REFINEMENT OF THE CRYSTAL STRUCTURE OF DIPARATOLYL DISULFIDE

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Abstract

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REFINEMENT OF THE CRYSTAL STRUCTURE OF DIPARATOLYL DISULFIDE

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Determination of the structure of the diparatolyl disulfide molecule was undertaken in order to clarify the role of the lone pair of electrons of sulfur atoms in aromatic disulfides.

The model of the molecule was established earlier in work ([1]) from one centrosymmetric projection of the electron density and a three-dimensional function of interatomic vectors. The molecule occupies a general position in the noncentrosymmetric space group $P2_1$. Refinement of the structure was begun with the construction of a three-dimensional Fourier synthesis of the electron density and continued by the least-squares method. In all, 4 refinement cycles were carried out. By the least-squares method the scale factor K, corrections K_l to the coefficient K for individual layer lines, atomic coordinates, the constant of the overall temperature factor B, and individual isotropic temperature corrections u_j were refined. The final value of the discrepancy factor is $R(hkl) = 17.8\%$.

Table 1

Atom	x	y	z	B_j, Å^2	ρ, el/Å^3	Atom	x	y	z	B_j, Å^2	ρ, el/Å^3
S(1)	0.204	0.028	0.136	−4.34	21.72	C(7)	0.0198	−0.047	0.159	−4.30	7.43
S(2)	0.271	0.342	0.124	−4.36	20.96	C(8)	0.321	0.408	0.336	−4.22	37.51
C(1)	0.0917	0.104	0.190	−5.48	7.17	C(9)	0.370	0.611	0.354	−4.41	06.97
C(2)	0.0818	0.321	0.274	−4.19	57.50	C(10)	0.416	0.650	0.514	−4.14	66.92
C(3)	−0.004	0.375	0.325	−3.80	07.17	C(11)	0.410	0.512	0.665	−4.87	67.45
C(4)	−0.078	0.233	0.290	−5.04	7.22	C(12)	0.455	0.591	0.838	−4.42	06.59
C(5)	−0.175	0.276	0.335	−6.35	07.43	C(13)	0.363	0.297	0.632	−4.81	66.79
C(6)	−0.065	0.019	0.212	−4.04	7.53	C(14)	0.318	0.248	0.472	−4.82	66.56

Table 1 gives the atomic coordinates x, y, z, individual isotropic temperature constants B_j, and the heights of the maxima ρ. The constant of the overall temperature factor is $B = -4.56$ Å^2. A picture of the three-dimensional electron-density distribution in the form of a superposition of sections along the b axis

Fig. 2

Figure 1: Fig. 2

is given in Fig. 1. The sections were drawn through the maxima of the peaks corresponding to individual atoms. For C atoms the contour lines were drawn at intervals of 1 el/Å^3, beginning with 2 el/Å^3. For S atoms the contour lines were drawn at intervals of 2 el/Å^3.

The interatomic distances and valence angles calculated from the data of Table 1 are shown in Fig. 2. The interatomic distance S(1)–S(2), equal to 2.075 Å, agrees with the data of work ([1]) and coincides with the length of a single bond (2.08 Å) found for inorganic disulfides ([2]). The interatomic distances S(1) –C(1) (1.78 Å); S(2)–C(8) (1.80 Å), C(4)–C(5) (1.51 Å), C(11)–C(12) (1.52 Å), respectively, are equal to the lengths of single S–C and C–C bonds, taking into account the shortening of the covalent radius of the carbon atom in sp^2-hybridization.

The accuracy of determination of the interatomic distances in the diparatolyl disulfide molecule was estimated from the magnitude of the deviation of bond lengths in the benzene-

···rings from the value accepted in the literature for the C–C distance in benzene (1.397 Å) and is $±$0.02 Å.

The errors in determining bond lengths, calculated by the formula of B. K. Vainshtein ([3]) with the constants given by M. A. Porai-Koshits ([4]), are, for S–S, $±$0.01 Å, for C–S, $±$0.015 Å, and for C–C $±0.02.*This correspondstoanaccuracyindeterminingvalenceanglesaccordingtoDarlow*(^{5}$) of $±$2°.

The normal equations of planes I and II of the benzene rings have the form:

$$0.152x - 0.434y + 0.887z - 1.231 = 0, \qquad \text{(I)}$$

$$0.826x - 0.470y - 0.309z - 1.892 = 0. \qquad \text{(II)}$$

The deviations of the carbon atoms from the corresponding planes of the benzene rings are given in Table 2.

Fig. 2

The deformation of the valence angles in the benzene rings agrees with the scheme of deformation of the benzene ring under the influence of donor groups, given in ([6]): – –b, where *b* denotes valence angles increased in comparison with 120°*. The deformation of the external angles at C(4) and C(11) is evidently caused by steric hindrance arising in the packing of the complex molecule.

Fig. 3

Figure 2: Fig. 3

* The average interatomic distances in the benzene ring of di-*p*-tolyl disulfide also correspond to this scheme.

The dihedral angle between the planes C(1)S(1)S(2) and C(8)S(2)S(1) is 89°50′. The angle of rotation of the benzene rings relative to one another is 86°. The angle of rotation of benzene ring (I) relative to the plane C(1)S(1)S(2) is 21°, and the angle of rotation of benzene ring (II) relative to the plane C(8)S(2)S(1) is 6°.

Figure 3 shows the arrangement of molecules in the unit cell in projections onto the planes (010), (001), and gives the shortest intermolecular distances.

Table 2

Atom	Deviation δ	Atom	Deviation δ
C(1)	−0.007	C(8)	+0.042
C(2)	−0.008	C(9)	−0.004
C(3)	+0.005	C(10)	−0.005
C(4)	−0.041	C(11)	−0.120
C(5)	−0.063	C(12)	−0.258
C(6)	0	C(13)	−0.020
C(7)	0	C(14)	+0.011

The available literature data on the structure of disulfide molecules make it possible to draw some conclusions about the role of the free $3p^2$-pair of electrons of sulfur atoms in the disulfide group. Thus, according to X-ray spectral analysis data (7), for the molecule

$$[\text{cyclohexyl ring}] - CH_2 - S - S - CH_2 - [\text{cyclohexyl ring}]$$

a shift of the $SK_{\alpha_{1,2}}$ line was established in comparison with rhombic sulfur and the dibenzyl sulfide molecule: $\Delta E = +0.12$ eV. Hence it followed that in this molecule the repulsion of the free electron pairs of neighboring sulfur atoms leads to an increase

Fig. 3

bond length S–S. In the structure of tetramethylthiuram disulfide, a shortened interatomic distance S–S, equal to 2.00 ± 0.01 Å, has been established ([8]). The dihedral angle in this molecule is equal to 88°. The shortening of the S–S distance in this case is associated with a decrease in repulsion as a result of partial unpairing of the $3p^2$-pair of electrons of the sulfur atoms in the disulfide

group and transfer of charge to the acceptor thiocarbonyl group. Analogous examples are given in ([9]).

According to X-ray diffraction data ([10]), in the molecule

$$Br-C_6H_4-S-S-C_6H_4-Br$$

the S–S bond length is equal to 2.15 Å. However, the value cited is apparently incorrect, since the configuration of the molecule was determined from a single projection of the electron density and from geometrical analysis.

The results of the present X-ray structural investigation of di-*p*-tolyl disulfide show that the S–S bond length is equal to the sum of the covalent radii. The $3p^2$ orbitals of the lone electron pairs of the sulfur atoms are situated in mutually perpendicular planes, and therefore the repulsion between them is minimal.

Our data are confirmed by the results of measurements of X-ray spectra. In di-*p*-tolyl disulfide $\Delta E \simeq 0$, which corresponds to single S–S and S–C bonds in the molecule studied ([11]).

It is interesting to note that the dihedral angle between the two OOH planes in the hydrogen peroxide molecule, as found by the neutron-diffraction method ([12]), is equal to 90.2°, i.e., in both structures—in di-*p*-tolyl disulfide and in hydrogen peroxide—the dihedral angles are identical.

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Note: Figure translations are in progress. See original paper for figures.