Folded Conformations. Part IX.[1] Crystal and Molecular Structure of *p*-Dimethylaminobenzyl *p*-Nitrophenyl Sulphone and *p*-Chlorophenyl *p*-Methoxybenzyl Sulphone

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The crystal and molecular structures of the two title compounds (Ia) and (Ib) have been determined by *X*-ray diffraction. The (low-temperature) structure determination of (Ia) showed that the molecules have a folded conformation in the solid state. For (Ib), the structure of which was determined at room temperature, the molecules have a stretched conformation in the crystal. Non-bonded energy calculations on the free molecules show that in both cases the lowest energy is found for a folded conformation, but the calculated energy difference between stretched and folded conformations is only small (*ca.* 1 kcal mol^{-1}). For the conformation observed for (Ia), the long wavelength charge-transfer interaction found in solution cannot be explained by ' through space ' overlap of the donor and acceptor groups.

THE observation of substantial intramolecular shielding effects in the n.m.r. spectra of benzyl phenyl sulphones (I) has led to the suggestion that these molecules in solution preferentially adopt folded conformations which

$$\mathrm{Ar^1SO_2CH_2Ar^2} \quad \text{(I)}$$

$$\text{a; } \mathrm{Ar^1} = p\text{-}\mathrm{NO_2C_6H_4},\ \mathrm{Ar^2} = p\text{-}\mathrm{Me_2NC_6H_4}$$

$$\text{b; } \mathrm{Ar^1} = p\text{-}\mathrm{ClC_6H_4},\quad \mathrm{Ar^2} = p\text{-}\mathrm{MeOC_6H_4}$$

allow the aryl rings (Ar^1 and Ar^2) to experience each other's magnetic anisotropy effect.[2] A significant parameter with which to describe the conformation of the sulphones (I) is the torsion angle ϕ of the central S–C bond. This angle is defined as zero for the eclipsed position of Ar^1 and Ar^2 and 180° for the *anti*-conformation. For the favoured folded conformations the aryl rings reside in a gauche-type position and ϕ is *ca.* 60°. For (Ib) the thermodynamic parameters for the equilibrium between folded and unfolded conformations, have been estimated from the temperature dependence of the aromatic proton chemical shifts ($K^{25°}$ 15, $\Delta G^{25°}$ -1.59 kcal mol^{-1}, ΔH -2.6 kcal mol^{-1}, $\Delta S^{25°}$ -3.5 e.u.).[2c] Interestingly, compound (Ia), which contains an aryl ring of low ionization potential (Ar$^2 = p$-Me$_2$NC$_6$H$_4$) and an aryl ring of high electron-affinity (Ar$^1 = p$-NO$_2$C$_6$H$_4$) exhibits an intramolecular charge-transfer (CT) absorption band (λ_m 368 nm, ε_m 526 l mol^{-1} cm^{-1}, 17.8 °C in CHCl$_3$). However, comparison of the intramolecular shielding effects observed for (Ia) and (Ib) (which shows no CT transition) indicates that electron donor–acceptor (D–A) interaction does not significantly affect the conformation preference [2b] and ground-state electron distribution [1a] for (Ia). It has been tentatively suggested that stabilization of the folded forms of (I) is obtained through minimizing $n \rightarrow \pi$ repulsive forces between the sulphonyl lone pairs and the π electrons of the Ar^2 aryl ring.[2]

In view of these results it appeared worthwhile to determine the molecular geometry of (Ia) and (Ib) by *X*-ray diffraction to see whether or not the folding tendency of the molecules is retained in the crystalline state and whether or not the intramolecular CT transition of the crystals of (Ia) can be rationalized in terms of inter- or intra-molecular ' through-space ' overlap of the donor and acceptor π-systems. Recently, considerable attention has been focussed on ' through-space ' and ' through-bond ' intramolecular CT interaction.[3-5]

EXPERIMENTAL

Compounds (Ia) and (Ib) were prepared by the method described in ref. 2. Suitable crystals were obtained by slow evaporation from a solution of (Ia) in methyl acetate and of (Ib) in acetone. The structure of (Ia) was determined at -160 °C. Cell dimensions were obtained from zero-layer Weissenberg (*hk*0, *h*0*l* and 0*kl*) photographs taken with Ni-filtered Cu-radiation and calibrated with NaCl reflexion spots. The structure of (Ib) was determined at room temperature as the mosaic spread appeared to increase strongly when cooling the crystal. Cell dimensions were obtained from the θ values measured on an Enraf–Nonius CAD4 diffractometer with Zr-filtered Mo-radiation.

Crystal Data.—(*a*) (Ia) (*at* -160 °C). C$_{15}$H$_{16}$N$_2$O$_4$S, $M = 320.3$, $a = 7.774(4)$, $b = 13.530(6)$, $c = 7.033(2)$ Å, $\alpha = 92.46(2)$, $\beta = 86.39(2)$, $\gamma = 93.71(2)°$, $U = 736.2$ Å^3, $D_m = 1.405$ (by flotation at 20 °C), $Z = 2$, $D_c = 1.455$. Space group $P\bar{1}$ (C_i^1, No. 2). Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 2.34 cm^{-1}. Crystal size 0.125 × 0.25 × 0.425 mm.

(*b*) (Ib) (*at room temperature*). C$_{14}$H$_{13}$ClO$_3$S, $M = 296.8$, $a = 29.52(7)$, $b = 5.43(1)$, $c = 8.78(1)$ Å, $\alpha = \gamma = 90°$, $\beta = 98.2(2)°$, $U = 1\,393$ Å^3, $Z = 4$, $D_c = 1.42$ g cm^{-3}. Space group $P2_1/c$ (C_{2h}^5, No. 14), μ(Mo-K_α) = 4.2 cm^{-1}. Crystal size *ca.* 0.25 × 0.25 × 0.35 mm.

For both compounds intensity data were collected on an Enraf–Nonius CAD4 diffractometer with Zr-filtered Mo-radiation. Crystal of (Ia) was cooled to -160 °C by a stream of cold N$_2$ gas produced by the apparatus described in ref. 6. Corrections for possible variations in the intensity

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[1] (*a*) Part VIII, I. P. Bleeker and J. B. F. N. Engberts, *Rec. Trav. chim.*, 1977, **96**, 58; (*b*) Part VII, R. M. Tel and J. B. F. N. Engberts, *J.C.S. Perkin II*, 1976, **95**, 483.

[2] (*a*) R. van Est-Stammer and J. B. F. N. Engberts, *Tetrahedron Letters*, 1971, 3215; (*b*) R. van Est-Stammer and J. B. F. N. Engberts, *Canad J. Chem.*, 1973, **51**, 1187; (*c*) R. van Est-Stammer, Ph.D. Thesis, University of Groningen, 1973.

[3] C. Worrell, J. W. Verhoeven, and W. N. Speckamp, *Tetrahedron*, 1974, **30**, 3525 and references therein.

[4] A. J. de Gee, J. W. Verhoeven, W. J. Sep, and Th. J. de Boer, *J.C.S. Perkin II*, 1975, 579.

[5] T. K. Brunck and F. Weinhold, *J. Amer. Chem. Soc.*, 1976, **98**, 4392 and references therein.

[6] F. van Bolhuis, *J. Appl. Cryst.*, 1971, **4**, 263.

of the primary beam were obtained from measurements of reference reflexions at frequent intervals. In order to obtain, as nearly as possible ' constant count ' statistics, each reflexion was scanned [θ—2θ for (Ia), and ω for (Ib)] first at fastest motor speed, and provided that the net integrated intensity obtained exceeded a preset value, the scan was repeated at the optimum motor speed; otherwise the intensity for the pre-scan was accepted and the reflexion assigned unobserved status in the subsequent least-squares refinement. For (Ia) 5 204 independent reflexions, of which 2 173 were considered unobserved, with $\sin \theta/\lambda < 0.75$ Å^{-1} were available for the structure determination. For (Ib) 3 407 reflexions with $\sin \theta/\lambda < 0.67$ Å^{-1} were measured of which 669 randomly distributed reflexions were lost owing to troubles with the CAD4 tape unit; of the remaining reflexions 783 were considered unobserved. Owing to the large mosaic spread of the crystal (2°, see later) the intensities for (Ib) are not very accurate. For both compounds the usual corrections for Lorentz and polarization effects were made. Absorption corrections were not applied.

TABLE 1

Compound (Ia): fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses. H atoms are numbered according to the carbon atoms to which they are bonded

	x/a	*y/b*	*z/c*
S	1 760(1)	4 648(1)	2 169(1)
O(1)	2 502(3)	4 785(1)	256(3)
O(2)	1 135(2)	5 505(1)	3 243(3)
O(3)	7 788(3)	2 184(2)	5 851(4)
O(4)	6 431(3)	2 703(2)	8 448(3)
N(1)	6 661(3)	2 654(2)	6 716(4)
N(2)	2 689(3)	172(2)	−1 326(4)
C(1)	3 299(3)	4 112(2)	3 502(4)
C(2)	4 605(3)	3 588(2)	2 544(4)
C(3)	5 727(3)	3 109(2)	3 606(4)
C(4)	5 504(3)	3 177(2)	5 571(4)
C(5)	4 224(3)	3 706(2)	6 547(4)
C(6)	3 090(3)	4 181(2)	5 473(4)
C(7)	33(3)	3 707(2)	2 116(4)
C(8)	623(3)	2 750(2)	1 212(4)
C(9)	1 062(4)	1 984(2)	2 332(4)
C(10)	1 714(4)	1 126(2)	1 511(5)
C(11)	1 967(4)	1 000(2)	−483(4)
C(12)	1 468(4)	1 766(2)	−1 600(4)
C(13)	815(4)	2 615(2)	−752(4)
C(14)	2 961(4)	−674(2)	−213(6)
C(15)	2 777(6)	29(3)	−3 370(6)
H(20)	−4 747	3 559	1 005
H(30)	6 747	2 694	2 913
H(50)	4 108	3 747	8 086
H(60)	2 076	4 598	6 171
H(71)	−981	3 958	1 309
H(72)	−461	3 579	3 560
H(90)	894	2 067	3 865
H(100)	2 020	543	2 413
H(120)	1 598	1 684	−3 136
H(130)	448	3 189	−1 638
H(141)	1 875	−923	524
H(142)	2 188	−1 330	−1 012
H(143)	3 688	−460	881
H(151)	1 636	−125	−3 803
H(152)	3 137	561	−4 090
H(153)	2 980	−736	−4 089

For neither (Ia) nor (Ib) could the structure be directly obtained by the symbolic addition method. For (Ia) analysis of the Patterson function, modified to correspond with point atoms at rest, was straightforward; the sulphur atom and the tetrahedral group of atoms bonded to it were readily located by means of the interatomic vectors to the centrosymmetrically related sulphur atom. For (Ib) the structure was obtained by combining information obtained from direct methods, visual inspection of the Patterson map, and difference Fourier syntheses. In both cases on the assumption of anisotropic thermal motion, the atomic parameters of all but the hydrogen atoms were refined by a least-squares program working with a full normal matrix.

TABLE 2

Compound (Ib): fractional co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
S	2 704(1)	5 935(4)	3 031(2)
Cl	4 656(1)	3 782(8)	6 483(4)
O(1)	2 663(2)	4 682(11)	1 586(6)
O(2)	2 632(2)	8 558(9)	3 020(6)
O(3)	517(2)	5 493(13)	1 286(8)
C(1)	3 257(3)	5 330(13)	4 030(9)
C(2)	3 477(3)	3 241(18)	3 651(11)
C(3)	3 919(4)	2 813(19)	4 396(12)
C(4)	4 112(4)	4 459(23)	5 522(12)
C(5)	3 889(4)	6 528(19)	5880(12)
C(6)	3 449(3)	6 965(15)	5 133(9)
C(7)	2 331(3)	4 524(13)	4 199(8)
C(8)	1 843(3)	4 754(14)	3 470(8)
C(9)	1 657(3)	3 109(15)	2 343(9)
C(10)	1 211(3)	3 428(15)	1 639(10)
C(11)	949(3)	5 376(17)	2 057(10)
C(12)	1 134(3)	6 995(16)	3 198(10)
C(13)	1 591(3)	6 716(16)	3 875(10)
C(14)	242(4)	7 589(24)	1 593(12)
H(20)	3 315	1 981	2 796
H(30)	4 107	1 225	4 109
H(50)	4 051	7 803	6 725
H(60)	3 261	8 560	5 416
H(71)	2 376	5 349	5 317
H(72)	2 416	2 616	4 333
H(90)	1 858	1 595	2 018
H(100)	1 067	2 157	761
H(120)	930	8 465	3 563
H(130)	1 743	8 031	4 713
H(141)	−97	7 451	903
H(142)	406	9 294	1 286
H(143)	208	7 645	2 821

The quantity minimized was $w(F_o\text{-}K^{-1}F_c)^2$ where K is the F_o scaling factor. For (Ia) the weighing scheme applied was $w = [\sigma_c^2(F_o) + 0.001\,2\ \ F_o^2]^{-1}$ and for (Ib) $w = [\sigma_c^2(F_o) + 0.006\,F_o^2 + 0.5 \sin\theta]^{-1}$, $\sigma_c^2(F_o)$ being the variance due to counting statistics. Scattering factors for nitrogen and sulphur (including the real part of the anomalous dispersion correction) were taken from ref. 7 and those for carbon, nitrogen, and oxygen from ref. 8. For (Ia) all sixteen hydrogen atoms, including those in the two methyl groups, could be located in a difference-Fourier synthesis; during the final stages of refinement the isotropic temperature factors of the hydrogen atoms were held constant and their positions maintained 1.08 Å from the respective bonded carbon atoms. Refinement was considered complete when the maximum ratio of shift-to-error was <0.1. The final conventional R index was 0.091 for 5 204 independent reflexions (R' 0.069). For (Ib) the refinement proceeded in essentially the same way as for (Ia) apart from the fact that in the final cycles isotropic temperature parameters were adjusted for the hydrogen atoms; the final R was 0.12, R' 0.15.

Final co-ordinates for (Ia) and (Ib) are given in Tables 1 and 2. Observed and calculated structure factors, and all

[7] ' International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[8] S. Harkema, Ph.D. Thesis, Technical University of Enschede, 1971.

thermal parameters are listed in Supplementary Publication No. SUP 22167 (30 pp., 1 microfiche).*

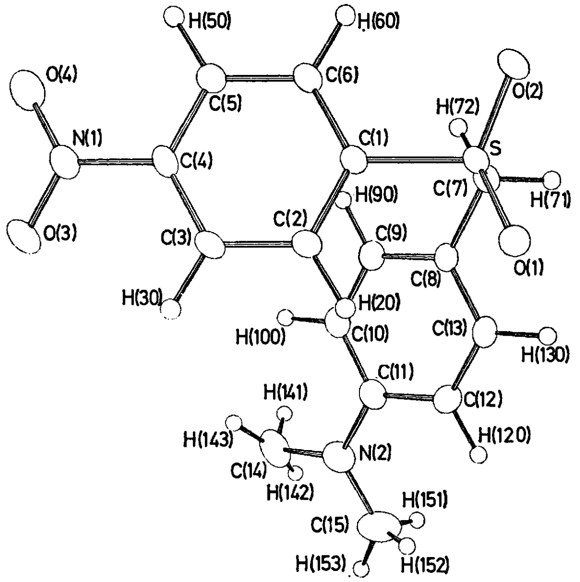

FIGURE 1 Structure of molecule (Ia) and the atom numbering scheme

The ' X-Ray ' system of crystallographic programs [9] was used for calculations.

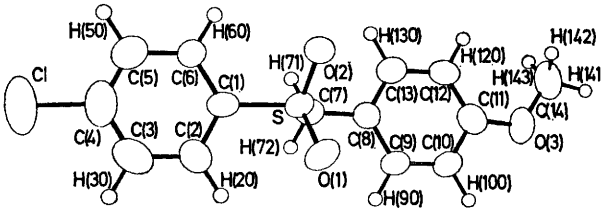

FIGURE 2 Structure of molecule (Ib) and numbering scheme

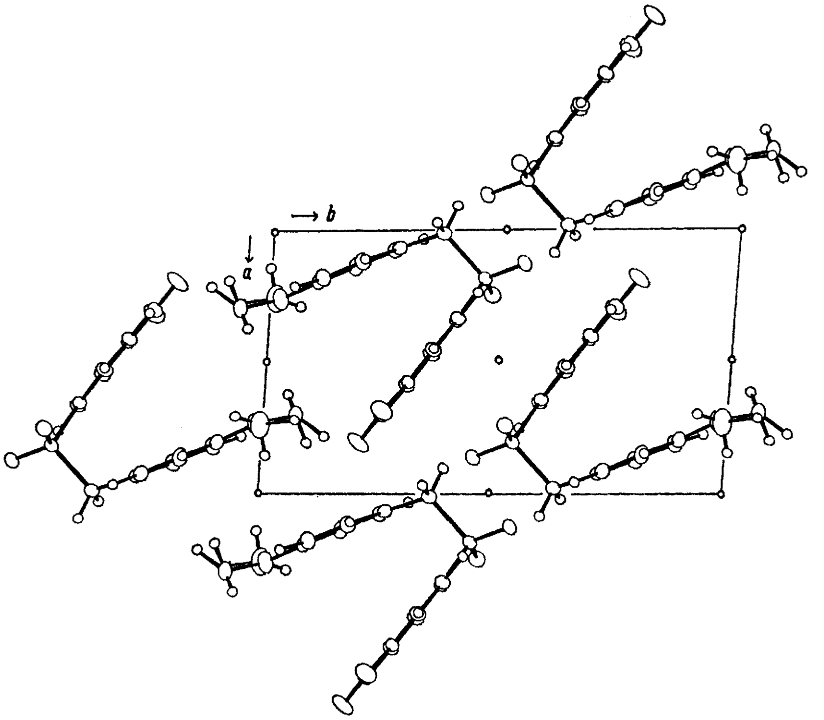

FIGURE 3 Crystal structure of (Ia) viewed along the c axis

RESULTS AND DISCUSSION

Crystal Packing.—The structures of the molecules (Ia) and (Ib) and the atom numbering scheme used are given in Figures 1 and 2 respectively. The packing of the molecules in the crystal is shown for (Ia) in Figure 3 and for (Ib) in Figures 4 and 5. Short intermolecular distances are given in Table 3. In both structures distances shorter than the sum of the relevant van der Waals radii [10] occur only between oxygen and hydrogen atoms of neighbouring molecules. Table 3 shows that in (Ia) the oxygen atoms of both the SO_2 and NO_2 groups have short distances with hydrogen atoms of neighbouring molecules, giving rise to a strongly packed three-dimensional structure. For (Ib) the short distances are depicted in Figure 5 which shows that the strong O • • • H interactions connect successive molecules in the b and c direction so that layers perpendicular to the a axis are formed (see also Figure 4). The presence of these layers explains the easy cleavage of the crystals along (100) as a result of which the crystals were easily deformed during experimental work and appeared to have a large mosaic spread. It may be noticed that

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[9] J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Technical Report TR 192, Computer Science Centre, University of Maryland, 1972.

[10] L. Pauling, ' The Nature of the Chemical Bond ', 3rd edn., Cornell University Press, Ithaca, New York, 1960.

short distances between SO_2 oxygen atoms and hydrogen atoms of neighbouring molecules are frequently observed, for instance in the structure of propenyl *p*-tolyl sulphone described in ref. 11*a*, in the further examples mentioned in this reference, and in the structure of *p*-tolylsulphonylmethyl perchlorate.[11b]

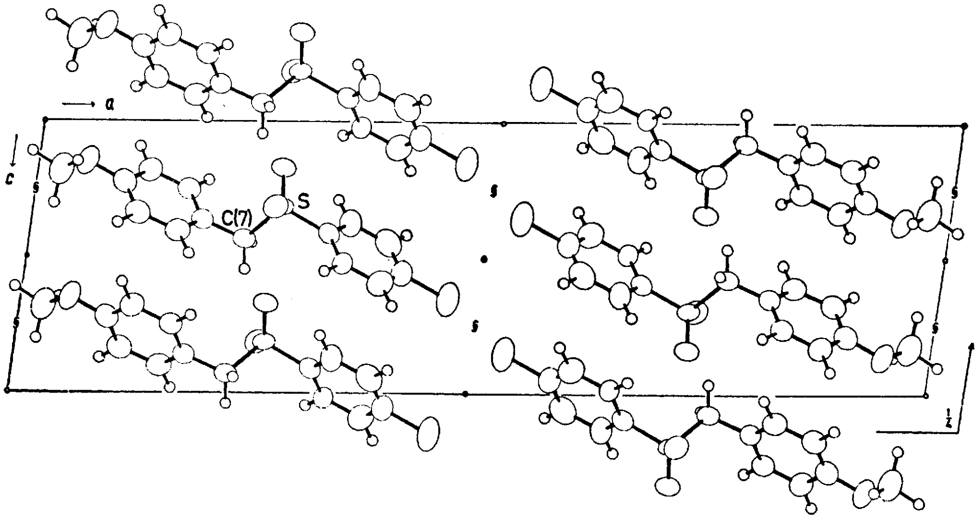

FIGURE 4 Crystal structure of (Ib) viewed along the *b* axis

Bond Lengths and Angles.—Interatomic distances and interbond angles with standard deviations are given in Table 3. The standard deviations were calculated on the assumption of an isotropic variance for each atomic position (covariances ignored) for (Ia) and by the program BONDLA of the '*X*-Ray' system for (Ib). Bonds in compound (Ia) are found to be slightly larger than corresponding bonds in (Ib) since for the low-temperature structure determination of (Ia) shortenings due to thermal motion[12] are less than for the room-temperature structure determination of (Ib).

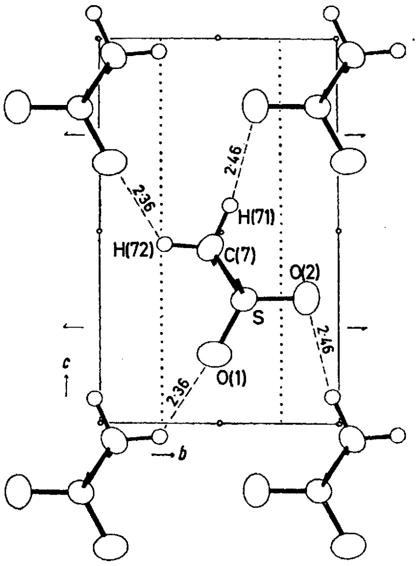

FIGURE 5 View of the portions of the molecules of (Ib) lying around $x = 1/4$, showing the short O · · · H distances between them

An interesting feature is the variation of the angles in the phenyl groups. Domenicano and Vaciago[13] have studied the variation of the angle α at the carbon atom bearing a substituent. In Table 4 literature values for α and C–X are compared with those for (Ia) and (Ib). Possible explanations of the variations are given by Domenicano *et al.*[14,15] In general our experimental values follow the same trend as for the literature values with the exception of values for X = SO_2 and $-NO_2$ which are somewhat larger. No explanation for this increase has yet been found. In (Ia) the C(Ph)–NMe_2 bond is considerably shorter than the C(Ph)–NO_2, owing to π conjugation of the dimethylamino-group with the phenyl ring. This conjugation also explains the trend in bond lengths for the $Me_2N\cdot C_6H_4-$ phenyl ring.[16] For the $NO_2\cdot C_6H_4-$ phenyl ring all C–C bonds are within 2σ of the mean (1.392 Å). For compound (Ib) the C–C bonds of the phenyl groups lie within a rather large experimental error equal to the mean (1.385 Å).

The geometries of the $-SO_2-$,[10,17] the NO_2,[18] and the NMe_2[19] groups in (Ia) and (Ib) do not show large

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[11] (*a*) A. H. Klazinga and A. Vos, *Rec. Trav. chim.*, 1973, **92**, 361; (*b*) J. B. F. N. Engberts, H. Morsink, and A. Vos, *J. Amer. Chem. Soc.*, in the press.

[12] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

[13] A. Domenicano and A. Vaciago, *Izvj. Jugoslav. Centr. Krist. (Zagreb)*, 1975, **10**, 37.

[14] A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.*, 1975, **B31**, 221.

[15] A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.*, 1975, **B31**, 1630.

[16] A. Domenicano and A. Vaciago, Collected Abstracts 3rd European Cryst. Meeting, 1976, p. 274, Abstract O 19 T.

[17] G. Chiari, D. Viterbo, A. Gaetani-Manfredotti, and C. Guastini, *Cryst. Struct. Comm.*, 1973, **2**, 539; I. J. Tickle and J. B. F. N. Engberts, *J.C.S. Perkin II*, 1973, 2031.

[18] G. Casalone, A. Gavezzotti, and M. Simonetta, *J.C.S. Perkin II*, 1973, 342; J. V. Barve and L. M. Pant, *Acta Cryst.*, 1971, **B27**, 1158.

[19] F. Bachechi and L. Zambonelli, *Acta Cryst.*, 1972, **B28**, 2489.

deviations from the geometries observed in other compounds. The shortening of the S–C(Ph) bond relative to the S–CH_2 bond may be ascribed to the relatively strong *s* character of the former.[20] The C_6H_4–O–Me portion of (Ib) is strongly analogous to that in other alkoxy-substituted phenyl groups.[21] In all these groups the Me moiety lies approximately in the plane of the phenyl ring. Due to the repulsion between the alkoxy-group and the phenyl ring, the angle at oxygen is large, whereas the bond C(Ph)–O lies asymmetrically in the plane of the phenyl ring. The difference of 0.09(2) Å between Me–O and O–C(Ph) in (Ib) is not significantly different from that [0.042(3) Å] observed between corresponding bonds in methyl *c*-4-*p*-methoxyphenyl-3-phenyl-Δ^1-pyrazoline-*r*-3-carboxylate.[22]

TABLE 3

Bond lengths (Å) and angles (°) in molecules (Ia) and (Ib), and short intermolecular O · · · H contacts (Å)

(*a*) Bond lengths

	(Ia)	(Ib)
S–O(1)	1.444(2)	1 433(6)
S–O(2)	1.449(2)	1.440(6)
S–C(1)	1.775(3)	1.768(9)
S–C(7)	1.791(3)	1.781(9)
C(1)–C(2)	1.398(4)	1.371(13)
C(2)–C(3)	1.392(4)	1.393(14)
C(3)–C(4)	1.382(4)	1.397(15)
C(4)–C(5)	1.393(4)	1.362(16)
C(5)–C(6)	1.400(4)	1.388(13)
C(6)–C(1)	1.385(4)	1.378(11)
C(4)–N(1)	1.476(4)	
N(1)–O(3)	1.230(4)	
N(1)–O(4)	1.219(4)	
Cl–C(4)		1.741(10)
C(7)–C(8)	1.503(4)	1.495(11)
C(8)–C(9)	1.401(4)	1.392(11)
C(9)–C(10)	1.386(4)	1.383(12)
C(10)–C(11)	1.408(4)	1.391(13)
C(11)–C(12)	1.414(4)	1.391(12)
C(12)–C(13)	1.383(4)	1.401(13)
C(13)–C(8)	1.386(4)	1.375(12)
C(11)–N(2)	1.380(4)	
N(2)–C(14)	1.449(5)	
N(2)–C(15)	1.440(5)	
C(11)–O(3)		1.355(11)
O(3)–C(14)		1.446(15)

(*b*) Angles

	(Ia)	(Ib)
O(1)–S–O(2)	118.2(1)	118.4(4)
O(1)–S–C(1)	108.4(1)	108.0(4)
O(2)–S–C(1)	108.6(1)	108.0(4)
O(1)–S–C(7)	109.3(1)	108.8(4)
O(2)–S–C(7)	108.2(1)	108.9(4)
C(1)–S–C(7)	103.0(1)	103.9(4)
S–C(1)–C(2)	119.4(1)	117.7(6)
S–C(1)–C(6)	118.1(1)	119.3(6)
C(6)–C(1)–C(2)	122.4(2)	123.1(7)
C(1)–C(2)–C(3)	118.8(2)	117.6(9)
C(2)–C(3)–C(4)	118.4(2)	119.3(10)
C(3)–C(4)–C(5)	123.5(2)	122.2(9)
C(4)–C(5)–C(6)	118.0(2)	118.6(9)
C(5)–C(6)–C(1)	118.9(2)	119.2(8)
C(3)–C(4)–N(1)	118.9(2)	
C(5)–C(4)–N(1)	117.6(2)	
C(4)–N(1)–O(3)	117.5(2)	
C(4)–N(1)–O(4)	118.3(2)	
O(3)–N(1)–O(4)	124.2(2)	
C(3)–C(4)–Cl		117.7(9)
C(5)–C(4)–Cl		120.1(8)
S–C(7)–C(8)	111.8(1)	110.9(5)
C(7)–C(8)–C(9)	120.9(2)	120.8(7)
C(7)–C(8)–C(13)	121.1(2)	118.3(7)
C(13)–C(8)–C(9)	118.0(2)	120.8(7)
C(8)–C(9)–C(10)	121.3(2)	119.7(8)
C(9)–C(10)–C(11)	120.8(2)	120.3(8)
C(10)–C(11)–C(12)	117.3(2)	119.8(8)
C(11)–C(12)–C(13)	120.9(2)	119.8(8)
C(12)–C(13)–C(8)	121.7(2)	119.6(8)
C(10)–C(11)–N(2)	121.8(2)	
C(12)–C(11)–N(2)	120.9(2)	
C(11)–N(2)–C(14)	120.8(2)	
C(11)–N(2)–C(15)	120.0(3)	
C(14)–N(2)–C(15)	117.4(3)	
C(10)–C(11)–O(3)		114.7(8)
C(12)–C(11)–O(3)		125.4(8)
C(11)–O(3)–C(14)		116.9(7)

TABLE 3 (*Continued*)

(*c*) Intermolecular contacts

(i) in (Ia)		(ii) in (Ib)	
O(1) · · · $\mathrm{H}(71^{\mathrm{I}})$	2.47	O(1) · · · $\mathrm{H}(72^{\mathrm{VI}})$	2.36
O(1) · · · $\mathrm{H}(50^{\mathrm{II}})$	2.38	O(1) · · · $\mathrm{H}(60^{\mathrm{VII}})$	2.37
O(2) · · · $\mathrm{H}(72^{\mathrm{III}})$	2.56	O(2) · · · $\mathrm{H}(71^{\mathrm{VII}})$	2.46
O(2) · · · $\mathrm{H}(60^{\mathrm{III}})$	2.50		
O(2) · · · $\mathrm{H}(130^{\mathrm{I}})$	2.56		
O(3) · · · $\mathrm{H}(153^{\mathrm{IV}})$	2.34		
O(4) · · · $\mathrm{H}(20^{\mathrm{V}})$	2.45		

Roman numeral superscripts denote the following equivalent positions with respect to the reference molecule at *x,y,z*.

I	$-x, -y + 1, -z$	V	$x, y, z + 1$
II	$x, y, z - 1$	VI	$x, -y + \frac{1}{2}, z - \frac{1}{2}$
III	$-x, -y + 1, -z + 1$	VII	$x, -y + 1\frac{1}{2}, z - \frac{1}{2}$
IV	$-x + 1, -y, -z$		

TABLE 4

Values for angles α (°) and bond lengths C–X (Å) [a]

	Literature		Present work		
Group	α	C–X	α	C–X	Cpd.
NMe_2	117.2(2) [b]	1.380(4) [c]	117.3(2)	1.380(4)	(Ia)
–CH_2	118.1(1) [d]	1.506(2) [d]	118.0(2)	1.503(4)	(Ia)
			120.8(7)	1.495(11)	(Ib)
OMe	119.9(2) [b]	1.370(2) [e]	119.8(8)	1.355(11)	(Ib)
SO_2	121.19(14) [f]	1.7534(14) [f]	122.4(2)	1.775(3)	(Ia)
			123.1(7)	1.768(9)	(Ib)
Cl	121.37(9) [f]	1.7404(11) [f]	122.2(9)	1.741(10)	(Ib)
NO_2	122.1(1) [d]	1.463(2) [d]	123.5(2)	1.476(4)	(Ia)

[a] In the system ArX, α is the angle C–C(X)–C. [b] Ref. 13. [c] Ref. 19. [d] Ref. 14. [e] Ref. 22. [f] Ref. 15.

Molecular Conformations.—The conformations of the two molecules, as observed in the solid state, are quite different. Molecule (Ia) has a folded conformation analogous to the preferred conformation in solution. In contrast, (Ib) exists in a stretched (*anti*) conformation in which the phenyl groups are situated in approximately parallel orientations. In an attempt to assess the favoured conformations, intramolecular potential-energy calculations were carried out for the free molecules, taking into account only non-bonded repulsion and van der Waals attraction. For these calculations Busing's program WMIN was used in the same way as described previously.[16b,23] Rotations around specific bonds were performed to find the conformation with minimal

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energy. Apart from these rotations the molecules were kept rigid with bond lengths and valence angles as observed in the crystal. For both (Ia) and (Ib) rotations were performed around:

S–C(7) Dihedral angle ϕ : C(1),S,C(7); S,C(7),C(8)
C(1)–C(7) Dihedral angle ν_1 : Ph[C(1)—C(6)]; C(1),S,C(7)
C(7)–C(8) Dihedral angle ν_2 : Ph[C(8)—C(13)]; S,C(7),C(8)

In the definition of the dihedral angles the following rules are obeyed: $\phi = 0$ for C(1) and C(8) eclipsed, and ν_1 and ν_2 are 90° when the normals to the benzene planes lie in the planes C(1),S,C(7) and S,C(7),C(8), respectively.

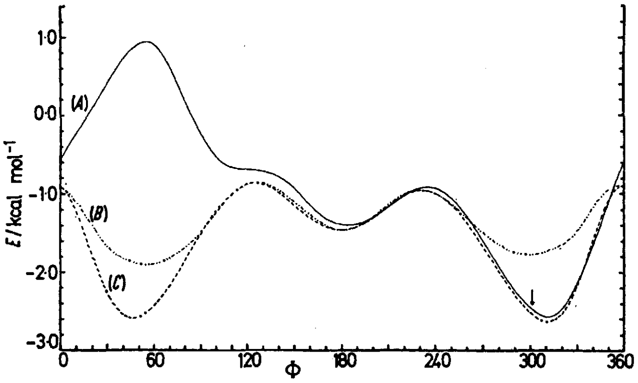

FIGURE 6 Variation of the calculated potential energy E as a function of ϕ for a free molecule of (Ia). For identification of curves see the text. The arrow indicates the ϕ value observed for the crystal

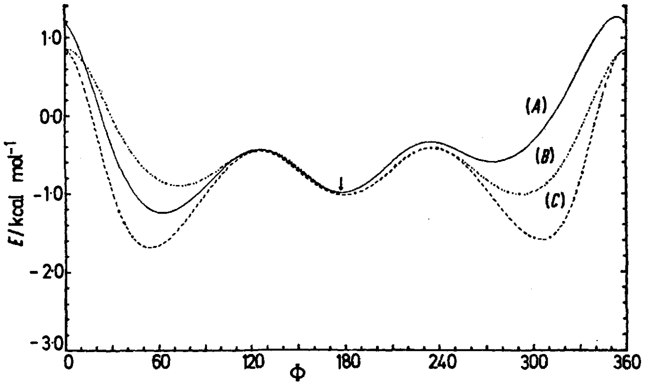

FIGURE 7 Variation of the calculated potential energy E as a function of ϕ for a free (Ib) molecule. See also legend of Figure 6

The changes in the angles are taken as positive, if in a Newman projection along the bond considered the rigid body of the front atom has to be rotated in clockwise direction to restore the original situation. Figures 6 and 7 show the potential energy for molecule (Ia) and (Ib), referred to an arbitrary zero, as a function of ϕ. For curve (A) the ν values are those of the conformation in the crystal. For curve (B) $\nu_1 = \nu_2 = 90°$. Curve (C) is obtained by choosing (stepwise) the best ν_1 and ν_2 (thus the values giving the minimum energy) for each ϕ. Dihedral angles for which minima of the energy are observed and the minimum E values are given in Table 5.

TABLE 5

Values for dihedral angles (°) for minimum values of E/kcal mol^{-1}. The three blocks correspond with curves (A), (B), and (C). The ν values for block (A) are those observed in the crystal. Values of ϕ for the crystal are 301 (Ia) and 177 (Ib)

	(1a)				(Ib)			
	ϕ	ν_1	ν_2	E	ϕ	ν_1	ν_2	E
					63	89	95	−1.25
(A)	186	85	81	−1.40	63	89	96	−0.99
	311	85	81	−2.57	17	89	96	−0.60
(B)	55	90	90	−1.90	73	90	90	−0.90
	181	90	90	−1.46	181	90	90	−1.02
	300	90	90	−1.77	292	90	90	−1.01
(C)	48	101	101	−2.59	55	101	102	−1.69
	183	89	93	−1.46	179	93	92	−1.02
	313	81	77	−2.63	307	81	80	−1.60

Figures 6 and 7 and Table 5 show that, in contrast to the situation in the solid state, a folded conformation is expected for both (Ia) and (Ib). We see, however, especially from block (C) in Table 5, which includes minimization of the energy with respect to all varied angles, that the difference in (minimum) energy $D(f - s)$ between the folded and stretched conformations is only small, −1.17 kcal mol^{-1} for (Ia) and −0.67 kcal mol^{-1} for (Ib). Differences between the conformations as observed in the crystals and those calculated for $E_{\min}$ may therefore well be attributed to packing forces. It may be noted that for molecule (Ia), for which a folded conformation is observed, $[D(f - s)]$ is approximately twice as large as for molecule (Ib), which has a stretched conformation in the crystal.

Charge Transfer.—In agreement with experiment for molecule (Ib) no CT is expected in view of the substituents at the phenyl groups and the large distances between these groups. For (Ia) in solution strong charge transfer, resulting in the reddish colour of the solution, is observed. Since the crystals of (Ia) also show a reddish colour the CT is expected to be maintained in the crystals. The present crystal structure determination of (Ia) shows, however, that the intramolecular overlap between the π orbitals of the acceptor (p-nitrophenyl) and donor (p-dimethylaniline) rings is not sufficiently large to explain the CT by 'through-space'[3-5] overlap. Neither does the arrangement of molecules in the lattice allow intermolecular overlap of this type, since the only significant plane-to-plane contacts (interplanar spacing 3.42 Å) occur between pairs of p-nitrophenyl rings related by the inversion centre at ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$). Quantum mechanical calculations will be carried out to assess the origin of the donor–acceptor interaction band of (Ia).

Calculations were carried out at the Computing Centre of the University of Groningen.

[7/1239 *Received, 13th July, 1977*]