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Torsion potentials and electronic structure of trifluoromethoxy- and trifluoromethylthiobenzene: an ab initio study

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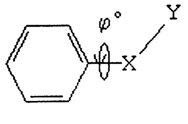
Abstract

Potential functions of internal rotation about the $C_{sp^2}-X$ bonds in molecules $C_6H_5XCF_3$ ($X = O, S$) were calculated at the second-order Møller–Plesset perturbation level of theory with 6-31G(d) basis set. The profile of the potential function and the rotation barrier ($\Delta E^{\#} = 3.0$ kJ/mol) found for $C_6H_5OCF_3$ suggest that, depending on experimental conditions, there can be either free rotation about the $C_{sp^2}-O$ bond or the conformational equilibrium is shifted to the side of the orthogonal form. The rotational barrier for $C_6H_5SCF_3$ is 14.7 kJ/mol and the molecule exists in the stable orthogonal conformation. The nature of hybridization, energy and population of lone electron pairs (LPs) on the oxygen and sulfur atoms were considered by using the Natural Bond Orbital (NBO) method. The energy of interactions of the LPs with antibonding π^*-orbitals of the aromatic moiety were estimated for different conformations. The distribution of electron density in the molecules was discussed. The results were compared with analogous calculations on the molecules $C_6H_5XCH_3$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio; Trifluoromethoxybenzene; Trifluoromethylthiobenzene; Methoxybenzene; Methylthiobenzene; Conformations; NBO analysis

1. Introduction

The conformation of trifluoromethoxybenzene and trifluoromethylthiobenzene is characterized by the torsion angle φ between the plane of benzene ring and the $C_{sp^2}-X-C_{sp^3}$ ($X = O, S$) bond plane:



∠φ from 0° to 90°

where $Y = CH_3$ or CF_3.

Studies of the molecules by structural physical methods (electron diffraction and X-ray analyses, microwave spectroscopy) have not been made. The first quantum-chemical investigation of the molecule $C_6H_5OCF_3$ was perfected by the CNDO/2 method [1]. The calculation was carried out with the use of idealized geometry and the torsion angle φ was estimated from the correlation between φ and substituent constants σ_R^0. It was inferred that the molecule exists in the orthogonal conformation due to steric interactions between the fluorine and *ortho*-hydrogen atoms. Based on analysis of long-range spin–spin coupling constants in NMR spectra of $C_6H_5OCF_3$ and on ab initio quantum-chemical calculations using minimal STO-3G and split valence 3-21G (with incomplete geometry optimization) basis sets, it was suggested that the molecule has a near-planar structure [2]. The minimum on the potential function of internal rotation about the $C_{sp^2}-O$ bond is located at $\varphi = 29.9°$ (STO-3G) or at $40.1°$ (HF/3-21G). However, according to calculations at the HF/6-31G level, the orthogonal conformation is energetically preferable [2]. It was concluded from the analysis of ^1H and ^{19}F NMR spectra of structurally related compounds p-$FC_6H_4OCF_3$ and p-$IC_6H_4OCF_3$ in a nematic liquid crystalline solvent that fluorinated anisoles possess the orthogonal conformation [3]. Trifluoromethylthiobenzene was also suggested to have the orthogonal structure on basis of its UV and IR spectra. However, a small amount, about 15%, of the planar conformer was also detected [4]. The X-ray emission K_β spectrum of the sulfur atom in $C_6H_5SCF_3$ suggests localization of lone electron pairs (LPs) on the sulfur atom [5]. The K_β spectrum is similar to that of t-$C_6H_5SC_4H_9$-t [6], which has the orthogonal conformation. Semiempirical quantum-chemical calculations at AM1 [7] and PM3 approximations [8,9] have shown that the $C_6H_5SCF_3$ molecule has a near-orthogonal conformation. The electronic effect of the OCF_3 and SCF_3 groups on the

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benzene ring is characterized by different substituent constants [10–13], i.e. 0.35 (σ_m), 0.32 (σ_p), 0.55 (σ_I), −0.18 (σ_R^0) for OCF_3 and 0.45 (σ_m), 0.48 (σ_p), 0.42 (σ_I), 0.06 (σ_R^0) for SCF_3. These values were used to discuss the influence of the substituents on the reactivity of the molecules [12–17]. From the values of constants σ_m and σ_p, the OCF_3 and the SCF_3 groups have large electron-acceptor effect on the aromatic ring. The inductive effect of the groups (see σ_I constants) is also electron-withdrawing and stronger as compared to substituents OCH_3 ($\sigma_I = 0.25$ [14]) or SCH_3 ($\sigma_I = 0.13$ [15]). In terms of a conjugative effect, the OCF_3 group is a weak π-donor with respect to the aromatic ring (see σ_R^0 constant), much weaker than OCH_3 ($\sigma_R^0 = -0.43$ [14]). The π-donor effect of the SCF_3 group ($\sigma_R^0 = -0.06$) is in contrast to that of SCH_3 ($\sigma_R^0 = -0.16$ [15]). Judging by shifts of K_β lines from the sulfur atom in X-ray emission spectra of $C_6H_5SCH_3$ and $C_6H_5SCF_3$, the substitution of hydrogen for fluorine atoms in the methyl group appreciably reduces the electron density on the sulfur atom [18]. The dipole moments of the $C_6H_5OCF_3$ (2.36 D [13], 2.27 D [19]) and $C_6H_5SCF_3$ (2.50 D [19]) molecules are greater than for $C_6H_5OCH_3$ (1.24 D [20]) and $C_6H_5SCH_3$ (1.31 D [21]). Some physicochemical characteristics and details on synthesis of $C_6H_5XCF_3$ are presented elsewhere [12,13,22–29].

The aim of the present work is to calculate potential functions of internal rotation about the $C_{sp^2}-O$ and $C_{sp^2}-S$ bonds in $C_6H_5OCF_3$ and the $C_6H_5SCF_3$, to determine stationary (minimum and maximum) points, geometric parameters and to clarify the nature of intramolecular interactions. These are given for comparison of the corresponding data obtained for the $C_6H_5OCH_3$ and $C_6H_5SCH_3$ molecules at the same level of theory.

2. Computational details

The ab initio computations at the second level Møller–Plesset perturbation theory (MP2) [30,31] have been carried out with the use of Gaussian 98W (Revision A.7) program [32]. All orbitals were active. The standard double-split valence basis set 6-31G(d) with Cartesian (6d) representation of the d functions was employed [33]. The standard convergence criteria were used. Torsional potentials for the molecules were constructed by constraining the torsion angle φ to fixed values 0, 15, 30, 45, 60, 75 and 90° and optimizing all other geometrical parameters. The positions of stationary points on PES were refined by re-optimization of all geometric parameters including the torsion angle φ. Vibrational frequencies were calculated numerically throughout. Stationary points on PES were verified as equilibrium geometries by the absence of imaginary frequencies, and transition states were characterized by the presence of a single imaginary frequency. Natural Bond Orbital (NBO) [34,35] population analysis was performed with the use of the NBO program, Version 3.1 (link 607, Gaussian 98W) [36].

3. Conformations

The total energies (E_{tot}, a.u.) for the $C_6H_5OCF_3$ and $C_6H_5SCF_3$ molecules are displayed in Table 1. The energies of the rotamers (ΔE, kJ/mol) relative to the minimum of the potential function of the internal rotation about the $C_{sp^2}-X$ bonds are given in parentheses. Such a minimum for the $C_6H_5OCF_3$ molecule is in the domain of the orthogonal conformation, whereas the maximum lies in the region of the planar conformation (see Fig. 1). The rotation barrier, calculated without ZPVE correction with accuracy determined by the 15°-increment, is 4.35 kJ/mol. The Hessian calculations revealed a negative eigenvalue ($-24.64\ \mathrm{cm}^{-1}$) at the point corresponding to the conformation $\varphi = 0°$. Therefore, this conformation is the maximum. The conformation with the torsion angle $\varphi = 90.1°$ ($E_{tot} = -642.7953837$ a.u.) is the minimum. The Hessian matrix has only positive eigenvalues at this point. The ZPVE correction is 0.106712 hartree per particle (a scaling factor of is used 0.9661 [37]) at the point of maximum and 0.107241 hartree per particle at the point of minimum. The ZPVE correction decreases the rotation barrier to 3.04 kJ/mol. The energy barrier $\Delta E^{\#} < kT$ (at RT = 2.5 kJ/mol) corresponds to free internal rotation [38]. Thus, a "border" situation is realized in the $C_6H_5OCF_3$ molecule. The molecular moieties have free rotation about the $C_{sp^2}-O$ bond or restricted motion with larger amplitude in the potential well with a broad flat bottom. The molecule is a conformationally non-rigid system. However, the conformational equilibrium is shifted to the orthogonal form. Note that experimental conditions can affect the conformational equilibrium.

Table 1
The total energies ($-E_{tot}$, a.u.) for $C_6H_5XCH_3$ and $C_6H_5XCF_3$ (X = O and S)[a]

Compound	φ°						
	0	15	30	45	60	75	90
$C_6H_5OCH_3$	345.6831291 (0.00)	.6827475 (1.00)	.6817110 (3.72)	.6804153 (7.13)	.6796587 (9.11)	.6795371 (9.43)	.6795188 (9.48)
$C_6H_5SCH_3$	668.3024735 (2.88)	.3025569 (2.66)	.3027167 (2.24)	.3029312 (1.67)	.3033128 (0.16)	.3035414 (0.07)	.3035681 (0.00)
$C_6H_5OCF_3$	642.7937269 (4.35)	.7938043 (4.15)	.7939728 (3.70)	.7941498 (3.24)	.7944747 (2.39)	.7950598 (0.85)	.7953834 (0.00)
$C_6H_5SCF_3$	965.3850386 (15.23)	.3857070 (13.60)	.3870953 (9.95)	.3885169 (6.22)	.3897743 (2.92)	.3906761 (0.55)	.3908858 (0.00)

[a] The energies of the rotamers (ΔE, kJ/mol) relative to the minimum are given in parentheses.

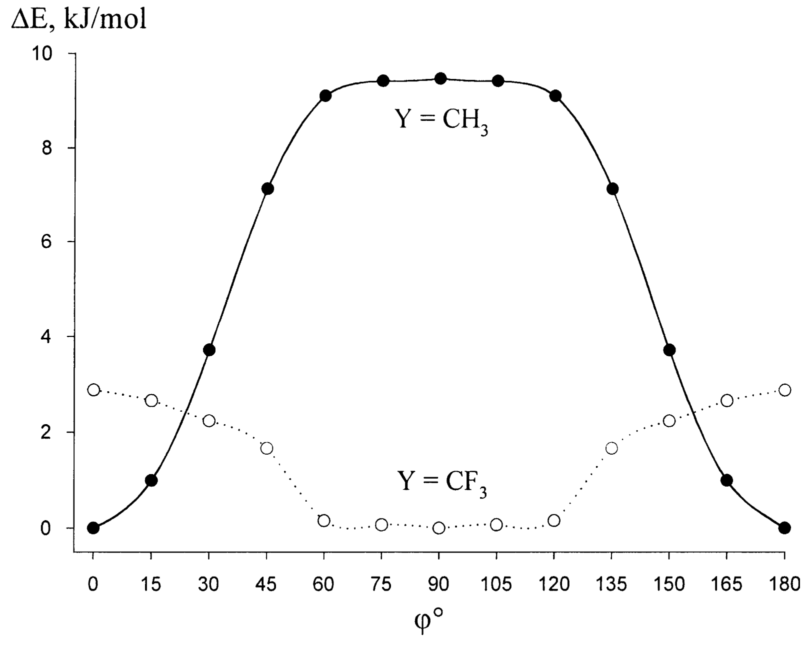

Fig. 1. Potential functions (at MP2/6-31G(d) level) for internal rotation about the C_{sp^2}–O bond in C_6H_5OY ($Y = CH_3$ or CF_3).

The energy minimum of the potential function of internal rotation about the C_{sp^2}–S bond in the $C_6H_5SCF_3$ molecule also lies close to the orthogonal conformation and the maximum is close to planar (see Fig. 2). The uncorrected barrier is 15.23 kJ/mol. The Hessian for conformation with the torsion $\varphi = 0°$ has a negative eigenvalue ($-54.46\ cm^{-1}$), therefore, it is the saddle point. The minimum corresponds to the conformation with $\varphi = 90°$. The ZPVE corrections for the points of maximum and minimum are 0.103337 and 0.103550 hartree per particle, respectively. The corrected rotational barrier is 14.67 kJ/mol. Thus, the $C_6H_5SCF_3$ molecule exists in the orthogonal conformation.

The planar conformation of the $C_6H_5OCH_3$ molecule is the energy minimum of the potential function of internal rotation about the C_{sp^2}–O bond, and the orthogonal form is the maximum (Fig. 1). This is in agreement with the results of electron diffraction [39], microwave spectroscopy [40] and quantum-chemical calculation at MP2/6-31G(d)//HF/6-31G(d) [41,42] and MP2/6-311 + G(d) [43] levels. The rotational barrier of the $C_6H_5OCH_3$ molecule, without ZPVE correction, is 9.48 kJ/mol. At the point of energy

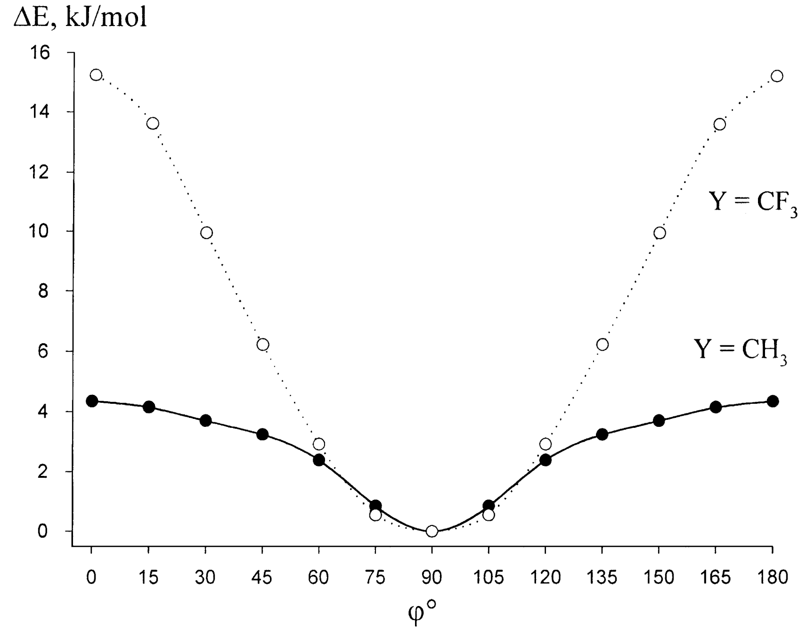

Fig. 2. Potential functions (at MP2/6-31G(d) level) for internal rotation about the C_{sp^2}–S bond in C_6H_5SY ($Y = CH_3$ or CF_3).

minimum ($\varphi = 0°$), the Hessian has all positive eigenvalues and at the point of maximum ($\varphi = 90°$) one negative eigenvalue ($-45.56\ \mathrm{cm}^{-1}$). The ZPVE corrections are 0.129984 hartree per particle ($\varphi = 0°$) and 0.129339 ($\varphi = 90°$). The corrected rotational barrier is 7.78 kJ/mol, which is in a good agreement with the value of 7.91 kJ/mol found at MP2/6-311 + G(d, p) [43] level of theory.

The energy minimum on the potential function of internal rotation about the $C_{sp^2}-S$ bond in the $C_6H_5SCH_3$ molecule is at the near-orthogonal conformation region and the planar conformation is the maximum (Fig. 2). The uncorrected rotation barrier is 2.88 kJ/mol. The complete geometrical optimization shows that the energy minimum is a conformer with the torsion $\varphi = 85.6°$ ($E_{tot} = -668.3035682$ a.u.). At this point, the Hessian matrix has only positive eigenvalues. The ZPVE correction for the total energy is 0.126353 hartree per particle. The major maximum is observed at the torsion angle $\varphi = 0°$. The Hessian matrix at this point has one negative eigenvalue ($-29.86\ \mathrm{cm}^{-1}$). The correction is 0.126433 hartree per particle. The ZPVE corrected barrier between the planar and non-planar (near-orthogonal) forms is 3.08 kJ/mol. The Hessian matrix for the structure with the torsion angle $\varphi = 90°$ has one negative eigenvalue ($-30.05\ \mathrm{cm}^{-1}$) and therefore can be identified as the point of the second maximum. The barriers between these two non-planar forms at $\varphi = 90°$ is assessed at the purely formal value of 0.02 kJ/mol which is comparable with the calculation error. Thus, the $C_6H_5SCH_3$ molecule, like $C_6H_5OCF_3$, is a conformationally non-rigid molecule. Experimental conditions can substantially influence the conformational equilibrium and the profile of the potential function. Physical methods on non-rigid molecules usually reveal only a so-called "effective" conformation, i.e. a hypothetical three-dimensional structure averaged over all possible conformations, having regard to their statistical weights. Electron diffraction identified the conformation of $C_6H_5SCH_3$ in the vapour phase having a torsion angle $\varphi = 45 \pm 10°$ [44]. When free rotation about the $C_{sp^2}-S$ bond occurs, such a value of φ reflects the "effective" conformation that is the average of 0 and 90°. This inference is confirmed by MP4(SDQ)/6-31G(d, p)//HF/6-31G(d, p) calculations on the $C_6H_5SCH_3$ molecule which estimate the rotational barrier at 2.19 kJ/mol [45]. At the same time, the values of *Kerr* constants suggest that in solution (CCl_4, C_6H_6) the conformational equilibrium is shifted to the side of a flatter structure ($\varphi = 23 \pm 5°$) [21].

Thus, the orthogonal or near-orthogonal conformers are the energy minima on the potential function of internal rotation about the $C_{sp^2}-X$ bonds for $C_6H_5OCF_3$, $C_6H_5SCF_3$ and $C_6H_5SCH_3$ and the major maxima are planar forms. $C_6H_5OCH_3$ has a planar structure. $C_6H_5OCH_3$ and $C_6H_5SCF_3$ exist in stable conformations while the $C_6H_5OCF_3$ and $C_6H_5SCH_3$ molecules belong to conformationally non-rigid structures. The conformation of the $C_6H_5XCF_3$ and $C_6H_5XCH_3$ molecules is determined by two major factors, by the effect of n,π-conjugation of the LP of the O and S atoms with the π-system of the aromatic ring, which increases stability of the planar forms, and by steric interactions between the CF_3 and CH_3 groups and the *ortho*-H atoms of the aromatic ring, which decreases stability of less strained non-planar forms. The CF_3 group is larger than CH_3 as follows, for instance, from the comparison of Van der Waals radii of hydrogen (1.20 Å) and fluorine (1.47 Å) atoms [46,47] or steric constants E_s^o of these groups, i.e. −1.24 (CH_3) and −2.40 (CF_3) [47].

Therefore, with the same X atoms, the planar conformations of the F_3CX-substituted benzenes are sterically more crowded than for the H_3CX-substituted molecules. In the series of the compounds with different atoms X (O or S) but identical groups CH_3 or CF_3, the molecules with $X = O$ have more flattened conformations and lower barriers to rotation about the $C_{sp^2}-X$ bonds owing to more effective n,π-conjugation of the oxygen LP with the aromatic ring compared to sulfur atom.

4. Geometrical parameters

Table 2 reports the optimized values of valence angles and bond lengths for the $C_6H_5OCF_3$ and $C_6H_5SCF_3$ molecules computed as the torsion angle varied from 0 to 90°.

It is likely that the CXC and CCX valence angles should depend noticeably on conformation. The lengths of the $C_{sp^2}-X$ and $C_{sp^3}-X$ bonds vary with conformation to a lesser extent. Interestingly, the $C_{sp^2}-O$ bond in $C_6H_5OCF_3$ is longer than the $C_{sp^3}-O$ bond. The reason for this might be the high polarity of the triad C_i–O–C_F that is reflected in substantial difference of charges on the atoms. The $C_6H_5SCF_3$ molecule shows the usual trend: the $C_{sp^2}-S$ bond is shorter than the $C_{sp^3}-S$. The C–F bond in $C_6H_5OCF_3$ is much shorter than in $C_6H_5SCF_3$ (see values of $\sum l(C-F)/3$) in Table 2. The length of the C–X bond in $C_6H_5XCH_3$ varies depending on conformation, in the ranges: 1.352–1.355 Å ($C_{sp^2}-O$), 1.422–1.429 Å ($C_{sp^3}-O$), 1.770–1.781 Å ($C_{sp^2}-S$) and 1.802–1.813 Å ($C_{sp^3}-S$). Thus, the bonds ($C_{sp^2}-X$) in $C_6H_5XCF_3$ are longer and the bonds ($C_{sp^3}-X$) are shorter than in the $C_6H_5XCH_3$ molecules with the same X atoms. The difference is particularly appreciable for compounds with $X = O$.

The valence angles in the $C_6H_5XCH_3$ molecules change in the ranges 117–112° (∠COC), 125–120° (∠CCO), 103–99° (∠CSC) and 125–120 (∠CCS). The CSC, CCO and CCS angles in all the molecules considered are rather similar and the COC angle in $C_6H_5OCF_3$ is slightly greater than in $C_6H_5OCH_3$ at corresponding torsion angles φ.

5. Intramolecular interactions

To analyse the intramolecular interactions, the wavefunctions obtained for the $C_6H_5XCF_3$ and $C_6H_5XCH_3$ molecules were represented as orbitals corresponding to traditional

Table 2
Variation of bond angles (°) and lengths (Å) in $C_6H_5OCF_3$ and $C_6H_5SCF_3$

Compound	φ°						
	0	15	30	45	60	75	90
$C_6H_5OCF_3$							
∠COC	119.93	119.71	119.06	118.11	116.94	115.56	114.77
∠CCO	125.08	124.80	124.04	124.02	121.86	120.36	118.93
$l(C_{sp^2}-O)$	1.402	1.402	1.403	1.405	1.408	1.409	1.409
$l(C_{sp^3}-O)$	1.352	1.352	1.353	1.354	1.354	1.354	1.355
$\sum l(C-F)/3$	1.344	1.344	1.343	1.344	1.344	1.343	1.343
$C_6H_5SCF_3$							
∠CSC	103.02	102.57	101.57	110.35	99.10	97.70	97.01
∠CCS	125.97	125.48	124.32	123.01	121.72	120.43	119.80
$l(C_{sp^2}-S)$	1.781	1.781	1.780	1.781	1.781	1.782	1.782
$l(C_{sp^3}-S)$	1.794	1.794	1.796	1.798	1.798	1.798	1.797
$\sum l(C-F)/3$	1.347	1.347	1.347	1.347	1.347	1.347	1.347

chemical terminology within the framework of the NBO technique. The energy and the hybridzation state of the heteroatom LPs were determined. LPs of the O and S atoms are non-equivalent. One of the pairs (LP1) comprises a hybridized orbital, as in accord with the NBO analysis the s-character of the LP1 is assessed at about 40% for the oxygen and 70% for the sulfur atom. With the same X atoms, the contribution of s-AO into LP1 depends only little on the nature of the CH_3 or CF_3 groups. The second lone electron pair (LP2) of the O and S atoms is practically pure p-AO. As a result, the LP1 of the O and S atoms noticeably differ in energy. Shown in Fig. 3 are the values of energy of LPs (E_{LP} in eV) in the conformationally non-rigid molecules ($C_6H_5OCF_3$ and $C_6H_5SCH_3$) throughout the range of the torsion angle φ and in the conformationally stable molecules ($C_6H_5SCF_3$ and $C_6H_5OCH_3$) only at the points of minimum of the potential function. For compounds with the CF_3 group E_{LP1} has greater magnitude than for the CH_3X-substituted molecules. With the same groups CF_3 or CH_3, the E_{LP1} is little dependent on the nature of the X atom. The influence of X atoms and CF_3 or CH_3, on the value of the E_{LP2} is more substantial. For compounds with the OCF_3 or OCH_3 groups, the values of E_{LP2} are located lower (in energy scale) than for their sulfur analogs. With the same X, for the compounds with the CF_3 group the energy of E_{LP2} is lower. Thus, the nature of the CF_3 or CH_3 groups has the major influence on the difference in energy of the LP1's, whereas the substituents interact mainly with the σ^*-type orbitals. The LP2's interact chiefly with π^*-orbitals and the differences in the energies of LP2's are mainly determined by the nature of the heteroatom X.

The interaction of the lone pairs of O and S with the aromatic ring and the CF_3 and CH_3 groups affect their population (see values of E_{LP} in Fig. 3). When passing from the planar to the orthogonal conformations, the population of LP1 is decreasing, while that of LP2 is increasing. The conformation-dependent changes in the population of LP2, are due to the steric disruption of the n,π-conjugation between the LP and the ring π-system. That is, with lowering of coplanarity, the delocalization of LP2 onto the aromatic moiety decreases and its localization on the heteroatom increases. However, the population of LP1 and LP2 cannot be a measure of the n,π-interaction with the ring as the lone pairs also interact with the antibonding σ^*-orbitals of C–F or C–H.

Table 3 lists the values of $E_{n,\pi}$ of the energy of donor–acceptor interaction of the LP1 and LP2 on the X atoms with antibonding π^*-orbitals of the aromatic ring. The calculations show that the hybridized lone pair (LP1) in planar and near-planar conformations ($\varphi = 0$–$30°$) does not interact with the ring π^*-orbitals. However, for torsion angles $\varphi = 30$–$45°$, such an interaction starts to occur and peaks in the orthogonal form. In the conformation with $\varphi = 90°$ the values of $E_{n,\pi}$ (LP1) for anisoles are four to five times greater that for thioanisoles evidently due to higher contribution of the p-component into LP1 of the oxygen as compared with the sulfur atom. LP2 interacts much more strongly with the antibonding π^*-orbitals of the aromatic ring in the planar and near-planar conformations, but in the orthogonal form such an interaction is absent as the p-orbital is displaced from the plane of the aromatic π-system. With the same conformations (excluding the orthogonal one), the value of $E_{n,\pi}$ (LP2) decreases in the sequence: $C_6H_5OCH_3 > C_6H_5OCF_3 > C_6H_5SCH_3 > C_6H_5SCF_3$. That is with the same X atoms and in the same conformation the substitution of the CF_3 for CH_3 groups reduces the interaction energy of LP2 with the antibonding π^*-orbitals. The reason may be the competitive donor–acceptor interactions of the LP2 with antibonding σ^*-orbitals of the C–F bonds. As the NBO analysis shows, such an interaction is possible with two C–F bonds pointing toward the benzene ring and it is calculated to be about 67–87 kJ/mol for OCF_3 and about 40–60 kJ/mol for the SCF_3 group. A similar interaction of LP2 with σ^*-orbitals of the C–H bonds is observed in the H_3CX-subsituted molecules, but its energy is appreciably lower, i.e. 25–30 kJ/mol for the OCH_3 group

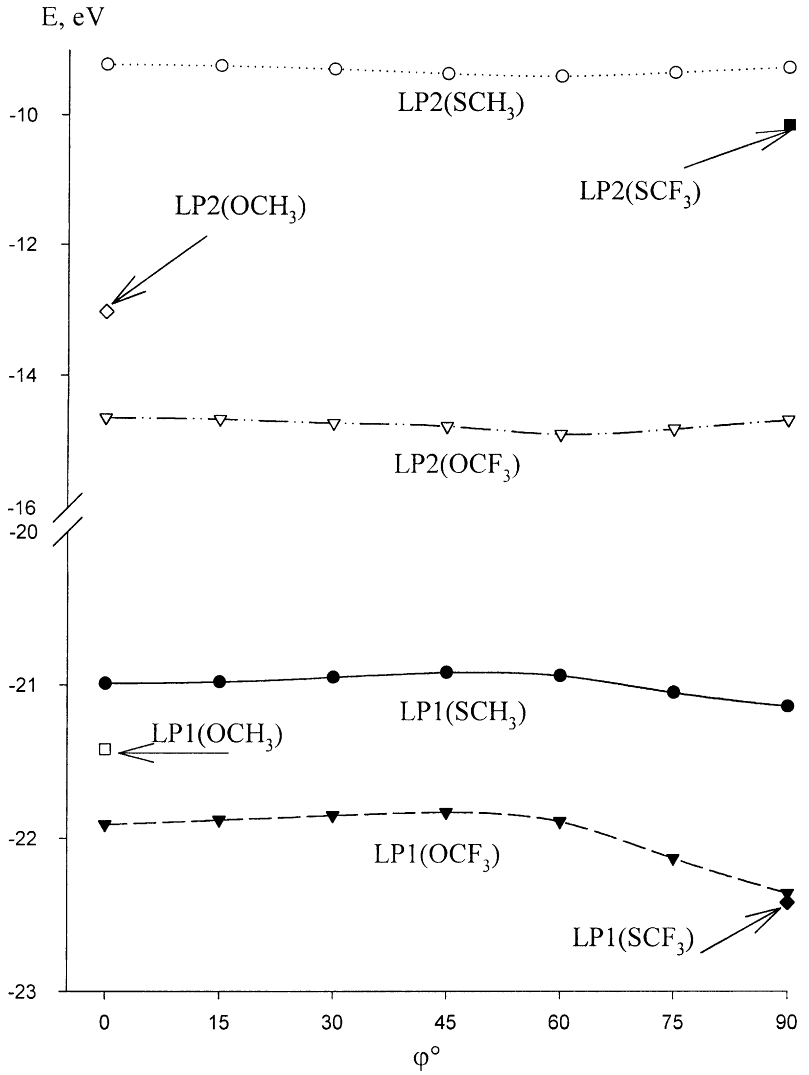

Fig. 3. The energies of LPs (E_{LP} in eV) at MP2/6-31G(d) level.

Table 3
Population (*P*, electron) and energy of LP, π*-interaction (*E*, kJ/mol) for $C_6H_5XCH_3$ and $C_6H_5XCF_3$ (X = O or S)

XY	Parameters	*φ*°						
		0	15	30	45	60	75	90
OCH_3	*P*(LP1)	1.94076	1.94050	1.93958	1.93745	1.93332	1.92778	1.92321
OCF_3	*P*(LP1)	1.95333	1.95305	1.95219	1.95060	1.94809	1.94554	1.94428
SCH_3	*P*(LP1)	1.95307	1.95305	1.95286	1.95223	1.95119	1.95009	1.94952
SCF_3	*P*(LP1)	1.97839	1.97843	1.97844	1.97812	1.97738	1.97675	1.97649
OCH_3	*P*(LP2)	1.83212	1.83583	1.84672	1.86419	1.88456	1.90081	1.90926
OCF_3	*P*(LP2)	1.88726	1.88873	1.89309	1.89978	1.90765	1.91468	1.91795
SCH_3	*P*(LP2)	1.84065	1.84460	1.85596	1.87290	1.88963	1.90096	1.90515
SCF_3	*P*(LP2)	1.88206	1.88434	1.89050	1.89923	1.90862	1.91578	1.91861
OCH_3	$E_{LP1,\pi}$	0.0	0.0	0.0	4.7	8.8	17.3	30.1
OCF_3	$E_{LP1,\pi}$	0.0	0.0	0.0	8.0	14.9	23.2	28.3
SCH_3	$E_{LP1,\pi}$	0.0	0.0	0.0	2.3	3.9	5.7	6.6
SCF_3	$E_{LP1,\pi}$	0.0	0.0	0.0	2.6	4.0	5.2	5.7
OCH_3	$E_{LP2,\pi}$	146.9	139.5	118.9	88.4	54.4	25.9	0.0
OCF_3	$E_{LP2,\pi}$	105.5	99.9	84.3	61.8	35.9	11.9	0.0
SCH_3	$E_{LP2,\pi}$	104.0	96.8	77.4	50.3	26.5	7.8	0.0
SCF_3	$E_{LP2,\pi}$	90.4	83.2	60.3	41.8	21.7	6.4	0.0

and 21–23 kJ/mol for the SCH_3 group. The interaction of LP1 with σ^*-orbitals of the C–F and C–H bonds is 4–8 kJ/mol (OCH_3 SCH_3, SCF_3) and 34–35 kJ/mol (OCF_3) and these energies are little dependent on the structure of the molecules.

Consequently, charge is transferred from the oxygen atom onto the aromatic ring in planar $C_6H_5OCH_3$ owing to interaction of the LP2 with antibonding π^*-orbitals of the ring ($E_{n,\pi} \approx 147$ kJ/mol). For $C_6H_5OCH_3$ with torsion angle φ varies from 45° (free rotation) to 90° and for this reason the donor effect of the LP2 on the ring is substantially weakened. If the conformational equilibrium is shifted to the orthogonal form, the LP2 does not interact with the antibonding π^*-orbitals of the ring, but at the same time donor interaction occurs between the LP1 and the π^*-orbitals ($E_{n,\pi} \approx 28$ kJ/mol). $C_6H_5SCF_3$ is orthogonal, where the interaction of LP1 with the antibonding π^*-orbitals is weak ($E_{n,\pi} \approx 6$ kJ/mol). In the conformation of $C_6H_5SCH_3$ with the torsion angle $\varphi = 45°$, the overall donor interaction of LP1 and LP2 with antibonding π^*-orbitals of the ring is estimated at about 53 kJ/mol. In the orthogonal conformation, only LP1 interact with the π^*-orbitals ($E_{n,\pi} \approx 7$ kJ/mol).

The fluorine atom has three lone electron pairs of which one (LP_F1) is represented according to the NBO analysis, by the hybrid sp-orbital (about 70% s-character) and two others (LP_F2 and LP_F3) are considered as practically pure p_y- and p_z-AO. In each fluorine atom LP2 interacts with the antibonding σ^*-orbitals of the X–C_F bond with the energy 57–59 kJ/mol in the $C_6H_5OCF_3$ molecule ($\varphi = 45$–$90°$) and of 37–43 kJ/mol in $C_6H_5SCF_3$ ($\varphi = 90°$). The lone pairs of the fluorine interact also with antibonding σ^*-orbitals of the neighbouring C–F bonds. In the CF_3 group, two C–F bonds (*syn*) point toward the benzene ring and the third C–F bond (*anti*) points in the opposite direction. In the planar and the orthogonal conformation, both *syn*-fluorine atoms are equivalent. At torsion angles $0° < \varphi < 90°$, the CF_3 group turns and the *syn*-atoms become non-equivalent. Depending on the spatial orientation of antibonding σ^*-orbitals of the C–F bonds with respect to the lone pairs on the neighbouring fluorine atoms, the energy of their interaction changes substantially and in particular situations exceeds 120 kJ/mol.

6. Charge distribution

The use of the set of natural aromatic orbitals (NAO) constructed in an arbitrary basis of AO allows compensation for the disadvantages of the Mulliken population analysis [48]. Table 4 lists the natural charges (q) on atoms of the $C_6H_5XCF_3$ and $C_6H_5XCH_3$ molecules in conformations with torsion angles of $\varphi = 0$, 45 and 90°.

It is convenient to consider the influence of the XCF_3 and XCH_3 groups on electron density distribution in the aromatic ring by comparing the differences of charges on the atoms in the molecules and in unsubstituted benzene, i.e. $\Delta q = q(C_6H_5XCF_3 \text{ or } C_6H_5XCH_3) - q(C_6H_6)$. The quantum-chemical calculation for benzene at MP2/6-31G(d) level followed by NBO analysis of the obtained wavefunction shows that the natural charges comprise −0.2350 electron on each carbon and 0.2350 electron on each hydrogen atom of the molecule. The calculated values of Δq are presented in Table 5. Increase in the negative value (or decrease in the positive value) of Δq corresponds to rise in the atomic charge compared to the corresponding atom (C or H) in unsubstituted benzene. Due to the higher electronegativity of oxygen compared to carbon, the $C_6H_5OCH_3$ and $C_6H_5OCF_3$ molecules bear excess electronic density on the oxygen and low electronic density on the C_i atom of the aromatic ring. The values of $\Delta q C_i$ (~0.5 electron) found for $C_6H_5OCH_3$ and $C_6H_5OCF_3$ indicates the strong acceptor

Table 4
Atomic natural charges (q, electron) for C_6H_5XY (X = O or S; Y = CH_3 or CF_3)

$\varphi°$	qX	$q\mathrm{C}_y$	$\sum(q\mathrm{Y})/3$	$q\mathrm{C}_i$	$q\mathrm{C}_o$	$q\mathrm{H}_o$	$q\mathrm{C}_m$	$q\mathrm{H}_m$	$q\mathrm{C}_p$	$q\mathrm{H}_p$
$C_6H_5OCF_3$										
0	−0.5710	1.3638	−0.3615	0.2877	−0.2896, −0.2598	0.2563, 0.2549	−0.2193, −0.2233	0.2425, 0.2424	−0.2412	0.2411
45	−0.5774	1.3629	−0.3625	0.2798	−0.2797, −0.2577	0.2588, 0.2550	−0.2195, −0.2222	0.2428, 0.2428	−0.2380	0.2415
90	−0.5826	1.3613	−0.3636	0.2660	−0.2583, −0.2575	0.2561, 0.2558	−0.2216, −0.2216	0.2431, 0.2431	−0.2349	0.2416
$C_6H_5SCF_3$										
0	0.2903	0.9402	−0.3588	0.2057	−0.2482, −0.2429	0.2489, 0.2437	−0.2175, −0.2209	0.2420, 0.2421	−0.2360	0.2405
45	0.2736	0.9415	−0.3604	−0.2166	−0.2401, −0.2365	0.2525, 0.2481	−0.2169, −0.2195	0.2427, 0.2426	−0.2311	0.2409
90	0.2583	0.9433	−0.3620	−0.2302	−0.2270, −0.2270	0.2523, 0.2522	−0.2186, −0.2186	0.2433, 0.2433	−0.2267	0.2414
$C_6H_5OCH_3$										
0	−0.5306	−0.3095	0.2092	0.3061	−0.3134, −0.2625	0.2385, 0.2470	−0.2270, −0.2325	0.2354, 0.2368	−0.2515	0.2358
45	−0.5489	−0.3037	0.2065	0.2990	−0.2908, −0.2628	0.2386, 0.2473	−0.2295, −0.2315	0.2361, 0.2370	−0.2466	0.2362
90	−0.5656	−0.2965	0.2037	0.2896	−0.2677, −0.2673	0.2448, 0.2450	−0.2321, −0.2321	0.2372, 0.2372	−0.2403	0.2368
$C_6H_5SCH_3$										
0	0.3038	−0.8395	0.2483	−0.2060	−0.2586, −0.2380	0.2340, 0.2413	−0.2245, −0.2273	0.2369, 0.2383	−0.2420	0.2368
45	0.2742	−0.8266	0.2447	−0.2109	−0.2426, −0.2363	0.2367, 0.2455	−0.2255, −0.2259	0.2367, 0.2388	−0.2367	0.2374
90	0.2507	−0.8183	0.2421	−0.2171	−0.2324, −0.2324	0.2459, 0.2461	−0.2270, −0.2270	0.2391, 0.2391	−0.2310	0.2379

Table 5
The differences of atomic charges in $C_6H_5XCF_3$, $C_6H_5XCH_3$ (X = O and S) and in unsubstituted benzene [$\Delta q = q(C_6H_5XCF_3 \text{ or } C_6H_5XCH_3) - q(C_6H_6)$]

φ°	$\Delta q C_i$	$\Delta q C_o$	$\Delta q H_o$	$\Delta q C_m$	$\Delta q H_m$	$\Delta q C_p$	$\Delta q H_p$
$C_6H_5OCF_3$							
0	0.5227	−0.0546, −0.0248	0.0213, 0.0199	0.0157, 0.0117	0.0075, 0.0074	−0.0062	0.0061
45	0.5148	−0.0447, −0.0227	0.0238, 0.0200	0.0155, 0.0128	0.0078, 0.0078	−0.0030	0.0065
90	0.5010	−0.0233, −0.0225	0.0211, 0.0208	0.0134, 0.0134	0.0081, 0.0081	0.0001	0.0066
$C_6H_5SCF_3$							
0	0.0293	−0.0132, −0.0079	0.0139, 0.0087	0.0175, 0.0141	0.0070, 0.0071	−0.0010	0.0055
45	0.0184	−0.0051, −0.0015	0.0051, 0.0015	0.0181, 0.0155	0.0077, 0.0076	0.0039	0.0059
90	0.0048	0.0080, 0.0080	0.0173, 0.0172	0.0164, 0.0164	0.0083, 0.0083	0.0083	0.0064
$C_6H_5OCH_3$							
0	0.5411	−0.0784, −0.0276	0.0035, 0.0120	0.0080, 0.0025	0.0004, 0.0018	−0.0165	0.0008
45	0.5340	−0.0558, −0.0278	0.0036, 0.0123	0.0055, 0.0035	0.0011, 0.0020	−0.0116	0.0012
90	0.5246	−0.0327, −0.0323	0.0098, 0.0100	0.0029, 0.0029	0.0022, 0.0022	−0.0053	0.0018
$C_6H_5SCH_3$							
0	0.0290	−0.0236, −0.0030	−0.0010, 0.0063	0.0105, 0.0077	0.0019, 0.0033	−0.0070	0.0018
45	0.0241	−0.0076, −0.0013	0.0017, 0.0105	0.0095, 0.0091	0.0017, 0.0038	−0.0017	0.0024
90	0.0179	0.0026, 0.0026	0.0109, 0.0111	0.0080, 0.0080	0.0041, 0.0041	0.0040	0.0029

effect of the OCH_3 and OCF_3 groups on the C_i atoms. The $C_6H_5SCH_3$ and $C_6H_5SCF_3$ molecules have lower electron density on the C_i atom. In the $C_6H_5OCH_3$ molecule in the planar conformation the most favourable conditions for interaction of the LP2 on the oxygen atom with π^*-orbitals of the ring are realized. For this reason, the values of Δq on the atoms C_o (−0.0784 and −0.0275 electron) and C_p (−0.0165 electron) are more negative than in other compounds. If the equilibrium in $C_6H_5OCF_3$ is shifted to near-orthogonal conformations ($\varphi = 45{-}90^\circ$), the excess of electron density is 0.02 electron on the CO and 0.003 electron on the C_p atoms (compared to unsubstituted benzene). In the orthogonal conformation, the charge on the C_p atom is practically equal to the charge on carbons in unsubstituted benzene. The SCH_3 group in $C_6H_5SCH_3$ has a donor effect on the *ortho-* and *para*-position of the ring only in near-planar conformations or when free rotation is present ($\varphi = 45^\circ$). In the orthogonal form SCH_3-groups acts on C_o and C_p as an acceptor. In orthogonal $C_6H_5SCF_3$, the SCF_3 substituent also displays an acceptor effect on the C_o and C_p atoms. In all molecules considered, the XCF_3 and XCH_3 groups produce the acceptor effect on the C_s and on hydrogen atoms of the aromatic ring.

On nitration, $C_6H_5OCF_3$ gives a *para*-isomer, whereas $C_6H_5SCF_3$ is nitrated both at the *ortho-* and *para*-position [12,13]. As is evident from the charge distribution, the charge on the C_o and C_p atoms in $C_6H_5OCF_3$ is higher than in $C_6H_5SCF_3$, that is, the SCF_3 group deactivates the benzene ring towards electrophilic agents to a greater extent than does the OCF_3 group. The selective *para*-directive effect of the OCF_3 group is evidently associated with a small rotational barrier in the $C_6H_5OCF_3$ molecule. As OCF_3 freely rotates about the $C_{sp^2}{-}O$ bond, it sterically hampers attack on the *ortho*-position of the aromatic ring and the agent is directed to the *para*-position (though the electronic charge on the C_o atoms is higher than on the C_p). The $C_6H_5SCF_3$ molecule has a stable orthogonal conformation with almost equal charges on the C_o and C_p atoms and for this reason one should expect an equimolar ratio of the *ortho-* and *para*-isomers. However, despite the orthogonal conformation of the molecule, there is a steric shielding of the *ortho*-position with the bulky CF_3 group and, as a result, $C_6H_5SCF_3$ gives 65% of the *para-* and 35% of the *ortho*-isomer.

Thus, the distribution of electron density in aromatic ring of the $C_6H_5XCF_3$ and $C_6H_5XCH_3$ molecules is governed by two major factors, the electronic nature of the substituents XCF_3 or XCH_3 and the molecular conformation and agree well with reactivity.

7. NMR spectra

Table 6 lists chemical shifts of ^1H, ^{13}C and ^{19}F signals in NMR spectra of compounds $C_6H_5XCF_3$ and $C_6H_5XCH_3$. It is known that in ^{13}C NMR spectra of monosubstituted benzenes, the change in shielding of the carbon nuclei in the *para*-position is correlated with relative charge on this atom [49–51]. To derive the relationship of the δC_p and the natural charge on the *para*-carbon atoms we calculated, in the MP2/6-31G(d) approximation, the values of qC_p in molecules C_6H_5R with the following R (the charge in *e* on C_p is given in parentheses): NH_2 (−0.2620), F (−0.2466), Cl (−0.2384), Br (−0.2369), CF_3 (−0.2265), and CN (−0.2261). The values of qC_p for the above compounds, unsubstituted benzene and the $C_6H_5OCH_3$ and $C_6H_5SCF_3$ molecules in the preferred conformations correlate reasonably well with δC_p for the compounds [24,51] though the linear equation:

$$\delta C_p = 231.29(\pm 3.55) + 436.43(\pm 14.83) qC_p,$$

$$r = 0.996, \quad S_0 = 0.5216, \quad n = 9$$

Table 6
Chemical shifis of ^{1}H (δH, ppm from TMS), ^{13}C (δC, ppm from TMS) and ^{19}F (δF, ppm from $CFCl_3$) signals in NMR spectra in $C_6H_5XCF_3$ and $C_6H_5XCH_3$ (X = O or S)[a,b]

Compound	δC_i	δC_o	δC_m	δC_p	δC_Y	δF	δH_Y
$C_6H_5OCH_3$	150.42 (21.92)	122.17 (−6.33)	131.31 (2.81)	128.50 (0.00)	121.81	−57.54	
$C_6H_5SCH_3$	159.93 (31.43)	114.01 (−14.49)	129.47 (0.97)	120.61 (−7.89)	54.59		3.76[c]
$C_6H_5OCF_3$	124.71 (−3.79)	137.07 (8.57)	130.51 (2.01)	131.93 (3.43)	130.75	−43.18	
$C_6H_5SCF_3$	139.35 (10.85)	126.90 (−1.60)	129.45 (0.95)	125.43 (−3.07)	15.40		2.44[c]

[a] In acetone-d_6 solution.

[b] The differences of chemical shifts on the atoms in the molecules and in unsubstituted benzene are given in parentheses.

[c] Taken from [54].

The correlation plot is shown in Fig. 4. If the values of δC_p for the conformationally non-rigid molecules $C_6H_5SCH_3$ and $C_6H_5OCF_3$ are placed on the curve and the points are projected onto the coordinate axis, it is possible to estimate the charge on the C_p atoms in the molecules. The results indirectly suggest that the conformational equilibrium in solution is shifted to orthogonal for $C_6H_5OCF_3$ or to planar for $C_6H_5SCH_3$. Qualitatively similar, but less pronounced dependence of δC and *q*C is also observed, for other atoms of the aromatic ring. However, the magnetic shielding of nuclei is determined by many factors, of which the charge distribution is not always the determining one. The ^{13}C

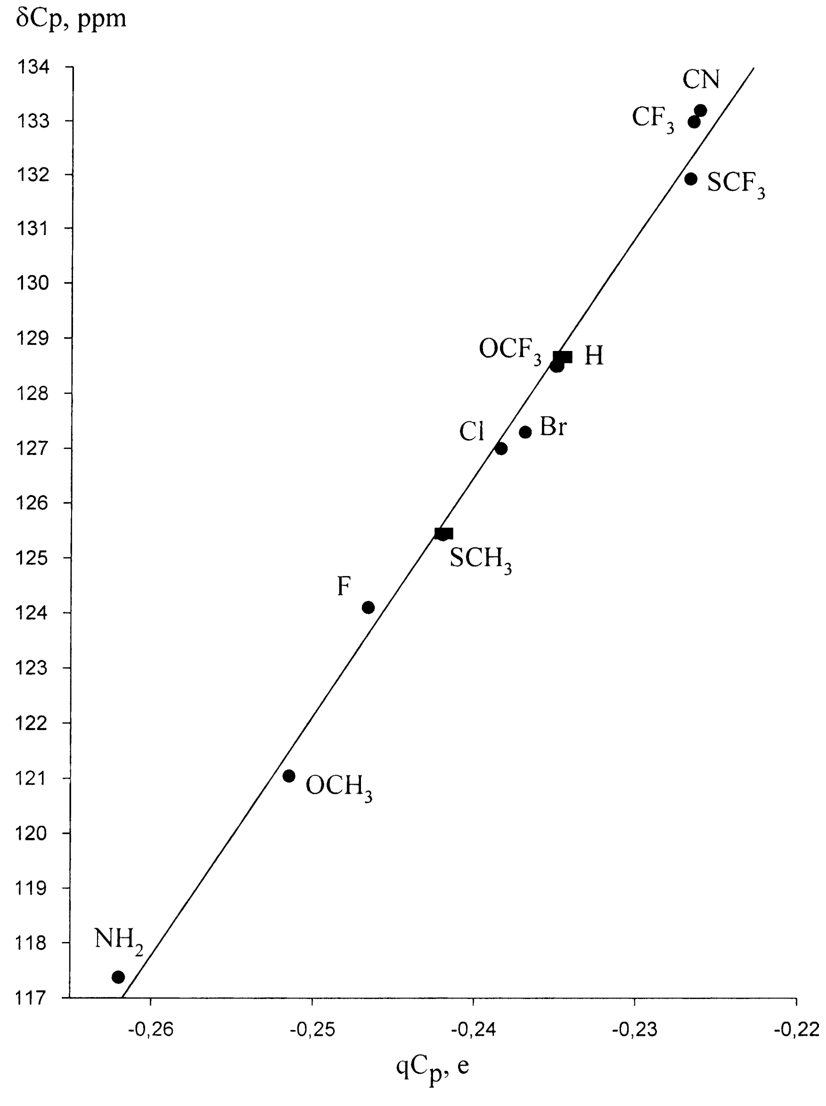

Fig. 4. Correlation between NMR ^{13}C (δC_p, ppm) chemical shifts of *para*-carbon atoms and natural charges (qC_p, electron) on these atoms in monosubstituted benzenes.

nuclei in the CH_3 group is substantially more shielded than in the CF_3 group which corresponds to the charges on these atoms, but, with a sulfur atom substituted for oxygen, the shielding of ^{13}C nuclei in the CF_3 group decreases, where in the CH_3 group it rises. In the CH_3 group, the change in δC parallels the change in the charge. In the CF_3 group, the shielding of the ^{13}C nucleus and the charge on this atom change in opposite directions as O is substituted by S. Such a substitution also causes opposite trends in the changes of shielding of the ^{19}F and ^{1}H nuclei in the CF_3 and CH_3 groups. In this case the changes in shielding of protons are opposite to the changes in the charge. The values of δO (ppm relative to H_2O; given in parentheses is the width at half-height) were found to be 112 ppm ($\nu_{1/2} = 160$ Hz) for $C_6H_5OCF_3$ and 49 ppm ($\nu_{1/2} = 190$ Hz) for $C_6H_5OCH_3$. They are in good agreement with the reported values of 113 ppm [25] ($C_6H_5OCF_3$), 45 ppm [52] and 48 ppm [53] ($C_6H_5OCH_3$). The spin–spin coupling constants ($^1J_{CF}$) are negative [49]. In absolute value the $^1J_{CF}$ in $C_6H_5OCF_3$ (−255.8 Hz) is smaller than in $C_6H_5SCF_3$ (−309.5 Hz). The $^1J_{CH}$ in $C_6H_5OCH_3$ (143.5 Hz [54]) is larger than in $C_6H_5SCH_3$ (140 Hz [54]) and the range of its variation in the thio analogs is substantially less wide.

8. Conclusion

Investigation of the potential function of internal rotation about the $C_{sp^2}{-}X$ bonds in the $C_6H_5XCF_3$ and $C_6H_5XCH_3$ ($X = O, S$) molecules at the MP2/6-31G(d) level of theory gives new information about spatial structures of these compounds. The $C_6H_5OCH_3$ molecule is planar while $C_6H_5SCF_3$ is orthogonal. $C_6H_5SCH_3$ and $C_6H_5OCF_3$ have either free rotation of the fragments about the $C_{sp^2}{-}O$ bond or molecular fragment motion with a large amplitude in the broad flat bottomed potential well and a small rotational barrier. Owing to the small rotation barrier, experimental conditions (solvent, temperature) can affect on the profile of the internal rotation potential function and markedly shift the conformation equilibrium in the $C_6H_5OCF_3$ and $C_6H_5SCH_3$ molecules. The hybridization of two LP's on the atoms O and S is different. One of the LP's comprises a hybrid orbital (with ≈40% of s-component for O and ≈70% for S). The second LP is a practically pure p-orbital. In near-planar conformations the second LP of O and S atoms interact strongly with π^*-system of the ring. In similar conformations such interaction is somewhat more effective for XCH_3 than for XCF_3 provided that the heteroatoms are the same. Interaction is substantially lowered in non-planar conformations and practically vanishes in the orthogonal form. However, in non-planar conformations, the hybridized LP of the oxygen or sulfur atom is involved in the interaction with π^*-orbitals, which peaks in the orthogonal form. For oxygen such interaction is more effective than for sulfur. The electron density in the aromatic ring is determined not only by differences in electronic effects of the XCF_3 and XCH_3 groups but also and to a large measure by their conformation.

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References

[1] I.W. Serfaty, T. Hodgins, E.T. McBee, J. Org. Chem. 37 (1972) 2651.

[2] T. Schaefer, G.H. Penner, J. Peeling, J. Baleja, Can. J. Chem. 69 (1991) 1047.

[3] M. Barnes, J.W. Emsley, T.J. Horne, G.M. Warms, G. Celebre, M. Longeri, J. Chem. Soc., Perkin Trans. 2 (1989) 1807.

[4] O.L. Shivernovskaya, G.V. Ratovskii, N.V. Kondratenko, V.N. Boyko, L.M. Yagupolskii, Ukr. Khim. Zh. 58 (1992) 687.

[5] G.N. Dolenko, N.V. Kondratenko, Izv. Akad. Nauk SSSR, Ser. Khim. (1987) 588.

[6] V.M. Bzhezovsky, G.N. Dolenko, G.A. Kalabin, Izv. Akad. Nauk SSSR, Ser. Khim. (1981)1784.

[7] V.M. Bzhezovsky, N.N. Ilchenko, N.I. Kulik, L.M. Yagupolskii, Zh. Obshch. Khim. 67 (1997) 1694.

[8] V.M. Bzhezovsky, V.V. Penkovskii, A.B. Rozhenko, S.V. Iksanova, N.V. Kondratenko, L.M. Yagupolskii, J. Fluorine Chem. 69 (1994) 41.

[9] V.M. Bzhezovsky, N.N. Illchenko, N.I. Kulik, L.M. Yagupolskii, Ukr. Khim. Zh. 63 (1997) 43.

[10] L.M. Yagupolskii, A.Ya. Ilchenko, N.V. Kondratenko, Uspekhi Khim. 43 (1974) 64.

[11] O. Exner, in: N.B. Chapman, J. Shorter (Eds.), Correlation Analysis in Chemistry. Recent Advances, Plenum Press, New York, London, 1978, p. 439.

[12] O. Exner, Correlation Analysis of Chemical Data, Plenum Press, New York, London, 1988, p. 275.

[13] L.M. Yagupolskii, Aromatic and Heterocyclic Compounds with Fluorine Containing Substituents, Naukova Dumka, Kiev, 1988.

[14] R.W. Taft, F. Price, I.R. Fox, I.C. Lewis, K.K. Andersen, G.T. Davis, J. Am. Chem. Soc. 85 (1963) 709,3146.

[15] W.A. Sheppard, R.W. Taft, J. Am. Chem. Soc. 94 (1972) 1919.

[16] W.A. Sheppard, J. Am. Chem. Soc. 85 (1965) 1314.

[17] F.S. Fawcet, W.A. Sheppard, J. Amer. Chem. Soc. 87 (1965) 4341.

[18] G.N. Dolenko, N.V. Kondratenko, V.I. Popov, L.M. Yagupolskii, Izv. Akad. Nauk SSSR, Ser. Khim. (1987) 336.

[19] A.E. Lutskii, L.M. Yagupolskii, E.M. Obuchova, Zh. Obshch. Khim. 34 (1964) 2641.

[20] M.J. Aroney, R.J.W. LeFevre, R.K. Pierens, M.G.N. The, J. Chem. Soc. B (1969) 666.

[21] M.J. Aroney, R.J.W. LeFevre, R.K. Pierens, M.G.N. The, J. Chem. Soc. B (1971) 1132.

[22] I.I.M. Schuster, J. Magn. Reson. 17 (1975) 104.

[23] R.A. Newmark, J.R. Hill, G.V.D. Tiers, Magn. Reson. Chem. 26 (1988) 612.

[24] V.M. Bzhezovsky, L.M. Yagupolskii, S.V. Iksanova, N.V. Kondratenko, I.A. Aliev, A.A. Kudryavtsev, R.Yu. Garlyauskayte, Ukr. Khim. Zh. 57 (1991) 1310.

[25] D.W. Boykin, Spectrosc. Lett. 24 (1991) 943.

[26] A.D. Baher, D.P. May, D.W. Turner, J. Chem. Soc. B (1968) 22.

[27] T. Yanagisawa, S. Tajima, M. lizuka, T. Matsumoto, Int. J. Mass Spectrom. Ion Processes 125 (1993) 55.

[28] W.A. Sheppard, C.M. Sharts, Organic Fluorine Chemistry, Benjamin, New York, 1969.

[29] G.A. Olah, T. Yamato, T. Hashimoto, J.G. Shih, N. Trivedi, B.P. Singh, M. Piteau, J.A. Olah, J. Am. Chem. Soc. 109 (1987) 3708.

[30] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

[31] Ch. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618.

[32] Gaussian 98W (Revision A.7), M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Adamo, S. Clifford, J. Ocherski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T.A. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

[33] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

[34] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

[35] F. Weinhold, J.E. Carpenter, in: R. Naaman, Z. Vager (Ed.), The Structure of Small Molecules and Ions, Plenum Press, New York, 1988, 227.

[36] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO, Version 3.1.

[37] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.

[38] W.J. Orville-Thomas (Ed.), Internal Rotation in Molecules, Wiley, London, New York, 1974.

[39] H.M. Seip, R. Seip, Acta Chem. Scand. 27 (1973) 4024.

[40] M. Onda, A. Toda, S. Mori, I. Yamaguchi, J. Mol. Struct. 144 (1986) 47.

[41] M.A. Vincent, I.H. Hillier, Chem. Phys. 140 (1990) 35.

[42] D.C. Spellmeyer, P.D.J. Grootenhuis, M.D. Miller, L.F. Kuyper, P.A. Kollman, J. Phys. Chem. 94 (1990) 4483.

[43] J.B. Nicholas, B.P. Hay, J. Phys. Chem. 103 (1999) 9815.

[44] N.M. Zaripov, Zh. Strukt. Khim. 17 (1976) 741.

[45] V.M. Bzhezovsky, E.G. Kapustin, N.N. Ilchenko, N.I. Kulik, L.G. Gorb, Zh. Obshch. Khim. 70 (2000) 1876.

[46] A. Bondi, J. Phys. Chem. 68 (1964) 441.

[47] B. Smart, Fluorinated Bioactive Compounds in Agricultural and Medicinal Fields, Brussels, September 1999, Paper No. 3.

[48] A.E. Reed, R.B. Weinstok, F. Weinhold, J. Chem. Phys. 83 (1985) 735.

[49] H.-O. Kalinowski, S. Berger, S. Braun, 13C-NMR-Spektroskopie, Georg Thieme, Stuttgart, 1984.

[50] W.J. Hehre, R.W. Taft, R.D. Topsom, Prog. Phys. Org. Chem. 12 (1976) 159.

[51] D.F. Ewing, Org. Magn. Reson. 12 (1979) 499.

[52] H.A. Christ, P. Diehl, H. Schneider, H. Dahn, Helv. Chim. Acta 44 (1961) 865.

[53] M. Katoh, T. Sugawara, Y. Kawada, H. Iwamura, Bull. Chem. Soc. Jpn. 52 (1979) 3475.

[54] G. Llabres, M. Baiwer, Can. J. Chem. 56 (1978) 2008.