Table 3. *Hydrogen bonding in α-D-galactosamine-*1-*phosphate monohydrate*

D–H···*A*	Symmetry code	*D*–H (Å)	*D*···*A* (Å)	H···*A* (Å)	*D*–H···*A* (°)
O(10)–H(O10)···O(6)	*a*	0·89 (5)	2·754 (5)	2·01 (6)	169 (6)
O(10)–H′(O10)···O(4)	*e*	0·71 (6)	2·871 (5)	2·25 (6)	147 (7)
O(4)–H(O4)···O(8)	*b*	1·07 (5)	2·614 (4)	1·65 (5)	149 (4)
O(6)–H(O6)···O(4)	*c*	1·02 (4)	2·889 (4)	1·99 (5)	146 (4)
N(2)–H(N2)···O(10)	*d*	0·97 (5)	2·696 (5)	1·73 (5)	170 (4)
N(2)–H′(N2)···O(9)	*d*	0·92 (4)	2·863 (4)	1·99 (4)	160 (4)
N(2)–H″(N2)···O(3)	*f*	1·12 (5)	2·911 (4)	1·80 (5)	169 (4)
O(3)–H(O3)···O(8)	*g*	1·04 (5)	2·653 (4)	1·71 (5)	150 (4)
O(7)–H(O7)···O(9)	*h*	0·94 (5)	2·652 (4)	1·74 (5)	149 (5)

Symmetry code

(*a*) x,y,z	(*e*) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$
(*b*) $x, 1-y, z$	(*f*) $-x, y-\frac{1}{2}, \frac{1}{2}-z$
(*c*) $\frac{1}{2}+x, \frac{1}{2}-y, -z$	(*g*) $-x, \frac{1}{2}+y, \frac{1}{2}-z$
(*d*) $\frac{1}{2}+x, \frac{3}{2}-y, -z$	(*h*) $\frac{1}{2}-x, 2-y, \frac{1}{2}+z$

phosphate group is engaged in only five hydrogen bonds. The presence of metal ions usually increases the number of hydrogen bonds (~9) to the phosphate by virtue of increasing the amount of water of hydration (Swaminathan & Sundaralingam, 1979). The O(9) atom of the phosphate group is hydrogen bonded to the NH_3^+ group and O(7)–H of a neighboring molecule to form an infinite spiral about the twofold screw axis parallel to the crystallographic *c* axis. The O(7)–H of the phosphate also accepts a hydrogen bond from the ammonium group. The water molecule is not hydrogen bonded to the phosphate group but bridges the O(6) and O(4) atoms of 2_1-related molecules and accepts a hydrogen bond from the ammonium group of a third molecule. The ring O(5) atom and the phosphate ester O(1) atom are not engaged in hydrogen bonding.

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The Structure of Methoin: an Anticonvulsant Drug

BY J. N. LISGARTEN AND R. A. PALMER

Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, England

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Abstract

$C_{12}H_{14}N_2O_2$, orthorhombic, *Pbca*, $a = 27{\cdot}336\ (24)$, $b = 10{\cdot}002\ (9)$, $c = 8{\cdot}477\ (8)$ Å, $Z = 8$, $D_c = 1{\cdot}249$ Mg m^{-3}, $\mu(\text{Cu } K\alpha) = 0{\cdot}622$ mm^{-1}. The crystal used for X-ray analysis was prepared from material purchased from Aldrich Chemical Co., Inc. $R_o = 0{\cdot}078$ for 1310 observed reflections and $R = 0{\cdot}098$ for 1673 measured

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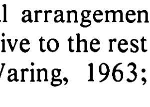
reflections. The structure is hydrogen bonded. Structure–activity relationships are presented for methoin and other anticonvulsant drugs.

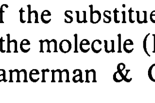
Introduction

The varying hypnotic and anticonvulsant properties exhibited by barbiturates and hydantoins depend upon the nature of the substituents at the C(5) position of the heterocyclic ring. Drug molecules having aliphatic side groups at this position are commonly used as sedatives, while those with phenyl groups are effective in grand-mal epilepsy. It has also been suggested that the mode of action of such compounds may be a function of the spatial arrangement of the substituents in this position relative to the rest of the molecule (Lien, 1970; Spinks & Waring, 1963; Camerman & Camerman, 1971).

Methoin, $C_{12}H_{14}N_2O_2$ [5-ethyl-3-methyl-5-phenylhydantoin, (II) (R_2 = C_2H_5, R_3 = CH_3)], is an anticonvulsant with actions similar to those of the extensively used phenytoin, $C_{15}H_{12}N_2O_2$ [5,5-diphenylhydantoin, (II) (R_2 = C_6H_5, R_3 = H)], but with less hypnotic effect. Methoin has been used in the treatment of grand-mal seizures and has also given good results in cases of psychomotor attacks, focal seizures and behavioural disorders (Martindale, 1977). In contrast to phenytoin, methoin also exhibits a sedative action, possibly due to the presence of the ethyl substituent at the C(5) position. This feature also occurs in phenobarbitone, $C_{12}H_{12}N_2O_3$ [5-ethyl-5-phenylbarbituric acid (I) (R_1 = =O)], and primidone, $C_{12}H_{14}N_2O_2$ [5-ethyl-5-phenylhexahydropyrimidine (I) (R_1 = H_2)], both of which are important anticonvulsant drugs.



(I)



(II)

Experimental

A sample of methoin was purchased from Aldrich Chemical Co., Inc. Slow evaporation of a chloroform solution produced clear, lustrous platey crystals elongated along **c** with D_m = 1·245 (5) Mg m^{-3}. The space group was determined unambiguously as *Pbca*. Accurate cell parameters were determined from fifteen 2θ values measured on a computer-controlled four-circle diffractometer (Hilger & Watts Y290) using Cu $K\alpha_1$ radiation (λ = 1·5405 Å).

Intensities were measured to $\theta < 60°$ on the same instrument using the ω–2θ scanning mode with 80 steps at intervals of 0·01° and a count time per step of 1·0 s. The background was counted for 8·0 s on either side of the extreme position for each reflection. Three standard reflections, monitored every 50 reflections during data collection, showed no significant fluctuations. A total of 1673 independent intensities were measured, of which 363 with $I < 3\sigma(I)$ were classified as unobserved. Lorentz and polarization corrections were applied but absorption effects were ignored (μ = 0·622 mm^{-1}, μr = 0·2 to 0·4).

Structure determination and refinement

Numerous attempts were made to solve the structure by direct methods using the program *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974), but none was completely successful. With the 107 reflections with $|E| > 1·9$ eight phase sets were produced and an E map calculated for the set with the highest figure of merit (0·823), lowest $R_{\rm Karle}$ (20·8) and highest combined figure of merit (2·619) revealed ten high peaks in stereochemically viable positions, several of which, however, subsequently proved to be erroneous. Positions for the 16 non-hydrogen atoms were eventually assigned after calculation of several Sim-weighted electron density syntheses. At this stage the R factor was 0·28, with an overall isotropic temperature factor $\bar{U}$ = 0·04 Å^2.

Isotropic full-matrix least-squares refinement of this model converged to R = 0·21 and anisotropic refinement to 0·12 for 1310 observed reflections. All fourteen H atoms were located on a difference map and included in subsequent refinement cycles. CH_3 groups were refined as rigid groups with H atoms riding on the corresponding C atom at a distance fixed at 1·08 Å and all three H atoms having a common isotropic temperature factor. The five phenyl H atoms were refined in a similar manner. Positional parameters and isotropic temperature factors were refined for the remaining three H atoms. A total of 166 parameters were thus refined. The final positions of all H atoms were close to the corresponding peak positions on the difference map. Final R values were 0·078 for the 1310 observed reflections and 0·098 for all data, the corresponding weighted R value being 0·15. A final difference map had no region with density greater than 0·3 e Å^{-3}. Weights in the final least-squares cycle were calculated as $w = [\sigma^2(|F|) + 0·0226|F|^2]^{-1}$. The distribution of $\sum w(\Delta F)^2$ with sin θ was approximately constant but fell off slightly with $(|F|/|F_{\rm max}|)^{1/2}$.* Refinement of the structure was undertaken using the program package *SHELX* (Sheldrick, 1976) on the University of London CDC 6600 computer.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35410 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

A view of the molecule with the numbering scheme is shown in Fig. 1. Fractional coordinates are listed in Table 1 and Table 2 lists bond lengths and angles involving all atoms whose positional parameters were refined. With the exception of C(15)–C(16) = 1·484 (6) Å, which, for no apparent reason, is very short, bond lengths are within the expected range of values. All bond angles are normal. Torsion angles are given in Table 3. The hydantoin ring is planar with O(8) and O(6) situated at −0·1 and 0·01 Å respectively from the plane through the five ring atoms. The geometry of the hydantoin group compares well with that in allantoin (Mootz, 1965) and diphenylhydantoin (Camerman & Camerman, 1971). The dihedral angle between the phenyl-ring plane and the hydantoin-ring plane is 77° while the torsion angle about the linkage bond [C(10)–C(9)–C(5)–C(4)] is −88°.

Table 1. *Refined positional parameters and isotropic thermal parameters, with e.s.d.'s in parentheses*

$\bar{U}^2_{\mathrm{iso}}$ is the isotropic temperature factor in the expression $B^2_{\mathrm{iso}} = 8\pi^2\bar{U}^2_{\mathrm{iso}}$.

Other than H(1), H(151) and H(152) all hydrogens have been refined as part of rigid groups with idealized geometry. Apart from these exceptions the e.s.d.'s relate only to the refinement and do not indicate the accuracy of the given H coordinates.

(*a*) Nonhydrogen atoms

	x	y	z	U_{iso} (Å^2)
N(1)	0·0820 (1)	0·3721 (3)	0·2041 (3)	0·054 (2)
C(2)	0·0797 (1)	0·3812 (3)	0·0452 (4)	0·050 (2)
N(3)	0·1034 (1)	0·4990 (3)	0·0017 (3)	0·053 (2)
C(4)	0·1198 (1)	0·5680 (3)	0·1318 (3)	0·045 (2)
C(5)	0·1086 (1)	0·4835 (3)	0·2769 (4)	0·047 (2)
O(6)	0·0614 (1)	0·3029 (2)	−0·0464 (3)	0·065 (3)
C(7)	0·1092 (2)	9·5429 (5)	−0·1596 (5)	0·082 (3)
O(8)	0·1386 (1)	0·6784 (2)	0·1312 (3)	0·060 (2)
C(9)	0·1563 (1)	0·4389 (3)	0·3502 (4)	0·047 (2)
C(10)	0·1788 (2)	0·3205 (4)	0·3005 (5)	0·065 (3)
C(11)	0·2228 (2)	0·2820 (5)	0·3630 (6)	0·077 (3)
C(12)	0·2451 (2)	0·3586 (5)	0·4768 (5)	0·074 (3)
C(13)	0·2239 (2)	0·4750 (5)	0·5273 (5)	0·075 (3)
C(14)	0·1791 (2)	0·5178 (4)	0·4623 (5)	0·065 (3)
C(15)	0·0745 (2)	0·5599 (5)	0·3885 (4)	0·061 (2)
C(16)	0·0282 (2)	0·6066 (6)	0·3157 (6)	0·087 (3)

(*b*) Hydrogen atoms

	x	y	z	$\bar{U}^2_{\mathrm{iso}}$ (×10^4)	
H(1)	0·0655 (18)	0·3037 (52)	0·2846 (64)	889 (154)	NH
H(71)	0·1307 (2)	0·6329 (5)	−0·1723 (5)	988 (90)	CH_3
H(72)	0·0734 (2)	0·5586 (5)	−0·2097 (5)	988 (90)	
H(73)	0·1271 (2)	0·4616 (5)	−0·2204	988 (90)	
H(10)	0·1610 (2)	0·2584 (4)	0·2136 (5)	963 (73)	C_6H_5
H(11)	0·2403 (2)	0·1923 (5)	0·3201 (6)	963 (73)	
H(12)	0·2792 (2)	0·3260 (5)	0·5283 (5)	963 (73)	
H(13)	0·2413 (2)	0·5350 (5)	0·6172 (5)	963 (73)	
H(14)	0·1624 (2)	0·6103 (4)	0·5002 (5)	963 (73)	
H(151)	0·0851 (16)	0·6311 (56)	0·4274 (54)	964 (126)	CH_2
H(152)	0·0699 (20)	0·5147 (55)	0·4779 (68)	830 (148)	
H(161)	0·0335 (2)	0·6646 (6)	0·2096 (6)	1045 (104)	CH_3
H(162)	0·0092 (2)	0·6665 (6)	0·4023 (6)	1045 (104)	
H(163)	0·0068 (2)	0·5189 (6)	0·2888 (6)	1045 (104)	

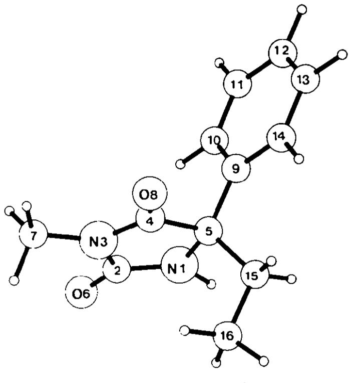

Fig. 1. View of the molecule down **b** showing the atom numbering scheme. (Radii of circles are approximately in proportion to atomic weight.)

Table 2. *Bond lengths* (Å) *and angles* (°) *with standard deviations in parentheses*

N(1)–C(2)	1·352 (4)	C(9)–C(10)	1·398 (5)
C(2)–N(3)	1·395 (4)	C(10)–C(11)	1·372 (6)
N(3)–C(4)	1·376 (4)	C(11)–C(12)	1·374 (7)
C(4)–C(5)	1·524 (4)	C(12)–C(13)	1·370 (7)
C(6)–N(1)	1·467 (4)	C(13)–C(14)	1·410 (6)
C(2)–O(6)	1·211 (4)	C(14)–C(9)	1·384 (5)
N(3)–C(7)	1·445 (5)	C(5)–C(15)	1·532 (5)
C(4)–O(8)	1·218 (4)	C(15)–C(16)	1·484 (6)
C(5)–C(9)	1·515 (5)		

N(1)–C(2)–N(3)	107·4 (2)	C(4)–C(5)–C(15)	110·2 (3)
N(1)–C(2)–O(6)	127·9 (3)	C(4)–C(5)–C(9)	108·7 (3)
O(6)–C(2)–N(3)	124·7 (3)	C(5)–C(15)–C(16)	114·9 (3)
C(2)–N(3)–C(4)	111·3 (2)	C(9)–C(5)–C(15)	114·8 (3)
C(2)–N(3)–C(7)	123·9 (3)	C(9)–C(10)–C(11)	120·5 (4)
C(7)–N(3)–C(4)	124·8 (3)	C(10)–C(11)–C(12)	120·2 (4)
N(3)–C(4)–C(5)	107·7 (2)	C(11)–C(12)–C(13)	120·4 (4)
N(3)–C(4)–O(8)	126·1 (3)	C(12)–C(13)–C(14)	120·3 (4)
O(8)–C(4)–C(5)	126·2 (3)	C(13)–C(14)–C(9)	119·1 (4)
C(4)–C(5)–N(1)	100·5 (2)	C(14)–C(9)–C(10)	119·5 (3)
C(5)–N(1)–C(2)	113·0 (2)	C(14)–C(9)–C(5)	120·1 (3)
N(1)–C(5)–C(9)	112·1 (3)	C(5)–C(9)–C(10)	120·3 (3)
N(1)–C(5)–C(15)	109·7 (3)		

H(1)–N(1)	1·07 (5)	H(152)–C(15)	0·89 (6)
H(151)–C(15)	0·84 (5)		

All other H–C lengths were fixed at 1·08 Å.

H(1)–N(1)–C(5)	115 (3)	H(151)–C(15)–C(16)	101 (3)
H(1)–N(1)–C(2)	131 (3)	H(152)–C(15)–C(5)	110 (3)
H(151)–C(15)–C(5)	117 (3)	H(152)–C(15)–C(16)	113 (4)

All other hydrogens were refined in rigid groups.

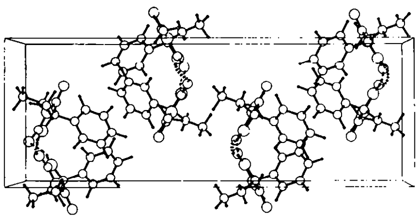

Fig. 2. The crystal structure viewed along **c**. Hydrogen bonds between molecules are shown as broken lines.

Table 3. *Torsion angles* (°) *determined for methoin*

The sign of the angle *A–B–C–D* is positive when a clockwise rotation about *B–C* is required to bring *A–B–C* into coincidence with *B–C–D*, viewed along *B–C*. E.s.d.'s are 0·5 to 0·7°.

A	*B*	*C*	*D*		*A*	*B*	*C*	*D*		*A*	*B*	*C*	*D*	
C(16)	C(15)	C(25)	N(1)	−54	C(9)	C(10)	C(11)	C(12)	+1	O(6)	C(2)	N(1)	C(5)	178
C(16)	C(15)	C(5)	C(4)	+55	C(10)	C(11)	C(12)	C(13)	−1	C(9)	C(5)	N(1)	C(2)	−112
C(16)	C(15)	C(5)	C(9)	+179	C(11)	C(12)	C(13)	C(14)	0	C(5)	N(1)	C(2)	O(6)	178
C(15)	C(5)	C(9)	C(14)	−35	C(12)	C(13)	C(14)	C(9)	+2	C(15)	C(5)	N(1)	C(2)	119
N(1)	C(5)	C(9)	C(14)	−161	C(13)	C(14)	C(9)	C(10)	−2	C(15)	C(5)	C(4)	N(3)	−120
N(1)	C(5)	C(9)	C(10)	+22	C(14)	C(9)	C(10)	C(11)	+1	O(8)	C(4)	N(3)	C(2)	−174
C(5)	N(1)	C(2)	N(3)	−1	C(9)	C(5)	C(4)	O(8)	−68	C(5)	C(4)	N(3)	C(7)	−177
N(1)	C(2)	N(3)	C(4)	−2	C(15)	C(5)	C(4)	O(8)	58	N(1)	C(2)	N(3)	C(7)	179
C(2)	N(3)	C(4)	C(5)	+4	C(10)	C(9)	C(5)	C(4)	−88	O(6)	C(2)	N(3)	C(7)	0
N(3)	C(4)	C(5)	N(1)	−4	C(14)	C(9)	C(5)	C(4)	89	C(5)	N(1)	C(2)	O(6)	180
C(4)	C(5)	N(1)	C(2)	+3										

Table 4. *Intramolecular distances* (Å) *and dihedral angles* (°)

E.s.d.'s are 0·01–0·05 Å and 0·3–0·8°.

(*a*) Oxygen–ring-centroid distances in methoin, phenytoin, phenobarbitone and primidone

Oxygen	Ring centroid	
Methoin		
O(6)	C(9) to C(14)	5·54
O(8)	C(9) to C(14)	4·06
Phenytoin		
O(6)	C(8) to C(13)	5·68
O(7)	C(8) to C(13)	3·97
O(6)	C(14) to C(19)	5·51
O(7)	C(14) to C(19)	4·23
Phenobarbitone		
O(4)	C(11) to C(16)	4·34
O(6)	C(11) to C(16)	4·27
O(2)	C(11) to C(16)	5·42
Primidone		
O(4)	C(11) to C(16)	4·46
O(6)	C(11) to C(16)	4·39

(*b*) Oxygen–oxygen distances in methoin, phenytoin, phenobarbitone and primidone

Oxygen	Oxygen	
Methoin		
O(6)	O(8)	4·56
Phenytoin		
O(6)	O(7)	4·56
Phenobarbitone		
O(4)	O(6)	4·79
Primidone		
O(4)	O(6)	4·51

(*c*) Dihedral angles in methoin, phenytoin, phenobarbitone and primidone

Methoin	
Hydantoin–phenyl C(9) to C(14)	76
Phenytoin	
Hydantoin–phenyl C(8) to C(13)	114
Hydantoin–phenyl C(14) to C(19)	113
Phenobarbitone	
Phenyl–pyrimidine N(1), C(2), N(3), C(4), C(6)	86
Primidone	
Phenyl–pyrimidine N(1), N(3), C(4), C(6)	87

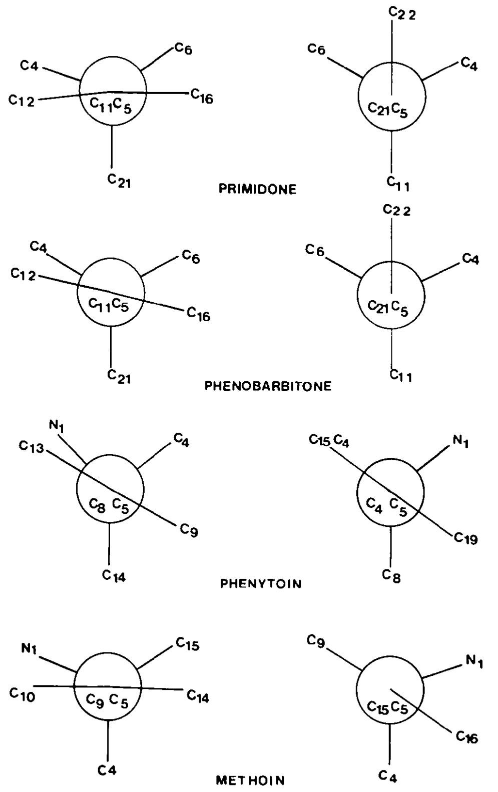

Fig. 3. Newman projections comparing the configuration about C(5) in methoin, primidone, phenobarbitone and phenytoin.

Hydrogen-bonded spirals parallel to **c** are formed (Fig. 2) between N(1) and the symmetry-related atom O(6′) at $x,\frac{1}{2}-y,\frac{1}{2}+z$, with N(1)···O(6′) = 2·802 (3) Å, H(1)···O(6′) = 1·79 (5) Å and N(1)–H(1)···O(6′) = 157 (2)°. The only other noteworthy intermolecular contact is C(7)···O(8″) = 3·400 (3) Å, O(8″) being at $x,\frac{3}{2}-y,-\frac{1}{2}+z$.

The carbonyl O atoms in the hydantoin rings of methoin and phenytoin, and in the pyrimidine rings of 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

By F. Mo and A. Gaasdal

*Institutt for Røntgenteknikk, Universitetet i Trondheim-NTH, N-*7034 *Trondheim-NTH, Norway*

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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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