

Conformations of β -Fluorophenetole and Their Reactivities Studied by Supersonic Jet/REMPI Spectroscopy

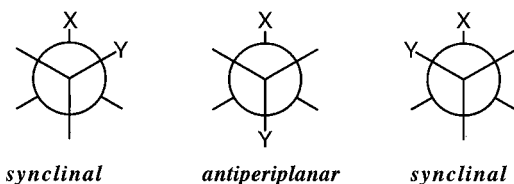
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The structure and spectroscopy of β -fluorophenetole (2-phenoxy-1-fluoroethane, FCH₂CH₂OPh) have been studied by X-ray crystallography and Raman scattering of the solid and by resonance-enhanced multiphoton ionization (REMPI) excitation spectra of a supersonic-jet-cooled gaseous sample, as well as by ab initio calculations. Fluorine and oxygen are synclinal (with an FCCO torsion angle near 70°) in the dominant conformational isomer for both the crystalline and gas phases. The minor conformer observed in the gas phase has antiperiplanar substituents (FCCO torsion angle = 180°), with a relative abundance comparable to that previously inferred from NMR measurements in solution. Hartree–Fock-based computations, as well as second-order Møller–Plesset and density functional geometry optimizations, predict the structural features closely, and the computed (unscaled) normal modes ≤ 350 cm⁻¹ have frequencies not far from those measured by vibrational spectroscopy. CI singles calculations give reasonable estimates of the isomeric differences in the UV absorptions and fit the observed overtones well, though they err in predicting the absolute wavelengths. Ab initio calculations of the electronic ground states do not give a useful ordering of the relative energies of the conformational isomers, for they predict high stability for a highly nonplanar structure for which no experimental evidence is seen. Atoms-in-molecules analysis of theoretical electron densities correlates the preferences for synclinal versus antiperiplanar geometries (in 1-phenoxypropane as well as β -fluorophenetole) with double bowing of the bond paths between two methylene carbons, which (in-planar conformations with C_s symmetry) cut across the lines of centers. Time-of-flight mass spectrometry of isotopically substituted analogues ionized by REMPI shows that deuterium substitution does not decelerate the rate of decomposition of radical cations nor do different conformers manifest any differences in their fragmentation patterns.

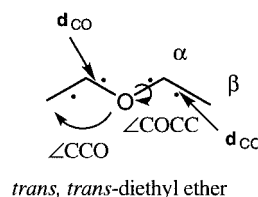
Chemists conventionally describe the three-dimensional structure of saturated chains in terms of the stable conformations of each pair of singly bonded, tetrahedral atoms. When two adjacent atoms have unique substituents (represented as X and Y in the Newman projections below), there are three regions of



stability for the torsional angle between the bond to X and the bond to Y.¹ The terminology for these regions of stability specifies domains of $\pm 30^\circ$. Two of the stable conformations represent nonsuperimposable mirror images, in which the substituents X and Y are synclinal (torsional angle near $+60^\circ$ or -60°), as depicted. In the third conformation, designated as antiperiplanar, the two substituents are separated by a dihedral angle of approximately 180° .

This description pertains if the chain contains at least four atoms other than hydrogen. When X and Y correspond to saturated carbon centers, thermodynamics favors the antiperiplanar geometry. Consider the example of diethyl ether, a molecule that prefers to have C_{2v} symmetry. The carbons directly attached to oxygen are often said to be in the α -position and the adjacent

carbons in the β -positions. The most stable structure (sometimes called the *trans,trans*) has only antiperiplanar orientations,



despite the fact that entropy favors synclinal geometries that have no symmetry (by a factor of 2 from mixing two mirror images and by a factor of 2 from the symmetry number for overall rotation of the *trans,trans*).

An atoms-in-molecules analysis of theoretical electron densities indicates that the extrema between nuclei do not lie on the lines of centers. Instead, the bonds bow slightly, with saddle points in the electron densities (referred to as bond critical points)² indicated schematically by the heavy dots superimposed on the structure of *trans,trans*-diethyl ether. The two equivalent carbon–oxygen bonds bow toward one another, and the two equivalent carbon–carbon bonds bow toward the central oxygen. The distances of the bond critical points from the lines of centers (represented as d_{CO} and d_{CC}) are typically = 0.02 Å, with the latter being much smaller than the former.

Figure 1 portrays a less stable conformation of diethyl ether viewed down one of the C–O bonds (with the oxygen in back and its lone pairs protruding). A CH₃ group and a CH₂ group

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sponding alcohol with DAST in CH_2Cl_2 , washing the crude reaction mixture with 10% aqueous KOH, removal of solvent under reduced pressure, and sublimation under vacuum to yield white crystals, mp 39–41 °C. GC/MS (70 eV): m/z (relative intensity) 142 (27), 109 (13), 96 (8), 95 (100), 81 (7), 77 (27), 67 (29), 65 (14), 63 (8), 51 (30), 49 (8).

Crystal data for undeuterated β -fluorophenetole were collected at 158 K: orthorhombic, space group $Pbca$, $a = 6.6799(9)$ Å, $b = 12.256(3)$ Å, $c = 17.611(4)$ Å, $V = 1441.8(5)$ Å³, $Z = 8$, $D_{\text{calcd}} = 1.291$ mg/m³, $\mu = 0.101$ mm⁻¹, GOF (on F) = 1.47, Mo K_{α} radiation, 1137 reflections (888 independent; 848 with $F > 2\sigma$). The structure was solved by the direct method (hydrogens located from a difference Fourier synthesis and included with isotropic thermal parameters) and refined by using the UCI-modified UCLA Crystallographic Computing Package and the SHELXTL PLUS program set. The final $R_w(F)$ was 0.036 with conventional $R(F) = 0.031$ for 128 parameters.

For jet/REMPI experiments, a molecular beam from a free expansion of gaseous β -fluorophenetole seeded into helium was intersected at right angles by the focused beam of the excitation laser in an apparatus that has been previously described.^{7,11} UV absorptions were monitored by the resonance-enhanced formation of ions observed by means of a time-of-flight (TOF) mass spectrometer. The excitation source was the frequency-doubled output of a dye laser (Spectra Physics Model PDL-2) pumped by a Nd:YAG laser (Spectra Physics Model DCR-3) in which the transverse beam profile is nearly Gaussian. Frequency doubling of dye fundamental lines was performed using a Spectra Physics Model WEX-1 wavelength extender, and UV from the WEX-1 was focused by a 20-cm focal length convex lens into the excitation region in the vacuum chamber. Ion intensity ratios for complete jet/REMPI TOF mass spectra were determined from data blocks that represented averages of 500 mass spectra, each spectrum containing 501 data points over the mass range 50–150. The m/z 94: m/z 95 abundance ratio from $\text{PhOCH}_2\text{CD}_2\text{F}$ was closely examined as a function of photon energy at three laser wavelengths, 273.96, 273.34, and 273.07 nm. For these experiments, each mass spectrum consisted of 501 data points over the m/z 93–96 mass range, and 3000 mass spectra were analyzed at each wavelength. The distribution of ion peak intensity ratios was found to be highly skewed, so statistical comparisons were performed as follows. Each of the 501-point mass spectra was least-squares fit as the sum of two Gaussians plus a constant, varying all parameters (amplitude, center position, and standard deviation for each Gaussian, as well as the constant baseline). The mass ratio was then computed as the ratio of the integrated areas of the two best-fit Gaussians, which generated 3000 ratios for each wavelength. These sets of ratios came closer to normal distributions (skewness = 0.88–1.05; kurtosis = 4.8–5.1) than did the distributions of ion peak intensity ratios.

All ab initio calculations were performed with the 6-31G** basis set using the GAUSSIAN94 (Gaussian, Inc.) program system on Cray YMP, C90, and T90 mainframes. Ground-state geometries were optimized using Hartree–Fock-based methods (SCF), while excited-state geometries were optimized using CI singles (CIS).¹³ Normal-mode calculations were performed at these levels and animated using SPARTAN (Wavefunction, Inc.) to display the effects of deuterium substitution. Additional ground-state geometry optimizations were performed using second-order Møller–Plesset (MP2) and density functional (B3LYP) methods. SCF normal-mode calculations give stretching frequencies that are too high but show no systematic deviation for the low-frequency modes discussed below; hence,

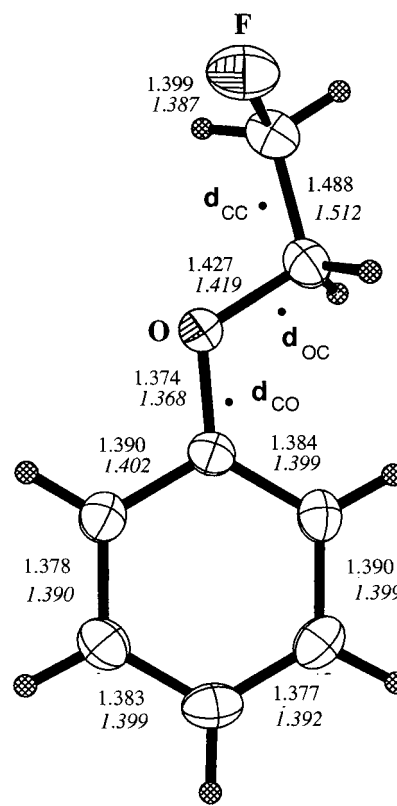


Figure 4. ORTEP drawing of the X-ray structure of β -fluorophenetole with a comparison of experimental with calculated (in italics) bond lengths in Å. Heavy dots symbolize the positions of the bond critical points from theory but with the distances from their respective lines of centers (d_{cc} , d_{oc} , and d_{co}) greatly exaggerated for pictorial purposes.

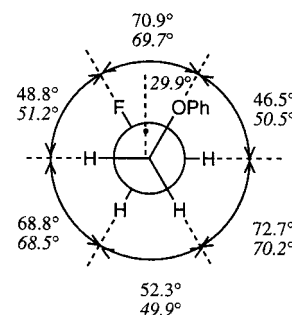


Figure 5. DFT-calculated (in italics) and X-ray dihedral angles for β -fluorophenetole. The position of the bond critical point for the sp^3 – sp^3 carbon–carbon bond is indicated by the heavy dot.

the calculated normal-mode harmonic frequencies reported here have not been scaled. Bond paths and extrema of electron densities were evaluated using the PROAIMS suite of programs (from the AIMPAC program package kindly provided by J. Cheeseman and R. F. W. Bader).

Results

Ab initio calculations predict three low-lying conformations of β -fluorophenetole: one with a completely planar skeleton (the planar) with fluorine antiperiplanar to oxygen and net C_s symmetry, one in which all the carbons in the side chain lie far outside of the plane of the ring (the gauche), and one in which all the carbons and the oxygen are very nearly coplanar but the fluorine is synclinal to the oxygen (the synclinal). X-ray crystallography shows that the solid consists only of the synclinal structure (structural data summarized in Figures 4 and 5 and Table 3). Bond lengths and angles for the FCH_2CH_2 side

TABLE 2: Calculated Electronic and Zero-Point Energies for the Conformational Isomers of β -Fluorophenetole in Its Ground and First Excited Singlet States, Along with 300 K Entropies and a Comparison of ab Initio with Experimental Vertical Electronic Transition Energies

	SCF ^a	MP2 ^a	CIS(S ₁) ^b	B3LYP ^a	exptl ^c
$-E_{el}$, au					
synclinal	482.483 64	483.898 76	482.260 29	485.326 50	
gauche	482.482 80	483.898 95	482.259 13	485.326 51	
planar	482.485 02	483.898 99	482.261 34	485.326 57	
vertical $E_{S_1} - E_{S_0}$, cm ⁻¹					
synclinal			49638 (MP2)		36 502
gauche			49687 (MP2)		not obsd
planar			49707 (MP2)		36 584
ZPE ^d kJ/mol					
synclinal	434.6		421.2		
gauche	434.4		422.1		
planar	434.8		421.3		
300 K vibrational entropy, ^d J/(mol K)					
synclinal	93.3		109.5		
gauche	95.2		105.8		
planar	94.0		110.4		

^a Ground electronic state (S₀). ^b Geometry optimized for the first electronically excited singlet state (S₁). ^c From jet/REMPI excitation spectrum, corresponding to the first excited singlet (S₁). ^d Based on unscaled harmonic frequencies.

TABLE 3: Selected Bond Angles from the X-ray Structure of β -Fluorophenetole and from DFT Geometry Optimizations (B3LYP/6-31G) ^a**

	obsd (X-ray)	calcd (B3LYP/6-31G**)		
		synclinal	gauche	planar
$\angle FCC$	110.1°	110.4°	111.9°	108.1°
$\angle CCO$	108.3°	108.1°	113.6°	106.4°
$\angle COC$	117.7°	118.7°	120.0°	118.6°
$\angle OCC$	124.6°	124.6°	124.3°	124.4°

^a CCO denotes the sp³ C–sp³ C–O bond angle and $\angle OCC$ sp³ C–sp² C–O corresponding to the edge of the ring on the same side as the chain.

chain differ from the corresponding values reported for the *p*-nitrobenzenesulfonate ester of β -fluoroethanol.¹³ Agreement between our crystal structure and the density functional (B3LYP/6-31G**) geometry optimization is much closer. The predicted orientation of the ring about the sp² C–O bond, $\angle CCOC = 2.3^\circ$, is not far from the value seen in the crystal, $\angle CCOC = 4.5^\circ$. The predicted orientation of the chain about the sp³ C–O bond, $\angle COCC = 177.5^\circ$, comes close to the value in the crystal, $\angle COCC = 176.6^\circ$. By using these angles (and rounding to the nearest quadrant), we could designate synclinal β -fluorophenetole as a [0,180] structure. The corresponding angles predicted by DFT for gauche β -fluorophenetole would be $\angle CCOC = -27.3^\circ$ and $\angle COCC = 99.9^\circ$, so it would be designated as a [0,90] structure. However, the gauche is not detected in any of the experiments reported here, so the quality of the theoretical predictions cannot be assessed for that conformer.

Distortions of bond angles provide evidence of steric repulsion within β -fluorophenetole. The angles that include the C–O bond from the ring deviate substantially from 120°. While the CCC bond angles within the ring range from 119.5° to 120.8°, the CCO bond angle opposite the chain is 115.4°, while (as tabulated in Table 3) the angle on the same side as the chain is much larger than 120°. The DFT calculations give excellent agreement with experiment and imply that the CH₂ group bonded to oxygen repels the CH of the ring that is closest to it. Similarly, the torsion angles summarized in Figure 5 exhibit the repulsion of the oxygen and fluorine, with an experimental dihedral angle $\angle FCCO = 71^\circ$ that is more than 1° larger than predicted.

The angles calculated for gauche β -fluorophenetole exhibit even greater distortion, as Table 3 summarizes. The FCC and

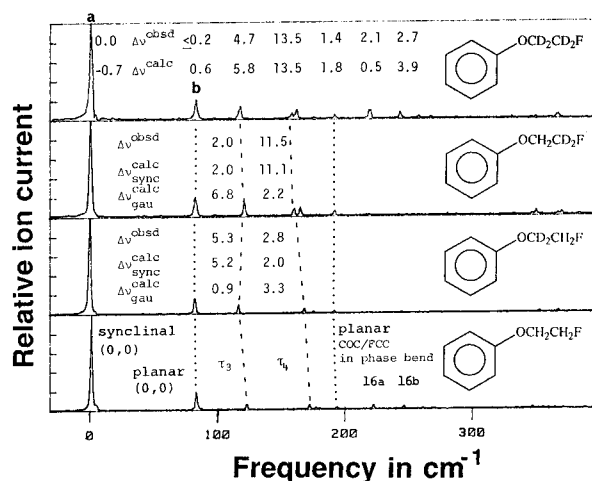


Figure 6. Jet/REMPI excitation spectra of β -fluorophenetole, along with one *d*₄ analogue and two *d*₂ analogues, with the origin bands designated as **a** and **b**. The dotted lines indicate the peaks < 350 cm⁻¹ assigned to the minor (planar) conformer, while the dashed lines indicate the overtones assigned to the τ_3 and τ_4 normal modes of the major (synclinal) conformer. Comparisons of observed and CIS-calculated isotopic shifts made for the *d*₄ analogue (relative to *d*₀) based on our peak assignments are tabulated in the top panel. Comparisons of observed and calculated isotopic shifts (contrasting synclinal and gauche) for the *d*₂ analogues are tabulated in the middle two panels.

COC bond angles open up further, and the CCO bond angle is larger than the tetrahedral value (rather than smaller, as it is in the synclinal). The calculated dihedral angle $\angle FCCO = 77^\circ$ is substantially larger than for the synclinal. Given this evidence for increased steric repulsion, it is surprising that the computed electronic energies at MP2 and B3LYP are lower for the gauche than for the synclinal. The following analysis of the jet/REMPI excitation spectra demonstrates that the experimental preference for synclinal versus gauche pertains to the gas phase as well as to the solid and does not result from crystal packing forces.

REMPI Excitation Spectra and Vibrational Analysis. Figure 6 reproduces the jet/REMPI excitation spectra of β -fluorophenetole and its deuterated analogues. The most intense peak occurs at 273.96 nm, with no features at longer wavelengths. This band is labeled **a** in Figure 6. Six major overtones appear in the domain ≤ 250 cm⁻¹ to the blue of **a**. Assignments of the conformations of β -fluorophenetole are based on a comparison of the observed vibrational progression with cal-

TABLE 4: Comparison of Raman Vibrational Frequencies for Crystalline β -Fluorophenetole between 175 and 750 cm^{-1} with SCF Normal-mode (6-31G) Calculations for the Synclinal and Gauche Conformations**

	obsd	synclinal	gauche
	188	189	192
	251	266	275
	303	314	354
	426	458	439
	472	462	466
	517	511	522
	614	571	573
$\Sigma\nu_i$	2771	2771	2821
ΔRMS	0	15.8	27.1

TABLE 5: Calculated Unscaled Harmonic Vibrational Frequencies for S_0 and S_1 States of Three Conformers of β -Fluorophenetole Compared with Experimental Values for S_1 from the Overtones of the Jet/REMPI Excitation Spectra in Figure 6

		SCF ^a	CIS(S_1) ^b	exptl ^c
synclinal	τ_1	45	46	42 ^d
	τ_2	65	62	57 ^d
	τ_3	136	131	122
	τ_4	189	185	171
	16a	267	207	222
	16b	314	215	246
gauche	τ_1	33	48	not obsd
	τ_2	69	69	not obsd
	τ_3	124	121	not obsd
	τ_4	192	191	not obsd
	16a	275	220	not obsd
	16b	354	248	not obsd
planar	τ_1^e	42	46	not obsd
	τ_2^e	107	91	not obsd
in-phase bend		117	117	110
	τ_3^e	150	145	not obsd
	16a ^e	266	208	not obsd
	16b ^e	320	213	not obsd

^a Ground electronic state (S_0). ^b Geometry optimized for the first electronically excited singlet state (S_1). ^c First excited singlet state (S_1). ^d Not observed for d_0 compound; extrapolated from overtones observed for deuterated analogues. ^e A'' symmetry, Franck–Condon-forbidden transition.

culated CI-singles normal-mode frequencies. Computed zero-point energy differences predict that (0,0) bands should shift by $< 1 \text{ cm}^{-1}$ as one goes from $\text{PhOCH}_2\text{CH}_2\text{F}$ to $\text{PhOCD}_2\text{CD}_2\text{F}$. Band **a** does not shift at all, and only one other peak within 400 cm^{-1} of **a** exhibits a comparably small shift. That peak, labeled **b**, lies 82 cm^{-1} to the blue of **a** and is assigned as the (0,0) band of a minor conformer. Band **b** has an intensity 0.18 that of **a**. Overtone frequencies relative to the corresponding (0,0) bands are listed in Table 5 and are compared with CI singles calculated values.

Ab initio normal-mode frequencies do not give perfect agreement with experiment at currently affordable levels of theory. Ordinarily the predicted total zero-point energy is too high. Here, however, we find that the sums of low-frequency vibrations deviate only slightly from experimental measurement.

This is demonstrated for crystalline $\text{PhOCH}_2\text{CH}_2\text{F}$, where there is no question as to which conformation is present. Table 4 compares 7 of the 10 lowest calculated frequencies for the electronic ground state of synclinal β -fluorophenetole with those measured by Raman spectroscopy on a solid sample (the three lowest frequency bands are obscured by the exciting line and are therefore not included). While individual frequencies differ between experiment and theory, their sums $\Sigma\nu_i$ are equal. In other words, some calculated frequencies are too high, while

others are too low. The net deviation is close to zero, although the average RMS deviation, $\Delta\text{RMS} = [\Sigma(\Delta\nu_i)^2/7]^{1/2}$, corresponds to 4% of the average frequency. Table 4 also compares the predicted frequencies for the gauche isomer with those for the synclinal. The average RMS deviation for the gauche is nearly 7%, and the sum of the seven frequencies is 50 cm^{-1} higher than for the synclinal.

The overtones observed by jet/REMPI represent the vibrations of the first excited singlet state (S_1) and are tabulated in Table 5 and assigned based on CIS¹² calculations. The sum of the first six observed normal-mode frequencies (relative to band **a**) is $\Sigma\nu_i = 860 \text{ cm}^{-1}$ for $\text{PhOCH}_2\text{CH}_2\text{F}$. CIS for S_1 gives $\Sigma\nu_i = 845 \text{ cm}^{-1}$ for the synclinal and $\Sigma\nu_i = 897 \text{ cm}^{-1}$ for the gauche conformers. That result by itself does not lead to an unambiguous distinction between the two candidates for the major conformer. Moreover, two other bands appear $\leq 250 \text{ cm}^{-1}$ from **a** in $\text{PhOCH}_2\text{CH}_2\text{F}$, at 176 and 192 cm^{-1} . We assign the latter to the in-plane, in-phase COC/FCC bend of the planar conformer, the only vibrational overtone below 350 cm^{-1} that is not Franck–Condon forbidden by the C_s symmetry of that conformation and its excited state. On this basis, peak **b** is ascribed to the (0,0) band of the planar, with an in-plane bending frequency of 110 cm^{-1} .

The four lowest normal modes of the nonplanar conformers have such large torsional components that they are identified as torsions τ_1 – τ_4 . Deuterium labeling clarifies the assignments of the overtones $< 200 \text{ cm}^{-1}$ for the major conformer. In particular, the torsion/bending modes τ_3 and τ_4 exhibit the shift predicted for the synclinal structure in passing from the d_0 compound to the two d_2 analogues. The agreement between the calculated and observed shifts allows us to assign band **a** and its associated overtones to the synclinal conformer. The predicted shifts of these two normal modes differ markedly for the gauche conformer, as tabulated in the middle pair of spectra reproduced in Figure 6. The agreement between the calculated and observed shifts for the d_4 analogues is summarized for the top spectrum. Overtones corresponding to the two lowest normal modes (τ_1 and τ_2) are too weak to detect in the d_0 compound but are observed in the deuterated analogues (though their intensities are too low for them to be seen in Figure 6). Thus, all six of the lowest normal modes (including the out-of-plane deformations of the ring, which correspond to modes **16a** and **16b** in benzene¹⁵) for synclinal β -fluorophenetole contribute overtones to the jet/REMPI spectra.

The only bands in the jet/REMPI of $\text{PhOCH}_2\text{CH}_2\text{F}$ $< 300 \text{ cm}^{-1}$ that cannot be assigned based on harmonic vibrational calculations are the 176-cm^{-1} overtone of **a** and the small, poorly resolved shoulder approximately 4 – 4.5 cm^{-1} to the blue of **a**. The former band exhibits a large isotopic shift (greater than the sum of the shifts for τ_1 and τ_3 individually), which rules out its being the (0,0) band of a third conformer. The observed isotopic shifts are also not consistent with assigning it as an overtone of the gauche conformer for which the shoulder of **a** represents the (0,0) band. It could conceivably be a $\tau_1 + \tau_3$ combination band from **a**, although the isotope effect is greater than that of either of the individual fundamentals. The intensity of this band increases markedly in going from the d_0 to the d_4 compound, which is consistent with its arising from absorption by a vibrationally excited ground state. We note that the geometry of the excited state is closer to planarity than the ground state: $\angle\text{COCC}$ gets larger and $\angle\text{CCOC}$ gets smaller, which corresponds to the motion of the τ_1 vibration. Therefore, Franck–Condon overlap for the τ_1 -excited ground-state molecule (which ought to be present in the jet at nonnegligible

TABLE 6. Percent of Total Ionization (% Σ) for Ions from 273.96-nm REMPI on a Mixture of β -Fluorophenetole- d_0 and - d_4 (Sample Standard Deviations Given in Parentheses)

ion mass	m/z 94	m/z 95	m/z 140	m/z 144	m/z 107	m/z 109
% Σ (SD)	5.2(0.6)	4.6(0.5)	48.8(1.2)	39.3(1.6)	1.1(0.4)	1.1(0.2)
mean ratio	1.14		1.25		0.97	
k_H/k_D (SD)	0.91(0.11)		0.78(0.19)			

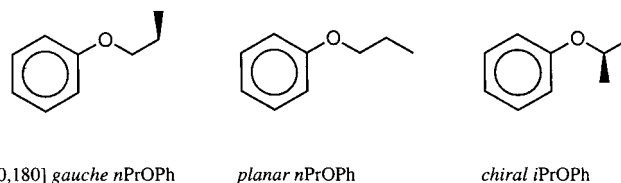
concentrations) should be no less favorable. Contributions from this hot band could account for the small shoulder 4–4.5 cm^{-1} to the blue of band **a**, whose position agrees qualitatively with the calculation that τ_1 has a higher frequency in the electronically excited state than in the ground electronic state and whose intensity relative to **a** accords with the Boltzmann factor expected for the $\nu = 1$ level of a 45- cm^{-1} vibration at 25 K. Strong anharmonic coupling between τ_1 and τ_4 might explain why the overtone from the latter in the hot band is comparatively large and why its intensity varies with isotopic substitution, but confirmation of the assignment of the 176- cm^{-1} peak to a hot band will require additional studies, which vary the temperature of the jet.

CIS calculations do not reliably predict the energies of electronic absorptions, but the ab initio difference between the vertical transition energies of the planar and synclinal conformations, 69 cm^{-1} (using MP2-optimized ground-state geometries), is not far from the 82- cm^{-1} difference between **b** and **a**. The gauche conformer, were it present, should have had a (0,0) band predicted between **a** and **b**, in a region where no peaks appear above the noise level in the jet/REMPI of $\text{PhOCH}_2\text{CH}_2\text{F}$.

REMPI TOF Mass Spectra. Time-of-flight mass spectra from single-wavelength REMPI were examined in order to probe ion decomposition processes. At low laser powers (<0.01 mJ per 8-ns pulse), only molecular ions are seen from β -fluorophenetole. At higher intensities, phenol $^+$ is observed, as well as a fragment corresponding to the loss of fluoromethyl radical. For the d_0 compound, the molecular ion occurs at m/z 140 and the fragment ions at m/z 94 and 107. For $\text{FCD}_2\text{CD}_2\text{OPh}$, the molecular ion occurs at m/z 144 and the fragment ions at m/z 95 and 109. For $\text{FCD}_2\text{CH}_2\text{OPh}$, the molecular ion occurs at m/z 142 and fragment ions at m/z 94, 95, and 107. The formation of both PhOH^+ and PhOD^+ from the d_2 precursors has been shown to result from the competition of three different mechanisms for expulsion of neutral fluoroethylene.

REMPI of a mixture of d_0 and d_4 compounds permits a measurement of the net kinetic isotope effect on molecular ion decomposition, which cannot be determined from intramolecular competition experiments owing to the complexity of the decomposition pathway. A 5:4 mixture of $\text{FCH}_2\text{CH}_2\text{OPh}$ and $\text{FCD}_2\text{CD}_2\text{OPh}$ in the supersonic jet was ionized using 0.01–0.02-mJ 273.96-nm laser pulses and the proportions of parent and fragment ions measured in four independent trials. Table 6 summarizes the data and converts the ion intensity ratios to the average isotope effects $k_H/k_D = (m/z\ 94:m/z\ 95)/(m/z\ 140:m/z\ 144)$ for expulsion of fluoroethylene and $(m/z\ 107:m/z\ 109)/(m/z\ 140:m/z\ 144)$ for expulsion of fluoromethyl radical.

The competition between the formation of PhOH^+ and PhOD^+ was found to be independent of wavelength. REMPI-TOF mass spectra were recorded for $\text{FCD}_2\text{CH}_2\text{OPh}$ using laser frequencies corresponding to band **a**, band **b**, and the τ_3 overtone of **a** (cf. Figure 6). The $m/z\ 94:m/z\ 95$ peak intensity ratios were measured as 1.41, 1.64, and 1.52, respectively, by averaging data blocks. The individual intensity ratios gave broad, non-

**Figure 7.** Lowest energy conformational isomers of phenoxypropanes.

normal distributions, which complicated the statistical analysis. A more robust approach (described above in the Experimental Section) fitted individual spectra using Gaussian functions and gave ratios of peak areas of 1.49 (SD = 0.25), 1.50 (SD = 0.26), and 1.50 (SD = 0.22), respectively. The area ratios did not give normal distributions, and no significant differences were found among them (as measured by skewness or kurtosis).¹⁶

Discussion

Two conformational isomers of β -fluorophenetole are observed in the gas phase by jet/REMPI spectroscopy. Analysis of vibrational overtones demonstrates that the more abundant one corresponds to the synclinal geometry, the same structure as is found by X-ray structural analysis of a crystalline sample. The minor conformer corresponds to the planar isomer, which has C_s symmetry, where the benzene ring lies in the mirror plane. There is no evidence for the gauche structure, even though geometry optimizations at the MP2/6-31G** or B3LYP/6-31G** level predict it to be more stable than the synclinal one.

REMPI spectroscopy in a supersonic jet not only probes the electronic transitions of isolated molecules but it also gives mass spectrometric data for individual conformations. We have used the mass spectra from the REMPI experiments to examine two aspects of the fragmentation of ionized β -fluorophenetole: the kinetic isotope effect on the dissociation of the molecular ion generated from the synclinal conformer and the dependence of the competition between the formation of PhOH^+ and PhOD^+ from $\text{FCD}_2\text{CH}_2\text{OPh}$ upon ionizing wavelength. Assuming the energetics of this fragmentation to be similar to the expulsion of propene from ionized propyl phenyl ether,^{7,18} ionization is a two-photon process, while ion decomposition requires at least three photons in the energy range studied here. The discussion below compares β -fluorophenetole with 1-phenoxypropane with regard to both conformational analysis of the neutral molecule and mass spectrometry of the ion.

The correlation between experiment and theory for the phenoxypropanes can be compared to the present results for β -fluorophenetole. For 1-phenoxypropane ($n\text{PrOPh}$), ab initio calculations predict two low-lying conformers, planar and [0,180] gauche, with nearly the same electronic energy, in addition to four other conformations that lie approximately 6–7 kJ mol^{-1} higher. Three conformers are seen by jet/REMPI, with a ratio of (0,0) band intensities of roughly 15:5:6 (Figure 7). The first two geometries have been assigned to the [0,180] gauche and planar geometries,⁷ which correspond closely to the synclinal and planar conformers of β -fluorophenetole, in which a methyl group replaces the fluorine. Those assignments (based upon isotopic shifts) are confirmed by CIS normal-mode calculations. The third conformation cannot yet be assigned unambiguously. Supersonic jet expansions tend to freeze out the conformational distribution that existed in the gaseous sample prior to expansion.¹⁷ For 1-phenoxypropane, theory would thus have predicted two dominant conformations in the jet: [0,180] gauche roughly twice as abundant as planar (due, for the most part, to the entropy of the former). Observation of a third conformer (but no others) contradicts that expectation.

CIS calculations confirm the assignment of the dominant conformer of 2-phenoxypropane (*i*PrOPh) to the chiral structure and identify the six most intense overtones = 300 cm⁻¹ from the origin (in addition to the higher frequency bands previously assigned¹⁸). Thus, theory and experiment agree well for the purposes of conformational analysis based on low-frequency normal modes and their isotopic shifts. However, the results for phenoxypropanes invite skepticism with regard to the accuracy of the calculated energy differences between conformers. β -Fluorophenetole presents a case where the structure calculated to have the lowest energy is not observed in the gas phase.

The B3LYP electronic energy of planar β -fluorophenetole is 0.18 kJ mol⁻¹ above that of the synclinal. Zero-point energies and vibrational entropies (computed at the SCF level and summarized in Table 2) are nearly the same so that the predicted equilibrium constant would be [synclinal]/[planar] = 2 near room temperature, due principally to the entropy of mixing of the nonsuperimposable mirror images of the nonplanar structure. This does not represent a serious discrepancy from the observed ratio of (0,0) band intensities, 5.5 (which does not differ greatly from the ratio inferred from NMR measurements,⁹ [synclinal]/[planar] = 4). However, calculated electronic and zero point energies favor the *gauche*, as does vibrational entropy. Were the calculated energy correct for the *gauche* its abundance ought to have exceeded that of the synclinal, even though the geometrical distortion of the *gauche* from conventional bond and torsional angles suggest that it has greater intramolecular steric repulsions.

Could *gauche* β -fluorophenetole be present in the supersonic jet but have a (0,0) band that lies outside the domain of Figure 6? Calculated differences in the UV absorption frequencies ($\Delta\nu$) argue against this. CIS-calculated shifts do not differ vastly from experiment, even though the energies of the vertical transitions are greatly in error. The predicted blue shift of planar 1-phenoxypropane with respect to its [0,180] *gauche* conformational isomer is not far from the experimental value ($\Delta\nu^{\text{expt}} = 17$ cm⁻¹; $\Delta\nu^{\text{CIS}} = 2$ cm⁻¹ for SCF-optimized ground-state geometries). The calculated and experimental shifts of chiral 2-phenoxypropane to the red of [0,180] *gauche* 1-phenoxypropane ($\Delta\nu^{\text{expt}} = 120$ cm⁻¹; $\Delta\nu^{\text{CIS}} = 257$ cm⁻¹ for SCF-optimized ground-state geometries) differ by roughly a factor of 2. The predicted shifts of *gauche* β -fluorophenetole to the blue of synclinal ($\Delta\nu^{\text{CIS}} = 282$ cm⁻¹ for SCF-optimized ground-state geometries; $\Delta\nu^{\text{CIS}} = 49$ cm⁻¹ for MP2-optimized ground-state geometries) indicate that the *gauche* conformer, had it been present, ought to have contributed a peak to Figure 6.

Why does theory err with regard to the stability of *gauche* β -fluorophenetole? An atoms-in-molecules analysis of the computed structure reveals a hydrogen bond between the fluorine and the ring hydrogen (represented in Figure 3) that is closest to it. These two atoms are 2.25 Å apart, but the calculation portrays their interaction as being attractive rather than repulsive, since there is a bond critical point (i.e., an extremum in the electron density that has one positive second derivative and two negative second derivatives). The atoms-in-molecules analysis also locates a ring point (i.e., an extremum in the electron density that has one negative second derivative and two positive second derivatives), besides the one within the benzene ring, which corresponds to the seven-membered ring formed by the hypothetical fluorine–hydrogen attraction. The calculated CH \cdots FC interaction (which appears at all levels of calculation investigated) contradicts the well-documented reluctance of carbon-bound fluorine to act as a hydrogen-bond

acceptor.¹⁹ Therefore, the conflict between experiment and this level of theory must be attributed to an artifact of the latter, which predicts a fictitious long-range attraction.

With this caveat in mind, consider the atoms-in-molecules analysis of synclinal versus planar β -fluorophenetole. Virtually the same results are obtained regardless of whether optimization was performed at SCF, MP2, or B3LYP. The following distances come from B3LYP calculations. The CH₂–CH₂ bond in the synclinal is bowed toward oxygen (just as is the synclinal CH₃–CH₂ bond in *trans,gauche*-diethyl ether in Figure 1) such that the bond path between the two singly bonded carbons is $\Delta r = 0.00043$ Å longer than the geometric distance between the bonded atoms. The bond critical point lies $d_{\text{CC}} = 0.0080$ Å away from the line of centers (cf. Figure 4). This is smaller than d_{CO} or d_{OC} , which have values in the same range as d_{CO} for diethyl ether in Table 1. For planar β -fluorophenetole, the bond critical point lies closer to the line of centers ($d_{\text{CC}} = 0.0016$ Å), on the side closer to oxygen (just as drawn for the C–C bonds of *trans,trans*-diethyl ether). The bond path for the planar is only $\Delta r = 0.00021$ Å longer than the geometric distance. Unlike the bond paths in diethyl ether, however, the path for the C–C single bond in the planar is doubly bowed, as represented in Figure 2 (where X = fluorine and Y = phenoxy). Double bowing results from having antiperiplanar substituents.

Qualitatively, bowing does not depend on the electronegativity of the substituents, since 1-phenoxypropane displays similar effects. While the deviations of the CH₂–CH₂ bond paths from geometrical distances are less ($\Delta r = 0.00026$ Å for [0,180] *gauche* and 0.00012 Å for planar 1-phenoxypropane), the distances of the bond critical points from their respective lines of centers are nearly the same as for β -fluorophenetole ($d_{\text{CC}} = 0.0076$ and 0.0016 Å for the [0,180] *gauche* and planar 1-phenoxypropane, respectively). Planar 1-phenoxypropane exhibits double bowing in the same sense as planar β -fluorophenetole, and the orientations of the bond critical points with respect to the oxygen are the same. The placement of substituent X at the β -position of an alkyl phenyl ether (as illustrated in Figure 2, where Y = phenoxy) thus perturbs the bond paths relative to those of an ethyl group. Given the experimental result that the proportion of planar conformers is nearly the same for 1-phenoxypropane and for β -fluorophenetole and a theoretical picture that shows only small differences between them, it seems reasonable to conclude that the energetic cost of double bowing is independent of whether substituent X is a fluorine or a methyl group.

Now consider the outcome of the REMPI TOF mass spectrometric studies. The results for β -fluorophenetole contrast with those reported for 1-phenoxypropane. First, ionized phenol is the only fragmentation product seen from phenoxypropanes in the range of laser powers corresponding to those used here. In the case of β -fluorophenetole, we could not reproducibly observe the formation of phenol⁺ without competition from loss of fluoromethyl radical (roughly 20% of phenol⁺). Second, whereas the PhOH⁺:PhOD⁺ ratio from CD₃CH₂CD₂OPh exhibits a significant variation (ANOVA: $F = 14.00$, $df = 37$) depending on which of the three most prevalent conformers is ionized, no conformational dependence is detected in FCD₂-CH₂OPh. Finally, if the isotope effect from intramolecular competition in 1-phenoxypropane (normal isotope effects $k_{\text{H}}/k_{\text{D}} = 1.24$ – 1.33 , depending on which (0,0) band the laser irradiates) is compared with the intermolecular deuterium isotope effect measured here, kinetic isotope effects are smaller for the dissociation of β -fluorophenetole: an inverse effect of deuterium on the formation of phenol⁺ as well as an inverse secondary

effect on fluoromethyl loss (though neither of these differs significantly from $k_H/k_D = 1$). Since the slight enhancement of decomposition for the d_4 analogue might result from an increase in the cross section for absorption of a third photon, the intermolecular competition experiment implies only that there is no evidence for a large normal isotope effect that decelerates decomposition (unless it happens to be fortuitously canceled by an equal and opposite increase in absorption cross section).

Ionized β -fluorophenetole dissociates to ionized phenol via three competing mechanisms: β -elimination (which transfers only deuterium to yield $\text{PhOD}^{+\bullet}$ from ionized $\text{FCD}_2\text{CH}_2\text{OPh}$), bridging to form ion-neutral complexes containing bridged fluoronium ions (which transfer α - and β -hydrogens with equal probability), and hydride shift to form ion-neutral complexes containing fluoroethyl cations (which transfer α - and β -hydrogens in a 1:2 ratio). Photoionization studies have shown that similar types of competing pathways operate in the decomposition of ionized 1-phenoxypropane.²⁰ Hence, one might have expected an analogous conformational dependence of fragmentation ratios. But we can see no conformational effect for β -fluorophenetole. However, the observed fragment ion ratios from REMPI on jet-cooled $\text{FCD}_2\text{CH}_2\text{OPh}$, $\text{PhOH}^{+\bullet}:\text{PhOD}^{+\bullet}=1.5$, have such large standard deviations that they turn out to be within experimental error of the value reported from 70-eV electron impact on heated samples, 1.33. The present experiments required comparatively low laser intensities in order to minimize the competition from other dissociation pathways (e.g., formation of free fluoroethyl cations, which appear at higher powers). The large errors in measuring relative abundances of ions produced by < 0.02 -mJ laser pulses may limit our ability to monitor the subtle consequences of the conformation of the precursor neutrals.

Photoionization (both single photon and multiphoton) displays aspects of the ground states, electronically excited states, and radical cations of the phenyl ethers. These compounds absorb UV in a domain convenient for laser spectroscopy, which (with the help of deuterium substitution) reveals the variety of structures accessible as a consequence of single-bond torsions. The lowest frequency vibrations of the first excited singlet become visible in the overtones of the excitation spectra, fundamentals that are usually difficult to observe directly in the ground electronic state. These normal modes are reasonably well predicted by ab initio calculations, as are structural features of the ground state. An atoms-in-molecules analysis of computed electronic structures accounts for the relative stability of synclinal conformations even though their through-space steric repulsion exceeds that of their antiperiplanar isomers. Calculated energetic orderings of conformational isomers do not yet agree as well with experiment, and atoms-in-molecules analysis helps interpret the limitations of the theoretical results. Photoionization mass spectra of deuterated analogues confirm the occurrence of multiple decomposition pathways for ions possessing enough internal energy to dissociate. The relationship between structure and reactivity of this class of compounds remains a subject of an ongoing inquiry.

Conclusions

(1) β -Fluorophenetole is the smallest known molecule containing a monofluoroethoxy group that remains solid at room temperature without any hydrogen bonding. Its crystal structure accords with the structure predicted by ab initio calculations.

(2) The dominant conformer in the gas phase, the synclinal, has the same structure as in the crystal, despite theoretical calculations that place the energy of another structure (the

gauche) lower than that of the synclinal. The only other conformational isomer detected has the planar structure, with oxygen and fluorine antiperiplanar to one another.

(3) Double bowing of the bond paths calculated for planar alkyl phenyl ethers, an effect that has been proposed to destabilize antiperiplanar geometries relative to their synclinal isomers, occurs to a nearly equal extent when the phenoxy is antiperiplanar to a methyl as when phenoxy is antiperiplanar to fluorine.

(4) Ab initio normal-mode calculations (unscaled) at the SCF and CIS levels display no systematic bias toward overestimating or underestimating the low-frequency vibrations (which make the major contributions the entropy differences among isomers) and predict isotopic shifts that accord well with experiment.

(5) REMPI time-of-flight mass spectra reveal no significant deceleration of the rate of decomposition of ionized deuterated β -fluorophenetole.

(6) The synclinal conformation of $\text{FCD}_2\text{CH}_2\text{OPh}$ exhibits a mass spectrum from multiphoton ionization at its origin band that is indistinguishable from the mass spectrum produced by REMPI at its τ_3 overtone or by REMPI of its planar isomer.

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Supporting Information Available: X-ray crystallographic data (11 pages). Ordering information is given on any current masthead page.

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