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Multinuclear NMR spectroscopy and semi-empirical MNDO-PM3 quantum chemical investigations of the compounds C_6H_5XY ($X=S$, SO, SO_2; $Y=CF_3$, CH_3)

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Abstract

The compounds $C_6H_5XCF_3$ and $C_6H_5XCH_3$ ($X=S$, SO, SO_2) have been investigated by multinuclear ^1H, ^{13}C, ^{17}O, ^{19}F and ^{33}S NMR spectroscopy and quantum chemical methods (MNDO in the PM3 parametrization). Compounds with XCF_3, $SOCH_3$ and SO_2CH_3 groups have been characterized with effective non-planar conformations. A nearly planar effective conformation has been found for $C_6H_5SCH_3$. As the two lone pairs (LP) of sulphur in the sulphides are essentially non-equivalent with their orbital energies differing considerably, only one LP (with a higher energy level) can participate in the p–π conjugation. In compounds with XCF_3, $SOCH_3$ and SO_2CH_3 groups, the electron-withdrawing π-inductive effect is the main factor determining the π-charge distribution in the benzene ring. The p–π conjugation is essentially distorted in $C_6H_5SCF_3$ due to its various conformations. Electron-donating p–π conjugation only contributes considerably to the π-charge distribution in the benzene ring in $C_6H_5SCH_3$. An interpretation of the NMR spectra of the considered compounds is given on the basis of the quantum chemical calculations.

Introduction

Intramolecular interactions in and the reactivity of trifluoromethyl and methyl phenyl sulphides and analogous sulphoxides and sulphones have been studied previously by various physical and chemical methods [1–4]. The structural constants characterizing the inductive and resonance effects of the XCF_3 and XCH_3 groups ($X=S$, SO, SO_2) are well known and there is no doubt concerning their electron-withdrawing effect [3–6]. The σ_I constants vary from 0.13 (SCH_3) to 0.78 (SO_2CF_3). The resonance constants are close to zero for the SCF_3 and SCH_3 groups while the $SOCF_3$, SO_2CH_3 and (especially) SO_2CF_3 substituents reveal a strong electron-withdrawing resonance effect; in contrast, the SCH_3 group is a weak resonance donor. In all cases, for the same X moieties, XCF_3 groups show stronger electron-withdrawing properties than XCH_3 groups.

The concept of the participation of the unoccupied 3d sulphur orbital in the chemical bonding (3d–π conjugation) is often used as an explanation of the electron-withdrawing effect of the XCF_3 and SO_2CH_3 groups on the π system of an aromatic moiety [1–4]. However, experimental methods and semi-empirical calculations have been incapable of supplying unambiguous arguments supporting this concept, whilst within the framework of *ab initio* calculations the role of the 3d sulphur orbitals has not been completely elucidated (see, for example, refs. 7 and 8). To our knowledge, no investigations concerning the possibility of 3d–π interaction between the sulphur atom and the unsaturated moieties have been performed hitherto using quantum chemical *ab initio* methods with extended basis sets. The mechanism of the interaction of the CF_3 and CH_3 groups with neighbouring atoms or fragments is also thought to be related to ‘negative’ and ‘usual’ hyperconjugation, polarization effects, etc. [1–4, 9]. However, many of these effects are open to criticism. Hence, simple and illustrative interpretation of the results of physical and chemical experiments requires the determination of the main types of intramolecular interactions.

This paper presents the results of investigation of compounds **1–6** using multinuclear ^1H, ^{13}C, ^{17}O, ^{19}F and ^{33}S NMR spectroscopy and the quantum chemical SCF MO LCAO method in the semi-empirical MNDO PM3 approximation [10].

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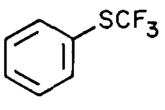

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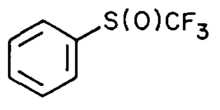

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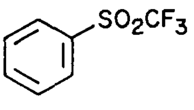

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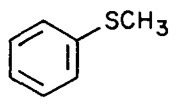

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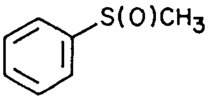

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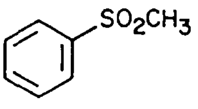

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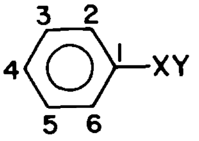
Quantum chemical calculations

The geometry of compounds **1**–**6** was completely optimized. The geometric parameters obtained are listed in Table 1. Because of the possible different orientations of the CF_3 and CH_3 groups relative to the Ph–S plane, the internal rotation of these groups about the C_{sp^2}–S bond was considered. The corresponding potential curves for compounds **1** and **4** are given in Figs. 1 and 2; the barriers to internal rotation $\Delta H^{\#}$ from the planar conformation (the CF_3 and CH_3 rotation angle $\varphi = 0°$) to the orthogonal one ($\varphi = 90°$) are 4.1 and 5.3 kJ mol^{-1}, respectively. The latter value agrees well with the results of the long-range spin–spin interaction measurement in the NMR spectrum of **4** (5.5 kJ mol^{-1}) and with the *ab initio* calculations using the STO-3G basis set [11]. A local minimum at $\varphi = 0°$ (enthalpy of formation $\Delta H = -448.9$ kJ mol^{-1}) and two deep minima at $\varphi = 70°$ ($\Delta H = -452.7$ kJ mol^{-1}) and $\varphi = 90°$ ($\Delta H = -453.0$ kJ mol^{-1}) are observed in the rotation potential curve of **1**. Analysis of the UV and IR spectra of **1** [12] leads to the conclusion that this compound is a mixture of planar and orthogonal conformers, the latter being predominant.

An analysis of the photoelectronic spectrum of **4** also indicates the existence of two conformers although the planar predominates (estimated 90% [13] or 77% [14]), whereas the difference in the total (binding and vibrational) energy of the conformer is 3.5 ± 0.3 kJ mol^{-1} [14]. Similar conclusions have been drawn from an interpretation of the UV and IR spectra of **4** [15, 16]. Measurement of the dipole moments and molar Kerr constants [17] indicate that $\varphi = 23°$ for molecule **4**. The gas-phase electron diffraction data for **4** show a best fit with the theoretical model at $\varphi = 45 \pm 10°$ [18].

TABLE 1. Geometrical parameters of trifluoromethyl phenyl sulphides, sulphoxides and sulphones and their methyl analogues (MNDO-PM3)



(X = S, SO, SO_2; Y = CF_3, CH_3)

Compound	Angles (°)			Bond lengths (pm)			
	φ	C_1SC_Y	C_1SO	$S-C_1$	$S-C_Y$	S=O	$C_Y-F(H)$
Y = CF₃							
1	0	106.8		176	192		135
	87	102.6		176	193		135
2	70	98.8	106.4	178	200	152	135
	90	98.8	106.6	178	200	152	135
3	76	98.2	112.4	175	202	143	135
	90	98.2	112.4	175	202	143	135
Y = CH₃							
4	0	105.8		176	180		110
	45	(105.6)[a]		(179)[a]	(180)[a]		
	90	102.3		177	181		110
5	71	99.5	106.0	180	182	156	110
	82	98.9	106.1	180	183	156	110
6	72	100.7	109.8	177	177	144	112
	86	99.9	109.9	178	179	147	110

[a] Gas-phase electron diffraction [18].

Fig. 1. The potential energy curve relating to internal rotation of the CF_3 group about the C_1-S bond for compound 1 (for notes see Table 1).

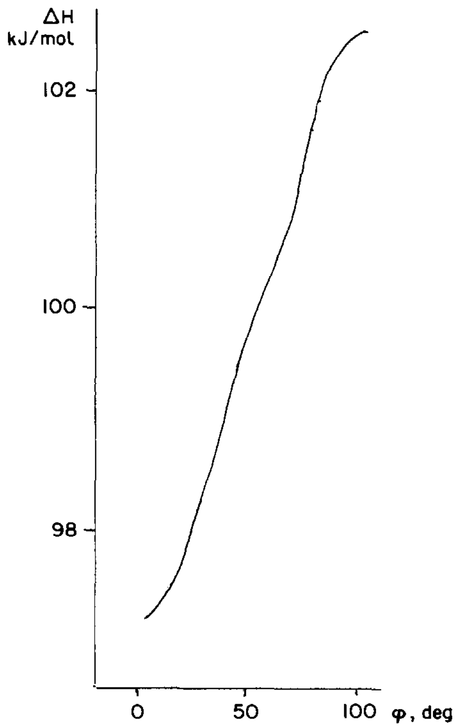


Fig. 2. The potential energy curve relating to internal rotation of the CH_3 group about the C_1-S bond for compound 4 (for notes see Table 1).

By optimizing the molecular geometry of the sulphoxides and sulphones we have established minima at the following φ values (the respective ΔH values in kJ mol^{-1} are given in brackets): **2**, 70° (−573.9) and 90° (−575.6); **3**, 76° (−725.6) and 90° (−724.2); **5**, 71° (−15.9) and 82° (−15.1); and **6**, 72° (−172.5) and 90° (−172.9). Studies of the molar Kerr constants of **5** and **6** [19] led to the conclusion that the most probable φ values are $70 \pm 5°$ and $58 \pm 8°$, respectively.

Hence the non-planar conformers (close to the orthogonal) predominate for compounds **1–3**, **5** and **6**, and a nearly planar conformation is characteristic of compound **4**. In fact, owing to the low energy barriers to internal rotation, the factors affecting conformational equilibrium in the above systems are rather provisional and depend on the methods of measurement or calculation. Hence, compounds **1–6** may be characterized, to a first approximation, by an 'effective' conformation statistically averaged over all the conformers.

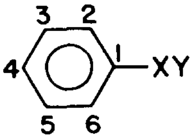
The charge distribution characteristics of compounds **1–6** are presented in Table 2. The charge on the sulphur atom is positive in all cases and increases for higher oxidation states or (at similar X) with the replacement of methyl by the trifluoromethyl group. It is compensated by negative charges on the C_6H_5, CF_3 or CH_3 groups (except for compound **4**) and by those on the oxygen atoms in sulphoxides and sulphones. The electron density on these fragments increases in the series sulphides < sulphoxides < sulphones, and is higher on the aromatic fragment and the oxygen atoms for methyl-substituted compounds with the same X moieties.

The bond orders $S-C(Y)$ in compounds **1–3** (**1**, 0.895; **2**, 0.671; **3**, 0.522) and compounds **4–6** (**4**, 0.999; **5**, 0.861; **6**, 0.741) decrease as the electronegativities of the X moieties increase; with unchanged X they are higher in compounds **4–6** since $S-C(CH_3)$ bonds are shorter than $S-C(CF_3)$ bonds. If the $C-F$ and $C-H$ bonds participated in the hyperconjugation, the opposite trend in these bond orders would be anticipated for various X moieties (the 'negative' and 'usual' hyperconjugation effects). However, the calculated $C-F$ and $C-H$ bond orders are nearly constant (0.966–0.967 and 0.978–0.980, respectively).

The charge on the C_1 atom and its π component increases for both compounds **1–3** and **4–6** in the series sulphides < sulphoxides < sulphones; the charge on the C_4 atom decreases in the same order. With X unchanged, the total and π-electron density on the C_1 atom in the series **1–3** is higher than for the series **4–6**; a reverse tendency is observed for the C_4 atom. These results indicate an increase in the aromatic ring polarization towards the XCF_3 (XCH_3) moiety with increasing electronegativity of the latter.

The most convincing indicators of aromatic ring polarization are the total charge (q_t) and the π charge (q_π) on the C_4 atom. The σ charge (q_σ) on the C_4 atom shows little change for compounds **1–6** (in the range 0.001e). Only for sulphide **4** is a small π-electron density excess (−0.001e) observed on the C_4 atom; in

TABLE 2. Torsion angles φ (°), enthalpies of formation ΔH (kJ mol^{-1}), total charges on atoms q_t(e) and π charges q_π(e) in compounds



(X=S, SO, SO_2; Y=CF_3, CH_3)

Parameter	Compound											
	1	1	1	2	2	3	3	4	5	5	6	6
φ	60	70	87	70	90	76	90	0	71	82	72	86
ΔH	−452.1	−452.7	−452.9	−573.9	−575.6	−723.6	−724.2	97.1	−15.9	−15.1	−172.5	−172.9
q_t(S)	0.122	0.120	0.118	1.060	1.055	2.302	2.303	0.085	0.995	0.998	2.240	2.239
q_t(O)				−0.622	−0.624	−0.793[a]	−0.793[a]		−0.692	−0.691	−0.836[a]	−0.836[a]
Σq_t(Ph)	−0.014	−0.009	−0.004	−0.140	−0.134	−0.258	−0.259	−0.108	−0.194	−0.192	−0.313	−0.312
Σq_t(Y)	−0.108	−0.111	−0.113	−0.300	−0.297	−0.457	−0.457	0.023	−0.110	−0.109	−0.255	−0.255
$q_t(C_1)$	−0.230	−0.239	−0.247	−0.418	−0.418	−0.610	−0.612	−0.173	−0.380	−0.382	−0.567	−0.569
$q_\pi(C_1)$	−0.121	−0.127	−0.133	−0.158	−0.158	−0.213	−0.214	−0.054	−0.109	−0.111	−0.158	−0.159
$q_t(C_4)$	−0.059	−0.052	−0.048	−0.043	−0.043	−0.025	−0.024	−0.104	−0.067	−0.065	−0.048	−0.047
$q_\pi(C_4)$	0.044	0.050	0.054	0.060	0.060	0.078	0.078	−0.001	0.035	0.036	0.054	0.054
$q_t(C_Y)$	0.276	0.274	0.273	0.098	0.099	−0.054	−0.054	−0.199	−0.365	−0.362	−0.559	−0.559
Σq_t/3(F,H)	−0.128	−0.128	−0.128	−0.132	−0.132	−0.134	−0.134	0.074	0.085	0.084	0.101	0.101

[a] Σq_t(O)/2 values.

other compounds, the q_π values on the C_4 atom are positive. The weak electron-donating effect of the SCH_3 group towards the aromatic ring in **4** is caused by the lone pair (LP) overlapping with the ring π system owing to the nearly planar conformation of **4**.

In sulphide **1** and sulphoxides **2** and **5**, the sulphur LPs deviate substantially from the aromatic π system, so that p–π overlap should be negligible. This fact, in combination with the strong S−O and C−F bond polarization in these compounds, leads to a predominance of the withdrawing effect of the XCF_3 (XCH_3) moiety which polarizes the π system towards the C_1 atom. This also occurs for sulphones **3** and **6**. These phenomena correspond to a π-inductive effect [9, 20]. This is local within the aromatic ring and manifests itself most probably via an electrostatic mechanism (monopole–monopole or monopole–dipole interaction). We believe that this effect, rather than p–π or d–π delocalization interactions, determines the resonance constant values of the XCF_3 (XCH_3) groups in the compounds under consideration.

Conformational perturbation of p–π conjugation in the alkyl aryl ethers, sulphides and selenides with various alkyl substituents has been considered experimentally [13, 21–24]. The conformational resonance inhibition in compounds **1** and **4** may be analyzed using the Σq_π, Σq_σ and Σq_t values for the aromatic ring, as well as the q_t(S), $\Sigma q_t(CF_3)$ and $\Sigma q_t(CH_3)$ values, in the range of φ values from 0° to 90° (Table 3). With increased tilting of the CF_3 and CH_3 groups towards the ring plane (i.e. with an increased φ value), the total and π-electron densities in **1** and **4** decrease over all the

TABLE 3. Charge distribution ($q \times 10^3$, e) with a change in φ angle from 0° to 90° in trifluoromethyl and methyl phenyl sulphides

Molecule	Parameter	Torsion angle φ									
		0	10	20	30	40	50	60	70	80	90
1	$\Sigma q_t(Ph)$	−40	−38	−37	−32	−24	−19	−14	−9	−6	−4
	$\Sigma q_\pi(Ph)$	−44	−42	−37	−26	−13	1	13	24	32	35
	$\Sigma q_\sigma(Ph)$	4	4	0	−6	−11	−20	−28	−33	−38	−39
	$q_t(S)$	135	133	134	130	125	124	122	120	119	118
	$\Sigma q_t(CF_3)$	−95	−96	−97	−98	−101	−105	−108	−111	−113	−113
4	$\Sigma q_t(Ph)$	−108	−107	−104	−99	−92	−86	−80	−74	−70	−69
	$\Sigma q_\pi(Ph)$	−59	−57	−52	−43	−32	−21	−10	0	6	9
	$\Sigma q_\sigma(Ph)$	−49	−50	−52	−56	−60	−65	−71	−74	−76	−77
	$q_t(S)$	85	84	82	78	72	66	60	56	53	51
	$\Sigma q_t(CH_3)$	23	22	22	22	21	20	20	18	18	18

benzene ring and increase on the sulphur atom, while the σ-electron density increases on the CF_3 and CH_3 groups, perhaps due to an decrease in sulphur electronegativity. The types of change for the Σq_π, Σq_σ and Σq_t values for the aromatic ring at φ variations from 0° to 90° are shown in Fig. 3 for compound **1**; qualitatively similar values apply to compound **4**. The charges on the aromatic ring atoms for this φ variation are: in **1**, −0.043e (C_1), 0.127e ($C_{2,6}$), −0.043e ($C_{3,5}$), 0.038e (C_4); in **4**, −0.036e (C_1), 0.108e ($C_{2,6}$), −0.035e ($C_{3,5}$), 0.031e (C_4), (where the negative sign indicates an increase in the π-electron density).

Additional data concerning the character of the interaction of the XCF_3 or XCH_3 groups (X = S, SO, SO_2) with the aromatic ring may be obtained from changes in the calculated MO energies and structure in the series **1**-**6** (Fig. 4). Comparison of the photoelectron spectra of compounds **4**–**6** [14, 25, 26] with our calculations show that these are reproduced at least as far as the sequence of the higher occupied orbitals is concerned, their energy being overestimated by only 0.4–0.7 eV. The conformational variance of **1** and **4** leads to striking differences for the HOMO energies. The sulphur LP orbital is a major contributor to the HOMO of both compounds. However, in the case of compound **4** it is combined with the contribution of the benzene π MO ($n\pi$ HOMO) while the HOMO of **1** belongs to the n type as it is completely localized on the sulphur atom, with its axis in the aromatic ring plane (the $p\sigma$ sulphur AO contributions are 74% and 24%); this provides evidence for the lack of p–π conjugation (n HOMO). For this reason, the degeneracy of the $\pi(e_g)$ benzene MO is almost completely retained in compound **1**. The next MO of σ type is localized on the C−S bond. The character of the occupied MO sequence of **1** is the same as that of the orthogonal conformer of **4** observed by photoelectron spectroscopy at elevated temperature [14]. As the conformation of **1** is close to orthogonal, the energies of the HOMO and occupied π MO are lower than those of compound **4** by 1.6 and 0.4 eV, respectively. In the conformations of **1** with $\varphi = 70°$ and $\varphi = 0°$, the sequence of occupied molecular orbitals remains unchanged, but in the latter case the HOMO energy increases by 0.9 eV while the $\pi(b_1)$ MO energy decreases by 1.0 eV.

In both compounds, the sulphur LP orbitals are energetically non-equivalent. In compound **1**, the second n MO level is lower than the HOMO by 10.3 eV (the sulphur s, p_x, p_y and p_z contributions are 3, 11, 34 and 1%, respectively). In compound **4**, the second n MO is combined with the benzene σ MO, due to the similar structure but higher energy; the level of the highest of these $n\sigma$ MOs is just below that of the $n\pi$ HOMO and the π MO, its energy being lower by 3.0 eV than the HOMO energy. The regularities in the spectra of compounds **2** and **3** and their methyl analogues **5** and **6** are similar. The HOMO of **2** and **5** is the antibonding combination of the sulphur and oxygen LP orbitals ($n_S - n_O$), the next two MOs are the π orbitals of the benzene ring. The latter MOs are highest in the case of sulphones **3** and **6** (with the HOMO being of the $\pi(a_2)$ type) followed by the $n\sigma$ MO. Due to the low symmetry of the molecules, all the MOs contain some contributions from other AOs. Our calculations indicate π MO splitting (about 0.3 eV) in all cases; this value seems to be an overestimate since it is equal to 0.08 eV [25] in the spectrum of **5** and is not observed at all for **6** [26].

Substitution of the methyl group by the more electronegative CF_3 groups leads to a lowering of the n and π MO energies by 0.5 and 1.0 eV, respectively. The influence of such substitution on the LUMO level in the series **1**–**6** is greater. The LUMO is of the $\pi^*(b_1)$ type. In the case of compounds **1**–**3**, a noticeable contribution is also made by the $\sigma(SC)$ MO, and the LUMO energy is lower by 0.9–1.3 eV as compared with the methyl analogues **4**–**6**. The π MO splitting increases from 0.3–0.5 eV for **4**–**6** to 1.0–1.5 eV for **1**–**3**. The

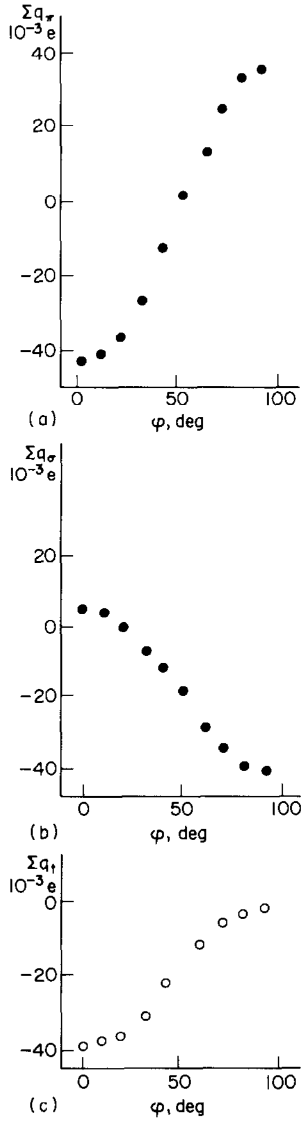


Fig. 3. Changes in the (a) Σq_π, (b) Σq_σ and (c) Σq_t values on the aromatic ring of compound **1** for variations in the angle φ from 0° to 90°.

phenyl ring σ* MO energy of **1–3** is also lowered due to the electron-withdrawing effect of the XCF_3 substituents and becomes lower than the $\pi^*(b_1)$ MO energy in contrast to the situation in compounds **4–6**.

Hence, the results of calculations of the electron-density distribution, as well as those of the MO energies and structure of **1–6**, indicate that the electronic effects of the SCF_3, XCF_3 and XCH_3 substituents (X = SO, SO_2) are mainly σ and π inductive in nature. In both series of compounds, the electron density increases on the $C(CF_3)$, $C(CH_3)$ and F atoms, and decreases on the methyl hydrogens in the series sulphides < sulphoxides < sulphones. A considerable electron-density deficiency is observed on the $C(CF_3)$ atoms as compared with the $C(CH_3)$ atoms, due to the strong polarization of the C−F bond.

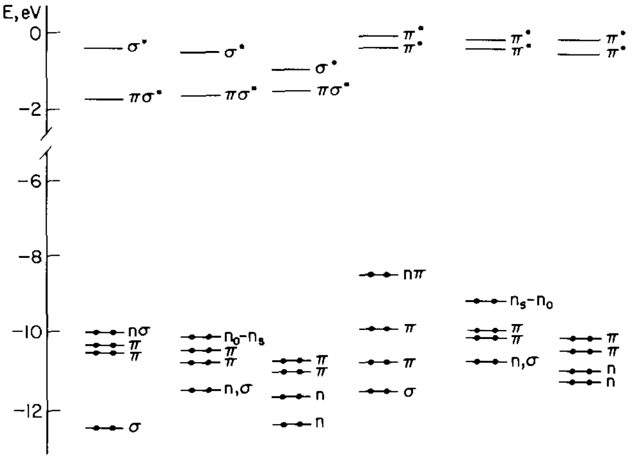


Fig. 4. MO energies and structure for compounds **1–6**.

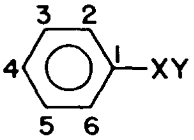
NMR spectra

Selected data on ^1H, ^{13}C and ^{19}F NMR chemical shifts (δH, δC and δF, respectively) of compounds **1–6** are presented in Table 4. Interpretations of the δC_1 and $\delta C_{2,6}$ values in aromatic sulphides, sulphoxides and sulphones have been attempted by various authors [27–29]. However, no definite conclusions were drawn about the dependence of the ^{13}C shielding on the steric and electronic effects. The changes in the δC_1 and $\delta C_{2,6}$ values for compounds **1–6** are difficult to explain starting from the usual concepts of the electronegativity increase of the X moieties in the series $S < SO < SO_2$. However, some regularities may be noted. Thus, with the same X moieties, the ^{13}C shielding is higher for compounds **1–3** relative to compounds **4–6**. The corresponding tendencies in the $^{13}C_{2,6}$, $^{13}C_{3,5}$ and $^{13}C_4$ shielding are opposite. The observed effect is obviously the consequence of the stronger polarization of the aromatic π system (π-inductive effect) by XCF_3 substituents as compared with XCH_3 groups. The prevailing σ-inductive effect should lead to opposite changes in the δC_1 value, owing to the increased C_1-X bond polarity.

Our experimental results indicate that in each of the series (**1–3** and **4–6**) studied the ^{13}C nuclei are the most shielded in sulphides and the least shielded in sulphones. This is possibly related to the through-space electrostatic interaction between the strongly polarized $\overset{\delta+}{S}=\overset{\delta-}{O}$ and $C_1 \cdots C_{2,6}$ bonds by a dipole-induced dipole ($\underset{\delta-}{C}_1 \cdots \underset{\delta+}{C}_{2,6}$) mechanism in sulphones which is less important in sulphoxides.

Correlations of the δC_4 values for the benzene derivatives C_6H_5X (where X is a functional group containing elements of the second period in the Periodic Table) with the total (σ+π) and π charge values on the C_4 atom are well known [30–32]. The charges were calculated using the CNDO method [30, 31] or *ab initio* method with the minimal STO-3G basis set [32]. We

TABLE 4. NMR chemical shifts ^1H (δH_i, ppm, TMS), ^{13}C (δC_i, ppm, TMS), ^{19}F (δF_i, ppm, $CFCl_3$), ^{17}O (δO, ppm, H_2O) and ^{33}S(δS, ppm, CS_2) for trifluoromethyl phenyl sulphides, sulphoxides and sulphones, and their methyl analogues



($X = S$, SO, SO_2; $Y = CF_3$, CH_3)

Compound	δC_1	$\delta C_{2,6}$	$\delta C_{3,5}$	δC_4	δC_Y	δF	δH^a	δO ($\nu_{1/2}$)^b	δS ($\nu_{1/2}$)^b
1	124.71	137.07	130.51	131.93	130.64	−43.18			
2	136.90	126.72	130.59	134.47	125.86	−75.14		−2.0 (120)	
3	131.87	131.28	131.61	138.12	120.85	−78.90		134.0 (110)	308 (1000)
4	139.35	126.90	129.45	125.43	15.40		2.35		
5	147.07	124.09	129.83	131.31	43.84		2.71	1.0 (120)	
6	142.19	127.88	129.96	134.08	44.24		3.12	154.0 (90)	319 (40)

[a] Methyl protons.
[b] Resonance signal line width, Hz.

found that the q_t and q_π values for the C_4 atom in compounds **1**–**6** calculated by the MNDO-PM3 method also correlate well with the δC_4 values in these compounds (Fig. 5):

$$\delta C_4 = 141.53(\pm 0.35) + 156.29(\pm 5.60) q_t(C_4),$$

$$r = 0.998,\ S_0 = 0.37,\ n = 5$$

$$\delta C_4 = 125.54(\pm 0.28) + 156.08(\pm 5.19) q_\pi(C_4),$$

$$r = 0.998,\ S_0 = 0.31,\ n = 5$$

Hence, it is reasonable to relate changes in the δC_4 values with the redistribution of total and π charges in **1**–**6**. We have shown above that the electron density changes on the C_4 atom of these compounds are mainly determined by the changes in the π charge. It follows from the δC_4 values that a π-electron density excess on the C_4 atom is only observed in compound **4**. The shielding of the C_4 nuclei in this molecule is higher than in benzene (128 ppm [33]). This is a consequence of the increased π charge on the C_4 atom due to the p,π conjugation of the sulphur atom with the aromatic ring, in agreement with our calculations. In other compounds, the C_4 nuclei are markedly deshielded (Table 4). Hence, the XY substituents in **1**–**3** and **5** and **6** are electron-withdrawing relative to the π system of the aromatic ring.

Considerable deviation from the linear plot presented in Fig. 5 is observed only for compound **1** when $\varphi = 90°$. If the strong dependence of the charge on the C_4 atom on the φ value in sulphides (see Table 3) is taken into account, one may assume that the effective conformation of **1** corresponds to an angle $\varphi \approx 60°$, i.e. close to a φ value of 70°, at the calculated potential energy minimum (Fig. 1). Based on the total π-charge value on the aromatic ring and assuming 100% distortion of the p–π interaction at $\varphi = 90°$ as compared with the planar

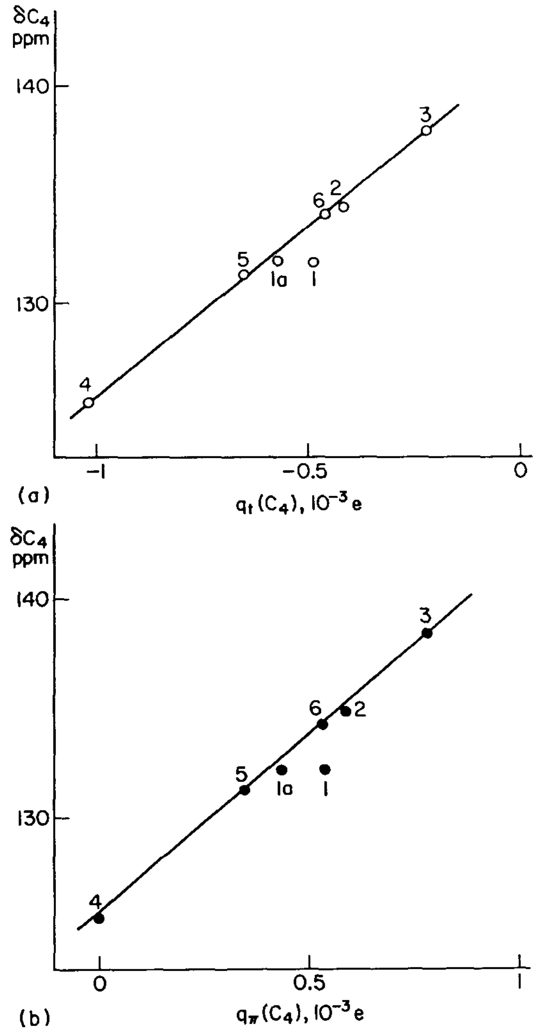


Fig. 5. The dependence of δC_4 on (a) the total charge q_t and (b) the π charge q_π on the carbon atom in the *para* position of the aromatic ring in compounds **1**–**6**. The point 1a corresponds to the conformation of molecule **1** with $\varphi = 60°$ in both cases.

conformer, we may estimate approximately that the reduction in the considered effect at $\varphi = 60°$ and $\varphi = 70°$ is 73% and 88%, respectively.

Interestingly, the δC_4 values in compounds **2** and **6** differ only by 0.39 ppm. Very close values for δC_4 have also been obtained for compounds **1** and **5**. Hence, substitution of atoms Y = H by Y = F in the CY_3 groups and oxidation of the sulphur atom ($S^{II} \rightarrow S^{IV}$, $S^{IV} \rightarrow S^{VI}$) are almost equivalent in their influence on the δC value in the *para* position of the benzene ring.

The ^{17}O NMR chemical shifts in compounds **2**, **3**, **5** and **6** are presented in Table 4. The shielding of the ^{17}O nuclei in **2** and **5** is nearly the same, whereas in sulphones it increases with substitution of the atoms Y = H by Y = F in the CY_3 group.

We have only measured the ^{33}S NMR chemical shifts in sulphones **3** and **6** (Table 4); in the ^{33}S NMR signals cannot be detected in sulphoxides as they are very broad [34]. Despite the large ^{33}S NMR signal linewidth, and hence the low accuracy of the chemical shift measurement, it should be noted that shielding of the ^{33}S nuclei, like ^{17}O, is higher in compounds with a CF_3 group than in methyl-substituted compounds. Comparison of the ^{13}C and ^{17}O NMR chemical shifts (δC and δO) in the carbonyl groups of the ketones $C_6H_5COCF_3$ (**7**) and $C_6H_5COCH_3$ (**8**) leads to the same result: compound **7**, δC = 180.52 ppm, δO = 543 ppm; compound **8**, δC = 197.75 ppm, δO = 552 ppm [35]. Hence, in compounds $C_6H_5XCF_3$ (X = S, SO_2 or CO) shielding of the ^{33}S, ^{17}O and ^{13}C nuclei is higher in comparison to compounds $C_6H_5XCH_3$ when the X moieties are the same. However, the results of our quantum chemical calculations of **2**, **3**, **5** and **6** indicate that the electron density on the O and S atoms is higher in the methyl-substituted compounds for similar X moieties. Hence an obvious discrepancy is observed between the electron-density changes on these atoms and the shielding of the ^{33}S and ^{17}O nuclei on the replacement of the CF_3 group by the CH_3 group.

With an increase in the sulphur oxidation state ($S < SO < SO_2$), the ^{13}C and ^{19}F shielding in the CF_3 group of compounds **1**–**3** increases while the ^{13}C and ^{1}H shielding in the CH_3 group of compounds **4**–**6** decreases. We believe that this occurs for the following reasons. In compounds **1**–**3** the carbon atom of the CF_3 group is strongly depleted of electron density owing to the high polarity and rigidity of the C−F bonds. This is shown by the δC values of this atom (120.85–130.64 ppm) and by the results of our quantum chemical calculations. Hence, the increase of the ^{13}C and ^{19}F shielding in the series **1** < **2** < **3** arises from the total electron density increase on the CF_3 group with increasing electron-density deficiency on the X moiety. The calculated charges on the C and F atoms of the CF_3 groups also increase in the same series.

The electron density on the $C(CH_3)$ atom in compounds **4**–**6** is much higher than on the $C(CF_3)$ atom in compounds **1**–**3**, due to the low polarization of the C−H bonds; the $\delta C(CH_3)$ values vary from 15.40 to 44.24 ppm. For this reason, the C−H bonds in **4**–**6** are much more labile and polarizable in comparison with **1**–**3**. Thus the increased electronegativity of the X moiety ($S < SO < SO_2$) leads to deshielding of the ^{13}C and ^{1}H nuclei in the CH_3 group, according to the usual inductive mechanism. The quantum chemical calculations confirm the electron density decrease on the hydrogen atoms of the CH_3 group in the series **4** < **5** < **6**; however, they predict the electron density increase on the methyl carbon atoms in this series.

Experimental

Compounds **1**–**3** were prepared according to procedures described previously [4]. All NMR spectra were recorded on a Varian VXR-300 spectrometer. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were obtained at working frequencies of 299.944 MHz and 75.43 MHz, respectively. The chemical shifts are referenced to TMS. The ^{33}S NMR spectra were recorded using a Varian VXR-300 spectrometer at 23.03 MHz, the 10 mm broadband probe being employed (frequency interval 30.1–125 MHz) with an additional frequency interval broadening towards low frequencies. To eliminate 'acoustic ringing', the pulse sequence ACOUSTIC [36] was used. The ^{33}S NMR spectra were measured using deuterium stabilization of the resonance. The exponential signal broadening was 5–20 Hz. The accuracy of the δS measurements was *c.* 0.3 ppm. Sulpholane was used as the internal reference; the δS values obtained were scaled relative to the ^{33}S signal in CS_2 (δS = 0 ppm). Proton decoupling was used to achieve additional narrowing of signals., The ^{17}O NMR spectra (40.67 MHz) were obtained without deuterium stabilization of the resonance conditions. Water (δO = 0 ppm) was used as the internal reference. To avoid baseline distortions due to acoustic ringing, a 100 μs delay was introduced before data acquisition. The exponential signal broadening was 10–100 Hz. The accuracy of the δO measurements was *c.* 0.5 ppm. The ^{19}F NMR spectra (292.21 MHz) were recorded under standard conditions ($CFCl_3$ as internal reference). The samples used for investigation were as 20%–30% solutions in acetone-d_6. The ^{33}S, ^{17}O and ^{13}C NMR spectra were recorded at room temperature in 10 mm sample tubes. The ^{1}H and ^{19}F NMR spectra were obtained using 5 mm sample tubes.

Conclusion

According to our results, compounds **1–3** and **5** and **6** are characterized by non-planar, nearly orthogonal effective conformations. The effective conformation of **4** is nearly planar. The two LPs of sulphur in sulphides are essentially non-equivalent, their orbital energies differing considerably, and only one LP (that with a higher energy level) can participate in p–π conjugation. The electron-donating effect associated with p–π conjugation contributes considerably to the electron-density distribution in the aromatic ring in **4**, owing to its nearly planar conformation. In compound **1**, the p–π conjugation is essentially distorted, due to the predominance of the non-planar rotational forms, and the resonance electron-donating effect of the sulphur atom is completely compensated by the electron-withdrawing π-inductive effect of the CF_3 group. The sulphur LP in sulphoxides **2** and **5** is sterically close to the ring plane and interacts with the oxygen LP, so that its participation in p–π conjugation is virtually excluded. The steric position of the $S=O$ bonds in sulphoxides and sulphones also excludes their resonance interaction with the aromatic π system. The π-charge distribution in the benzene ring in **1–3**, **5** and **6** is mainly determined by the electron-withdrawing π-inductive influence of the SCF_3 and SCH_3 groups via electrostatic effects.

With increasing electron density deficiency on the X moiety ($S<SO<SO_2$), the electron density on the CF_3 and CH_3 groups increases. Owing to the high polarity and the rigidity of the C—F bonds and the deficiency of the electron density on the carbon atom in the CF_3 group, the latter may be considered as a rather independent fragment of the molecule. Shielding of the ^{13}C and ^{19}F nuclei increases in the series $\mathbf{1}<\mathbf{2}<\mathbf{3}$, as a result of the total electron-density increase on the CF_3 group. In contrast, the C—H bonds of the methyl groups are labile and easily polarizable; hence, increasing electronegativity of the X moiety leads to deshielding of the ^1H and ^{13}C nuclei according to the inductive mechanism. The calculated C—F and C—H bond order values remain almost unchanged as the X groups are varied.

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