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The Crystal Structure of Di-*p*-Tolyl Sulfide*

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Di-*p*-tolyl sulfide belongs to the orthorhombic system and has cell dimensions, $a = 25{\cdot}07$, $b = 7{\cdot}92$ and $c = 5{\cdot}81$ Å. There are four molecules per cell, and the space group is $P2_12_12_1$. The crystal structure has been determined, and 284 terms were used in double-Fourier-series and least-squares procedures to refine the atomic coordinates of the 45 positional parameters. The intensities were measured visually by two independent observers. The S–C bond length is 1·75 Å and the C–S–C bond angle is 109°. The normals to the two aromatic rings form an angle of 56° with each other.

Introduction

The distribution of the valency bonds in divalent sulfur in various environments has received considerable attention. In some inorganic polysulfides the S–S bond length has shown an alternating tendency (Abrahams & Grison, 1953; Abrahams, 1954), and a similar effect has been reported in dimethanesulfonyl disulfide (Sörum, 1953), in barium tetrathionate dihydrate (Foss, Furberg & Zachariasen, 1954) and in barium pentathionate dihydrate (Foss & Zachariasen, 1954). A partial summary of the various determinations of the S–C bond length, and the C–S–C bond angle is given in Table 1.

Crystal data

Di-*p*-tolyl sulfide, $(p\text{-}CH_3.C_6H_4)_2S$; m.p. 57° C.; $D_{meas.} = 1{\cdot}22$ g.cm.$^{-3}$ (measured by flotation in aqueous $NaNO_3$ solution); $D_{calc.} = 1{\cdot}227$ g.cm.$^{-3}$; orthorhombic with $a = 25{\cdot}07 \pm 0{\cdot}02$, $b = 7{\cdot}92 \pm 0{\cdot}02$ and $c = 5{\cdot}81 \pm 0{\cdot}02$ Å.

(Toussaint (1943) reported these constants to be $a = 25{\cdot}02$, $b = 7{\cdot}92$, $c = 5{\cdot}85$ Å, and the refractive indices as $n_a = 1{\cdot}545$, $n_b = 1{\cdot}700$ and $n_c = 1{\cdot}894$, using 578 $m\mu$ light.) Absent spectra: ($h00$) only with $h = 2n+1$, ($0k0$) only with $k = 2n+1$ and ($00l$) only with $l = 2n+1$. The space group is uniquely $P2_12_12_1$. There are four molecules per cell. No molecular symmetry is required. The absorption coefficient for Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) is 2·50 cm.$^{-1}$, and for Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) is 21·9 cm.$^{-1}$. The volume of the unit cell is 1159·2 Å^3. The total number of electrons per unit cell, $F(000)$, is 456.

Analysis of the structure

The near isomorphism of the di-*p*-tolyl telluride (Blackmore & Abrahams, 1955*a*) and di-*p*-tolyl selenide (Blackmore & Abrahams, 1955*b*) crystals and the close resemblance of the cell edges of di-*p*-tolyl sulfide to those of the other two, encouraged the belief that all three might be nearly isostructural.§ Thus an initial set of x, z coordinates for the sulfide was obtained by a consideration of the coordinates taken

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§ Di-*p*-tolyl ether also crystallizes in the space group $P2_12_12_1$ with $a = 25{\cdot}44$, $b = 7{\cdot}80$ and $c = 5{\cdot}89$ Å. However, the intensity distribution for this crystal differs considerably from that of the sulfide, selenide and telluride, indicating widely different atomic coordinates.

Table 1. S–C *bond lengths and the* S *valency angle*

Molecule	S–C distance (Å)	S valency angle (°)	Method	Reference
Dimethanesulfonyl disulfide	1·77±0·05	105±3	X-ray	Sörum (1953)
Dimethyl sulfide	1·82	105	Spectroscopy	Siebert (1952)
Dimethyl disulfide	1·78±0·03	107±2	Electron diffraction	Stevenson & Beach (1938)
Dimethyl trisulfide	1·78±0·04	104	X-ray	Donohue & Schomaker (1948)
Thiophthene	1·72±0·013 1·74±0·013	91·2±0·6	X-ray	Cox, Gillot & Jeffrey (1949)
p,p'-Dibromodiphenyl sulfide	1·75±0·03	109±5	X-ray	Toussaint (1945)
p,p'-Dibromodiphenyl disulfide	1·80±0·03	107	X-ray	Toussaint (1945)
Diphenyl sulfide	—	113±3	Dipole moments	Hampson, Farmer & Sutton (1933)
Phenyl-*p*-tolyl sulfide	—	115–116·5	Dipole moments	Chien & Lay (1937)

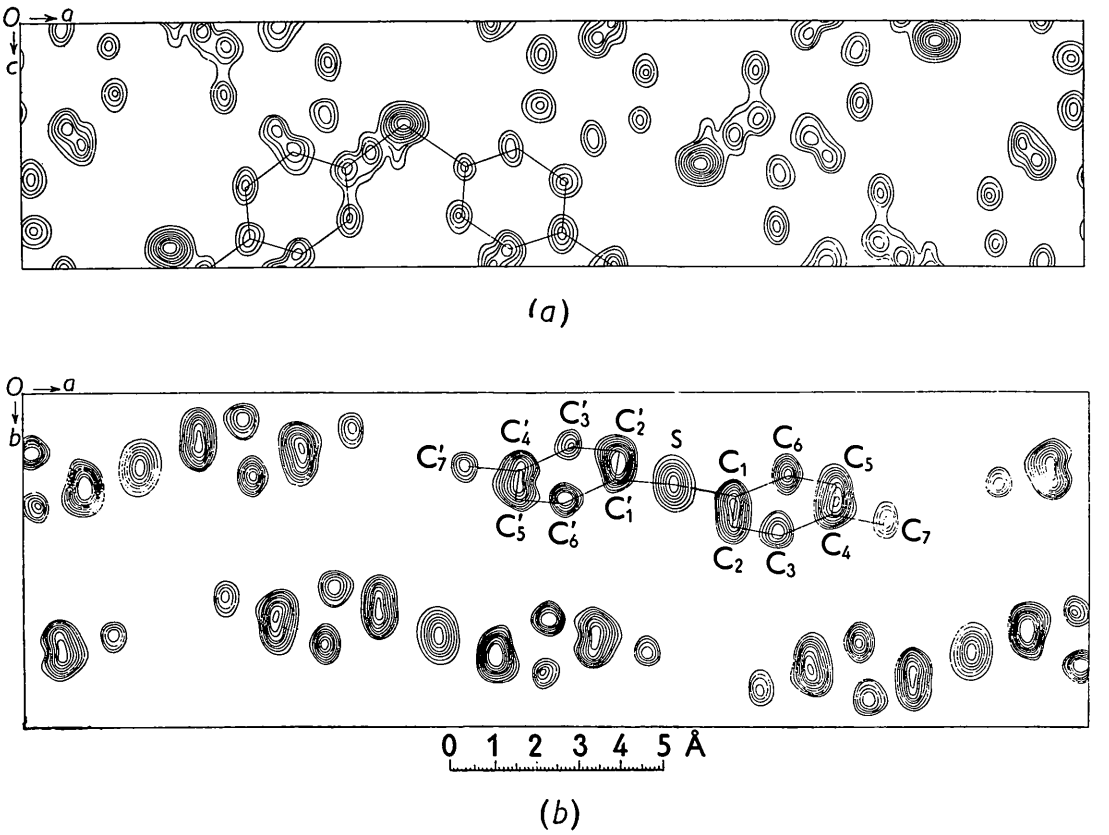


Fig. 1. (*a*) Projection of the unit cell of di-*p*-tolyl sulfide along the *b* axis. Each contour for the carbon atoms represents a density increment of 1 e.Å^{-2}, and for the sulfur atom of 2 e.Å^{-2}. The first contour is of 4 e.Å^{-2} for both. One molecule is outlined.

(*b*) Projection of the unit cell along the *c* axis. Contour scale as in (*a*), except that the carbon atoms represent a density increment of 0·5 e.Å^{-2}.

from the final (*h*0*l*) Fourier series of the other two crystals. The temperature factor B in the expression $\exp\{-B[(\sin\theta)/\lambda]^2\}$ was determined by Wilson's (1942) method to be 6·3 Å^2. This value was later changed to 4·7 Å^2. Using the former value of B, the coordinates derived as above, and the James & Brindley (1931) atomic scattering factors for carbon and sulfur, the agreement between the resulting calculated and measured structure factors was given by $R_1 = 0{\cdot}35$.

One Fourier-series cycle with the (*h*0*l*) data reduced R_1 to 0·29, and this series is shown in Fig. 1(*a*). It was observed that, in general, $F_c > F_o$ for $2\sin\theta < 0{\cdot}70$, and less for larger values of $2\sin\theta$. A new empirical atomic scattering factor for carbon was then derived (Table 5), retaining the James & Brindley curve for sulfur, and this made $R_1 = 0{\cdot}255$. Four least-squares cycles applied to these atomic coordinates, and using the new f_C values, led to a stationary R_1 of 0·19. During the course of the last two cycles, it was noticed that the signs of 25 of the $\Delta\xi_j$'s to be added on to the ξ_j's (ξ_j is the atomic coordinate of the jth atom) had changed. At this stage, the iteration process was taken as having converged. In the least-squares process, weights of unity were given to all the observational equations, and the off-diagonal terms were omitted.

In the (*hk*0) layer, a similar procedure led to a set of atomic coordinates which, after two double Fourier series, gave the projection in Fig. 1(*b*). This corresponded to $R_1 = 0{\cdot}248$. Three least-squares iterations reduced this to 0·186, and again it was found that R_1 had become stationary, accompanied by considerable oscillation in the signs of the $\Delta\xi_j$'s from one cycle to the next. Thus a state of convergency was again assumed. The same f_C values were used in this layer as in (*h*0*l*). All the values of R_1 given above were computed only for those structure factors which were actually observed.

No attempt was made to evaluate the contribution of the hydrogen atoms to the calculated structure factors, since almost half these atoms are in the methyl group, and the effort of investigating the many possible orientations of this group was not thought worth while in the absence of other evidence. In the above refinement process 284 terms were used to determine 45 unknowns.

Atomic coordinates

The final set of atomic coordinates was chosen in the way described by Blackmore & Abrahams (1955*a*) for the case of di-*p*-tolyl telluride. The final coordinates from the (*h*0*l*) and (*hk*0) layers are combined in Table 2. The (*h*1*l*) intensities were recorded to serve as an independent check of these coordinates. The values of R_1 based on these coordinates, using all the structure factors in Table 3, are 0·219 for (*hk*0), 0·220 for (*h*0*l*) and 0·236 for (*h*1*l*).

Table 2. *Atomic coordinates in* $(p\text{-}CH_3.C_6H_4)_2S$

The origin is half way between three pairs of non-intersecting screw axes

	Atom	*x*	*y*	*z*
	S	0·1391	0·2233	0·1701
Ring *A*	C_1	0·0822	0·1881	0·3392
	C_2	0·0860	0·0977	0·5431
	C_3	0·0409	0·0693	0·6776
	C_4	0·9920	0·1314	0·6071
	C_5	0·9876	0·2220	0·4029
	C_6	0·0323	0·2502	0·2698
	C_7	0·9438	0·1020	0·7498
Ring *B*	C_1'	0·1950	0·2404	0·3454
	C_2'	0·1906	0·3263	0·5510
	C_3'	0·2360	0·3402	0·6918
	C_4'	0·2850	0·2698	0·6267
	C_5'	0·2893	0·1845	0·4225
	C_6'	0·2441	0·1685	0·2789
	C_7'	0·3330	0·2811	0·7796

Dimensions in the di-*p*-tolyl sulfide molecule

There are two S–C distances in this molecule, unrelated crystallographically, and these were measured as 1·76 and 1·74 Å. The valency angle C–S–C is 109°. The angles made by the normals to ring *A* (Table 2) with the *a*, *b* and *c* axes are 80°, 32° and 62°, respectively. The corresponding angles for ring *B* are 104°, 149° and 63°. These normals form an angle of 56° with each other.

Intermolecular distances

The intermolecular distances were all found to be greater than 3·5 Å, excluding H–H contacts. It is therefore assumed that only van der Waals forces are present between molecules in this crystal.

Accuracy of the coordinates

The treatment used in the study of di-*p*-tolyl telluride (Blackmore & Abrahams, 1955*a*) was employed in the present case. Although the effect on the atomic coordinates of placing all the weights equal to unity rather than to some other values has not been examined, the assumption that the determinant *D* formed from the coefficients of the normal equations is diagonal, has been studied. There are 30 unknowns in the (*h*0*l*) determination, and the 465 different coefficients in the symmetric determinant based upon the final (*x*, *z*) coordinates were computed. It should be noted that this layer contains only 136 observations, which is fewer than in the other layer in this study or in any layer used for refinement in the studies on di-*p*-tolyl telluride or selenide. Since the diagonal elements are sums of squares, and the off-diagonal elements are sums of products which may be of either sign, in general it may be expected that the larger the number of observational equations available for a given set of unknowns, the smaller the ratio of off-diagonal to diagonal element will be.

An examination of these 465 coefficients showed that the ratio of the off-diagonal to the diagonal element in the normal equation for a Δx_j was less, on average, than the corresponding ratio in a normal equation for a Δz_j. It was also observed that of those off-diagonal elements which were large (i.e. of comparable size with the diagonal element in the same equation), all were of the form

$$\sum_{hl}\left(\frac{\partial F(h0l)}{\partial z_i}\right)\left(\frac{\partial F(h0l)}{\partial x_j}\right)$$

in a normal equation for Δz_i as compared with coefficients of the form

$$\sum_{hl}\left(\frac{\partial F(h0l)}{\partial z_i}\right)\left(\frac{\partial F(h0l)}{\partial z_j}\right)$$

in that equation. A solution of this 30th order determinant showed that the r.m.s. error in Δx_j caused by assuming *D* to be diagonal is 0·03 Å and in Δz_j is 0·04 Å. Only in the case of two carbon atoms was this error equal to or greater than the standard deviation in the coordinates of the carbon atoms derived below. The solution obtained for this determinant was necessarily an approximation (see 'Experimental' below), and the figures above are subject to an error of ±0·01 Å.

The method of Blackmore & Abrahams (1955*a*), using the same nomenclature, gave $\sigma(\Delta x_S)=0{\cdot}010$ Å and hence $\sigma(r_S) = 0{\cdot}010$ Å. The ratio $\bar{f}_S/\bar{f}_C$ was 3·7 and hence $\sigma(r_C) = 0{\cdot}04$ Å. The standard deviation in each C–S bond length is 0·04 Å and in the averaged bond length is 0·03 Å. The standard deviation in the C–S–C bond angle is 1·9°.

Discussion

The S–C bond length measured in di-*p*-tolyl sulfide is 1·75±0·03 Å. The principal values for this bond length previously reported are given in Table 1, and from these it may be seen that the value found here is very close to the average. Cox, Gillot & Jeffrey (1949) have suggested that 1·79 Å be regarded as the standard length of a single covalent C–S bond, and 1·60 Å as the length of a standard double bond. They further assume a straight-line relation between bond

Table 3. *Observed and calculated structure factors for di-p-tolyl sulfide*

h0ℓ	F_{obs}	F_{calc}	h0ℓ	F_{obs}	F_{calc}	h0ℓ	F_{obs}	F_{calc}	hk0	F_{obs}	F_{calc}
200		-17	23, 0, 2	11	+12	605	17	-18	020	155	-152
400	45	+50	24, 0, 2	< 2	0	705	< 2	+ 4	040	20	+ 23
600	14	+18	25, 0, 2	< 2	0	805	< 2	+ 4	060	12	- 14
800	< 1	+ 4	26, 0, 2	< 2	- 2	905	< 2	- 2	080	14	+ 1
10, 0, 0	18	-11	27, 0, 2	2	- 4	10, 0, 5	6	- 3	100	2	0
12, 0, 0	6	- 7	28, 0, 2	< 2	+ 2	11, 0, 5	3	+ 1	110	11	+ 11
14, 0, 0	23	+24	29, 0, 2	2	+ 2	12, 0, 5	2	- 5	210	73	- 74
16, 0, 0	< 2	+ 2	30, 0, 2	2	+ 4	13, 0, 5	2	- 2	310	21	- 24
18, 0, 0	26	-26	31, 0, 2	< 2	+ 2	14, 0, 5	10	- 8	410	8	+ 9
20, 0, 0	9	+ 7	103	8	+ 8	15, 0, 5	18	-14	510	5	+ 5
22, 0, 0	13	+13	203	16	+18	16, 0, 5	6	+ 4	610	32	+ 32
24, 0, 0	2	+ 4	303	14	-12	17, 0, 5	10	+ 7	710	18	+ 16
26, 0, 0	3	- 4	403	12	-12	18, 0, 5	4	- 2	810	7	+ 9
28, 0, 0	2	+ 2	503	6	+ 7	19, 0, 5	3	+ 2	910	< 3	- 1
30, 0, 0	2	+ 1	603	29	-30	20, 0, 5	4	- 4	10, 1, 0	7	- 8
002	54	+62	703	< 2	+ 4	21, 0, 5	4	- 4	11, 1, 0	< 3	+ 2
004	22	-10	803	8	+11	22, 0, 5	2	+ 1	12, 1, 0	12	- 16
006	9	- 4	903	< 2	+ 1	23, 0, 5	2	- 2	13, 1, 0	< 3	- 1
008	< 1	- 2	10, 0, 3	13	+13	24, 0, 5	2	+ 1	14, 1, 0	13	+ 11
101	30	+35	11, 0, 3	2	+ 8	25, 0, 5	5	+ 3	15, 1, 0	< 3	- 6
201	9	-11	12, 0, 3	15	-13	26, 0, 5	5	- 4	16, 1, 0	14	+ 17
301	67	-70	13, 0, 3	< 2	- 1	27, 0, 5	< 2	0	17, 1, 0	< 5	- 1
401	14	-22	14, 0, 3	5	- 6	28, 0, 5	< 2	- 1	18, 1, 0	< 4	- 2
501	< 1	+ 1	15, 0, 3	5	- 4	106	3	0	19, 1, 0	12	+ 13
601	10	-15	16, 0, 3	23	+21	206	< 2	+ 4	20, 1, 0	43	- 45
701	46	+43	17, 0, 3	3	- 6	306	< 2	+ 4	21, 1, 0	6	- 9
801	17	+19	18, 0, 3	< 2	0	406	13	+11	22, 1, 0	9	- 7
901	1	+ 2	19, 0, 3	< 2	- 4	506	< 2	- 1	23, 1, 0	8	+ 6
10, 0, 1	43	+42	20, 0, 3	2	- 2	606	< 2	+ 1	24, 1, 0	9	- 9
11, 0, 1	11	- 8	21, 0, 3	< 2	0	706	< 2	- 1	25, 1, 0	9	+ 2
12, 0, 1	18	-17	22, 0, 3	< 2	+ 4	806	5	- 3	26, 1, 0	< 5	+ 5
13, 0, 1	8	+10	23 0, 3	< 2	+ 2	906	3	- 3	27, 1, 0	< 5	+ 2
14, 0, 1	< 1	0	24, 0, 3	15	+12	10, 0, 6	6	+ 5	28, 1, 0	< 3	- 2
15, 0, 1	8	11	25, 0, 3	3	+ 4	11, 0, 6	< 2	0	29, 1, 0	< 3	+ 3
16, 0, 1	17	+16	26, 0, 3	7	- 6	12, 0, 6	3	+ 3	30, 1, 0	5	+ 2
17, 0, 1	21	-20	27, 0, 3	< 2	+ 1	13, 0, 6	< 2	0	31, 1, 0	< 3	0
18, 0, 1	< 1	0	28, 0, 3	< 2	- 1	14, 0, 6	3	- 3	32, 1, 0	< 1	+ 1
19, 0, 1	11	-15	29, 0, 3	< 2	+ 3	15, 0, 6	< 2	0	120	77	- 78
20, 0, 1	16	+14	30, 0, 3	< 2	+ 2	16, 0, 6	2	0	220	53	- 50
21, 0, 1	2	+ 1	104	4	+ 7	17, 0, 6	2	+ 4	320	36	+ 33
22, 0, 1	< 2	+ 2	204	< 2	+ 1	18, 0, 6	11	+ 6	420	6	- 2
23, 0, 1	< 2	+ 2	304	< 2	+ 2	19, 0, 6	3	- 2	520	23	+ 22
24, 0, 1	14	+13	404	< 2	+ 2	20, 0, 6	< 2	0	620	45	+ 38
25, 0, 1	2	- 5	504	15	-11	21, 0, 6	< 2	- 1	720	9	+ 13
26, 0, 1	3	- 4	604	12	-10	22, 0, 6	5	- 4	820	16	- 20
27, 0, 1	< 2	0	704	3	- 5	23, 0, 6	2	+ 3	920	7	+ 11
28, 0, 1	< 2	- 3	804	6	- 9	107	< 2	- 1	10, 2, 0	5	- 3
29, 0, 1	3	+ 5	904	23	+24	207	< 2	- 2	11, 2, 0	7	0
30, 0, 1	6	+ 6	10, 0, 4	16	-11	307	5	+ 3	12, 2, 0	8	+ 9
31, 0, 1	< 2	0	11, 0, 4	2	0	407	< 2	+ 1	13, 2, 0	21	- 14
102	19	+23	12, 0, 4	2	+ 5	507	< 2	+ 3	14, 2, 0	26	+ 22
202	< 1	- 2	13, 0, 4	23	-20	607	< 2	+ 1	15, 2, 0	7	+ 6
302	17	+14	14, 0, 4	19	-16	707	10	- 4	16, 2, 0	< 3	0
402	< 1	+ 1	15, 0, 4	2	+ 4	807	2	- 2	17, 2, 0	6	+ 3
502	17	-16	16, 0, 4	2	0	907	< 2	+ 1	18, 2, 0	24	- 21
602	5	- 2	17, 0, 4	2	- 3	10, 0, 7	2	- 1	19, 2, 0	< 5	0
702	< 1	- 5	18, 0, 4	2	+ 3	11, 0, 7	< 2	+ 2	20, 2, 0	5	0
802	13	+12	19, 0, 4	< 2	- 3	12, 0, 7	2	+ 2	21, 2, 0	6	- 5
902	33	+35	20, 0, 4	< 2	- 1	13, 0, 7	< 2	- 2	22, 2, 0	8	+ 4
10, 0, 2	48	-47	21, 0, 4	2	- 2	14, 0, 7	< 2	- 1	23, 2, 0	9	+ 8
11, 0, 2	< 1	- 1	22, 0, 4	3	- 3	15, 0, 7	7	- 5	24, 2, 0	< 5	+ 2
12, 0, 2	< 2	- 6	23, 0, 4	4	+ 5	16, 0, 7	2	+ 2	25, 2, 0	< 5	0
13, 0, 2	21	-19	24, 0, 4	< 2	0	17, 0, 7	< 2	+ 1	26, 2, 0	7	- 5
14, 0, 2	3	- 4	25, 0, 4	< 2	+ 1	18, 0, 7	< 2	0	27, 2, 0	< 3	- 2
15, 0, 2	4	+ 7	26, 0, 4	< 2	0	108	4	- 3	28, 2, 0	5	- 4
16, 0, 2	< 2	+ 1	27, 0, 4	7	- 4	208	< 2	+ 2	29, 2, 0	< 3	0
17, 0, 2	< 2	+ 5	28, 0, 4	< 2	- 2	308	< 2	0	30, 2, 0	5	+ 2
18, 0, 2	2	- 6	105	13	-11	408	2	+ 2	130	8	- 10
19, 0, 2	9	- 7	205	< 2	- 1	508	3	+ 1	230	21	+ 24
20, 0, 2	< 2	+ 1	305	21	+17	608	< 2	0	330	11	+ 12
21, 0, 2	6	- 8	405	2	- 1				430	< 3	+ 2
22, 0, 2	2	+ 3	505	3	+ 3				530	11	+ 9

F(200) was cut off by the layer-line screen and was not observable.

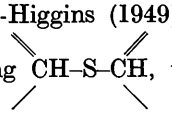
Table 3 (*cont.*)

hk0	F_{obs}	F_{calc}
630	20	-21
730	29	-25
830	24	-23
930	< 3	- 4
10, 3, 0	6	+11
11, 3, 0	8	- 8
12, 3, 0	7	+14
13, 3, 0	12	+13
14, 3, 0	22	-19
15, 3, 0	12	+ 9
16, 3, 0	14	-16
17, 3, 0	< 5	- 6
18, 3, 0	9	+ 4
19, 3, 0	9	-13
20, 3, 0	15	+14
21, 3, 0	9	+ 5
22, 3, 0	8	+11
23, 3, 0	< 5	- 4
24, 3, 0	< 5	0
25, 3, 0	< 5	- 3
26, 3, 0	8	- 6
27, 3, 0	8	- 7
28, 3, 0	< 3	+ 4
29, 3, 0	< 3	- 2
30, 3, 0	< 1	- 1
140	7	+ 8
240	8	+10
340	8	+13
440	20	-20
540	10	-10
640	28	-28
740	26	-28
840	< 3	+ 8
940	5	+ 3
10, 4, 0	3	+ 7
11, 4, 0	6	± 3
12, 4, 0	22	-18
13, 4, 0	19	+15
14, 4, 0	7	-10
15, 4, 0	6	- 7
16, 4, 0	8	- 7
17, 4, 0	5	- 4
18, 4, 0	11	+11
19, 4, 0	6	+ 6
20, 4, 0	< 5	- 3
21, 4, 0	< 5	- 1
22, 4, 0	< 5	- 1
23, 4, 0	< 5	- 1
24, 4, 0	< 5	- 2
25, 4, 0	< 3	- 3
26, 4, 0	< 3	+ 3
27, 4, 0	7	+ 1
28, 4, 0	< 3	+ 4
150	9	+11
250	6	-14
350	5	- 8
450	5	+ 5
550	8	- 8
650	6	+ 7
750	14	+ 8
850	21	+18
950	12	+12
10, 5, 0	8	-10
11, 5, 0	7	+ 5
12, 5, 0	< 5	- 1
13, 5, 0	9	-17
14, 5, 0	9	+11
15, 5, 0	< 5	- 3
16, 5, 0	14	+11
17, 5, 0	8	+ 9
18, 5, 0	< 5	+ 7
19, 5, 0	5	+ 6
20, 5, 0	5	- 6
21, 5, 0	< 5	+ 2
22, 5, 0	6	0
23, 5, 0	< 3	- 4
24, 5, 0	< 3	+ 2
25, 5, 0	7	+ 1
26, 5, 0	7	+ 3
160	7	-11
260	14	+14
360	16	-15
460	9	+10
560	< 5	+ 2
660	12	+11
760	9	+12
860	6	+ 3
960	< 5	+ 2
10, 6, 0	5	- 6
11, 6, 0	9	-11
12, 6, 0	8	+11
13, 6, 0	6	- 4
14, 6, 0	< 5	+ 4
15, 6, 0	< 5	+ 2
16, 6, 0	< 5	+ 6
17, 6, 0	< 5	+ 5
18, 6, 0	< 5	- 2
19, 6, 0	< 5	- 6
20, 6, 0	< 3	0
21, 6, 0	< 3	- 2
22, 6, 0	< 3	+ 4
23, 6, 0	< 3	+ 2
24, 6, 0	< 3	0
170	9	- 8
270	< 5	+ 3
370	9	+ 8
470	< 5	+ 2
570	< 5	+ 5
670	< 5	- 5
770	6	- 2
870	6	- 3
970	< 5	- 7
10, 7, 0	< 5	+ 4
11, 7, 0	< 5	0
12, 7, 0	< 5	- 1
13, 7, 0	< 5	+ 7
14, 7, 0	< 5	- 3
15, 7, 0	< 5	+ 2
16, 7, 0	5	- 5
17, 7, 0	3	- 6
18, 7, 0	5	- 6
19, 7, 0	7	- 8
20, 7, 0	< 3	+ 2
21, 7, 0	3	+ 4
22, 7, 0	3	- 4
180	< 5	+13
280	9	- 4
380	< 5	+10
480	< 5	0
580	< 5	+ 2
680	7	- 6
780	< 5	- 2
880	< 5	+ 3
980	< 5	- 1
10, 8, 0	< 5	0
11, 8, 0	< 3	+ 5
12, 8, 0	< 3	- 1
13, 8, 0	< 3	+ 3
14, 8, 0	< 3	- 2
15, 8, 0	< 3	- 4
16, 8, 0	< 3	+ 1
17, 8, 0	< 3	- 2
18, 8, 0	< 3	- 1
19, 8, 0	< 1	+ 2
20, 8, 0	< 1	0
190	< 3	+ 2
290	< 3	0
390	< 3	- 2
490	5	- 3
590	< 3	- 8
690	< 3	- 2
790	< 3	+ 4
890	< 3	+ 2
990	< 3	+ 1
10, 9, 0	< 3	- 2
11, 9, 0	< 3	0
12, 9, 0	< 3	- 1
13, 9, 0	< 3	- 3
14, 9, 0	< 1	+ 3
15, 9, 0	< 1	- 1
1, 10, 0	< 1	- 4
2, 10, 0	3	- 2
3, 10, 0	< 1	- 6
4, 10, 0	< 1	- 4

h1ℓ	F_{obs}	$\lvert F_{calc}\rvert$
011	*	60
111	*	43
211	23	18
311	70	51
411	73	70
511	14	13
611	5	11
711	< 2	5
811	24	13
911	18	26
10, 1, 1	46	36
11, 1, 1	13	9
12, 1, 1	19	11
13, 1, 1	20	23
14, 1, 1	< 4	6
15, 1, 1	< 4	7
16, 1, 1	< 4	1
17, 1, 1	24	21
18, 1, 1	10	11
19, 1, 1	24	21
20, 1, 1	< 5	4
21, 1, 1	5	3
22, 1, 1	8	11
23, 1, 1	5	7
012	< 4	6
112	14	14
212	18	28
312	32	30
412	5	5
512	6	11
612	4	10
712	35	33
812	7	8
912	10	11
10, 1, 2	36	33
11, 1, 2	20	23
12, 1, 2	7	10
13, 1, 2	4	7
14, 1, 2	4	3
15, 1, 2	7	9
16, 1, 2	4	12
17, 1, 2	< 5	5
18, 1, 2	< 5	0
19, 1, 2	6	6
20, 1, 2	12	11
21, 1, 2	7	11
22, 1, 2	< 5	5
013	< 4	2
113	< 4	6
213	< 4	6
313	7	12
413	46	42
513	13	16
613	23	21
713	< 4	4
813	20	15
913	< 4	6
10, 1, 3	22	17
11, 1, 3	< 4	3
12, 1, 3	8	10
13, 1, 3	5	7
14, 1, 3	12	13
15, 1, 3	< 5	2
16, 1, 3	< 5	2
17, 1, 3	< 5	6
18, 1, 3	< 5	7
19, 1, 3	< 5	5
20, 1, 3	< 5	1
21, 1, 3	< 5	0
22, 1, 3	5	7
014	< 5	2
114	5	6
214	12	9
314	5	9
414	< 5	3
514	< 5	7
614	23	16
714	25	25
814	< 5	7
914	< 5	3
10, 1, 4	7	10
11, 1, 4	25	18
12, 1, 4	6	13
13, 1, 4	7	10
14, 1, 4	6	7
15, 1, 4	< 5	3
16, 1, 4	< 5	0
17, 1, 4	< 5	2
18, 1, 4	< 5	1
19, 1, 4	< 5	2
20, 1 4	< 5	5
015	6	10
115	10	9
215	< 5	2
315	5	8
415	< 5	6
515	16	17
615	13	15
715	< 5	5
815	< 5	5
915	< 5	3
10, 1, 5	< 5	4
11, 1, 5	< 5	3
12, 1, 5	< 5	2
13, 1, 5	< 5	3
14, 1, 5	13	12
15, 1, 5	< 5	4
16, 1, 5	< 5	5
17, 1, 5	8	9
18, 1, 5	< 5	3
19, 1, 5	5	5
016	< 5	0
116	< 5	3
216	13	12
316	< 5	9
416	< 5	5
516	< 5	3
616	< 5	2
716	5	6
816	< 5	3
916	< 5	1
10, 1, 6	< 5	3

* Not observable; cut off by layer-line screen.

length and order, from which the length 1·75 Å corresponds to a bond order of 1·21. The value of the standard deviation in this bond length clearly requires caution to be used in this interpretation, but it does appear that some double-bond character may be present in the C–S bonds in di-*p*-tolyl sulfide. If there were complete freedom of rotation about the C–S bond, the closest intramolecular contact between *ortho* carbon atoms of adjacent aromatic rings would be 2·58 Å if the molecule were coplanar. If each ring were normal to the C–S–C plane, this distance would be increased to the maximum separation of 3·99 Å, assuming no change in the present S valency angle. In di-*p*-tolyl sulfide, ring *A* forms an angle of 32·5° and ring *B* of 35° with this C–S–C plane, resulting in an intermediate C_2–C_2' distance of 3·19 Å. This approach suggests a fairly strong interaction between these two atoms, which must be one of repulsion. Hence, the C–S bond apparently does not permit free rotation, and is probably not a pure single bond. The normal steric repulsion between these two atoms could be balanced by a tendency towards conjugation in the C–S bonds. Unfortunately, there does not yet appear to be any information available regarding the variation in the degree of conjugation in a system, such as the present, with changing dihedral angle.

There is also other evidence favoring the view that sulfur tends to conjugate with aromatic systems with which it is linked. Longuet-Higgins (1949) has suggested that in the grouping  the sulfur atom may expand its valency shell to a decet by using the available 3*d* orbitals. A tendency such as this will produce some double-bond character in the C–S bond, and Longuet-Higgins has ascribed the high degree of aromaticity in thiophene to a mechanism of this kind. On the basis of the reactivity of monomers such as methyl vinyl sulfide in copolymerization, and also of the ultraviolet absorption spectra, Price & Zomlefer (1950) suggested that the octet of the sulfide sulfur atom might expand to permit some conjugation with the adjacent bonds.

The dihedral angle between the normals to the planes of the aromatic rings in di-*p*-bromophenyl sulfide (Toussaint, 1945) is 72±2°, which may be compared with the corresponding angle in di-*p*-tolyl sulfide of 56°.

The C–S–C angle in di-*p*-tolyl sulfide is 109°, and the average value for this angle in Table 1 is about 106°. In di-*p*-tolyl selenide and telluride the valency angle of the group VI_b atom is respectively 106° and 101°, and the corresponding oxygen angle is reported to be 116±4° in diphenyl ether (Leonard & Sutton, 1948) on the basis of electric dipole measurements, and 123±2° in *p,p'*-diiodophenoxybenzene (Plieth, 1947) by X-ray measurement. This valence angle thus tends to decrease with increasing atomic number, and may be the result of diminished steric repulsion between adjacent carbon atoms as the central atom gets larger. It may be noted that in group V_b, a similar decrease in the valence angle occurs, as shown in Table 4.

Table 4. *Values of the valency angle in compounds of group* V_b

All measurements are by spectroscopic methods

V_b atom	Valency angle	Molecule	Reference
N	106° 47′	NH_3	Herzberg (1945)
P	93° 50′	PH_3	Nielsen (1952)
As	91° 35′	AsH_3	Nielsen (1952)
Sb	91° 31′	SbH_3	Nielsen (1952)

Experimental

The colorless needles of di-*p*-tolyl sulfide were prepared by the method of Rosenmund & Harms (1920), and recrystallized from aqueous alcohol solution. The crystals have a tendency to volatilize, and hence were mounted in very thin-walled glass capillaries to avoid loss of weight during the X-ray exposure. The largest of the five crystals employed was 0·30×0·40×1·20 mm.³ and the smallest was 0·07×0·09×0·50 mm.³, the larger crystals being used only for the weakest intensities, and the strong intensities being measured with the smallest crystal. The experimental procedures were the same as those described by Blackmore & Abrahams (1955*a*), except that the upper layer was photographed using a precession camera and the multiple-exposure technique. The correction for the Lorentz and polarization effect was made by the method of Burbank (1952) and Grenville-Wells & Abrahams (1952). The ratio of the strongest to the weakest intensity in each layer was 2916:1 in (*hk*0), 6292:1 in (*h*0*l*) and 1000:1 in (*h*1*l*). The complete set of coefficients for the normal equations were computed on International Business Machines. A close approximation to the solution of the 30th-order determinant was obtained by a variation of the method of conjugate gradients (Hestenes & Stiefel, 1952) on Whirlwind,* the Massachusetts Institute of Technology high-speed digital computer.

The empirical atomic-scattering-factor curve for carbon was obtained by assuming the James & Brindley curve for sulfur to be correct, and with $B = 4{\cdot}7$ Å² computing the ratio $f_C = (F_o - F_c^S)/G_C$, where f_C is the empirical form factor for carbon, F_o is the observed structure factor, F_c^S is the calculated contribution of sulfur to the structure factor, and G_C is the geometric contribution of the carbon atoms to that structure factor. The values of f_C thus derived were plotted

Table 5. *Empirical atomic scattering factor for carbon in di-p-tolyl sulfide at* 25° C.

$(\sin\theta)/\lambda$	0·0	0·1	0·2	0·3	0·4	0·5	0·6
f_C	6·0	4·5	2·6	1·3	0·8	0·5	0·3

* Availability of Digital Computer Laboratory time for this problem was made possible by the Office of Naval Research.

versus $(\sin\theta)/\lambda$ and a smooth curve was drawn. This is represented in Table 5.

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Friedel's Law in the Dynamical Theory of Diffraction

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The significance and validity of Friedel's law are critically discussed by means of the dynamical theory of diffraction. It is proved that in some cases diffraction phenomena are not invariant under the operation of inversion exerted on the crystal; this means that Friedel's law fails. The cause of the failure is not the effect of absorption, but is found in the dynamical relation of reflexions which are excited simultaneously.

1. Introduction

Friedel's law (Friedel, 1913) was originally proposed as an empirical rule for the diffraction phenomena of X-rays by crystals. The law implies:

> Intensities of reflexions of indices (hkl) and $(\bar{h}\bar{k}\bar{l})$ are equal to each other. (Form I)

This rule can be readily derived from the kinematical theory of diffraction, because the structure amplitudes $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ are generally complex conjugate to each other and the integrated intensity of the diffraction spot given by this theory is proportional to $|F|^2$. The same law is expected to hold similarly for electron and neutron waves when the diffraction takes place in accordance with the kinematical theory.

Friedel's law is sometimes expressed in another form (e.g. Zachariasen, 1944):

> The diffraction phenomena of waves by a crystal are invariant under an inversion of the crystal with respect to the incident beam. (Form II)