Crystal and Molecular Structures of Ring-substituted Methyl Phenyl Sulfoxides: an X-Ray and Molecular Orbital *Ab Initio* Investigation

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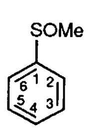
The solid-state crystal and molecular structure of a number of ring-substituted methyl phenyl sulfoxides, containing mainly fluorine substituents, has been obtained by X-ray analysis. The conformation found for the molecules has geometrical features very close to those of the most stable conformer(s) predicted by *ab initio* molecular orbital calculations. In those compounds without *ortho* substituents the S=O bond is only slightly twisted from being coplanar with the ring plane, while a larger twist is present when both *ortho* positions are substituted. In the presence of one *ortho* substituent the S=O bond adopts an *anti* orientation and is almost coplanar with the ring. With the unsymmetrically substituted derivatives two conformers are possible and in the case of *ortho* substitution the energy difference (18–24 kJ mol^{-1}) is large enough to have crystals only of the lower energy conformer. When the *ortho* positions are both free, the energy difference is quite low (0.6 kJ mol^{-1}) and both conformers are found in the same crystal.

Molecular orbital (MO) *ab initio* calculations have shown[1] that in the energy profile for rotation around the C_{ar}–S bond one minimum is present and corresponds to the S=O bond which is nearly eclipsed with the phenyl ring (twist angle 7.3°). When one fluorine atom is placed at the *ortho* position, two energy minima are found and the more stable conformation corresponds[1] to the S=O bond coplanar with the ring and *anti* with respect to the *ortho* substituent. Two *ortho* fluorine substituents determine only one conformational minimum and the S=O bond is twisted by 45° with respect to the ring plane. These results cannot be compared with the experimental behaviour since geometrical parameters for methyl phenyl sulfoxides were, and still are, seldom known. From the limited number of available experimental results it is possible to observe that the S=O bond is almost coplanar with the aromatic ring in methyl *p*-tolyl sulfoxide[2] and it is confined[3] to the *anti* orientation by the presence of an *ortho*-methoxycarbonyl group. A multinuclear (^1H, ^{13}C and ^{17}O) NMR investigation[4] of substituted methyl phenyl sulfoxides showed that, in solution, conformations qualitatively similar to those predicted by the theoretical approach are the most populated ones. In the compounds containing fluorine substituents in the ring, the long-range $^nJ_{C,F}$ and $^nJ_{H,F}$ coupling constants, where C and H are nuclei of the methyl group, were found[5] to be conformationally dependent and empirical correlations with torsional angles are useful conformational probes for these molecules. Nevertheless, to set up the empirical correlations, it is necessary to have compounds with unequivocally known geometrical structures.

A number of ring-substituted methyl phenyl sulfoxides (**1**–**7**), solid at room temperature and obtainable in suitable crystal form, were subjected to X-ray analysis in order to determine their molecular structure. On the same molecules MO *ab initio* calculations were carried out in order to examine the trend of the conformational ground state of the 'free' molecules. Comparison of the results from the two approaches will provide information on the influence of packing interactions on the solid-state conformation of these molecules.



1; 2,3-F_2
2; 3,4-F_2
3; 2,5-F_2
4; 3,5-F_2
5; 2,4,6-F_3
6; 2,6-Cl_2
7; 2-NO_2

Results

X-Ray Analysis.—Table 1 quotes the final atomic coordinates of the seven compounds and Table 2 enables comparison of bond distances and angles in them. Fig. 1 shows the ORTEP[6] drawings of the molecules together with the Newman projections, along the S–C(1) bond, which assist in getting a clear picture of the orientation of the methylsulfinyl group with respect to the benzene ring.

Considering the lone pair, the sulfinyl group is tetrahedral, as expected, and deformed so as to have the bond angles at sulfur smaller than the theoretical value of 109.5° (Table 2), according to the valence shell electron pair repulsion (VSEPR) theory.[7] The sulfur atom is on average 0.7 Å out of the plane through O,C(1),C(7), but this distance is much larger [1.177(1) Å] in the case of the nitro derivative.

The geometry of the sulfinyl group is practically the same in all the compounds; the following averaged values agree quite well with those found in the methylsulfinyl derivatives of furan and thiophene[8] (averages in square brackets): S–O = 1.495(4) [1.487(2)]; S–C(ar) = 1.765(4) [1.799(4)]; S–CH_3 = 1.793(6) [1.792(2)] Å, C–S–C = 98.2(2) [97.1(2)]°, O–S–C(ar) = 106.0(3) [105.7(2)]°; O–S–CH_3 = 106.3(3) [106.1(2)]°.

From the Newman projections in Fig. 1 the following considerations can be made: (i) when the two *ortho* positions are both unsubstituted, the oxygen atom shows a tendency to eclipse an *ortho* carbon (O–S–C–C = 1.9/14.8°); (ii) when the two *ortho* positions are both substituted, the O–S–C(7) system

Table 1 Atomic co-ordinates ($\times 10^4$); esds in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Compound **1**			
S	2 039.8(8)	4 843.0(3)	8 565.8(8)
O	−84(3)	5 203(1)	7 837(2)
F(2)	5 278.4(19)	3 537.0(8)	9 676.6(23)
F(3)	4 722.5(25)	1 935.1(9)	9 386.0(28)
C(1)	1 680(3)	3 767(1)	8 314(3)
C(2)	3 335(3)	3 245(1)	8 922(3)
C(3)	3 036(3)	2 425(1)	8 771(3)
C(4)	1 091(4)	2 106(1)	8 026(3)
C(5)	−574(4)	2 623(2)	7 445(3)
C(6)	−300(4)	3 451(2)	7 590(3)
C(7)	3 469(5)	4 973(2)	6 720(4)
Compound **2**			
S(A)	7 793.2(13)	2 380.2(10)	6 219.2(5)
F(3A)	5 391(3)	7 445(3)	5 570(1)
F(4A)	4 882(3)	8 066(3)	6 758(1)
O(A)	8 372(4)	2 487(3)	5 588(1)
C(1A)	6 859(4)	4 099(4)	6 372(2)
C(2A)	6 467(5)	5 111(4)	5 891(2)
C(6A)	6 593(5)	4 422(4)	6 986(2)
C(3A)	5 800(5)	6 425(4)	6 032(2)
C(4A)	5 539(5)	6 746(4)	6 634(2)
C(5A)	5 903(5)	5 754(5)	7 119(2)
C(7A)	5 872(8)	1 343(6)	6 090(4)
S(B)	10 338.8(14)	1 481.6(11)	4 066.3(5)
F(3B)	7 676(4)	6 411(3)	4 483(1)
F(4B)	7 499(3)	7 235(3)	3 272(1)
O(B)	10 919(5)	856(3)	3 490(2)
C(1B)	9 348(5)	3 199(4)	3 817(2)
C(2B)	8 831(5)	4 128(4)	4 260(2)
C(3B)	8 197(5)	5 469(4)	4 062(2)
C(4B)	8 098(5)	5 890(4)	3 441(2)
C(5B)	8 606(5)	4 973(5)	2 995(2)
C(6B)	9 241(6)	3 603(5)	3 191(2)
C(7B)	8 501(8)	497(6)	4 204(3)
Compound **3**			
S	2 005.5(3)	1 623.2(7)	699.3(9)
F(2)	885.7(8)	735.7(17)	−3 275.1(21)
F(5)	−714.4(8)	4 111.6(20)	3 226.8(24)
O	2 249.3(9)	2 164.4(27)	3 067.1(25)
C(1)	928(1)	2 147(2)	265(3)
C(2)	479(1)	1 588(2)	−1 662(3)
C(3)	−355(1)	1 867(3)	−1 979(4)
C(4)	−760(1)	2 713(3)	−322(4)
C(5)	−314(1)	3 266(2)	1 590(4)
C(6)	527(1)	2 997(3)	1 942(3)
C(7)	2 397(1)	3 181(4)	−1 183(4)
Compound **4**			
S	784(3)	1 766(2)	2 989(1)
F(3)	3 234(7)	4 220(5)	5 790(2)
F(5)	−3 769(6)	1 167(5)	5 668(2)
O	3 366(7)	2 144(6)	2 817(3)
C(1)	341(10)	2 193(7)	4 065(4)
C(2)	2 026(10)	3 092(7)	4 518(4)
C(3)	1 640(10)	3 330(7)	5 340(4)
C(4)	−303(12)	2 718(7)	5 753(4)
C(5)	−1 896(10)	1 833(7)	5 271(4)
C(6)	−1 655(10)	1 525(7)	4 450(4)
C(7)	−984(12)	3 372(9)	2 582(4)
Compound **5**			
S	8 764.3(11)	4 851.6(10)	3 564.2(8)
O	9 405(3)	5 688(3)	2 887(2)
F(2)	6 594(3)	6 451(2)	2 706(2)
F(4)	4 419(3)	7 480(3)	5 540(2)
F(6)	7 924(3)	4 716(2)	5 565(2)
C(1)	7 337(4)	5 565(3)	4 123(3)
C(2)	6 476(4)	6 335(4)	3 661(3)
C(3)	5 507(5)	7 001(4)	4 114(4)
C(4)	5 376(5)	6 847(4)	5 075(4)
C(5)	6 162(5)	6 087(4)	5 585(3)
C(6)	7 130(4)	5 473(4)	5 086(3)
C(7)	7 793(7)	3 838(5)	2 882(5)
Compound **6**			
S	1 562(6)	8 101(4)	3 238(4)
Cl(6)	162(7)	8 236(5)	5 572(4)
Cl(2)	145(7)	5 588(5)	1 371(4)
O	1 080(13)	8 430(10)	1 887(9)
C(1)	30(17)	6 891(15)	3 474(12)
C(2)	−626(18)	7 044(13)	4 470(11)
C(3)	−1 921(23)	6 219(20)	4 647(18)
C(4)	−2 545(21)	5 247(17)	3 824(17)
C(5)	−1 913(25)	5 077(16)	2 819(15)
C(6)	−620(20)	5 890(17)	2 644(12)
C(7)	3 480(18)	7 123(16)	3 594(14)
Compound **7**			
S	3 572.0(8)	3 203.3(15)	1 171.2(6)
O(1)	990(2)	−3 326(5)	889(2)
O(2)	2 417(3)	−736(4)	1 713(2)
O(3)	3 995(2)	5 539(4)	825(2)
N	1 737(2)	−1 585(5)	947(2)
C(1)	2 608(3)	1 636(6)	93(2)
C(2)	2 640(3)	2 645(6)	−773(3)
C(3)	1 948(3)	1 598(8)	−1 630(3)
C(4)	1 198(4)	−465(7)	−1 640(3)
C(5)	1 131(3)	−1 483(7)	−797(2)
C(6)	1 833(3)	−441(5)	62(2)
C(7)	5 055(4)	1 320(8)	1 385(3)

rotates about S–C(1) giving a O–S–C–C torsion angle in the range 36.7/38°; (iii) when only one *ortho* position is substituted, the oxygen atom shows a tendency to eclipse the carbon of the unsubstituted *ortho* position (O–S–C–C = −1/9.5°), probably as a consequence of an intramolecular C–H • • • O hydrogen bonding.

The sulfur atom in some cases shows quite significant displacements from the plane of the benzene ring (Table 2), probably as a consequence of packing effects.

Concerning compound **2** it is worth noting that the two independent molecules of the asymmetric unit are different conformers arising as a consequence of the asymmetric substitution of the phenyl group. Molecule **2B** becomes equal to molecule **2A** by rotating the substituted phenyl ring by *ca.* 180° around the C(1)–S direction. The energy barrier from atom–atom potential energy calculation for this transformation is fairly low (*ca.* 30 kJ mol^{-1} = *ca.* 7 kcal mol^{-1}), as shown by the potential energy profiles illustrated in Fig. 2. The peaks in the curves of Fig. 2 are due to the repulsive interactions between the hydrogens or the *ortho*-substituents and the methyl group.

The curves of Fig. 2 are calculated considering free molecules, and positive values of the rotation angle φ correspond to counter-clockwise rotations. The $\varphi = 0°$ value is for the conformation found in the crystal and the energy values are relative to the energy corresponding to that conformation. From the plots of Fig. 2 it can be seen that, by adding the coulombic contributions (calculated using the atom charges from the *ab initio* calculations) to the van der Waals energy, the broadening of the minima are reduced and the minima themselves are shifted nearer the positions found experimentally, excepting the case of the chlorine derivative, for which addition of the coulombic contribution does not change the curves significantly.

The internal motions considered in the atomic anisotropic displacement analysis, whose results are shown in Table 3,

Table 2 Bond distances/Å and angles/°; esds in parentheses

Compound	**1**	**2A**	**2B**	**3**	**4**	**5**	**6**	**7**
S–O	1.486(2)	1.478(3)	1.478(4)	1.485(2)	1.498(4)	1.492(3)	1.48(1)	1.499(3)
S–C(1)	1.798(2)	1.786(4)	1.800(4)	1.797(2)	1.788(6)	1.788(4)	1.82(2)	1.820(3)
S–C(7)	1.792(3)	1.789(6)	1.779(6)	1.793(3)	1.785(8)	1.782(6)	1.78(2)	1.803(4)
F(2)–C(2)	1.348(2)	—	—	1.359(2)	—	1.354(5)	—	—
F(3)–C(3)	1.355(2)	1.356(4)	1.346(5)	—	1.351(7)	—	—	—
F(4)–C(4)	—	1.354(5)	1.346(4)	—	—	1.349(6)	—	—
F(5)–C(5)	—	—	—	1.360(3)	1.355(7)	—	—	—
F(6)–C(6)	—	—	—	—	—	1.345(5)	—	—
Cl(2)–C(2)	—	—	—	—	—	—	1.73(2)	—
Cl(6)–C(6)	—	—	—	—	—	—	1.72(1)	—
C(1)–C(2)	1.372(3)	1.377(5)	1.370(6)	1.384(3)	1.391(8)	1.381(6)	1.38(2)	1.386(5)
C(2)–C(3)	1.372(3)	1.362(6)	1.366(5)	1.370(3)	1.359(9)	1.369(6)	1.39(3)	1.375(5)
C(3)–C(4)	1.364(3)	1.351(6)	1.361(6)	1.373(3)	1.380(9)	1.369(7)	1.37(3)	1.378(6)
C(4)–C(5)	1.368(4)	1.369(6)	1.364(6)	1.373(3)	1.377(8)	1.365(8)	1.35(3)	1.369(5)
C(5)–C(6)	1.382(4)	1.380(6)	1.389(6)	1.382(3)	1.353(8)	1.368(6)	1.40(2)	1.379(4)
C(6)–C(1)	1.379(3)	1.377(6)	1.365(6)	1.380(3)	1.400(8)	1.373(6)	1.37(2)	1.395(4)
O(1)–N	—	—	—	—	—	—	—	1.222(4)
O(2)–N	—	—	—	—	—	—	—	1.228(3)
N–C(6)	—	—	—	—	—	—	—	1.462(4)
C(1)–S–C(7)	96.9(1)	97.0(2)	98.6(2)	97.1(1)	96.4(3)	97.7(2)	98.4(7)	95.7(2)
O–S–C(7)	105.9(1)	105.6(3)	107.6(2)	106.7(1)	106.6(3)	107.6(2)	108.0(7)	104.2(2)
O–S–C(1)	105.7(1)	107.4(2)	105.7(2)	106.0(1)	107.1(3)	107.5(2)	108.5(6)	105.3(1)
S–C(1)–C(6)	120.2(2)	119.0(3)	118.9(3)	120.0(2)	118.5(4)	120.6(3)	118(1)	126.1(2)
S–C(1)–C(2)	120.9(2)	120.7(3)	120.0(3)	120.5(2)	120.4(4)	123.8(3)	124(1)	116.2(2)
C(2)–C(1)–C(6)	118.8(2)	120.3(4)	120.8(4)	119.3(2)	121.0(5)	115.2(4)	118(1)	117.8(3)
C(1)–C(2)–C(3)	120.6(2)	118.8(4)	118.6(4)	122.2(2)	117.8(5)	123.8(4)	121(1)	120.8(3)
C(2)–C(3)–C(4)	121.0(2)	121.0(4)	121.1(4)	119.0(2)	123.9(6)	116.6(4)	120(2)	120.3(3)
C(3)–C(4)–C(5)	118.6(2)	121.3(4)	120.8(4)	118.8(2)	115.4(6)	123.5(5)	120(2)	120.3(4)
C(4)–C(5)–C(6)	121.0(2)	118.4(4)	118.5(4)	123.0(2)	124.9(5)	116.4(4)	120(2)	119.3(3)
C(1)–C(6)–C(5)	119.8(2)	120.1(4)	120.1(4)	117.7(2)	117.0(5)	124.4(4)	121(1)	121.5(3)
F(2)–C(2)–C(1)	120.1(2)	—	—	118.2(2)	—	118.6(4)	—	—
F(2)–C(2)–C(3)	119.3(2)	—	—	119.7(2)	—	117.6(4)	—	—
F(3)–C(3)–C(2)	118.4(2)	120.4(4)	120.3(4)	—	118.8(5)	—	—	—
F(3)–C(3)–C(4)	120.6(2)	118.6(3)	118.6(3)	—	117.2(5)	—	—	—
F(4)–C(4)–C(3)	—	119.4(4)	118.9(3)	—	—	118.1(4)	—	—
F(4)–C(4)–C(5)	—	119.3(4)	120.3(4)	—	—	118.4(4)	—	—
F(5)–C(5)–C(4)	—	—	—	118.8(2)	116.6(5)	—	—	—
F(5)–C(5)–C(6)	—	—	—	118.2(2)	118.5(5)	—	—	—
F(6)–C(6)–C(1)	—	—	—	—	—	117.5(4)	—	—
F(6)–C(6)–C(5)	—	—	—	—	—	118.1(4)	—	—
Cl(2)–C(2)–C(1)	—	—	—	—	—	—	122(1)	—
Cl(2)–C(2)–C(3)	—	—	—	—	—	—	117(1)	—
Cl(6)–C(6)–C(1)	—	—	—	—	—	—	121(1)	—
Cl(6)–C(6)–C(5)	—	—	—	—	—	—	118(1)	—
O(1)–N–O(2)	—	—	—	—	—	—	—	123.4(3)
O(1)–N–C(6)	—	—	—	—	—	—	—	118.8(2)
O(2)–N–C(6)	—	—	—	—	—	—	—	117.8(3)
N–C(6)–C(1)	—	—	—	—	—	—	—	120.8(2)
N–C(6)–C(5)	—	—	—	—	—	—	—	117.6(3)
S···(C,C,O)[a]	0.717(1)	0.702(1)	0.689(1)	0.706(1)	0.703(2)	0.683(1)	0.667(4)	1.117(1)
S···Ph[b]	0.045(1)	0.051(1)	0.139(1)	0.122(1)	0.060(2)	0.222(2)	0.162(4)	0.003(1)
C(2)–C(1)–S–O	−177.6(2)	13.4(4)	−173.1(3)	−170.7(2)	14.8(6)	36.7(4)	38.2(14)	9.5(3)

[a] (C,C,O) refers to the plane through C(1),C(7),O. [b] Ph refers to the plane through the benzene ring.

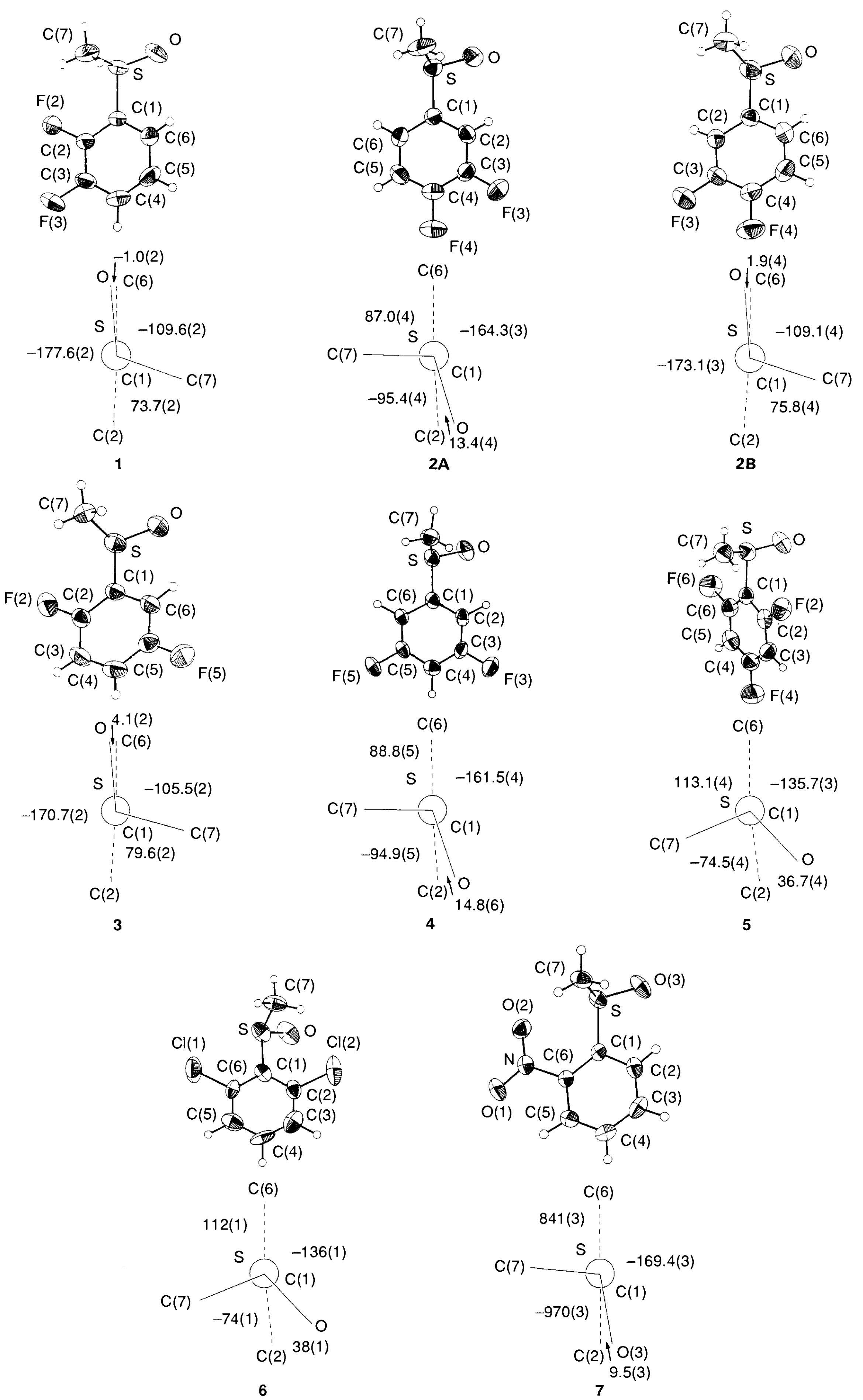
correspond, in general, to librations of the sulfinyl group about the C(1)–S bond and of the halogens along directions lying in the benzene plane. In the case of the nitro derivative libration of the NO_2 group along the N–C direction was also considered.

No regular trends are observed in the bond distances of the phenyl rings, whereas clear evidence is found for widening of the endocyclic angles at the carbon atoms bound to fluorine in the case of compounds **3**, **4** and **5**: these angles are larger than 120° by 2.2–4.9°. The widenings of the corresponding angles in the other compounds are much smaller, their range being 0.6–1.5°. These widenings, as for those present in the nitro and chloro derivatives, are related to the electronegativity of the substituents.[9]

Relevant asymmetry for the exocyclic S–C–C angles is observed in the case of compounds **6** and particularly **7**, where the coplanarity of the nitro group with the benzene ring, required by π-conjugation, causes the widening of the S–C(1)–C(6) and N–C(6)–C(1) angles. In this last compound the S···O(2) = 2.709(3) Å interaction is probably the one most responsible for the orientation of the sulfinyl group.

No significant differences are observed for the C(ar)–F distances and their average, 1.354(1) Å, agrees quite well with the average of the values found in the literature: 1.362(1) Å on 58 compounds retrieved from the files of the Cambridge Crystallographic Data Centre (CCDC),[10] using the screening criterion $R \leqslant 0.05$ and $\sigma(C–C) < 0.01$ Å. The C(ar)–Cl distances found in compound **6** are in agreement with the average, 1.739(1) Å, of 447 values retrieved from the CCDC files using the same screening criterion, in spite of the low accuracy of the results of its analysis.

MO ab Initio *Calculations*.—Calculations were performed



1 **2A** **2B**

3 **4** **5**

6 **7**

Fig. 1 ORTEP drawings and Newman projections along the C(1)–S bond for compounds **1–7**. Ellipsoids are at the 50% probability level.

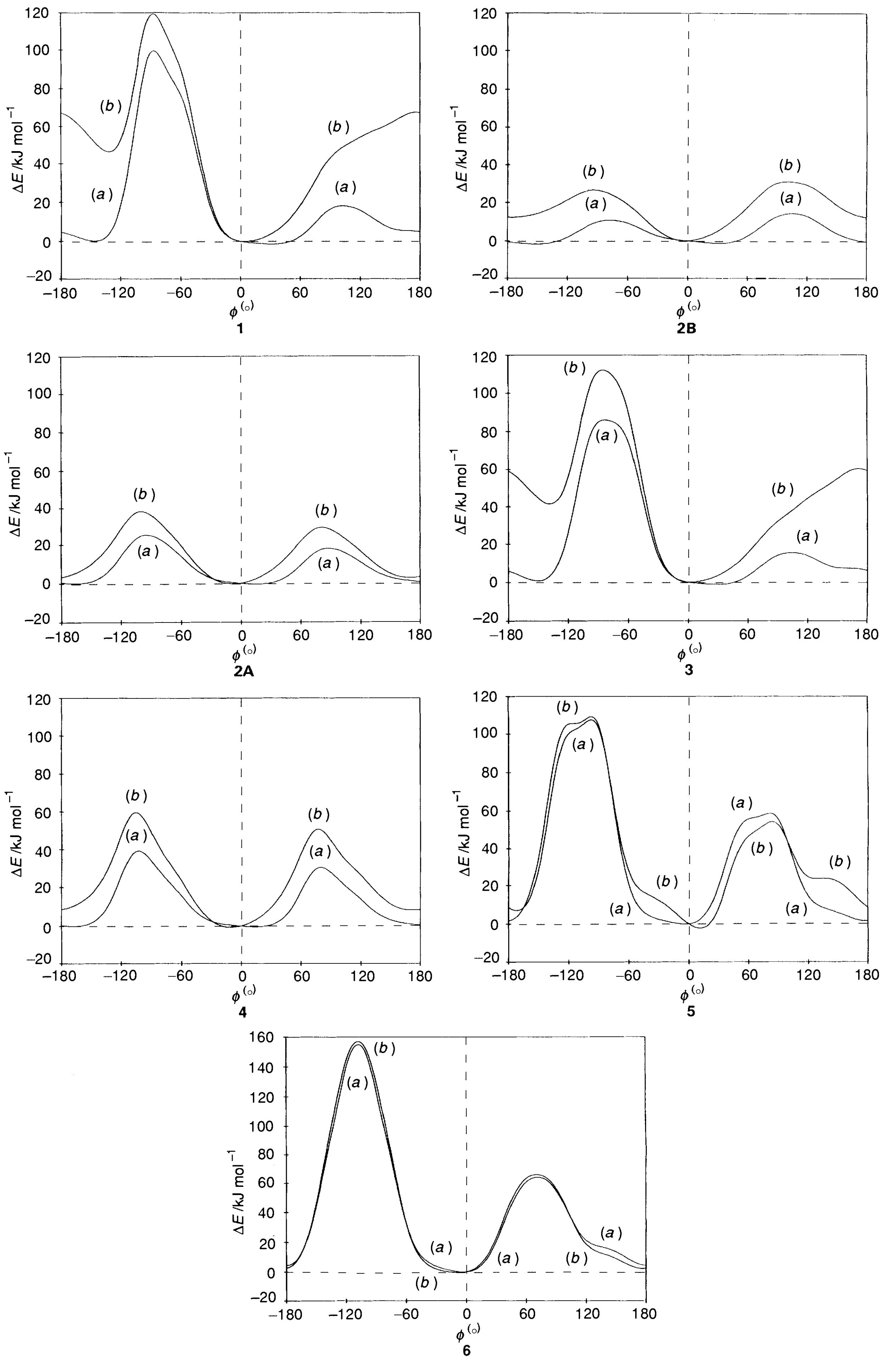


Fig. 2 Calculated difference potential energy profiles for the rotation of the sulfinyl group about the C(1)–S bond: (*a*) van der Waals energy alone; (*b*) including the coulombic energy.

Table 3 Results of the atomic anisotropic displacement analysis

Compound	Treatment[a]	$\bar{\Delta}$[b]	$\bar{\sigma}(U_o)$[c]	$\sigma(\omega\Delta U)$[d]	R_{wU}[e]
1	RB	0.0028(35)	0.0011	0.0017	0.054
	IM			0.0013	0.042
2A	RB	0.0041(54)	0.0022	0.0025	0.069
	IM			0.0019	0.052
2B	RB	0.0040(51)	0.0023	0.0024	0.061
	IM			0.0016	0.041
3	RB	0.0029(37)	0.0009	0.0023	0.071
	IM			0.0015	0.047
4	RB	0.0045(57)	0.0031	0.0025	0.070
	IM			0.0019	0.053
5	RB	0.0047(60)	0.0024	0.0025	0.055
	IM			0.0018	0.039
6	RB	0.0112(138)	0.0087	0.0047	0.090
	IM			0.0036	0.069
7	RB	0.0035(46)	0.0016	0.0021	0.075
	IM			0.0015	0.055

[a] RB = rigid-body, IM = internal motions. [b] $\bar{\Delta}$ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for pairs of atoms. [c] $\bar{\sigma}(U_o)$ = mean esd of U_o values. [d] $\sigma(\omega\Delta U) = [\Sigma(\omega\Delta U)^2/\Sigma\omega^2]^{\frac{1}{2}}$. [e] $R_{wU} = [\Sigma(\omega\Delta U)^2/\Sigma(wU_o)^2]^{\frac{1}{2}}$.

Table 4 Geometrical parameters relaxed at the 3-21G* level, absolute (a.u.) and relative energies (kJ mol^{-1}) for compounds **1**–**7**

Parameter[a]	**1**[b]		**2**[b]		**3**[b]	
S–O	1.484	1.491	1.491	1.491	1.484	1.491
S–C(1)	1.784	1.779	1.777	1.777	1.784	1.778
S–C(7)	1.790	1.790	1.792	1.792	1.790	1.791
C(7)–H	1.081	1.081	1.082	1.082	1.081	1.081
C(1)–S–O	110.73	105.08	105.68	105.73	110.49	105.13
C(2)–C(1)–S	122.16	122.06	122.81	117.28	122.65	122.77
C(7)–S–O	107.70	108.16	107.18	107.16	107.62	108.19
H–C(7)–S	109.15	109.00	109.29	109.30	109.15	108.99
H–C(7)–S–O	66.64	70.25	69.56	69.62	66.68	70.46
C(7)–S–C(1)	96.59	96.46	96.70	96.64	96.49	96.42
C(2)–C(1)–S–O	48.49	−177.66	−173.24	6.84	48.16	−177.74
E(a.u.)	−934.928 028	−934.937 319	−934.934 487	−934.934 716	−934.934 986	−934.944 279
E/kJ mol^{-1}	24.39	0	0.60	0	18.67	0

Parameter[a]	**4**	**5**	**6**	**7**
S–O	1.490	1.484	1.482	1.491
S–C(1)	1.778	1.788	1.818	1.818
S–C(7)	1.792	1.790	1.794	1.795
C(7)–H	1.082	1.081	1.082	1.080
C(1)–S–O	105.89	109.66	111.59	103.79
C(2)–C(1)–S	117.70	121.88	123.55	127.86
C(7)–S–O	107.28	107.45	108.35	105.48
H–C(7)–S	109.28	109.19	109.35	108.86
H–C(7)–S–O	69.65	67.62	65.46	68.28
C(7)–S–C(1)	96.32	96.26	95.33	96.59
C(2)–C(1)–S–O	6.38	45.84	32.42	5.29
E(a.u.)	−934.941 155	−1033.253 212	−1651.917 892	−940.585 909
E/kJ mol^{-1}	—	—	—	—

[a] C(1) and C(2) refer to the carbon atoms of the ring: C(1) is that bonded to the sulfinyl group; C(7) and H refer to the methyl group. Bond lengths/Å; angles/°. [b] The two columns relative to compounds **1**–**3** refer to the two conformers of the ground state.

with the GAUSSIAN-86 package[11] by employing a CRAY-X-MP48 supercomputer. The 3-21G* basis set level was chosen and geometry relaxation was allowed for the parameters of the methylsulfinyl group. The geometry of the substituted rings was derived from the experimental structures. The optimized parameters are reported in Table 4. Employment of the 3-21G basis set, without d-orbitals on the sulfur atom, gave unreliable S=O bond distances: 1.66–1.67 Å *vs.* 1.48–1.49 Å from the 3-21G* basis set, to be compared with the experimental values of 1.48–1.50 Å. Minor and less significant differences are found for the other geometrical parameters calculated with the two basis sets. In Table 4 the absolute energies of the conformational minima are also reported.

Discussion and Conclusions

The calculated bond length C(1)–S is slightly longer in compounds **6** and **7** in comparison with the other molecules examined. This is not an artifact of calculations since the same trend is observed in the experimental results of Table 2. The

Table 5 Atomic charges[a] from 3-21G* *ab initio* calculations on the S and O atoms of the sulfinyl group for the conformers of compounds **1–7**

Compound	O	S
1	−0.6843	1.1325
	−0.6541	1.0870
2	−0.6849	1.1109
	−0.6801	1.1109
3	−0.6830	1.1311
	−0.6555	1.0878
4	−0.6809	1.1151
5	−0.6581	1.1160
6	−0.6544	1.1170
7	−0.6989	1.1596

[a] Where two entries are reported, the first refers to the more stable conformation.

origin is probably to be found, as regards compound **6**, in the steric interactions between the methylsulfinyl group and the two chlorine substituents, whereas for compound **7** polar bonding between the positive sulfur atom and one of the negative oxygens of the nitro group takes place and should lower the bond order in the C(1)–S bond.

In the unsymmetrically-substituted compounds the two conformational minima have different energies. The corresponding values are rather different in compounds **1** and **3** where one fluorine atom is in the *ortho* position, while quite close values are found in compound **2**. For the former compounds it is thus expected that one conformation should predominate in different physical conditions, while for compound **2** conformational equilibria should be possible. These conclusions agree with the behaviour found[5] for these compounds in solution. Furthermore, for compound **2** the solid state structure shows that two independent molecules are present in the unit cell and they correspond to these conformers.

Comparing the calculated torsional angles C(1)–C(2)–S–O in the conformational minima (Table 4) and the experimental values (Table 2) it appears that the values are reasonably close and the interactions taking place in the solid state seem to influence the torsional angle of the equilibrium geometry of the 'free' molecule only within a few degrees. In the preferred conformation of the compounds having one fluorine atom in the *ortho* position, **1** and **3**, the orientation of the S=O bond is *anti* with respect to the substituent and almost coplanar with the ring, as found previously[1] for the calculated structure of 2-fluorophenyl methyl sulfoxide. For the compounds without *ortho* substituents, **2** and **4**, in the calculated ground state conformation(s) the S=O bond is slightly distorted (*ca.* 7°) from the coplanarity with the ring as occurs[1] in methyl phenyl sulfoxide, and the calculated twist is smaller than that found in the solid state structures (13–15°). This also occurs for one of the two conformers of compound **2**, while they show almost the same twist in the calculated structures. The presence of two *ortho* substituents causes large twists of the S=O bond from coplanarity with the ring plane both in the calculated and experimental structures. Nevertheless, while calculations show that the effect is higher in the case of fluorine (compound **5**) than chlorine (compound **6**) substituents, in the solid state this peculiarity is not observed. Conformations with high twist were postulated[5] for these molecules, even in solution, in order to explain their experimental behaviour.

The high polarity of the S=O bond is a well-known property.[12] Total atomic charges from *ab initio* calculations agree with this peculiarity and those of the compounds examined are reported in Table 5. For those molecules with two ground-state conformations the negative charge on the oxygen atom is almost the same in the conformers with similar energy content (compound **2**). The charges differ and the oxygen atom becomes less negative, when in one conformation the twist increases and the stability gets lower with respect to the other, *i.e.* compounds **1** and **3**. The lower negative charge on the oxygen atom of this conformer is practically the same as that occurring in compounds **5** and **6**, which have only one twisted conformation. The highest polarity of the S=O bond is found in compound **7** where the positive character of the sulfur atom should contribute in establishing bonding polar interactions between this atom and the negative oxygens of the nitro group. This finding is in agreement with the highest value for the S • • • (C,C,O) distance found experimentally.

Experimental

Compounds.—The sulfoxides **1–7** were obtained as described in previous work.[4,5] Samples for X-ray analysis were obtained by slow crystallization from the solvent of already purified materials. The m.p. of the crystals and the solvent used were: **1**, 59–61 °C, diisopropyl ether; **2**, 43–45 °C, diisopropyl ether; **3**, 49–51 °C, hexane; **4**, 80–82 °C, diisopropyl ether; **5**, 81 °C, hexane; **6**, 97–99 °C, hexane; **7**, 61–62 °C, diisopropyl ether.

Crystal Structure Analyses.—Table 6 summarizes the relevant data concerning the crystal structure analyses. The lattice parameters were refined by a least-squares procedure[13] using the Nelson and Riley extrapolation function.[14] All reflections were corrected for Lorentz and polarization effects but not for absorption, and secondary extinction was considered only for compound **3** according to Zachariasen.[15]

The crystals of compound **6** were of poor quality and consequently the results of the analysis are less accurate with respect to those of the other compounds.

All structures were solved using the direct methods of SHELX86[16] and refined by full matrix least-squares, using the SHELX76[17] program. The hydrogen atoms were localized in the final $\Delta\rho$ map and refined, excepting those of compounds **4** and **6** which were put in calculated positions riding on the attached carbon atoms.

The results of the anisotropic atomic displacement analysis, shown in Table 3, are quite satisfactory. This analysis was carried out in the rigid body approximation of Schomaker and Trueblood[18] considering also the internal motions according to the one-parameter model of Dunitz and White[19] by using the THMV[20] program. The data of Table 1 are not corrected for these displacements, the differences being less than 2σ.

For the analysis of the geometry of the molecules the PARST[21] program was used and the drawings were obtained by using the ORTEP[6] program. The atom–atom potential energy calculations were carried out with the ROTENER program[22] which makes use of a function of the type: $E_{ij} = B_{ij}\exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6}$, and the atom charges, necessary for the calculation of the coulombic energy, were from *ab initio* calculations. Atomic scattering factors and anomalous scattering coefficients were taken from ref. 23. The crystallographic calculations were carried out on the ENCORE-POWERNODE 6040 computer of the *Centro di Studio per la Strutturistica Diffrattometrica del CNR* (*Parma*).

Additional material deposited at the Cambridge Crystallographic Data Centre (CCDC) comprises hydrogen atom coordinates, thermal parameters and the remaining bond lengths and bond angles.*

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* For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

Table 6 Experimental data for the crystallographic analyses

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_7H_6F_2OS$	$C_7H_6F_2OS$	$C_7H_6F_2OS$	$C_7H_6F_2OS$	$C_7H_5F_3OS$	$C_7H_6Cl_2OS$	$C_7H_7NO_3S$
M	176.18	176.18	176.18	176.18	194.17	209.09	185.20
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Pcab$	$P2_1/n$	$P2_1/c$
a/Å	6.470(1)	7.980(2)	16.179(16)	5.536(1)	9.655(2)	7.976(2)	10.301(2)
b/Å	16.531(3)	9.124(1)	7.944(7)	8.438(2)	11.573(6)	10.334(3)	5.5469(5)
c/Å	7.232(1)	21.162(3)	5.850(5)	16.052(5)	14.060(8)	11.154(3)	14.527(2)
β/°	102.36(1)	98.20(2)	92.88(2)	91.67(2)	—	106.84(2)	106.52(2)
U/Å^3	755.6(2)	1525.04(48)	750.9(12)	749.5(3)	1571(1)	879.9(4)	795.8(2)
Z	4	8	4	4	8	4	4
D_x/mg m^{-3}	1.549	1.535	1.558	1.561	1.642	1.578	1.546
Diffractometer	CAD4	CAD4	SIEMENS AED	CAD4	PHILIPS-PW1100	CAD4	CAD4
Reflections for lattice parameters: number	25	25	28	25	25	25	23
Reflections for lattice parameters: θ range/°	12/17.5	11/17	14/19	10/18	11/18.5	10/17	13/19
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
F(000)	360	720	360	360	784	424	384
Crystal size/mm	0.62 × 0.42 × 0.23	0.51 × 0.30 × 0.27	0.29 × 0.34 × 0.63	0.23 × 0.42 × 0.53	0.43 × 0.36 × 0.23	0.39 × 0.28 × 0.19	0.33 × 0.28 × 0.65
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
μ/mm^{-1}	0.382	0.378	0.384	0.385	0.392	0.906	0.352
Extinction parameter g	—	—	$1.77(2) \times 10^{-7}$	—	—	—	—
Scan speed/deg min^{-1}	3.30	3.30	3–12	3.30	6	3.30	3.30
Scan width/°	$0.80 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$	$1.10 + 0.14 \tan\theta$	$0.80 + 0.35 \tan\theta$	1.10	$0.80 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
θ range/°	3–27	3–25	3–27	3–25	3–25	3–25	3–27
h range	−7/7	−9/9	−20/20	−6/6	0/11	−7/7	−12/11
k range	0/19	0/10	0/9	0/9	0/13	0/10	0/6
l range	0/8	0/25	0/7	0/17	0/16	0/12	0/16
Standard reflection	2 10 3	2 −6 −4	−10 3 1	−3 0 7	2 4 5	3 4 2	−7 0 4
Intensity variation	none	none	none	none	none	none	none
No. of measured reflections	1491	2942	1914	1163	1619	1378	1611
Condition for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 1.5\sigma(I)$	$I > 2\sigma(I)$
No. of reflections used in refinement	1011	1217	1099	598	640	432	818
R(int)	0.021	0.010	0.017	0.014	—	0.052	0.030
Max. LS shift to error ratio	0.014	0.014	0.009	0.07	0.13	0.6	0.006
Min./Max. height in final $\Delta\rho$/e Å^{-3}	−0.11/0.10	−0.10/0.09	−0.12/0.11	−0.21/0.22	−0.07/0.06	−0.18/0.26	−0.12/0.12
No. of refined parameters	124	247	124	115	129	118	137
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0278	0.0290	0.0311	0.0518	0.0296	0.0513	0.0285
$R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$	0.0405	0.0374	0.0413	0.0640	0.0290	0.0549	0.0343
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$ [a]	0.2920	0.3922	0.5404	0.6008	0.9385	1.871	0.5980
k, g ($w = k/[\sigma^2(F_c) + gF_o^2]$)	0.2199, 0.0022	1.0000, 0.0050	1.0000, 0.0037	1.0000, 0.0081	w = 1	w = 1	1.0000, 0.0005

[a] P = number of parameters, N = number of observations.

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