Conformational Properties of 2-Fluoroanisole in the Gas Phase

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Molecular structure and conformational properties of 2-fluoroanisole have been studied by gas electron diffraction and quantum chemical methods (HF/6-31G*, MP2/6-31G*, and B3LYP/6-31G*). All methods predict the existence of two minima on the potential to internal rotation around the C(sp^2)-O bond corresponding to planar and nonplanar forms, but they give rather different results on the geometry and the relative energy of the nonplanar conformation. The electron diffraction data were treated with two different procedures for obtaining the scattering intensities (scanner and densitometer) and two different procedures of structural analysis used in laboratories of Moscow and Tübingen. With all data sets and procedures used in analysis, geometrical parameters and conformational composition were found to be very close. The preferred conformation of 2-fluoroanisole is a planar anti form, 70 ± 12%, whereas the minor conformation is a nonplanar form with the CH_3 group rotated toward the F atom with $\varphi(C{=}C{-}O{-}C) = 57(8)°$. The structural parameters are compared with those obtained for related compounds. Stereochemical peculiarities in ortho derivatives of anisole, which result in the existence of a nonplanar conformer, are discussed in terms of a natural bond orbital (NBO) analysis.

1. Introduction

Experimental and theoretical methods lead to contradicting results for the conformational properties of anisole (methoxybenzene) $C_6H_5{-}O{-}CH_3$. Photoelectron spectra were interpreted in terms of a mixture of planar ($\varphi(CCOC) = 0°$) and perpendicular ($\varphi(CCOC) = 90°$) conformers, with the latter form being 1.4(2) kcal/mol higher in energy.[1] Similarly, from dynamic NMR measurements in solutions, the presence of planar and perpendicular conformers is concluded.[2] On the other hand, gas electron diffraction (GED) intensities which were recorded at 55 and 260 °C were interpreted in terms of a planar equilibrium structure with a large amplitude torsional motion around the C(sp^2)−O bond.[3] This result is confirmed by microwave spectroscopy (MW). The rotational constants demonstrate planarity of the heavy atom skeleton and no transitions corresponding to a second conformation were observed.[4] Several ab initio calculations at the Hartree−Fock level using different basis sets (STO-3G, 3-21G, 4-21G, 6-31G, and 6-31G*) predict potential functions for internal rotation around the C(sp^2)−O bond with two minima at planar and perpendicular orientations, with the latter minimum higher in energy by 0.1−1.8 kcal/mol.[2,5−7] However, ab initio calculations which include electron correlation (MP2, MP3, MP4(SDQ), CCSD, and CCSD(T) with different large basis sets) result in potential functions with a single minimum at the planar orientation and a flat maximum at the perpendicular orientation which lies 2.1−3.0 kcal/mol above the planar structure.[8] Considering the experimental GED and MW results for the gas phase and the high-level ab initio calculations, we conclude that anisole exists only as a single conformer with planar heavy atom skeleton. This sterically unfavorable structure is stabilized by conjugation between the p-shaped electron lone pair of oxygen and the C═C π bonds.

A strong conformational change occurs upon fluorination of the methyl group. Two independent experimental studies for α,α,α-trifluoroanisole (trifluoromethoxybenzene) based on GED, vibrational spectroscopy, and quantum chemical calculations lead to slightly different results. Whereas one of these studies results in a mixture of 30(21)% planar and 70(21)% perpendicular conformers,[9] the other study results in the presence of the perpendicular form only.[10] Quantum chemical calculations also predict different conformational properties for this compound.[9,10] HF and MP2 methods result in a potential function for internal rotation around the C(sp^2)−O bond with a single minimum at the perpendicular orientation of the CF_3 group and a maximum for planar orientation, DFT (B3LYP) calculations predict a mixture of perpendicular and planar conformers. The slight discrepancy between the two experimental studies may be due to differences in GED intensities, which were recorded at the universities of Antwerp[9] and Tübingen,[10] or because of different procedures applied in the analysis of the experimental intensities. It has to be pointed out that calculated molecular intensities or radial distribution functions of this compound depend very weakly on the orientation of the CF_3 group.

In the present study, we are interested in the effect of fluorination of the phenyl ring on the conformational properties of anisole. It should be noted that the GED study of 2-chloroanisole[11] gave the evidence of two conformers, planar and perpendicular forms, with the ratio 70:30%. The latter form is very unusual and needs to be checked on other ortho derivatives of anisole.

Because the molecular intensities (and radial distribution curves) of 2-fluoroanisole depend very little on the orientation of the methyl group, the result for the conformational composition may strongly depend on the experimental data and on the procedures used in the structure refinement (mean square

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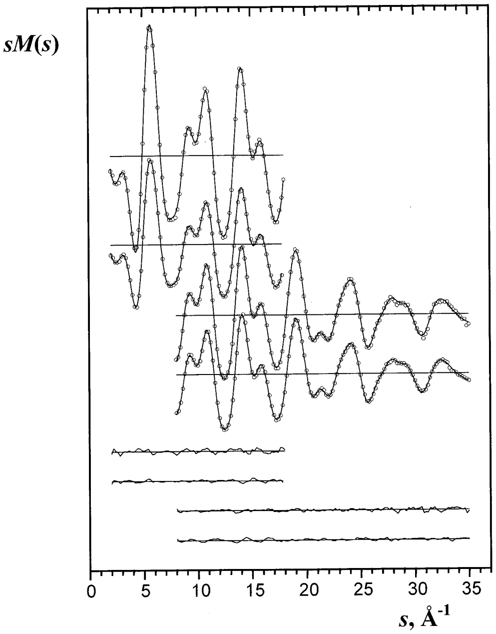

Figure 1. Data set obtained by scanner. Experimental (circles) and theoretical (full line) molecular intensity curves and residuals for the final model of 2-fluoroanisole.

amplitudes and vibrational corrections). Therefore, we used scattering intensities, which were obtained from a densitometer and from a scanner and different procedures for refinement. We report a gas-phase investigation of the conformational properties of 2-fluoroanisole based on the GED intensities recorded at the University of Tübingen, which were analyzed with procedures used in the GED laboratories of Moscow (refinement M) and Tübingen (refinement T).

2. Experimental Section

A commercial sample (Aldrich 98%) was used without further purification. Possible volatile impurities were pumped off at room temperature. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[12] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was heated to 37 °C, and the inlet system and nozzle were heated to 60 °C. Two photographic plates for each camera distance were analyzed with the densitometer ELSCAN and with the Agfa Duoscan HiD scanner.

For scanning the plates, we used a special plastic holder with the empty central part of the exact size of the photographic plate. This holder also contained a slit for mounting the optical wedge, which was used to calibrate the optical density measured by the scanner. Thus, the holder allows us to obtain the images of the wedge and the plate from the same scan and to eliminate a possible instability of the scanner light unit. The control of the stability of the light unit and calibration of the scanner optical density were carried out by the program GIST2. The total scattering intensity curves were obtained from the TIFF file with the image of the photographic plate using the program SCAN3[13] that was slightly modified to be suitable for standard processing of the GED data in Tübingen.

Experimental intensities were obtained in the range $s = 2-18$ and $8-35$ Å^{-1} with steps $\Delta s = 0.2$ Å^{-1} for the long and short camera distances, respectively, ($s = (4\pi/\lambda) \sin \theta/2$, where λ is the electron wavelength and θ is the scattering angle) and are shown in Figure 1 (scanner) and Figure 2 (densitometer).

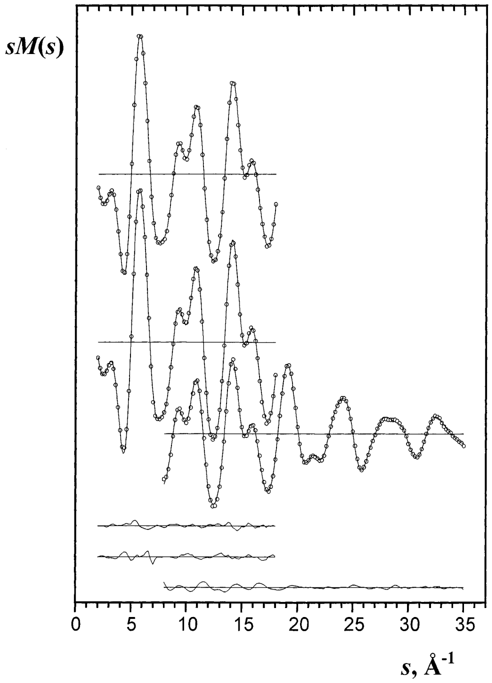

Figure 2. Data set obtained by densitometer. Experimental (circles) and theoretical (full line) molecular intensity curves and residuals for the final model of 2-fluoroanisole.

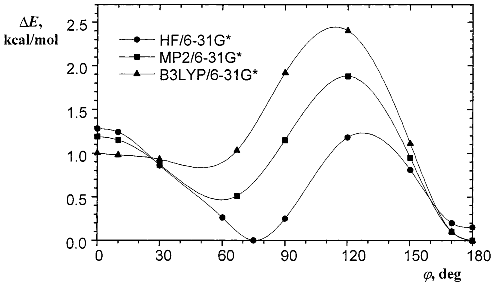

Figure 3. Potential functions of internal rotation of the OCH_3 group in 2-fluoroanisole calculated by different theoretical methods.

3. Quantum Chemical Calculations

Geometry optimizations for 2-fluoroanisole were performed with HF, MP2, and B3LYP methods and 6-31G* basis sets at different torsional angles around the C(sp^2)−O bond. The calculated potential functions (Figure 3) possess minima for the planar structure with the CH_3 group pointing away from the ortho-fluorine atom (φ(C2=C1−O−C) = 180°) and for a nonplanar structure with the CH_3 group bent toward the fluorine atom (Figure 4). This second minimum is predicted at torsional angles of 74.9° (HF), 66.9° (MP2), and 32.4° (B3LYP). The energy and Gibbs free enthalpy differences between the non-planar and the planar conformer are listed in Table 1. The $\Delta G°$ values also account for the different multiplicities of the two conformers (one for planar and two for nonplanar). According to the MP2 approximation and the DFT method, the nonplanar form is higher in energy than the planar conformer, and the HF approximation results in a slightly lower energy of the nonplanar form. Becasue of the higher entropy of the nonplanar structure and its multiplicity of 2, all methods predict negative $\Delta G°$ values, i.e., a preference of the nonplanar conformer. Vibrational frequencies and Cartesian force constants were calculated for both conformers with the MP2 and B3LYP methods. Both methods predict rather different values for the torsional frequencies around the C(sp^2)−O bond in the nonplanar conformer,

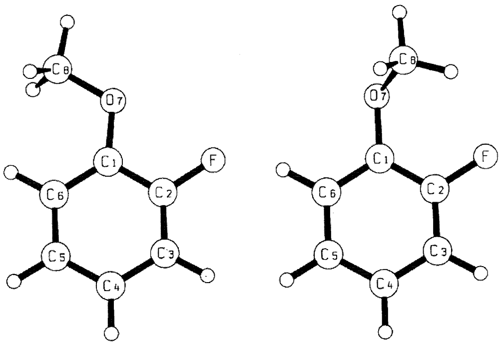

Figure 4. Planar conformer with φ(C2−C1−O−C) = 180° (left) and nonplanar conformer with φ(C2−C1−O−C) = 57(8)° (right) of 2-fluoroanisole.

TABLE 1: Energy and Gibbs Free Enthalpy Differences between Nonplanar and Planar Conformers of 2-fluoroanisole ($\Delta E = E$(nonplanar) − E(planar))

	HF/6-31G*	MP2/6-31G*	B3LYP/6-31G*
ΔE (kcal/mol)	−0.15	+0.51	+0.93
$\Delta G°$ (kcal/mol) [a]	−0.99	−0.31	−0.07

[a] Including the term $-RT \ln 2$ because of multiplicity of 2 for the nonplanar form.

74 (MP2) and 47 cm^{-1} (B3LYP). The force constants derived with the MP2 method were used to calculate vibrational frequencies and corrections $\Delta r = r_\alpha - r_a$, using the programs ASYM40[14] and SHRINK.[15,16] All quantum chemical calculations were performed with the program suite Gaussian 98.[17] The geometric parameters (MP2), mean-square amplitudes and vibrational corrections derived with the program SHRINK are listed together with the experimental values in the respective tables.

4. Structural Analysis

4.1. Parametrization. The numbering of atoms is shown in Figure 4. On the basis of the results from quantum chemical calculations, the following assumptions were adopted to describe the molecular geometry of 2-fluoroanisole: (a) all atoms of the C_6H_4F−O group lie in the same plane; (b) all C−H bond lengths in the ring are equal and bisect the adjacent CCC angles; (c) CH_3 group has C_{3v} symmetry and the C−H bonds are oriented such that the molecule with $\varphi = 180°$ has C_s symmetry and a staggered conformation about the C−O bond. With these assumptions, we used 20 independent geometric parameters: 11 bond distances (C1−C2, C1−C6, C6−C5, C4−C5, C3−C4, C2−C3, C1−O, C8−O, C2−F, C−H_{Ph}, and C−H_{Me}), 7 bond angles (C2−C1−C6, C1−C6−C5, C1−C2−C3, C−O−C, C1−C2−F, C6−C1−O, and HCH), tilt of CH_3 group which describes the deviation of C_3 axis from the C8−O bond, and the torsional angle φ(C2−C1−O−C).

The starting values for these parameters were taken from the MP2/6-31G* calculations. To take into account changes in geometry of different conformations, we used the following relaxation constraints as fixed differences between geometrical parameters of nonplanar and planar conformations (δ) from ab initio calculations: δr(C1−O) = δr(C8−O) = 0.01 Å, $\delta\angle$COC = −2.7°, $\delta\angle$C6C1O = 6.5°, δ(tilt CH_3) = −0.6°.

4.2. Refinement. The structural analysis was carried out using two different procedures, which are currently used in the GED laboratories of Moscow (refinement M) and Tübingen (refinement T). Both of them are based on the least-squares method applied to the reduced molecular intensities, $sM(s)$, within the static model. To calculate the root-mean-square amplitudes (u) and vibrational corrections ($\Delta r = r_\alpha - r_a$), we used two techniques: (M) the approach suggested by Sipachev[15,16] as incorporated in the program SHRINK and (T) the standard procedure[18] as represented by the program ASYM40.[14] The standard method is based on rectilinear displacements of the atoms during molecular vibrations, whereas Sipachev's approach is based on curvilinear displacements which implies a nonlinear transformation of internal coordinates into Cartesian displacements of the atoms.

The nonlinear transformation technique[15,16] gives vibrational corrections with clearer physical meaning if the molecule possesses low-frequency vibrations. We therefore intended to estimate the difference in the results of the structural analysis using two different approaches.

At the first stage of the structural analysis (refinement M), we tested different models with the fixed angles φ in the range 0−180°. It was found that the minimal R-factor values correspond to the planar ($\varphi \cong 180°$) and nonplanar ($\varphi \cong 70°$) forms. The mixture of these forms gives much lower R factor than the model with single conformer. Thus, refinement of the conformational composition α and the angle φ for the nonplanar conformation leads to the model, which agrees well with experiment ($R \cong 5.5\%$), even if other structural parameters are kept at their starting values.

Afterward, the background correction was carried out using the spline-smoothing algorithm.[19] At the final stage of refinement, the conventional scheme of the structural analysis was used.[20] Geometrical parameters and amplitudes were sequentially added to the set of parameters under determination according to their contributions to the scattering intensities. All C−C and C−O bond lengths and CCC valence angles could not be refined individually because of high correlations. Therefore, they were refined with fixed differences from ab initio calculations (MP2/6-31G*). The amplitudes for bonded and nonbonded distances were varied in groups with the differences fixed at the calculated values. In the final analysis, eight geometric parameters of the planar conformer, its contribution α, and the torsional angle φ of the nonplanar conformer were refined together with seven groups of vibrational amplitudes.

The same scheme of the structural analysis was also applied to the total intensity $I(s)$ obtained by densitometer. The final results of the structural analysis for refinement M are presented in Tables 2 and 3. The corresponding reduced molecular intensities $sM(s)$ and the radial distribution curve $f(r)$ are shown in Figures 1, 2, and 5.

Refinement T was carried out by the very similar way used in refinement M. The main difference was that amplitudes were calculated by ASYM40 program, and no vibrational corrections were used in this refinement. Furthermore, vibrational amplitudes for bonded distances were fixed at the calculated values. The comparison of the main geometric parameters obtained by different procedures is given in Table 4.

5. Discussions

5.1. Different Data Sets and Procedures of Structural Analysis. The comparison of the main geometric parameters of 2-fluoroanisole obtained by the use of different data sets and different procedures of refinement (Table 4) shows that they differ very insignificantly and deviations do not exceed a half of error limits except for the C−F bond length. This bond length depends very strongly on the vibrational amplitudes for bonded distances. The difference between two methods of refinement (M and T) is due to fixing these amplitudes in the T refinement. The error limits in Table 4 were obtained by varying the

TABLE 2: Interatomic Distances, Experimental and Calculated Mean-Square Amplitudes and Vibrational Corrections $\Delta r = r_\alpha - r_a$ in Å (without Nonbonded Distances Involving Hydrogens) for the Planar Conformer

atoms	R	u (exp.)	u (calc.)	$\Delta r = r_\alpha - r_a$
$(C-C)_{av}$	1.394	0.050 (2)	0.044	0.0004
$C_{Ph}-O$	1.360	0.051	0.045	0.0001
$C_{Me}-O$	1.420	0.054	0.048	0.0005
$C-F$	1.357	0.049	0.043	0.0005
$C-H_{Ph}$	1.076	0.078 (4)	0.075	0.0019
$C-H_{Me}$	1.079	0.080	0.077	0.0013
C1•••F	2.37	0.064 (3) $*^1$	0.058	0.0058
C3•••F	2.36	0.063	0.057	0.0045
C1•••C3	2.43	0.060	0.054	0.0053
C1•••C5	2.41	0.060	0.054	0.0056
C3•••C5	2.40	0.060	0.054	0.0028
C2•••C4	2.40	0.060	0.054	0.0055
C2•••C6	2.40	0.061	0.055	0.0053
C4•••C6	2.43	0.060	0.054	0.0025
C1•••C4	2.81	0.064 (7) $*^2$	0.060	0.0065
C2•••C5	2.75	0.063	0.060	0.0067
C3•••C6	2.79	0.065	0.061	0.0040
C6•••F	3.63	0.067 (4) $*^3$	0.059	0.0104
C4•••F	3.63	0.066	0.058	0.0093
C5•••F	4.10	0.066	0.061	0.0117
		Planar Conformer		
C2•••O	2.33	0.063 $*^1$	0.057	0.0057
C3•••O	3.62	0.068 $*^3$	0.059	0.0105
C4•••O	4.16	0.067 $*^4$	0.062	0.0111
C5•••O	3.70	0.062 $*^3$	0.058	0.0085
C6•••O	2.46	0.062 $*^1$	0.056	0.0033
O•••F	2.63	0.097 $*^1$	0.091	0.0101
C8•••F	4.02	0.104 $*^4$	0.100	0.0393
C8•••C1	2.38	0.067 $*^1$	0.061	0.0031
C8•••C2	3.62	0.073 $*^3$	0.065	0.0234
C8•••C3	4.79	0.067 (20) $*^5$	0.070	0.0247
C8•••C4	5.06	0.080	0.082	0.0144
C8•••C5	4.26	0.096 $*^4$	0.091	−0.0009
C8•••C6	2.88	0.094 $*^2$	0.090	−0.0123
		Nonplanar Conformer		
C2•••O	2.42	0.068 $*^1$	0.062	0.0064
C3•••O	3.68	0.069 $*^3$	0.061	0.0107
C4•••O	4.17	0.067 $*^4$	0.062	0.0115
C5•••O	3.67	0.069 $*^3$	0.061	0.0087
C6•••O	2.40	0.068 $*^1$	0.062	0.0038
O•••F	2.76	0.113 $*^2$	0.107	0.0120
C8•••F	2.86	0.177 $*^2$	0.173	−0.0038
C8•••C1	2.36	0.077 $*^1$	0.071	0.0060
C8•••C2	2.97	0.109 $*^2$	0.105	−0.0015
C8•••C3	4.26	0.113 $*^4$	0.108	0.0062
C8•••C4	4.95	0.118 $*^5$	0.121	0.0184
C8•••C5	4.61	0.141 $*^5$	0.144	0.0277
C8•••C6	3.44	0.153 $*^3$	0.145	0.0284

$*^n$ Mean-square amplitudes were refined in the group n.

TABLE 3: Independent Geometrical Parameters for the Planar Conformer of 2-fluoroanisole, Torsional Angle for Non-planar Conformer and Conformational Composition (α) as Determined by GED (scanner intensities, Moscow programs) and ab Initio Calculations[a]

parameter[b] (r/Å, ∠/deg)	GED (r_a, $\angle_\alpha$)	MP2/6-31G* (r_e)
$(C-C)_{av}$	1.394(2)	1.396
C1−C6	1.396 (2)	1.398
C6−C5	1.399	1.401
C4−C5	1.390	1.392
C3−C4	1.398	1.400
C2−C3	1.381	1.383
C1−C2	1.403	1.405
$(C-O)_{av}$	1.390(7)	1.395
$C_{Ph}-O$	1.360 (7)	1.365
$C_{Me}-O$	1.420	1.425
C−F	1.357(15)	1.354
$(C-H)_{av}$	1.077(4)	1.086
$C-H_{Ph}$	1.076 (4)	1.085 (av.)
$C-H_{Me}$	1.079	1.088 (av.)
C2−C1−C6	118.1 (3)	118.2
C1−C6−C5	119.9	120.0
C1−C2−C3	122.0	122.1
C−O−C	117.9(12)	116.2
C1−C2−F	118.8(17)	118.0
C2−C1−O	115.1(17)	115.4
H−C−H	109.7 fixed	109.7 (av.)
tilt (CH_3) [c]	4.1 fixed	4.1
α (planar), %	70(12)	30
∠φ (planar)	180.0 fixed	180.0
∠φ (nonplanar)	57.1(80)	66.9
R factor, %	3.69	

[a] Geometry of nonplanar conformer was refined with the relaxation constraints from ab initio calculations (see text). [b] Numbering of the atoms is shown in Figure 4. Errors are given as three times the standard deviation including the scale error. The parameters in braces were refined in groups with the fixed differences from ab initio calculations. [c] Tilt angle between C_3 axis and $C_{Me}-O$ bond, toward oxygen lone pairs.

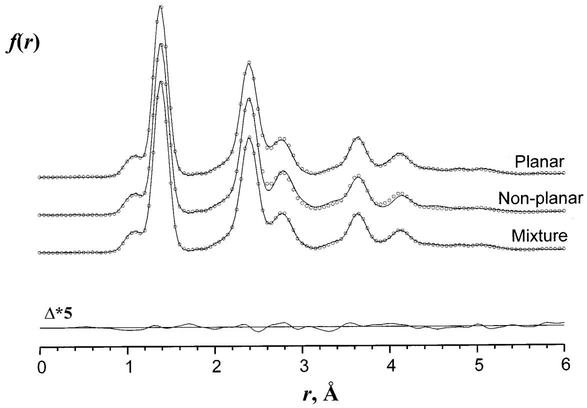

Figure 5. Experimental (circles) and theoretical (full line) radial distribution curves for different conformers of 2-fluoroanisole. The difference curve corresponds to the final model with the mixture of two conformers (refinement M, scanner data).

amplitudes for bonded distances by ±0.005 Å. Lower R factors obtained in refinement M demonstrate that refinement of these amplitudes and inclusion of the vibrational corrections (refinement in terms of r_α structure) lead to a better fit as compared with refinement T. Despite different approaches used in refinements M and T, both of them give very similar structural parameters which agree well with results of the MP2/6-31G* calculations.

Comparing R factors for the data sets obtained by scanner and densitometer (Table 4), we can see that the scanner data are better in refinement M and nearly the same as the densitometer data in refinement T. In fact, we believe that the scanner processing of GED data has more advantages, especially in cases where photographic plates have larger defects on the emulsion that produce errors in the densitometer data. In the case of the scanner data, these errors can easily be eliminated without any loss of data accuracy.[13] For example, because of a lot of coarse errors on one of the photographic plates obtained from short camera distance, we had to remove its densitometer data from structural analysis, but the scanner data from this plate appeared to be of the same quality as from the “good” plate (see Figure 1). Taking into account the above considerations, we consider the results obtained in refinement M with the scanner data as the final results of our structural study (Tables 2 and 3).

TABLE 4: Main Geometric Parameters of Planar Conformer, Torsional Angle for Nonplanar Conformer, and Conformational Composition as Derived from Densitometer and Scanner Data with Different Analyzing Procedures and from MP2/6-31G* Calculations

	Moscow		Tübingen		ab initio MP2/6-31G*
	densitometer	scanner	densitometer	scanner	
$(C-C)_{av}$	1.393(3)	1.394(2)	1.392(2)	1.393(3)	1.396
$(C-O)_{av}$	1.397(11)	1.390(7)	1.397(6)	1.402(8)	1.395
C−F	1.345(21)	1.357(15)	1.326(18)	1.329(22)	1.354
$(C-H)_{av}$	1.076(6)	1.078(4)	1.078(6)	1.077(6)	1.089
C−C1−C	118.2(4)	118.1(4)	118.2(3)	118.1(2)	118.2
C2−C1−O	114.2(22)	115.1(17)	114.3(9)	115.5(9)	115.4
C−O−C	116.8(19)	117.9(12)	115.2(13)	116.0(13)	116.2
C1−C2−F	118.8(28)	118.8(17)	118.6(14)	117.1(15)	118.0
φ(C2−C1−O−C) planar (fixed)	180.0	180.0	180.0	180.0	180.0
φ(C2−C1−O−C) nonplanar	63(9)	57(8)	66(7)	61(8)	66.9
%(planar)	67(16)	70(12)	63(14)	67(12)	37
R factor (%)	3.93	3.69	4.21	4.23	−

TABLE 5: Sum of Orbital Interaction Energies (kcal/mol) between the Oxygen Lone Pairs and the Ring Orbitals for Various Orientations of the Methoxy Group in Anisole and 2-Fluoroanisole

φ (C2−C1−O−C)	0°	180°	90°	67°
$C_6H_5OCH_3$	46.1	46.1	27.3	
$2F-C_6H_4OCH_3$	47.5	46.9	29.9	31.7

5.2. Geometrical Parameters. Fluorination of the benzene ring in 2-fluoroanisole does not change the $C_{Ph}-O$ and $C_{Me}-O$ bond lengths (Table 4) as compared with anisole where these lengths are 1.361(15) and 1.423(15) Å,[3] respectively. The C−F bond in 2-fluoroanisole is also of nearly the same length as in fluorobenzene, $r_s = 1.354(10)$ Å[21] and $r_g = 1.356(4)$ Å.[22] The same tendency is found in 2-chloroanisole:[11] there are no differences in the C−Cl, $C_{Ph}-O$, and $C_{Me}-O$ bond lengths in comparison with anisole[3] and chlorobenzene.[23,24] It should be noted that, unlike the methoxy group, the nitro group produces an essential shortening of the C−F bond in 2-fluoronitrobenzene[25] by 0.05 Å and of the C−Cl bond in 2-chloronitrobenzene[26] by 0.016 Å as compared with fluoro- and chlorobenzene, respectively.

5.3. Conformation. The conformational properties of 2-fluoroanisole do not conform with chemical intuition. Naively, one would expect the presence of only one planar conformer with anti orientation of the methyl group with respect to fluorine, $\varphi = 180°$. The presence of a second nonplanar form with the methyl group rotated toward the fluorine atom ($\varphi \approx 60°$) is surprising. It is attempted to rationalize this experimental result as follows.

The orientation of the methoxy group around the $C(sp^2)-O$ bond in anisoles depends primarily on two opposing effects, steric repulsion between the methyl group and the benzene ring which favors perpendicular orientation and orbital interactions between the oxygen lone pairs and the benzene ring which favor the planar conformation. Steric repulsions can be estimated only qualitatively, but orbital interaction energies can be derived from a natural bond orbital (NBO) analysis.

The oxygen lone pairs (n_σ with approximately sp^2 hybridization and n_π with p shape) can interact with the σ^* orbitals of the benzene ring (anomeric effects) or with π^* orbitals (conjugation). Their relative contributions depend strongly on the torsional angle φ. The sum of all interaction energies, as derived with the MP2 approximation, is listed in Table 5 for different orientations in anisole and in 2-fluoroanisole. This sum is largest for planar orientations ($\varphi = 0°$ or 180°) where conjugation between the n_π lone pair and the π^* orbitals of the ring is by far the largest contribution. It is the smallest for perpendicular orientation where anomeric effects contribute about twice as much as conjugation between the n_σ lone pair and the π^* orbitals.

In anisole, the gain in orbital interaction energies in the planar conformer ($\varphi = 0°$ and 180°) relative to the perpendicular structure exceeds steric repulsion and leads to a planar structure as discussed in the Introduction. The same situation occurs in 2-fluoroanisol for the planar conformation with $\varphi = 180°$. For the planar conformation with $\varphi = 0°$ (CH_3 group toward the fluorine atom), steric repulsions between the methyl group and fluorine exceed stabilization due to orbital interactions and the methyl group is rotated around the $C(sp^2)-O$ bond out of the plane. Balance between repulsions and orbital interactions occurs at $\varphi = 67°$ (according to MP2 calculations). This orientation corresponds to a minimum in the calculated torsional potential (see Figure 3). If the methoxy group in 2-fluoroanisole is rotated from the perpendicular orientation ($\varphi = 90°$) toward the fluorine atom ($\varphi = 67°$), stabilization due to orbital interactions increases by about 2 kcal/mol (from 29.9 to 31.7 kcal/mol). In this orientation, the shortest contact between fluorine and a methyl hydrogen atom (2.35 Å) is shorter than the van der Waals distance (2.55 Å), but electrostatic attraction between fluorine (−0.40 au) and hydrogen (+0.20 a.u) seems to favor this orientation toward the fluorine atom. Thus, the existence of the nonplanar conformer can be rationalized by a delicate balance between steric, electrostatic, and orbital interactions.

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