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Structural elucidation of 2-fluorothiophenol from Fourier transform microwave spectra and *ab initio* calculations

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TOC graphic

-Rotational spectrum of 2-fluorothiophenol was measured

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-^{13}C, ^{34}S substitution used to identify geometry effects of fluorination

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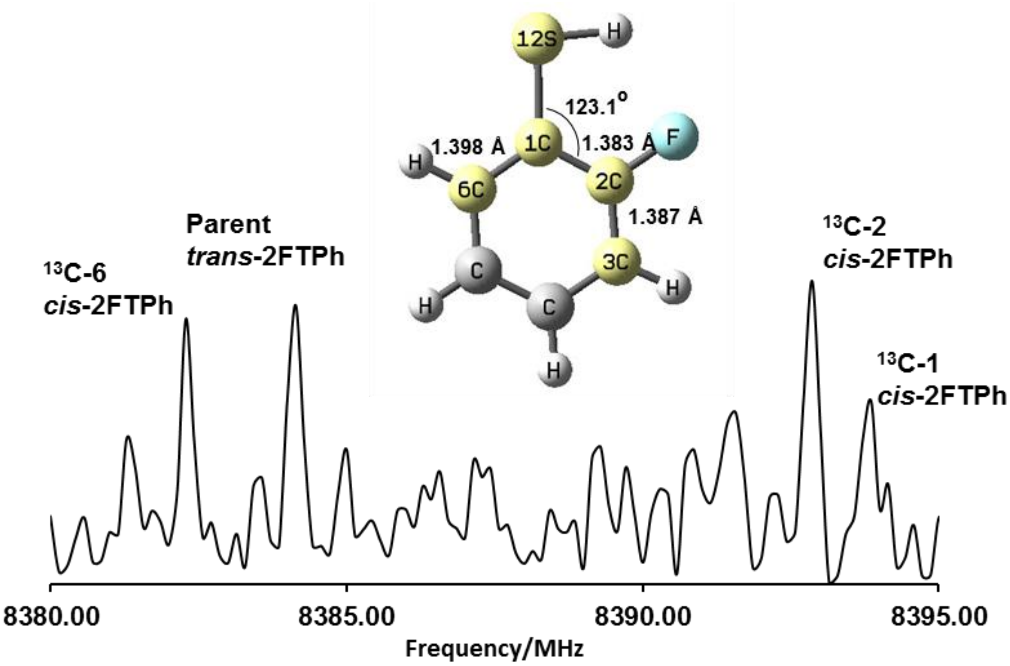

Abstract

Pure rotational transitions corresponding to the ground vibrational state of 2-fluorothiophenol (2FTPh) were recorded via Fourier transform microwave (FTMW) spectroscopy in the range of 4 to 26 GHz. The observed transitions were assigned to two planar conformers in which the SH bond is directed toward (*cis*-2FTPh) or away from (*trans*-2FTPh) the fluorine substituent with the former predicted to lie 3.88 kJ/mol lower in energy from *ab initio* calculations (MP2/6-311++G(2d,2p)). The rotational constants determined from the spectral analysis were used to derive effective ground state (r_0) structures of the lower energy *cis*-2FTPh conformer using spectra of the corresponding ^{13}C and ^{34}S isotopologues which were observed in natural abundance. Geometry optimization at the MP2/6-311++G(2d,2p) level provided the equilibrium (r_e) structure which is in close agreement with the experimentally-derived geometry. Comparison with results from natural bond orbital (NBO) calculations provide evidence of a weak intramolecular interaction between the lone pair on sulfur and the CF moiety in *cis*-2FTPh that is not found in *trans*-2FTPh or thiophenol (TPh). This interaction stabilizes the *cis*-2FTPh conformer by 2.18 kJ/mol.

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1. Introduction

The importance of non-covalent interactions in chemistry has been broadly investigated for nearly a century[1] and yet these phenomena continue to inspire a multitude of new studies each year. As fluorinated species find increasing use in industry to tune the physiochemical properties of materials,[2] pharmaceuticals[3] and agrochemicals,[4] the role of fluorine in non-covalent interactions such as hydrogen bonding and halogen bonding has been explored in a rapidly expanding range of both inter- and intramolecular systems using a range of experimental techniques including NMR spectroscopy[5,6,7] and microwave spectroscopy.[8,9,10] Previously overlooked functional groups, such as divalent sulfur compounds, are also gaining interest in part because of the key role that weak interactions with sulfur play in determining protein structures.[11] Although less electronegative than other atoms typically involved in non-covalent bonding, the strength of the interaction can still be significant as shown, for example, via infrared spectroscopy of the methanol-dimethyl sulfide complex in which the enthalpy of hydrogen bond formation was determined to be only ~23% smaller (-14.8(15) kJ/mol) than that of the oxygen analogue methanol-dimethyl ether (-19.1(20) kJ/mol).[12]

Gas phase spectra provide useful information for identifying the effects of non-covalent interactions on molecular geometry in isolation. For example, 2-fluorophenol has been extensively studied both spectroscopically[13,14,15,16,17] and theoretically[17,18,19] for this reason. Two planar conformers were identified via gas phase far infrared spectroscopy[14] that differ by the orientation of the OH group and whether it is directed toward (*cis*) or away from (*trans*) fluorine on the neighbouring carbon. The *cis*-conformer is estimated to be 12.1 kJ/mol lower in energy based on MP2 (aug-cc-pVDZ) calculations[18] due to the presence of a stabilizing intramolecular OH•••F interaction. Recently, the effect of this interaction on the geometry of *cis*-2-

fluorophenol was investigated via Fourier transform microwave (FTMW) spectroscopy and *ab initio* calculations (MP2/6-311++G(2d,2p) of the *cis* conformer.[17] Based on the rotational spectra of the ^{13}C isotopologues, the geometry of the benzene backbone was experimentally derived and compared to that of phenol to elucidate i) the effect of fluorination and ii) any structural changes consistent with formation of an intramolecular hydrogen bond. As in other fluorine-substituted aromatic rings such as fluorobenzene,[20,21,22] fluoropyridine,[23,24] and fluorocyanobenzene,[25] the largest geometry changes appear near the substitution site with an increase in the ring angle at that site by 3-4^{o} and a shortening of the adjacent C-C bonds by 0.006-0.015 Å. This was attributed to inductive effects due to the highly electronegative fluorine atom. In deducing the role of an intramolecular OH•••F interaction in *cis*-2-fluorophenol, it was noted that both the OH and CF bonds are longer than those of phenol and 3-fluorophenol. Furthermore, the CO and CF bonds are each tilted ~2 degrees toward each other relative to their orientations in phenol bringing the OH and F substituents closer together. These results were interpreted in reference to natural bond orbital (NBO) analysis which revealed a 3.1 kJ/mol stabilization due to donation of electron density from fluorine (n) to the σ* orbital of OH. This value is nearly identical to that found for *cis*-2-cyanophenol 3.0 kJ/mol[26] which was classified as a hydrogen-bonding interaction.

In this work, the isovalent 2-fluorothiophenol (2FTPh) molecule is investigated to identify geometry changes that accompany fluorination and any effects involving interaction between the neighbouring SH and F groups. This paper describes the first rotational spectroscopic study of 2FTPh including the parent and singly substituted ^{13}C and ^{34}S minor isotopologues of *cis*-2FTPh in natural abundance as well as the parent species of the higher energy *trans*-2FTPh conformer. The rotational constants derived from the fit were used to determine the experimental ground state effective geometry (r_0) of *cis*-2FTPh for comparison with the equilibrium geometry (r_e) calculated at the MP2/6-311++G(2d,2p) level. Comparison with the *ab initio* geometry (r_e) of thiophenol and study of the natural bond orbitals (NBO) allows identification of subtle geometric changes that accompany fluorination as well as investigation of the origin of the conformational preference for *cis*-2FTPh.

2. Experimental

A sample of liquid 2FTPh (97%) was obtained from Sigma-Aldrich Canada and used without further purification. Due to the low vapour pressure (35 mmHg at 61-62^{o}C), a few mL of 2FTPh was transferred to a glass bubbler that was seated in a temperature-controlled water bath maintained at 37^{o}C. Approximately one bar of neon was bubbled through the liquid sample and served as a carrier gas to deliver 2FTPh to the spectrometer's pulsed nozzle for supersonic expansion into the vacuum chamber. The broadband rotational spectrum was first recorded in 2 GHz segments in the range of 8 to 18 GHz using the chirped-pulse FTMW spectrometer.[27] This allowed the identification of the strongest transitions of each conformer and refinement of their rotational constants. The Balle-Flygare FTMW spectrometer[28] was then used to record individual rotational transitions with higher resolution in the range of 4 to 26 GHz and to seek out lower intensity transitions. Spectra recorded with the cavity-based instrument have linewidths (FWHM) of ~7 kHz and individual frequencies are typically measured to within ±1 kHz. Rotational lines due to the singly-substituted minor isotopologues of ^{34}S and ^{13}C were predicted by appropriate scaling of the rotational constants of the parent species and sought by scanning small frequency ranges with the Balle-Flygare instrument.

3. Spectral assignment and fitting

As there are no previous reports on the microwave spectra of the title species, the rotational transition frequencies were initially predicted using the equilibrium structures obtained from *ab initio* calculations. Geometry optimization was conducted for both the planar *cis*- and *trans*-2FTPh conformers at the MP2/6-311++G(2d,2p) level using Gaussian 09 software.[29] The resulting structures are shown in Figure 1 in their principal inertial axis systems.

The *cis*-2FTPh conformer lies 3.88 kJ/mol lower in energy and has dipole components μ_a=1.71 D and μ_b=0.48 D confirming that the spectrum is dominated by *a*-type rotational transitions. In total, 253 transitions were observed for the parent species including 116 *b*-type transitions and 137 *a*-type transitions for which ΔK_a=0, 2. The observed intensities were sufficient to proceed with observation of 61 rotational transitions due to the ^{34}S species (including 4 *b*-type) and more than 20 *a*-type transitions for each of the six ^{13}C analogues. The full list of observed lines is provided as Supplementary data to this article.

For *trans*-2FTPh, the dipole components are sizeable (μ_a=1.90 D and μ_b=2.13 D) but in the room temperature sample, only ~21% of molecules would adopt this conformation due to its higher energy. During the supersonic expansion, molecular motions are cooled such that the rotational temperature of molecules is a few Kelvin. In this case, the barrier to convert from one conformer to the other will establish whether a metastable conformer such as *trans*-2FTPh is abundant in the expansion. The interconversion pathway between *cis*- and *trans*-2FTPh was thus calculated (MP2/6-311++G(2d,2p)) by twisting the SH moiety by 180^o around the CS bond in steps of 10^o. At each dihedral angle (CCSH), all other geometric parameters were optimized to minimize the energy. The resulting energy profile is shown in Figure 2 and reveals that the barrier for re-arrangement to the lower energy conformer is 5.46 kJ/mol or 456 cm^{-1} which is higher than that derived in thiophenol (3.31 kJ/mol) and 4-fluorothiophenol (0.75 kJ/mol) via microwave spectroscopy.[30] Previous microwave studies on a range of species seeded in a supersonic jet provide a useful rule of thumb that barriers greater ~400 cm^{-1} allow observation of the metastable species while those with smaller barriers result in facile relaxation to the lowest energy conformer.[31] The observation of transitions due to *trans*-2FTPh in the present study is consistent with this as the barrier is only ~6% higher than 2kT (~430 cm^{-1}). In total, a mixture of 116 transitions (both *a*- and *b*-type) was observed for the higher energy *trans*-conformer with about 1-2% the intensity of the analogous transitions of *cis*-2FTPh as shown in Figure 3. Based on the similar dipole moments and the height of the barrier for interconversion, one would expect higher intensity for the *trans*-conformer which suggests that some relaxation to the *cis*-conformer must occur in the expansion. The reduced intensity relative to the spectrum for *cis*-2FTPh made it impossible to observe minor isotopic species of *trans*-2FTPh. A list of observed transitions for *trans*-2FTPh is provided in the Supplementary Information.

Rotational and centrifugal distortion constants were obtained by fitting all observed transitions using Pickett's SPFIT software[32] set to Watson's A-reduced Hamiltonian. The parameters determined for *cis*-2FTPh and *trans*-2FPh are compiled in Table 1 along with the *ab initio* values for comparison. The rms error of each fit was below 1 kHz suggesting that the model Hamiltonian provides a good representation of the various species.

4. Structural Determination

4.1 Equilibrium Geometry (r_e)

The internal coordinates for the MP2/6-311++G(2d,2p) optimized geometries of *cis*-2FTPh, *trans*-2FTPh and thiopenol (TPh) are provided as Supplementary data to this article. To better understand the changes to the geometry that accompany fluorination, natural bond order (NBO) analysis using the POP = NBO command in G09 was also performed for all three species. The key geometric parameters related to the carbon backbone of *cis*-2FTPh are summarized in Table 2 under the r_e heading along with those of TPh and *trans*-2FTPh for comparison.

4.2 Ground State Effective Geometry (r_0)

The r_0 structure of *cis*-2FTPh was derived using the rotational constants of the observed isotopologues via least squares fitting of key geometric parameters of *cis*-2FTPh in Kisiel's STRFIT program.**Error! Bookmark not defined.** As the molecule is assumed to be planar, there are only two independent moments of inertia and thus, the fit was performed using only two rotational constants (*A* and *B*) for each isotopologue as reported for the related 2-fluorophenol species.[17] The S-H, C-F and C-H bond lengths, along with the C1-S-H angle, were kept fixed at their *ab initio* values while the C-S and C-C bond lengths (except C1-C6) were varied. In order to preserve the orientation of the C-X bonds (X=H, F, S) relative to the ring, the difference of each pair of external angles (for example ∠C1C2F −∠C3C2F) was held fixed to the *ab initio* value while one of the angles was varied. The internal ring angles (for example ∠C1C2C3) were then readily determined by trigonometry as were any remaining parameters (C6-C1). The resulting r_0 parameters are given in Table 3. The maximum discrepancy between the observed and calculated rotational constants from this fitting procedure was 0.002%.

5. Discussion

The spectroscopic constants obtained from fitting the spectra of *cis*-2FTPh and *trans*-2FTPh are well-determined and are in good agreement with *ab initio* estimates at the MP2/6-

311++G(2d,2p) level provided in Table 1. The inertial defects (Δ_o) derived from the rotational constants of each species are small and negative (*cis*: -0.101 μÅ^2, t*rans*: -0.052 μÅ^2) which is often indicative of low-frequency out-of-plane motions in planar molecules.[33] For 2FTPh, the lowest energy vibration corresponds to torsion about the C-S bond that moves the thiol hydrogen atom out of the plane of the ring. These are calculated to be at ~180 and 211 cm^{-1} for *cis*- and *trans*-FTPh (this work, B3LYP/6-311++G(2d,2p)), respectively suggesting that this vibration is more hindered in the *trans*-conformer resulting in the smaller inertial defect. This is the opposite trend observed for this out-of-plane OH torsion mode in 2-fluorophenol in which the band of the *cis*-conformer is ~40 cm^{-1} higher than that of the *trans*-conformer which was attributed to an intramolecular interaction between OH and F.[14]

In Table 2, a comparison of geometric parameters for *cis*-2FTPh reveals that most experimental bond lengths and angles (r_0) of the aromatic ring match the *ab initio* values (r_e) to within the 1σ uncertainties derived from the least squares fit with the exception of the C1-C2 bond which agrees within 2σ. When compared with the geometry of the TPh backbone and the *trans*-conformer, which are also provided in Table 2, the most significant changes occur near the fluorine substituent as expected. The C1-C2-C3 angle increases at the site of fluorination by ~2.4-2.7° which is similar to the change observed in fluorine-substituted benzenes,[20,21,22] pyridines,[23,24] benzonitriles[25] and phenols[17] that were previously investigated via FTMW spectroscopy. This is indicative of a change in the hybridization at C2 as the orbital directed along the C-F bond has more p-character due to its polarity while the orbitals forming the σ-framework within the aromatic ring have enhanced s-character. This is supported by the NBO calculations which show ~7% change in p-character of the orbital on C2 when directed to fluorine (21.4% s, 78.2% p) in *cis*-2FTPh compared to the analogous orbital in TPh (28.4% s, 71.4% p).

A second effect of fluorination is the observation that the C-C bond lengths involving the substituted carbon are shortened by 0.005-0.010 Å relative to those of the TPh parent. A similar trend was observed in the singly substituted fluorobenzonitriles[25] and in 3-fluorophenol.[17] The observed structural changes are consistent with inductive effects caused by the fluorine substituent which leads to a positive natural charge at C2 (+0.434) in *cis*-2FTPh and shortens the bonds to the neighbouring C1 (-0.232) and C3 (-0.187) atoms compared to TPh in which all carbon atoms hold a positive partial charge. Interestingly, the same effect was not observed in the C1-C2 bond of the oxygen-analogue, 2-fluorophenol,[17] but in that case, the site of the OH substituent (C1) bore a positive partial charge whereas in 2FTPh, the natural charge at C1 is negative (-0.232) while that at sulfur is positive (+0.069).

If a non-covalent SH•••F interaction in *cis*-2FTPh is the reason for the relative stability of this conformer over its *trans* counterpart, one would expect subtle geometry changes involving the thiol and fluorine substituents as reported in *cis*-2-fluorophenol.[17] In that study, the CF and CO bonds were each titled by ~2^{o} closer to each other relative to the analogous substituents in phenol. In this work, a similar comparison reveals little change with the CF bond titled by only 0.8^{o} more toward the CO bond than in TPh. Careful study of the second order perturbation energy corrections from the NBO analysis shows a 2.18 kJ/mol stabilization of *cis*-2FTPh by donation of electron density from the sulfur lone pair (n) to the σ* orbital of CF although the alignment of the affected orbitals seems non-ideal. This interaction is not found in the parent molecule or *trans*-2FTPh but such hyperconjugative effects involving σ* (CF) have been documented in other rings. For example, donation of electron density into σ* (CF) from the lone pair on oxygen in fluoropyran was used to explain its anomeric stabilization to favour an axial position of fluorine and the preferred orthogonal conformer of benzyl fluoride has been explained via donation of π-electron density into σ* (CF).[34] Interestingly, the interaction in *cis*-2FTPh is not mirrored in its oxygen analogue, *cis*-2-fluorophenol, in which the conformer stabilizing interaction (3.05 kJ/mol) involved donation of electron density from the fluorine lone pair (n) to σ* (OH). The difference is presumably due to the different size and electronegativity of oxygen versus sulfur.

In summary, the rotational spectrum of 2-fluorothiophenol (2FTPh) is reported for the first time in this work and confirms the presence of two planar conformers. As in 2-fluorophenol, the *cis* conformer lies lower in energy than the *trans* form but the energy difference in 2-FTPh (3.86 kJ/mol) is about a third that reported for the oxygen analogue (12.1 kJ/mol).[18] The effective ground state structure (r_0) of *cis*-2FTPh was derived using the rotational constants of the parent, ^{13}C and ^{34}S minor isotopologues and the results are consistent with the *ab initio* r_e geometry (MP2/6-311++G(2d,2p)). When compared with the structure of the parent thiophenol (TPh), the largest geometry changes occur around C2, the site of fluorination with similar effects predicted in both conformers. To address the presence of a non-covalent interaction between neighbouring SH and F substituents, NBO calculations were performed. The results suggest a 2.18 kJ/mol stabilization of *cis*-2FTPh relative to *trans*-2FTPh arising from n(S) to σ*(CF) electron donation. This interaction is ~1 kJ/mol smaller in magnitude and opposite in direction to the hydrogen bonding-type interaction found in 2-fluorophenol which was reported as donation of electron density from n(F) to σ*(OH).[17] The smaller magnitude of the interaction in the present work is consistent with the r_e geometries of *cis*- and *trans*-2FTPh which are very similar (Supplementary Information, Appendix 1) relative to those of *cis*- and *trans*-2-fluorophenol. For example, while the C-F bond in *cis*-2FTPh (1.356 Å) is 0.003 Å longer than in the *trans* counterpart (1.353 Å) as one would expect for a non-covalent interaction that adds electron density to σ*(CF) in the former, the lengthening is four times greater (0.013 Å) when one compares the C-F bond lengths in *cis*- and *trans* 2-fluorophenol (1.361 and 1.348 Å, respectively). The similarity in the geometric parameters of the ring (Table 2) and the C-F, S-H and C-S bonds of *cis*- and *trans*-2FTPH suggests that any intramolecular interaction between the neighbouring thiol and F groups in the former is minor.

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Table 1. Ground State Spectroscopic Constants of *cis*-2-fluorothiophenol and its ^{34}S and ^{13}C Isotopologues and Parent Species of *trans*-2-fluorothiophenol

	cis-2FTPh	^{13}C1	^{13}C2	^{13}C3	^{13}C4	^{13}C5	^{13}C6	^{34}S12	*trans*-2FTPh
Rotational Constants[a] /MHz									
A	2881.80948(2)	2879.6916(7)	2869.348(1)	2864.476(1)	2881.726(1)	2852.5106(9)	2845.5855(9)	2871.2446(4)	2940.95799(5)
B	1551.61932(1)	1550.9818(1)	1551.4313(2)	1539.5483(2)	1524.5662(2)	1535.7587(1)	1550.7199(1)	1509.86006(5)	1545.43846(4)
C	1008.78474(1)	1008.25768(6)	1007.1747(1)	1001.5590(1)	997.2702(1)	998.48868(8)	1003.93322(8)	989.70967(3)	1013.18381(2)
Centrifugal Distortion Constants[b] /kHz									
Δ_J	0.05041(9)	0.049(1)	0.050(2)	0.050(1)	0.046(2)	0.048(1)	0.052(1)	0.0495(3)	0.0490(2)
Δ_{JK}	0.1777(3)	0.188(5)	0.174(7)	0.168(7)	0.176(9)	0.161(6)	0.161(6)	0.181(1)	0.243(1)
Δ_K	0.3198(7)	[0.3198]	[0.3198]	[0.3198]	[0.3198]	[0.3198]	[0.3198]	[0.3198]	0.375(1)
δ_J	0.01618(4)	0.0149(6)	0.016(1)	0.015(1)	0.014(1)	0.0158(8)	0.0164(7)	0.0159(1)	0.0148(1)
δ_K	0.1502(3)	0.155(9)	0.15(1)	0.16(1)	0.14(1)	0.14(1)	0.17(1)	0.157(3)	0.172(1)
rms /kHz	0.8	0.6	0.8	0.8	0.8	0.7	0.7	0.6	0.9
# lines	253	27	25	24	23	26	25	61	116

[a] Calculated rotational constants (MP2/6-311++G(2d,2p)) for *cis*-2-fluorothiophenol: A = 2881.5 MHz, B = 1545.4 MHz, C = 1005.9 MHz, for trans-2-fluorothiophenol: A = 2939.4 MHz, B = 1539.5 MHz, C = 1010.3 MHz

[b] Centrifugal distortion constant Δ_K for the isotopologues was held fixed to the parent values during the fit of minor isotopologues.

Table 2. 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-fluorothiophenol

	Thiophenol[a]	*cis*-2FTPh		*trans*-2FTPh
	r_e	r_e	r_0	r_e
C1-C2	1.398	1.393	1.383(6)	1.393
C2-C3	1.394	1.386	1.387(2)	1.384
C3-C4	1.395	1.394	1.392(5)	1.395
C4-C5	1.395	1.396	1.402(6)	1.395
C5-C6	1.394	1.392	1.395(4)	1.394
C6-C1	1.399	1.400	1.398(7)	1.398
S12-C1	1.778	1.769	1.772(6)	1.772
∠(C1-C2-C3)	120.2	122.7	122.6(7)	122.9
∠(C2-C3-C4)	120.4	119.0	118.8(5)	118.9
∠(C3-C4-C5)	119.4	119.6	119.8(6)	119.7
∠(C4-C5-C6)	120.4	120.2	120.2(6)	120.3
∠(C5-C6-C1)	120.2	121.0	120.3(8)	120.9
∠(C6-C1-C2)	119.4	117.4	118.3(6)	117.4
∠(F(H)7-C2-C1)	120.1	118.9	118.9(7)	118.1
∠(S12-C1-C2)	122.8	123.1	123.1(6)	118.1

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

Figure 1: Principal inertial axis systems of *cis*-2-fluorothiophenol and *trans*-2-fluorothiophenol based on *ab initio* predictions (MP2/6-311++G(2d,2p)).

Figure 2: Calculated barrier (MP2/6-311++G(2d,2p)) for re-arrangement between the *cis*-2FTPh and *trans*-2FTPh conformers.

Figure 3: 80 MHz portion of the chirped-pulse spectrum of 2-fluorothiophenol showing the relative intensity of the 312-211 (J K_a K_c) transition for the two conformers and ^{13}C isotopologues. The spectrum is an average of 60 000 gas pulses.

Figure 1: Sun and van Wijngaarden

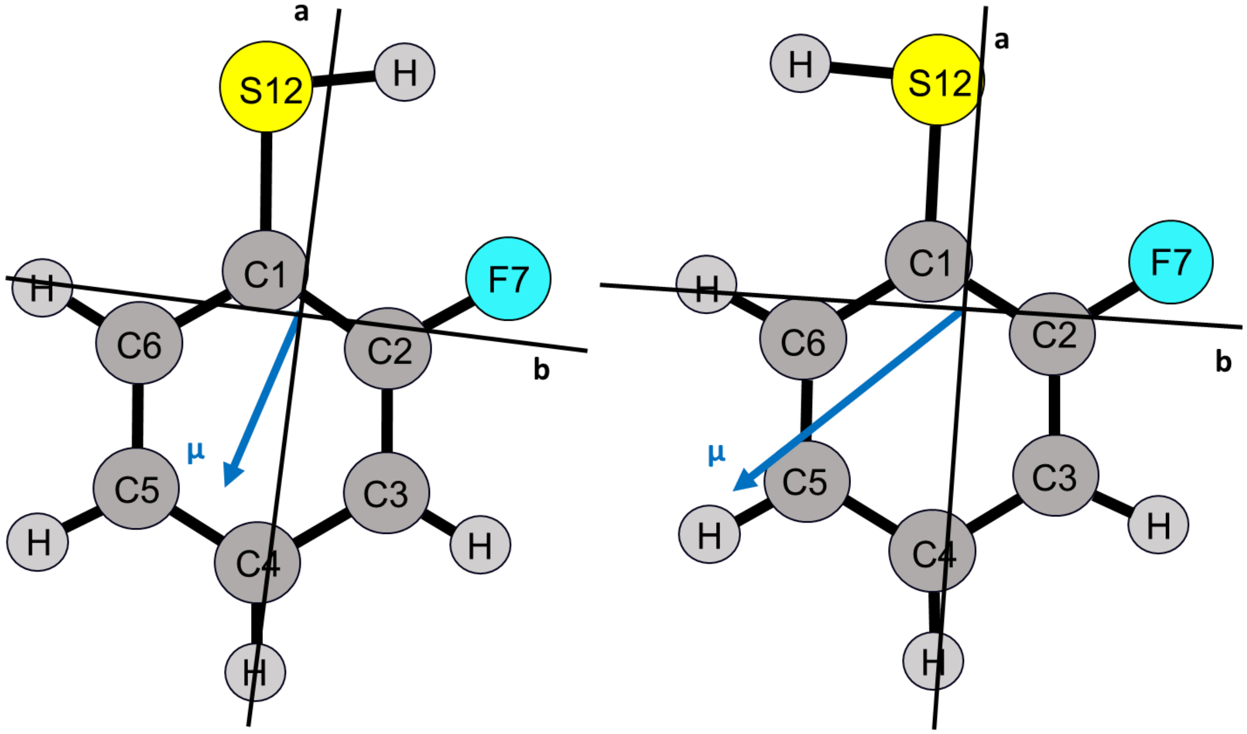


Figure 2: Sun and van Wijngaarden

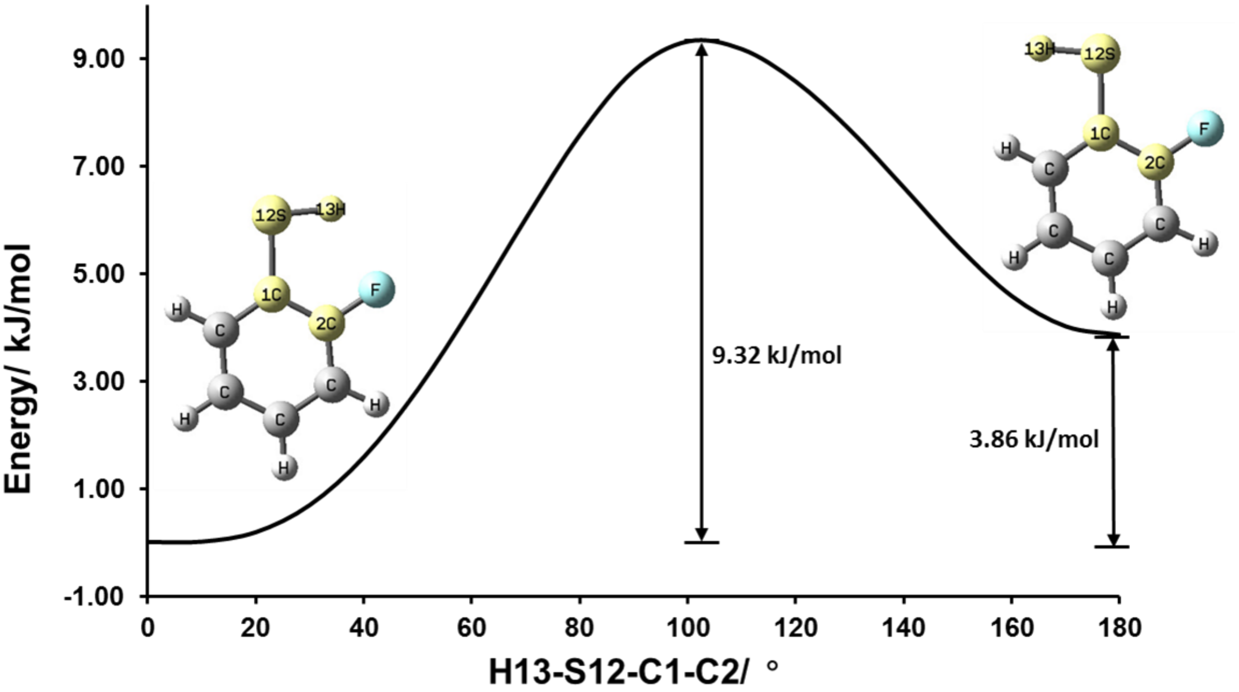
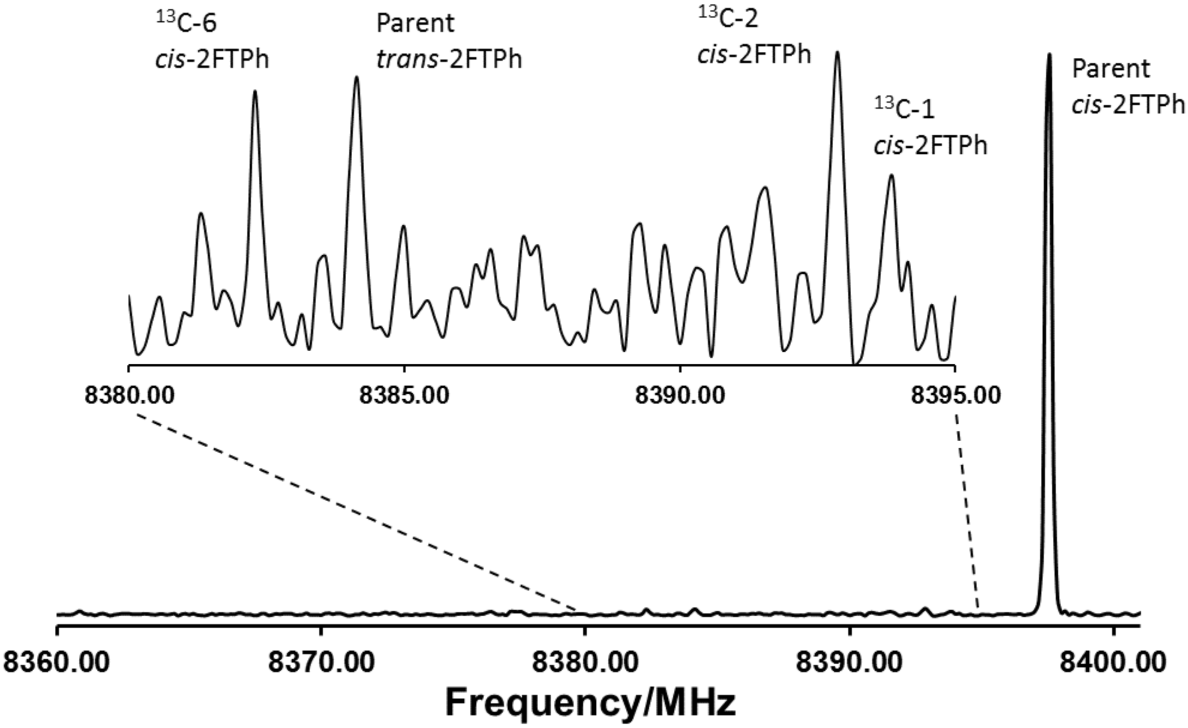


Figure 3: Sun and van Wijngaarden



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