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Structure and Conformation of 4-Fluoro(trifluoromethoxy)benzene: Gas Electron Diffraction and Quantum Chemical Calculations

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The geometric structure and conformational properties of 4-fluoro(trifluoromethoxy)benzene, 4-F-$C_6H_4OCF_3$, were investigated independently in two laboratories (Moscow State University and Universität Tübingen) using gas electron diffraction (GED), quantum chemical calculations, and matrix infrared spectroscopy. Both experimental GED studies result in a perpendicular conformation (C−O−C plane perpendicular to the benzene ring). Analyses of the GED intensities with a simple two-conformer model cannot exclude a small contribution of up to 25% (Moscow) or 13% (Tübingen) of a planar conformer. Quantum chemical calculations lead to rather different potenial functions for internal rotation around the C(sp^2)−O bond. HF, MP2, and B3LYP methods with 6-31G* basis sets predict potential functions with a single minimum for perpendicular orientation. The planar structure is predicted to correspond to a transition state, 0.6−1.8 kcal/mol higher in energy. B3LYP/cc-pVTZ calculations predict an additional very shallow minimum for the planar conformer, about 0.6 kcal/mol higher than that for the perpendicular structure. Infrared spectra demonstrate the presence of a single conformer in a Ne matrix at 15 K and no second conformer is expected to be present in the gas phase, assuming an adiabatic cooling process.

Introduction

According to gas electron diffraction (GED),[1] microwave spectroscopy (MW),[2] and high-level ab initio calculations,[3] anisole, $C_6H_5OCH_3$, exists in the gas phase as a single conformer with a planar heavy atom skeleton and a torsion angle around the C(sp^2)−O bond of $\varphi(C-O) = 0°$. Earlier photoelectron spectra[4] and dynamic NMR measurements,[5] however, were interpreted in terms of a mixture of planar and perpendicular conformers. Ab initio calculations in the HF approximation also predict a potential function for internal rotation around the C−O bond with minima at $\varphi(C-O) = 0°$ and 90°.[5−7] Recently, a conformational study of α,α,α-trifluoroanisole (trifluoromethoxybenzene), $C_6H_5OCF_3$ (**1**), was performed independently in two laboratories. Both GED analyses resulted in a main conformer with perpendicular orientation of the CF_3 group $\varphi(C-O) = 90°$ and a small contribution of 30(21)%,[8] and 12(8)%,[9] respectively, of a planar form. Unfortunately, electron diffraction intensities depend very little on the orientation of the CF_3 group and, thus, GED does not prove unambiguously the existence of a mixture of two conformers. IR spectra of gaseous, liquid, and crystalline $C_6H_5OCF_3$ were interpreted in terms of a mixture,[8] whereas MW and IR (matrix) spectroscopy lead to the conclusion that only the perpendicular conformer corresponds to a stable structure.[9] The results of quantum chemical calculations depend on the computational method. Whereas HF and MP2 approximations with 6-31G* basis sets predict the presence of a single perpendicular conformer,[8] the B3LYP method[9] and MP2 approximation with cc-pVTZ basis sets[10] predict the existence of a mixture, with the perpendicular form prevailing. Recent quantum chemical calculations with the B3LYP method and large basis sets (pc2 and 6-311G++(3df,2dp)) resulted in a potential function with its global minimum at $\varphi(C-O) = 90°$ and a very flat plateau in the region $-50° < \varphi(C-O) < +50°$ with a very shallow minimum at $\varphi(C-O) = 0°$.[11]

CHART 1

planar orthogonal

To obtain additional information about the effect of CH_3/CF_3 substitution on the conformation of anisole, we decided to perform two independent studies for 4-fluoro(trifluoromethoxy)benzene, 4-F-$C_6H_4OCF_3$ (**2**). It is expected that fluorine substitution in para position has only a minor effect on the conformational properties and that GED intensities are more characteristic for the orientation of the CF_3 group due to additional interatomic distances between the *p*-fluorine atom and the CF_3 group. From ^1H and ^{19}F NMR spectra of this compound in a nematic solvent, a potential function for internal rotation around the C−O bond with a minimum at $\varphi(C-O) = 90°$ (perpendicular conformer) was derived.[12] The data, however, cannot differentiate between a potential function with a single minimum at $\varphi(C-O) = 90°$ and one with two minima at $\varphi(C-O) = 90°$ and 0°, i.e., between a single perpendicular conformer and a mixture of both forms. On the other hand, long-range NMR coupling constants are interpreted in terms of a planar or nearly planar structure, with the barrier to internal rotation lower than that in anisole.[13] This interpretation is in agreement with low-level ab initio calculations (HF/STO-3G and HF/3-21G).[13]

Quantum Chemical Calculations

The geometry of **2** was optimized for different fixed torsion angles $\varphi(C-O)$ between 0° and 90°. HF, MP2, and B3LYP

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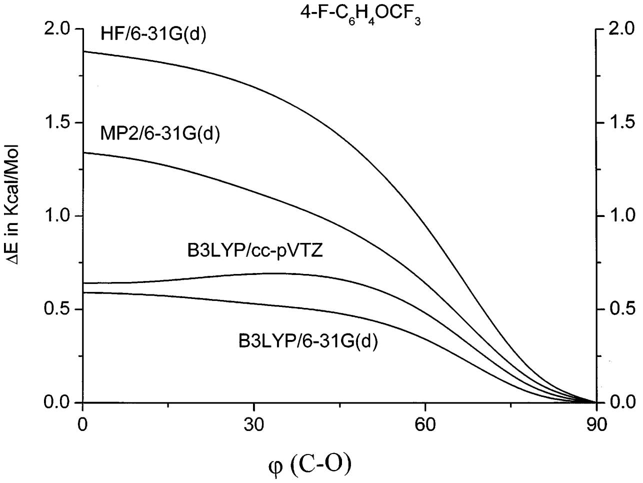

Figure 1. Calculated potential functions for internal rotation around the $C(sp^2)-O$ bond.

calculations with 6-31* basis sets and additional B3LYP/cc-pVTZ calculations were performed. The calculated potential functions for internal rotation about the C−O bond depend on the computational method and on basis sets (see Figure 1). All methods with 6-31* basis sets result in a single minimum corresponding to perpendicular orientation. Calculated geometric parameters are very similar. The B3LYP method with cc-pVTZ basis sets, however, results in a second very flat minimum for the planar structure, about 0.6 kcal/mol higher in energy. Very recent calculations with the B3LYP method and with basis sets that have been developed especially for DFT methods [pc1, pc2, and 6-311++G(3df,2pd)] predict a potential curve that is extremely flat in the region $-50° < \varphi(C-O) < +50°$ and possesses a very shallow minimum at the planar orientation.[11] This minimum is only 0.07 kcal/mol deep and about 0.5 kcal/mol above the global minimum for the perpendicular conformer. If the energies are corrected by the zero point vibrational energy (ZPE), the minimum at the planar structure disappears in the potential function obtained with the B3LYP/cc-pVTZ method and is only 0.01 kcal/mol deep in the potential obtained with the B3LYP/6-311++G(3df,2pd) method.

Structural parameters for the perpendicular conformer derived with the B3LYP/cc-pVTZ and MP2/6-31G* methods are included in Table 1. Vibration frequencies were calculated for the perpendicular form with MP2/6-31G* approximation and for perpendicular and planar conformers with the B3LYP/cc-pVTZ method. All quantum chemical calculations were performed with the GAUSSIAN98 program package.[14] Vibrational amplitudes and vibrational corrections for interatomic distances were derived from the calculated force fields using the method of Sipachev and the program SHRINK.[15] This method takes the nonlinear relation between Cartesian and internal coordinates into account and corrects r_a distances to r_{h1} values.

TABLE 1: Experimental and Calculated Geometric Parameters[a] of Perpendicular Conformer

	GED Moscow	B3LYP/ cc-pvtz	GED Tübingen		MP2/ 6-31G*
$(C-C)_{av}$	1.386(3)	1.386	1.389(3)	p1	1.393
C1−C2	1.386(3)	1.386	1.388(3)	p1	1.392
C2−C3	1.388(3)	1.388	1.391(3)	p1	1.395
C3−C4	1.384(3)	1.384	1.387(3)	p1	1.391
C1−O	1.416(28)	1.406	1.405(14)	p2	1.409
O−C7	1.362(28)	1.352	1.354(14)	p2	1.358
C7−F1	1.333(18)	1.329	1.321(5)	p3	1.334
C7−F2	1.350(18)	1.346	1.336(5)	p3	1.349
C4−F4	1.354[d]	1.347	1.343(5)	p3	1.356
$(C-H)_{av}$	1.115(21)	1.085	1.077(15)	p4	1.085
C−C1−C	122.8(15)	121.7	120.8(17)	p5	122.2
C−C4−C	121.2(16)	122.2	123.3(14)	p6	122.5
C−O−C	114.8(15)	117.1	117.2(14)	p7	114.8
F−C−F	106.7(9)	106.8	107.5(6)	p8	108.1
tilt (CF_3)[b]	3.2[d]	3.2	3.1[d]	3.1[d]	3.1
oop (C1−O)[c]	3.5[d]	3.5	3.2[d]	3.2[d]	3.2
ϕ(C−O)	90.0[e]	90.0	90.0[e]	90.0[d]	90.0

[a] r_g distances in Å, r_{h1} angles in degree; uncertainties are 3σ values; for atom numbering see Figure 3. r_e is the equilibrium parameter. [b] Tilt angle of CF_3 group, away from the C1−O bond. [c] Out-of-plane angle of the C1−O bond. The direction is such that the C1···C7 distance increases. [d] Not refined.

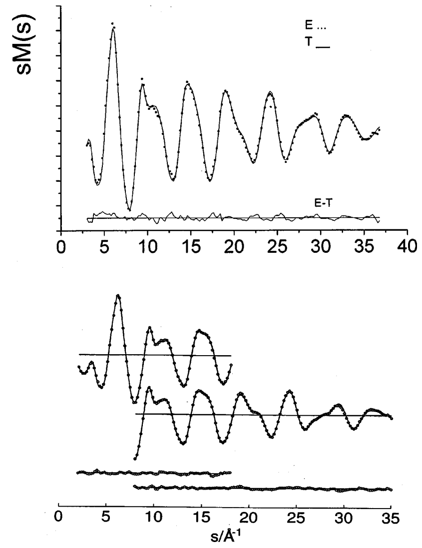

Figure 2. Experimental (dots) and calculated (full line) molecular intensities and residuals of Moscow (above) and Tübingen (below) analysis (upper curves are for long and lower curves for short nozzle-to-plate distance).

Experimental Section

A commercial sample of **2** (Aldrich, 99%) was used. Electron diffraction patterns were recorded at nozzle-to-plate distances of 169.8 and 375.3 mm on Kodak Electron Image films with the Moscow State University apparatus. This apparatus was reconstructed in 1998 from an ER-100 M commercial unit and equipped with an r^3-sector. The wavelength of the incident electrons (nominal accelerating voltage of 50 kV) was determined from diffraction photographs of benzene that were obtained in the same experiment as those for **2.** The data were processed with standard procedures.[16] The experiment yielded leveled intensities in the following s-ranges for short and long nozzle-to-plate distance, respectively: $11.4 \leq s \leq 36.8$ Å^{-1} and $3.0 \leq s \leq 18.4$ Å^{-1}, in intervals of $\Delta s = 0.2$ Å^{-1} ($s = (4\pi/\lambda)\sin\theta/2$, where λ is the electron wavelength and θ is the scattering angle). The resulting sM(s) curve is shown in Figure 2.

Electron diffraction intensities were also recorded at the University of Tübingen with a Gasdiffraktograph KD-G2 [17] at 250 and 500 mm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was cooled to 3 °C and the inlet system and nozzle were at room temperature. The Kodak Electron Image plates (18 × 13 cm) were analyzed with an Agfa Duoscan HiD scanner and total scattering intensity curves were obtained from the TIFF files using the program SCAN3.[18] Experimental molecular intensities were derived in the s-ranges 2−18 and 8−35 Å^{-1} for the long and short camera distances, respectively, in steps of $\Delta s = 0.2$ Å^{-1} and are shown in Figure 2.

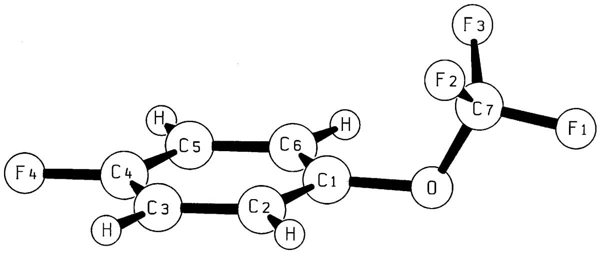

Figure 3. Molecular model for perpendicular conformer with atom numbering.

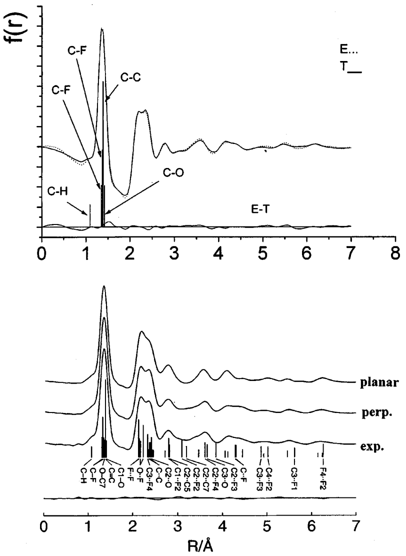

Figure 4. Experimental and calculated radial distribution functions and difference curve of Moscow analysis (above) and Tübingen analysis (below). Negative values occur in the curve of the Moscow analysis, since molecular intensities for $s < s_{\min}$ were set to zero in the Fourier transformation. In the Tübingen analysis, calculated intensities were used for this *s*-region.

Structure Analysis

The experimental GED intensities were analyzed independently in Moscow and in Tübingen. Both analyses were based on geometrically consistent r_{h1} structures. The structure of **2** can be described by five independent bond distances, $r(\text{C}-\text{H})_{\text{av}}$, $r(\text{C}-\text{C})_{\text{av}}$, $r(\text{C}-\text{O})_{\text{av}}$, $r(\text{C}-\text{F})_{\text{av}}$ in the CF_3 group, and $r(\text{C}-\text{F4})$ and by the angles ∠CC1C, ∠CC4C, ∠COC, and ∠FCF, and tilt(CF_3). An additional out of plane angle of O−C1 bond from the plane of the benzene ring was used for the perpendicular conformer and the C2−C1−O angle for the planar form. The torsional angle $\varphi(\text{C}-\text{O})$ around the C1−O bond was set to 90° (perpendicular) or 0° (planar). C_S symmetry was assumed for both conformers. Atom numbering is shown in Figure 3.

In the Moscow analysis the differences between the $r(\text{C}-\text{C})$ bonds, the $r(\text{O}-\text{C})$ and the $r(\text{C}-\text{F})$ bonds in the CF_3 were fixed to the respective values derived from the B3LYP/cc-pVTZ calculation. The C−F4 bond distance was assumed to be equal to that in C_6H_5F.[19] This bond length could not be refined, because the value of $r(\text{C}-\text{F4})$ is close to the mean value of the bonds in the CF_3 group and refinement caused large correlations. The hydrogen atoms were assumed to lie on the bisector of the ∠CCC angles and in the plane of the benzene ring. The CF_3 group was fixed to staggered orientation.

The radial distribution function (RDF) was obtained by Fourier transformation of the molecular intensities (Figure 4). Since nonbonded interatomic distances between the CF_3 group and ring atoms possess large vibrational amplitudes due to a low-frequency torsional vibration around the C1−O bond, no distinct peaks that are characteristic for a perpendicular or planar structure appear in the region $r > 3$ Å. The B3LYP/cc-pVTZ method predicts torsional frequencies of 29 and 14 cm^{-1} for perpendicular and planar conformer, respectively. This leads to very broad peaks for torsion dependent distances, and as a consequence the RDF is not very sensitive toward the conformational properties of this anisole.

The perpendicular conformer reproduces the RDF better than a planar structure. Least-squares refinements were performed for both conformers and for mixtures. Initial values for independent geometric parameters and vibrational amplitudes were taken from B3LYP/cc-pVTZ calculations. Preliminary refinements of geometric parameters were performed with an iterated step-by-step procedure,[20] in which vibrational amplitudes were fixed to calculated values. The step-by-step approach was chosen to obtain a molecular model that is closer to the final experimental structure than the B3LYP result. In the next step a conventional least-squares procedure of Andersen et al. [21] was used. These refinements demonstrated that the perpendicular conformer reproduces the experimental molecular intensities considerably better (agreement factor $R = 10\%$) than the planar conformer ($R = 20\%$). In the final step the vibrational amplitudes that were collected in 13 groups were included in the refinement. The agreement factors for both conformers decreased to 6% and 9%, respectively. The following correlation coefficients for the perpendicular conformer had absolute values greater than 0.7: $r(\text{C}-\text{C})/r(\text{C}-\text{O}) = -0.73$, $\angle\text{COC}/\angle\text{FCF} = -0.78$ and $r(\text{C}-\text{C})/r(\text{C}-\text{F}) = -0.93$. The results for the perpendicular conformer are listed in Table 1 (geometric parameters) and Table 2 (interatomic distances and vibrational amplitudes).

Furthermore, a step-by-step analysis was performed for mixtures of perpendicular and planar conformers with different compositions. The contribution of each conformer was changed from 0% to 100% in steps of 5%. From the increase of *R* factors and Hamilton's test[22] at the 5% level of significance we conclude that the electron diffraction data of **2** can be described by a mixture of both conformers with the following contributions: 75%−100% for perpendicular and 0%−25% for planar.

The same geometric parameters as described above were used also in the structure analysis performed in Tübingen, with the exception that the C4−F4 bond length was included in $(\text{C}-\text{F})_{\text{av}}$. The constraints for differences between bond lengths and other geometric parameters were taken from the MP2/6-31G* result. Since the MP2 approximation predicts an imaginary frequency for the planar conformer, this force field could not be used to derive vibrational amplitudes and corrections for this structure. Therefore, the Cartesian force field calculated for the perpendicular structure was transformed to an internal force field, which was then used to derive amplitudes and corrections for both structures.

The experimental RDF together with functions calculated for both conformers is shown in Figure 4. The perpendicular structure reproduces the experimental curve better in the region $r > 3$ Å. Least-squares fitting of the molecular intensities was performed for both conformers. Eight geometric parameters and eight vibrational amplitudes collected in four groups for distances that do not depend on the torsion around the C1−O bond were refined simultaneously. The agreement factor for the intensities of the long nozzle-to-plate distance, R_{long}, which is more sensitive toward conformational properties, is 4.3% and 9.1% for perpendicular and planar conformers, respectively. If

TABLE 2: Interatomic Distances (r_a Values) and Experimental and Calculated Vibrational Amplitudes (without nonbonded distances involving hydrogen atoms) from Moscow Analysis[a]

		amplitude		
	distance	GED	B3LYP	code[b]
$(C-H)_{av}$	1.110(21)	0.076	0.076	*
$(C-C)_{av}$	1.384(3)	0.048(4)	0.045	i
C1−O	1.414(28)	0.049(4)	0.045	ii
O−C7	1.360(28)	0.051	0.047	ii
C4−F4	1.354*	0.049	0.045	ii
C7−F1	1.331(18)	0.049	0.045	ii
C7−F2	1.348(18)	0.050	0.046	ii
F1$\cdots$F2	2.137(58)	0.056	0.056	*
F2$\cdots$F3	2.138(120)	0.056	0.056	*
O$\cdots$F1	2.215(27)	0.056	0.056	*
O$\cdots$F2	2.310(10)	0.057	0.057	*
C1$\cdots$C7	2.338(43)	0.064	0.064	*
O$\cdots$C6	2.355(21)	0.064	0.064	*
C1$\cdots$C5	2.368(18)	0.054	0.054	*
C3$\cdots$F4	2.373(3)	0.058	0.058	*
C3$\cdots$C5	2.390(9)	0.054	0.054	*
C2$\cdots$C4	2.410(9)	0.054	0.054	*
C2$\cdots$C6	2.429(18)	0.054	0.054	*
C1$\cdots$C4	2.741(15)	0.059	0.059	*
C2$\cdots$C5	2.778(6)	0.061	0.061	*
C1$\cdots$F2	2.829(33)	0.110(30)	0.139	iii
C1$\cdots$F3	2.831(33)	0.114	0.143	iii
C2$\cdots$F3	3.108(30)	0.163(93)	0.234	iv
C2$\cdots$C7	3.168(37)	0.121(91)	0.114	v
C1$\cdots$F1	3.461(15)	0.093(12)	0.063	vi
O$\cdots$C3	3.604(21)	0.092	0.062	vi
C2$\cdots$F4	3.641(6)	0.089	0.059	vi
C6$\cdots$F3	3.857(43)	0.283	0.283	*
C1$\cdots$F4	4.090(15)	0.072(18)	0.061	vii
O$\cdots$C4	4.096(21)	0.074	0.063	vii
C2$\cdots$F1	4.276(18)	0.102(27)	0.118	viii
C2$\cdots$F3	4.278(36)	0.233	0.249	viii
C3$\cdots$C7	4.396(33)	0.110	0.126	viii
C5$\cdots$F2	4.837(57)	0.288(45)	0.302	ix
C4$\cdots$C7	4.904(36)	0.087	0.103	ix
C3$\cdots$F2	5.022(51)	0.220	0.234	ix
O$\cdots$F4	5.444(21)	0.083(38)	0.065	x
C3$\cdots$F1	5.585(21)	0.108(43)	0.107	xi
C4$\cdots$F1	6.144(20)	0.112(45)	0.085	xii
C7$\cdots$F4	6.222(39)	0.140	0.113	xii
F2$\cdots$F4	6.261(58)	0.286	0.259	xii
F1$\cdots$F4	7.479(21)	0.173(120)	0.092	xiii

[a] For atom numbering see Figure 3. [b] Refined in groups i−xiii; amplitudes with * are not refined.

amplitudes for torsion dependent interatomic distances are included in the refinement, the R factors decrease to 3.7% and 6.1%, but some amplitudes for the planar conformer adopt unreasonable values. The following correlation coefficients had values larger than $|0.7|$ in the refinement of the perpendicular conformer: $r(C-C)/r(C-O) = -0.86$, $r(C-O)/r(C-F) = -0.78$, and $\angle(CC1C)/\angle(CC4C) = -0.80$. The final results for the geometric parameters are included in Table 1. Interatomic distances and vibrational amplitudes derived in this analysis are equal to those obtained in the Moscow analysis within their experimental uncertainties and are not given.

In the refinement of mixtures of both conformers, only the geometric parameters and vibrational amplitudes of the perpendicular form were refined. The geometric parameters of the planar conformer were set to those derived in the above analysis for this structure and vibrational amplitudes were constrained to calculated values. R_{long} has its minimum for pure perpendicular conformer and increases with increasing contribution of the planar form. Thus, its contribution is between 0% and 13%, according to Hamilton's test.

Matrix Infrared Spectra

Matrix infrared spectra were recorded in the range 4000−400 cm^{-1} with a Bruker IFS 66v spectrometer and with a resolution of 1 cm^{-1}. Mixtures of **2** with Ar or Ne (1:1000) were deposited at 15 K on an aluminum-plated copper mirror in a He-cooled cryostat. Details of the matrix-isolation apparatus have been given elsewhere.[23] The temperature of the mixture before deposition in the matrix was 21 and 330 °C. Only the Ne spectra were analyzed, since the Ar spectra showed splitting of several bands due to matrix effects.

Most bands are readily assigned on the basis of calculated (B3LYP/cc-pVTZ) frequencies and intensities for the perpendicular conformer. Shifts of several bands by up to 20 cm^{-1} are predicted for the planar conformer. Such a splitting is not observed in the Ne spectra. Furthermore, no significant shifts of relative band intensities in the spectra at 21 and 330 °C occur. These spectra demonstrate that only a single conformer is present in the matrix at 15 K.

Conclusions

Independent GED studies of 4-fluoro(trifluoromethoxy)benzene performed in two laboratories result in equal geometric parameters and conformational composition within their experimental error limits. The uncertainties for some bond lengths, which are reported by the Tübingen group, are smaller, because no vibrational amplitudes for bonded distances were refined in this analysis. In the Moscow analysis, however, vibrational amplitudes for bonded distances were refined in two groups (see Table 2), leading to larger uncertainties due to higher correlations.

Both investigations demonstrated that CH_3/CF_3 substitution has a strong effect on the conformation of anisols. The parent compound $C_6H_5OCH_3$ possesses a planar structure, as pointed out in the Introduction. A recent GED investigation of 4-fluoroanisole also resulted in a planar structure.[24] These experimental results are in agreement with high-level quantum chemical calculations that include electron correlation. On the other hand, anisols **1** and **2**, in which the methyl group is substituted by a CF_3 group**,** exist predominantly as perpendicular conformers. For both compounds the analyses of the GED intensities cannot exclude some contribution of the planar form. Quantum chemical calculations result in rather different shapes of the potential functions for internal rotation around the $C(sp^2)-O$ bond for the two trifluoromethoxybenzenes. In the case of **2**, HF, MP, and B3LYP methods with 6-31G* basis set predict a single minimum for the perpendicular form and a transition state for the planar structure 0.6−1.8 kcal/mol higher in energy. The B3LYP method with large basis sets [cc-pVTZ, pc1, pc2, and 6-311++G(3df,2pd)] predicts a second shallow minimum for a planar conformation, about 0.6 kcal/mol above the global minimum for the perpendicular structure. These minima disappear or become extremely shallow if the energies are corrected by ZPE.

Independent of the detailed shape of the potential function, whether it possesses a flat maximum or a shallow minimum at $\varphi(C-O) = 0°$, we expect structures for all torsional angles to be populated at room temperature. Obviously, the adequate model for analyzing the GED intensities would be a dynamic one, using many pseudoconformers with different torsional angles and appropriate weight. However, we cannot expect to derive the shape of the potential function from such an analysis, since even a two-conformer model did not allow for an unambiguous determination of the presence of the second conformer. Referring to the calculated potential functions shown in Figure 1, even the presence of a shallow minimum at φ(C−O) = 0° would not lead to a stationary planar conformer at room temperature. The IR(matrix) spectra demonstrate that no such conformer is trapped in the matrix upon deposition of the gas heated to 21 or 330 °C, respectively. This makes the existence of a second, high-energy conformer in the gas phase before deposition of the sample in the matrix very unlikely. The possible small contribution of a planar conformer that was derived from the GED intensities with a two-conformer model represents the population of structures around the planar form that occur during internal rotation around the C(sp^2)−O bond.

CH_3/CF_3 substitution has also a strong effect on the C−O bond lengths. In anisol the C1−O [C(sp^2)−O] bond [1.361(15) Å][1] is considerably shorter than the O−C7 [O−C(sp^3)] bond [1.423(15) Å]. On the other hand, in the CF_3-substituted compound **2** the C1−O bond [1.42(3) or 1.405(14) Å] is considerably longer than the O−C7 bond [1.36(3) or 1.354(14) Å]. The short C1−O bond in anisol can be rationalized by strong conjugation between the p-shaped oxygen lone pair and the π-system of the benzene ring, which occurs only in the planar structure. The short O−C7 bond in **2** can be rationalized by orbital interactions (anomeric effects) between the oxygen lone pairs and the σ^*(C−F) orbitals and by polar effects ($O^{(-)}$−$C^{(+)}$).

Although fluorination of the benzene ring in the para position has no effect on the principal conformational properties of compounds **1** and **2**, it increases the barrier to internal rotation around the C1−O bond. According to quantum chemical calculations this barrier increases from 0.9 to 1.3 kcal/mol (MP2/6-31G*) or from 0.4 to 0.6 kcal/mol (B3LYP/cc-pVTZ). The B3LYP/6-311++G(3df,2pd) method predicts an increase from 0.21 to 0.55 kcal/mol.[11] This trend is confirmed by the GED analyses using a simple two-conformer model. The contribution of the planar conformer decreases upon fluorination from 70(30)%[8] or 12(8)%[9] in **1** to 0−25% (Moscow analysis) or 0−13% (Tübingen analysis) in **2**.

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