

**The Distribution of Conformers in Some *Ortho* and *Meta*-Substituted  
Benzaldehydes  
in Polar and Nonpolar Solvents**

by

Kerry James Cox

A Thesis

Submitted to the Faculty of Graduate Studies  
in Partial Fulfilment of the Requirements for the Degree of

MASTER OF SCIENCE

Department of Chemistry

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### Abstract

Monosubstituted derivatives of benzaldehyde, like benzaldehyde itself, have barriers to rotation of the aldehyde groups around the exocyclic  $C_{sp^2}-C_{sp^2}$  bonds of a magnitude sufficient to allow a discussion in terms of two planar conformers; these have the carbonyl oxygen pointing away from (O-trans), or toward (O-cis), the ring substituent. The magnitudes of the observed stereospecific five bond coupling constants in the  $^1H$  nmr spectra of these molecules are the most precise indicators of conformational populations in solution. The  $^1H$  nmr spectra are analyzed for benzaldehyde derivatives with Cl, Br,  $NO_2$ ,  $CH_3$ , and CN substituents at the *meta* position<sup>a</sup>, and for those with Cl, Br, I,  $NO_2$ , OMe, CN, and  $CH(CH_3)_2$  substituents at the *ortho* position, as dilute solutions in acetone- $d_6$  and  $CS_2/C_6D_{12}$  solutions.

The O-trans conformer is slightly favoured in *m*-chloro, bromo, and nitrobenzaldehydes; however, for *m*-tolualdehyde this form makes up slightly less than half of the molecules in solution, at 300 K. O-trans is also the principal form of the *ortho*-substituted Cl, Br, I,  $NO_2$ , and OMe derivatives, accounting for 80 to 100 % of these compounds in solution, at 300 K. Computations at various levels of molecular orbital theory support these findings and confirm the planar nature of the rotamers. Several experimental methods have been used to measure conformer distributions in these compounds, with varying degrees of agreement. The populations, and free energy differences, implied by the five bond coupling constants are compared to these measurements.

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<sup>a</sup> For ease of writing, the prefixes, *ortho* and *meta* (o- and m-), will be used in the textual parts of this thesis; however many of the tables presented make use of numbers to express the substituent's position on the aromatic ring.



o- and m-Cyanobenzaldehyde are discussed in some detail because these compounds provide an excellent example of how substituents with high dipole moments can interact with each other, and with the surrounding solvent, to determine conformer populations. Reaction field theory is used to extrapolate equilibrium constants from the solution state to the vapour. It is found that a slight excess of the O-trans form of m-cyanobenzaldehyde is present in both acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> at 300 K. Specific interactions with benzene-d<sub>6</sub> solvent increase the O-trans population in that solvent. The conformational equilibrium of o-cyanobenzaldehyde displays a relatively large solvent dependence; the O-cis form is stabilized in acetone-d<sub>6</sub> by 2.2 kJ/mol with respect to benzene-d<sub>6</sub>, and 4.6 kJ/mol with respect to CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solutions.

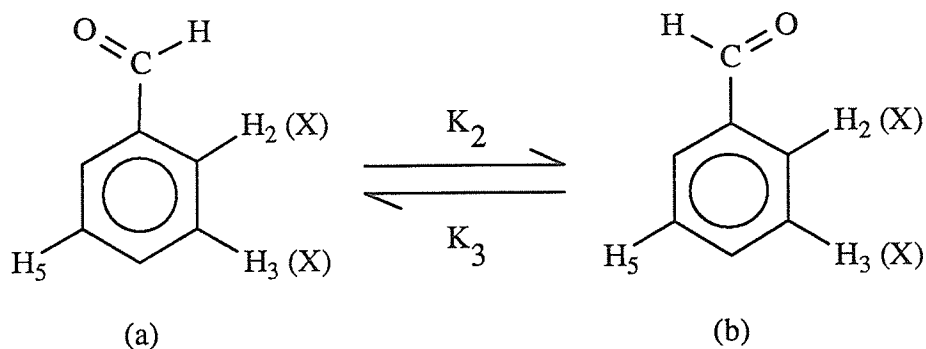
The analysis of o-isopropylbenzaldehyde is also presented in a separate chapter. These analyses deal with conformational populations not only with respect to the aldehyde group, but also with respect to the isopropyl moiety. A slight majority of the molecules in solution have the O-trans orientation of CHO, with a slight decrease in population of these forms being caused by an increase in solvent polarity. The proportion of conformers with the methine C-H bond of the isopropyl group directed away from CHO is found to be small, regardless of solvent polarity. The sign of the proximate coupling constant between the methine and aldehyde protons was found by double resonance experiments to be negative.

## **1.0 Introduction**

The aldehyde group in benzaldehyde and its monosubstituted derivatives has been shown by several different methods (including nmr [1-6], ir [7-11] and microwave [12] spectroscopies, and also dipole moment [13-17] and electron diffraction [18,19] studies) to be coplanar with the aromatic ring. This is the result of a high internal barrier to rotation about the exocyclic  $C_{sp^2}-C_{sp^2}$  bond. The value determined experimentally [3, 4] for this barrier in benzaldehyde itself in solution is near 32 kJ/mol. *Ab initio* molecular orbital calculations carried out for these molecules [20-23] indeed show appropriate minima in the potential curve for rotation of the aldehyde group for the planar conformations, with those utilizing a minimal basis set giving the closest agreement with experimentally determined barriers. Semiempirical computational methods [21] also support the planar nature of the molecule. However, the barrier arrived at by these methods is much too low.

Hence there are two possible planar conformers for benzaldehyde and its derivatives at ambient temperatures: O-trans (fig. 1a) where the C=O bond of the aldehyde is oriented away from a ring substituent (or away from a specified ring proton for benzaldehyde itself) and O-cis (fig. 1b) where the carbonyl is pointed toward the ring substituent (or toward the specified ring proton for benzaldehyde). Of course in the case of benzaldehyde these conformers are equivalent.

Spin-spin coupling between the aldehyde proton and the ring protons has been described many times in the literature [1-4, 24, 25-27]. In the past, the use of these couplings to gain insight into the preferred conformation of these molecules has been restricted by the relatively low resolution attainable from the equipment in use at that time. Coupling constants between the aldehyde proton and the ring protons at



**Figure 1.** a) O-trans and b) O-cis benzaldehyde and their derivatives.

positions 3 and 5 have been demonstrated [1, 25, 27, 29, 30] to be stereospecific, with only those between protons having a zig-zag (all-trans) bond pathway between them being observable. Thus, in the structure of benzaldehyde seen in figure 1a the coupling constant between the aldehyde proton and that at position 5 is observable while coupling between the aldehyde proton and that at position 3 is not detectable. The coupling constant,  $^5J(\text{CHO}, \text{H}_5)$ , obtained from the spectrum of benzaldehyde arises from a 50:50 mixture of the two conformers (figure 1a and 1b) and is therefore an average of the coupling in each. The following equation may be used to arrive at a value for  $^5J(\text{CHO}, \text{H}_5)$  from the splitting observed in an nmr spectrum:

$$^5J(\text{CHO}, \text{H}_5)_{\text{obs}} = P_t \cdot ^5J(\text{CHO}, \text{H}_5)_t + P_c \cdot ^5J(\text{CHO}, \text{H}_5)_c \quad (1)$$

where  $^5J(\text{CHO}, \text{H}_5)_{\text{obs}}$  is the coupling constant measured in the nmr spectrum and  $P_t$  and  $P_c$  are the fractions of molecules with O-trans and O-cis orientation, respectively

(in this case meaning those molecules where the C=O bond is pointed away from or toward proton 3, as in figures 1a and 1b). As stated previously,  $P_t$  and  $P_c$  must both be 0.5 in benzaldehyde since both conformers are chemically identical.

$^5J(\text{CHO},\text{H5})_{\text{obs}}$  for benzaldehyde [29] in acetone- $d_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solutions at 300 K is 0.430(1) and 0.431(2) Hz, respectively. As already mentioned, for the O-cis rotamer (fig. 1b)  $^5J(\text{CHO},\text{H5})_c$  is zero so that  $^5J(\text{CHO},\text{H5})$  becomes, from equation (1):

$$^5J(\text{CHO},\text{H5})_t = 0.430(1) \text{ Hz.} / 0.5 = 0.862(2) \text{ Hz} \quad (2)$$

in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution.  $^5J(\text{CHO},\text{H3})_c$  can be found in an analogous manner.

When a substituent is placed on the ring *ortho* or *para* to the aldehyde group, the sum of the couplings to H3 and H5 remains very nearly the same as when the substituent is absent [1, 25, 27, 31, 32], and appears to be nearly independent of the nature of the substituent. Thus, from equation (1), the magnitudes of these couplings can yield accurate proportions of molecules with O-trans and O-cis orientations. Similarly, a *meta* substituent, being far from the pathway between the aldehyde proton and the proton at the other *meta* position, does not appear to alter the magnitude of the coupling [29, 31].

Although, as mentioned at the outset, several methods have been used to determine the preferred orientation and the relative populations of the two rotamers in molecules of this kind, a general agreement has been lacking. An early study, conducted by Miller et al [7], used ir spectroscopy to conclude that for m-fluoro, chloro, bromo and methylbenzaldehyde there were indeed two rotamers present in the

vapour phase and that the O-cis conformation was more stable. These researchers also concluded, on the basis of the intensities of two observed low frequency bands, that the ratios, O-cis/O-trans, for these compounds were 10, 2.5, 7 and 11, respectively. The barrier to rotation in these molecules in the vapour phase was determined to be 16.8 - 20.9 kJ/mole with the O-cis rotamer being more stable than the O-trans by 2.9 - 7.1 kJ/mole. For the *ortho* substituted molecules the O-trans was found to be the more stable conformation, as expected from steric considerations. In the case of o-bromo and o-methylbenzaldehyde only one rotamer was detected.

The results of this ir study were in direct conflict with those of Karabatsos and Vane [1], who had previously examined these compounds in solution by  $^1\text{H}$  nmr spectroscopy. Using the stereospecificity of the five bond coupling between the aldehyde proton and the *meta* protons of benzaldehyde derivatives, they found that 60-70% of m-nitro, chloro and bromobenzaldehyde were present as the O-trans conformers. For o-nitro, fluoro, chloro, bromo and methoxybenzaldehydes only a doublet was observed in the aldehyde region, indicating only one rotamer, judged to be O-trans.

A later solution state ir study [11] contradicted the results of Miller et al for the *meta* substituted benzaldehydes when it was reported that the O-trans rotamers of the fluoro, chloro and bromo compounds constituted 70, 78 and 83%, respectively. These [11] results for the *ortho*-substituted molecules showed the O-cis rotamer to be in greater abundance than the O-trans, which contradicted not only Miller, but also Karabatsos and Vane. Later ir investigations of these molecules supported the findings of Miller et al in concluding that rotational isomerism does occur [9] and that for

m-fluoro, chloro and bromobenzaldehydes the O-cis conformer is the more stable in both the liquid and vapour states [10]. The vastly different results in [11] could in part be due to the use of solvated versus vapour phase samples and also to the use of peak intensities rather than integrated peak areas to determine the ratios of the two rotamers; peak intensities have been shown to change with temperature with no significant change in total peak area [10 and reference 5 therein].

Interpretation of the electronic spectra [33] of *ortho* and *meta*-substituted fluoro- and chlorobenzaldehydes lead to conclusions supported by the results of gas phase electron diffraction studies of o- and m- chlorobenzaldehyde [18, 19] in that it suggests that the more stable rotamer of the *ortho*-substituted benzaldehydes in the vapour phase is the O-trans. These studies differ from the vapour phase ir studies, however, in indicating that the O-trans rotamer is also more stable in the *meta*-substituted molecules, as was concluded in the early nmr work in solution.

There has been rough agreement among researchers investigating the dipole moments and molar Kerr constants of these molecules. The O-trans conformers of *meta*-substituted benzaldehydes are concluded to be the more stable in nonpolar solvents [13-17]. The populations determined for the O-cis conformers range, however, from 20% [14] to 47% [15] for m-chlorobenzaldehyde. The O-trans rotamer of o-chlorobenzaldehyde may be exclusively favoured [14]; however, a discrepancy between the calculated and the experimentally determined molar Kerr constant suggests a small amount of a second isomer, perhaps as much as 10%.

The results of an investigation of o- and m-fluorobenzaldehydes by  $^1\text{H}$  nmr [25] again showed the O-trans conformer to be the more stable form of

o-fluorobenzaldehyde, by 4.6 kJ/mol in free energy. The population of the O-trans conformer was determined to be 0.86. The size of the coupling constant between the aldehyde proton and the *meta* ring proton in the spectrum of m-fluorobenzaldehyde indicates a slight preference for the O-cis rotamer, whereas INDO MO FPT [34, 35] calculations on this molecule gave the O-trans rotamer as 0.67 kJ/mol lower in energy than the O-cis rotamer.

A  $^{13}\text{C}$  nmr study [5] also showed the O-trans form to be favoured in o-fluoro and o-chlorobenzaldehydes in a Freon mixture solution at  $-150^\circ\text{C}$ , this time exclusively. For o-tolualdehyde, however, the populations of O-trans and O-cis conformers appear to be effectively equal. The reason suggested was that the more closely aligned dipoles in the O-cis form of the *ortho*-substituted halobenzaldehydes favour the O-trans conformer but that this dipole - dipole repulsion effect is absent in the o-methyl substituted molecule. The populations arrived at for the O-trans conformer of the m-fluoro, chloro and bromo derivatives are 0.26, 0.35 and 0.41 respectively. This goes against the previous INDO calculations but agrees qualitatively with the aforementioned  $^1\text{H}$  nmr work that suggests a polar solvent would tend to increase the stability of the more polar O-cis conformer. The trend of decreasing proportion of O-cis conformer as the electronegativity of the *meta*-substituent is increased was explained by a hydrogen bond type of interaction between the aldehyde oxygen and the slightly positive ring proton between the aldehyde and the electronegative substituent. A second explanation suggested a dipole - dipole interaction between the C2-H bond and the aldehyde C-H bond.

A far more recent  $^1\text{H}$  nmr analysis of o- and m-fluorobenzaldehyde [31] at



300 K found that  $4.4 \pm 0.1$  % of o-fluorobenzaldehyde exists as the O-cis conformer in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solution and  $13.5 \pm 0.2$  % in acetone-d<sub>6</sub>. Once again the proposal that the more polar solvent favours the more polar conformer to a greater extent than a does nonpolar solvent, such as CS<sub>2</sub>, is supported. For m-fluorobenzaldehyde, on the other hand, the population of the O-cis rotamer was found to be 0.538(4) in CS<sub>2</sub>, the O-trans rotamer being less stable by 0.38(4) kJ/mole in CS<sub>2</sub> and 0.27(4) kJ/mole in acetone-d<sub>6</sub> solution. This result is in qualitative agreement with the ir study [7]; however, the energy difference between the two rotamers in this case is somewhat lower.

In this thesis several benzaldehyde derivatives with various substituents at either the *ortho* or the *meta* position have been examined by very high resolution nmr spectroscopy in both polar and nonpolar solvents. *Ab initio* and semiempirical MO calculations have been conducted on selected molecules and the results discussed in light of the spectroscopic data. CNDO and INDO MO FPT predictions of coupling to the aldehyde proton in some of the molecules are also presented. An attempt has been made to reconcile some of the previous results obtained by the various methods mentioned above. Part 3 deals with *ortho* and *meta*-substituted chloro-, bromo-, and nitrobenzaldehydes as well as o-iodo-, o-methoxy-, and m-methylbenzaldehyde. Part 4 is devoted to o- and m-cyanobenzaldehyde, found to have characteristically interesting features. Part 5 involves the examination of the conformational behaviour of o-isopropylbenzaldehyde, for which no other measurements, in these solvents, or at temperatures near 300 K, are known. The synthesis of this compound is given in Part 2.

The magnitude of the coupling between the aldehyde proton and the ring proton at position 4 in benzaldehyde is known [1,36] to depend on the dihedral angle between the plane containing the atoms of the aldehyde group and the plane of the aromatic ring. It has also been reported [36] that this coupling is generated by a  $\sigma - \pi$  mechanism whereby spin information is transferred via both the sigma and pi electrons and therefore varies as a function of  $\sin^2\theta$  [29, 36], where  $\theta$  is the dihedral angle described in the previous sentence. Its magnitude is greatest when the C-H bond of the aldehyde group is at  $90^\circ$  to the plane of the aromatic ring,  $^6J_{90}$ , and at a minimum when this bond is coplanar with the ring,  $^6J_0$ . The sign of this coupling was assumed to be always negative until some *meta*-substituted benzaldehydes [29] were found to exhibit a positive six bond coupling. Some of the compounds in this work lend further support to this observation and comments about this have been made where it has been deemed appropriate.

## **2.0 Experimental Methods**

## 2.1 Synthesis

2-isopropylbenzaldehyde was prepared as follows:

14.3 mmol of lithium metal was added to 6.13 mmol of 2-bromoisopropylbenzene from Lancaster Synthesis Ltd. in 25 mL of diethyl ether under nitrogen atmosphere. The vessel was allowed to sit at room temperature in an ultrasound bath for two hours at which point the bulk of the metal had reacted. Still under nitrogen, 6.13 mmol of N,N-dimethylformamide was added to the lithiate mixture and was allowed to react, with constant stirring, for 30 minutes. The reaction was then quenched with excess aqueous  $\text{NH}_4\text{Cl}$  (saturated). 25 mL more of diethyl ether was shaken with the mixture. After separation, the ether layer was dried over  $\text{MgSO}_4$  and then evaporated to leave the product. The product was purified on a silica gel column with hexane as the solvent.

The yield, as calculated from the area of the aldehyde proton peak at 10.37 ppm in the wide sweep width acetone- $\text{d}_6$  survey spectrum versus the total area of the aromatic proton peaks (the only source of aromatic ring protons being the initial 6.13 mmol of 2-bromoisopropylbenzene), was approximately 40%.

That the aldehyde peak in the survey spectra did not belong to N,N-dimethylformamide or formaldehyde impurity is evident since the chemical shifts [37] of these aldehyde protons are 8.01<sup>1</sup> and 9.57<sup>2</sup>, respectively.

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<sup>1</sup> 10 mol% in acetone.

<sup>2</sup> Either neat with 5% TMS or in TMS with 5% formaldehyde, reference is not specific.

## 2.2 Sample Preparation

Solutions of *ortho* and *meta*-substituted benzaldehydes were prepared in acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. Approximately 100 mg of each sample was accurately measured into glass vials and sufficient solvent was added to dilute the sample solutions to 4 mol%. One drop of tetramethylsilane (TMS) was then added to the acetone-d<sub>6</sub> solutions for spectral reference. In the case of the CS<sub>2</sub> solutions, a previously prepared solvent mixture was used, containing 10 mol% C<sub>6</sub>D<sub>12</sub>, for a lock signal, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% TMS. *Ortho*-iodo-, cyano-, and nitrobenzaldehyde, as well as *meta*-bromo and *meta*-nitrobenzaldehyde, being very nearly insoluble in CS<sub>2</sub>, were simply prepared as saturated solutions containing less than 4 mol% of solute. *Ortho*-iodobenzaldehyde and *ortho*-nitrobenzaldehyde, which are also relatively insoluble in acetone-d<sub>6</sub>, were similarly prepared as saturated solutions in this solvent.

*Ortho* and *meta*-cyanobenzaldehyde were also prepared as benzene-d<sub>6</sub> solutions. Both these compounds are only sparingly soluble in this solvent and had to be prepared as saturated solutions.

All solutions were filtered through a cotton plug into 0.5 mm outside diameter nmr tubes which then were connected to a vacuum line apparatus and degassed through 3 or 4 freeze-pump-thaw cycles. After being degassed, the tubes were flame sealed.

All compounds examined in this study were commercially available, with the exception of *o*-isopropylbenzaldehyde.

## 2.3 Spectroscopic Method

All spectra were acquired on a Bruker AM 300 spectrometer operating with a probe temperature of 300 K. The positions, with respect to TMS, of the ring and functional group protons were first located from wide sweep width survey spectra. Regions of the spectra which were of interest were then examined in detail by adjusting the spectral range and the number of data points collected until acquisition times of from 35 to 68 seconds were arrived at. In each case the magnet was shimmed manually on the free induction decay (FID) for the TMS protons. Up to 32 scans were accumulated for each region to give an acceptable signal to noise ratio, S/N. The FIDs collected were zero-filled to two to four times the original number of data points and enhancements were applied with Gaussian broadening and line broadening factors of 0.5 to 0.6 and -0.07 to -0.13, respectively, before Fourier transformation was performed.

Many of the FIDs were transferred to a Bruker X32 workstation for processing and plotting.

The highly precise chemical shift frequencies and coupling constants reported in this thesis, along with their respective standard deviations are those given by the analysis program, NUMARIT [38]. The standard deviations arise from the fitting of the spectroscopic data to the Hamiltonian and indirectly reflect error in the positioning of the peaks in the spectra; errors in peak position, as measured by the peak picking routine, cause a poor fit to the Hamiltonian and thus a higher RMS. The peak picking routine cannot determine the position of any line in the spectrum with an accuracy

poorer than the digital resolution. In fact, the accuracy of the peak position will be greater than the digital resolution since the peak picking routine fits the data points which describe the peak to a Lorentzian line-shape. In each of the analyses presented in this thesis the digital resolution is quite high, in most cases being 0.004 Hz/pt and so the frequencies submitted to the analysis program are reliable.

In deciding on the credibility of the standard errors given by the analysis program it is important to take note of several points:

- i) the digital resolution used during acquisition of the spectrum
- ii) the RMS deviation
- iii) the number of transitions assigned compared to the number calculated, and compared also to the number of peaks observed, and
- iv) the largest difference between the observed and theoretical frequencies.

It must be kept in mind that the analysis program has been modified so that spectral transitions far from their theoretical frequencies are ignored in order to facilitate autoassignment by the program; however, the number of peaks ignored is usually very small.

In calculations which make use of the spectroscopic data, error limits have been overestimated to the next highest order of magnitude to increase confidence in the results.

## 2.4 Computations

*Ab initio* and semiempirical molecular orbital calculations were performed on an Amdahl 5870 computer system using the Gaussian 86 [39] program. In each instance geometry optimization procedures kept the benzene ring moiety planar, with all bond lengths and angles being allowed to vary.

The rotational barrier energies computed were then fit to a function of the form:

$$V(\theta) = V_1 \sin^2\left(\frac{\theta}{2}\right) + V_2 \sin^2(\theta) + V_3 \sin^2\left(\frac{3\theta}{2}\right) \\ + V_4 \sin^2(2\theta) + V_6 \sin^2(3\theta) + V_8 \sin^2(4\theta)$$

using the SAS nonlinear least squares program, NLIN [40]. SAS/GRAPH [41] programs were written to plot the resulting curves using a spline interpolation which is part of the SAS/GRAPH library.

All spectra were analyzed using the iterative program, NUMARIT (modified extensively by R. Sebastian) on an Amdahl 5870 computer system. The results of each analysis were then submitted to a plotting routine. This program and plotting routine were also used to simulate analyzed spectra, with various magnitude and sign combinations assigned to certain spin-spin coupling constants. These simulations were used to verify the sign and magnitudes of the iteratively calculated values for many of the molecules analyzed.



### **3.0 Chloro, bromo, iodo, nitro, methoxy and methyl benzaldehydes**

### 3.1 Experimental Results

### 3.1.1

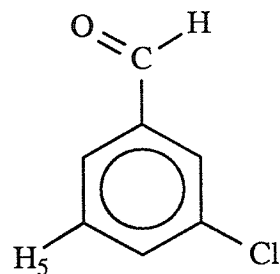
The 300 MHz  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for 4 mol% solutions of 3-chlorobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  at 300 K are given in tables 1 and 2, respectively.

The aldehyde spectrum of m-chlorobenzaldehyde in acetone- $\text{d}_6$  is seen in figure 2, along with the computer simulation. The spectra of the ring protons are shown in figure 3. The half-height linewidth in this spectrum is 0.02 Hz. The signs of the coupling constants and initial guesses as to their magnitudes were taken from a previous analysis of m-fluorobenzaldehyde [31]. The sign of  $^6\text{J}(\text{H4},\text{CHO})$  was verified by simulation of the aldehyde proton (in the  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution) spectrum with different sign and magnitudes assigned to this coupling. The results are shown in figure 4.

The only difficulty in these analyses was due to the small chemical shift difference between the ring protons at positions 2 and 6; in figure 3c the transitions for H2 are seen to be interspersed among the high frequency transitions of H6.

Table 1. Spectral parameters<sup>a</sup> for 4.0 mol% 3-chlorobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2) <sup>b</sup>	2372.933	0.0004
v(H4)	2316.014	0.0003
v(H5)	2291.524	0.0004
v(H6) <sup>c</sup>	2367.742	0.0004
v(CHO)	3114.825	0.0003



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	2.228	0.0005	J(H5,H6)	7.655	0.0006
J(H2,H5)	0.475	0.0006	J(H5,CHO)	0.439	0.0005
J(H2,H6)	1.489	0.0005			
J(H2,CHO) <sup>d</sup>	-0.083	0.0005			
J(H4,H5)	8.010	0.0005	J(H6,CHO)	-0.131	0.0005
J(H4,H6)	1.068	0.0005			
J(H4,CHO)	0.021	0.0005			

91 Transitions

Largest Difference = 0.003 Hz

73 Observed Peaks

RMS Deviation of Transitions = 0.0012

69 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Correlated with  $\nu(\text{H6})$  by -0.2071, with  $J(\text{H2},\text{H4})$  by -0.1815, with  $J(\text{H2},\text{H5})$  by 0.1995, and with  $J(\text{H5},\text{H6})$  by -0.2039.
- <sup>c</sup> Correlated with  $J(\text{H2},\text{H5})$  by -0.2100 and with  $J(\text{H5},\text{H6})$  by 0.2055.
- <sup>d</sup> Correlated with  $J(\text{H6},\text{CHO})$  by -0.1988.
- <sup>e</sup> Sign determined by spectrum simulations using the program, NUMARIT, with various values assigned to the coupling constant  $J(\text{H4},\text{CHO})$  and all other parameters kept constant.

Figure 2. The 300 MHz spectrum of the aldehyde proton of 4 mol% 3-chlorobenzaldehyde in acetone-d<sub>6</sub> at 300K.

A) The experimental spectrum.

B) The simulated spectrum.

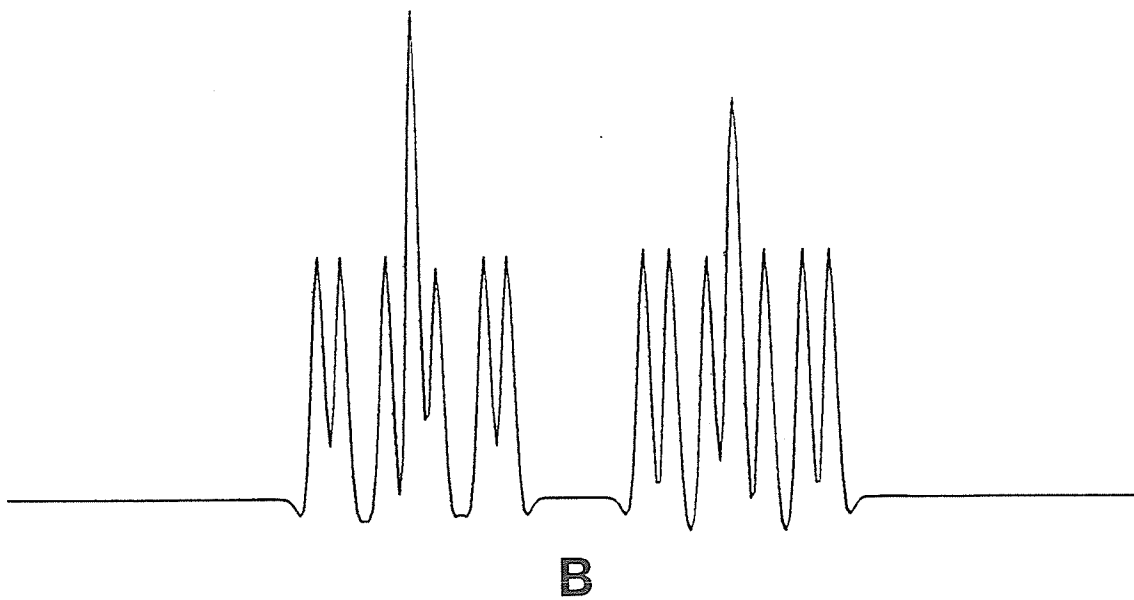
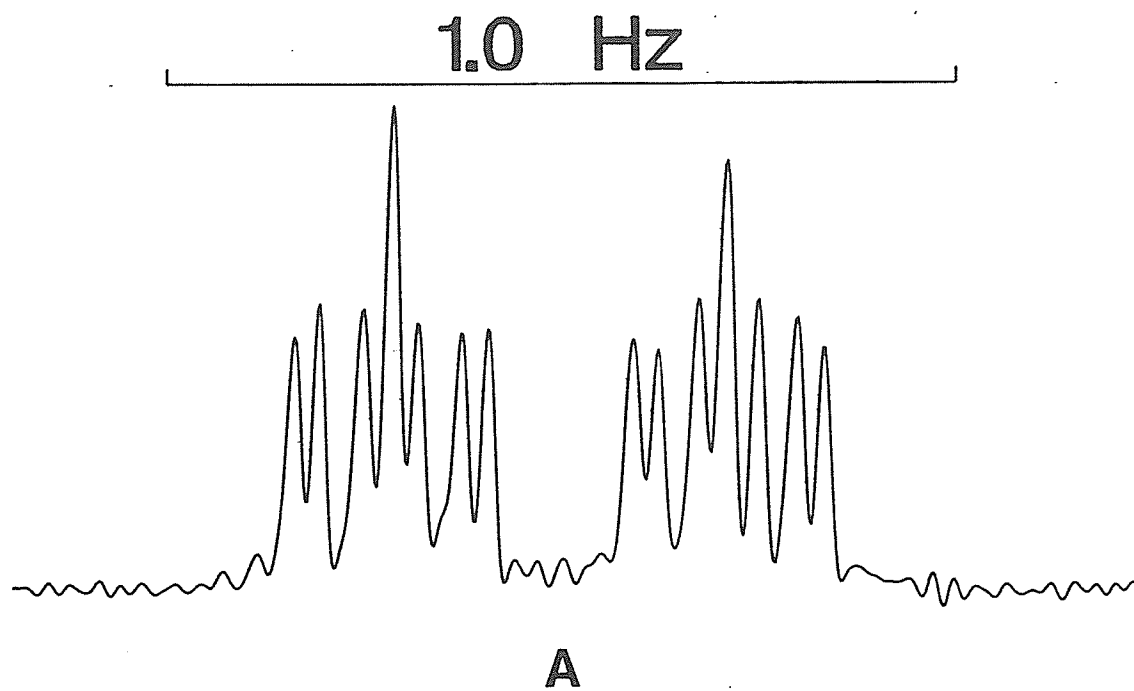


Figure 3. The 300 MHz spectrum of the ring protons of 4 mol% 3-chlorobenzaldehyde in acetone-d<sub>6</sub> at 300K.

A) Ring proton H5.

B) Ring proton H4<sup>1</sup>.

C) Ring protons H2 and H6<sup>2</sup>.

---

<sup>1</sup> In B, 0.021 Hz splitting due to <sup>6</sup>J(CHO,H4) can be observed.

<sup>2</sup> In C, the transitions for ring proton H2 are interspersed within the eight high frequency transitions of proton H6.



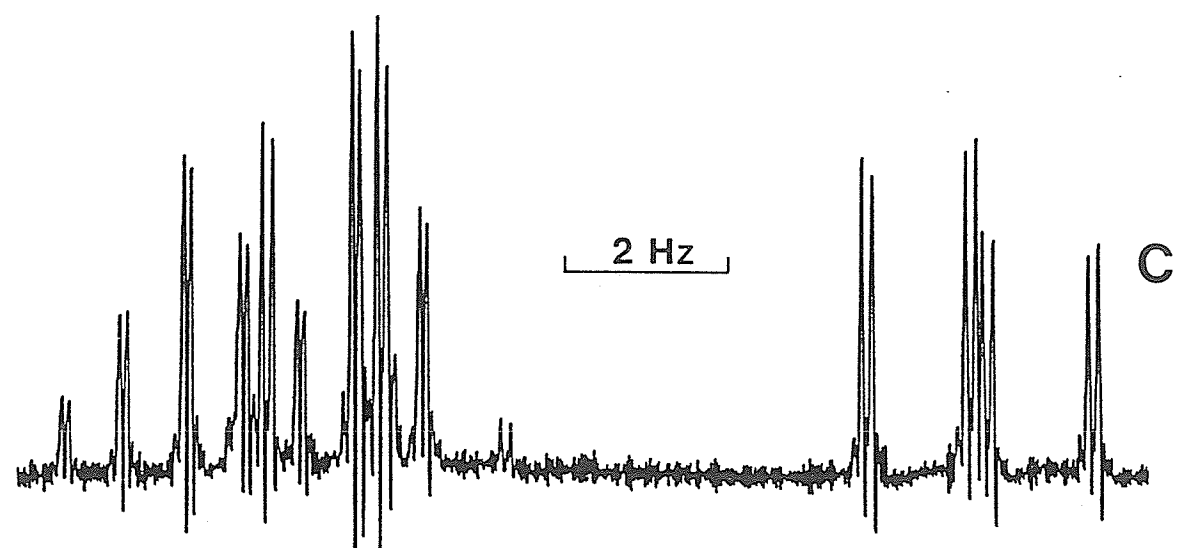
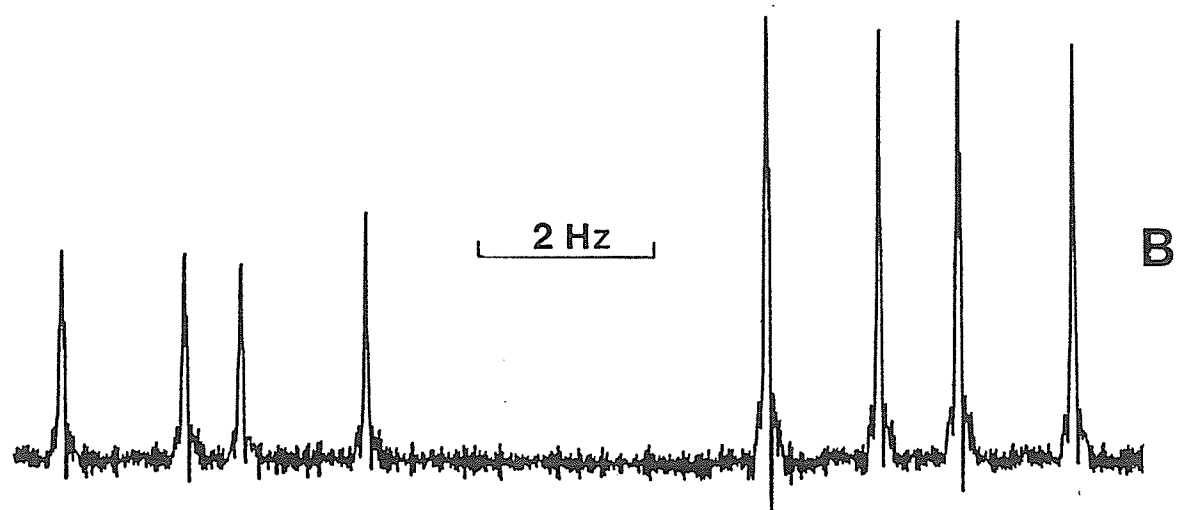
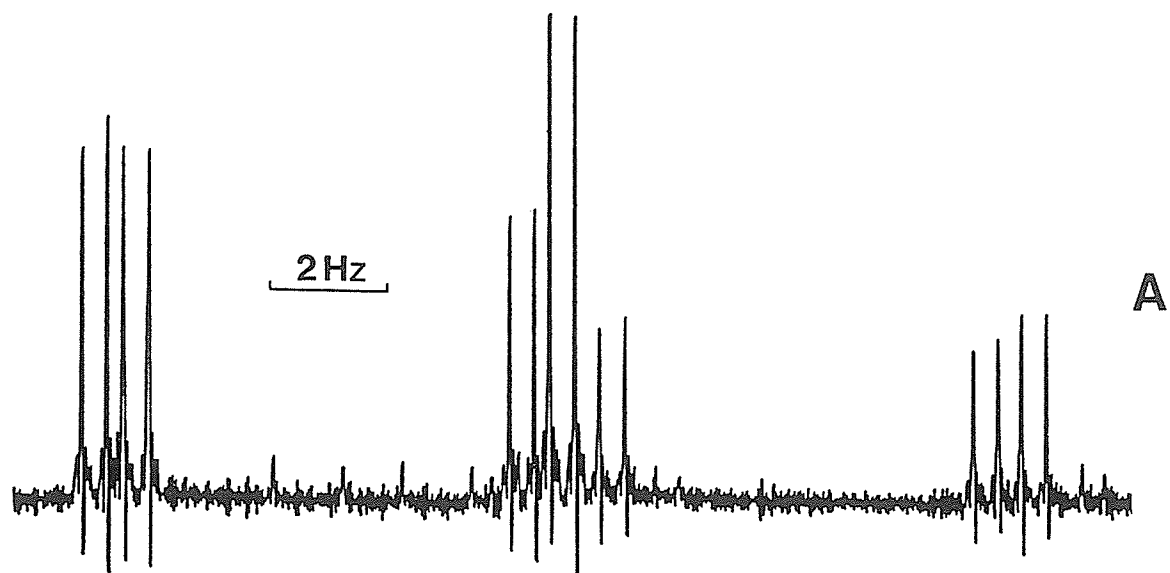
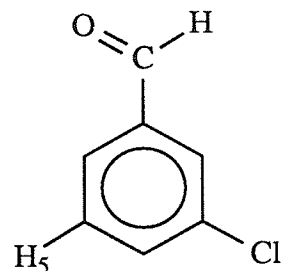


Table 2. Spectral parameters<sup>a</sup> for 4.8 mol%<sup>b</sup> 3-chlorobenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2322.679	0.0002
v(H4)	2252.985	0.0003
v(H5)	2228.121	0.0003
v(H6)	2304.844	0.0002
v(CHO)	2970.014	0.0003



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	2.187	0.0004	J(H5,H6)	7.621	0.0004
J(H2,H5)	0.467	0.0003	J(H5,CHO)	0.444	0.0004
J(H2,H6)	1.496	0.0003			
J(H2,CHO) <sup>c</sup>	-0.085	0.0004			
J(H4,H5)	7.958	0.0004	J(H6,CHO)	-0.132	0.0004
J(H4,H6)	1.103	0.0004			
J(H4,CHO) <sup>d,e</sup>	0.024	0.0004			

80 Transitions

Largest Difference = 0.002 Hz

89 Observed Peaks

RMS Deviation of Transitions = 0.0009

71 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained 4.8 mol% m-chlorobenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with J(H6,CHO) by -0.1312.
- <sup>d</sup> Correlated with  $\nu$ (H4) by -0.1412, with J(H2,CHO) by -0.1364, with J(H4,H6) by 0.1921, and with J(H6,CHO) by -0.1448.
- <sup>e</sup> Sign determined by spectral simulations with various values assigned to the coupling constant J(H4,CHO) while all other parameters were kept constant.

Figure 4. A) The experimental 300 MHz spectrum of the aldehyde proton of 4 mol% 3-chlorobenzaldehyde in CS<sub>2</sub>.

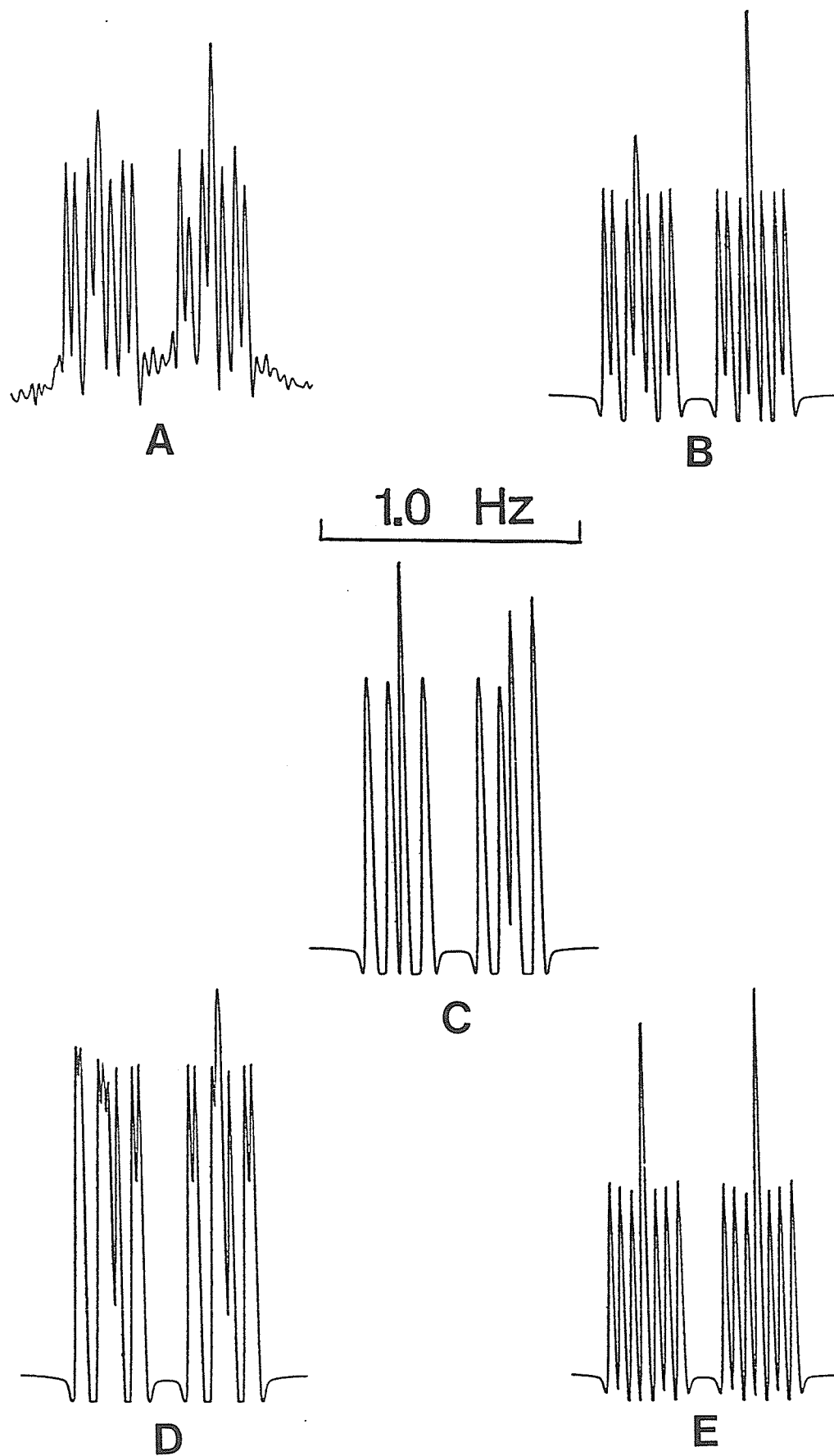
B) The iteratively determined spectrum where  ${}^6J(\text{CHO},\text{H}_4)$  is 0.024 Hz.

The sign and magnitude of  ${}^6J(\text{CHO},\text{H}_4)$  are verified by simulations calculated with this six bond coupling being:

C) -0.024 Hz

D) 0.014 Hz

E) 0.034 Hz



### 3.1.2

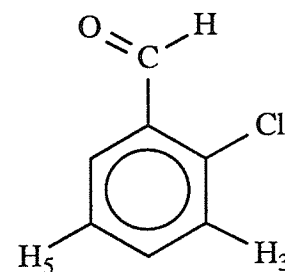
Tables 3 and 4 display the  $^1\text{H}$  nuclear magnetic resonance spectral parameters for 4 mol% solutions of 2-chlorobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively, measured at 300K and 300 MHz. Chemical shift differences were sufficiently large that the analyses of these first order spectra were straightforward.

The aldehyde proton spectra for both solvent solutions are seen in figure 5. Only a doublet is seen for the  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution, owing to the absence of coupling between this proton and the ring proton at position 3. In the spectrum for the acetone- $\text{d}_6$  solution, the doublet of triplets shows significant spin-spin coupling to both ring protons H3 and H6.

The relative energies and dipole moments computed for 2-chlorobenzaldehyde with the aldehyde group rotated, in steps of 15 degrees, from 0 to 180 degrees out of the plane of the benzene ring are presented in table 5. These values were computed by both ab initio molecular orbital calculations at the STO-3G level, and the semiempirical method, AM1.

Table 3. Spectral parameters<sup>a</sup> for 4.0 mol% 2-chlorobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2272.557	0.0004
v(H4)	2304.694	0.0004
v(H5)	2256.845	0.0004
v(H6)	2369.852	0.0004
v(CHO) <sup>b</sup>	3134.514	0.0007



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	8.098	0.0006	J(H5,H6)	7.760	0.0006
J(H3,H5)	1.090	0.0006	J(H5,CHO)	0.800	0.0007
J(H3,H6)	0.427	0.0006			
J(H3,CHO) <sup>c</sup>	0.065	0.0007			
J(H4,H5)	7.384	0.0006	J(H6,CHO)	-0.081	0.0007
J(H4,H6)	1.778	0.0006			
J(H4,CHO)	-0.006	0.0007			

82 Transitions

Largest Difference = 0.004 Hz

63 Observed Peaks

RMS Deviation of Transitions = 0.0016

69 Assigned Transitions

Notes:

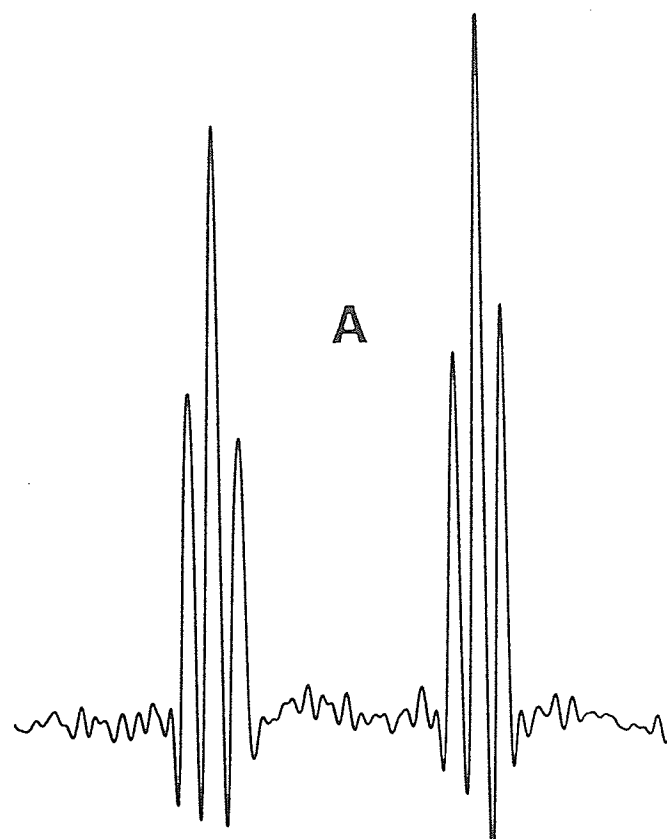
<sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.

<sup>b</sup> Correlated with J(H4,CHO) by -0.2567 and with J(H5,CHO) by 0.2579.

<sup>c</sup> Correlated with J(H6,CHO) by 0.2272.



Figure 5. The 300 MHz spectrum of the aldehyde proton of 2-chlorobenzaldehyde in A) acetone-d<sub>6</sub> and B) CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>, at 300 K.



1.0 Hz

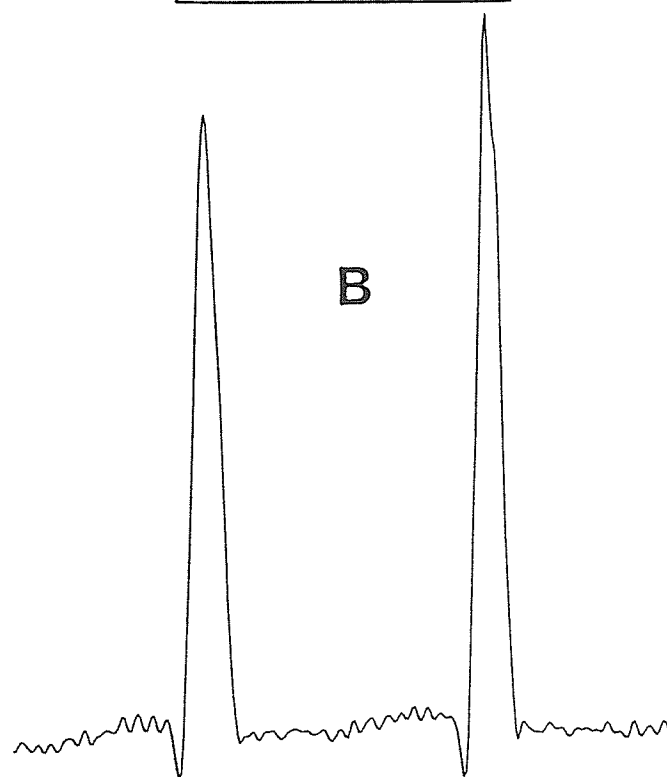
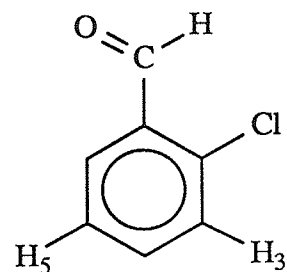


Table 4. Spectral Parameters<sup>a</sup> for 4.0 mol%<sup>b</sup> 2-chlorobenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2212.440	0.0015
v(H4) <sup>c</sup>	2237.866	0.0019
v(H5)	2198.907	0.0014
v(H6)	2347.099	0.0015
v(CHO) <sup>d</sup>	3115.501	0.0021



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	8.063	0.0022	J(H5,H6)	7.753	0.0021
J(H3,H5)	1.116	0.0021	J(H5,CHO)	0.856	0.0024
J(H3,H6)	0.428	0.0021			
J(H3,CHO)	-0.002	0.0024			
J(H4,H5)	7.342	0.0024	J(H6,CHO)	-0.036	0.0026
J(H4,H6)	1.794	0.0023			
J(H4,CHO) <sup>e</sup>	-0.026	0.0031			

84 Transitions

Largest Difference = 0.012 Hz

53 Observed Peaks

RMS Deviation of Transitions = 0.0059

69 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained 4 mol% 2-chlorobenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with J(H4,CHO) by -0.3679, with J(H4,H5) by 0.2731, and with J(H6,CHO) by -0.1423.
- <sup>d</sup> Correlated with J(H4,CHO) by -0.2622 and with J(H6,CHO) by -0.1015.
- <sup>e</sup> Correlated with J(H6,CHO) by 0.3872.

Table 5. *Ab initio* and Semiempirical Molecular Orbital Calculations for 2-Chlorobenzaldehyde.

$\theta(\text{deg})$	Energy <sub>rel</sub> (kJ/mole)	
	STO-3G	AM1
0	0.000	0.000
15	1.166	0.349
30	4.475	1.512
45	-----	3.556
60	14.540	6.071
75	18.802	8.287
90	21.061	9.699
105	20.882	10.319
120	18.580	10.473
135	-----	10.651
150	12.364	11.228
165	10.643	12.049
180	10.127	12.461

Note:

The carbon and hydrogen atoms of the benzene ring moiety were kept planar while all bond lengths and angles in the molecule were allowed to vary during optimization.  $\theta = 0^\circ$  corresponds to the O-trans conformer.

Figure 6. The STO-3G potential of 2-chlorobenzaldehyde upon rotation of the aldehyde group through 180 degrees<sup>1</sup>. The solid line is the fitted potential function:

$$V(\theta) = 9.36(8)\sin^2\left(\frac{\theta}{2}\right) + 16.11(7)\sin^2(\theta) \\ + 0.68(8)\sin^2\left(\frac{3\theta}{2}\right) - 0.80(1)\sin^2(2\theta)$$

and the triangles are the energies from individual molecular orbital computations.

---

<sup>1</sup>  $\Theta = 0^\circ$  corresponds to the O-trans rotamer while  $\Theta = 180^\circ$  corresponds to the O-cis rotamer.

## 2-Chlorobenzaldehyde ST0-3G

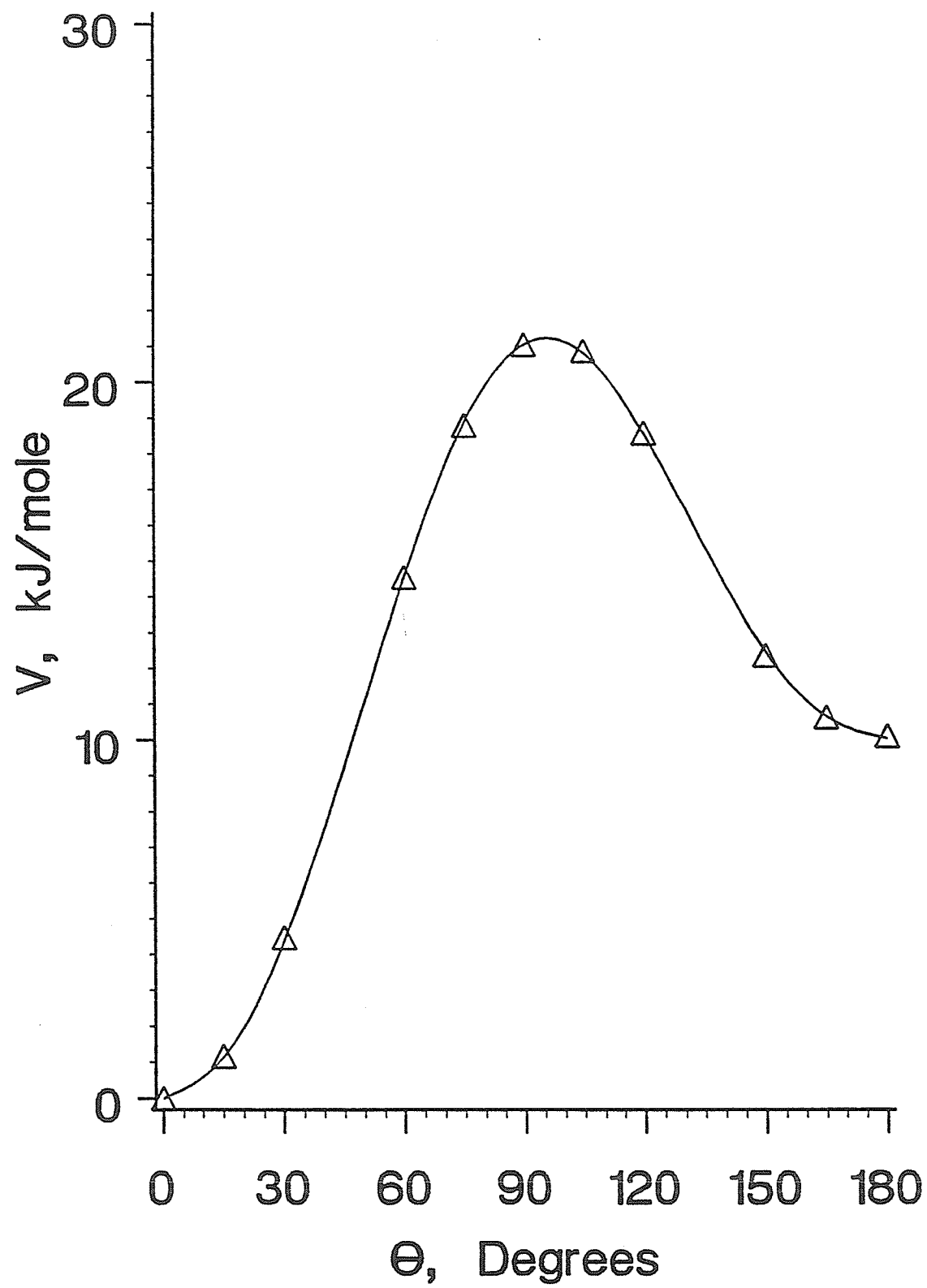


Figure 7. The AM1 potential of 2-chlorobenzaldehyde upon rotation of the aldehyde group through 180 degrees<sup>1</sup>. The solid line is the fitted potential function:

$$\begin{aligned}
 V(\theta) = & 11.23(1)\sin^2\left(\frac{\theta}{2}\right) + 3.58(1)\sin^2(\theta) \\
 & + 1.22(1)\sin^2\left(3\frac{\theta}{2}\right) - 0.86(1)\sin^2(2\theta) \\
 & + 0.11(1)\sin^2(3\theta)
 \end{aligned}$$

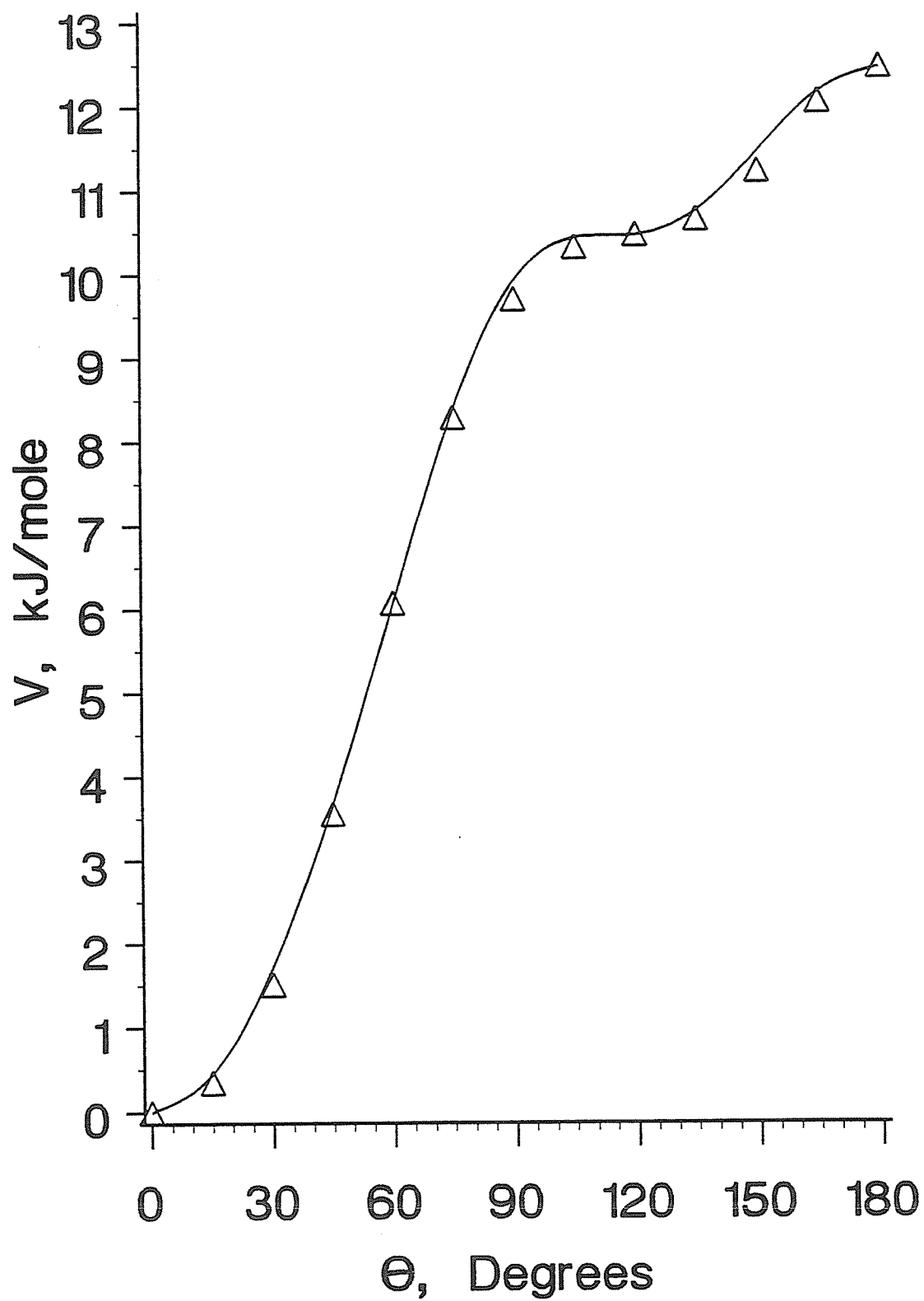
and the triangles are the energies from individual molecular orbital computations.

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<sup>1</sup>  $\Theta = 0^\circ$  corresponds to the O-trans rotamer while  $\Theta = 180^\circ$  corresponds to the O-cis rotamer.



## 2-Chlorobenzaldehyde AM1



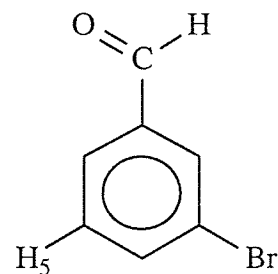
### 3.1.3

The  $^1\text{H}$  nuclear magnetic resonance chemical shifts and coupling constants for 3-bromobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  are shown in tables 6 and 7, respectively. The acetone- $\text{d}_6$  solution contained 4 mol% 3-bromobenzaldehyde while the  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution was a saturated solution containing less than 1.5 mol% solute.

For the acetone- $\text{d}_6$  solution, all shifts were well separated and no trouble was encountered in the analysis. In  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , however, the chemical shift difference between H2 and H6 is only 4 Hz (as shown in figure 8) and slight second order effects are witnessed in the spectral region corresponding to the aldehyde proton. Figure 9 shows this proton to exhibit a triplet and a quartet instead of the doublet of quartets that would be predicted in 1st order.

Table 6. Spectral parameters<sup>a</sup> for 4.0 mol% 3-bromobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2417.707	0.0005
v(H4)	2359.829	0.0004
v(H5)	2272.210	0.0006
v(H6)	2380.211	0.0004
v(CHO)	3009.856	0.0004



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	2.093	0.0006	J(H5,H6) <sup>c</sup>	7.651	0.0007
J(H2,H5) <sup>b</sup>	0.451	0.0008	J(H5,CHO)	0.448	0.0007
J(H2,H6)	1.495	0.0006			
J(H2,CHO)	-0.086	0.0006			
J(H4,H5)	7.981	0.0007	J(H6,CHO)	-0.130	0.0006
J(H4,H6)	1.068	0.0006			
J(H4,CHO) <sup>d</sup>	-0.001	0.0006			

80 Transitions

Largest Difference = 0.004 Hz

60 Observed Peaks

RMS Deviation of Transitions = 0.0017

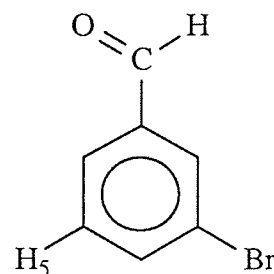
70 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H nmr at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Correlated with  $\nu(\text{H2})$  by 0.1421, with  $\nu(\text{H5})$  by -0.3162, and with  $J(\text{H5,CHO})$  by -0.1723.
- <sup>c</sup> Correlated with  $\nu(\text{H5})$  by -0.2977 and with  $J(\text{H5,CHO})$  by 0.1597.
- <sup>d</sup> Using the program, NUMARIT, the aldehyde spectrum was simulated with various values assigned to the coupling constant  $J(\text{H4,CHO})$  with all other parameters kept constant. This coupling was thus shown to be  $-0.015 \text{ Hz} < J(\text{H4,CHO}) < +0.010 \text{ Hz}$ .

Table 7. Spectral parameters<sup>a</sup> for a saturated<sup>b</sup> solution of 3-bromobenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2) <sup>c</sup>	2416.034	0.0012
v(H4)	2345.090	0.0005
v(H5)	2292.051	0.0004
v(H6) <sup>d</sup>	2412.245	0.0012
v(CHO)	2999.263	0.0005



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	1.670	0.0008	J(H5,H6)	7.773	0.0023
J(H2,H5) <sup>e</sup>	0.641	0.0023	J(H5,CHO)	0.476	0.0007
J(H2,H6)	1.620	0.0009			
J(H2,CHO)	-0.076	0.0008			
J(H4,H5)	7.686	0.0007	J(H6,CHO)	-0.112	0.0008
J(H4,H6)	1.248	0.0008			
J(H4,CHO) <sup>f</sup>	-0.003	0.0007			

88 Transitions

Largest Difference = 0.004 Hz

63 Observed Peaks

RMS Deviation of Transitions = 0.0020

77 Assigned Transitions

## Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained probably less than 1.5 mol% 3-bromobenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with  $\nu(\text{H6})$  by -0.7359, with  $J(\text{H2},\text{H6})$  by 0.8756, and with  $J(\text{H5},\text{H6})$  by -0.8301.
- <sup>d</sup> Correlated with  $J(\text{H2},\text{H5})$  by -0.8303, and with  $J(\text{H5},\text{H6})$  by 0.8759.
- <sup>e</sup> Correlated with  $J(\text{H5},\text{H6})$  by -0.8802.
- <sup>f</sup> Sign determined by spectrum simulations with various values assigned to the coupling constant  $J(\text{H4},\text{CHO})$  while all other parameters were kept constant.

Figure 8. The  $^1\text{H}$  nmr spectrum of the ring protons at positions 2 and 6 of 3-bromobenzaldehyde in  $\text{CS}_2/\text{C}_6\text{D}_{12}$ .

A) The experimental spectrum.

B) The computer simulation.

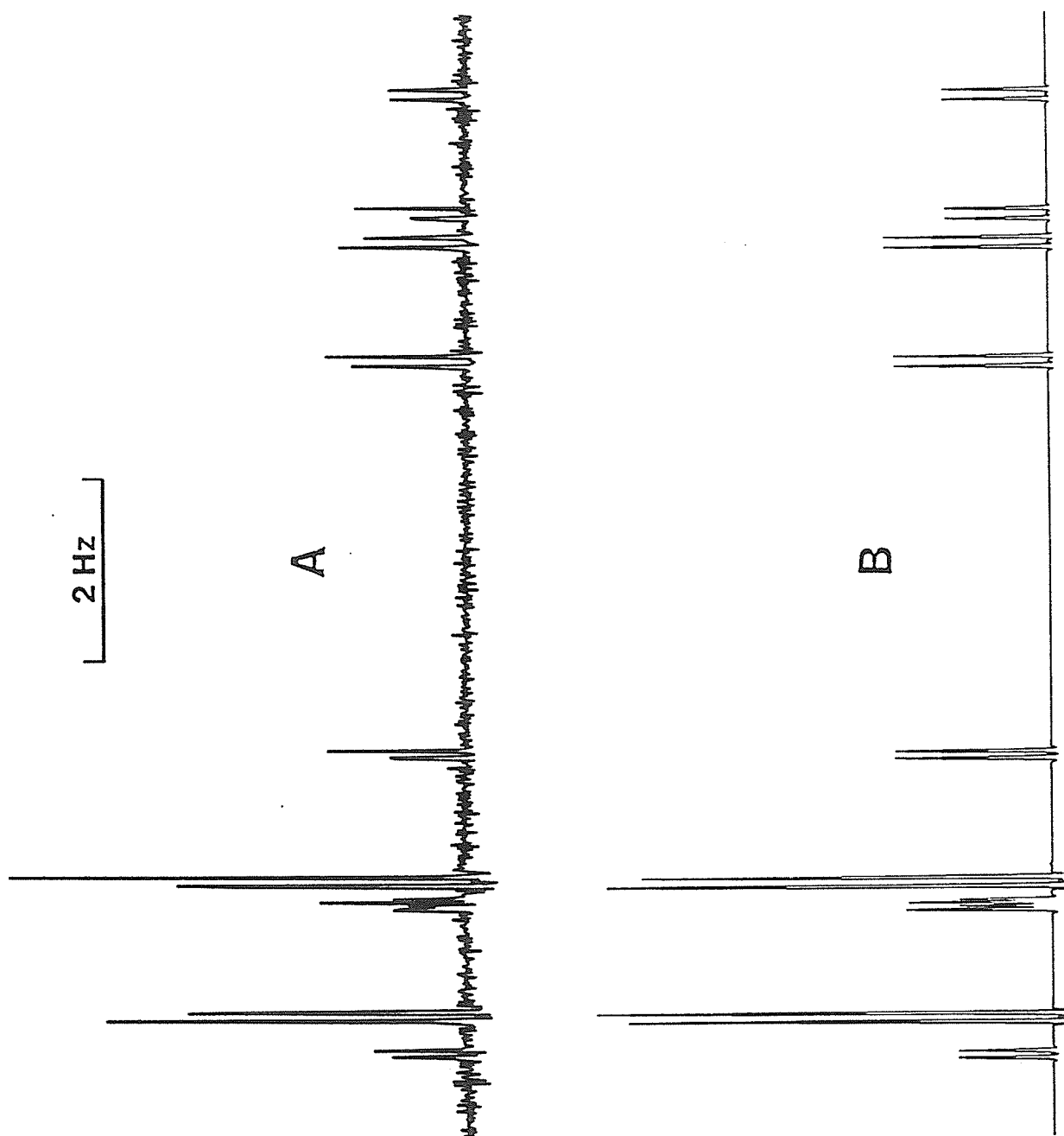
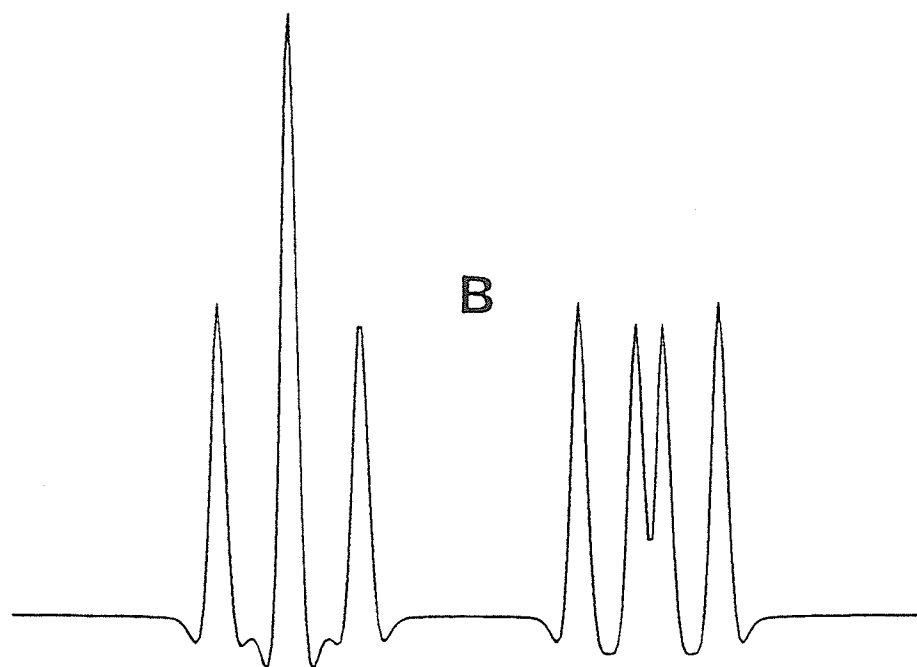
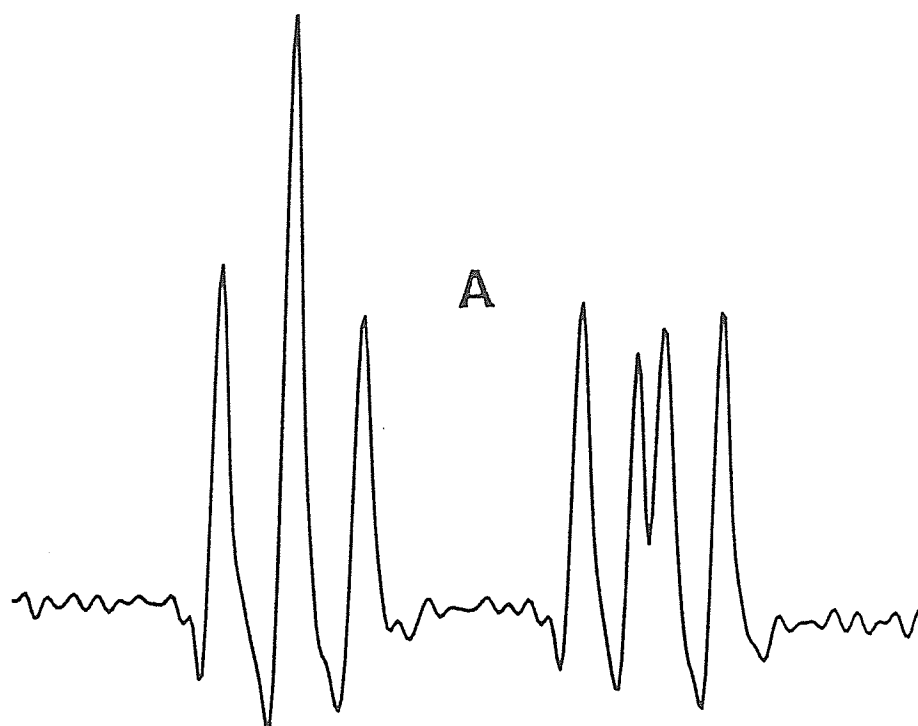




Figure 9.     A) The experimental spectrum for the aldehyde proton of  
3-bromobenzaldehyde in  $\text{CS}_2/\text{C}_6\text{D}_{12}$ .  
  
B) The computer simulation.



1.0 Hz



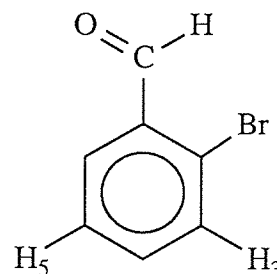
### 3.1.4

The  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for a 4 mol% solution of 2-bromobenzaldehyde in acetone- $\text{d}_6$ , measured at 300 K and 300 MHz, are given in table 8.

The aldehyde proton spectrum and the optimized computer simulation are shown in figure 10. The signs of the coupling constants shown in table 8 are confirmed by the computer simulations of the aldehyde spectrum seen in figure 11, which have various combinations of signs assigned to these coupling constants.

Table 8. Spectral parameters<sup>a</sup> for 3.9 mol% 2-bromobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2329.522	0.0004
v(H4)	2281.244	0.0005
v(H5)	2269.889	0.0005
v(H6)	2366.214	0.0005
v(CHO)	3099.251	0.0006



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4) <sup>b</sup>	8.060	0.0007	J(H5,H6)	7.733	0.0007
J(H3,H5)	1.089	0.0007	J(H5,CHO) <sup>d</sup>	0.801	0.0008
J(H3,H6)	0.403	0.0006			
J(H3,CHO)	0.065	0.0007			
J(H4,H5)	7.353	0.0006	J(H6,CHO)	-0.060	0.0007
J(H4,H6) <sup>c</sup>	1.812	0.0007			
J(H4,CHO) <sup>e</sup>	-0.031	0.0008			

92 Transitions

Largest Difference = 0.004 Hz

82 Observed Peaks

RMS Deviation of Transitions = 0.0017

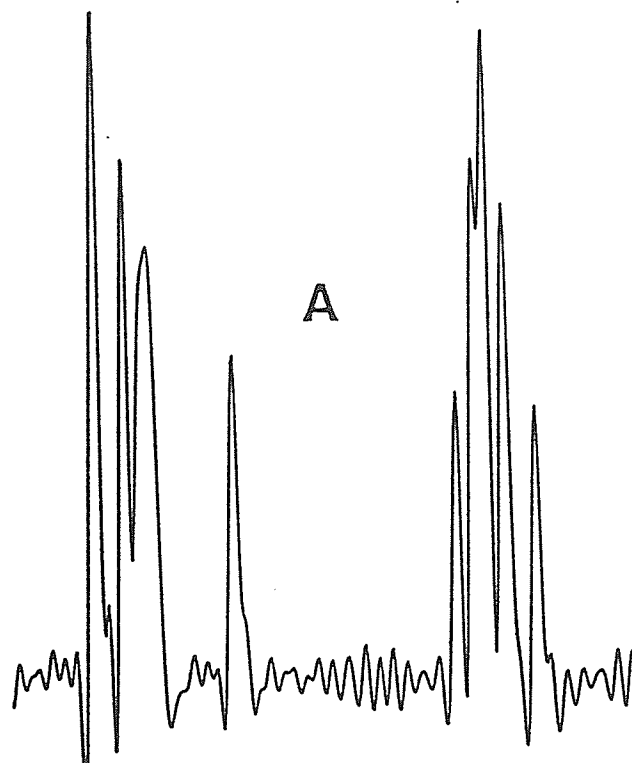
68 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Correlated with J(H3,H5) by -0.3552.
- <sup>c</sup> Correlated with J(H5,H6) by -0.3085.
- <sup>d</sup> Correlated with  $\nu(\text{CHO})$  by -0.2422 and with J(H4,CHO) by -0.2852.
- <sup>e</sup> The sign of this and other coupling constants was verified by simulating the aldehyde spectrum, using the program NUMARIT, with different combinations of signs attributed to the coupling constants.

Figure 10.    A) The experimental 300 MHz spectrum of the aldehyde proton of  
4 mol% 2-bromobenzaldehyde in acetone-d<sub>6</sub>.

                  B) The theoretical spectrum where  ${}^6J(\text{H}_4, \text{CHO})$  is -0.031 Hz.



1.0 Hz

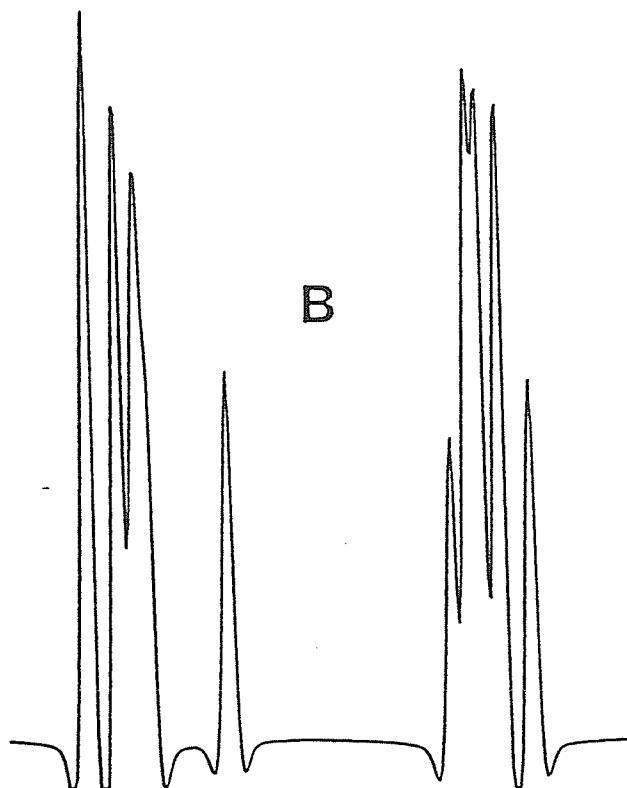
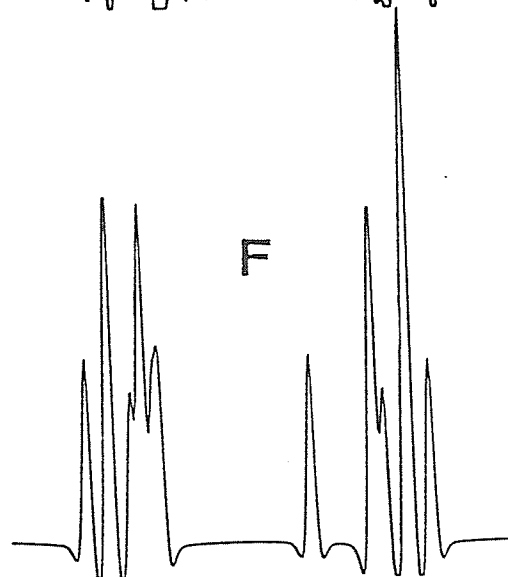
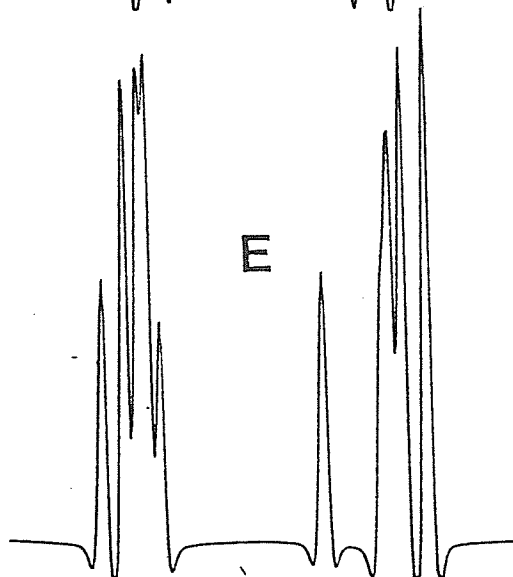
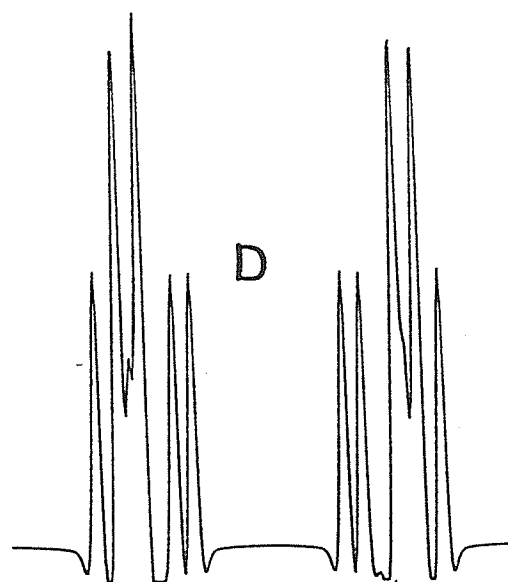
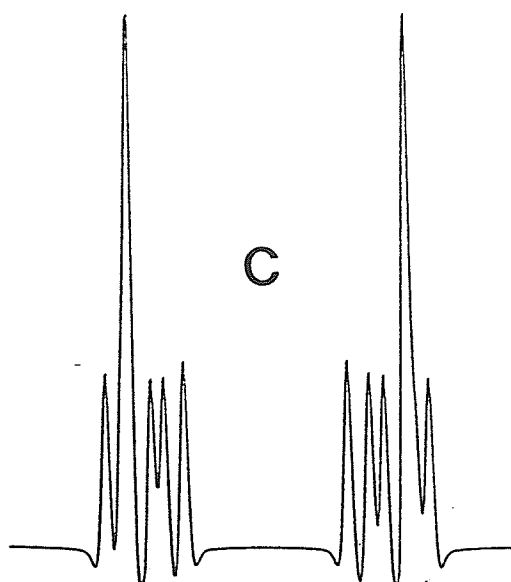
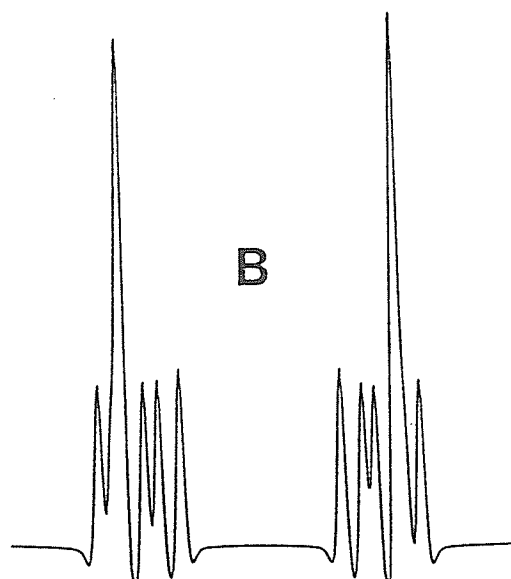
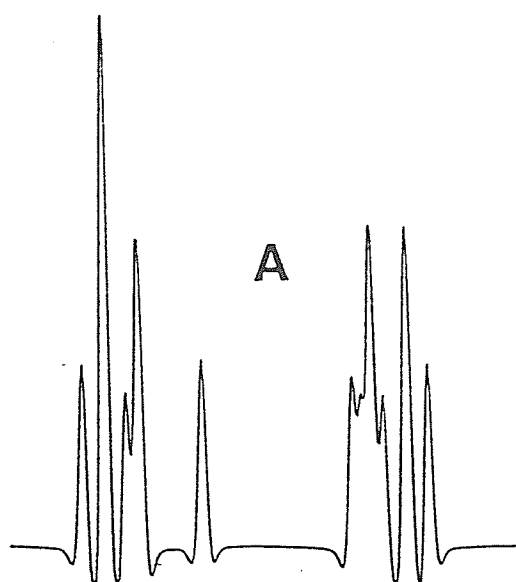


Figure 11. The theoretical spectrum of the aldehyde proton of 2-bromobenzaldehyde in acetone-d<sub>6</sub>, simulated with the coupling constants (Table 7) having the same magnitudes as in the optimized spectrum (Figure 5A) but with various combinations of the signs of these coupling constants.

A)	$^5J(\text{H3,CHO})$	+	B)	$^5J(\text{H3,CHO})$	+
	$^6J(\text{H4,CHO})$	+		$^6J(\text{H4,CHO})$	-
	$^5J(\text{H5,CHO})$	+		$^5J(\text{H5,CHO})$	+
	$^4J(\text{H6,CHO})$	-		$^4J(\text{H6,CHO})$	+
C)	$^5J(\text{H3,CHO})$	-	D)	$^5J(\text{H3,CHO})$	-
	$^6J(\text{H4,CHO})$	-		$^6J(\text{H4,CHO})$	+
	$^5J(\text{H5,CHO})$	+		$^5J(\text{H5,CHO})$	+
	$^4J(\text{H6,CHO})$	-		$^4J(\text{H6,CHO})$	-
E)	$^5J(\text{H3,CHO})$	-	F)	$^5J(\text{H3,CHO})$	-
	$^6J(\text{H4,CHO})$	-		$^6J(\text{H4,CHO})$	+
	$^5J(\text{H5,CHO})$	+		$^5J(\text{H5,CHO})$	+
	$^4J(\text{H6,CHO})$	+		$^4J(\text{H6,CHO})$	+





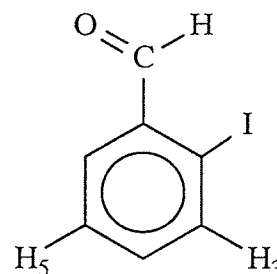
### 3.1.5

The  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for saturated solutions of 2-iodobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , measured at 300 K are given in tables 9 and 10, respectively.

The spectrum for the aldehyde proton for 2-iodobenzaldehyde in acetone- $\text{d}_6$  is shown in figure 12 along with the computer simulation. The spectrum for the ring proton *para* to the aldehyde group is seen in figure 13 and clearly shows splitting due to spin-spin coupling to the aldehyde proton.

Table 9. Spectral parameters<sup>a</sup> for a saturated<sup>b</sup> solution of 2-iodobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2416.616	0.0004
v(H4)	2226.562	0.0004
v(H5)	2275.320	0.0005
v(H6)	2353.721	0.0004
v(CHO) <sup>c</sup>	3014.382	0.0007



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	7.925	0.0006	J(H5,H6)	7.720	0.0006
J(H3,H5)	1.106	0.0006	J(H5,CHO)	0.769	0.0008
J(H3,H6)	0.414	0.0006			
J(H3,CHO) <sup>d</sup>	0.092	0.0008			
J(H4,H5)	7.327	0.0006	J(H6,CHO)	-0.045	0.0008
J(H4,H6)	1.787	0.0006			
J(H4,CHO)	-0.023	0.0008			

80 Transitions

Largest Difference = 0.006 Hz

84 Observed Peaks

RMS Deviation of Transitions = 0.0018

71 Assigned Transitions

Notes:

<sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.

<sup>b</sup> A saturated solution of less than 1.5 mol% 2-iodobenzaldehyde.

<sup>c</sup> Correlated with J(H4,CHO) by -0.1494 and with J(H6,CHO) by 0.1450.

<sup>d</sup> Correlated with J(H4,CHO) by 0.2515.

Figure 12. The experimental, (A), and the computer simulated, (B), spectrum for the aldehyde proton of 2-iodobenzaldehyde in acetone-d<sub>6</sub>.

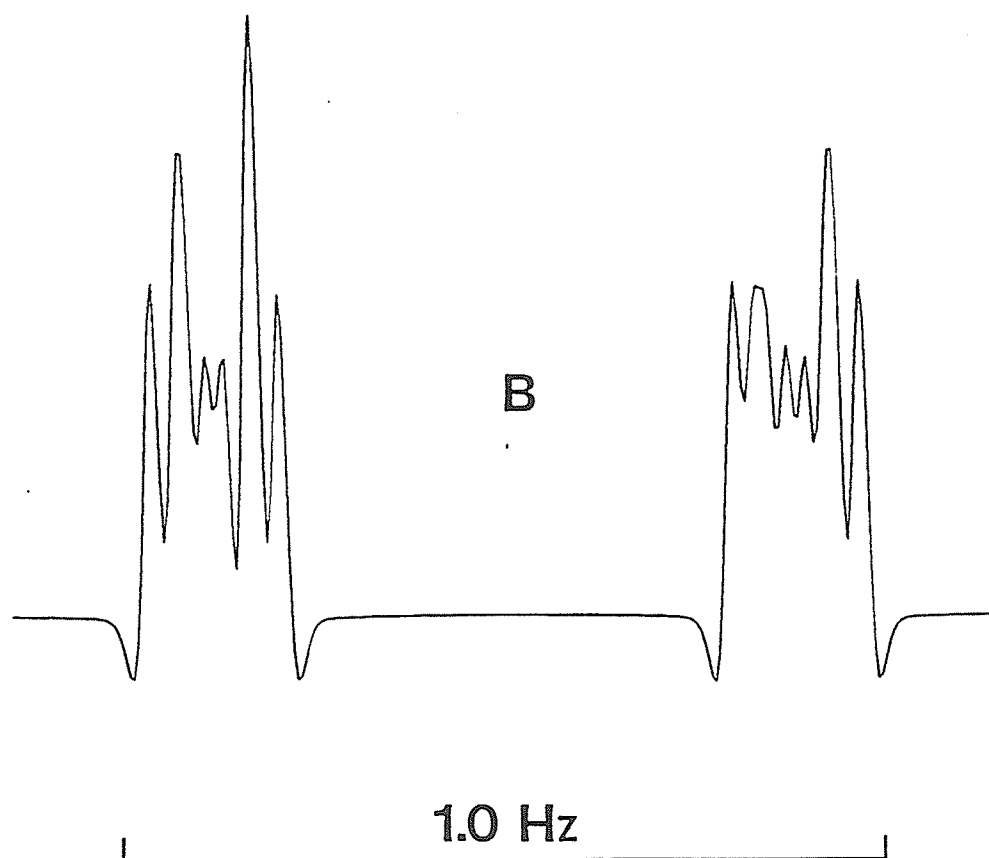
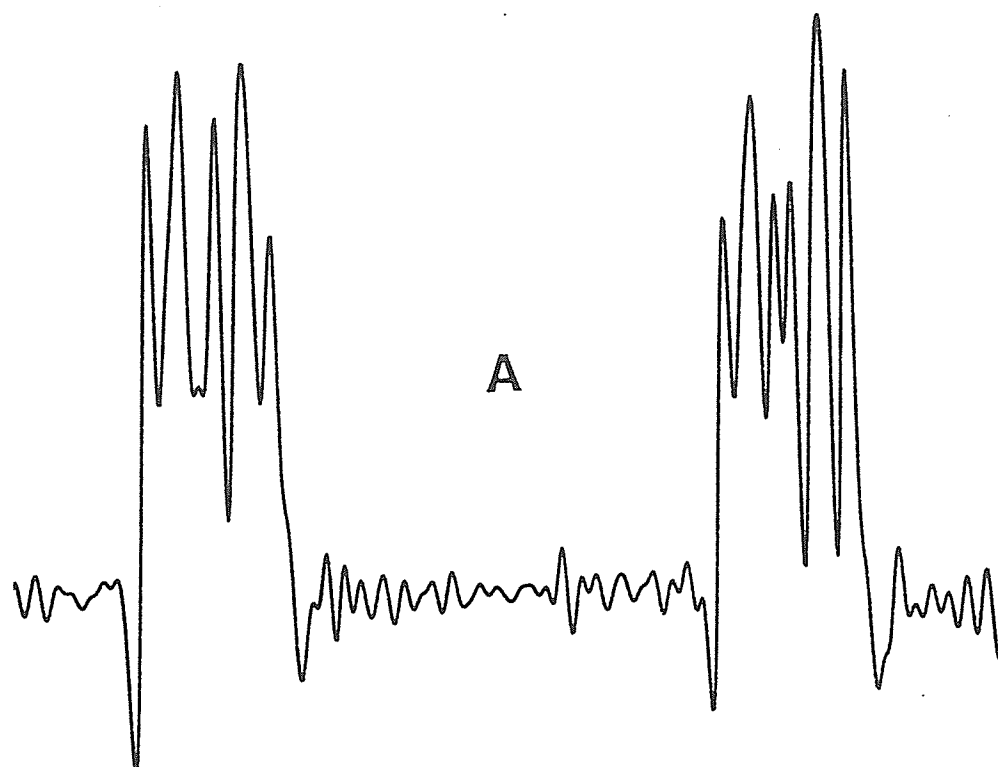


Figure 13. The  $^1\text{H}$  nmr spectrum of the ring proton para to the aldehyde group of 2-iodobenzaldehyde in acetone- $\text{d}_6$ <sup>1</sup>.

(A) The experimental spectrum.

(B) The computer simulated spectrum.

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<sup>1</sup> Several small peaks in the spectrum correspond to a small amount of impurity in the sample. These peaks can be identified by their absence in the computer simulated spectrum.

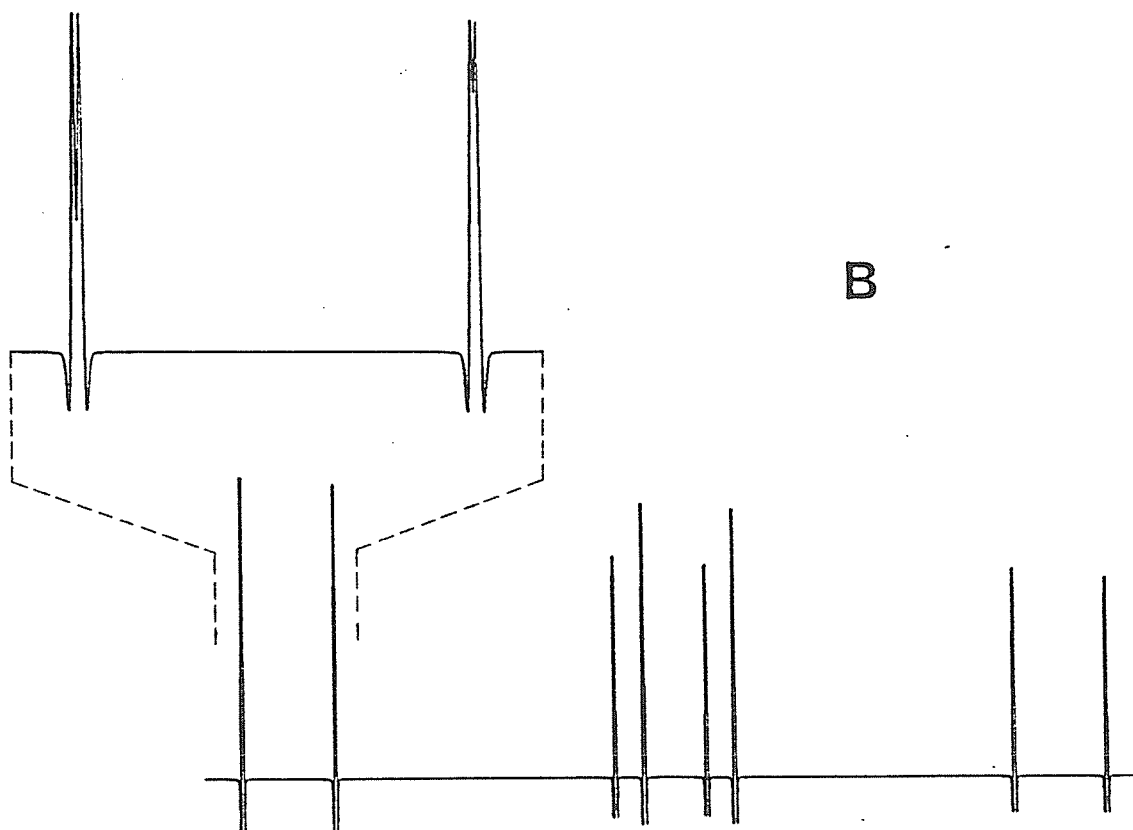
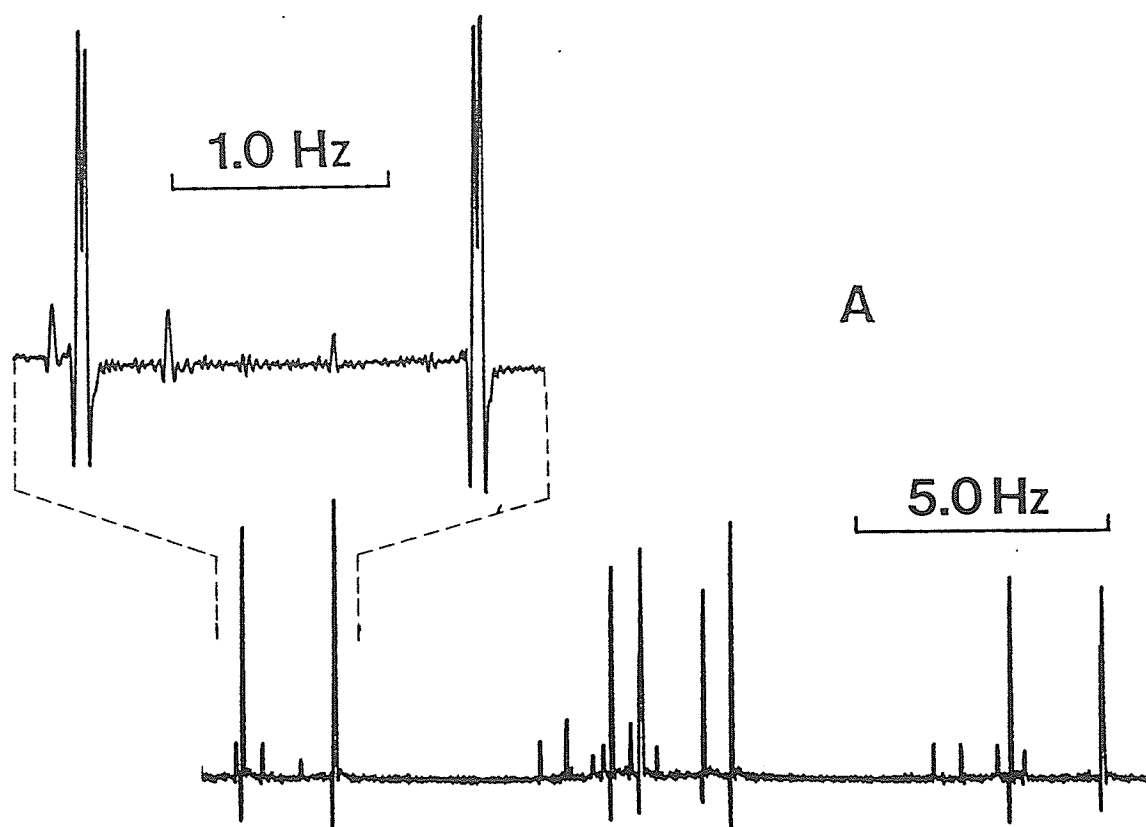
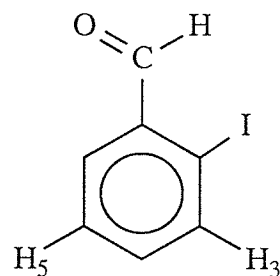




Table 10. Spectral parameters<sup>a</sup> for a saturated<sup>b</sup> solution of 2-iodobenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2364.155	0.0003
v(H4)	2165.450	0.0003
v(H5)	2221.130	0.0003
v(H6)	2337.316	0.0003
v(CHO) <sup>c</sup>	2989.317	0.0009



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	7.912	0.0004	J(H5,H6)	7.709	0.0004
J(H3,H5)	1.124	0.0004	J(H5,CHO)	0.825	0.0005
J(H3,H6)	0.407	0.0004			
J(H3,CHO)	0.051	0.0005			
J(H4,H5)	7.279	0.0004	J(H6,CHO)	-0.001	0.0005
J(H4,H6)	1.816	0.0004			
J(H4,CHO)	-0.004	0.0005			

80 Transitions

Largest Difference = 0.003 Hz

84 Observed Peaks

RMS Deviation of Transitions = 0.0011

66 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> A saturated solution of less than 1.5 mol% 2-iodobenzaldehyde.
- <sup>c</sup> Correlated with J(H3,CHO) by -0.3016, with J(H5,CHO) by 0.3009, and with J(H6,CHO) by 0.3012.

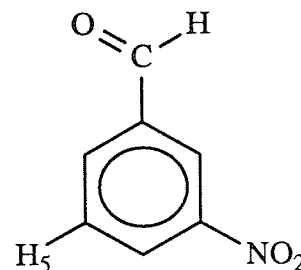
### 3.1.6

Tables 11 and 12 show the  $^1\text{H}$  nmr parameters for 3-nitrobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively, at 300 K. The acetone- $\text{d}_6$  solution contained 4 mol% 3-nitrobenzaldehyde and the  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution was a saturated solution, probably containing less than 1.5 mol% solute.

Nuclei having a quadrupole moment, such as  $^{14}\text{N}$ , relax rapidly via not only a dipolar but also a quadrupolar relaxation mechanism. The effects of this rapid relaxation can be observed as line broadening in the nmr spectra of nuclei which are spin coupled to the quadrupolar nucleus. In the analyses of 3-nitrobenzaldehyde, extensive line broadening was encountered in the spectra for ring protons H2 and H4, arising from quadrupolar relaxation in the  $^{14}\text{N}$  nucleus of the nitro group. Because of these effects, several of the spectral parameters in this analysis could not be accurately determined.

Table 11. Spectral parameters<sup>a</sup> for 4 mol% 3-nitrobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2615.515	0.0004
v(H4)	2562.235	0.0005
v(H5)	2381.485	0.0005
v(H6)	2511.583	0.0004
v(CHO)	3065.131	0.0004



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	2.374	0.0006	J(H5,H6)	7.633	0.0007
J(H2,H5)	0.496	0.0007	J(H5,CHO) <sup>d</sup>	0.459	0.0007
J(H2,H6)	1.510	0.0006			
J(H2,CHO)	0.000	0.0006			
J(H4,H5) <sup>b</sup>	8.201	0.0007	J(H6,CHO)	-0.115	0.0006
J(H4,H6)	1.115	0.0006			
J(H4,CHO) <sup>c</sup>	0.000	0.0006			

80 Transitions

Largest Difference = 0.006 Hz

66 Observed Peaks

RMS Deviation of Transitions = 0.0017

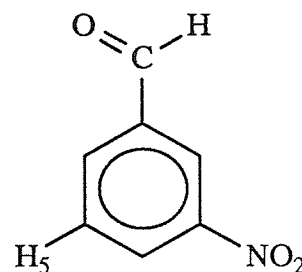
72 Assigned Transitions

## Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H nmr at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Correlated with  $\nu(\text{H4})$  by 0.1264, with  $J(\text{H2},\text{H5})$  by -0.1322, and with  $J(\text{H5},\text{H6})$  by -0.1222.
- <sup>c</sup> The value of  $J(\text{H4},\text{CHO})$  is somewhat uncertain due to the quadrupolar relaxation effects of the <sup>14</sup>N of the nitro group causing extensive line broadening in the region of the spectrum for the ring proton at position 4.
- <sup>d</sup> Correlated with  $\nu(\text{H5})$  by 0.1920 and with  $J(\text{H5},\text{H6})$  by 0.1280.

Table 12. Spectral parameters<sup>a</sup> for a saturated<sup>b</sup> solution of  
3-nitrobenzaldehyde in CS<sub>2</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2584.094	0.0019
v(H4) <sup>c</sup>	2523.149	0.0024
v(H5)	2316.004	0.0014
v(H6)	2450.717	0.0014
v(CHO)	3022.094	0.0014



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4) <sup>d</sup>	2.297	0.0029	J(H5,H6)	7.606	0.0020
J(H2,H5)	0.502	0.0024	J(H5,CHO)	0.520	0.0020
J(H2,H6) <sup>e</sup>	1.519	0.0022			
J(H2,CHO)	-0.029	0.0022			
J(H4,H5)	8.128	0.0023	J(H6,CHO)	-0.121	0.0020
J(H4,H6)	1.171	0.0023			
J(H4,CHO)	-0.027	0.0028			

80 Transitions

Largest Difference = 0.010 Hz

89 Observed Peaks

RMS Deviation of Transitions = 0.0055

64 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained probably less than 1.5 mol% 3-nitrobenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with J(H4,CHO) by 0.5774.
- <sup>d</sup> Correlated with  $\nu$ (H2) by -0.2761 and with J(H2,H5) by 0.2695.
- <sup>e</sup> Correlated with J(H2,CHO) by 0.1304.

### 3.1.7

The  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for saturated solutions of 2-nitrobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  are shown in tables 13 and 14, respectively.

As with the analysis of 3-nitrobenzaldehyde, quadrupolar relaxation effects involving the  $^{14}\text{N}$  nucleus of the nitro group are apparent in the spectrum of the ring proton at the position ortho to the nitro group, i.e. proton H3. Some difficulty in the analysis also arose from the small chemical shift differences between ring protons H4, H5, and H6. However, in the spectrum of the  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution, larger differences between chemical shifts lead to a more first order spectrum and hence a simpler analysis.

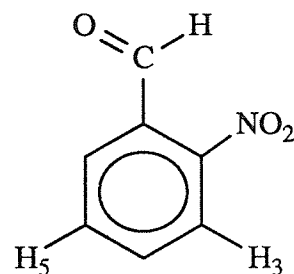
The aldehyde proton spectrum for 2-nitrobenzaldehyde in acetone- $\text{d}_6$  is seen in figure 14 and that for the ring protons H4, H5, and H6 is shown in figure 15. The sign of  $J(\text{H4}, \text{CHO})$  was verified by simulation of the aldehyde spectrum with all parameters the same as the optimized spectrum except for  $J(\text{H4}, \text{CHO})$ , for which the sign was changed. This simulation is also seen in figure 14. The aldehyde proton spectrum for 2-nitrobenzaldehyde in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  is seen in figure 16 along with the computer simulated spectrum.

The relative AM1 energies of 2-nitrobenzaldehyde at various degrees of rotation of the aldehyde group with respect to the plane of the ring are shown in table 15. The data in table 15 were fit to the potential curve plotted in figure 17.



Table 13. Spectral parameters<sup>a</sup> for a saturated<sup>b</sup> solution of 2-nitrobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2447.6 <sup>c</sup>	
v(H4)	2376.609	0.0037
v(H5)	2383.625	0.0081
v(H6)	2387.776	0.0067
v(CHO)	3108.908	0.0026



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4) <sup>d</sup>	8.134	0.0062	J(H5,H6)	7.675	0.0055
J(H3,H5)	1.165	0.0087	J(H5,CHO) <sup>b</sup>	0.645	0.0072
J(H3,H6) <sup>e</sup>	0.393	0.0063			
J(H3,CHO)	0.179				
J(H4,H5) <sup>f</sup>	7.502	0.0135	J(H6,CHO)	-0.127	0.0061
J(H4,H6) <sup>g</sup>	1.489	0.0146			
J(H4,CHO)	-0.095	0.0046			

102 Transitions

Largest Difference = 0.023 Hz

62 Observed Peaks

RMS Deviation of Transitions = 0.0102<sup>i</sup>

76 Assigned Transitions

Notes:

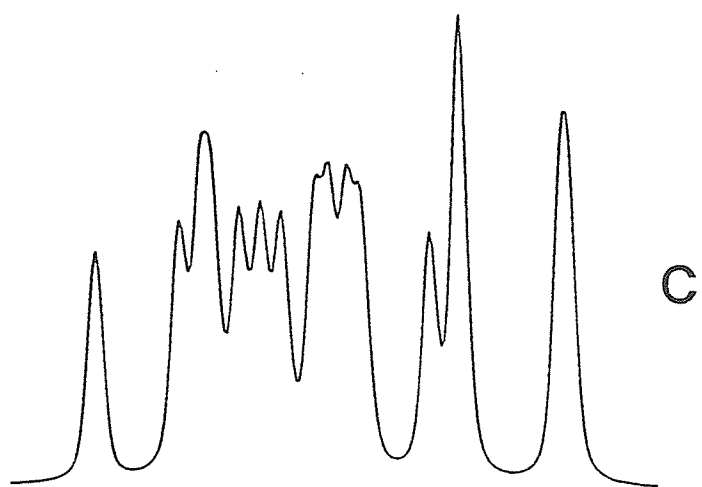
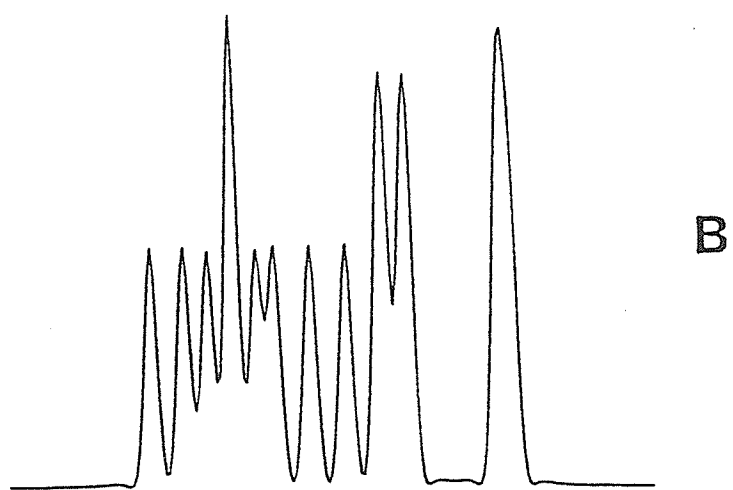
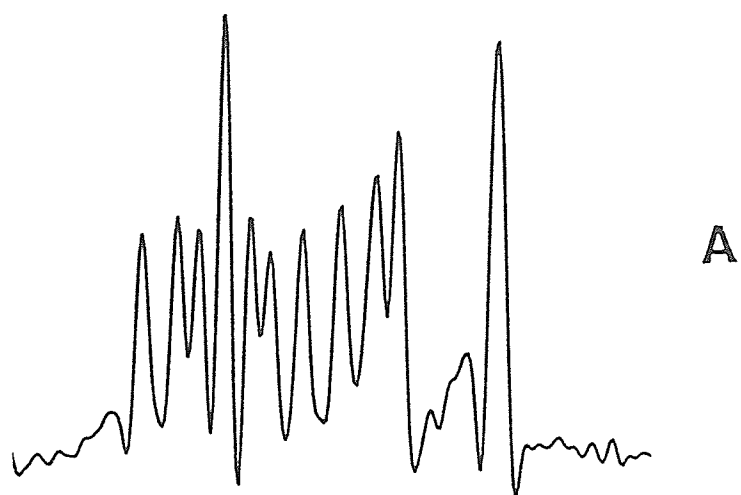
- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The concentration of 2-nitrobenzaldehyde was probably less than 1.5 mol%.
- <sup>c</sup>  $\nu(\text{H3})$  and  $J(\text{H3},\text{CHO})$  were not iterated upon because the area in the spectrum corresponding to the ring proton at position 3 displays extensive line broadening due to the quadrupolar relaxation effects of the <sup>14</sup>N nucleus of the nitro group, and hence it became impossible to pick the peaks with any accuracy.
- <sup>d</sup> Correlated with  $\nu(\text{H4})$  by 0.5166 and with  $J(\text{H3},\text{H5})$  by -0.5173.
- <sup>e</sup> Correlated with  $J(\text{H3},\text{H5})$  by -0.5186.
- <sup>f</sup> Correlated with  $\nu(\text{H5})$  by 0.7878, with  $\nu(\text{H4})$  by -0.7716, and with  $J(\text{H4},\text{H6})$  by -0.8980.
- <sup>g</sup> Correlated with  $\nu(\text{H5})$  by -0.7044.
- <sup>h</sup> Correlated with  $J(\text{H6},\text{CHO})$  by -0.5827.
- <sup>i</sup> The RMS deviation is much greater than usual due to the inaccuracy of peak picking because of quadrupolar effects.

Figure 14. The  $^1\text{H}$  nmr spectrum of the aldehyde proton of 2-nitrobenzaldehyde in acetone- $\text{d}_6$  at 300K.

(A) The experimental spectrum.

(B) The computer simulated spectrum with  $J(\text{H}_4, \text{CHO}) = -0.095 \text{ Hz}$ .

(C) As (B) but with  $J(\text{H}_4, \text{CHO}) = 0.095 \text{ Hz}$ .



1.0 Hz

Figure 15. The  $^1\text{H}$  nmr spectrum corresponding to the ring protons at positions 4, 5, and 6 of 2-nitrobenzaldehyde in acetone- $\text{d}_6$  at 300K.

(A) The experimental spectrum.

(B) The computer simulated spectrum.

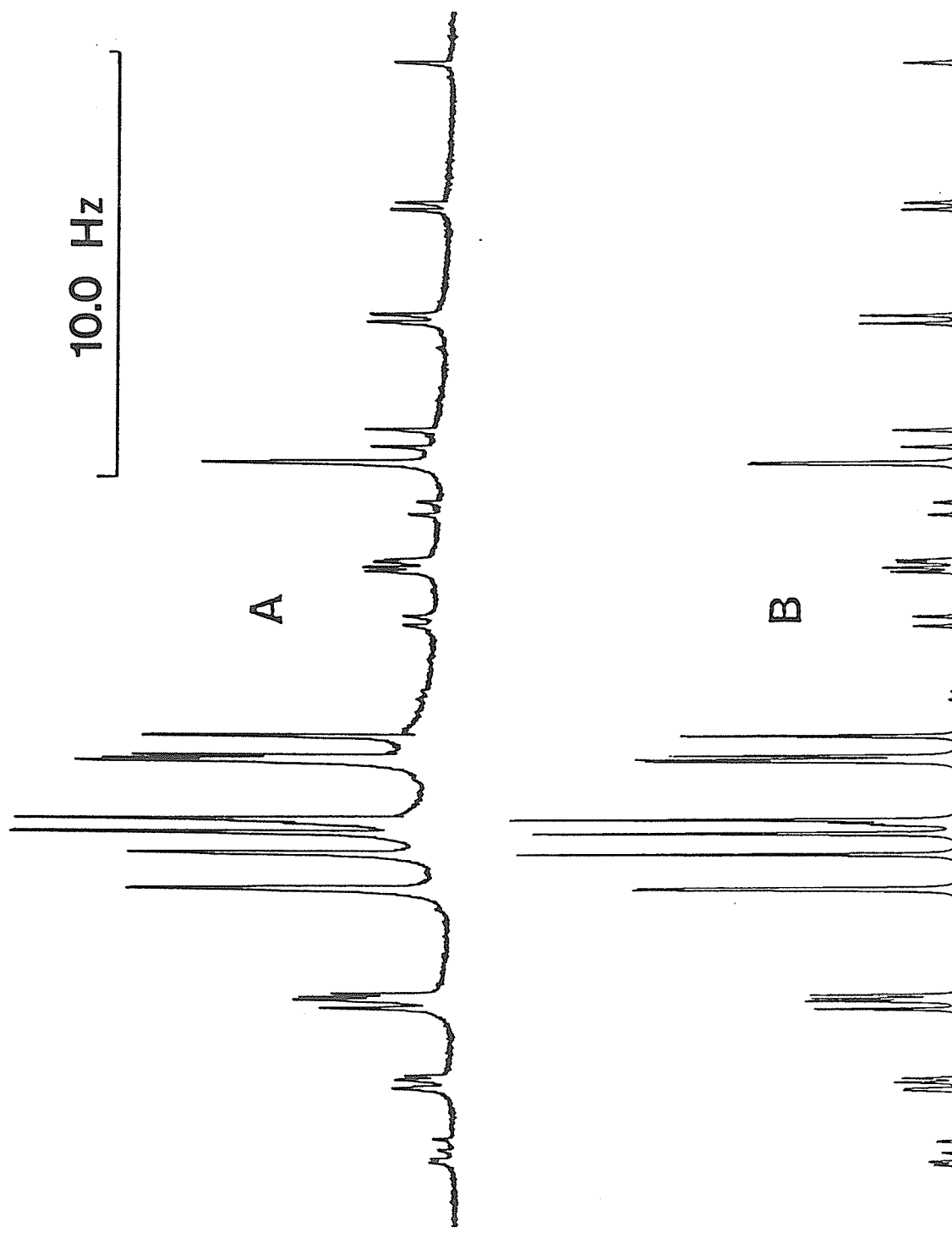
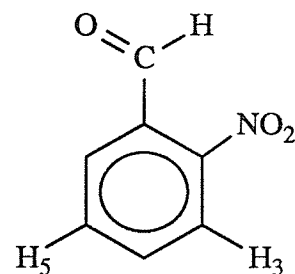


Table 14. Spectral Parameters<sup>a</sup> for a saturated<sup>b</sup> solution of 2-nitrobenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
$\nu(\text{H3})$	2405.517	0.0020
$\nu(\text{H4})^c$	2314.374	0.0012
$\nu(\text{H5})^d$	2324.843	0.0011
$\nu(\text{H6})$	2361.098	0.0009
$\nu(\text{CHO})$	3083.960	0.0010



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
$J(\text{H3}, \text{H4})^e$	8.146	0.0022	$J(\text{H5}, \text{H6})$	7.690	0.0016
$J(\text{H3}, \text{H5})$	1.168	0.0020	$J(\text{H5}, \text{CHO})$	0.738	0.0016
$J(\text{H3}, \text{H6})$	0.411	0.0016			
$J(\text{H3}, \text{CHO})$	0.115	0.0018			
$J(\text{H4}, \text{H5})$	7.435	0.0014	$J(\text{H6}, \text{CHO})$	-0.036	0.0013
$J(\text{H4}, \text{H6})^f$	1.522	0.0016			
$J(\text{H4}, \text{CHO})^g$	-0.088	0.0016			

94 Transitions

Largest Difference = 0.009 Hz

76 Observed Peaks

RMS Deviation of Transitions = 0.0035

60 Assigned Transitions

Notes:

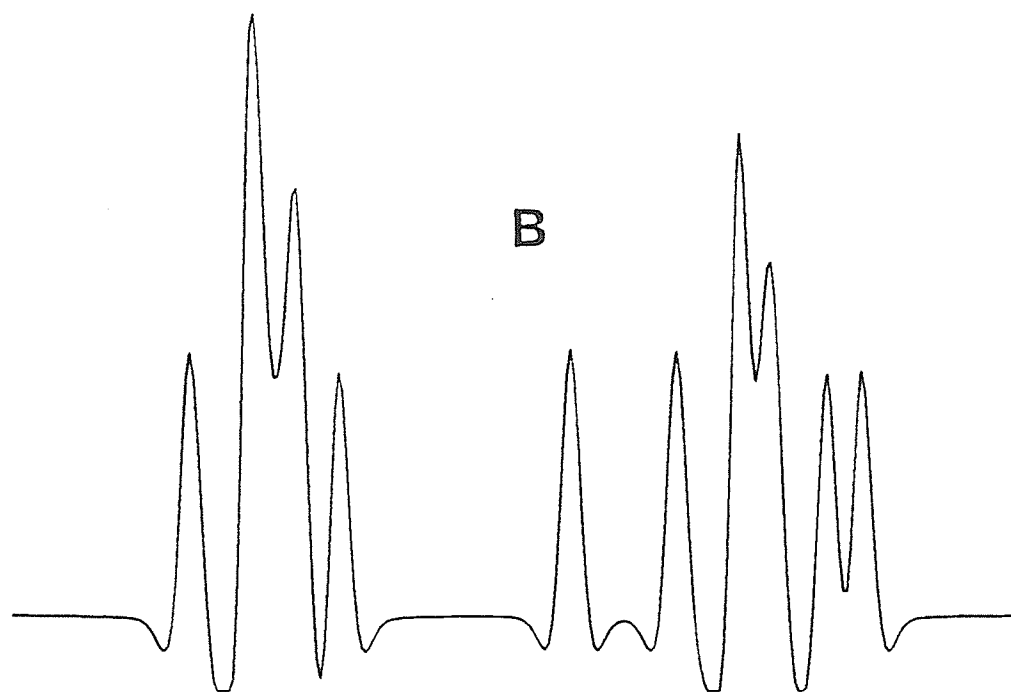
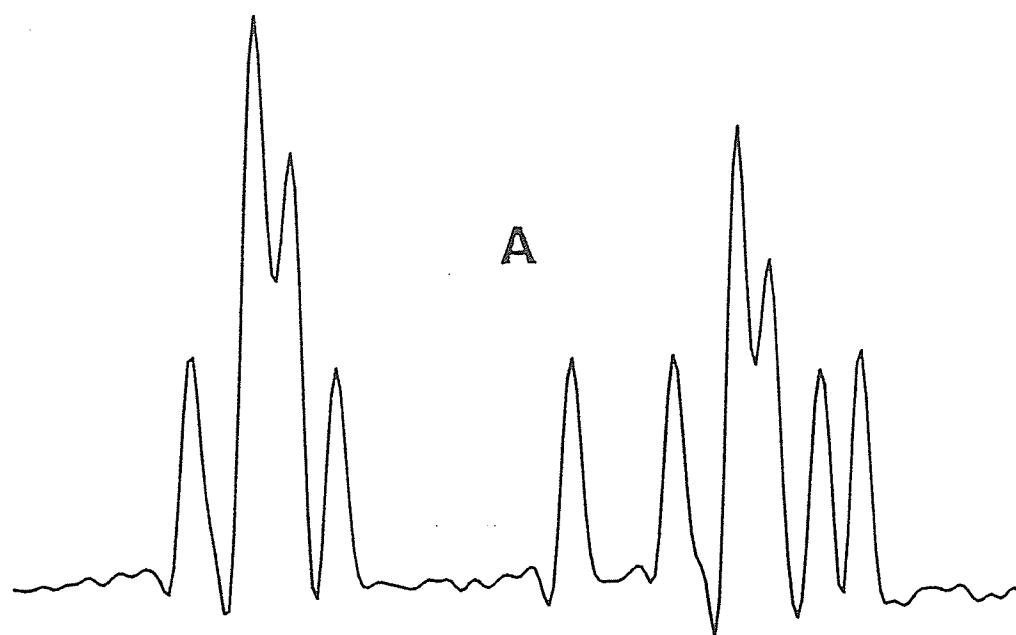
- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H nmr at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained probably less than 1.5 mol% 3-nitrobenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with J(H4,H6) by -0.3401.
- <sup>d</sup> Correlated with  $\nu$ (H4) by -0.3180, with J(H3,H5) by 0.3086 and with J(H5,H6) by -0.2862.
- <sup>e</sup> Correlated with  $\nu$ (H3) by 0.4564 and with J(H3,H5) by -0.2688.
- <sup>f</sup> Correlated with J(H5,H6) by -0.3286.
- <sup>g</sup> Correlated with J(H5,CHO) by -0.3161.



Figure 16. The  $^1\text{H}$  nmr spectrum of the aldehyde proton of 2-nitrobenzaldehyde in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  at 300K.

(A) The experimental spectrum.

(B) The computer simulated spectrum.



1.0 Hz

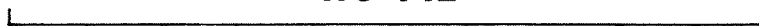


Table 15. Semiempirical AM1 Molecular Orbital Calculations for  
o-Nitrobenzaldehyde.

$\theta(\text{deg})$	Energy <sub>rel</sub> (kJ/mol)
0	0.000
15	-0.747
30	-1.254
45	-0.997
60	0.041
75	1.587
90	3.181
105	1.576
120	0.221
135	1.135
150	2.996
165	5.391
180	7.347

Note:

The benzene ring moiety was kept planar; however, all bond lengths and angles in the molecule were allowed to vary during optimization.  $\theta = 0$  corresponds to the O-trans rotamer. It was found in a previous set of AM1 calculations on o-nitrobenzaldehyde that if the initial input conformation had both the nitro and aldehydes group in plane, the optimization procedure did not allow the nitro group to rotate out of plane. Consequently, the nitro group was initially  $15^\circ$  out of plane for each calculation presented in table 15. These calculations showed the nitro group out of plane in both the O-trans and O-cis conformers.

Figure 17. The AM1 potential of 2-nitrobenzaldehyde upon rotation of the aldehyde group through 180°<sup>1</sup>. The solid line is the fitted potential function:

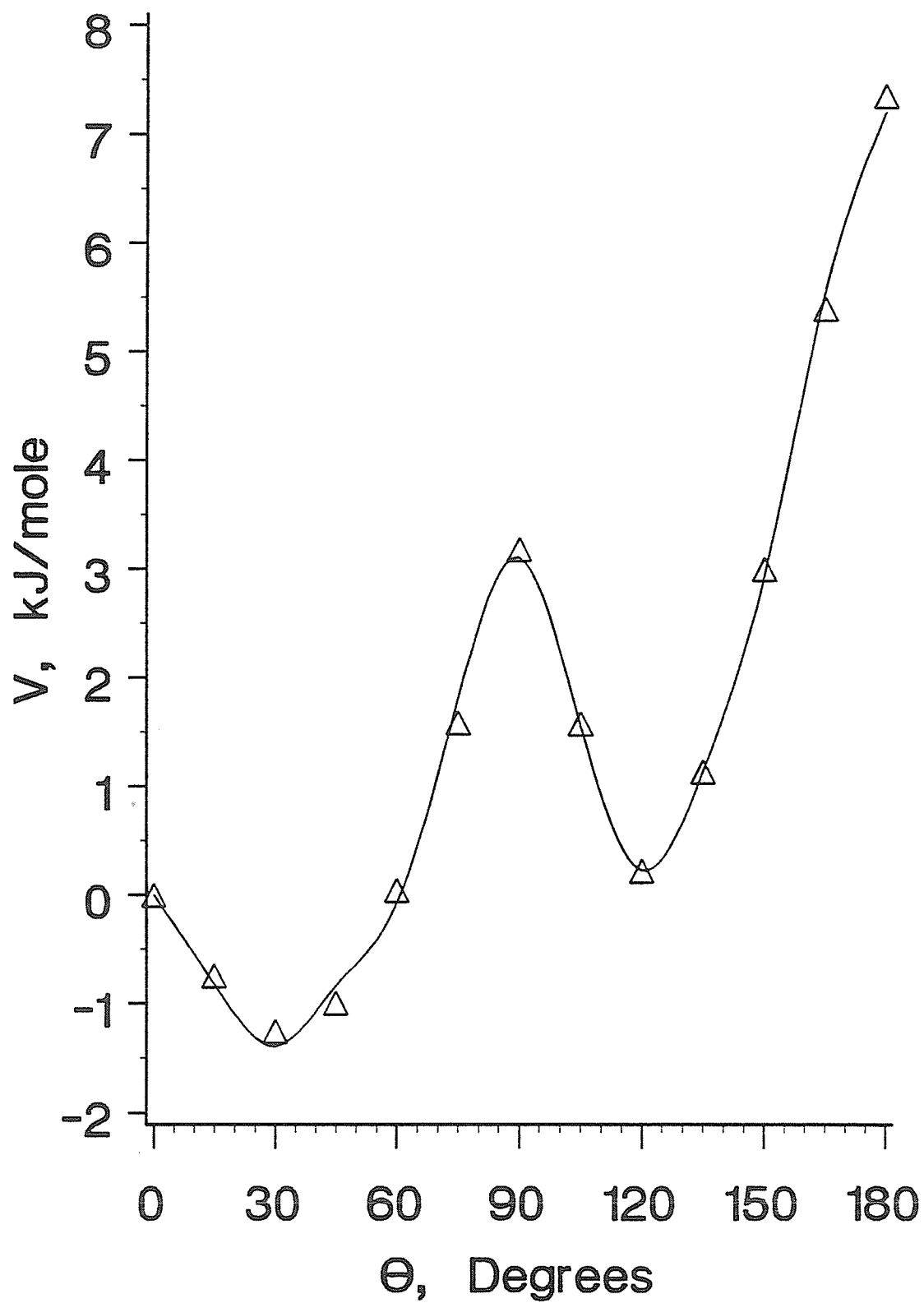
$$\begin{aligned}
 V(\theta) = & 5.0(1)\sin^2\left(\frac{\theta}{2}\right) - 0.8(1)\sin^2(\theta) \\
 & + 2.2(1)\sin^2\left(\frac{3\theta}{2}\right) - 3.2(1)\sin^2(2\theta) \\
 & + 0.3(1)\sin^2(3\theta) - 0.7(1)\sin^2(4\theta)
 \end{aligned}$$

and the triangles are the energies from the individual molecular orbital computations.

---

<sup>1</sup>  $\theta = 0^\circ$  corresponds to the O-trans rotamer while  $\theta = 180^\circ$  corresponds to the O-cis rotamer.

## 2-Nitrobenzaldehyde AM1

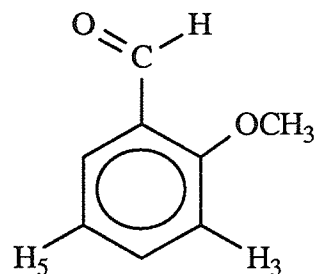


### 3.1.8

The  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for 4 mol% solutions of 2-methoxybenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  are shown in tables 16 and 17, respectively.

Table 16. Spectral parameters<sup>a</sup> for 4.0 mol% 2-methoxybenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2157.187	0.0002
v(H4) <sup>b</sup>	2287.190	0.0002
v(H5)	2116.486	0.0002
v(H6)	2322.684	0.0001
v(CHO)	3134.390	0.0001
v(OMe) <sup>c</sup>	1188.90	



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	8.467	0.0002	J(H5,H6)	7.688	0.0002
J(H3,H5)	0.936	0.0002	J(H5,CHO)	0.838	0.0002
J(H3,H6)	0.433	0.0002	J(H5,OMe)	-0.044	0.0004
J(H3,CHO)	0.000	0.0002			
J(H3,OMe) <sup>d</sup>	-0.300	0.0002			
J(H4,H5)	7.312	0.0002	J(H6,CHO)	-0.167	0.0002
J(H4,H6)	1.863	0.0002	J(H6,OMe)	0.000	0.0002
J(H4,CHO)	0.000	0.0002			
J(H4,OMe)	0.091	0.0002	J(CHO,OMe)	0.000	0.0002

608 Transitions

Largest Difference = 0.005 Hz

136 Observed Peaks

RMS Deviation of Transitions = 0.0015

407 Assigned Transitions

Notes:

<sup>a</sup> In Hz at 300K. <sup>1</sup>H nmr at 300.135 MHz to high frequency of TMS.

<sup>b</sup> Correlated with J(H4,OMe) by -0.1445.

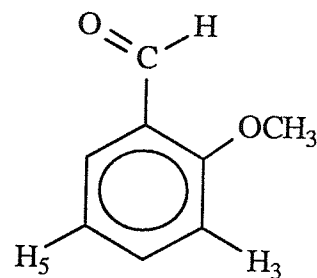
<sup>c</sup> Not optimized.

<sup>d</sup> Correlated with J(H3,H5) by 0.1140 and ith J(H3,H6) by 0.1037.



Table 17. Spectral parameters<sup>a</sup> for 4.0 mol%<sup>b</sup> 2-methoxybenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2069.844	0.0013
v(H4)	2228.948	0.0007
v(H5) <sup>c</sup>	2074.056	0.0008
v(H6)	2302.598	0.0007
v(CHO)	3106.171	0.0007
v(OMe)	1162.000	0.0007



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	8.339	0.0013	J(H5,H6)	7.648	0.0013
J(H3,H5)	0.932	0.0014	J(H5,CHO)	0.859	0.0010
J(H3,H6) <sup>d</sup>	0.434	0.0015	J(H5,OMe)	0.001	0.0007
J(H3,CHO)	-0.006	0.0012			
J(H3,OMe) <sup>e</sup>	-0.338	0.0011			
J(H4,H5)	7.306	0.0011	J(H6,CHO) <sup>f</sup>	-0.134	0.0010
J(H4,H6)	1.870	0.0010	J(H6,OMe)	0.001	0.0007
J(H4,CHO)	0.000	0.0009			
J(H4,OMe)	0.090	0.0007	J(CHO,OMe)	0.001	0.0006

661 Transitions

Largest Difference = 0.017 Hz

99 Observed Peaks

RMS Deviation of Transitions = 0.0056

362 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300K. <sup>1</sup>H resonance at 300.135 to high frequency of TMS.
- <sup>b</sup> The solution contained 4.0 mol% 2-methoxybenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with J(H3,H6) by 0.2236 and with J(H5,H6) by -0.3865.
- <sup>d</sup> Correlated with J(H5,H6) by -0.4961.
- <sup>e</sup> Correlated with  $\nu$ (H3) by 0.2933 and with  $\nu$ (OMe) by 0.2966.
- <sup>f</sup> Correlated with  $\nu$ (CHO) by -0.2158.

### 3.1.9

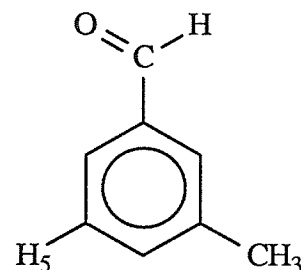
Tables 18 and 19 show the  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for 4 mol% solutions of 3-tolualdehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively.

A second radio frequency was used to decouple the protons of the methyl group from the ring protons to aid in the analysis. The small chemical shift difference between ring protons H2 and H6 (1.50 Hz in acetone- $\text{d}_6$ ) caused some problems in the analysis, but all parameters for the ring protons were eventually determined.

The experimental  $^1\text{H}$  nmr spectrum for the aldehyde proton of 3-tolualdehyde in acetone- $\text{d}_6$  is shown in figure 18 along with simulations which verify the sign and magnitude of  $J(\text{H}_4, \text{CHO})$ . The experimental and computer simulated spectrum of ring protons H4 and H5 with the methyl group decoupled are seen in figure 19 and those for protons H2 and H6 are seen in figure 20. The ring proton spectra without decoupling of the methyl protons are seen along with the computer simulations in figure 21. The methyl proton spectrum is shown in figure 22.

Table 18. Spectral parameters<sup>a</sup> for 4.0 mol% 3-tolualdehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2315.605	0.0008
v(H4) <sup>b</sup>	2253.310	0.0016
v(H5) <sup>c</sup>	2242.420	0.0013
v(H6)	2314.101	0.0009
v(CHO)	3002.151	0.0005
v(CH3)	725.826	0.0005



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	1.871	0.0014	J(H5,H6)	7.626	0.0016
J(H2,H5) <sup>d</sup>	0.572	0.0015	J(H5,CHO)	0.418	0.0010
J(H2,H6) <sup>e</sup>	1.645	0.0012	J(H5,CH3)	0.343	0.0009
J(H2,CHO)	-0.162	0.0010			
J(H2,CH3)	-0.739	0.0008			
J(H4,H5)	7.565	0.0021	J(H6,CHO)	-0.164	0.0010
J(H4,H6)	1.205	0.0015	J(H6,CH3)	-0.601	0.0009
J(H4,CHO) <sup>f</sup>	0.015	0.0011			
J(H4,CH3) <sup>g</sup>	-0.718	0.0009			

653 Transitions

Largest Difference = 0.020 Hz

98 Observed Peaks

RMS Deviation of Transitions = 0.0052

371 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Correlated with  $\nu(\text{H5})$  by -0.6315, with  $J(\text{H4},\text{H5})$  by 0.7615.
- <sup>c</sup> Correlated with  $J(\text{H4},\text{H5})$  by -0.6900.
- <sup>d</sup> Correlated with  $J(\text{H2},\text{H4})$  by -0.3022 and with  $J(\text{H5},\text{H6})$  by -0.2930.
- <sup>e</sup> Correlated with  $J(\text{H5},\text{H6})$  by 0.3462.
- <sup>f</sup> The sign and magnitude of  $J(\text{H4},\text{CHO})$  were verified by simulation of the aldehyde spectrum using the program NUMARIT.
- <sup>g</sup> Correlated with  $H(\text{H5},\text{CH3})$  by -0.3008.

Figure 18. The 300 MHz spectrum of the aldehyde proton of 3-tolualdehyde in acetone-d<sub>6</sub> at 300 K.

- (A) The experimental spectrum.
- (B) The theoretical spectrum with optimized parameters  
where  $J(\text{H4}, \text{CHO}) = +0.014 \text{ Hz}$ .
- (C) The theoretical spectrum with  ${}^6J(\text{H4}, \text{CHO}) = -0.014 \text{ Hz}$  but all  
other parameters the same as in (C).
- (D) As (C), but with  ${}^6J(\text{H4}, \text{CHO}) = 0.000 \text{ Hz}$ .

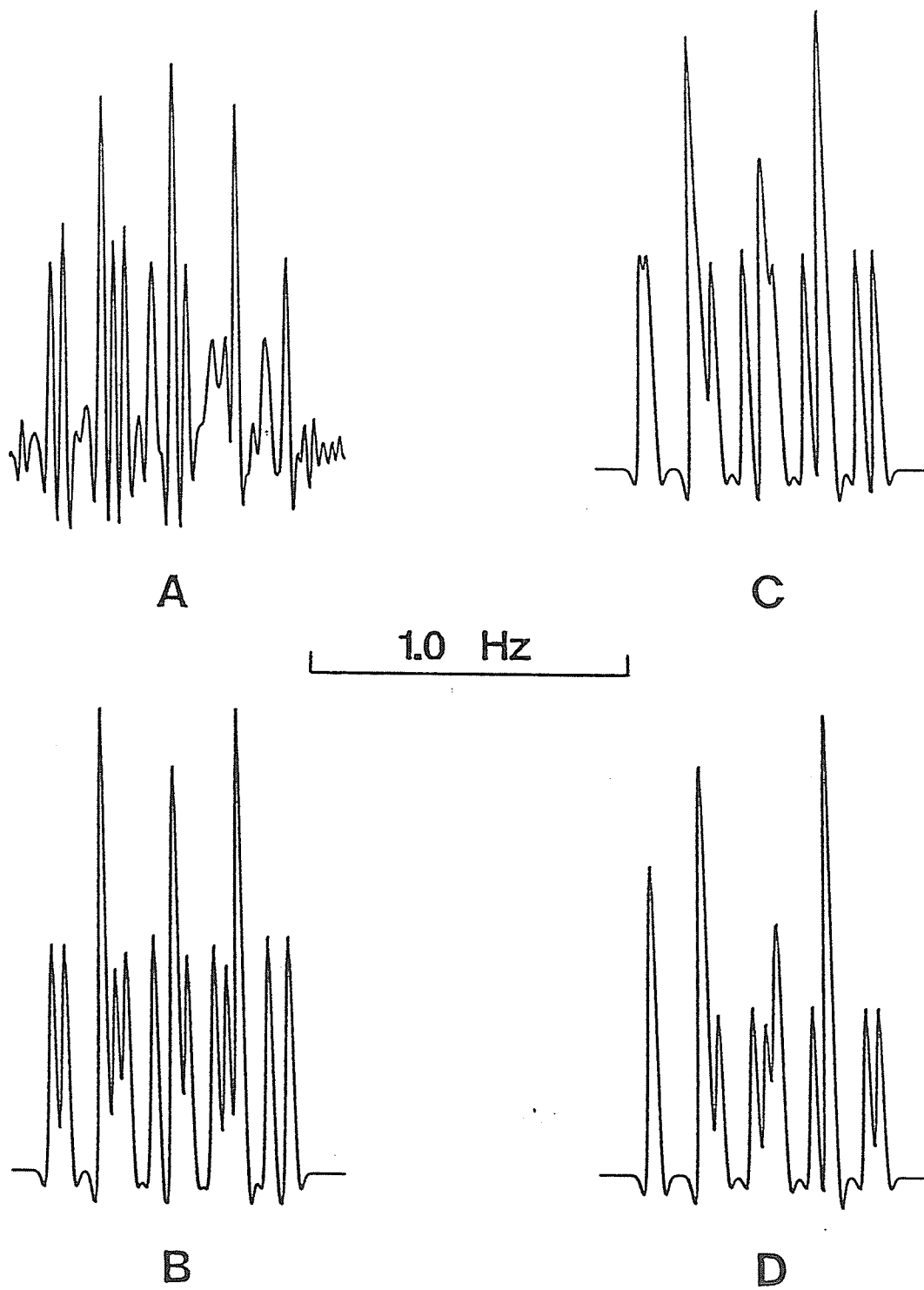


Figure 19. A portion of the 300 MHz spectrum of the aromatic region of 3-tolualdehyde in acetone-d<sub>6</sub>, with methyl group decoupling. Transitions for the ring protons at positions 4 and 5 are shown.

(A) The experimental spectrum.

(B) The computer simulated spectrum.



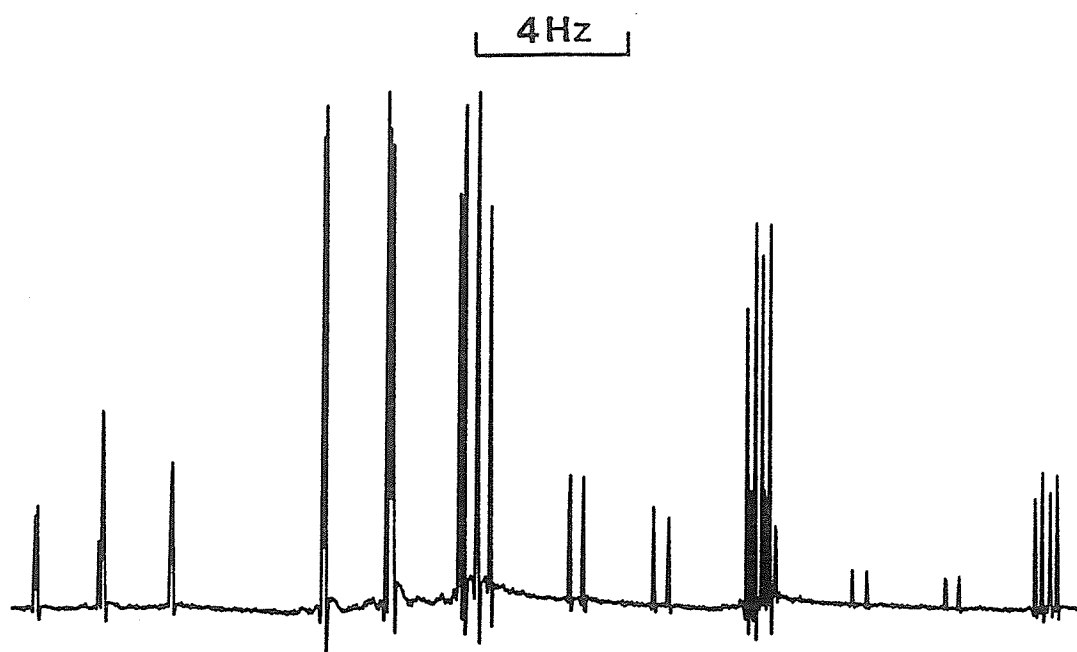
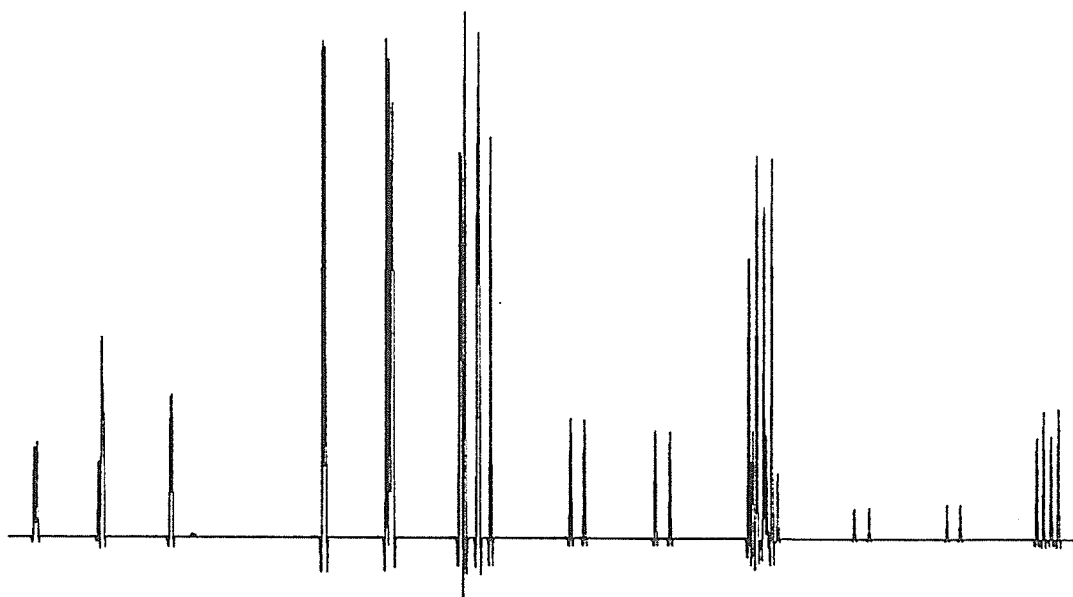
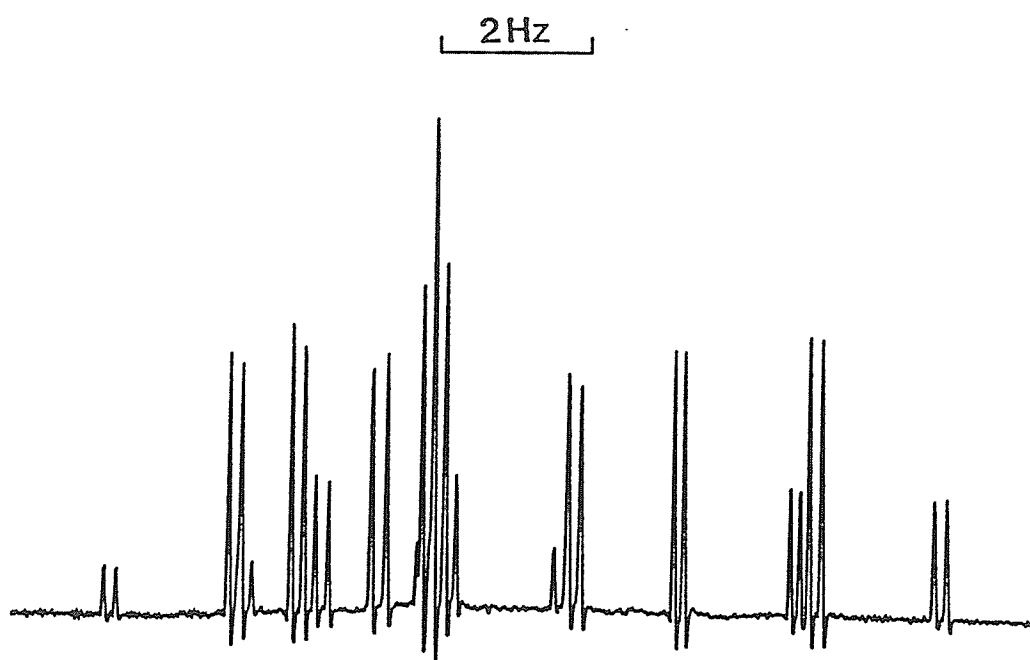
**A****B**

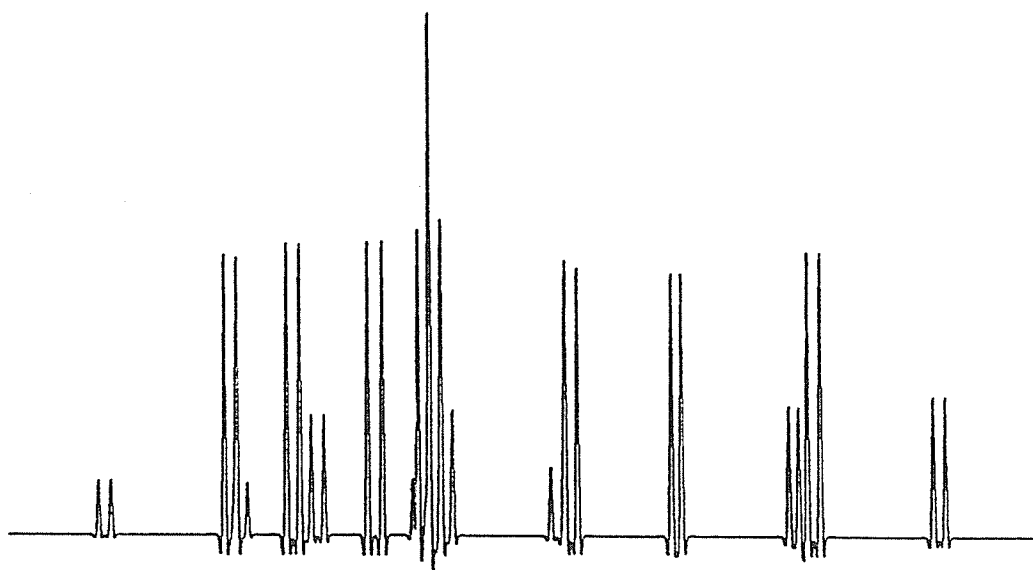
Figure 20. The portion of the  $^1\text{H}$  nmr spectrum of 3-tolualdehyde in acetone- $\text{d}_6$  (with methyl group decoupling) corresponding to ring protons H2 and H6.

(A) The experimental spectrum.

(B) The theoretical spectrum.



A



B

Figure 21. The 300 MHz  $^1\text{H}$  nmr spectrum of the ring protons of 3-tolualdehyde in acetone- $\text{d}_6$  without methyl group decoupling.

(A) The experimental spectrum of ring protons H2 and H6.

(A') The theoretical spectrum corresponding to (A).

(B) The experimental spectrum of ring protons H4 and H5.

(B') The theoretical spectrum corresponding to (B).

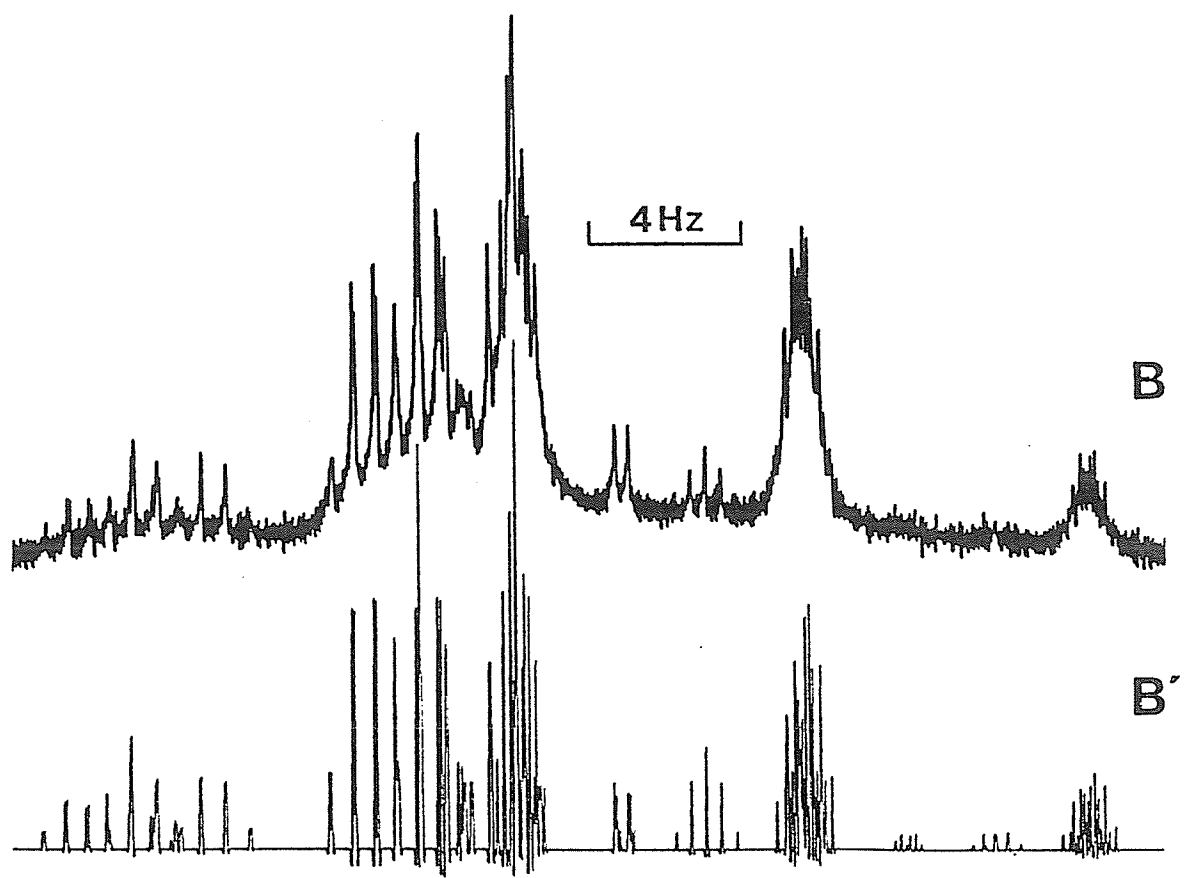
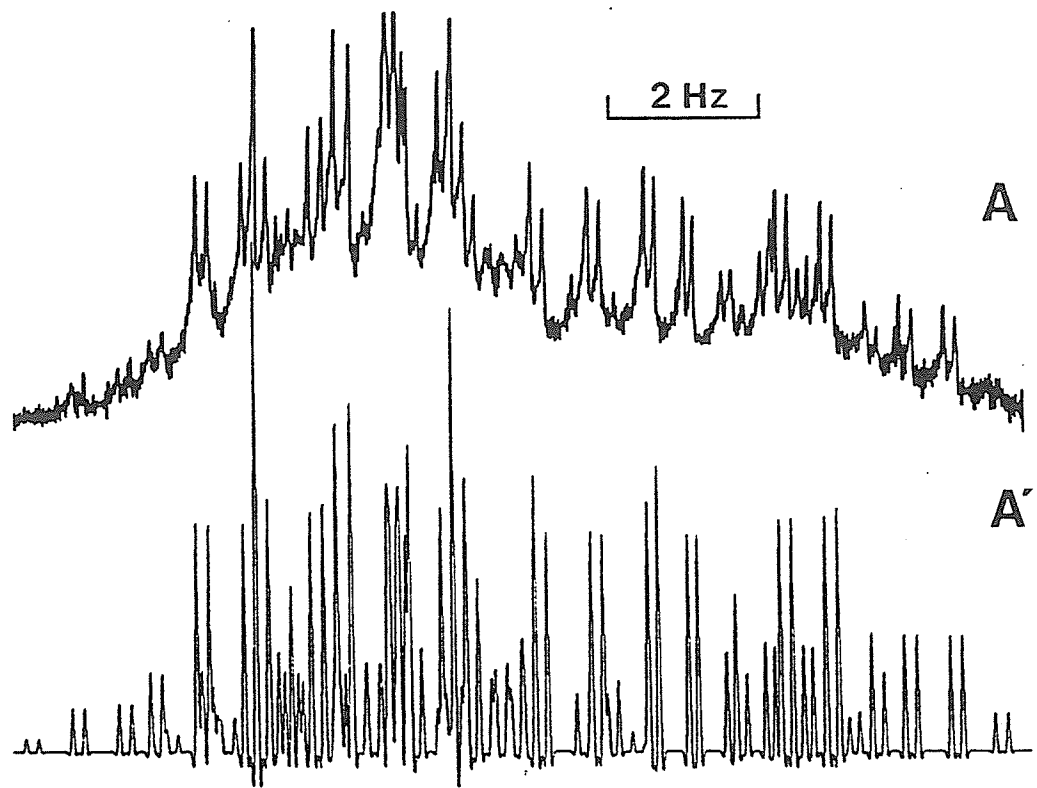
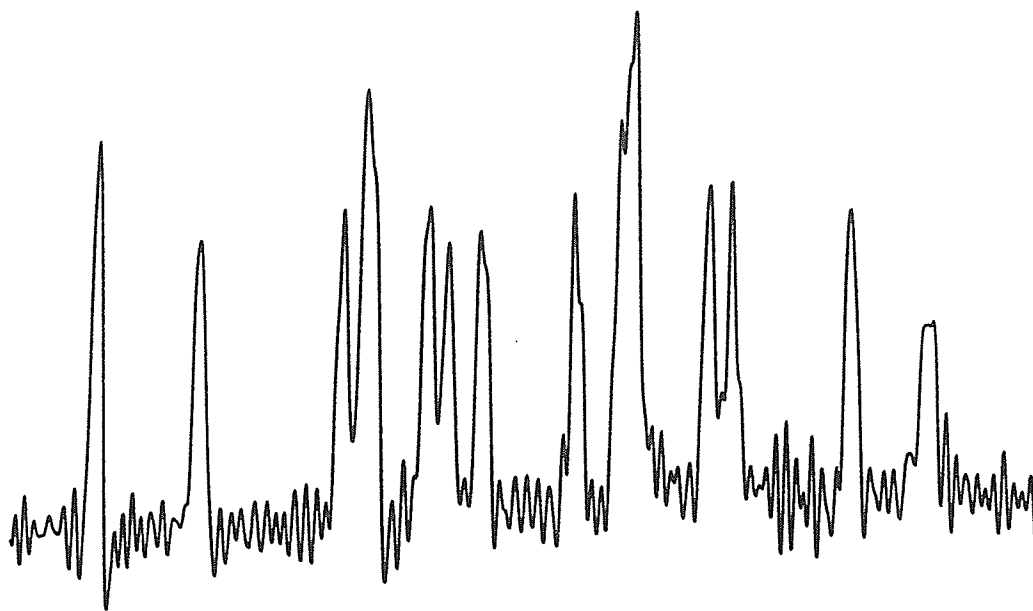


Figure 22. The 300 MHz  $^1\text{H}$  nmr spectrum for the methyl protons of 3-tolualdehyde in acetone- $\text{d}_6$ .

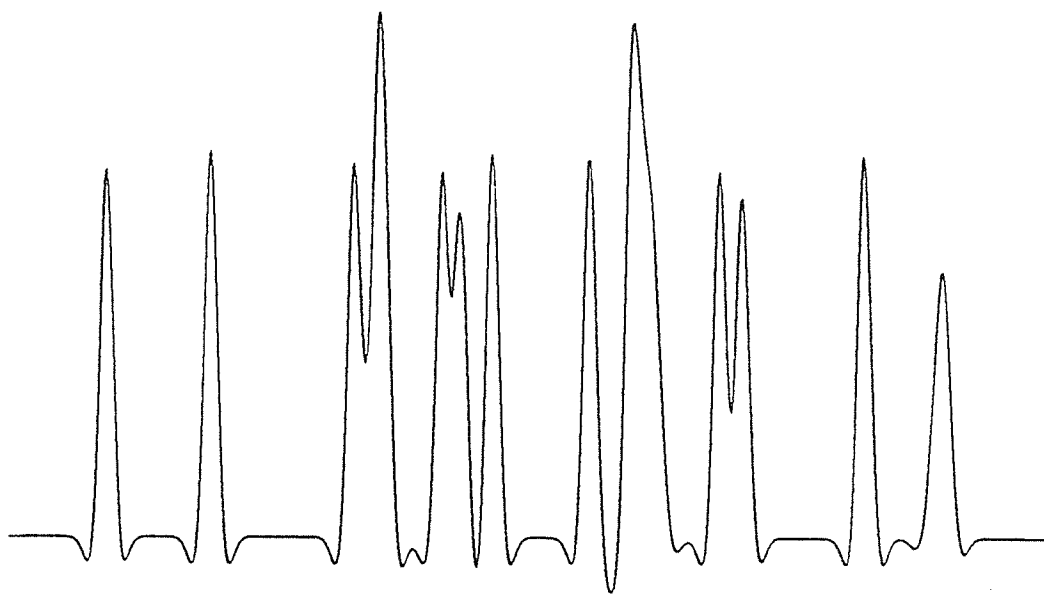
(A) The experimental spectrum.

(B) The computer simulated spectrum.

1.0 Hz



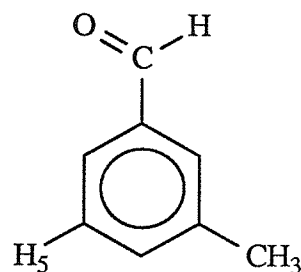
A



B

Table 19. Spectral parameters<sup>a</sup> for 4.0 mol%<sup>b</sup> 3-tolualdehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2266.184	0.0013
v(H4) <sup>c</sup>	2198.052	0.0039
v(H5) <sup>d</sup>	2195.199	0.0041
v(H6)	2263.799	0.0013
v(CHO) <sup>e</sup>	2959.953	
v(CH3)	719.395	0.0010



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	1.863	0.0028	J(H5,H6)	7.616	0.0066
J(H2,H5)	0.573	0.0032	J(H5,CHO)	0.413	0.0030
J(H2,H6)	1.631	0.0017	J(H5,CH3)	0.325	0.0022
J(H2,CHO)	-0.160	0.0018			
J(H2,CH3)	-0.741	0.0011			
J(H4,H5)	7.498	0.0025	J(H6,CHO)	-0.147	0.0018
J(H4,H6) <sup>f</sup>	1.191	0.0070	J(H6,CH3)	-0.588	0.0012
J(H4,CHO) <sup>g</sup>	0.024	0.0029			
J(H4,CH3)	-0.697	0.0021	J(CHO,CH3)	-0.006	0.0010

653 Transitions

Largest Difference = 0.022 Hz

98 Observed Peaks

RMS Deviation of Transitions = 0.0095

405 Assigned Transitions



Notes:

- <sup>a</sup> In Hz at 300K. <sup>1</sup>H nmr at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Contained 3.99 mol% 3-tolualdehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub> and 0.25 mol% TMS.
- <sup>c</sup> Correlated with  $\nu(\text{H5})$  by -0.8789 and with  $J(\text{H5},\text{H6})$  by -0.6946.
- <sup>d</sup> Correlated with  $J(\text{H4},\text{H6})$  by -0.7699 and with  $J(\text{H5},\text{H6})$  by 0.6934.
- <sup>e</sup> Not optimized.
- <sup>f</sup> Correlated with  $J(\text{H5},\text{H6})$  by -0.8942.
- <sup>g</sup> Correlated with  $J(\text{H5},\text{CHO})$  by -0.6569.

## 3.2 Discussion

*Some notes on the reliability of the method*

The available data [1-6, 8-19, 28] on benzaldehyde and its substituted derivatives all indicate that, although the barrier to rotation of the aldehyde group is somewhat altered when a substituent is placed on the ring, it is still high enough to allow a discussion in terms of two planar conformers at 300 K.

The salient pieces of information in the determination of conformer populations from spin-spin coupling constants in these molecules are the magnitudes of the coupling constants over five bonds between the aldehyde proton and the ring protons *meta* to the aldehyde group. The method depends both on the absence of a five bond coupling between protons not related by bonds in an all-trans pattern, and upon the assertion that the sum of the five bond coupling constants in the substituted molecule does not vary substantially from that in benzaldehyde.

The former assumption has been justified by studies of *ortho*-salicylates [1, 27, 28] where, in each instance, hydrogen bonding involving the carbonyl and the hydroxyl groups precludes the existence of an O-trans isomer. The latter has also been substantiated by several researchers [1, 25, 27, 31, 32] and is corroborated by the sums given in table 20 for the *ortho* substituted benzaldehydes. The sum of the five bond coupling constants to the aldehyde proton of benzaldehyde [31] is 0.860(2) Hz in acetone-d<sub>6</sub> and 0.862(4) Hz in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. The sums in this table are, in general, so similar to the sum in benzaldehyde that the value for benzaldehyde was used in determining the conformer populations for the *meta*-substituted compounds.

The sums of the five bond aldehyde coupling constants for o-nitrobenzaldehyde

Table 20. Populations of, and energy differences between O-cis and O-trans rotamers of *ortho* and *meta*-substituted benzaldehydes.

X	Solvent	$^5J(\text{CHO}, \text{H}3)$	$^5J(\text{CHO}, \text{H}5)$	$^5J_{\text{sum}}^a$	% O-cis	$K^b$	$\Delta G^c$ (kJ/mol)
m-Cl	acetone-d6	-----	0.439(1)	0.860(2)	49.0(2)	1.04(1)	0.10(5)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	-----	0.444(1)	0.862(4)	48.5(3)	1.06(1)	0.15(5)
o-Cl	acetone-d6	0.065(1)	0.800(1)	0.865(2)	7.5(1)	12.3(2)	6.27(7)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	-0.002(2) <sup>d</sup>	0.856(2)	0.856(4)	0.0(2)	>500	>15
m-Br	acetone-d6	-----	0.448(1)	0.860(2)	47.9(2)	1.09(1)	0.21(5)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	-----	0.476(1)	0.862(4)	44.8(3)	1.23(1)	0.52(4)
o-Br	acetone-d6	0.065(1)	0.801(1)	0.866(2)	7.5(1)	12.3(2)	6.27(7)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub> <sup>e</sup>	0.064(6)	0.828(9)	0.89(2)	7.2(8)	13.0(2)	6.4(6)
o-I	acetone-d6	0.092(1)	0.769(1)	0.861(2)	10.7(1)	8.35(9)	5.29(5)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	0.051(1)	0.825(1)	0.876(2)	5.8(1)	16.2(3)	6.95(9)
m-NO <sub>2</sub>	acetone-d6	-----	0.459(1)	0.860(2)	46.6(2)	1.15(1)	0.35(4)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	-----	0.520(2)	0.862(4)	39.7(3)	1.52(2)	1.04(7)
o-NO <sub>2</sub>	acetone-d6	0.179 <sup>f</sup>	0.645(7)	0.824(7)	21.7(2)	3.61(4)	3.20(6)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	0.115(2)	0.738(2)	0.853(4)	13.5(3)	6.4(2)	4.6(1)
o-OCH <sub>3</sub>	acetone-d6	0.000(1)	0.838(1)	0.838(2)	0.0(2)	>500	>15
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	-0.006(1) <sup>d</sup>	0.859(1)	0.859(2)	0.0(2)	>500	>15
m-CH <sub>3</sub>	acetone-d6	-----	0.418(1)	0.860(2)	51.4(2)	0.95(1)	0.13(5)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	-----	0.413(3)	0.862(4)	52.1(6)	0.92(2)	0.21(11)

Notes:

- <sup>a</sup> For the *meta* substituted benzaldehydes the sums of  $^5J(\text{CHO},\text{H3}) + ^5J(\text{CHO},\text{H5})$  are from a previous study of *ortho* and *meta* fluorobenzaldehyde [31].
- <sup>b</sup> The equilibrium constants,  $K$ , are calculated as  $N_{\text{O-trans}}/N_{\text{O-cis}}$ .
- <sup>c</sup> The free energy differences are calculated from  $\Delta G = -RT \ln K$ .
- <sup>d</sup> These are the values as given by the analysis program, NUMARIT. As these values are extremely small and as there is no evidence that this coupling is ever negative, these coupling constants should be taken to be zero.
- <sup>e</sup> This analysis did not converge. First order analysis to get  $^5J(\text{CHO},\text{H3})$  and  $^5J(\text{CHO},\text{H5})$  was not possible because of the second order nature of the spectrum. These are the best values that could be obtained and reproduce the spectra of H3 and H5 accurately.
- <sup>f</sup> Line broadening effects prevented optimization of this parameter; the  $^{14}\text{N}$  nucleus of the nitro group undergoes rapid quadrupolar relaxation, the effects of which are observed in the spectra for nuclei, in this case ring proton H3, which are spin coupled to the quadrupolar nucleus.

and o-methoxybenzaldehyde in acetone-d<sub>6</sub> at 0.824(7) Hz and 0.838(2) Hz, respectively, show the greatest differences from the other sums in table 20. The results pertaining to o-nitrobenzaldehyde will now be discussed as a "worst case scenario" to show the reliability of the method. In table 20,  $^5J(\text{CHO},\text{H3})$  for o-nitrobenzaldehyde in acetone-d<sub>6</sub> is given as 0.179 Hz. Optimization of this parameter was prevented by line broadening due to coupling to the quadrupolar  $^{14}\text{N}$  nucleus of the nitro group. Judging from the closeness with which the experimental spectrum is reproduced using this value of  $^5J(\text{CHO},\text{H3})$ , 0.01 Hz should be a reasonable estimate of the uncertainty in this coupling constant. Although the reason for the difference in sums for these large functional group molecules is not clear, the following possibilities may be considered.

First, perhaps this large group perturbs the system such that the passage of spin information between the ring proton at the position next to it and the aldehyde proton is diminished while that between the ring proton at position 5 and the aldehyde proton is unchanged. The difference between the sum of the five bond couplings for o-nitrobenzaldehyde and the same sum for benzaldehyde itself is 0.036(9) Hz. Suppose for the sake of argument that  $^5J(\text{CHO},\text{H3})$  in o-nitrobenzaldehyde were decreased in the O-cis form while  $^5J(\text{CHO},\text{H5})$  in the O-trans form remained at 0.860(2) Hz, as in benzaldehyde. If this were so, the population of the O-trans rotamer would be  $0.645(7)/0.860(2) = 0.75(1)$ , making the O-cis population 0.25(1). According to equation (1) this would entail a  $^5J(\text{CHO},\text{H3})$  in the O-cis form is 0.72(3) Hz. The equilibrium constant,  $K_3$ , would then be 3.0(2) as opposed to the 3.61(4) for  $K_3$  shown in table 20. On the other hand, what if it were  $^5J(\text{CHO},\text{H5})$  in the O-trans

form that decreased while  $^5J(\text{CHO},\text{H3})$  in the O-cis form remained as in benzaldehyde? The population of O-cis isomer would be  $0.18(1)/0.860(2) = 0.21(1)$  making the O-trans population 0.79(1). Equation (1) then gives  $^5J(\text{CHO},\text{H5})$  as 0.82(2) Hz. The value of  $K_3$  would then become 3.8(2). These outside limits for the equilibrium constant can be encompassed by a value of 3.4(6) which gives a free energy difference of 3.1(5) kJ/mol between O-cis and O-trans rotamers.

Second, and alternatively, what if the aldehyde group in the O-cis conformer is forced out of the plane of the benzene ring by the nearby nitro group? The six bond coupling,  $^6J(\text{CHO},\text{H4})$ , has been determined to be a  $\sigma$ - $\pi$  coupling which varies as  $\sin^2\theta$  [29, 36]. When the aldehyde proton lies in the plane of the aromatic ring this coupling,  $^6J_0$ , is at its minimum and increases in magnitude as the aldehyde group is rotated about the  $\text{C}_{\text{sp}^2}$ - $\text{C}_{\text{sp}^2}$  bond, to reach a maximum,  $^6J_{90}$ , when the formyl C-H bond lies perpendicular to the ring. Providing  $^6J_0$  is negligible [28, 29] and  $^6J_{90}$  is known or can be reasonably estimated, the expectation value  $\langle \sin^2\theta \rangle$  can be obtained [42] from the relationship:

$$^6J_{\text{obs}} = ^6J_0 + ^6J_{90} \langle \sin^2\theta \rangle \quad (3) .$$

Table 13 shows  $^6J(\text{CHO},\text{H4})$  to be -0.095(5) Hz, which indicates that the aldehyde group is rotated out of the plane of the aromatic ring much of the time. The O-trans rotamer is the low energy form, as indicated by the magnitudes of  $^5J(\text{CHO},\text{H3})$  and  $^5J(\text{CHO},\text{H5})$ . Furthermore, it may be reasonable, as a first approximation, to assume that only the O-cis rotamer is forced out of plane; since the

polar functional groups are aligned near each other in this form, dipolar repulsion forces may be acting to rotate the formyl group out of plane. The value of  ${}^6J_{90}$  has been estimated [36] to be -0.33 Hz for benzaldehyde. The value of  $\langle \sin^2 \theta \rangle$  which is obtained by using this value of  ${}^6J_{90}$  in equation (3) is an average over all forms of the molecule present in the solution. Equation (3) can be modified to accommodate the assumption of two stable rotamers, giving:

$${}^6J_{\text{obs}} = P_t {}^6J_{90} \sin^2 \theta_t + P_c {}^6J_{90} \sin^2 \theta_c \quad (4)$$

where  $P_t$  and  $P_c$  are again the populations of the O-trans and O-cis rotamers, respectively.  $\theta_t$  and  $\theta_c$  are the angles by which the aldehyde C-H bond is rotated out of plane in the two forms. Assuming that the trans form is planar, ie  $\theta_t = 0^\circ$ , the entire O-trans term in equation (4) drops out. The value of  $\sin^2 \theta_c$  obtained from equation (4), using  ${}^6J_{90} = -0.33$  Hz and the value of  $P_c$  from the last argument ( $P_c = 0.21(1)$ ), is 1.37. If  ${}^6J_{90}$  in o-nitrobenzaldehyde is -0.33 Hz as it is in benzaldehyde, then this model must be rejected.

The final approach that will be considered still assumes that two stable rotamers exist, but that both are nonplanar. Equation (4) is now left with four unknowns and an approximation must be made as to the rotation angles in both rotamers<sup>1</sup>. AM1 [43] calculations were performed on this molecule with the angle of rotation of CHO varied from  $0^\circ$  to  $180^\circ$  in steps of  $15^\circ$ . The O-trans form

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<sup>1</sup> Although both rotamers of o-nitrobenzaldehyde will now be considered non-planar, the O-trans/O-cis nomenclature will be maintained.



corresponds to  $\theta = 0^\circ$ . The nitro group was allowed to rotate freely out of plane during optimization. The results of these calculations on the free molecule are seen in table 15 and figure 17. Energy minima are observed at  $\theta = 30^\circ$  and at  $\theta = 120^\circ$  with a barrier of approximately 4.4 kJ/mol to be overcome on rotation from O-trans to O-cis. This twofold barrier at  $\theta = 90^\circ$  is notoriously underestimated by AM1 for molecules possessing high degrees of conjugation. AM1 gives [21] a twofold barrier of 11.17 kJ/mol for the free benzaldehyde molecule compared to *ab initio* calculations at the STO-3G level [20, 23], which give close agreement to vapour phase experiments with a barrier of 24.5 kJ/mol. It may be noted here that although the barrier determined by the semiempirical method is too low, it is found at  $\theta = 90^\circ$ , in agreement with the *ab initio* results.

Similar agreement in the placement of the twofold barrier between the two computational methods is seen in figures 6 and 7 for o-chlorobenzaldehyde. A maximum potential is again observed when the aldehyde C-H bond is perpendicular to the plane of the benzene ring. This rise in potential in figure 7 is not prominent but is still evident. The energy difference between the two rotamers of o-chlorobenzaldehyde is given by STO-3G [44, 45] calculations as 10.1 kJ/mol. The same energy difference is 12.5 kJ/mol when calculated using the semi-empirical approach.

As will be shown in a subsequent chapter, both methods show the appropriate maxima and minima for rotation of the aldehyde group of m-cyanobenzaldehyde, though once again the height of the twofold barrier is much too low when calculated by the AM1 approach. For that molecule the differences in energy between the planar

rotamers are 0.46 kJ/mol and 0.76 kJ/mol as calculated by STO-3G and AM1, respectively.

The important point demonstrated by these few examples is that, as far as the simple rotation of an aldehyde group is concerned, the high and low energy planar conformations of the free molecule can be extracted approximately from the results of AM1 calculations; however, the energies of rotation of the aldehyde group given by the AM1 method for these types of molecules are not reliable. For *ortho*-substituted benzaldehydes,  $V_2$  is too low and prior knowledge of the placement of the twofold barrier is of advantage.

However, AM1 calculations more closely approximate the experimentally determined internal rotational barrier of nitrobenzene than does the *ab initio* approach. The twofold barrier was found by microwave experiments to be 12.3 kJ/mol [46] and 11.6 kJ/mol [47]. The Raman overtone spectrum [48] yields a torsional barrier of 13.6 kJ/mol. These values are appreciably lower than the barrier of 20.9 kJ/mol calculated using the STO-3G basis set [49]. The twofold barrier in nitrobenzene is computed to be 14.53 kJ/mol [21] by the AM1 method.

Taking the above relationships into account when considering the results of MO calculations on o-nitrobenzaldehyde, it is logical that the given rotation angles of CHO are too great, since AM1 underestimates the twofold rotational barriers of aldehyde groups in like molecules. Similarly, as the barrier to rotation of the nitro group in nitrobenzene is slightly overestimated by AM1, it is reasonable to assume that the nitro group in o-nitrobenzaldehyde can relax to a lower energy conformation in both rotamers by twisting somewhat further out of plane than is predicted by AM1.

This would also tend to reduce the angle that the aldehyde group makes with the ring. It is also logical that the angle in the O-cis form is overestimated to a greater degree than that in the O-trans form, owing to the greater steric and dipolar interactions involved in this orientation. That the aldehyde group is rotated out of the plane of the ring in the O-trans form is substantiated by an X-ray diffraction analysis of o-nitrobenzaldehyde [50] where it is concluded that in the crystal (consisting of only O-trans rotamer) the C-H bond of the aldehyde lies out of plane by  $31^\circ$  while the dihedral angle that the nitro group makes with the plane is  $27^\circ$ .

It is be expected that the *ab initio* method would tend to give minima at torsion angles that are too small since the nitrobenzene barrier arrived at by this approach is much too high. The extreme escalation in computing time upon going from the semiempirical to the *ab initio* approaches prohibited the use of the latter method for o-nitrobenzaldehyde; however, one STO-3G calculation was performed having CHO held in the plane of the ring while the nitro group was allowed to rotate during optimization. In this case the optimized conformation had the nitro group in the plane of the ring as well as the aldehyde group. This is in keeping with the above expectation.

Now, it has been shown that  $^5J(\text{CH}_3, \text{H})$  in toluene can be described [51] by:

$$^5J = ^5J_{90}^\pi \sin^2(\theta) + ^5J_{180}^\sigma \sin^2(\theta/2) \quad (5).$$

It has also been suggested [29, 31] that  $^5J(\text{CHO}, \text{H})$  in benzaldehyde is a pure  $\sigma$

coupling. This proposal can be illustrated with a comparison to toluene. In that molecule,  ${}^5J_{90}^\pi$  and  ${}^6J_{90}$  are estimated to be 0.336 Hz [52] and -1.20 Hz [51], respectively. If the ratio  ${}^5J_{90}^\pi/{}^6J_{90} = -0.280$  for toluene holds true for benzaldehyde as well, then from the value of  ${}^6J_{90}$  above,  ${}^5J_{90}^\pi$  for benzaldehyde is about 0.09 Hz. If the value of -0.33 Hz is accepted for  ${}^6J_{90}$  at 300 K then, from equation (3),  $\langle \sin^2 \theta \rangle$  is about 0.04, making the  $\pi$  term in equation (5)  $<0.004$  Hz.

Suppose that the true angles of rotation of CHO in o-nitrobenzaldehyde are the same as in the crystal, for the O-trans rotamer, and 80 % of that predicted by the AM1 calculations, for the O-cis form. Then the aldehyde C-H bond is rotated  $31^\circ$  out-of-plane in the O-trans form and  $48^\circ$  out-of-plane in the O-cis form. Assuming then that  ${}^5J(\text{CHO},\text{H})$  in the two isomers of o-nitrobenzaldehyde varies as  $\sin^2(\theta/2)$ , and also that  ${}^5J_{180}^\sigma$  is the same as in benzaldehyde for both rotamers, the following values of the five bond coupling constants are obtained from equation (5):

$${}^5J(\text{CHO},\text{H5})_t = 0.822(2) \text{ Hz}$$

$${}^5J(\text{CHO},\text{H3})_t = 0.085(2) \text{ Hz}$$

$${}^5J(\text{CHO},\text{H5})_c = 0.192(2) \text{ Hz}$$

$${}^5J(\text{CHO},\text{H3})_c = 0.767(2) \text{ Hz.}$$

By substituting these values into equation (1) the following two equations are obtained:

$$(i) \quad {}^5J(\text{CHO},\text{H5}) = P_i 0.822(2) + P_e 0.192(2) = 0.645(7) \text{ Hz}$$

$$(ii) \quad {}^5J(\text{CHO},\text{H3}) = P_i 0.085(2) + P_e 0.767(2) = 0.18(1) \text{ Hz}$$

These equations yield  $P_e = 0.20(5)$  and  $P_i = 0.80(5)$ . Using these populations in equation (4) gives  ${}^6J(\text{CHO},\text{H4}) = -0.109(14) \text{ Hz}$ . As stated above, the observed value of this coupling constant is  $-0.095(5) \text{ Hz}$ . This model adequately fits the experimental results and may be nearer the actual situation. These populations correspond to the equilibrium constant being  $3.5(1.0)$ , which is within the limits of uncertainty of the equilibrium constant of  $3.4(6)$  arrived at in the preceding argument.

In the spectrum of o-methoxybenzaldehyde in acetone-d<sub>6</sub> there is no splitting observed in the aromatic region corresponding to  ${}^6J(\text{CHO},\text{H4})$ ; therefore the aldehyde group is not significantly rotated out of the plane of the aromatic ring. The spectrum of the aldehyde proton shows only two doublets, due to  ${}^5J(\text{CHO},\text{H5})$  and  ${}^5J(\text{CHO},\text{CH}_3)$ . A simulated spectrum with  ${}^5J(\text{CHO},\text{H3}) = 0.035 \text{ Hz}$  shows modest but visible splitting in the H3 region but only broadening of the four lines in the aldehyde region. Since  ${}^5J(\text{CHO},\text{H5})$  is  $0.838(2) \text{ Hz}$ ,  ${}^5J(\text{CHO},\text{H3})$  need only be  $0.022 \text{ Hz}$  for the sum to be the same as for benzaldehyde. The spectral quality and the multiplicity of peaks in the aldehyde region of this spectrum are such that that a coupling constant of  $0.022 \text{ Hz}$  would not be detectable. If indeed a  $0.022 \text{ Hz}$  coupling constant is present, the equilibrium constant for o-methoxybenzaldehyde in acetone-d<sub>6</sub> at  $300 \text{ K}$  is then  $38.09(5)$  and  $\Delta G$  is  $9.07(1) \text{ kJ/mol}$ .

*The meta substituted benzaldehydes:*

i) *meta*-chlorobenzaldehyde

For m-chlorobenzaldehyde in acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solutions the magnitude of <sup>5</sup>J(CHO,H5) is 0.439(1) Hz and 0.444(1) Hz, respectively. Assuming that <sup>5</sup>J(CHO,H5) for the O-trans conformer in both solvents is the same as it is in benzaldehyde itself, the percentage of the O-cis conformer is 49.0(2) % in acetone-d<sub>6</sub> and 48.5(3) % in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. Although the proportions of the two forms are very nearly the same in both solvents, a slight excess of the O-trans rotamer is indicated.

ii) *meta*-bromobenzaldehyde

For m-bromobenzaldehyde, the fractions of O-cis rotamers in the two solvents (0.479(2) and 0.448(3) in acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>, respectively) indicate a slight propensity for the more polar O-cis to exist in the more polar acetone-d<sub>6</sub> solvent than in the non-polar CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solvent. The fit of the spectral data to the Hamiltonian was very good in both of these analyses, with the largest difference between theoretical and experimental transition frequencies being 0.004 Hz. Since the difference in <sup>5</sup>J(CHO,H5) in the two solvents is a relatively substantial 0.028(2) Hz, the indicated inequality of the rotamer population may well be significant.

iii) *meta*-nitrobenzaldehyde

m-Nitrobenzaldehyde shows a greater difference in rotamer populations between the two solvents than do m-chloro and m-bromobenzaldehyde. Fortunately,

there is a large enough number of intervening bonds between the ring proton at position 5 and the  $^{14}\text{N}$  nucleus of the nitro group that quadrupolar relaxation effects do not prevent  $^5\text{J}(\text{CHO}, \text{H}_5)$  from being determined with precision. The difference between the values of this coupling constant in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution is 0.061(3) Hz. The coupling constants given in table 20 correspond to free energy differences between O-trans and O-cis rotamers of 0.35(4) kJ/mol and 1.04(7) kJ/mol in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively. Again, an increase in the amount of O-cis rotamer appears to be brought about by the switch to the more polar acetone- $\text{d}_6$  solvent.

iv) *meta*-tolualdehyde

The values of  $^5\text{J}(\text{CHO}, \text{H}_3)$  for m-tolualdehyde at 300 K in acetone- $\text{d}_6$  and in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  are 0.418(1) Hz and 0.413(3) Hz, respectively. Using the sum of the five bond coupling constants in benzaldehyde, the population of O-cis rotamer in acetone- $\text{d}_6$  is 0.514(2) and is 0.521(6) in the  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution. Within the limits of uncertainty, there is no change in rotamer population upon changing to the more polar solvent. This is not surprising since the negligible dipolar contribution of the methyl group results in essentially no difference in dipole moment between the O-cis and O-trans conformers. Why a slightly higher fraction of the O-cis form exists at 300 K is not known.

*The ortho-substituted benzaldehydes:*

i) *ortho*-chlorobenzaldehyde

The sums of the five bond coupling constants involving the aldehyde proton in *o*-chlorobenzaldehyde in acetone- $d_6$  and in  $CS_2/C_6D_{12}$  are 0.865(2) Hz and 0.858(4) Hz, respectively. Within experimental uncertainty these values are the same as that for benzaldehyde where the average of the values of  $^5J(CHO,H)$  in acetone- $d_6$  and  $CS_2/C_6D_{12}$  is 0.861(5) Hz. The chlorine substituent on the ring does not appear to perturb the coupling pathway between the aldehyde proton and the ring protons *meta* to it. It is unlikely that the spin coupling between the aldehyde proton and H5 of the ring would be enhanced by precisely the amount by which  $^5J(CHO,H3)$  were diminished. The relatively large 0.065(1) Hz coupling to H3 for *o*-chlorobenzaldehyde in acetone- $d_6$  demonstrates that the *O*-cis rotamer exists in a substantial concentration at 300 K in acetone- $d_6$ . This coupling constant corresponds to a population of *O*-cis rotamer of 0.075(1), which in turn results in an equilibrium constant of 12.4(2) in this solvent. A free energy difference of 6.27(7) kJ/mol between the *O*-cis and *O*-trans forms is indicated. In  $CS_2/C_6D_{12}$  solution on the other hand, the coupling constant  $^5J(CHO,H3)$  is not observed while  $^5J(CHO,H5)$  is seen to be 0.856(2) Hz. The spectrum for *o*-chlorobenzaldehyde in this non-polar solvent is that of the *O*-trans form exclusively. For this molecule there is an unmistakable solvent induced increase in population of the more polar *O*-cis rotamer, which is stabilized by at least  $15 - 6.3 = 8.7$  kJ/mol relative to the *O*-trans form upon passing from  $CS_2/C_6D_{12}$  to acetone- $d_6$  solution.



ii) *ortho*-bromobenzaldehyde

As shown in table 20, there is little difference between the magnitudes of  $^5J(\text{CHO},\text{H3})$  observed in the spectra of the acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solutions of *o*-bromobenzaldehyde. For this latter sample solution a precise analysis was not achieved. A good simulated spectrum could be attained for the aromatic region of the spectrum; however, attempts to simulate the aldehyde proton region fell short of the precision achieved in the other analyses performed in this study. The sample was prepared a second time and a second analysis was attempted, with the same results. The values for  $^5J(\text{CHO},\text{H3})$  and  $^5J(\text{CHO},\text{H5})$  which appear in table 20 are those from what was felt to be the best of the several analyses performed for this molecule in this solvent. The uncertainties shown should be treated as a somewhat optimistic minimum. The spectra were simulated using values for these coupling constants which were more in line with the results for *o*-chlorobenzaldehyde in  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , i.e.  $^5J(\text{CHO},\text{H3}) = 0.000 \text{ Hz}$  and  $^5J(\text{CHO},\text{H5}) = 0.860 \text{ Hz}$ . The resulting simulation differed significantly from the experimental spectrum. The results shown in table 20 for *o*-bromobenzaldehyde in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  were included mainly for completeness. All that is intended is to show what is judged to be a finite *O*-cis rotamer population in this solvent. A plausible explanation for the existence of this polar form in the non-polar solvent is not presented.

iii) *ortho*-iodobenzaldehyde

In both solvents the spectrum for *o*-iodobenzaldehyde displays a finite coupling constant between the aldehyde proton and H3 of the aromatic ring. Once again,

however, the relatively sizable  $^5J(\text{CHO}, \text{H}_3)$  in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  is markedly dissimilar from the corresponding coupling constant in o-chlorobenzaldehyde. A notable proportion, 5.8(1)%, of the O-cis rotamer is indicated in this solvent as well as in acetone-d6 where the O-cis rotamer accounts for 10.7(1) % of the total sample. The coupling constants shown in table 20 correspond to free energy differences of 5.29(5) kJ/mol and 6.95(9) kJ/mol in acetone-d6 and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively, between the O-cis and O-trans forms of o-iodobenzaldehyde. The equilibrium constant in acetone-d6 solution is calculated to be 8.35(9) while in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution,  $K_3 = 16.2(3)$ . Although the existence of such a large amount of O-cis form in the non-polar solvent was not expected, based upon the results of the analyses for o-chlorobenzaldehyde, the expected higher fraction of polar rotamer (O-cis) in the more polar solvent (acetone-d6) is observed. Upon passage from  $\text{CS}_2/\text{C}_6\text{D}_{12}$  to acetone-d6 the O-cis rotamer is stabilized by 1.7(2) kJ/mol relative to the O-trans form.

#### iv) *ortho*-nitrobenzaldehyde

The results of the analysis of o-nitrobenzaldehyde have already been discussed in terms of the reliability of the results of calculations which make use of the spectroscopic data from the analyses presented in this thesis. The important points to take note of here are the considerable presence of the O-cis rotamer in both solvents and the stabilization of this form by 1.4(2) kJ/mol relative to the O-trans form in going from  $\text{CS}_2/\text{C}_6\text{D}_{12}$  to acetone-d6.

v) *ortho*-methoxybenzaldehyde

The absence of an observable  $^5J(\text{CHO}, \text{H}_3)$  in *o*-methoxybenzaldehyde has been discussed above with reference to the reliability of the method.

*Comparisons to other methods*

The results of investigations by several experimental methods into the conformational behaviour of *ortho* and *meta*-substituted benzaldehydes are shown in table 21. In most instances solvent effects on conformational preferences in these molecules were not studied; the data were accumulated using only one, usually non-polar, solvent. The investigations were performed at temperatures ranging from 123 K to 393 K, depending on the method employed. In most cases, table 21 reflects a very slight preponderance of O-trans rotamer for the *meta*-substituted molecules at ambient temperature in such relatively non-polar solvents as  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ . *o*-Chlorobenzaldehyde and *m*-chlorobenzaldehyde are the most extensively studied of the compounds included in this thesis; consequently a good deal of the following discussion is centred on these molecules.

The equilibrium constants calculated for *m*-chlorobenzaldehyde from the results of the three dipole moment investigations seen in table 21 all agree with each other within their associated uncertainties. The value of the equilibrium constant from one of these investigations [15],  $K_3 = 1.4(3)$  at 298 K, encompasses the other two results and so should be a reliable value corresponding to this method. These equilibrium constants are in agreement with the  $^1\text{H}$  nmr study of Karabatsos and Vane [1] whose

Table 21. Equilibrium constants obtained by various methods.

X	Method <sup>a</sup>	State <sup>b</sup>	K <sub>3</sub> <sup>c</sup>	
			<i>meta</i>	<i>ortho</i>
Cl	ir [7]	vapour, 323 - 360 K	0.43	2.6
	<sup>1</sup> H nmr coupling constants [1]	CCl <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> , acetone	1.9(4)	∞
	<sup>1</sup> H nmr coupling constants	acetone-d <sub>6</sub> , 300 K	1.04(1)	12.3(2)
		CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub> , 300 K	1.06(1)	>500
	<sup>13</sup> C nmr chemical shifts [5]	Freon mixture, 123 K	0.54	∞
	M.O. constrained ̄ diffraction[19]	vapour, 393 K	2(1)	----
	dipole moment [13]	CCl <sub>4</sub> , 298 K	1.2(1)	∞
	dipole moment [15]	C <sub>6</sub> H <sub>6</sub> , 298 K	1.34	----
Br	dipole moment [16]	CCl <sub>4</sub> , 298 K	1.4(3)	∞
	ir [7]	vapour, 323 - 360 K	0.14	∞
	<sup>1</sup> H nmr coupling constants [1]	CCl <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> , acetone	1.9(4)	----
	<sup>1</sup> H nmr coupling constants	acetone-d <sub>6</sub> , 300 K	1.09(1)	12.3(2)
		CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub> , 300 K	1.23(1)	13(1)
	<sup>13</sup> C nmr chemical shifts [5]	Freon mixture, 123 K	0.69	----
	dipole moment [13]	CCl <sub>4</sub> , 298 K	1.4(1)	----
	dipole moment [16]	CCl <sub>4</sub> , 298 K	1.3(2)	∞
NO <sub>2</sub>	<sup>1</sup> H nmr coupling constants [1]	CCl <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> , acetone	1.9(4)	----
	<sup>1</sup> H nmr coupling constants	acetone-d <sub>6</sub> , 300 K	1.15(1)	3.4(6)
		CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub> , 300 K	1.52(2)	6.4(2)
	dipole moment [13]	CCl <sub>4</sub> , 298 K	1.7(1)	----
	dipole moment [16]	CCl <sub>4</sub> , 298 K	1.9(2)	∞
CH <sub>3</sub>	ir [7]	vapour, 323 - 360 K	0.09	∞
	<sup>1</sup> H nmr coupling constants [1]	acetone	< 0.4(1)	----
	<sup>1</sup> H nmr coupling constants	acetone-d <sub>6</sub> , 300 K	0.95(1)	----
		CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub> , 300 K	0.92(2)	----
	<sup>13</sup> C nmr chemical shifts [5]	Freon mixture, 123 K	0.81	1

## Notes

- <sup>a</sup> Where no reference is given, the results are from this study.
- <sup>b</sup> Where no temperature is given, no mention of temperature was made in the reference; room temperature is assumed.
- <sup>c</sup>  $K_3 = \text{O-trans/O-cis}$ . For those references where no estimate of the uncertainty in rotamer populations or equilibrium constants was given, no error estimates are given in table Y.

results give 1.9(4) for  $K_3$  at an undisclosed temperature, presumably ambient. The molecular orbital constrained electron diffraction method [19] also agrees with these results, giving  $K_3$  as 2(1) for *m*-chlorobenzaldehyde at 393 K in the vapour state. The results of research performed for this thesis,  $K_3 = 1.04(1)$  and  $1.06(1)$  at 300 K in acetone- $d_6$  and  $CS_2/C_6D_{12}$ , respectively, are compatible with the above results taken at their lower uncertainty limits.

The results of a vapour phase ir investigation at 323 - 360 K [7] find the O-cis rotamer to be the more stable of the two forms. Another ir investigation [9] of the vapour, liquid, and solid phases of *m*-chlorobenzaldehyde also shows the O-cis rotamer to be more stable than the O-trans form in the pure compound and is explained as being due to a hydrogen bond type of interaction involving H2, which is made slightly positive by the electron withdrawing substituent next to it on the ring, and the polarized carbonyl group; however, this does not account for *m*-bromobenzaldehyde appearing to have a higher fraction of the O-cis form than does *m*-chlorobenzaldehyde in this same [9] ir investigation, because the electronegativity of the bromine substituent is less than that of the chlorine substituent.

A recent  $^1H$  nmr examination [31] by Schaefer and Takeuchi found that the O-cis form of *m*-fluorobenzaldehyde was slightly favoured in both acetone- $d_6$  and  $CS_2/C_6D_{12}$ , solutions with the population of O-cis rotamer increasing upon passing from acetone- $d_6$  to the much less polar  $CS_2/C_6D_{12}$ . Provided that this trend of increasing O-cis population with decreasing solvent dielectric constant ( $\epsilon_{acet}^{25^\circ} = 20.7$ ,  $\epsilon_{CS_2}^{25^\circ} = 2.63$ ) continues, these results agree qualitatively with the ir investigation [7] which also found the O-cis rotamer to be the most stable form in the vapour where

$\epsilon = 1$ . The results of the research performed on m-chlorobenzaldehyde for this thesis are in direct conflict with these findings as not only is O-trans found to be more stable, but the fraction of the O-cis form decreases with decreasing solvent dielectric constant. This implies that the O-trans rotamer would be the more stable form even in the vapour.

The O-cis rotamer was also found to be the most stable form of m-chlorobenzaldehyde in a  $^{13}\text{C}$  nmr experiment at 123 K [5]. The solvent in this case was a Freon mixture. While these authors agreed with the vapour phase ir investigation about which is the more stable isomer of the m-halobenzaldehydes, the relative proportions of O-cis form in these molecules was found to decrease as  $\text{F} > \text{Cl} > \text{Br}$  in the  $^{13}\text{C}$  nmr experiment but  $\text{F} > \text{Br} > \text{Cl}$  by the ir method.

Although the results of this thesis contradict those from the vapour phase ir method and the low temperature  $^{13}\text{C}$  nmr method, the agreement between the results of Karabatsos and Vane, the dipole moment investigations, and this coupling constant method are encouraging. It seems safe to say that in such relatively non-polar solvents as  $\text{CS}_2/\text{C}_6\text{D}_{12}$  and  $\text{CCl}_4$ , or in solvents as polar as acetone- $\text{d}_6$ , the O-trans form of m-chlorobenzaldehyde is slightly more stable at ambient temperatures than the O-cis form.

Researchers have observed evidence for two rotational isomers of o-chlorobenzaldehyde in the ir spectra of the vapour [7] and liquid [9]. Although both of these groups found the O-trans rotamer to be far more stable than the O-cis form, only one [7] gives an estimate as to the fraction of O-cis present. This group gives  $K_3$  a value of 2.6 in the vapour at 323 - 360 K. An electron diffraction study [18] gives

an approximate ratio of 4:1 favouring the O-trans form but states that a model consisting of solely the O-trans rotamer gives only slightly poorer agreement with experiment.

Evidence for the existence of the O-cis rotamer of o-chlorobenzaldehyde is also found in early  $^1\text{H}$  nmr work [26,27]. The earlier of the two investigations [27] gave  $^5\text{J}(\text{CHO},\text{H5}) = 0.78(2)$  Hz and  $^5\text{J}(\text{CHO},\text{H3}) = 0.04(2)$  Hz for the neat liquid with 10% hexamethyldisiloxane as an internal reference. The temperature of the experiment was not given, but was likely room temperature. The spectrum was obtained on a 60 MHz CW spectrometer. The splitting due to  $^5\text{J}(\text{CHO},\text{H3})$  was not observed in the spectrum but was a result of the computer aided analysis. That  $^5\text{J}(\text{CHO},\text{H3})$  does exist was shown by irradiating the aldehyde signal and observing the resulting narrowing of the spectral lines for H3. Using the sum of these coupling constants as the value of the observable five bond coupling in the O-cis and O-trans forms gives the O-trans population as 0.95(7).

The other report [26] states that decoupling experiments were used to show that the aldehyde protons of o-chloro-, bromo-, iodo-, fluoro-, and nitrobenzaldehyde are coupled to the ring protons at position 3. The researchers did not report the magnitudes of the coupling constants and so all that can be gathered is that the O-cis population is small.

Table 20 shows  $^5\text{J}(\text{CHO},\text{H3})$  for o-chlorobenzaldehyde in acetone- $\text{d}_6$  to be 0.065(1) Hz. Clearly, 7.5(1)% of the molecules must lie in the O-cis form to account for this coupling constant, provided that the basis of this method is sound. The same coupling constant for this molecule in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  is evaluated to be -0.002(2) Hz; as



there is no evidence that this coupling constant can ever be negative, and since it is of the same order of magnitude as its associated uncertainty, this coupling constant should be considered to be 0.000(2) Hz, implying that none of the O-cis isomer is present in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> at 300 K. The sum of the five bond coupling constants for this molecule in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> is 0.856(4) Hz. If the sum for this compound were really 0.865(2) Hz, as it is for the same compound in acetone-d<sub>6</sub>, this would imply that a coupling constant of 0.865(2) - 0.856(2) = 0.009(4) Hz might exist between the aldehyde proton and H3, but would not be visible in the spectrum. Even using these values for the sum and for <sup>5</sup>J(CHO,H3) there is present at most 1% of the O-cis form. On this basis it is concluded that the O-cis rotamer is much less stabilized by CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> than by acetone-d<sub>6</sub>, and that only the O-trans rotamer exists in the non-polar solvent.

Dipole moment investigations of o-chlorobenzaldehyde [13,16] consistently find the O-trans rotamer to be present exclusively. Since these investigations were carried out in CCl<sub>4</sub> at 298 K, which is of very nearly the same polarity as CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> at 300 K, the failure of these investigators to detect any evidence of the O-cis isomer is understandable.

An explanation for why the vapour phase ir study showed evidence for an appreciable O-cis fraction is not apparent. The data of table 20 clearly show that as the dielectric character of the solvent decreases, so does the fraction of O-cis isomer. Since this fraction is at most scarcely greater than zero in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>, there should be none of this isomer present in the vapour. Even at the elevated temperatures (323 - 360 K) used in that experiment the O-cis population should not have been detectable.

The results of previous analyses of the conformations of o- and m-bromobenzaldehyde closely follow those for their chloro-substituted counterparts, except that in this case the ir studies failed to produce any evidence of an O-cis rotamer of o-bromobenzaldehyde. The  $^1\text{H}$  nmr study [26] mentioned above does present evidence for the O-cis isomer in  $\text{CCl}_4$  solution.

In the case of m-nitrobenzaldehyde there is again reasonable agreement between the results for the  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution seen in table 20 and those from dipole moment measurements [13,16]. The equilibrium constants calculated from these dipole moment experiments are seen in table 21 to be 1.7(1) and 1.9(2). The fraction of O-cis isomer calculated from the  $^1\text{H}$  nmr coupling constants in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  is 0.397(3), making  $K_3 = 1.52(2)$ . The dielectric constant of a 9:1 mixture of  $\text{CS}_2$  and  $\text{C}_6\text{D}_{12}$  is approximately 2.57 while that of  $\text{CCl}_4$  is 2.23. The somewhat lower dielectric constant of the solvent used in the dipole moment studies ( $\text{CCl}_4$ ) could be partially responsible for the difference in the equilibrium constants based on the two methods.

The only reference to a conformational study of o-nitrobenzaldehyde in solution is a dipole moment paper [16], where it is concluded that in  $\text{CCl}_4$  at 298 K the solute is totally in the O-trans form. This is surprising since the fraction of O-cis rotamer in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  at 300 K is determined to be 0.135(3) by the coupling constant method. The authors of this paper mention that their predicted values for the O-cis and O-trans forms are uncertain since effects due to interaction of the two polar groups, and effects due to steric crowding, are not taken into account. In fact, the dipole moment they determine experimentally is smaller than that predicted for an entirely O-trans sample, indicating that the assumed moments of 6.80 D and 4.68 D

for the O-cis and O-trans rotamers, respectively, are exaggerated.

For m-tolualdehyde, very few references could be found, with most involving some form of nmr method. Table 21 shows that there is general agreement between the solution state and vapour phase investigations in that they all find the O-cis form to be the stable form. The values of  $K_3$  determined in solution range from 0.4(1) [1] to that of 0.95(1), obtained in acetone-d<sub>6</sub> in this thesis. For the vapour, Miller et al [7] claim a far greater proportion of O-cis form, giving 0.09 for the equilibrium constant. The results in table 20 indicate little or no change in the proportions of the two forms on going from polar to non-polar solvents, with  $K_3 = 0.95(1)$  in acetone-d<sub>6</sub> and  $K_3 = 0.92(2)$  in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

#### *A positive ${}^6J(\text{CHO}, \text{H4})$ in meta-substituted benzaldehydes*

As stated in the introduction, the  $\sigma - \pi$  mechanism responsible for the six bond coupling constant between the aldehyde proton and the ring proton *para* to the formyl group gives rise to an observable coupling constant which varies as  $\langle \sin^2 \theta \rangle$ . If CHO is forced out of the plane of the benzene ring by steric or electrostatic interactions with one or two *ortho*-substituted derivatives, or if the height of the internal barrier to rotation of CHO is lowered by *ortho* or *meta*-substituents,  $\langle \sin^2 \theta \rangle$  becomes non-zero and  ${}^6J(\text{CHO}, \text{H4})$  may be observed. In most instances the sign of this coupling constant is negative, as it is in toluene [51], where  ${}^6J_{90}$  is -1.20 Hz. Recently, some *meta*-substituted derivatives of benzaldehyde have been shown to display a small positive six bond coupling constant, rationalized by an ionic valence bond model [29].

The value of  ${}^6J(\text{CHO},\text{H}_4)$  in *m*-fluorobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  is  $+0.047(2)$  Hz [29].

In the work done for this thesis, two *meta*-substituted derivatives of benzaldehyde display positive six bond coupling constants to the aldehyde protons. One of these compounds is *m*-chlorobenzaldehyde, where the best iterative fit to the experimental  ${}^1\text{H}$  nmr spectrum has  ${}^6J(\text{CHO},\text{H}_4)$  as  $+0.024(1)$  Hz. The aldehyde proton spectrum is seen in figure 4. Several theoretical spectra were prepared (using NUMARIT) with different signs and magnitudes attributed to this six bond coupling constant. These spectra are also shown in figure 4, with the values of  ${}^6J(\text{CHO},\text{H}_4)$  for each given in the caption. Clearly, the only two simulated spectra resembling the experimental one are 4B and 4E where  ${}^6J(\text{CHO},\text{H}_4)$  is  $+0.024$  Hz and  $+0.034$  Hz, respectively. Figure 4E is dissimilar enough to the experimental spectrum that  ${}^6J(\text{CHO},\text{H}_4)$  in 4B is quite certainly of the correct sign and magnitude.

The other compound possessing a positive  ${}^6J(\text{CHO},\text{H}_4)$  is *m*-tolualdehyde where this coupling constant is  $+0.015(1)$  Hz in acetone- $\text{d}_6$  and  $+0.024(3)$  Hz in  $\text{CS}_2/\text{C}_6\text{D}_{12}$ . The  ${}^1\text{H}$  nmr spectrum of the aldehyde proton is shown in figure 18A. The iteratively fit spectrum is seen in figure 18B. The spectra in figures 18C and 18D have all parameters the same as in 18B except that  ${}^6J(\text{CHO},\text{H}_4)$  is  $-0.015$  Hz in 18C and is  $0.000$  Hz in 18D. A good fit of the theoretical spectrum to the experimental one is seen in figure 18B only.

#### 4.0 *Ortho* and *meta*-cyanybenzaldehyde

## **4.1 Experimental Results**

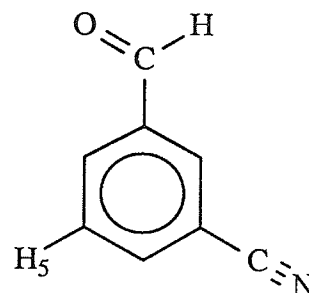
#### 4.1.1

The  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for 4 mol% solutions of 3-Cyanobenzaldehyde in acetone- $\text{d}_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$  are given in tables 22 and 23, respectively.

The STO-3G and AM1 computed energies of conformers of the free molecule having CHO rotated from  $0^\circ$  to  $180^\circ$  out of plane, in steps of  $15^\circ$ , are shown in table 24. The O-trans rotamer has  $\theta = 0^\circ$ . The STO-3G and AM1 energies are plotted versus  $\theta$  in figures 23 and 24.

Table 22. Spectral parameters<sup>a</sup> for 4.0 mol% 3-cyanobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2493.900	0.0001
v(H4)	2430.330	0.0002
v(H5) <sup>b</sup>	2356.567	0.0001
v(H6)	2474.964	0.0002
v(CHO)	3036.289	0.0000



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4)	1.701	0.0003	J(H5,H6)	7.820	0.0003
J(H2,H5)	0.642	0.0003	J(H5,CHO)	0.451	0.0003
J(H2,H6)	1.623	0.0003			
J(H2,CHO)	-0.072	0.0003			
J(H4,H5)	7.735	0.0003	J(H6,CHO)	-0.115	0.0003
J(H4,H6)	1.211	0.0003			
J(H4,CHO) <sup>c</sup>	-0.001	0.0003			

80 Transitions

Largest Difference = 0.002 Hz

62 Observed Peaks

RMS Deviation of Transitions = 0.0009

73 Assigned Transitions

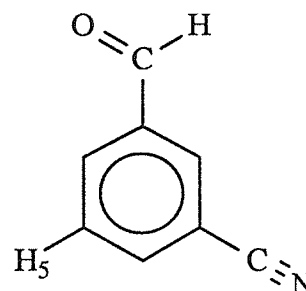


Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Correlated with J(H4,H5) by 0.1161, with J(H5,H6) by -0.1163, and with J(H5,CHO) by -0.1190.
- <sup>c</sup> The sign of J(H4,CHO) could not be determined by spectral simulation; however, its magnitude was determined to be 0.20 Hz or less.

Table 23. Spectral parameters<sup>a</sup> for 4.0 mol%<sup>b</sup> 3-cyanobenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H2)	2370.223	0.0003
v(H4)	2299.370	0.0003
v(H5)	2208.984	0.0003
v(H6)	2317.614	0.0003
v(CHO)	2965.010	0.0003



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H2,H4) <sup>c</sup>	2.054	0.0004	J(H5,H6)	7.617	0.0004
J(H2,H5)	0.447	0.0004	J(H5,CHO)	0.454	0.0004
J(H2,H6)	1.497	0.0004			
J(H2,CHO)	-0.087	0.0004			
J(H4,H5)	7.929	0.0004	J(H6,CHO)	-0.133	0.0004
J(H4,H6)	1.103	0.0004			
J(H4,CHO) <sup>d</sup>	0.000	0.0004			

80 Transitions

Largest Difference = 0.002 Hz

59 Observed Peaks

RMS Deviation of Transitions = 0.0011

74 Assigned Transitions

Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained 4.0 mol% 3-cyanobenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with J(H<sub>4</sub>,CHO) by 0.0845.
- <sup>d</sup> The sign of J(H<sub>4</sub>,CHO) could not be determined by spectral simulation<sup>e</sup> however, it was determined to be between -0.015 Hz and +0.020 Hz.

Table 24. *Ab initio* and Semiempirical Molecular Orbital Calculations for m-Cyanobenzaldehyde.

$\theta$ (deg)	Energy <sub>rel</sub> (kJ/mole)	
	STO-3G	AM1
0	0.00	0.00
15	1.46	0.67
30	5.58	2.60
45	11.50	5.41
60	17.72	8.34
75	22.40	10.50
90	24.13	11.29
105	22.48	10.58
120	17.97	8.56
135	11.95	5.81
150	6.12	3.18
165	1.95	1.38
180	0.46	0.76

Note:

The benzene ring moiety was kept planar while all bond lengths and angles within the ring were allowed to optimize. All other bond lengths and angles were allowed to vary during optimization.  $\theta = 0^\circ$  corresponds to the O-trans rotamer.

Figure 23. The STO-3G potential of 3-cyanobenzaldehyde upon rotation of the aldehyde group through 180<sup>10</sup>. The solid line is the fitted potential function:

$$V(\theta) = 0.5(1)\sin^2\left(\frac{\theta}{2}\right) + 23.8(1)\sin^2(\theta) - 0.4(1)\sin^2(2\theta)$$

and the triangles are the free energies from the individual molecular orbital computations.

---

<sup>1</sup>  $\theta = 0^\circ$  corresponds to the O-trans rotamer while  $\theta = 180^\circ$  corresponds to the O-cis rotamer.

## 3-Cyanobenzaldehyde ST0-3G

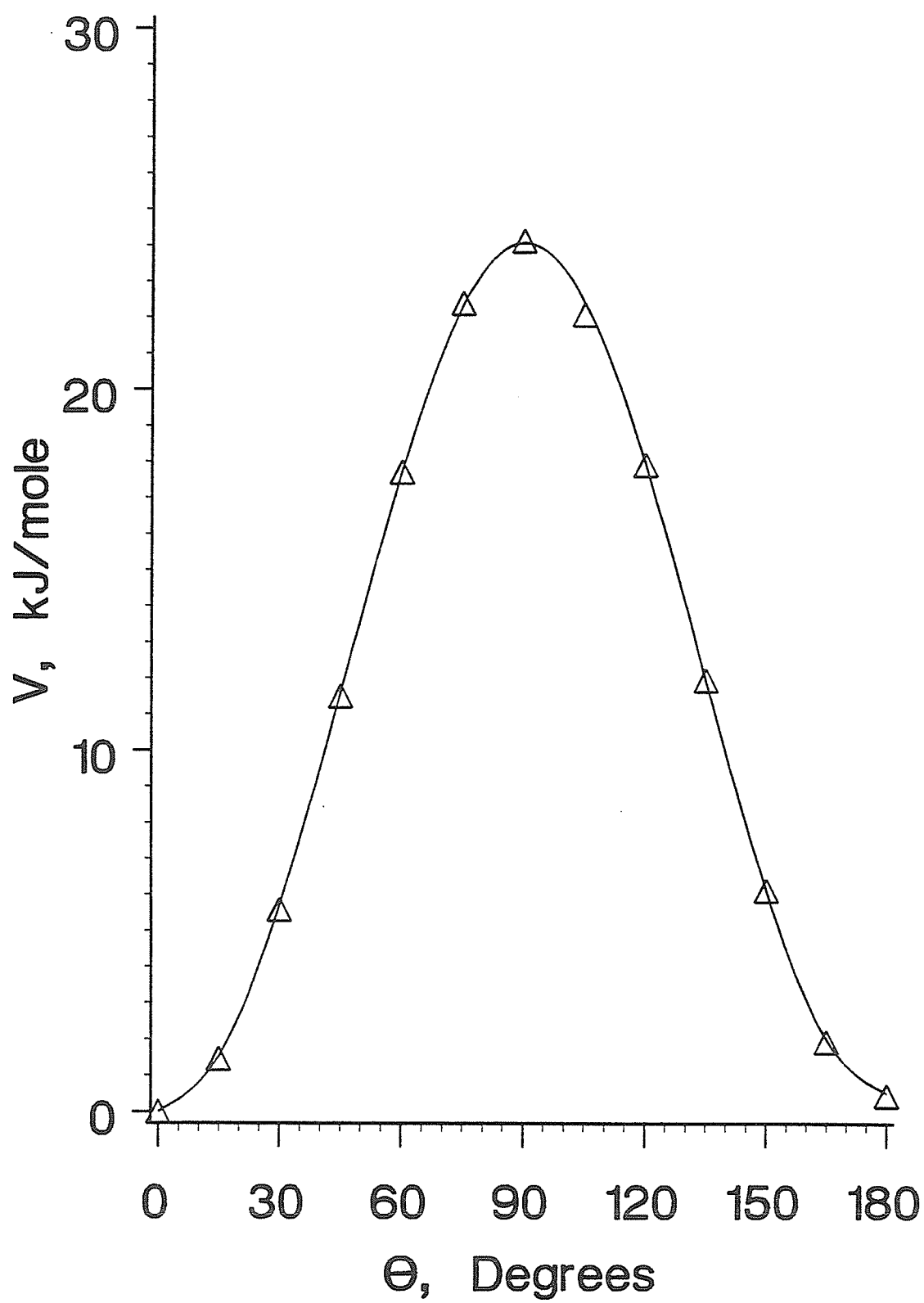


Figure 24. The AM1 potential of 3-cyanobenzaldehyde upon rotation of the aldehyde group through 180°<sup>1</sup>. The solid line is the fitted potential function:

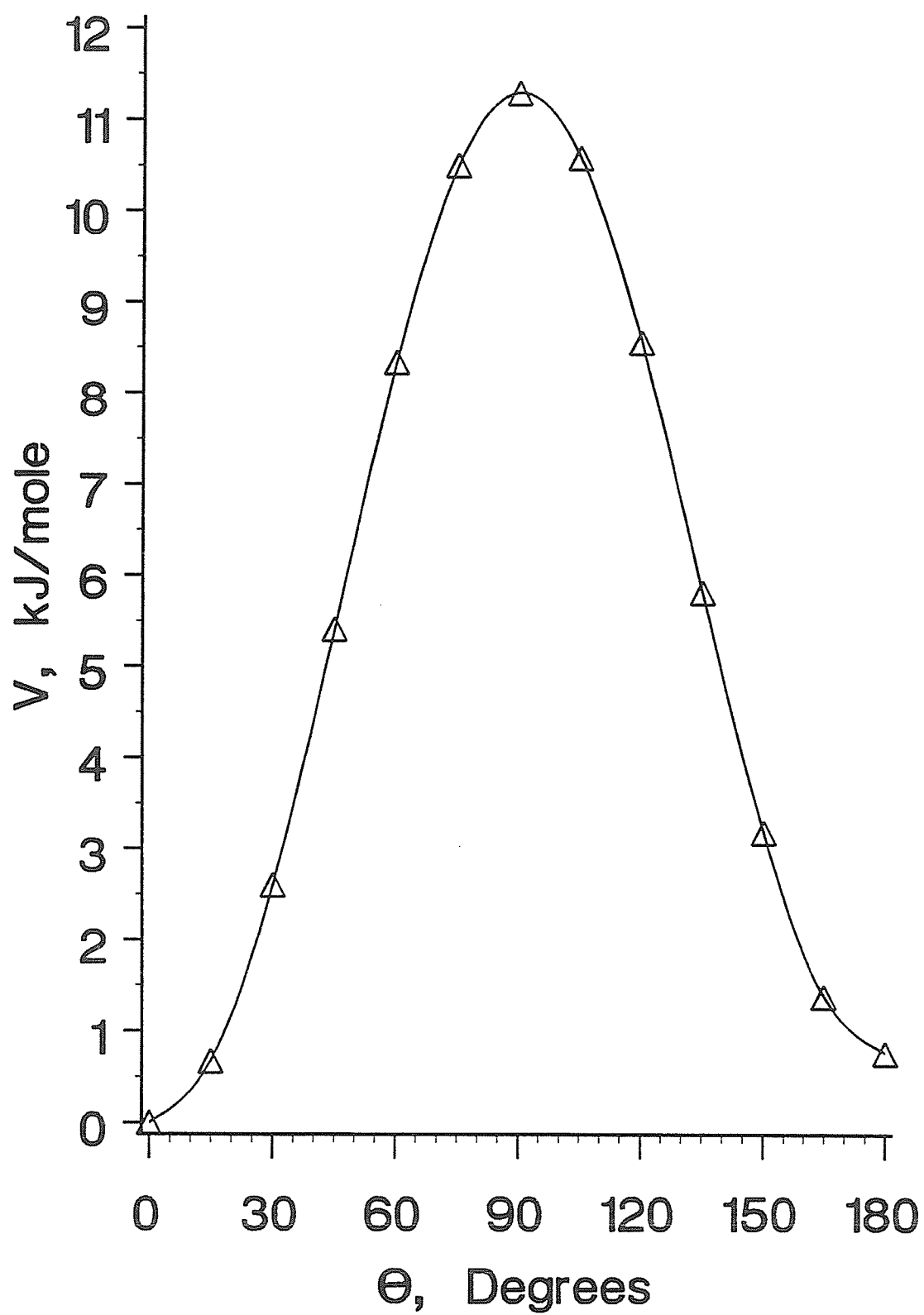
$$\begin{aligned}
 V(\theta) = & 0.66(1)\sin^2\left(\frac{\theta}{2}\right) + 10.98(1)\sin^2(\theta) \\
 & + 0.11(1)\sin^2\left(\frac{3\theta}{2}\right) - 0.23(1)\sin^2(2\theta) \\
 & - 0.07(1)\sin^2(3\theta)
 \end{aligned}$$

and the triangles are the free energies from the individual molecular orbital computations.

---

<sup>1</sup>  $\theta = 0^\circ$  corresponds to the O-trans rotamer while  $\theta = 180^\circ$  corresponds to the O-cis rotamer.

## 3-Cyanobenzaldehyde AM1





#### 4.1.2

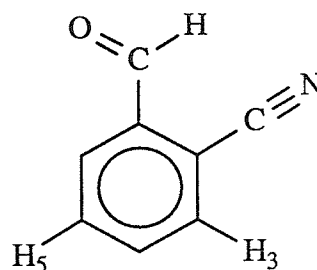
The  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for a 4 mol% solution of o-cyanobenzaldehyde in acetone- $\text{d}_6$ , measured at 300K is given in table 25. The parameters for a saturated solution of o-cyanobenzaldehyde in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  are given in table 26.

Figure 25 shows the aldehyde proton spectrum for o-cyanobenzaldehyde in acetone- $\text{d}_6$  along with the iterated computer simulation. Also shown are several computer simulations which verify the sign and magnitude of  $^6J(\text{CHO},\text{H}_4)$ .

The STO-3G energies for conformers of the free molecule with CHO rotated through  $180^\circ$ , in steps of  $15^\circ$ , are tabulated in table 27 and plotted against the angle of rotation in figure 26.

Table 25. Spectral parameters<sup>a</sup> for 4.0 mol% 2-cyanobenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2400.530	0.0004
v(H4) <sup>b</sup>	2375.044	0.0005
v(H5)	2387.770	0.0005
v(H6)	2439.262	0.0004
v(CHO)	3083.554	0.0005



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4) <sup>c</sup>	7.703	0.0007	J(H5,H6)	7.797	0.0007
J(H3,H5)	1.206	0.0007	J(H5,CHO)	0.480	0.0007
J(H3,H6)	0.562	0.0006			
J(H3,CHO) <sup>d</sup>	0.378	0.0007			
J(H4,H5)	7.602	0.0007	J(H6,CHO)	-0.130	0.0007
J(H4,H6)	1.307	0.0007			
J(H4,CHO)	-0.009	0.0008			

92 Transitions

Largest Difference = 0.005 Hz

73 Observed Peaks

RMS Deviation of Transitions = 0.0017

72 Assigned Transitions

Notes:

<sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.

<sup>b</sup> Correlated with J(H4,H6) by 0.2286.

<sup>c</sup> Correlated with J(H3,H5) by -0.1936.

<sup>d</sup> Correlated with  $\nu(\text{H3})$  by -0.1958 and with J(H4,CHO) by -0.2551.

Figure 25. A) The experimental 300 MHz spectrum of the aldehyde proton of 2-cyanobenzaldehyde in dilute (<1.5 mol%) acetone-d<sub>6</sub> solution at 300 K. B) The iteratively determined spectrum. The sign and magnitude of  ${}^6J(\text{CHO},\text{H}_4)$  is verified by simulating the spectrum with this coupling constant set to C) 0.000 Hz, D) 0.010 Hz, and E) -0.020 Hz.

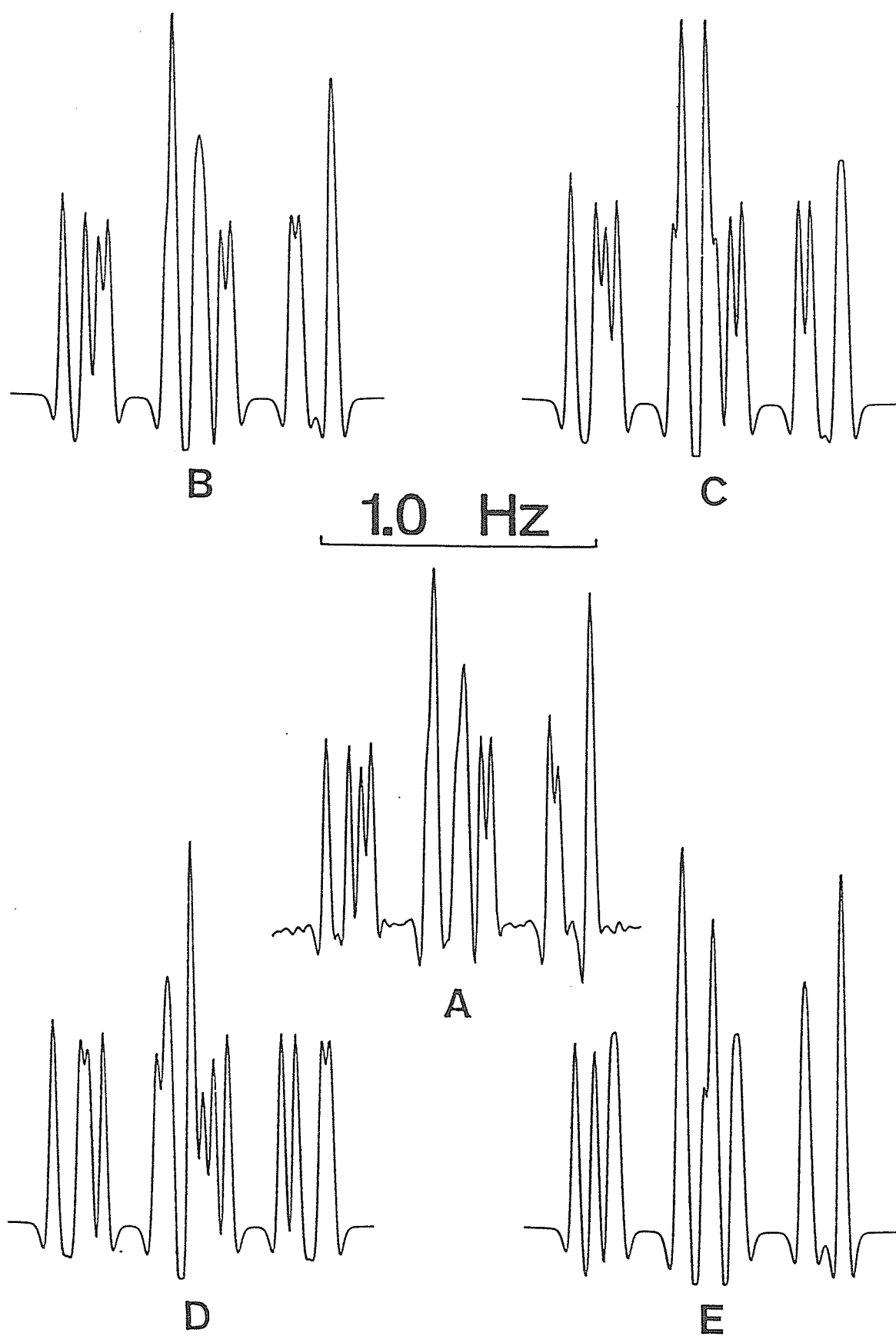
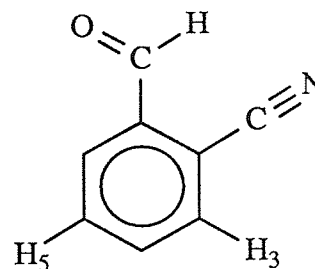


Table 26. Spectral parameters<sup>a</sup> for a saturated<sup>b</sup> solution of 2-cyanobenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3)	2320.561	0.0008
v(H4) <sup>c</sup>	2304.404	0.0011
v(H5) <sup>d</sup>	2312.081	0.0010
v(H6)	2399.714	0.0008
v(CHO) <sup>e</sup>	3099.799	0.0011



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4) <sup>f</sup>	7.709	0.0015	J(H5,H6)	7.847	0.0014
J(H3,H5)	1.229	0.0015	J(H5,CHO)	0.796	0.0014
J(H3,H6)	0.588	0.0012			
J(H3,CHO)	0.098	0.0013			
J(H4,H5)	7.520	0.0014	J(H6,CHO)	-0.099	0.0012
J(H4,H6)	1.340	0.0015			
J(H4,CHO) <sup>g</sup>	-0.010	0.0017			

100 Transitions

Largest Difference = 0.008 Hz

68 Observed Peaks

RMS Deviation of Transitions = 0.0032

72 Assigned Transitions

## Notes:

- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained less than 1.5 mol% 2-cyanobenzaldehyde with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with  $\nu(\text{H3})$  by -0.3012, with  $J(\text{H4},\text{H6})$  by -0.3030, and with  $J(\text{H5},\text{H6})$  by 0.2458.
- <sup>d</sup> Correlated with  $J(\text{H3},\text{H5})$  by 0.2663 and with  $J(\text{H5},\text{H6})$  by 0.2751.
- <sup>e</sup> Correlated with  $J(\text{H4},\text{CHO})$  by 0.3761 and with  $J(\text{H5},\text{CHO})$  by -0.2042.
- <sup>f</sup> Correlated with  $J(\text{H3},\text{H5})$  by -0.3451.
- <sup>g</sup> Spectral simulations with various values of  $J(\text{H4},\text{CHO})$  demonstrates it as negative and smaller than 0.020 Hz in magnitude.

Table 27. *Ab initio* Molecular Orbital Calculations for o-Cyanobenzaldehyde.

$\theta(\text{deg})$	Energy <sub>rel</sub> (kJ/mole)
	STO-3G
0	0.00
15	0.88
30	4.52
45	9.88
60	15.67
75	20.27
90	22.33
105	21.39
120	17.87
135	12.98
150	8.36
165	5.25
180	4.19

Note:

The benzene ring moiety was kept planar while all bond lengths and angles within the ring were allowed to optimize. All other bond lengths and angles were allowed to vary during optimization.  $\theta = 0^\circ$  corresponds to the O-trans rotamer.



Figure 26. The STO-3G potential of 2-cyanobenzaldehyde upon rotation of the aldehyde group through 180<sup>o1</sup>. The solid line is the fitted potential function:

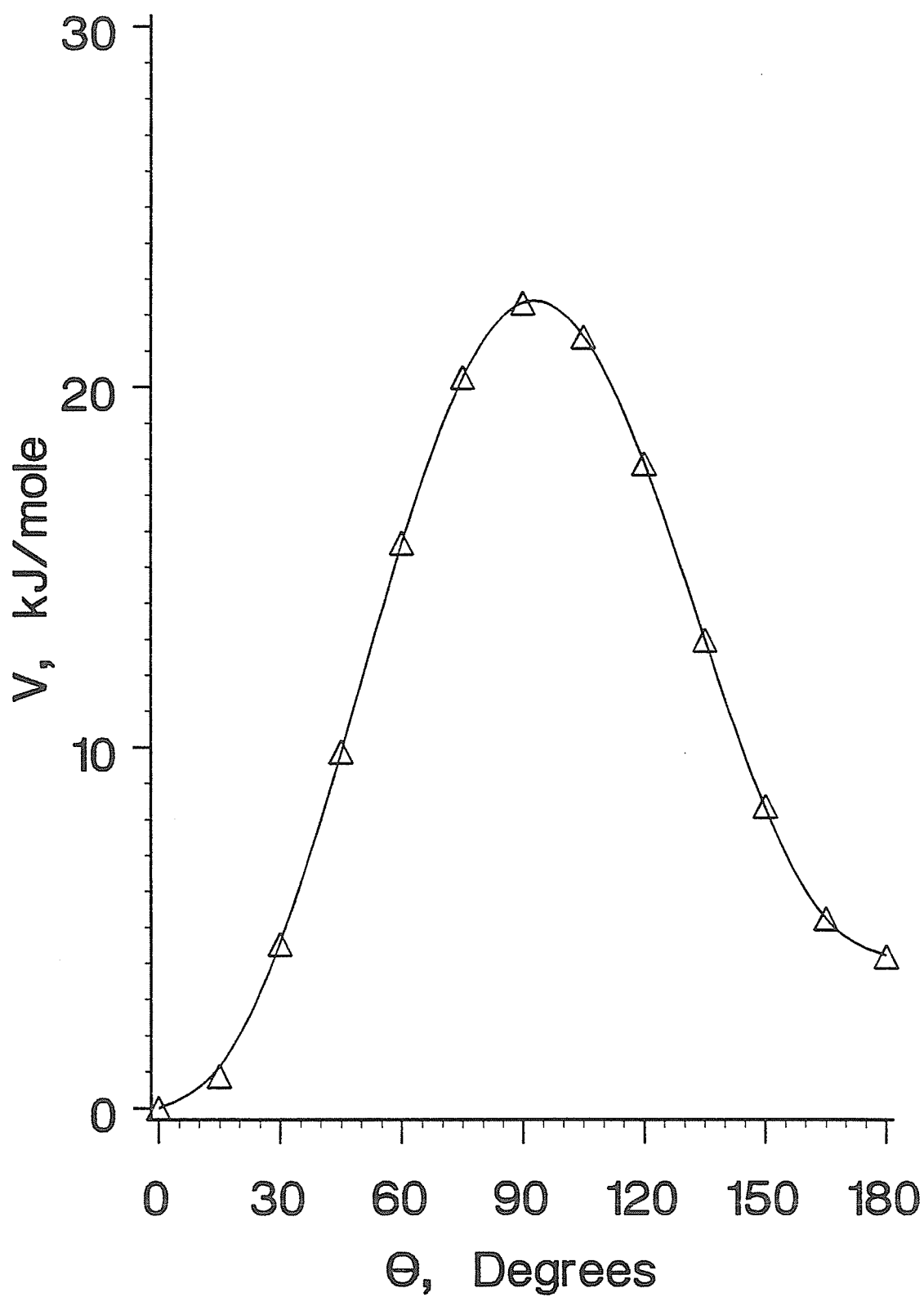
$$\begin{aligned}
 V(\theta) = & 4.31(3)\sin^2\left(\frac{\theta}{2}\right) + 20.37(3)\sin^2(\theta) \\
 & - 0.08(3)\sin^2\left(\frac{3\theta}{2}\right) - 0.80(3)\sin^2(2\theta) \\
 & - 0.15(3)\sin^2(3\theta)
 \end{aligned}$$

and the triangles are the free energies from the individual molecular orbital computations.

---

<sup>1</sup>  $\theta = 0^\circ$  corresponds to the O-trans rotamer while  $\theta = 180^\circ$  corresponds to the O-cis rotamer.

## 2-Cyanobenzaldehyde ST0-3G



## 4.2 Discussion

The distribution of conformers in m- and o-cyanobenzaldehyde in acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> varied significantly from those in the benzaldehyde derivatives presented in the previous chapter. The only other measurement of conformer populations in these compounds has been a dipole moment study [16] carried out in benzene. To facilitate a more accurate comparison of the results of these two methods, <sup>1</sup>H nmr analyses of m- and o-cyanobenzaldehyde were performed in benzene-d<sub>6</sub> as well in as acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. The quality of the spectra obtained for m- and o-cyanobenzaldehyde in benzene-d<sub>6</sub> was not as high as that obtained in the other solvents; however, the large magnitudes of the five bond coupling constants to the aldehyde protons, and the first order nature of the spectra, made it possible to determine the magnitudes of these coupling constants with reasonable precision. These analyses in benzene-d<sub>6</sub> are not tabulated but <sup>5</sup>J(CHO,H3) and <sup>5</sup>J(CHO,H5) are shown in table 28.

As was mentioned in the previous chapter, the computing time required for performing MO calculations escalates rapidly upon moving from semiempirical to *ab initio* approaches, and also upon employing higher level basis sets in the *ab initio* calculations. Because the results of the nmr analyses of m- and o-cyanobenzaldehyde were rather striking, perhaps because of the high dipole moments of these molecules, it was felt that the time needed for a more extensive MO evaluation would be justified. The results of these computations are discussed in this chapter.

Table 28. Populations of, and energy differences between, O-cis and O-trans rotamers of *ortho* and *meta*-cyanobenzaldehyde.

X	Solvent	$^5J(\text{CHO}, \text{H}3)^1$	$^5J(\text{CHO}, \text{H}5)^1$	$^5J_{\text{sum}}^2$	% O-cis	K <sup>3</sup>	$\Delta G^4$ (kJ/mol)
m-CN	acetone-d <sub>6</sub>	-----	0.451(1)	0.860(2)	47.6(2)	1.10(1)	0.23(3)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	-----	0.454(1)	0.862(4)	47.3(2)	1.11(1)	0.26(2)
	benzene-d <sub>6</sub> <sup>5</sup>	-----	0.542(2)	0.861(6)	37.0(5)	1.70(4)	1.3(1)
o-CN	acetone-d <sub>6</sub>	0.378(1)	0.480(1)	0.858(2)	44.1(2)	1.27(1)	0.60(2)
	CS <sub>2</sub> /C <sub>6</sub> D <sub>12</sub>	0.098(1)	0.796(1)	0.894(2)	11.0(1)	8.09(8)	5.21(3)
	benzene-d <sub>6</sub> <sup>5</sup>	0.210(7)	0.654(4)	0.864(11)	24.3(8)	3.1(1)	2.8(1)

<sup>1</sup> In Hz at 300 K. <sup>1</sup>H nmr at 300.135 MHz to high frequency of TMS.

<sup>2</sup> The sums for m-cyanobenzaldehyde in acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> are those from benzaldehyde. The sum for m-cyanobenzaldehyde in benzene-d<sub>6</sub> is the average of the sums for benzaldehyde in the two solvents.

<sup>3</sup> K is defined as  $P_{\text{O-trans}}/P_{\text{O-cis}}$ .

<sup>4</sup>  $\Delta G = -RT \ln K$

<sup>5</sup> These values are from simple first order inspection of the corresponding spectra.

*<sup>1</sup>H nmr Analyses*i) *meta*-cyanobenzaldehyde

Table 28 shows the percentage of O-cis rotamer of m-cyanobenzaldehyde in three solvents at 300 K. It is observed that, within the limits of uncertainty, the proportions of rotamers in acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> are the same. In both solvents there is a slight, < 3%, predominance of the O-trans form, favoured by 0.3(1) kJ/mol in free energy. The percentages in table 28 presuppose that a ring substituent *meta* to the aldehyde group causes no change in the coupling constants over five bonds between the aldehyde proton and H5. This assumption is reasonable in that the substituent is placed far from the coupling pathway and from the aldehyde group.

In benzene-d<sub>6</sub> the population of the O-cis form drops appreciably from that in the other two solvents. The coupling constant between the aldehyde proton and H5 in this solvent is 0.542(2) Hz compared to 0.451(1) Hz in acetone-d<sub>6</sub> and 0.454(1) Hz in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. The proportion of O-cis rotamer in benzene-d<sub>6</sub> at 300 K is 0.37(1), provided that the extremum of <sup>5</sup>J(CHO, H<sub>m</sub>) is not different from that of benzaldehyde, where 0.861(4) Hz is the average of the five bond coupling constants measured in acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

The dipole moment of the O-cis form is seen in table 29 to be much higher than that for the O-trans form, with STO-3G computations giving 4.32 D for the former and 1.97 D for the latter. Similarly large differences in the dipole moments determined by group moments and other MO approaches are seen in table 29. Those calculated by the AM1 calculations are much too small; however, even by this

Table 29. Relative conformational energies, populations, and dipole moments of o- and m-cyanobenzaldehyde.

<i>Meta</i> -cyanobenzaldehyde					
Method	Dipole moments (D)			$E_c - E_t$ (kJ/mol)	$P_t$
	O-cis	O-trans	$C_6H_6$		
$\mu/C_6H_6^a$	5.31 <sup>a</sup>	1.75 <sup>a</sup>	3.45 <sup>a</sup>	1.5(2) <sup>b</sup>	0.65(2)
$^5J(CHO, H_m)/C_6D_6$	————	————	(3.5) <sup>g</sup>	1.3(1)	0.63(1)
$^5J(CHO, H_m)/CS_2$	————	————	————	0.2(1) <sup>c</sup>	0.52(1)
$^5J(CHO, H_m)/acet$	————	————	————	0.2(1) <sup>c</sup>	0.53(1)
vapour/extrap	————	————	————	0.2(1) <sup>d</sup>	0.52(1)
STO-3G MO	4.32	1.97	(3.1) <sup>f</sup>	0.46 <sup>e</sup>	0.55
6-31G MO	6.36	1.93	(4.2) <sup>f</sup>	1.12	0.61
CNDO/2 MO	4.42	1.08	(2.8) <sup>f</sup>	0.35	0.54
INDO MO	4.41	1.15	(2.8) <sup>f</sup>	0.29	0.53
AM1 MO	1.81	0.45	(1.2) <sup>f</sup>	0.76	0.58
<i>Ortho</i> -cyanobenzaldehyde					
$\mu/C_6H_6^a$	6.89 <sup>a</sup>	4.74 <sup>a</sup>	4.94 <sup>a</sup>	6.1 <sup>b</sup>	0.92
$^5J(CHO, H_m)/C_6D_6$	————	————	(5.3) <sup>g</sup>	2.6(3)	0.76(1)
$^5J(CHO, H_m)/CS_2$	————	————	————	5.1(3) <sup>c</sup>	0.89(1)
$^5J(CHO, H_m)/acet$	————	————	————	0.4(3) <sup>c</sup>	0.56(1)
vapour/extrap	————	————	————	10.3±1.2 <sup>d</sup>	0.98(1)
STO-3G MO	5.16	3.50	(4.0) <sup>f</sup>	4.19 <sup>e</sup>	0.84
6-31G MO	7.87	5.21	(6.0) <sup>f</sup>	14.71 <sup>e</sup>	0.99
CNDO/2 MO	5.46	4.22	(4.5) <sup>f</sup>	1.42	0.64
INDO MO	5.51	3.54	(4.1) <sup>f</sup>	0.32	0.53

## Notes:

- <sup>a</sup> Dipole moment measured in benzene at 298 K [16]; the dipole moments of the two conformers are estimated from group dipoles [16].
- <sup>b</sup> The free energy difference at 298 K, calculated from the fractional population,  $P_t$ , of the O-trans rotamer;  $P_t$  follows from the measured dipole moment of 4.94 D and the estimated conformer moments.
- <sup>c</sup> The free energy difference between the O-cis and O-trans rotamers at 300 K, as deduced from  $^5J(\text{CHO}, H_m)$  by methods described in the text.
- <sup>d</sup> The free energy difference in the vapour at 300 K, obtained by extrapolation of solution data on the basis of a dielectric model discussed in the text.
- <sup>e</sup> The energy differences between the conformers, obtained from the molecular orbital computations, are assumed to be free energy differences in the calculation of  $P_t$  at 300 K.
- <sup>f</sup> The dipole moments in parentheses are those calculated for a benzene solution in which the computed dipole moments in the same row are used and the conformer populations are those implied by  $^5J(\text{CHO}, H_m)/C_6D_6$ . Of course, the predicted dipole moment follows from  $\mu^2 = P_t \mu_t^2 + (1 - P_t) \mu_c^2$ .
- <sup>g</sup> Calculated with the dipole moments of the conformers as estimated from the group moments in the row above and from the value of  $P_t$  obtained from  $^5J(\text{CHO}, H_m)/C_6D_6$ .



method, O-cis is the much more polar form of m-cyanobenzaldehyde. It appears from the proportions of the rotamers in the three solvents that there is a specific interaction between the benzene solvent molecules and the solute molecules causing stabilization of the less polar form of m-cyanobenzaldehyde. A free energy difference of 1.3(1) kJ/mol between the conformers at 300 K agrees well with that of 1.5(2) kJ/mol obtained from the dipole moment measurement [16], mentioned above.

ii) *ortho*-cyanobenzaldehyde

A pronounced change in rotamer populations occurs upon passage from acetone-d<sub>6</sub> to CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. Table 28 shows that the O-cis population in acetone-d<sub>6</sub> is 0.441(2) but is only 0.110(1) in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. The free energy difference between rotamers rises from 0.60(2) kJ/mol in acetone-d<sub>6</sub> to 5.21(3) kJ/mole in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

The above values are calculated using the sums of the two five bond coupling constants for each solvent. This sum in acetone-d<sub>6</sub> is 0.858(2) Hz which is within the uncertainty limits of 0.860(2) Hz determined for benzaldehyde in that solvent [29]. In CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solution, however, the two  $^5J(\text{CHO}, \text{H}_m)$  values sum to 0.894(2) Hz. If the extrema in  $^5J(\text{CHO}, \text{H}_5)$  and  $^5J(\text{CHO}, \text{H}_3)$  are both taken as 0.894(2) Hz, then K follows as 8.09(8), the fractional population of the O-cis form being 0.110(1), and the free energy difference between conformers being 5.21(3) kJ/mol at 300 K.

As was explained in the previous chapter, the sums of the five bond aldehyde coupling constants in molecules of this kind are commonly very similar to the corresponding sum for benzaldehyde. Relatively large differences in this sum contribute only a small uncertainty to the equilibrium constant and, hence, the

calculated free energy difference between rotamers. For instance, if  ${}^5J(\text{CHO},\text{H3})_c$  and  ${}^5J(\text{CHO},\text{H5})_t$  are independent of solvent and the antizigzag  ${}^5J(\text{CHO},\text{H}_m)$  vanish, the following system of equations is obtained:

$${}^5J(\text{CHO},\text{H5})_{\text{Ac}} = P_t^{\text{Ac}} \cdot {}^5J(\text{CHO},\text{H5})_t = 0.480(1) \text{ Hz}$$

$${}^5J(\text{CHO},\text{H3})_{\text{Ac}} = P_c^{\text{Ac}} \cdot {}^5J(\text{CHO},\text{H3})_c = 0.378(1) \text{ Hz}$$

$${}^5J(\text{CHO},\text{H5})_{\text{CS}_2} = P_t^{\text{CS}_2} \cdot {}^5J(\text{CHO},\text{H5})_t = 0.796(1) \text{ Hz}$$

$${}^5J(\text{CHO},\text{H3})_{\text{CS}_2} = P_c^{\text{CS}_2} \cdot {}^5J(\text{CHO},\text{H3})_c = 0.098(1) \text{ Hz} \quad .$$

Solution of this system of equations yields  ${}^5J(\text{CHO},\text{H5})_t = 0.907 \text{ Hz}$  and  ${}^5J(\text{CHO},\text{H3})_c = 0.803 \text{ Hz}$ . The fractional population of the O-cis form becomes 0.12 in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  and 0.44 in acetone- $\text{d}_6$ . Hence K is 7.2 in the former and 1.13 in the latter solution, corresponding to free energy advantages of 4.9 and 0.3 kJ/mol, respectively.

Comparison of these magnitudes with those in table 28 suggests an uncertainty of 0.3 kJ/mol in the derived energy differences. From this point on in this discussion, the free energy differences will be considered to be 0.4(3) and 5.0(3) kJ/mol in the polar and non-polar media, respectively.

It is interesting that  ${}^5J(\text{CHO},\text{H5})$  is implied by this treatment to be about 0.05 Hz greater than in benzaldehyde. Consider that in the O-trans conformer, the very polar cyano group (the dipole moment of cyanobenzene is 4.0 D [53] compared, for example, to 1.4 D for fluorobenzene) lies parallel to the C-H bond of the aldehyde group and the dipolar field of  $\text{C}\equiv\text{N}$  will act to polarize the aldehyde C-H bond in the sense of  $\text{C}^-\text{H}^+$ . That this polarization occurs is demonstrated by the chemical shift of

the aldehyde proton (table 25) in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution. Perhaps coincidentally, CNDO/2 MO FPT computations done for the optimized STO-3G geometries gave  $^5\text{J}(\text{CHO},\text{H5})_t$  as 0.926 Hz and  $^5\text{J}(\text{CHO},\text{H3})_c$  as 0.842 Hz, in qualitative support of the treatment above. In any event, the uncertainty introduced into the populational distribution by such perturbations is reasonably small in solution.

For a <1.3 mol% solution of o-cyanobenzaldehyde in benzene-6,  $^5\text{J}(\text{CHO},\text{H3})$  is 0.210(7) Hz and  $^5\text{J}(\text{CHO},\text{H5})$  is 0.654(4) Hz. Their sum is 0.864(11) Hz which, within experimental uncertainty, is the same as that in acetone-d<sub>6</sub> and that for benzaldehyde in acetone-d<sub>6</sub>. As is seen in table 28, the population of the O-cis rotamer follows as 0.243(8) at 300 K and the free energy difference between the conformers as 2.8(1) kJ/mol, midway between the free energy differences determined for o-cyanobenzaldehyde in the other two solvents.

### *Extrapolation to the vapour*

The reaction field model arises from the general theory of dielectrics and asserts that the proportion of each rotamer will vary corresponding to interactions between the electric field of the solute rotamers and the dielectric solvent [54]. The electric fields originate in the polarization of the solvent molecules that surround each solute molecule. Since the rotamers being discussed are not charged bodies, a first approximation within this theory deals with dipole moments only. Quadrupolar and higher terms, which can sometimes be significant, are neglected. Abraham and Bretschneider [54] give:

$$\Delta E^v - \Delta E^s = \frac{(m_A^2 - m_B^2)}{a^3} \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) \quad (6)$$

to describe the equilibrium between two rotamers, A and B. In this equation  $\Delta E^v$  and  $\Delta E^s$  are the differences in energy between conformers in the vapour and solvent, respectively. The dipole moments of the rotamers are  $m_A$  and  $m_B$  and  $a$  is the radius of the spherical solute cavity.  $\epsilon$  is the dielectric constant of the solvent. The reaction field model yields free energy differences [55,56] so equation (6) can be rewritten as:

$$\ln K_{eq}^s = \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) (m_A^2 - m_B^2) + \ln K_{eq} \quad (7)$$

Simple extrapolation of a plot of  $\ln K_{eq}^s$  versus  $(\epsilon - 1)/(2\epsilon + 1)$  to  $\epsilon = 1$  (vapour) should yield the equilibrium constant of the vapour. Equation (7) demonstrates the well known principle that solvents of high dielectric constant favour the rotamer of greater dipole moment. Empirically it is found that the change in the free energy difference between rotamers upon going from acetone to  $CS_2$  is close to that in going from  $CS_2$  solution to the vapour (see equation 13.18 and p. 562 of ref. 45 for a rationalization of this finding).

It is known [54] that, in the reaction field model of solvent perturbation of conformational energies, benzene behaves as if it had a much higher dielectric constant

than its static value of 2.3. Perusal of the available data [54] suggests that the effective dielectric constant varies from solute to solute and that it can be as low as 4.3 or even as high as 35, with 7.5 being a more common value. Specific interactions with the polar solute molecules are indicated by these observations.

i) *meta*-cyanobenzaldehyde

As mentioned above, the conformer populations do not vary on passage from the non-polar  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solution to the polar acetone- $\text{d}_6$  solution. At first glance this is surprising, considering the large difference in the dipole moments of the two conformers. If the constituent dipoles are sufficiently far apart (p. 507 of ref. 45), then the reaction field model becomes inappropriate and, at least for *m*-cyanobenzaldehyde, the orientation of the local aldehyde dipole relative to that of a local dipole centred at the cyano group is effectively unaltered by the surrounding medium (an accidental cancellation of dipolar and quadrupolar stabilization energies, such as to leave the conformational distribution unaltered in the two solvents, cannot be ruled out, however). The free energy difference between conformers, calculated from the five bond coupling constants is 0.24(4) kJ/mol at 300 K. Accordingly, in the vapour the O-trans form will be slightly the more abundant form and measurements at ambient temperatures will involve both conformers.

ii) *ortho*-cyanobenzaldehyde

The difference in free energies between the conformers of *o*-cyanobenzaldehyde are 0.60(2) and 5.21(3) kJ/mol in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  and acetone- $\text{d}_6$ ,

respectively. Empirically, the reaction field model implies this energy difference to be 9.6(6) kJ/mol in the vapour at 300 K, O-trans favoured. Alternatively, if  $(\epsilon - 1)/(2\epsilon + 1)$  is taken as 0.25 for the CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solvent mixture and as 0.46 for the acetone-d<sub>6</sub> solution, the extrapolation procedure mentioned above gives a free energy difference of 10.9(6) kJ/mol in the vapour at 300 K. It appears that a reasonable, semiempirical, estimate is  $10.3 \pm 1.2$  kJ/mol at 300 K. This free energy difference corresponds to a value of 0.98(1) for the fractional population of the O-trans form of o-cyanobenzaldehyde in the vapour. In this instance the effective dielectric constant of the benzene-d<sub>6</sub> solvent appears to lie between those of acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>; a value of 5 is indicated by the results. Accordingly, measurements on the vapour at ambient temperatures are predicted to involve the O-trans form almost exclusively.

### ***Molecular orbital computations and comparison to dipole moment results [16]***

#### **i) The internal barrier and relative energies**

As was discussed in the introduction, *ab initio* molecular orbital computations using a minimal basis set reproduce the internal rotational potential in benzaldehyde much more faithfully [20] than those using split valence bases such as 6-31G and 6-31G\*. Accordingly, the internal rotational potentials in o- and m-cyanobenzaldehyde were computed with the basis, STO-3G. The results of these calculations for m-cyanobenzaldehyde are seen in table 24 and figure 23. The equation to which the computed energies were fit is seen in the caption to figure 23. The barrier to rotation of CHO from the more stable O-trans form to  $\theta = 90^\circ$  (the O-trans barrier) is

essentially that computed for benzaldehyde [20], as is the fourfold component, in  $\sin^2 2\theta$ .

As a matter of curiosity, the same computations were carried out using the semiempirical AM1 approach. These results are also seen in table 24 and figure 24. The O-trans barrier at about 11.3 kJ/mol is seen to be much too low. The AM1 value of 0.76 kJ/mol favouring the O-trans rotamer, however, is in qualitative agreement with the STO-3G result, 0.46 kJ/mol. CNDO/2 and INDO computations were also conducted for the two conformers of this molecule; the results are seen in table 29. The closest agreement between computed O-trans fractional populations and  $^1\text{H}$  nmr results is that of the INDO calculations, where  $P_t$  is implied as 0.53 compared to the experimental result, 0.52(1). A slightly greater abundance of the O-trans form is suggested by all of the MO approaches, in qualitative agreement with the magnitudes of  $^5\text{J}(\text{CHO}, \text{H3})$  and  $^5\text{J}(\text{CHO}, \text{H5})$ . According to the reaction field model mentioned above, this is also the expected result for the vapour.

The STO-3G computed energies for o-cyanobenzaldehyde are seen in table 27 and figure 26. The equation describing these potentials is seen in the caption to figure 26. The standard deviation in this case is 0.03 kJ/mol, except that the energy at  $\theta = 15^\circ$  is overestimated by 0.26 kJ/mol by this expression. The O-trans rotamer has  $\theta = 0^\circ$ . The height of the barrier at  $\theta = 90^\circ$ , relative to  $\theta = 0^\circ$  (the O-trans barrier), is computed as 2.0 kJ/mol lower than in benzaldehyde [26]. The only internal barriers known for *ortho*-substituted benzaldehydes are those measured for the alkyl derivatives by dynamic nmr [5,6]. For o-tolualdehyde, the O-trans barrier is 3.6 kJ/mol [6] lower than for benzaldehyde in the same solvent system. The lower barrier is attributed to

destabilization of the planar forms due to steric interactions. For o-cyanobenzaldehyde, the O-cis barrier is computed to be 6.1 kJ/mol lower than in benzaldehyde, presumably due to destabilization of the O-cis conformer by dipole-dipole repulsion of the two dipolar groups and by a decrease of the  $C_{sp^2}-C_{sp^2}$  mobile bond order caused by the cyano group which competes with the carbonyl group for  $\pi$  electrons. This competition could also account for the barrier decrease computed for the O-trans conformer. Measurement of the internal barrier in o-cyanobenzaldehyde by dynamic nmr would require the use of a rather polar solvent because otherwise very little of the O-cis conformer would exist at the requisite low temperatures.

## ii) Comparison to the dipole moment results

The only previous investigation into the conformational behaviour of o- and m-cyanobenzaldehyde determined rotamer populations through comparison of dipole moments measured in benzene solution to the dipole moments estimated for the two planar forms using group moments [16]. The authors report that no consideration was given for mutual inductive or steric effects in arriving at the estimated moments of the conformers. The fractional population of the O-trans form of m-cyanobenzaldehyde obtained by these researchers was 0.65(2). The value of  $P_t$  obtained from the five bond coupling constants in benzene-d<sub>6</sub> solution is 0.63(1). These coincident results support the observation that there are specific interactions between the benzene solvent molecules and the O-cis form of m-cyanobenzaldehyde.

The results for o-cyanobenzaldehyde by the two methods above are not as congruent. The population of the O-trans isomer indicated by  $^5J(\text{CHO}, H_m)$  is 0.76(1)



compared to 0.92(1) by the dipole moment method. The authors [16] realize the uncertainty of their predicted dipole moments and conclude only that the O-trans form is strongly favoured. Perhaps a closer approximation to the rotamer dipole moments, which takes into account the proximity of the polar groups, can be had by considering the moments computed by the MO calculations in table 29, and the populations implied by the coupling constants.

If the populations determined from  $^5J(\text{CHO}, \text{H}_m)$  are assumed correct, then the estimated dipole [16] moments of the rotamers imply that the measured dipole moment should be 5.3 D; the measured value is 4.9 D [16]. Therefore, at least one of the estimated [16] dipole moments of the conformers is presumably too large. Once more assuming that the populations based on  $^5J(\text{CHO}, \text{H}_m)$  are correct, but this time using the STO-3G dipole moments, a value of 4.0 D is implied in benzene solution. Therefore, at least one of these theoretical dipole moments is underestimated. This minimal basis set underestimates [57] the dipole moments of benzaldehyde and cyanobenzene by 1.08 D and about 0.5 D, respectively, so that this conclusion is expected. If, arbitrarily, the STO-3G values are each increased by 1.0D, then, together with the populations given by  $^5J(\text{CHO}, \text{H}_m)$ , the dipole moment of o-cyanobenzaldehyde in benzene at 300 K is calculated as 4.95(4) D, precisely as measured [16].

## **5.0 *Ortho*-isopropyl benzaldehyde**

## **5.1 Experimental Results**

### 5.1.1

The  $^1\text{H}$  nuclear magnetic resonance shifts and coupling constants for 4 mol% solutions of *o*-isopropylbenzaldehyde in acetone- $\text{d}_6$ , and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , measured at 300 K, are given in tables 30 and 31, respectively.

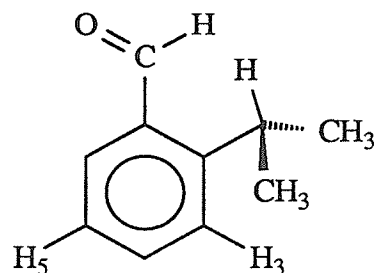
Spin-spin coupling between the ring protons and those of the methyl groups necessitated the use of a second radio frequency to decouple the methyl group transitions from the rest of the spectrum. In order to determine whether or not the aldehyde proton was coupled to the methyl group protons, the spectral window over which the decoupled FIDs were acquired was extended to a frequency just higher than that of the aldehyde proton signal.

A spin tickling experiment was performed to determine the sign of the sizable proximate coupling constant between the aldehyde proton and the methine proton of the isopropyl substituent. In this procedure, one transition in the spectrum is weakly perturbed by irradiation with a second radio frequency. Other transitions, which share one of the spin states of the irradiated transition, are consequently perturbed as well. In the spectrum, this is observed as a small splitting of the peaks due to these transitions. Two transitions of the ring proton at position 5 were weakly irradiated, one at a time, with a second radio frequency during acquisition of the aldehyde proton FID. H5 was chosen because it is measurably spin coupled to the aldehyde proton and to the methine proton, as well as to H3 and H6 which are also measurably spin coupled to the aldehyde proton. Since the signs of these other coupling constants are known, the sign of the proximate coupling constant can be ascertained by observing

which transitions in the aldehyde region of the spectrum are affected. The aldehyde proton spectra resulting from this experiment are seen in figure 28. First order representations of the spectra of the aldehyde proton, and the high frequency octet of the spectrum of H5, are seen in figure 27.

Table 30. Spectral parameters<sup>a</sup> for 4.0 mol% 2-isopropylbenzaldehyde in acetone-d<sub>6</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3) <sup>b</sup>	2262.350	0.0005
v(H4)	2281.980	0.0004
v(H5)	2218.858	0.0004
v(H6)	2349.096	0.0004
v(CHO) <sup>c</sup>	3112.755	0.0005
v(CH3) <sup>d</sup>	1214.000	



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	7.905	0.0006	J(H5,H6)	7.721	0.0006
J(H3,H5)	1.179	0.0007	J(H5,CHO)	0.473	0.0006
J(H3,H6)	0.515	0.0007	J(H5,CH)	-0.252	0.0008
J(H3,CHO)	0.341	0.0007			
J(H3,CH) <sup>e</sup>	-0.555	0.0011			
J(H4,H5)	7.340	0.0000	J(H6,CHO)	-0.264	0.0006
J(H4,H6)	1.545	0.0006	J(H6,CH)	0.168	0.0008
J(H4,CHO)	-0.017	0.0006			
J(H4,CH)	0.503	0.0009	J(CHO,CH) <sup>f,g</sup>	-0.388	0.0009

192 Transitions

Largest Difference = 0.006 Hz

122 Observed Peaks

RMS Deviation of Transitions = 0.0022

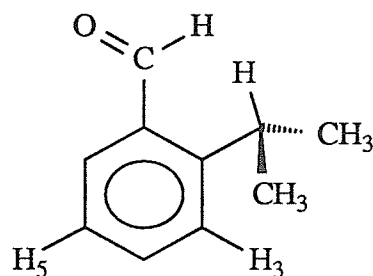
138 Assigned Transitions

## Notes:

- <sup>a</sup> In Hz at 300 K.  $^1\text{H}$  resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> Correlated with  $J(\text{H3},\text{H5})$  by 0.1905.
- <sup>c</sup> Correlated with  $J(\text{H5},\text{CHO})$  by 0.1812.
- <sup>d</sup> Not optimized.
- <sup>e</sup> Correlated with  $J(\text{H3},\text{H6})$  by 0.2754.
- <sup>f</sup> Correlated with  $J(\text{H4},\text{CHO})$  by 0.1281 and with  $J(\text{H5},\text{CHO})$  by 0.1393.
- <sup>g</sup> The sign of  $^5J(\text{CHO},\text{CH})$  was determined by a double resonance experiment.

Table 31. Spectral parameters<sup>a</sup> for 4.0 mol%<sup>b</sup> 2-isopropylbenzaldehyde in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>.

<u>Proton</u>	<u>Shift</u>	<u>Std.Dev.</u>
v(H3) <sup>c</sup>	2208.959	0.0005
v(H4)	2230.121	0.0005
v(H5)	2175.037	0.0004
v(H6)	2300.599	0.0004
v(CHO)	3059.957	0.0006
v(CH3) <sup>d</sup>	1185.50	



<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>	<u>Coupling</u>	<u>Magnitude</u>	<u>Std.Dev.</u>
J(H3,H4)	7.877	0.0007	J(H5,H6)	7.687	0.0006
J(H3,H5)	1.191	0.0007	J(H5,CHO) <sup>e</sup>	0.421	0.0008
J(H3,H6)	0.503	0.0007	J(H5,CH)	-0.265	0.0009
J(H3,CHO)	0.383	0.0008			
J(H3,CH)	-0.559	0.0011			
J(H4,H5)	7.326	0.0007	J(H6,CHO)	-0.273	0.0007
J(H4,H6)	1.546	0.0007	J(H6,CH)	0.167	0.0009
J(H4,CHO)	-0.014	0.0008			
J(H4,CH)	0.500	0.0009	J(CHO,CH)	-0.376	0.0013

192 Transitions

Largest Difference = 0.007 Hz

127 Observed Peaks

RMS Deviation of Transitions = 0.0025

137 Assigned Transitions

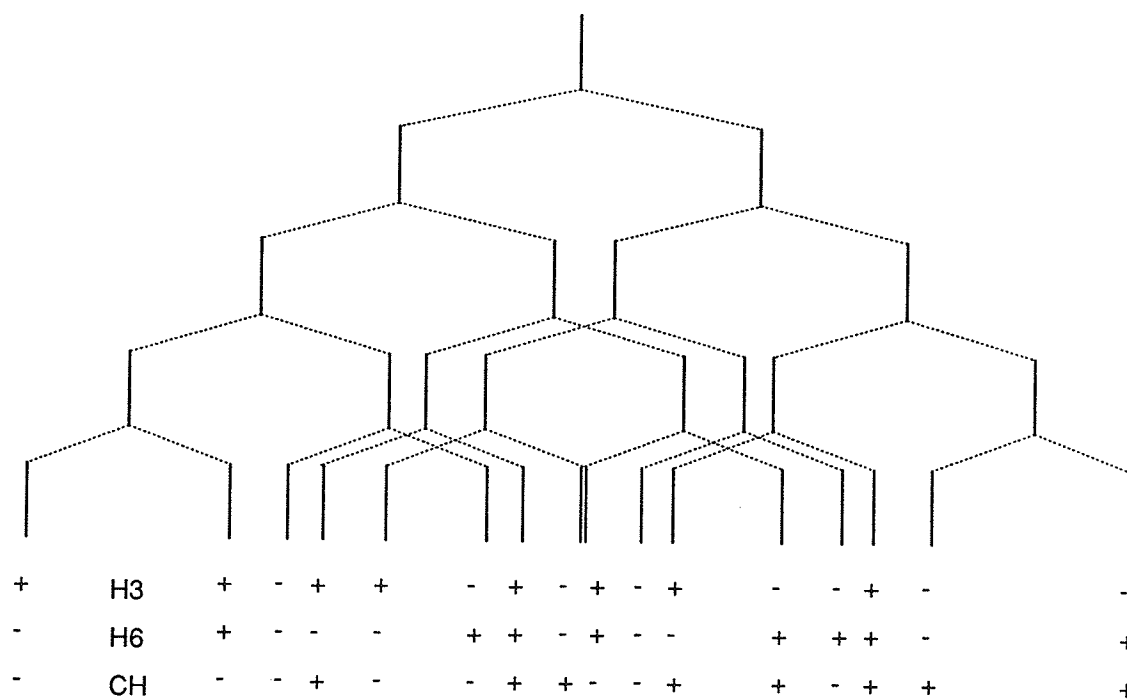
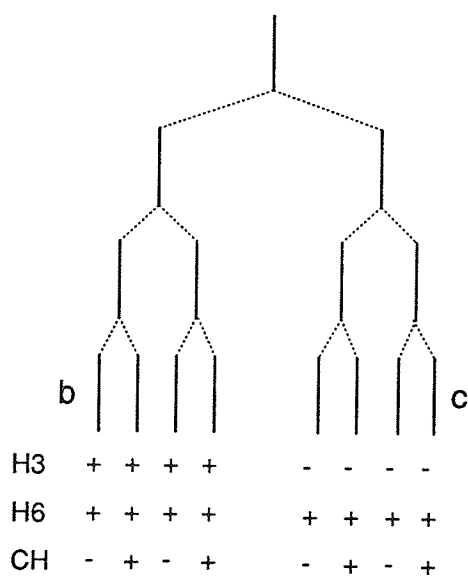


## Notes:

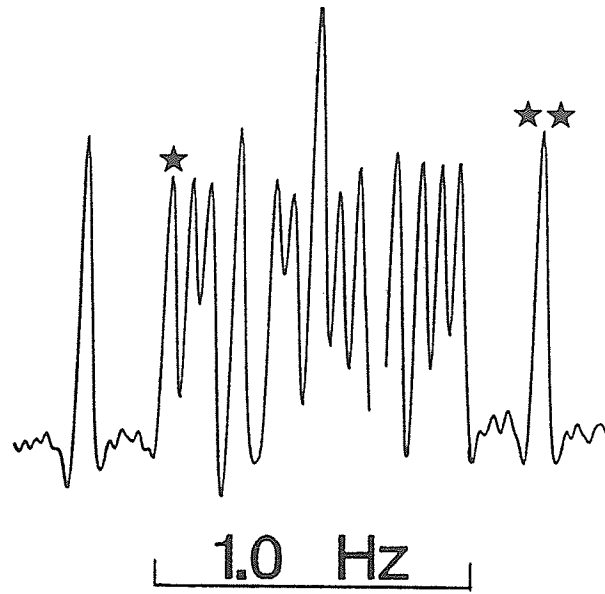
- <sup>a</sup> In Hz at 300 K. <sup>1</sup>H resonance at 300.135 MHz to high frequency of TMS.
- <sup>b</sup> The solution contained 4.0 mol% 2-isopropylbenzaldehyde, with 10 mol% C<sub>6</sub>D<sub>12</sub>, 0.25 mol% C<sub>6</sub>F<sub>6</sub>, and 0.25 mol% tetramethylsilane.
- <sup>c</sup> Correlated with J(H3,H5) by -0.2389.
- <sup>d</sup> Not optimized.
- <sup>e</sup> Correlated with  $\nu(\text{CHO})$  by -0.1821, with J(H3,CHO) by -0.2637, and with J(CHO,CH) by 0.1833.
- <sup>f</sup> The sign of <sup>5</sup>J(CHO,CH) was determined by a double resonance experiment with the acetone-d<sub>6</sub> solution.

Figure 27. A) A first order representation of the  $^1\text{H}$  nmr spectrum for the aldehyde proton of o-isopropylbenzaldehyde in acetone- $\text{d}_6$  at 300 K, showing the observed splittings. The sign of each transition is labelled + or - with respect to protons H3, H6, and the methine proton. The high frequency transitions associated with each splitting are labelled +, by convention.

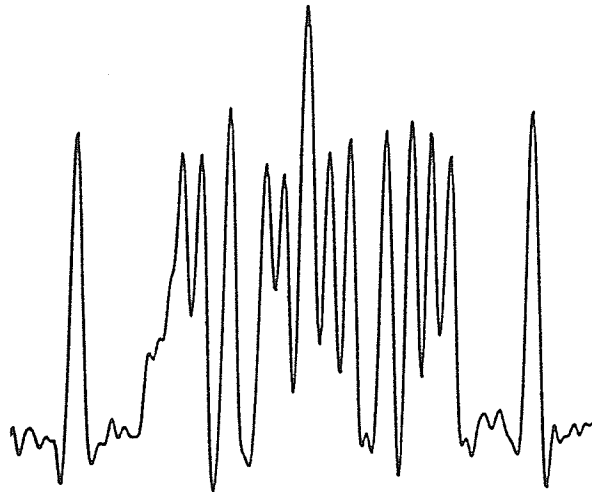
B) A first order representation of the high frequency multiplet in the spectrum for ring proton H5. The sign of each transition is labelled + or - with respect to protons H3, H6, and the methine proton. The small characters, b and c, in this representation show which transitions were weakly irradiated with a second radio frequency to yield spectra B and C of figure 28.

**A****B**

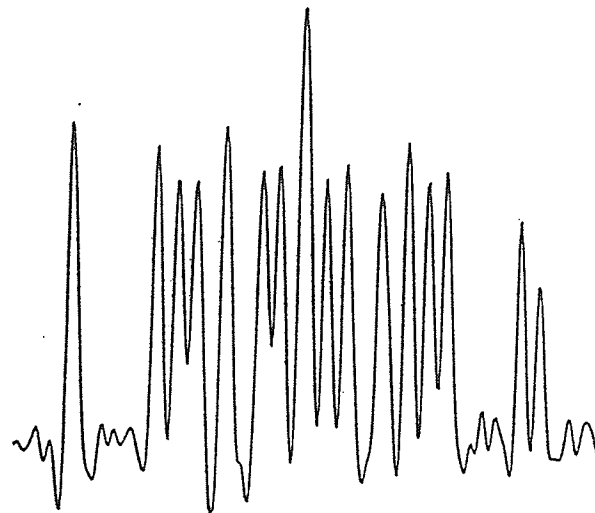
- Figure 28.
- A) The experimental spectrum of the aldehyde proton of o-isopropylbenzaldehyde in acetone-d<sub>6</sub> at 300 K.
  - B) The spectrum obtained with weak irradiation of the transition marked b in figure 27B. Note the reduction in intensity, and splitting, of the transition marked \* in spectrum A.
  - C) The spectrum obtained with weak irradiation of the transition marked c in figure 27B. Note the splitting of the transition marked \*\* in spectrum A.



A



B



C

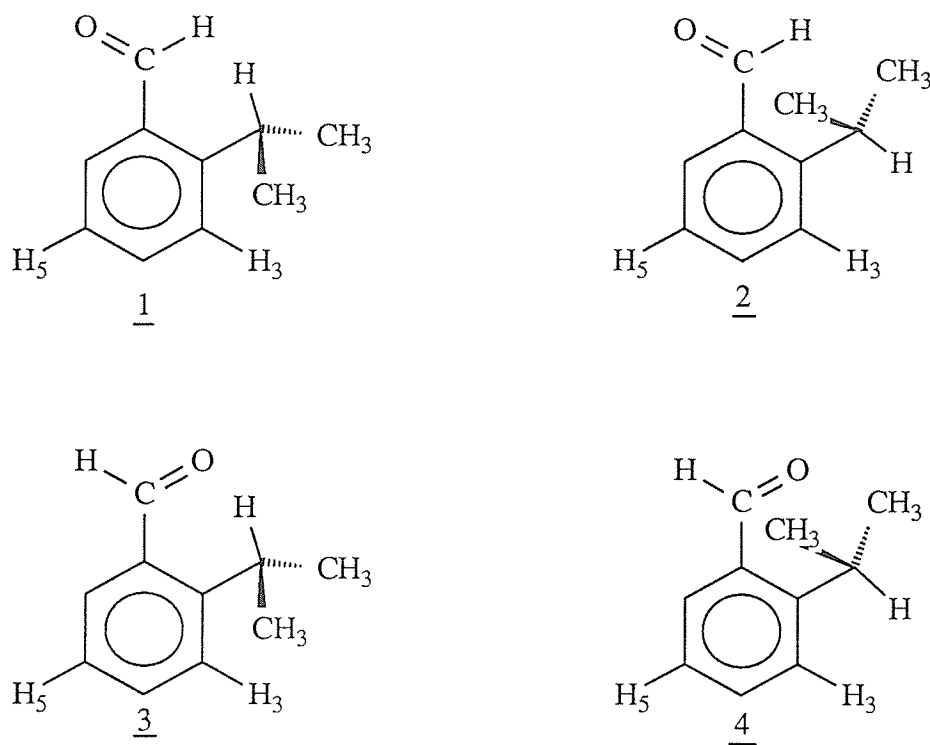
## 5.2 Discussion

### *The Populations $P_1 + P_2$ and $P_3 + P_4$*

The method of determining conformer populations from five bond coupling constants is now applied to o-isopropylbenzaldehyde. That the aldehyde group in this type of molecule is confined to the plane of the aromatic ring, has been shown in the previous two chapters, this being a consequence of the relatively high conjugative barrier to rotation about the exocyclic  $C_{sp^2}-C_{sp^2}$  bond. In benzaldehyde, in solution, this barrier is  $>30$  kJ/mol [3, 4]. In contrast, the barrier to rotation about the  $C_{sp^2}-C_{sp^3}$  bond in isopropylbenzene is very likely less than 10 kJ/mol [58]. AM1 computations on conformers of o-isopropylbenzaldehyde having CHO in-plane, and in the O-trans orientation, give a barrier height of  $>24$  kJ/mol. Considering that AM1 calculations closely reproduce the barrier in isopropylbenzene, it should be a reasonable approximation to speak of the four planar conformers presented in figure 29.

The  $^5J(\text{CHO}, H_m)$  in table 32 are indicative of the sums  $P_1 + P_2$  and  $P_3 + P_4$ , where  $P_n$  represents the fractional population of the conformers in figure 29. In acetone- $d_6$ ,  $P_1 + P_2 = 0.581(3)$ , while in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  this sum is  $0.524(3)$ . This observation is consistent with the STO-3G computed dipole moments given in table 33, which imply greater moments for the O-trans forms, which should therefore be stabilized in polar solvents.

The population sums given in table 32 are based on the sum of the observed  $^5J(\text{CHO}, H_m)$  values. Clearly, these sums,  $0.814(2)$  Hz and  $0.804(2)$  Hz in acetone- $d_6$  and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively, are significantly different from their counterparts in



**Figure 29.** Planar conformations of o-isopropylbenzaldehyde

benzaldehyde, 0.860(2) Hz and 0.862(4) Hz. In the previous two chapters it was shown that relatively large perturbations of  ${}^5J(\text{CHO},\text{H}_3)$  and/or  ${}^5J(\text{CHO},\text{H}_5)$  contribute in a minor fashion to the derived equilibrium constants and, hence, free energy differences between O-cis and O-trans rotamers.

In a treatment similar to that described for o-cyanobenzaldehyde, a system of four equations with four unknowns can be solved to yield  $P_1 + P_2$  in both acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>, as well as  ${}^5J(\text{CHO},\text{H}_3)_c$  and  ${}^5J(\text{CHO},\text{H}_5)_t$ , which are assumed to be independent of solvent. The solution of these equations gives  ${}^5J(\text{CHO},\text{H}_3)_c = 0.723$  Hz and  ${}^5J(\text{CHO},\text{H}_5)_t = 0.895$  Hz.  $P_1 + P_2$  is 0.53 in acetone-d<sub>6</sub>, and 0.47 in



Table 32. Conformational populations of o-isopropylbenzaldehyde from  $^1\text{H}$  nmr coupling constants.

	Solvent	
	Acetone-d6	$\text{CS}_2/\text{C}_6\text{D}_{12}$
$^5\text{J}(\text{CHO}, \text{H3})^{\text{a}}$	0.341(1)	0.383(1)
$^5\text{J}(\text{CHO}, \text{H5})^{\text{a}}$	0.473(1)	0.421(1)
$^5\text{J}_{\text{CHO, sum}}^{\text{a}}$	0.814(2)	0.804(2)
$\text{P}_1 + \text{P}_2$	0.581(3)	0.524(3)
$\text{K}^{\text{b}}$	1.39(2)	1.10(1)
$\Delta\text{G}_{\text{CHO}}^{\text{c}}$	0.82(4)	0.24(3)
$^5\text{J}(\text{CH}, \text{H4})^{\text{a}}$	0.503(1)	0.500(1)
$^5\text{J}(\text{CH}, \text{H6})^{\text{a}}$	0.168(1)	0.167(1)
$^5\text{J}_{\text{CH, sum}}^{\text{a}}$	0.671(2)	0.667(2)

<sup>a</sup> In Hz.  $^1\text{H}$  resonance at 300.135 MHz to high frequency of TMS.

<sup>b</sup>  $\text{K} = (\text{P}_1 + \text{P}_2) / (\text{P}_3 + \text{P}_4)$

<sup>c</sup> In kJ/mol.  $\Delta\text{G} = -RT \ln \text{K}$

Table 33. Dipole moments and relative energies of planar conformers 1 to 4, from geometry optimized STO-3G and AM1 computations.

Conformer	STO-3G		AM1		Dipole Moment <sup>a</sup>	
	Energy <sup>b</sup>	P <sub>i</sub> <sup>c</sup>	Energy <sup>b</sup>	P <sub>i</sub> <sup>c</sup>	STO-3g	AM1
1 <sup>d</sup>	4.107	0.16	0.000	0.63	2.068	0.738
2 <sup>e</sup>	11.291	0.01	5.297	0.08	2.071	1.209
3 <sup>f</sup>	0.000	0.81	1.953	0.29	1.637	1.032
4 <sup>g</sup>	9,197	0.02	14.647	0.00	1.720	1.032

<sup>a</sup> Debye

<sup>b</sup> kJ/mol

<sup>c</sup> The fractional population at 300 K based on a Boltzmann weighting.

<sup>d</sup> Proximate C-H bonds in the sidechains (see text), an O-trans conformer.

<sup>e</sup> Proximate C=O bond and C-H bond in the side chains, an O-cis conformer.

<sup>f</sup> Proximate C-H bond and CH<sub>3</sub> groups in sidechains.

<sup>g</sup> Proximate C=O bond and CH<sub>3</sub> groups in sidechains.

$\text{CS}_2/\text{C}_6\text{D}_{12}$ . Comparison of these populations to those in table 32 indicates that 0.55(3) and 0.50(3) are reasonable estimates of  $P_1 + P_2$  in acetone-d6 and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively, at 300 K.

### *Extrapolation to the Vapour*

The values of the equilibrium constants and free energy differences in table 32 were calculated using the values of  $P_1 + P_2$  and  $P_3 + P_4$  implied by the coupling constants, and the sums of  $^5\text{J}(\text{CHO}, \text{H}_m)$  in each solvent. These values have the O-trans rotamers favoured by free energy differences of 0.82(4) kJ/mol and 0.24(3) kJ/mol in acetone-d6 and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ , respectively. In the last section, arguments were presented which yielded populations which should encompass perturbations of  $^5\text{J}(\text{CHO}, \text{H}_m)$ . These populations correspond to equilibrium constants of 1.22(14) in acetone-d6 and 1.00(12) in  $\text{CS}_2/\text{C}_6\text{D}_{12}$ . The free energy difference in acetone-d6 is 0.5(3) kJ/mol, O-trans favoured. In  $\text{CS}_2/\text{C}_6\text{D}_{12}$  neither form appears predominant, this less polar solvent not appreciably stabilizing the more polar rotamers.

In the previous chapter it was noted that, to a good approximation, the changes in free energy on going from acetone to  $\text{CS}_2$  is the same as that for passage to the vapour from  $\text{CS}_2$ . Hence, an estimate of the free energy difference between O-cis and O-trans rotamers in the vapour follows as 0.5(6) kJ/mol, but with the O-cis form favoured.

*The Populations  $P_1 + P_3$  and  $P_2 + P_4$*

Just as  $^5J(\text{CHO}, \text{H}_m)$  are indicative of the proportions of molecules having O-cis and O-trans orientations of the aldehyde group,  $^5J(\text{CH}, \text{H}_4)$  and  $^5J(\text{CH}, \text{H}_6)$  can be used to arrive at the fractional populations of conformers having the methine C-H of the isopropyl group pointed toward, or away from, the aldehyde group. In terms of the planar conformers in figure 29, these fractional populations are  $P_1 + P_3$  and  $P_2 + P_4$ . The twofold barrier implied by the large magnitude of  $^6J(\text{CH}, \text{H}_5)$ , which varies as  $\langle \sin^2 \theta \rangle$ , in isopropylbenzene, using a hindered rotor model, is about 7 kJ/mol [58]. Thus, there is a good deal of internal motion around the  $\text{C}_{\text{sp}^2}\text{-C}_{\text{sp}^3}$  bond. For this reason, a somewhat different tack will be taken to derive conformer populations, than was used for o-nitrobenzaldehyde in a previous chapter.

In a trivial approach, the fractional population sums  $P_1 + P_3$  and  $P_2 + P_4$  can be approximated from  $^5J(\text{CH}, \text{H}_4)/(^5J(\text{CH}, \text{H}_4) + ^5J(\text{CH}, \text{H}_6))$  in the acetone solution as 0.75 and 0.25, respectively. These values are obviously inaccurate, since they do not take into account the significant  $\pi$  contribution to these five bond coupling constants, or the diminished  $\sigma$  contribution, arising from internal rotation (see equation (5) in part 3). A much better approximation to the fractional populations can be had by ignoring these  $\pi$  contributions, and considering only the  $\sigma$  components of  $^5J(\text{CH}, \text{H}_m)$ , which vary as  $\langle \sin^2 \theta/2 \rangle$ . This approach will be discussed next.

The value of  $\langle \sin^2 \theta \rangle$  can be obtained from the observed  $^6J(\text{CH}, \text{H}_5)$  using equation (3) if  $^6J_{90}$  is known or can be approximated.  $^6J_{90}$  for isopropylbenzene is -1.12 Hz [58] compared to -1.20 Hz for toluene [51], the lower value for

isopropylbenzene being due to the two methyl groups attached to the  $\alpha$  carbon; ethylbenzene has  ${}^6J_{90}$  as -1.16 Hz [59]. Assuming that  ${}^6J_{90}$  is the same in o-isopropylbenzaldehyde as it is in isopropylbenzene, which seems reasonable since  ${}^6J(\text{CH},\text{H5})$  is the same in both compounds,  $\langle \sin^2 \theta \rangle$  follows as 0.231(6). Equation (5) shows the  $\pi$  component of the five bond coupling constant to be  ${}^5J_{90}^\pi \langle \sin^2 \theta \rangle$ . If it is also assumed that  ${}^5J_{90}^\pi$  in isopropylbenzene decreases from the corresponding value in toluene in proportion to the decrease in  ${}^6J_{90}$ , and that  ${}^5J_{90}^\pi$  in o-isopropylbenzaldehyde is the same as that for isopropylbenzene, then the  $\pi$  component of  ${}^5J(\text{CH},\text{H}_m)$  is 0.073(2) Hz. Subtracting this from the observed  ${}^5J(\text{CH},\text{H4})$  and  ${}^5J(\text{CH},\text{H6})$  in acetone-d<sub>6</sub> leaves 0.430(3) Hz and 0.095(3) Hz, respectively. These are the  $\sigma$  contributions to the five bond coupling constants.

$\theta$  has been defined as the dihedral angle between the exocyclic C-H bond being considered, in this case the methine C-H bond, and the C-H bond *meta* to the ring proton involved in the five bond coupling constant. If  $\theta$  is the angle of rotation which governs the magnitude of, say  ${}^5J(\text{CH},\text{H4})$ , then the angle responsible for the magnitude of  ${}^5J(\text{CH},\text{H6})$  is, of course,  $180^\circ - \theta$ . The sum of  $\langle \sin^2 \theta/2 \rangle$  and  $\langle \sin^2 (180^\circ - \theta)/2 \rangle$  is 1, always. Now, for the acetone-d<sub>6</sub> solution, write:

$${}^5J(\text{CH},\text{H4}) = {}^5J_{180}^\sigma \langle \sin^2 \theta/2 \rangle = 0.095(3) \text{ Hz}$$

and

$${}^5J(\text{CH},\text{H6}) = {}^5J_{180}^\sigma \langle \sin^2 (180^\circ - \theta)/2 \rangle = 0.430(3) \text{ Hz}.$$

Adding these equations gives  ${}^5J_{180}^\sigma = 0.529(4) \text{ Hz}$ . This is the extremum in  ${}^5J(\text{CH},\text{H}_m)$

in any of the four rotamers.

In acetone-d<sub>6</sub>,  $P_1 + P_3$  follows from these pure  $\sigma$  coupling constants as  $0.430(3)/(0.430(3) + 0.095(3)) = 0.82(2)$ . Hence, the two conformers having the two methyl groups near CHO make up 18(2) % of the molecules in the polar solvent, at 300 K.

The sum  $^5J(\text{CH},\text{H}_4) + ^5J(\text{CH},\text{H}_6)$ , at 0.669(2) Hz in o-isopropylbenzaldehyde, in both acetone-d<sub>6</sub> and CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>, is larger than its counterpart in isopropylbenzene [58] by 0.078(7) Hz. As the six bond coupling constants to the methine protons are effectively the same in both molecules, this difference is not caused by an increase in the  $\pi$  components of  $^5J(\text{CH},\text{H}_m)$ , but must be attributed to an increase in the  $\sigma$  components of one, or both, of these five bond coupling constants in the derivative. In order to gain some insight into which of  $^5J(\text{CH},\text{H}_4)$  or  $^5J(\text{CH},\text{H}_6)$  increases in o-isopropylbenzaldehyde, CNDO/2 and INDO MO FPT computations were performed using the optimized STO-3G geometries of each conformer. These computations imply  $^5J(\text{CH},\text{H}_4)$  as larger than  $^5J(\text{CH},\text{H}_6)$  by 0.1 Hz. Attributing  $0.430(3) + 0.078(7) = 0.51(1)$  Hz to  $^5J(\text{CH},\text{H}_4)$ , and leaving  $^5J(\text{CH},\text{H}_6)$  at 0.095(3) Hz, gives the observed sum, and dictates that the fractional population  $P_2 + P_4$  is 0.16(1). It appears then, that fractional populations of 0.83(3) and 0.17(3) are reasonable estimates of  $P_1 + P_3$  and  $P_2 + P_4$ , respectively, in both solvents.

Recall that the proportion of O-trans conformers falls by about 10 % on changing from acetone-d<sub>6</sub> to CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>. That there is no concurrent change in  $P_1 + P_3$ , suggests that C=O $\cdots$ H-C and C-H $\cdots$ H-C repulsions in the side chains are nearly the same in magnitude. Furthermore, these interactions are relatively strongly

favoured over those between CHO and the methyl groups in conformers having the methine C-H directed away from CHO.

One assumption the previous two treatments have in common is that the values of  $\langle \sin^2 \theta \rangle$  in equation (5) for conformers 1 and 3, and conformers 2 and 4, are the same. In fact,  $\langle \sin^2 \theta \rangle$ , as implied by  ${}^6J(\text{CH}, \text{H5})$ , is an average over all forms present. Or, in other words, it is assumed that the methine C-H bond oscillates across the plane of the ring through the same angle, and at the same frequency, in either orientation of the isopropyl group. What if this is not the case? It seems, from visual inspection of a model, that steric interactions between the methyl groups and CHO in conformer 2 and, particularly, conformer 4, could significantly limit motion about the exocyclic  $\text{C}_{\text{sp}^2}\text{-C}_{\text{sp}^3}$  bond. At present not enough information can be culled from the  ${}^1\text{H}$  nmr coupling constants to explore this possibility. The coupling constants between the methyl groups and H3 of the ring, however, support the relatively low proportions of conformers 2 and 4. In o-isopropylbenzaldehyde, the spectrum of the methyl protons shows splitting of 0.10 Hz magnitude due to spin coupling to H3. The corresponding coupling constant in isopropylbenzene [58] is only  $\pm 0.04(1)$  Hz. If this coupling constant is mediated by direct interactions, then it is expected to have a sizeable magnitude in only conformers 1 and 3. That the coupling constant in o-isopropylbenzaldehyde is twice that of isopropylbenzene is consistent with the low proportion of conformers 2 and 4.

### *Molecular Orbital Computations*

The results of *ab initio* molecular orbital calculations at the STO-3G level are presented in table 33 along with the results of AM1 computations. Large differences in energies and dipole moments of the free molecules are observed between these two approaches. The populations given in table 33 result from a simple exponential weighting, at 300 K, and indicate a large discrepancy between the two methods for conformers 1 and 3. However, there is general agreement as far as  $P_2$  and  $P_4$  are concerned, with these populations being much lower than  $P_1$  and  $P_3$ , by both methods.  $P_4$  is calculated by both approaches to be 0.01(1). The STO-3G computed dipole moments presented in table 33 suggest that conformer 2 is additionally favoured over conformer 4 in polar solution, the latter having the smaller dipole moment. Dipole moments computed for other compounds in this thesis are consistently underestimated by AM1. The STO-3G computed dipoles are, however, consistently nearer the measured dipole moments. In the case of o-isopropylbenzaldehyde, the AM1 dipole moments for conformers 2 and 4 are qualitatively in agreement with STO-3G, however, they are, as expected, too small.

The instability of conformer 4 is also understandable in terms of the proximity of the methine hydrogen and the carbonyl oxygen. This distance can be as small as 1.6 Å in the planar molecule, clearly a strongly destabilizing situation.

The STO-3G results of o-tolualdehyde, optimized with the nuclei of the aromatic moiety in a plane, have the energies of conformers 1 to 4 as 7.41, 1.22, 3.70, and 0.00 kJ/mol, respectively, the methyl groups in figure 27 corresponding to the



methyl hydrogens of o-tolualdehyde. In other words, 2 and 4 are the stable conformers in that molecule, implying that in o-isopropylbenzaldehyde C-H...H-C and C=O...H-C interactions are both repulsive, but less so than the C-H...(CH<sub>3</sub>)<sub>2</sub> and C=O...(CH<sub>3</sub>)<sub>2</sub> interactions in conformers 1 and 3.

The experimental data above, extrapolated to the vapour, suggested that O-cis is the somewhat favoured form in the vapour, the C=O...H-C interaction being favoured over the C-H...H-C interaction of conformers 1 and 2. This is qualitatively consistent with the STO-3G calculations for the free molecule, which imply that the C=O...H-C interaction is attractive. AM1, however, favours H,H over H,O. Similar results are obtained for o-tolualdehyde.

The STO-3G computations on 1 and 3 allowed both groups to rotate freely during optimization; however, the twists about the exocyclic bonds did not exceed 0.2°, implying the local stability of the planar conformers. The small magnitude of <sup>6</sup>J(CHO,H4), -0.015(3) Hz, indicates that the aldehyde group does not deviate substantially from the aromatic plane. This coupling constant was not manifested by a detectable splitting in the <sup>1</sup>H nmr spectra, but is a result of the least squares fits of the hamiltonian to the spectra. Please see the previous chapters for a discussion of how <sup>6</sup>J(CHO,H4) relates to coplanarity of CHO with the aromatic ring. According to the above MO calculations the local barrier to planarity is so small, compared to the barrier of rotation of CH(CH<sub>3</sub>)<sub>2</sub>, that relatively stable, planar, conformers are suggested. However, STO-3G methods rather overestimate the barrier to rotation about the exocyclic bond in isopropylbenzene [58], but not in benzaldehyde. Accordingly, it is noted that it is an approximation to speak of planar conformers,

although the long range coupling constants suggest no greater an average twist about the  $C_{sp^2}-C_{sp^3}$  bond in the present molecule than in isopropylbenzene.

*The proximate coupling constant  $^5J(CHO,CH)$*

The computer assisted analysis of the spectrum of o-isopropylbenzaldehyde resulted in values of  $^5J(CHO,CH)$  which were -0.388(1) Hz in acetone-d<sub>6</sub> and -0.376(1) Hz in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solution. If this coupling constant is indeed a proximate one, then it seems likely that only for conformation 1 will it have a significant magnitude. These coupling constants are very sensitive to the interatomic distance [60, 61], the contact contribution depending on the overlap of orbitals on the atoms or bonds carrying the coupled nuclei. Consequently, CNDO/2 and INDO FPT computations were performed on the four conformers, using the optimized STO-3G geometries. These calculations give -0.30 Hz for  $^5J(CHO,CH)$  in conformer 1. In the other conformers, small positive values were indicated. Whether these were simply a result of the parameterization, or not, these calculations are taken as confirmation that this coupling has a large negative value only when the aldehyde proton and the methine proton are very close to each other, and, hence, that it is proximate.

The slightly larger value determined for CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> is consistent with the greater proportion of conformer 1 in that solvent. The population of P<sub>1</sub> in both solvents is <0.5, so that the magnitude of  $^5J(CHO,CH)$  in this conformer is likely near 1 Hz. At the present time, this sort of coupling constant cannot be used to deduce P<sub>1</sub>.

There was no difference in the spectra of the aldehyde proton, either with, or

without decoupling of the methyl group protons. If some evidence had been seen for coupling between these nuclei, this would be evidence for the existence of conformer 2, where the methyl groups lie quite close to the C-H bond of the aldehyde group.

## **6.0 Summary and Conclusions**

The coupling constants between the aldehyde and aromatic ring protons of substituted benzaldehydes yield precise conformer populations and, hence, free energy differences between O-trans and O-cis rotamers. Molecular orbital computations at various levels of sophistication can be used to substantiate, and sometimes help to explain, certain observations. It is found that, in general, polar solvents tend to stabilize the more polar O-cis form of these molecules, thus increasing their fractional populations in these solvents. In most instances, the O-trans forms of the *meta*-substituted molecules are found to be slightly favoured, in solution, over the more polar O-cis forms. The O-trans forms of *ortho*-substituted benzaldehydes are found to be favoured extensively over the O-cis forms, in CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> solutions. Upon passage to acetone-d<sub>6</sub> solvent, the O-cis form appears to be stabilized, causing an increase in the fractional population of these more polar forms. The idea of planar conformers appears to be insufficient to explain the data observed for o-nitrobenzaldehyde; however, a slight modification to the approach allows a reasonable discussion in terms of stable, nonplanar, rotamers.

The conformational behaviour of m- and o-cyanobenzaldehyde is seen to be distinctly different from the other molecules analyzed. The close proximity of the polar cyano and aldehyde groups in o-cyanobenzaldehyde tends to cause a large increase in the population of the polar O-cis rotamer in acetone-d<sub>6</sub> with respect to CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub>, and benzene-d<sub>6</sub>. This population increases from 0.11 to 0.24 to 0.44 on passage from CS<sub>2</sub>/C<sub>6</sub>D<sub>12</sub> to benzene-d<sub>6</sub> to acetone-d<sub>6</sub>, respectively. It is predicted on the basis of reaction field theory that, in the vapour, the population of the O-trans form of o-cyanobenzaldehyde increases to 0.98(1). The substituents in

m-cyanobenzaldehyde are far enough apart that no significant change in rotamer populations occurs on going from  $\text{CS}_2/\text{C}_6\text{D}_{12}$  to acetone-d<sub>6</sub>; however, specific interactions with benzene-d<sub>6</sub> solvent molecules appear to take place, causing a 20 % decrease in the O-cis population in that medium, compared to acetone-d<sub>6</sub> and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ .

The population of O-trans rotamers of o-isopropylbenzaldehyde is found to be 0.55(3) in acetone-d<sub>6</sub> and 0.50(3) in  $\text{CS}_2/\text{C}_6\text{D}_{12}$  solutions. The proportion of molecules having the methine C-H of the isopropyl group directed toward CHO is found to be 0.83(3) in both acetone-d<sub>6</sub> and  $\text{CS}_2/\text{C}_6\text{D}_{12}$ . Sufficient information is not available in the  $^1\text{H}$  nmr parameters to find precise proportions of the individual conformers; however, *ab initio* and semiempirical molecular orbital computations on the free molecules indicate that the conformer with O-cis orientation of CHO and the trans orientation of the isopropyl methine bond, is nearly nonexistent at 300 K.

## 7.0 References

1. G.J.Karabatsos and F.M.Vane. *J.Am.Chem.Soc.* **85**, 3886 (1963).
2. F.A.L.Anet and M.Ahmad. *J.Am.Chem.Soc.* **86**, 119 (1964).
3. L.Lunazzi, D.Maccientelli and A.Boicelli. *Tetrahedron Lett.* 1205 (1975).
4. T.Drakenberg, R.Jost and J.Sommer. *J.C.S.Chem.Comm.* 1011 (1974).
5. T.Drakenberg, R.Jost and J.M.Sommer. *J.Chem.Soc. Perkin Trans. 2*, 1682 (1975).
6. L.Lunazzi, A.Ticca, D.Macciantelli, and G.Spunta. *J.Chem.Soc.Perkin Trans.2*, 1121 (1976).
7. F.A.Miller, W.G.Fateley and R.E.Witkowski. *Spectrochim.Acta.* **23A**, 891 (1967).
8. H.G.Silver and J.L.Wood. *Trans.Faraday Soc.* **60**, 5 (1964).
9. J.H.S.Green and D.J.Harrison. *Spectrochim.Acta*, **32A**, 1265 (1976).
10. G.A.Crowder and F.J.Northam. *J.Chem.Phys.* **50(11)**, 4865 (1969).
11. A.R.Katritzky, A.R.Sinnott, T.T.Tidwell, and R.D.Topsom. *J.Am.Chem.Soc.* **91**, 628 (1969).
12. J.L.Alonso and R.M.Villamañán. *J.Chem.Soc.Faraday Trans.2*, **85**, 137 (1989).
13. C.T.Aw, H.H.Huang and E.L.K.Tan, *J.Chem.Soc. Perkin Trans. 2*, 1638 (1972).
14. C.L.Cheng, R.J.W.LeFèvre, G.L.D.Ritchie, P.A.Goodman, and P.H.Gore. *J.Chem.Soc.(B)*, 1198 (1971).
15. R.A.Y.Jones, A.R.Katritzky, and A.V.Ochkin. *J.Chem.Soc.(B)*, 1795 (1971).
16. E.A.W.Bruce, G.L.D.Richie, and A.J.Williams. *Aust.J.Chem.* **27**, 1809 (1974).
17. C.Grosse, M.Magdalena, and P.Brito. *Can.J.Chem.* **63**, 1031 (1985).
18. L.Schäfer, S.Samdal, and K.Hedberg. *J.Mol.Struct.* **31**, 29 (1976).
19. N.S.Chin, J.D.Ewbank, M.Askari, and L.Schäfer. **54**, 185 (1979).
20. G.H.Penner, P.George, and C.W.Bock. *J.Mol.Struct.(Theochem)*. **152**, 201 (1987).



21. W.M.F.Fabian. *J.Comp.Chem.* **9**(4), 369 (1988).
22. A.Lakshmi, S.Walker, B.J.McClelland, and J.H.Calderwood. *J.Mol.Struct.* **95**, 249 (1982).
23. T.Schaefer, T.A.Wildman, and R.Sebastian. *J.Mol.Struct. (Theochem)* **89**, 93 (1982).
24. R.H.Contreras, D.G.Kowalewski, and A.Osella. *Org.Mag.Res.* **12**(9), 542 (1979).
25. R.Wasylishen and T.Schaefer. *Can.J.Chem.* **49**, 3216 (1971).
26. W.B.Smith, D.L.Deavenport and A.M.Ihrig. *J.Am.Chem.Soc.* **94**, 1959 (1972).
27. D.G.DeKowalewski and S.Castellano. *Mol.Phys.* **16**, 567 (1969).
28. T.Schaefer, R.Sebastian, R.Laatikainen, and S.R.Salman. *Can.J.Chem.* **62**, 326 (1984).
29. T.Schaefer and C.Takeuchi. *Can.J.Chem.* **67**, 827 (1989).
30. T.Schaefer, G.H.Penner, K.J.Davie, and R.Sebastian. *Can.J.Chem.* **63**, 777 (1985).
31. T.Schaefer and C.Takeuchi. *Can.J.Chem.* **68**, 339 (1990).
32. T.Schaefer, S.R.Salman, and T.A.Wildman. *Can.J.Chem.* **58**, 2364 (1970).
33. M.K.Haque and S.N.Thakur. *Chem.Phys.Lett.* **66**(3), 561 (1979).
34. J.A.Pople, J.W.McIver, and N.S.Ostlund. *J.Chem.Phys.* **49**, 2965 (1968).
35. P.Dobosh and N.S.Ostlund. *QCPE*, **11**, 281 (1975).
36. T.Schaefer, J.Peeling, G.H.Penner, and A.Lemire. *Can.J.Chem.* **64**, 1859 (1986).
37. W.Brügel, *Handbook of NMR Spectral Parameters*, Heyden & Sons Ltd., London (1979) p 400.
38. J.S.Martin, A.R.Quirt, and K.E.Worvill. *The NMR Program Library*. Daresbury Laboratory, Daresbury, U.K.

39. M.J.Frisch, J.S.Binkley, H.B.Schlegel, K.Raghavachari, C.F.Meliuus, R.L.Martin, J.J.P.Stewart, F.W.Bobrowicz, D.F.Rohlfing, L.R.Kahn, D.J.Defrees, R.Seeger, R.A.Whiteside, D.J.Fox, E.M.Fluder, and J.A.Pople. Carnegie-Mellon Quantum Publishing Unit, Pittsburgh, PA (1984).
40. SAS User's Guide: Statistics, A.A.Roy (Ed.), Statistical Analysis System Institute (1982).
41. SAS/GRAPH User's Guide. K.A.Council and J.T.Helwig (Ed.), Statistical Analysis System Institute (1982).
42. W.J.E.Parr and T.Schaefer. *Acc.Chem.Res.* **13**, 400 (1980).
43. M.J.S.Dewar, E.J.Zoeibisch, E.F.Healy, and J.J.P.Stewart. *J.Am.Chem.Soc.* **107**, 3902 (1985).
44. W.J.Hehre, R.F.Stewart, and J.A.Pople. *J.Chem.Phys.* **51**, 2657 (1969).
45. W.J.Hehre, R.Ditchfield, R.F.Stewart, and J.A.Pople. *J.Chem.Phys.* **52**, 2769 (1970).
46. J.H.Høg, L.Nygaard, and G.O.Sørensen. *J.Mol.Struct.* **17**, 111 (1971).
47. T.Correll, N.W.Larsen, and T.Pedersen. *J.Mol.Struct.* **65**, 43 (1980).
48. L.A.Carreira and T.G.Towns. *J.Mol.Struct.* **41**, 1 (1977).
49. G.H.Penner. *J.Mol.Struct.(Theochem)*. **137**, 121 (1986).
50. P.Coppens and G.M.J.Schmidt. *Acta.Chryst.* **17**, 222 (1964).
51. T.Schaefer, R.Sebastian, and G.H.Penner. *Can.J.Chem.* **63**, 2597 (1985).
52. T.Schaefer and R.Laatikainen. *Can.J.Chem.* **61**, 2785 (1983).
53. A.L.McClellan. Tables of experimental dipole moments. Freenam and Co. San Fransisco (1963) p 233.
54. R.J.Abraham and E.Bretschneider in *Internal Rotation in Molecules*. Ed. W.J.Orville-Thomas. J.Wiley & Sons. New York, 1974, Chapter 13.
55. J.J.Moura Ramos, L.Dumont, M.L.Stien, and J.Reisse. *J.Am.Chem.Soc.* **102**, 4150 (1980).
56. A.Y.Meyer. *J.Mol.Struct.* **195**, 147 (1989).

57. W.J.Hehre, L.Radom, and J.A.Pople. *J.Am.Chem.Soc.* **94**, 1496 (1972).
58. T.Schaefer, R.Sebastian, and G.H.Penner. *Can.J.Chem.* **66**, 1495 (1988).
59. T.Schaefer, G.H.Penner, and R.Sebastian. *Can.J.Chem.* **65**, 873 (1987).
60. J.Hilton and L.H.Sutcliffe. *Prog.Nucl.Magn.Reson.Spectrosc.* **10**, 27 (1975).
61. R.H.Contreras, M.A.Natiello, and G.E.Scuseria. *Magn.Reson.Rev.* **9**, 239 (1985).
62. M.C.Ruiz de Azua, A.C.Diz, G.G.Giribet, R.H.Contreras, and I.D.Rae. *Int.J.Quant.Chem.* **S20**, 585 (1986) and references therein.