phenobarbitone and primidone, are important in determining the pharmacological properties of these drug molecules. In order to compare the relative positions of the carbonyl O atoms in these molecules we may consider the distances O···(ring centroid), O···O across the ring, and the respective interplanar dihedral angles. These quantities are listed in Table 4 for methoin, together with those for phenytoin (Camerman & Camerman, 1971), phenobarbitone (Williams, 1973) and primidone (Yeates & Palmer, 1975). In order to investigate the molecular properties further, a more detailed geometrical comparison is to be undertaken and possible additional stable configurations sought through calculation of energy functions for the above-mentioned molecules. Newman projections comparing the configurations about C(5) in the four molecules are shown in Fig. 3.

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X-ray Study of Structure and Charge Density of 1-Methylsulfonyl-2-phenylsulfonylethane

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Abstract

A study has been made of the electronic structure and charge density of Me—SO_2—CH_2—CH_2—SO_2—Ph by X-ray diffraction at room temperature. The space group is $P\bar{1}$, $a = 5{\cdot}985\,(1)$, $b = 9{\cdot}144\,(3)$, $c = 10{\cdot}913\,(3)$ Å, $\alpha = 101{\cdot}14\,(3)$, $\beta = 108{\cdot}66\,(3)$, $\gamma = 93{\cdot}22\,(3)^\circ$, $Z = 2$. Counter data collected to a limit in $(\sin\theta)/\lambda = 0{\cdot}807$ Å^{-1} were corrected for absorption and averaged. Least-squares refinement with reflexions below $(\sin\theta)/\lambda = 0{\cdot}65$ Å^{-1} (2431F) and all reflexions (4501F) gave $R = 0{\cdot}030$ and $0{\cdot}042$, respectively. The high-order data [$(\sin\theta)/\lambda > 0{\cdot}65$ Å^{-1}] yielded a significantly improved model of the aromatic ring compared with that based on the low-order data. Small angular distortions of the ring reflect perturbations of the π-electron system caused by the SO_2R substituent. Other structure details such as the short central C—C bond, also found in related molecules, have been discussed with reference to the Walsh–Bent rehybridization theory. For the study of deformation density, atomic parameters were taken from the high-order refinement, except for H coordinates which correspond to normalized C—H lengths of 1·09 Å. Density maps were calculated with a cutoff in $(\sin\theta)/\lambda$ of 0·65 Å^{-1}. Elongated maxima in the aromatic C—C bonds, 0·27–0·36 e Å^{-3}, show π character. All S—C bonds appear purely σ symmetric. There are maxima in four of the five exocyclic C—H bonds. Details in the vicinity of the S and O atoms are less well-defined, peaks are broad and, where present, the lone-pair density near the O atoms is merged with the density in the S—O bonds. Taking into account the possible core-electron polarization of these atoms, more data at considerably higher resolution will be needed for an analysis of charge density in the SO_2 regions.

Introduction

Sulfur is a constituent of a variety of inorganic, organic and biological molecules with interesting physicochemical properties. In particular this element appears to play an important role for electron transport in widely different systems such as the inorganic polymeric semimetal $(SN)_x$ (Mikulski, Russo, Saran, MacDiarmid, Garito & Heeger, 1975; Yoffe, 1976) and in proteins (Morgan, Gushard, Carpenter & Chalfin,

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1976). Such properties must be associated with its exceptional versatility in bonding. S—S distances in various compounds are distributed almost continuously in the range from 1·86 Å in SSF_2 to van der Waals distances; valency angles range between 90 and 180° (Steudel, 1975). For example, in linear multisulfur systems such as thiathiophthene with three S atoms the two S—S lengths can be equal or unequal; variations from 2·16 to 2·56 Å reflect the ease with which the bond is perturbed by the presence of substituents and by crystal-packing forces (Hansen, Hordvik & Sæthre, 1975). The normal S—S single-bond length is 2·06 Å (Steudel, 1975) and the sum of the van der Waals radii, 3·40–3·60 Å (Bondi, 1964; Walker, Folting & Merritt, 1969). Linear systems with four and five S atoms exhibit an even larger spread, 2·00–3·00 Å; a prerequisite for the formation of bonds of intermediate length in these systems is the possible delocalization of excess electrons (Sletten, 1976).

The structures of various cyclic sulfur systems provide further information on bonding properties of this element. The average S—S lengths in S_6 (Donohue, Caron & Goldish, 1961), S_8 (Caron & Donohue, 1965), S_{12} (Kutoglu & Hellner, 1966), S_{18} and S_{20} (Schmidt, Wilhelm, Debaerdemaeker, Hellner & Kutoglu, 1974) are closely similar, 2·047–2·059 Å, with little scatter about the mean. Much larger variations are found in S_7 (Steudel, Reinhardt & Schuster, 1977) and the oxides S_7O (Steudel, Reinhardt & Sandow, 1977) and S_8O (Luger, Bradaczek, Steudel & Rebsch, 1976), for instance in S_7O: 1·97–2·28 Å. The shortest transannular S···S contacts in these molecules are in the range 3·20–3·35 Å, corresponding to short van der Waals distances. In the cyclic ion S_8^{2+}, however, there are three short transannular S···S contacts, 2·86–3·00 Å, implying partial bonding (Davies, Gillespie, Park & Passmore, 1971).

Similar through-space interactions characterize several cyclic S—N compounds; for a review of this class of molecules see Roesky (1979). Tetrasulfur tetranitride, S_4N_4, in a cradle-like conformation with D_{2d} symmetry has two S···S distances about 2·60 Å across the ring (Sharma & Donohue, 1963; DeLucia & Coppens, 1978). The preference for this particular bonding arrangement has been rationalized from considerations of symmetry and MO calculations (Gleiter, 1970; Cassoux, Labarre, Glemser & Koch, 1972). The S_4N_4 cradle is a structure element in other SN cage compounds where the short bottom S···S contact of the cradle is preserved. In S_5N_6 it is 2·425 Å (Chivers & Proctor, 1978) and in the anions $[S_4N_4O_2(OCH_3)]^-$: 2·482 Å (Roesky, Witt, Krebs & Korte, 1979) and $[S_4N_5O]^-$: 2·632 Å (Luger, Bradaczek & Steudel, 1976). Slight changes in the ring electron density furthermore can have a drastic effect on the spatial structures of cyclic S and SN compounds. This is amply illustrated in the series $S_8 \rightarrow S_8^{2+} \rightarrow S_4N_4$ (isoelectronic with S_8^{4+}) $\rightarrow S_4N_4^{2+}$ where the number of π electrons decreases by 2 in each successive member (Davies *et al.*, 1971; Gillespie, Slim & Tyrer, 1977).

A rational explanation of the large variability in sulfur bonding is still incomplete. A major problem pertains to the possible participation of 3*d* orbitals (*cf.* for example Brill, 1973). With proper orbital symmetry, significant mixing and bond formation with adjacent atoms require similarity both in energy and radial size of these orbitals. Contraction of the 3*d* orbitals in S necessary for significant bonding depends largely on the number of electrons promoted from lower orbitals and the effective nuclear charge (Coulson, 1969). Thus, participation of *d* orbitals is more plausible when electronegative first-row elements like N, O and F are involved. A small calculated 3*d*-orbital contribution to bonding in non-empirical MO—SCF studies has been ascribed to the use of inadequate *s*- and *p*-type basis sets (Clark, 1970), or to some polarization of *s* and *p* orbitals which can be simulated by mixing in *d*-orbital functions (Coulson, 1969). Recent MO—SCF calculations on ethylene episulfide, episulfoxide and episulfone, however, have indicated that the 3*d*-orbital population does become significant with increasing positive charge on S in these and other molecules with S—O and S—F bonds (Rohmer & Roos, 1975). Participation of *d* orbitals also seems to be important in some reactions involving S-containing molecules (Tatsumi, Yoshioka, Yamaguchi & Fueno, 1976).

We have initiated diffraction studies of electronic structure and charge density in small organic molecules containing S. Preliminary results for a group of compounds with the general formula R_1—SO_2—CH_2—CH_2—SO_2—R_2 were presented recently (Mo, Berg, Thorkildsen & Gaasdal, 1979). The present X-ray study of the species with R_1 = Me and R_2 = Ph was conducted at room temperature and the data are of limited resolution. Some S-containing molecules studied by combined X-ray and neutron diffraction are given in a compilation by Coppens (1978). Other relevant structures subject to X-ray studies at varying resolution are: 2,5-dimercaptothiadiazole (Bats, 1976), sodium sulfanilate dihydrate (Bats, 1977*a*), dicyanotrisulfane (Bats, 1977*b*), tetrasulfur tetranitride (DeLucia & Coppens, 1978), pyrite (Stevens, DeLucia & Coppens, 1980), thiotrithiazyl nitrate (Moss, Guru Row & Coppens, 1980) and potassium iron disulfide (Stevens, 1979).

Experimental

Single crystals of 1-methylsulfonyl-2-phenylsulfonylethane, hereinafter $MPSO_2$, from acetone were long prismatic with well-developed faces (100), (010), (001) and (011).

Table 1. *Crystal data*

1-Methylsulfonyl-2-phenylsulfonylethane, $C_9H_{12}O_4S_2$

a = 5·985 (1) Å	M_r = 248·32
b = 9·144 (3)	Space group: $P\bar{1}$
c = 10·913 (3)	λ = 0·71073 Å
α = 101·14 (3)°	Z = 2
β = 108·66 (3)	D_x = 1·497 Mg m^{-3}
γ = 93·22 (3)	μ = 0·454 mm^{-1}*
V = 550·7 Å^3	Size: ~0·23 × 0·40 × 0·49 mm
T = 293·0 (5) K	M.p.: 447·0–448·0 K

* Mass absorption coefficients taken from *International Tables for X-ray Crystallography* (1974).

Lattice constants were determined from the setting angles of 20 reflexions (Table 1). The measurements were made at the beginning and twice during data collection. Changes in all parameters were $<2\sigma$. Intensities were measured without attenuators to a limit in $(\sin\theta)/\lambda$ of 0·807 Å^{-1} with Nb-filtered Mo $K\alpha$ radiation on a diffractometer controlled by the Vanderbilt disk-oriented program system (Lenhert, 1975). At this $(\sin\theta)/\lambda$ only about 57% of the reflexions had $I > 3\sigma(I)$. Data set 1 comprised 5235 $-h \pm k \pm l$ reflexions including 376 equivalent pairs $0 \pm k \pm l$; a partial set 2 of 1307 $h \pm k \pm l$ reflexions was also collected. The scan mode was $\omega/2\theta$ at 2° min^{-1} in 2θ, basic scan width was $2\theta(\alpha) - 0{\cdot}75$ to $2\theta(\alpha) + 0{\cdot}9°$, and backgrounds were measured for 20 s at each limit of the scan. Intensities below $2\theta = 12°$ were remeasured semi-manually with reduced low-angle scans to minimize errors caused by the Nb K absorption edge. Three standard reflexions were monitored at intervals of 70 reflexions. The data were scaled with a polynomial fit to the average standard decay and corrected for coincidence loss (Chipman, 1969; Mo & Jensen, 1975). The experimental recovery constant with this crystal was $9{\cdot}0 \times 10^{-8}$ counts^{-1}. Absorption coefficients were in the range 1·096 to 1·206, and corrections were applied to the intensities with a locally modified version of the program *ABSOR* (Templeton & Templeton, 1973) which is based on the analytical method (de Meulenaer & Tompa, 1965).

Weighted averages (w) of F^2 and $\sigma(F^2)$ were calculated for the equivalent reflexion pairs of set 1 and sets 1 and 2. For an F_i^2, $\sigma(F_i^2) = \sigma(I_i)\,(\mathrm{Lp})^{-1}(\text{scale})$ and $\sigma^2(I_i) = \sigma^2_{i\text{count}} + (SI_{i\text{net}})^2$; $i = 1, 2$. $D = \sum|F_1^2 - F_2^2|/\sum F_w^2$ for 1683 equivalent pairs was 0·0187. Assuming a normal distribution of the weighted mean of the differences $\Delta_i = |F_i^2 - F_w^2|$ the parameter S was adjusted to 0·014 following a frequency test of $z = \Delta_w/\sigma_w$. Eleven reflexions were deleted at this stage: two at $2\theta < 5°$ due to interference of the Nb K absorption edge with the peak itself, eight because counting rates were well outside the range for coincidence-loss corrections and one because of diffractometer malfunction. Another 347 reflexions with $F^2 < \sigma(F^2)$ were given zero weight.

A set of local programs was used for analyses and reduction of the data (Svinning & Mo, 1978). Calculations of residual electron density in an arbitrary plane were made with the subroutine *SPFT* (van de Waal, 1975). Other crystallographic programs were from XRAY 76 (Stewart, 1976). Molecular drawings were made with *ORTEP* (Johnson, 1976).

Structure determination and refinement

Tentative positions for the two S atoms of one molecule were found from a Patterson map. The correct pair of atomic sites and their position relative to a center of symmetry were readily established from a ΔF map after relaxing the space-group symmetry to $P1$. Identification of C and O atoms was by standard methods. Isotropic and later anisotropic refinement of the non-H atoms converged at $R(F) = 0{\cdot}057$; H positions were then located in maxima of density 0·5–0·75 e Å^{-3}.

Least-squares refinement

The quantity $\sum w(|F_o| - k|F_c|)^2$ with $w = 1/\sigma^2(F_o)$ was minimized by full-matrix least squares. Scattering factors were those of Doyle & Turner (1968) except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion values for S were taken from Cromer & Liberman (1970). Anisotropic temperature factors were assigned to C, O and S but not to H.

Separate refinements were carried out with reflexions below (LO) and above (HO) $s = (\sin\theta)/\lambda = 0{\cdot}65$ Å^{-1}. In the HO refinement atomic parameters of H were fixed at values obtained from a refinement with data above $s = 0{\cdot}30$ Å^{-1}. A review of various refinements is given in Table 2. Final atomic coordinates are given in Table 3.*

Deformation density maps

Deviations from the idealized charge density implicit in the harmonic description of the molecule as an

Table 2. *Survey of refinements*

Refinement	LO	ALL	HO
$(\sin\theta)/\lambda$ range (Å^{-1})	0–0·65	0–0·807	0·65–0·807
Number of reflexions with $w \neq 0$, NO	2431	4501	2070
Number of reflexions with $w = 0$	87	347	260
Number of variables, NV	184	184	136
Scale factor, k	8·852 (14)	8·795 (10)	8·403 (67)
$R(F) = \sum\|F_o - kF_c\|/\sum\|F_o\|$	0·030	0·042	0·063
$R_w(F) = [\sum w(F_o - kF_c)^2/\sum wF_o^2]^{1/2}$	0·035	0·037	0·038
$R(F^2) = \sum\|F_o^2 - (kF_c)^2\|/\sum F_o^2$	0·040	0·045	0·064
GOF = $[\sum w(F_o - kF_c)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$	3·80	3·05	1·34
Max. shift/error	0·09	0·15	0·08
Max. correlation	0·52	0·54	0·89

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* Tables of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35333 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional parameters* ($\times 10^5$ *for* S; $\times 10^4$ *for* C *and* O; $\times 10^3$ *for* H)

For non-H atoms: first row: low-order refinement (LO); second row: refinement with all reflexions (ALL); third row: high-order refinement (HO). For H atoms: first row: LO refinement; second row: refinement with reflexions beyond $(\sin\theta)/\lambda$ = 0·30 Å^{-1}. E.s.d.'s are in parentheses.

	x	y	z		x	y	z
S(1)	73628 (7)	40208 (4)	65534 (3)	C(7)	3844 (4)	2614 (2)	−168 (2)
	73626 (5)	40210 (3)	65530 (2)		3844 (3)	2614 (2)	−169 (1)
	73616 (8)	40227 (4)	65506 (3)		3843 (5)	2623 (3)	−179 (2)
S(2)	80206 (7)	7289 (4)	32852 (3)	C(8)	6284 (4)	2986 (2)	376 (2)
	80207 (6)	7287 (3)	32851 (2)		6285 (3)	2988 (1)	376 (1)
	80224 (9)	7277 (4)	32845 (4)		6306 (5)	2999 (3)	376 (2)
O(1)	7868 (2)	5336 (1)	6090 (1)	C(9)	7556 (3)	2418 (2)	1443 (1)
	7869 (2)	5337 (1)	6089 (1)		7560 (2)	2418 (1)	1443 (1)
	7858 (4)	5347 (2)	6084 (2)		7572 (3)	2425 (2)	1448 (2)
O(2)	9210 (2)	3679 (1)	7628 (1)				
	9211 (2)	3679 (1)	7628 (1)	H(11)	359 (3)	440 (2)	626 (2)
	9235 (6)	3679 (3)	7624 (2)		350 (4)	439 (2)	622 (2)
O(3)	6543 (2)	−496 (1)	3407 (1)	H(12)	525 (3)	499 (2)	770 (2)
	6542 (2)	−497 (1)	3407 (1)		515 (4)	499 (2)	772 (2)
	6542 (5)	−501 (2)	3411 (2)	H(13)	446 (3)	335 (2)	723 (2)
O(4)	10272 (2)	458 (1)	3133 (1)		435 (3)	327 (2)	720 (2)
	10274 (2)	458 (1)	3133 (1)	H(21)	611 (3)	169 (2)	546 (2)
	10287 (5)	459 (3)	3133 (2)		601 (3)	165 (2)	548 (2)
C(1)	4796 (4)	4184 (2)	6982 (2)	H(22)	524 (3)	268 (2)	447 (2)
	4796 (3)	4184 (2)	6981 (1)		512 (3)	272 (2)	446 (2)
	4786 (5)	4182 (2)	6986 (2)	H(31)	982 (3)	188 (2)	534 (2)
C(2)	6525 (3)	2449 (2)	5166 (1)		995 (3)	191 (2)	539 (1)
	6524 (2)	2449 (1)	5167 (1)	H(32)	927 (3)	303 (2)	453 (1)
	6513 (3)	2452 (2)	5172 (2)		929 (3)	310 (1)	454 (1)
C(3)	8651 (3)	2198 (2)	4728 (1)	H(51)	312 (3)	51 (2)	177 (2)
	8653 (2)	2198 (1)	4728 (1)		321 (3)	53 (2)	178 (2)
	8659 (3)	2197 (2)	4729 (1)	H(61)	116 (3)	140 (2)	−1 (2)
C(4)	6349 (3)	1484 (1)	1951 (1)		91 (4)	138 (2)	−5 (2)
	6348 (2)	1484 (1)	1951 (1)	H(71)	301 (3)	295 (2)	−84 (2)
	6351 (3)	1480 (2)	1951 (1)		300 (4)	301 (2)	−91 (2)
C(5)	3905 (3)	1115 (2)	1417 (2)	H(81)	716 (3)	363 (2)	0 (2)
	3903 (2)	1114 (1)	1418 (1)		714 (4)	368 (2)	0 (2)
	3899 (4)	1107 (3)	1417 (2)	H(91)	918 (3)	268 (2)	182 (1)
C(6)	2672 (3)	1703 (2)	346 (2)		927 (3)	267 (1)	182 (1)
	2670 (3)	1703 (2)	345 (1)				
	2652 (4)	1693 (4)	338 (2)				

assembly of isolated, spherical atoms are commonly studied by deformation density maps (Coppens, 1975). Such maps can be obtained as the difference between the observed and the calculated electron density from modified spherical X-ray refinements. Positional and thermal parameters for C, O and S from the HO refinement were used here as the best model available for the nuclear positions of these atoms.

As predicted from theory (Cochran, 1956; Stewart *et al.*, 1965; O'Connell, Rae & Maslen, 1966) and experimental evidence (*e.g.* Cochran, 1953; Hanson, Sieker & Jensen, 1973; Kvick, 1974) the positional parameters of bonded H atoms from conventional X-ray least-squares refinement are systematically affected by the strong asphericity of the electron density near H. Combined X-ray and neutron diffraction studies have shown that the X-ray shift of the charge centroid relative to the nuclear position is along the X—H vector. The effect is shortening but not, as a rule, any significant angular distortion at this bond (Kvick, 1974; Thomas, 1977). Thus, in the absence of unbiased parameters for H a reliable and significant correction for the X-ray shortening of X—H lengths can be applied. In the present work all C—H distances were normalized to 1·09 Å. Thermal parameters for the H atoms were from the ALL refinement (Table 2).

Deformation density maps were calculated with data below s = 0·65 Å^{-1} corrected for anomalous dispersion. The scale factor, k = 8·60 (1), was obtained from refinement of this parameter alone with atomic parameters fixed at values as described above. $R(F)$ was 0·040.

Discussion

The molecular structure

The molecular structure is shown in Fig. 1. The fragment C(Me)—S—C—C—S is approximately planar;

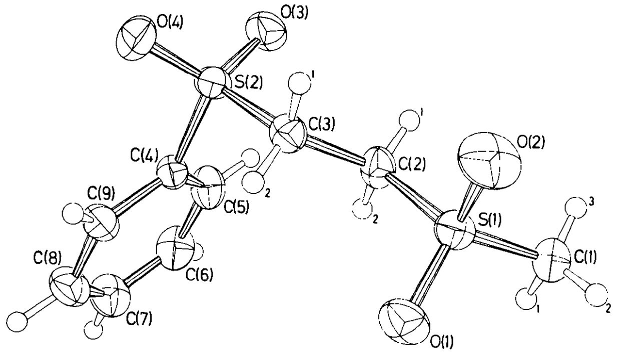

Fig. 1. Molecular conformation and atomic labelling. Sequential numbering of H atoms is given only where necessary. Thermal ellipsoids of the non-H atoms correspond to a 50% probability.

Table 4. *Asphericity shifts* (Å)

	HO–LO	HO–ALL
S(1)	0·0037 (5)	0·0032 (4)
S(2)	0·0018 (7)	0·0016 (6)
O(1)	0·014 (2)	0·013 (2)
O(2)	0·017 (4)	0·016 (4)
O(3)	0·007 (2)	0·006 (2)
O(4)	0·009 (3)	0·008 (3)
C(1)	0·010 (4)	0·010 (4)
C(2)	0·011 (3)	0·010 (3)
C(3)	0·005 (2)	0·004 (2)
C(4)	0·005 (2)	0·004 (2)
C(5)	0·008 (3)	0·006 (3)
C(6)	0·014 (3)	0·013 (3)
C(7)	0·016 (3)	0·015 (3)
C(8)	0·017 (3)	0·016 (3)
C(9)	0·011 (2)	0·009 (2)

S(1) through S(2) deviate from this plane by 0·02–0·03 Å. The sequence C(2)–C(3)–S(2)–C(4) is oriented *gauche*.

There are systematic differences between atomic positions from the LO and HO refinements (Table 4). (Values from the LO and ALL refinements are not different.) Shifts of the C atoms are in the range 0·005–0·017 Å. The major effect of HO refinement on the ring is a slight expansion and rotation relative to the LO structure. The apparent contraction of aromatic rings in LO refinements has been observed repeatedly, *e.g.* O'Connell *et al.* (1966).

As expected, HO shifts of the O atoms are directed largely away from the attached S atoms towards the lone-pair region. The present HO data set is too restricted in range, however, to yield nuclear positions of the bonded O atoms free of errors. Scattering on the lone-pair density persists into the region beyond $s = 0{\cdot}75$ Å^{-1} (Wang, Blessing, Ross & Coppens, 1976), in some cases as far out as $1{\cdot}0$ Å^{-1}, even at room temperature (Stevens, 1977). At low temperatures lone-pair scattering can be significant at still higher Bragg angles (Coppens & Lehmann, 1976). On the other hand the contribution from bonding electrons to the HO data is negligible due to their more diffuse character. Ottersen & Hope (1976) obtained the maximum asphericity shifts for all atoms from a refinement with $s_{\rm min} = 0{\cdot}50$ Å^{-1} in a liquid nitrogen X-ray study of diformylhydrazine. Similarly, the maximum shifts for O in sulfamic acid studied at 78 K appeared in the refinement with s in the range 0·65–0·85 Å^{-1} (Bats, Coppens & Koetzle, 1977).

Bond lengths and angles from the LO and HO refinements are given in Tables 5 and 6. The values are not corrected for libration shortening.

The average phenyl C–C bond increased from 1·383 Å, range 1·366–1·391 Å, in the LO refinement to 1·393 Å and a considerably narrower range, 1·388–1·398 Å, with the HO data. These results show the improved quality of the HO data, at least for describing the hydrocarbon part of the molecule, and illustrate the relative contribution of bonding electrons to the apparent shrinkage of benzene rings in LO refinements. There are three categories of endocyclic bond angles relative to the position of the electronegative SO_2 substituent: α(*ipso*), β(*ortho*), γ(*meta*) and δ(*para*) (Table 6). Deviations from 120° in the angles α (121·8°) and $\beta_{\rm mean}$ (118·8°) are in qualitative agreement with predictions from the Walsh–Bent rehybridization theory which considers only

Table 5. *Bond lengths* (Å) *with e.s.d.'s*

Results from the LO and HO refinements are given. H parameters in the HO set were fixed at values from a refinement with $s > 0{\cdot}30$ Å^{-1}.

	LO	HO
S(1)–O(1)	1·444 (1)	1·452 (2)
S(1)–O(2)	1·430 (1)	1·439 (3)
S(1)–C(1)	1·749 (2)	1·759 (3)
S(1)–C(2)	1·789 (1)	1·783 (2)
S(2)–O(3)	1·441 (1)	1·446 (2)
S(2)–O(4)	1·439 (2)	1·445 (3)
S(2)–C(3)	1·781 (2)	1·782 (2)
S(2)–C(4)	1·770 (2)	1·768 (2)
C(2)–C(3)	1·511 (3)	1·525 (3)
C(4)–C(5)	1·384 (2)	1·389 (3)
C(5)–C(6)	1·391 (3)	1·398 (4)
C(6)–C(7)	1·366 (3)	1·388 (5)
C(7)–C(8)	1·383 (3)	1·396 (4)
C(8)–C(9)	1·384 (2)	1·390 (3)
C(9)–C(4)	1·389 (3)	1·396 (3)
C(1)–H(11)	0·95 (2)	1·00 (2)
C(1)–H(12)	0·92 (2)	0·94 (2)
C(1)–H(13)	0·89 (2)	0·95 (2)
C(2)–H(21)	0·87 (2)	0·94 (2)
C(2)–H(22)	0·96 (2)	1·02 (2)
C(3)–H(31)	0·91 (2)	0·97 (2)
C(3)–H(32)	0·92 (2)	0·97 (1)
C(5)–H(51)	0·91 (2)	0·87 (2)
C(6)–H(61)	0·87 (2)	0·99 (2)
C(7)–H(71)	0·87 (2)	0·94 (2)
C(8)–H(81)	0·99 (2)	1·00 (2)
C(9)–H(91)	0·92 (2)	0·96 (2)

Table 6. *Valency angles* (°) *with e.s.d.'s*

The values are from the HO refinement, H parameters were fixed at values from a refinement with $s > 0{\cdot}30$ Å^{-1}.

C(1)S(1)C(2)	103·9 (1)	S(1)C(1)H(13)	109 (1·3)
C(1)S(1)O(1)	108·6 (1)	H(11)C(1)H(12)	110 (1·7)
C(1)S(1)O(2)	109·6 (2)	H(11)C(1)H(13)	111 (1·5)
C(2)S(1)O(1)	107·9 (1)	H(12)C(1)H(13)	110 (1·8)
C(2)S(1)O(2)	109·0 (1)	S(1)C(2)H(21)	106 (0·9)
O(1)S(1)O(2)	117·0 (2)	S(1)C(2)H(22)	106 (0·8)
S(1)C(2)C(3)	108·1 (1)	C(3)C(2)H(21)	113 (1·2)
C(2)C(3)S(2)	113·2 (1)	C(3)C(2)H(22)	113 (1·2)
C(3)S(2)C(4)	105·5 (1)	H(21)C(2)H(22)	110 (1·4)
C(3)S(2)O(3)	108·1 (1)	C(2)C(3)H(31)	113 (1·1)
C(3)S(2)O(4)	106·2 (1)	C(2)C(3)H(32)	112 (0·9)
C(4)S(2)O(3)	108·7 (1)	S(2)C(3)H(31)	105 (0·9)
C(4)S(2)O(4)	108·7 (1)	S(2)C(3)H(32)	108 (0·8)
O(3)S(2)O(4)	118·9 (2)	H(31)C(3)H(32)	107 (1·2)
S(2)C(4)C(5)	120·1 (2)	C(4)C(5)H(51)	119 (1·1)
S(2)C(4)C(9)	118·1 (1)	C(6)C(5)H(51)	123 (1·1)
C(4)C(5)C(6)β*	118·3 (2)	C(5)C(6)H(61)	117 (1·2)
C(5)C(6)C(7)γ*	120·6 (2)	C(7)C(6)H(61)	122 (1·2)
C(6)C(7)C(8)δ*	120·5 (2)	C(6)C(7)H(71)	121 (1·3)
C(7)C(8)C(9)γ*	119·6 (2)	C(8)C(7)H(71)	119 (1·3)
C(8)C(9)C(4)β*	119·2 (2)	C(7)C(8)H(81)	120 (1·0)
C(9)C(4)C(5)α*	121·8 (2)	C(9)C(8)H(81)	121 (1·0)
		C(8)C(9)H(91)	120 (1·0)
S(1)C(1)H(11)	108 (1·4)	C(4)C(9)H(91)	121 (0·9)
S(1)C(1)H(12)	107 (1·5)		

* Endocyclic angles α, β, γ and δ are *ipso*, *ortho*, *meta* and *para*, respectively, to the position of the SO_2 group.

σ-bonding (Walsh, 1947; Bent, 1961). There is also a significant distortion of the angle δ. This particular deformation, presumably mainly due to perturbations of the π-electron system by the substituent, has been noted and analyzed in other recent studies of substituted benzene rings (Norrestam & Schepper, 1978, 1979; Domenicano & Vaciago, 1979). The observed angular deviations from 120° in MPSO$_2$: $\Delta\alpha = +1{\cdot}8$, $\Delta\beta = -1{\cdot}2$, $\Delta\gamma = +0{\cdot}1$ and $\Delta\delta = +0{\cdot}5°$ are in good agreement with the values in a comparative analysis by Domenicano & Murray-Rust (1979). S(2)—C(4) is significantly longer, however, than the mean value given for corresponding S—C bonds, 1·753 Å (Domenicano, Vaciago & Coulson, 1975).

A short central C—C bond in the fragment $-SO_2-CH_2-CH_2-SO_2-$ can be anticipated as a secondary effect of rehybridization at S (Svinning, Mo & Bruun, 1976). This bond is slightly longer in MPSO$_2$, 1·525 (3) Å, than in some closely related structures: 1·516 (2) Å in *meso*-1,2-bis(methylsulfinyl)ethane (Svinning *et al.*, 1976), 1·515 (3) Å in 1-methylsulfonyl-2-methylsulfinylethane (Berg, Bruun & Mo, 1978) and 1·515 (2) Å in 1,2-bis(methylsulfonyl)ethane (Mo *et al.*, 1979). The mean S—O length from the HO refinement is 1·446 Å with range 1·439–1·452 Å.

According to the Walsh–Bent theory, substitution of the terminal methyl with the more electronegative phenyl ring will effect less p character in the σ bonds from S towards both O and the central C atom. Since less p character implies larger valency angles we expect for a purely σ-bonded system angles O—S—O and C(central)—S—O to be larger in the phenyl end of the molecule. This is true for the O—S—O angles which differ by about 2°. However, the average C(central)—S—O angle near phenyl is *smaller* by about 1·5°. The C(terminal)—S—O angles seem hardly influenced by the nature of the end group while C—S—C is slightly larger at the phenyl end. The apparent small anomalies in some of the angles must be viewed in conjunction with the fact that the two substituents do not differ much in electronegativity [the dipole moment of toluene is $1{\cdot}3 \times 10^{-30}$ Cm with methyl as the positive end (Gould, 1964)]. On the other hand they are distinct with respect to their ability to form π bonds. The spread within each type of angle further indicates some influence of intra- and intermolecular forces.

With one exception, refinement with data beyond $s = 0{\cdot}30$ Å^{-1} increased all C—H lengths over the LO result by an average ~0·05 Å (Table 5). The H parameters became unstable in refinements with higher $s_{\min}$, presumably due to a critical lowering of the statistical accuracy of the data and the dominance of S scattering.

The crystal structure

The aromatic and aliphatic parts constitute separate regions of the crystal structure (Fig. 2). Double layers of phenyl rings are generated by the translation repetition **a**, see for example molecules 2* and 1, and by inversion through symmetry centers at $m \times \frac{1}{2}$ along x where m is an odd integer. Molecules 1 and 8 are

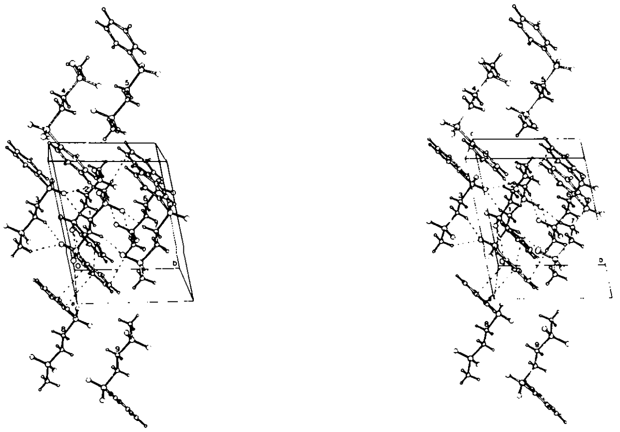

Fig. 2. Stereodrawing of the molecular packing with shortest interatomic contacts drawn as broken lines. Molecular numbering corresponds to the following symmetry code: (1) x,y,z; (2) $-1+x,y,z$; (3) $1-x,-y,1-z$; (4) $1+x,y,1+z$; (5) $2-x,1-y,2-z$; (6) $1-x,1-y,1-z$; (7) $2-x,1-y,1-z$; (8) $1-x,-y,-z$; (9) $x,y,-1+z$.

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* 2 denotes molecule at $-1+x, y, z$. The symmetry code is explained in the legend of Fig. 2.

related by inversion. The rings within one layer are connected through van der Waals contacts of the type $\mathrm{C}(9)^{*}_{2}\cdots\mathrm{C}(6)$, 3·665 (4) Å. Adjacent rings of neighboring layers are displaced laterally by $\frac{1}{2}$ ring width relative to each other. C(4) and C(6) of one ring are thus positioned directly above C(6) and C(4), respectively, of the other. The distance between the ring planes is 3·654 Å.

The O atoms play a key role in the packing of chain ends and are also involved in contacts to the aromatic rings. Eight O···C contacts are in the normal van der Waals range (Kitaigorodskii, 1973), 3·326–3·483 Å; the mean value is 3·381 Å. There are several short O···H contacts. With normalized C—H lengths the range of contact distances narrows considerably. The five shortest O···H distances then range from 2·36 to 2·41 Å compared with 2·44–2·53 Å when uncorrected H coordinates were taken from the refinement with data beyond $s = 0{\cdot}30$ Å^{-1}.

Deformation density maps

The deformation density calculated as described previously has been mapped in various planes through the molecule. The standard deviation in the density away from the nuclear positions has been estimated at 0·03–0·05 e Å^{-3} from the density variations in the general regions.

The map in the plane of the phenyl ring is shown in Fig. 3. There are fairly regular maxima of density 0·27–0·36 e Å^{-3} in every C—C bond; the density in the C(4)—S(2) bond is lower, 0·20 e Å^{-3}. The presence of distinct maxima in four of the five exocyclic C—H bonds must be ascribed largely to the corrections applied to the H coordinates. The densities in perpendicular sections through the midpoints of the aromatic C—C bonds are reproduced in Fig. 4 along with the C(4)—S(2) and the central C(2)—C(3) bonds. Except for the C(5)—C(6) bond peak which has a nearly circular profile the densities in the aromatic bonds are extended in the direction perpendicular to the ring plane. This is in consonance with the theoretical model for sp^2 bonding. As to the C(5)—C(6) bond also the in-plane details of the bonding density near C(6) are somewhat atypical (Fig. 3). The density contours in the C—S bonds are approximately circular; thus there is no strong evidence of conjugation in the C(4)—S(2) bond. There appears to be some deficit of charge both above and below this bond relative to the ring plane. Analyses of subtle effects of this character clearly require more high-angle data collected at low temperature. It is interesting, however, that there was also no significant

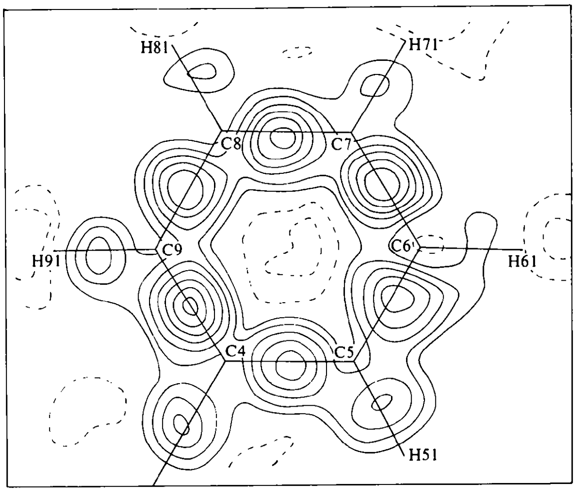

Fig. 3. Deformation density in the plane of the phenyl ring. Contours are at 0·05 e Å^{-3} with negative contours broken. Zero contour not shown.

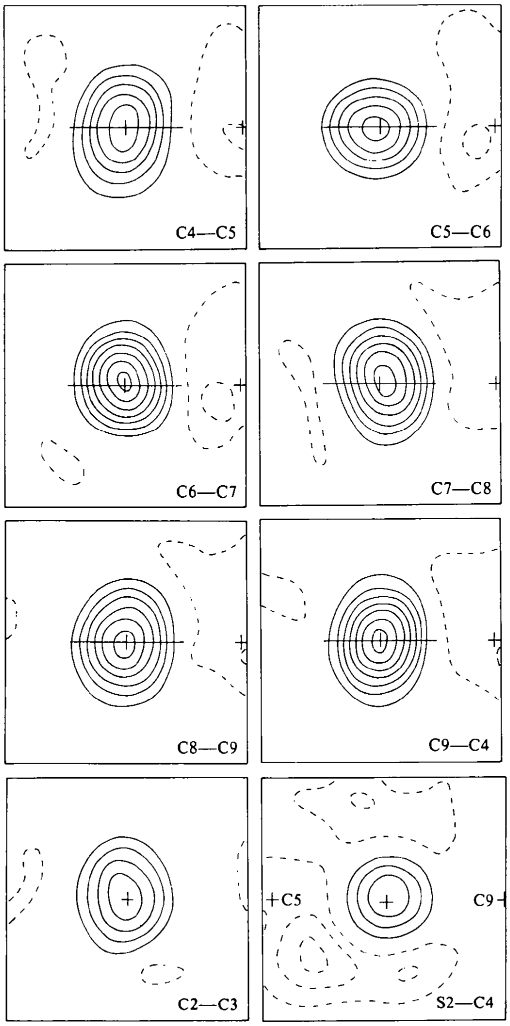

Fig. 4. Deformation density sections through the midpoints of, and perpendicular to, various bonds. Horizontal line and cross in phenyl C—C bond sections mark plane and center of ring, respectively. Contours as in Fig. 3.

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* See previous footnote.

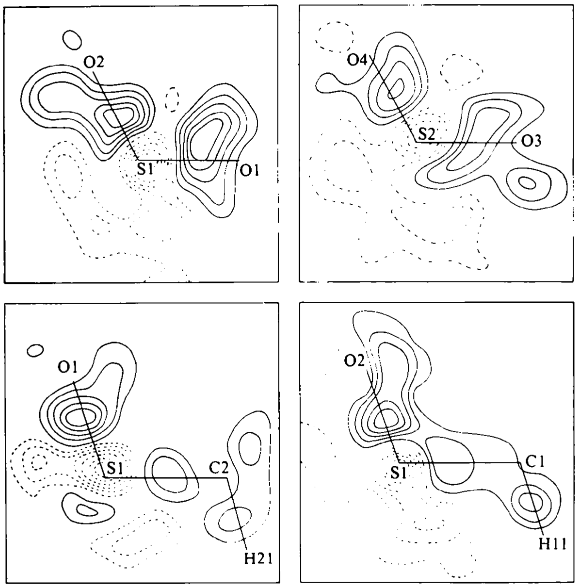

Fig. 5. Deformation density in various sections through S—O bonds. Contours as in Fig. 3.

deviation from cylindrical symmetry in the exocyclic C—S bond of sodium sulfanilate studied at 78 K (Bats, 1977*a*). In general, the experimental charge-density distribution in the C-containing parts of the molecule is very consistent in detail. We take this to imply that the data are free from large systematic errors and that the limited HO set is adequate to provide a decent model of the hydrocarbon part of the molecule.

The situation is different in the vicinity of the S and O atoms. Fig. 5 is a collection of density maps in and near the SO_2 groups. Peaks in the S—O bonds, 0·20–0·30 e Å^{-3}, are broad and irregular and, where present, lone-pair peaks near the O atoms are merged with the density in the bond. From the previous discussion it is clear that the atomic positions for O and S from the HO refinement are affected to some extent by the narrow range in *s*. In addition to the lone-pair scattering at higher angles there are other potent sources of errors such as the use of a harmonic model for the thermal motion at room temperature and the possible polarization of the core-electron density at O as discussed, for example, by Craven & McMullan (1979). A similar polarization of S due to bonding is also possible. If the latter effects are significant, an unbiased analysis of the charge-density distribution will require X-ray data at a considerably higher resolution than considered sufficient to distinguish lone-pair scattering.

A recurring feature in our density maps of $MPSO_2$ and other molecules containing S in tetrahedral bonding is the negative trough at the S atomic sites surrounded by negative lobes in an approximately trigonal arrangement (Mo *et al.*, 1979). Similar details appear in the density maps of sulfamic acid (Bats *et al.*, 1977) and sodium sulfanilate (Bats, 1977*a*). Leaving out the details close to the atomic positions where large errors preclude a meaningful interpretation, these observations consistently indicate quite large deficiencies in the spherical model of bonded S. X-ray work at liquid-nitrogen temperature is in progress on related molecules to obtain data for more precise studies of charge density associated with S bonding. The present results will then also become valuable for comparative purposes.

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