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Rotational Spectra and Conformer Geometries of 2-Fluorophenol and 3-Fluorophenol

Aimee Bell, James Singer, Durell Desmond, Omar Mahassneh and Jennifer van Wijngaarden*

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

*Corresponding author

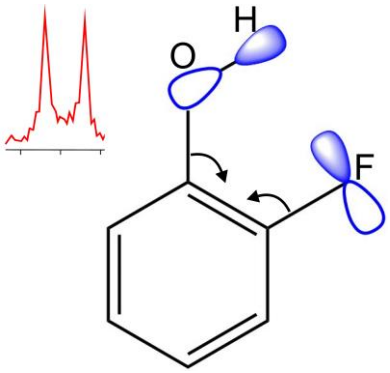
Email: vanwijng@cc.umanitoba.ca

Phone: (204)474-8379

Fax: (204)474-7608

TOC graphic

The microwave spectrum of 2-fluorophenol in comparison to that of 3-fluorophenol provides evidence of a non-covalent intramolecular interaction in the former.



Abstract

The ground states of 2-fluorophenol (2FPh) and 3-fluorophenol (3FPh) and their ^{13}C isotopologues were investigated using Fourier transform microwave (FTMW) spectroscopy in the range of 6 to 26 GHz. Two planar conformers were observed for 3FPh, corresponding to *cis* and *trans* orientations of OH relative to F, while only the *cis* conformer of 2FPh was detected. The rotational constants determined were used to derive substitution (r_s) and effective ground state (r_0) structures of the lowest energy conformer of each compound: *cis*-2FPh and *trans*-3FPh. Geometry optimization at the MP2/6-311++G(2d,2p) level provided equilibrium (r_e) structures which are in close agreement with the experimental parameters. The derived structures along with results from natural bond orbital (NBO) calculations provide evidence of an intramolecular interaction in *cis*-2FPh between the fluorine atom and OH moiety that stabilize this conformer by 0.72 kcal/mol.

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1. Introduction

Hydrogen bonding interactions involving fluorine have received marked attention in recent years as fluorinated species find expanded use in industry from new drugs[1] to materials processing.[2] The proliferation of such compounds arises as fluorine substitution at various sites provides an effective way to tune key molecular properties such as the stability, reaction rates, solubility and acidity.[3] The nature of hydrogen bonding interactions with fluorine has been the subject of controversy in the crystallography community,[4] however, gas phase spectra can simplify the interpretation of structures by providing a means to probe non-covalent interactions in isolation. Fourier transform microwave (FTMW) spectroscopy, in particular, is an ideal tool for such investigations as the compound of interest is interrogated in a collision-free supersonic jet. A number of FTMW studies of weakly bound dimers involving small fluorinated molecules[5,6,7] have been reported in recent years but similar high resolution investigations of *intra*molecular interactions with fluorine are scarce. In such cases, the classification of an interaction as a hydrogen bond may be ambiguous as the optimal 180^{o} angle for X-H••• F may not be possible.[8]

Fluorophenols (FPh) are convenient prototypes to investigate non-covalent intramolecular interactions involving fluorine via spectroscopic methods and their size makes them highly amenable to theoretical calculations. The potential for OH•••X interaction in 2-fluorophenol (2FPh), and other *ortho*-halophenols, has been explored using infrared spectroscopy of the neat liquid, solutions, Ar matrices and gas samples[9,10,11,12] as well as through computational studies.[12,13] For the chloro-, bromo- and iodo- analogs, the OH stretching modes provided conclusive proof of an intramolecular interaction through the observation of different vibrational band centers and intensities corresponding to geometries in which the OH moiety is

oriented in the plane toward (*cis*) or away from (*trans*) the halogen substituent.[9] For 2FPh, however, only one band was observed in the OH stretching region. Carlson *et al.*[10] provided the first evidence for the existence of two planar conformers of 2FPh from analysis of the far infrared spectrum of the OH out-of-plane torsion mode below 400 cm^{-1}. The band for the lower energy *cis* conformer, which is stabilized by the OH•••F interaction, is blue-shifted by ~40 cm^{-1} from that of the *trans* conformer. According to DFT and MP2 calculations using various basis sets, *cis*-2FPh is more stable than *trans*-2FPh by 2.8-2.9 kcal/mol[12,13] which is greater than the experimental estimate provided by Carlson *et al.* of 1.63 kcal/mol.[10] For the equivalent conformers of 3FPh, the substituents are too far to interact and are predicted to differ in energy by only 0.2 kcal/mol (MP2/aug-cc-pVDZ)) with the *trans* form being more stable.[12]

The rotational spectra of 2FPh and 3FPh have been reported above 12.5 GHz using Stark modulated microwave spectroscopy with experimental uncertainties in the measured line positions reported to be 0.1 to 0.2 MHz.[14,15,16,17,18] For 2FPh, only transitions corresponding to the lower energy *cis* conformer were observed in the ground vibrational state for the normal and singly deuterated (OD) analog.[14] As only four independent rotational constants were derived in this study, the subsequent structural analysis via least squares fitting was limited to the approximation of three bond lengths (CF, CO and OH). As the angles (in particular CCF, CCO, COH) were fixed to literature values of related molecules, the nature of the OH•••F interaction on the molecular geometry could not be explored with confidence. Although gas phase electron diffraction (GED) results are available for 2FPh, the large uncertainties made it difficult to extract specific geometric parameters in part because the results could not clearly establish the conformer composition of the sample which was estimated to be 66±23% *cis*-2FPh. For 3FPh, ground state rotational spectra of both the *cis* and *trans* conformers[15,17] have been reported as has

the spectrum of the first two excited OH torsional states of the latter which was confirmed via rf-microwave double resonance experiments.[18] Observation of transitions for the singly-deuterated (OD) isotopologue of the *trans* conformer[16] was used to estimate the geometry around the OH substituent within similar confines as described above for 2FPh. While limited in range and resolution, these studies have laid important ground work for the current investigation.

In order to better elucidate the role of non-covalent interactions in the FPh molecules, more reliable experimental geometries are required. These can be derived from high resolution FTMW spectra of the heavy atom substituted analogues of 2FPh and 3FPh. In this paper, we report the first rotational spectra of the six singly substituted ^{13}C isotopologues of *cis*-2FPh and *trans*-3FPh, the lowest energy conformer of each, recorded in natural abundance (1.07% for ^{13}C). The rotational constants derived from the fit of the minor isotopologues were used to determine the substitution geometry (r_s) and ground state effective geometry (r_0) of the parent molecules. The experimental structures compare well with the equilibrium geometry (r_e) calculated at the MP2/6-311++G(2d,2p) level and the results allow the investigation of subtle geometric changes in the ring backbone that accompany fluorination at the *ortho* and *meta* sites of the ring relative to the hydroxyl (OH) group. These are interpreted in the context of the results from natural bond orbital (NBO) calculations. We also report the re-assignment of the FTMW spectrum of the higher energy *cis*-3FPh conformer (parent) which is in agreement with *ab initio* results but is inconsistent with the previously reported spectrum and analysis.[17]

2. Experimental

Commercial samples of 2FPh and 3FPh (both 98%) were purchased from Sigma-Aldrich. These samples were not purified further. The rotational spectra of both compounds were

recorded over a range of 6 to 26 GHz using a Balle-Flygare FTMW spectrometer that has been previously described.[19] The observed transitions typically have linewidths (FWHM) of ~7 kHz and the uncertainty in line positions is ±1 kHz. Since these compounds have relatively high boiling points (171-172^{o}C for 2FPh, 178^{o}C for 3FPh), the liquid samples were kept in glass vessels through which a carrier gas (Ar at ~1 bar) was bubbled. The glass vessels were seated in a temperature controlled water bath to increase the vapour pressure of the compounds of interest (40^{o}C for 2FPh, 60^{o}C for 3FPh). The seeded gas sample was pulsed through a General Value nozzle (1 mm orifice) installed parallel to the cavity axis.

3. Spectral Analysis

3.1 Rotational Spectrum of 2-Fluorophenol

The geometries of *cis*-2FPh and *trans*-2FPh in their respective principal axis systems are shown in Figure 1. According to *ab initio* calculations from this work (MP2/6-311++G(2d,2p)), *cis*-2FPh has dipole components of μ_a = 1.17 D and μ_b = 0.45 D while *trans*-2FPh has values of μ_a = -0.74 D and μ_b = -3.04 D. Even though *trans*-2FPh has a larger dipole moment, this conformer is too high in energy (1.63(6) kcal/mol from the torsional frequencies,[10] 2.9 kcal/mol from MP2/aug-cc-pVDZ calculations,[12] 2.8 kcal/mol from this work) for observation due to the low rotational temperatures in the supersonic jet (<5 K). The rotational spectra of *cis*-2FPh and its isotopologues were successfully recorded over a range of 6 to 19 GHz with *a*-type and *b*-type transitions ranging from J = 2 to 7. A list of observed transitions is provided in the Supplementary Information.

3.2 Rotational Spectrum of 3-Fluorophenol

Cis-3FPh and *trans*-3FPh are shown within their principal axis systems in Figure 1. *Cis*-

3FPh is predicted to have dipole components of μ_a = 0.73 D and μ_b = 0.13 D while the *trans* conformer is expected to have larger values of μ_a = 2.07 D and μ_b = 2.29 D (this work: MP2/6-311++G(2d,2p)). Based on our calculations, the two conformers differ in energy by only 0.15 kcal/mol (0.2 kcal/mol from MP2/aug-cc-pVDZ calculations)[12] with the *trans* form being more stable. Due to the small energy gap, transitions of both conformers were readily detected, however, the low intensities observed for *cis*-3FPh (as a result of the smaller dipole moment) prevented the detection of its minor isotopologues. A comparison of the intensities of a typical rotational transition of the *cis* and *trans* conformers is shown in Figure 2. Rotational transitions were recorded from 8 to 26 GHz with *a*-type and *b*-type transitions ranging from J = 3 to 9. The Supplementary Information provides a list of all observed transitions.

3.3 Determination of Spectroscopic Constants

Rotational and centrifugal distortion constants were obtained by fitting all observed transitions using Pickett's SPFIT software[20] set to Watson's A-reduced Hamiltonian. The parameters determined for 2FPh are compiled in Table 1 and those for 3FPh are shown in Tables 2 (*trans*) and 3 (*cis*). For the fits involving minor isotopologues, the centrifugal distortion constants were held fixed to the parent values as fewer transitions were observed.

4. Structural Determination

The inertial defect ($\Delta I = I_c - I_a - I_b$) values of *cis*-2FPh, *trans*-3FPh and *cis*-3FPh were calculated using the experimental rotational constants in Tables 1 through 3. The values were found to be 0.0018(4) amu•Å^2 (*cis*-2FPh), -0.01677(9) amu•Å^2 (*trans*-3FPh) and -0.01866(3) amu• Å^2 (*cis*-3FPh) and are consistent with planar equilibrium structures. The small negative values for 3-FPh may arise due to contributions from low frequency out-of-plane motions (for

example OH-torsion) which are more hindered in *cis*-2FPh due to intramolecular interaction. Planarity was thus assumed in the subsequent structural analysis.

4.1 Equilibrium Geometry (r_e)

The molecular structures for both conformers of 2FPh and 3FPh were optimized at the MP2/6-311++G(2d,2p) level using Gaussian 09 software.[21] The key r_e structural parameters for of *cis*-2FPh and *trans*-3FPh are listed in Table 4. The optimized geometries of all four molecules and that of phenol were also subject to natural bond order (NBO) calculations using the POP = NBO command in G09 to better understand the relationship between equilibrium geometry and electronic structure for fluorine substitution at various sites.

4.2 Substitution Geometry (r_s)

As rotational spectra were observed for all six ^{13}C isotopologues of *cis*-2FPh and *trans*-3FPh, their rotational constants were used to estimate the bond lengths and angles for the carbon backbone of each. This was accomplished via Kraitchman analysis[22] using Kisiel's KRA program.[23] As the Kraitchman equations provide only absolute values of the coordinates, *ab initio* results were used to establish their signs. The coordinates and their corresponding Costain errors[24] were then input into the EVAL routine[23] to calculate the C-C bond lengths and CCC angles. The determined geometric parameters are shown in Table 4 under the r_s heading. It is important to note that the a-coordinate of C2 in *trans*-3FPh was imaginary due to its proximity to the b- inertial axis and was set to zero when determining geometric parameters. The Costain error for the a-coordinate of C5 in this species was larger than the coordinate itself which is also a consequence of its position near the b-axis and consequently, the geometric parameters involving C2 and C5 have large uncertainties. This made it difficult to compare the r_s structure of *trans*-3FPh with results from other methods.

4.3 Ground State Effective Geometry (r_0)

The r_0 structures of *cis*-2FPh and *trans*-3FPh were estimated from the A and B rotational constants of all observed isotopologues via least squares fitting of key geometric parameters in the STRFIT program.[23,25] While fitting the r_0 parameters of the ring backbone, the C-O, O-H, C-F and C-H bond lengths, along with the C1-O-H angle, were kept fixed at their *ab initio* r_e values. In the first step, all C-C bond lengths (except C6-C1) and one CCH or CCF angle for each carbon (except C1 and C6) were fitted. The related CCH or CCF angle for each carbon was varied simultaneously but the difference between the angles (for example, <C1-C2-F − <C3-C2-F) was fixed to the *ab initio* value to ensure that the orientation of the CH or CF bond was preserved relative to the ring. Next, these geometric parameters were held fixed and a second fit was performed in which the angles about C1 and C6 were determined. The process was repeated iteratively until the parameters no longer varied within their determined uncertainties. The resulting r_0 parameters are given in Table 4 for each. The maximum discrepancy between the observed and calculated rotational constants from this fitting procedure was 0.004%.

5. Discussion

The rotational constants obtained for the parent molecules of 2FPh and 3FPh are compared with previous literature values and *ab initio* estimates in Tables 1-3. For the lowest energy conformers, *cis*-2FPh and *trans*-3FPh, the ground state spectroscopic parameters are more precisely determined in this work due to the superior resolution of FTMW spectroscopy compared with conventional methods. For the higher energy *cis*-3FPh, while the experimentally derived parameters are in good agreement with *ab initio* results (as for the other two species), there is an obvious discrepancy with the previous literature values.[17] The earlier report was based

on a narrow frequency range (23-25 GHz) that overlaps with that of the present study (4-26 GHz) but we were unable to observe transitions at the frequencies reported in reference 17. Based on the extent and quality of the present fit and its correspondence with theory, we are confident in our assignment.

In Table 4, a comparison of the r_0 (experimental) and r_e (*ab initio*) structures for *cis*-2FPh and *trans*-3FPh reveals that most bond lengths and angles of the aromatic ring agree with the theoretical values to within the 1σ uncertainties derived from the least squares fit and all match within two standard deviations. When compared with the geometry of the phenol backbone, which is also provided in Table 4, the most significant changes occur near the fluorine substituent as one would expect. The CCC ring angle increases at the site of fluorination by ~3° which is similar to the change observed in substituted benzenes,[26,27] benzonitriles[28] and pyridines[29,30] investigated via FTMW spectroscopy. This is indicative of a change in the hybridization of the substituted carbon such that the orbital directed along the CF bond has more p-character as a result of its polarity while the orbitals forming the σ-framework within the ring have enhanced s-character. This is supported by the NBO calculations which show ~3% change in the hybridization character at C2 in 2FPh (s: 37.5%, p: 62.4%) and at C3 in 3FPh (s: 38.6%, p: 61.2%) for the orbitals directed to the adjacent carbon atoms compared with the hybridization in phenol (s: 35%, p: 65%).

A second effect of fluorination is the observation that the C-C bond lengths involving the substituted carbon are shortened by 0.010-0.015 Å relative to those of the phenol parent with the exception of C1-C2 in *cis*-2FPh. The same effect was noted in 2- and 3-fluorobenzonitrile.[28] Although it is known that fluorine can behave as a π-donor, the second order perturbation analysis within the NBO calculations does not support donation of electron density from the

fluorine lone pair into the π-bonding system of the ring. The observed structural changes may instead be explained with a more standard inductive argument in which the electron withdrawing nature of fluorine increases the positive charge at the substituted carbon which strengthens the adjacent C-C bonds. This is consistent with the calculated natural charges. The differences in natural charges between neighbouring carbon atoms (C2: -0.292, C3: 0.148, C4: -0.241) in phenol become larger in *trans*-3FPh, as shown in Figure 3, with the addition of the electronegative fluorine at C3. While the C2-C3 bond in *cis*-2FPh is similarly shortened, there is little change in C1-C2 compared with phenol. The natural charges at both C1 and C2 are positive in 2FPh because of the attached electronegative atoms (O, F) and thus, a shorter C1-C2 bond would not be favourable.

To address the effects of a non-covalent OH•••F interaction in *cis*-2FPh, it is necessary to compare the geometric parameters involving the hydroxyl and fluorine substituents with those of phenol and other isomers of FPh. The r_e values are provided in Table 5 for this purpose. While some of these values were fixed when determining the effective ground state parameters (r_0), the angles of the C-F and C-O bond with the ring were fit and are in excellent agreement with theoretical estimates. For *cis*-2FPh, these were found to be 116.75(13) for ∠(F-C2-C1) and 121.74(3) for ∠(O-C_1-C_2); for *trans*-3FPh, they are 117.7(13) for ∠(F-C3-C2) and 116.70(8) for ∠(O-C_1-C_2). As a result of this correspondence, the r_e values are assumed to be accurate and used in the remaining discussion as they provide a more complete set of parameters for comparing various isomers. Table 5 shows that the r_e parameters involving the OH and fluorine substituents are nearly identical in both conformers which is expected as the OH and fluorine groups are too far apart to interact. For 2FPh, the O-H and C-F bonds are longer in the *cis* form which supports the assertion that a non-covalent OH•••F interaction is present. Also noteworthy is the

observation that the C-F bond tilts toward C1 by ~2^{o} in *cis*-2FPh which brings the OH and fluorine groups closer together. A similar result is found for the orientation of the C-O bond which can be derived by comparing the O-C1-C2 and O-C1-C6 angles. In phenol, for example, the C-O bond tilts away from the bisector of the C6-C1-C2 angle by 2.7^{o} to increase the separation between the hydrogen of the hydroxyl group and the hydrogen of the vicinal carbon. In *cis*-2FPh, the tilt angle is only 0.8^{o} which reduces the distance between OH and fluorine while in *trans*-2FPh, the angle is larger (3.3^{o}). This presumably minimizes the repulsion between the neighbouring electronegative oxygen and fluorine atoms.

Finally, the nature of the non-covalent interaction in *cis*-2FPh is provided by the NBO results which show a potential stabilization of 0.73 kcal/mol from donation of electron density of the fluorine lone pair (n) to the σ* orbital of OH. This interaction is not present in *trans*-2FPh (or 3FPh) and is in close agreement with the value reported for *cis*-2-cyanophenol (0.72 kcal/mol)[31] which was itself classified as a hydrogen-bonding interaction. Two additional structural parameters are potentially useful for determining whether this interaction may be classified as a hydrogen bond: the OH•••F separation and angle. The OH•••F separation (2.212 Å) is 15% less than the sum of the van der Waals radii of hydrogen and fluorine (2.56 Å)[32] which has historically been used as an indicator for a hydrogen bond. For comparison, the analogous distance in phenol (OH•••H) (2.289 Å) is larger despite the fact that the sum of the van der Waals radii of two hydrogen atoms (2.18 Å) is less. Based on the report of a recent IUPAC task group,[8] the ∠(OH•••X) angle provides a better benchmark with the ideal angle being 180^{o} in hydrogen bonded systems and a lower limit of 110^{o}. For *cis*-2FPh, the present study supports an (OH•••F) angle of 112.3^{o} which is consistent with this recommendation despite the constraints introduced by the geometry of the resulting five-membered ring (C1-O-H•••F-C2).

Acknowledgements

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Table 1. Ground State Spectroscopic Constants of *cis*-2-Fluorophenol and its ^{13}C Isotopologues

	Normal	$^{13}C1$	$^{13}C2$	$^{13}C3$	$^{13}C4$	$^{13}C5$	$^{13}C6$
Rotational Constants[a,b] /MHz							
A	3337.90081(11)	3326.2850(4)	3328.7144(4)	3295.5680(5)	3326.8265(4)	3328.7520(4)	3295.8458(4)
B	2231.93426(9)	2229.88769(5)	2229.89418(5)	2227.10318(5)	2196.06356(5)	2195.16856(5)	2226.17495(5)
C	1337.55132(7)	1334.94979(4)	1335.34338(4)	1328.98299(4)	1322.83702(4)	1322.81607(4)	1328.69712(4)
Centrifugal Distortion Constants[c] /kHz							
Δ_J	0.0819(15)	0.0819	0.0819	0.0819	0.0819	0.0819	0.0819
Δ_{JK}	0.0546(41)	0.0546	0.0546	0.0546	0.0546	0.0546	0.0546
Δ_K	0.6050(48)	0.6050	0.6050	0.6050	0.6050	0.6050	0.6050
δ_J	0.02902(68)	0.02902	0.02902	0.02902	0.02902	0.02902	0.02902
δ_K	0.1074(28)	0.1074	0.1074	0.1074	0.1074	0.1074	0.1074
rms /kHz	1.2	0.63	0.88	1.2	0.64	1.7	1.4
# lines	79	16	16	15	16	16	16

[a]Rotational constants from ref 14: A = 3337.86(2) MHz, B = 2231.92(1) MHz, C = 1337.52(1) MHz.

[b]Calculated rotational constants (MP2/6-311++G(2d,2p)) from this work: A = 3340.8 MHz, B = 2227.0 MHz, C = 1336.2 MHz.

[c]Centrifugal distortion constants for the isotopologues were held fixed to the parent values during the fit.

Table 2. Ground State Spectroscopic Constants of *trans*-3-Fluorophenol and its ^{13}C Isotopologues

	Normal	$^{13}C1$	$^{13}C2$	$^{13}C3$	$^{13}C4$	$^{13}C5$	$^{13}C6$
Rotational Constants[a,b] /MHz							
A	3748.56150(3)	3746.40579(12)	3721.79808(18)	3747.00581(11)	3713.48601(16)	3660.28816(17)	3715.55890(16)
B	1797.766571(15)	1788.23250(4)	1797.85497(6)	1789.48924(4)	1788.94828(4)	1797.77460(6)	1787.78373(7)
C	1215.094056(12)	1210.506592(18)	1212.31096(3)	1211.145098(17)	1207.374600(20)	1205.668340(20)	1207.06293(3)
Centrifugal Distortion Constants[c] /kHz							
Δ_J	0.06475(11)	0.06475	0.06475	0.06475	0.06475	0.06475	0.06475
Δ_{JK}	-0.0056(4)	-0.00562	-0.00562	-0.00562	-0.00562	-0.00562	-0.00562
Δ_K	0.6154(10)	0.6154	0.6154	0.6154	0.6154	0.6154	0.6154
δ_J	0.02243(6)	0.022427	0.022427	0.022427	0.022427	0.022427	0.022427
δ_K	0.1328(6)	0.13276	0.13276	0.13276	0.13276	0.13276	0.13276
rms /kHz	0.484	0.919	1.379	0.797	1.007	0.893	1.241
# lines	154	44	41	39	40	36	37

[a]Rotational constants from ref 15 for *trans*-3FPh: A = 3748.524(4) MHz, B = 1797.751(2) MHz, C =1215.084(2) MHz

[b]Calculated rotational constants (MP2/6-311++G(2d,2p)) from this work for *trans*-3FPh: A = 3744.2 MHz, B =1793.8 MHz, C = 1212.8 MHz

[c]Centrifugal distortion constants for the isotopologues were held fixed to the parent values during the fit.

Table 3. Ground State Spectroscopic Constants of *cis*-3-Fluorophenol

A /MHz	3754.1500(5)
B	1792.78498(5)
C	1213.40619(3)
Δ_J /kHz	0.0664(4)
Δ_{JK}	-0.0224(16)
Δ_K	0.49(9)
δ_J	0.0235(2)
δ_K	0.126(8)
rms /kHz	0.38
# lines	47

From ref 17 for *cis*-3FPh: A = 3789.57(6) MHz, B = 1795.15(6) MHz, C =1217.89(5) MHz.

[b]Calculated rotational constants for *cis*-3FPh: A = 3756.4 MHz, B = 1786.6 MHz, C =1210.7 MHz.

[c]Centrifugal distortion constants for the isotopologues were held fixed to the parent values during the fit.

Table 4. Equilibrium (r_e) (MP2/6-311++G(2d2p)), Substitution (r_s) and Ground State Effective (r_0) Structural Parameters (Bond Lengths in Å, Angles in Degrees) Determined for *cis*-2-Fluorophenol and *trans*-3-Fluorophenol

	Phenol[a]	*cis*-2Fph		
	r_e	r_e	r_s	r_0
C1-C2	1.395	1.394	1.379(3)	1.392(2)
C2-C3	1.395	1.383	1.374(4)	1.380(3)
C3-C4	1.395	1.397	1.401(2)	1.396(3)
C4-C5	1.396	1.396	1.392(3)	1.402(4)
C5-C6	1.394	1.395	1.399(2)	1.396(3)
C6-C1	1.394	1.393	1.385(4)	1.391(3)
∠(C1-C2-C3)	119.8	122.7	123.3(3)	122.9(3)
∠(C2-C3-C4)	120.3	118.5	118.0(2)	118.4(3)
∠(C3-C4-C5)	119.4	119.9	119.8(1)	119.7(4)
∠(C4-C5-C6)	120.6	120.6	120.7(1)	120.7(4)
∠(C5-C6-C1)	119.6	120.0	119.4(1)	119.7(3)
∠(C6-C1-C2)	120.2	118.3	118.9(3)	118.6(3)
	Phenol[b]	*trans*-3FPh		
	r_e	r_e	r_s	r_0
C1-C2	1.394	1.395	1.416(11)	1.395(5)
C2-C3	1.394	1.385	1.367(11)	1.383(5)
C3-C4	1.396	1.388	1.376(6)	1.385(2)
C4-C5	1.395	1.394	1.341(93)	1.398(3)
C5-C6	1.395	1.395	1.448(93)	1.394(3)
C6-C1	1.395	1.396	1.384(6)	1.398(2)
∠(C1-C2-C3)	119.6	118.1	116.8(3)	117.4(5)
∠(C2-C3-C4)	120.6	123.1	124.6(4)	123.9(5)
∠(C3-C4-C5)	119.4	117.7	118.7(23)	117.3(3)
∠(C4-C5-C6)	120.3	120.9	120.8(2)	121.0 (4)
∠(C5-C6-C1)	119.8	119.6	118.1(21)	119.3(3)
∠(C6-C1-C2)	120.2	120.5	120.9(3)	121.0 (5)

[a]For ease of comparison, the carbon atom numbering follows that of *cis*-2-fluorophenol such that OH is directed toward C2.

[b]For ease of comparison, the carbon atom numbering follows that of *trans*-3-fluorophenol such that OH is directed away from C2; as such the parameters are labelled different than above, eg. C1-C2(*trans*) = C6-C1(*cis*) etc.

Table 5. Equilibrium (r_e) (MP2/6-311++G(2d2p)) Structural Parameters (Distance in Å, Angles in Degrees) for the Hydroxyl and Fluorine Substituents in Phenol, 2-Fluorophenol and 3-Fluorophenol.

	Phenol	*cis*-2FPh	*trans*-2FPh	*cis*-3FPh	*trans*-3FPh
C-O	1.373	1.365	1.366	1.370	1.371
O-H	0.961	0.963	0.961	0.961	0.961
C-F		1.361	1.348	1.354	1.353
∠(C1-O-H)	108.7	108.1	108.4	109.0	108.7
∠(F-C-C)[a]		116.9	118.5	118.0	118.1
∠(O-C1-C2)[b]	122.6 117.2	121.7	117.6	122.3	116.7
OH•••X	2.289	2.212			
∠(OH•••X)	103.7	112.3			

[a] Defined as F-C2-C1 for 2FPh and F-C3-C2 for 3FPh.

[b] The O-C1 bond is tilted from the bisector of the C6-C1-C2 angle to minimize repulsion between the hydrogen of OH and the hydrogen of the vicinal carbon leading to two possible numbering schemes.

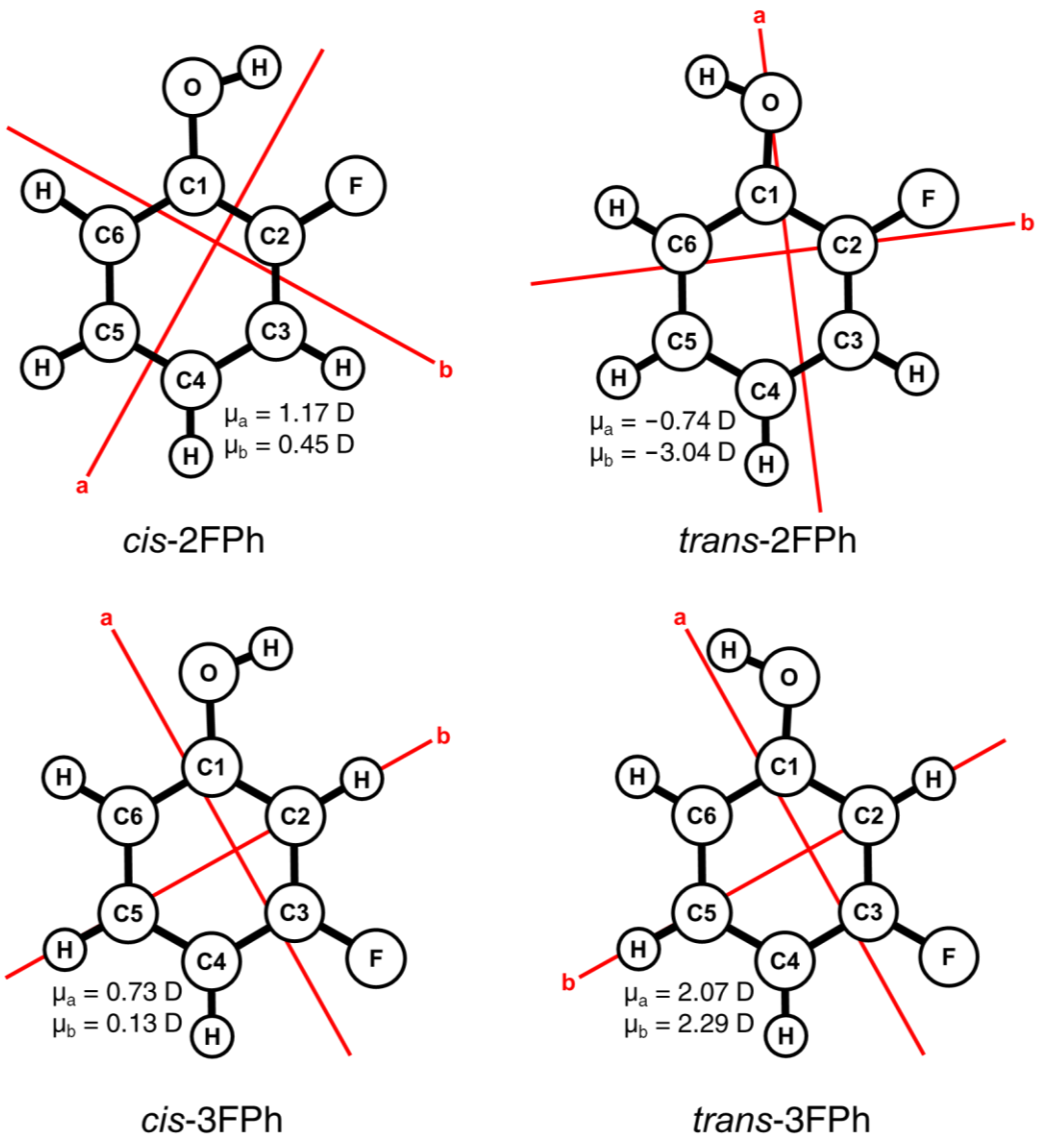

Figure 1: Principal axis systems of 2-fluorophenol and 3-fluorophenol based on *ab initio* predictions (MP2/6-311++G(2d,2p)). Note that *trans*-2FPh was not observed in this work as it is calculated to be 2.8 kcal/mol higher in energy than the *cis* conformer.

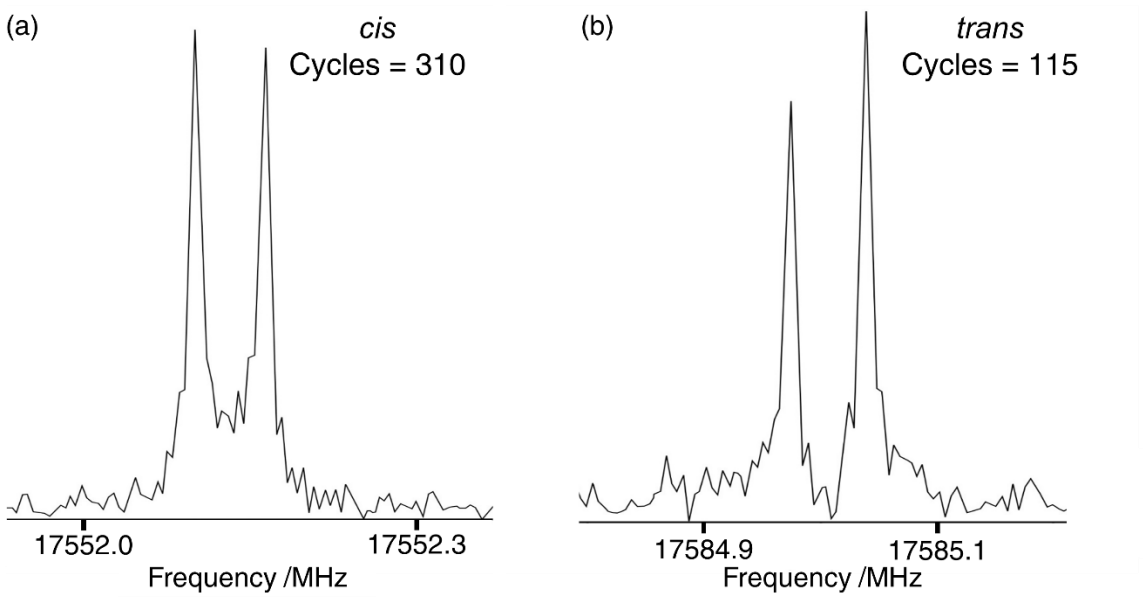

Figure 2: Sample spectra of the 6_{25} - 5_{24} rotational transition of: a) *cis*-3FPh and b) *trans*-3FPh. To obtain the same signal-to-noise ratio, the former required the averaging of nearly three times as many FIDs.

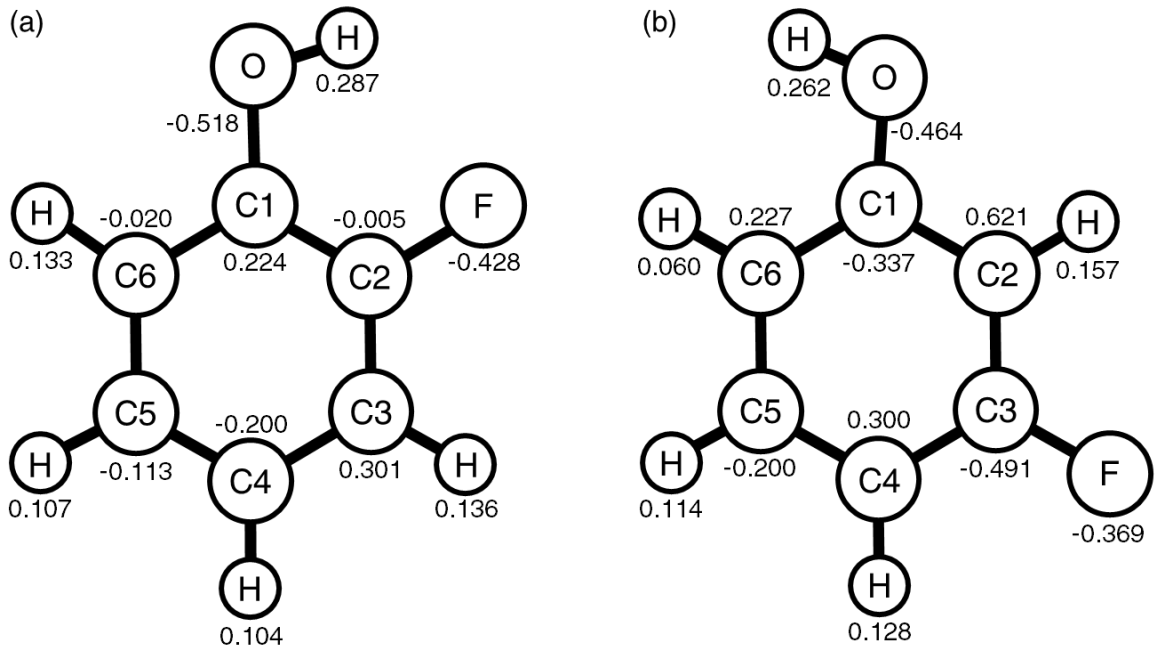

Figure 3: Natural charges in (a) *cis*-2FPh and (b) *trans*-3FPh from NBO analysis (MP2/6-311++G(2d,2p)).

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