

SHORT COMMUNICATIONS

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Comparison of two independent structure determinations of diphenyl disulphide. By M. SACERDOTI and G. GILLI, *Centro di Strutturistica Diffraattometrica, Università di Ferrara, Ferrara, Italy* and P. DOMIANO, *Centro di Studio per la Strutturistica Diffraattometrica del CNR, Università di Parma, Parma, Italy*

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The results of two independent structure determinations of diphenyl disulphide are compared by means of half-normal probability plots. No systematic errors are detected except in the temperature factors of the sulphur atoms.

The structure of diphenyl disulphide (DDS) has been determined by Lee & Bryant (1969) (hereinafter LB) from 963 visually estimated reflexions. We have determined the same structure from 1134 reflexions collected on a Siemens four-circle diffractometer. In general the atomic coordinates are in good agreement with those of the previous determination but the standard deviations are about four times smaller. A comparison of the two independent structure determinations is of interest in view of the different methods used for data collection.

In Table 1 are compared the two sets of experimental data; the refinement conditions, which are strictly similar, are also reported. We used the scattering factors reported by Cromer & Waber (1965) for the C and S atoms and by Stewart, Davidson & Simpson (1965) for the H atoms. LB used the scattering factors of Hanson, Herman, Lea & Skillman (1964).

Tables 2–5 list the results of our structure determination.* Table 2 shows the positional and thermal parameters of the non-hydrogen atoms. The parameters of the hydrogen atoms are reported in Table 3. The atom numbering scheme is the same as that of LB, the first phenyl ring, C(1)–C(6), being bonded through C(1) to S(1) and the second, C(7)–C(12), through C(7) to S(2). Tables 4 and 5 show a selection of bond distances and angles. The C–H distances are not reported; they are in the range 0.87–1.02 Å.

Comparison of the two structure determinations has been carried out by half-normal probability (HNP) plots (Abra-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30660 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Comparison of experimental data and refinement conditions*

	Lee & Bryant	Present work
Space group	$P2_12_12_1$	$P2_12_12_1$
<i>a</i>	23.78 (3) Å	23.691 (4) Å
<i>b</i>	8.13 (2)	8.136 (3)
<i>c</i>	5.64 (2)	5.636 (3)
<i>Z</i>	4	4
Crystal dimensions	0.3 × 0.15 × 0.15 mm	0.34 × 0.21 × 0.15 mm
Radiation	Ni-filtered Cu $K\alpha$	Ni-filtered Cu $K\alpha$
Intensity measurements	Weissenberg photographs, visual estimation	Automatic Siemens diffractometer, ω -2 θ scan
Number of independent reflexions		1227
Number observed	963	1134
Absorption and extinction correction	No	No
Refinement	Full-matrix	Full-matrix
Unobserved reflexions	Not used	Not used
Weights	Cruickshank scheme	Cruickshank scheme
Anomalous scattering correction	Yes	Yes
S and C atoms	Refined anisotropically	Refined anisotropically
H atoms	Calculated positions	Refined isotropically
<i>R</i>	0.09	0.027
<i>R_w</i>		0.033

Table 2. Positional ($\times 10^4$) and thermal parameters of the non-hydrogen atoms

Thermal parameters (\AA^2) have been multiplied by 10^2 . E.s.d.'s are shown in parentheses. The anisotropic temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	3075.8 (2)	-344.9 (10)	1774.1 (14)	4.44 (3)	4.21 (3)	7.34 (4)	0.39 (3)	1.25 (3)	-0.22 (4)
S(2)	3432.9 (2)	325.2 (9)	-1339.6 (12)	4.70 (3)	5.24 (3)	5.93 (4)	-0.22 (3)	-0.89 (3)	0.74 (4)
C(1)	3190 (1)	-2509 (3)	2074 (5)	3.4 (1)	4.0 (1)	5.5 (1)	-0.4 (1)	-0.1 (1)	-0.6 (1)
C(2)	3482 (1)	-3461 (3)	457 (5)	5.1 (1)	4.9 (1)	5.5 (1)	-0.1 (1)	0.5 (1)	-0.6 (1)
C(3)	3552 (1)	-5117 (4)	872 (6)	6.3 (1)	4.6 (2)	7.3 (2)	0.4 (1)	-0.6 (1)	-1.6 (1)
C(4)	3339 (1)	-5829 (4)	2905 (7)	6.9 (2)	4.1 (2)	8.2 (2)	-0.6 (1)	-1.6 (2)	-0.1 (1)
C(5)	3047 (1)	-4879 (4)	4519 (6)	6.1 (2)	6.0 (2)	6.4 (2)	-1.8 (1)	-0.8 (1)	0.8 (2)
C(6)	2974 (1)	-3215 (4)	4128 (5)	4.5 (1)	5.5 (1)	5.5 (1)	-0.7 (1)	0.4 (1)	-0.3 (1)
C(7)	4160 (1)	681 (3)	-665 (4)	4.4 (1)	3.4 (1)	4.8 (1)	0.1 (1)	0.2 (1)	-0.3 (1)
C(8)	4459 (1)	1569 (4)	-2359 (5)	5.8 (1)	5.8 (2)	5.7 (2)	0.3 (1)	0.6 (1)	1.2 (1)
C(9)	5033 (1)	1829 (4)	-2033 (6)	5.8 (2)	6.9 (2)	7.8 (2)	-0.9 (2)	1.8 (2)	1.2 (2)
C(10)	5305 (1)	1221 (4)	-67 (6)	4.6 (1)	7.0 (2)	7.8 (2)	-1.0 (1)	0.3 (1)	-0.9 (2)
C(11)	5006 (1)	348 (4)	1602 (6)	5.1 (1)	7.5 (2)	6.0 (2)	-0.5 (1)	-0.8 (1)	-0.2 (2)
C(12)	4431 (1)	74 (4)	1301 (5)	4.9 (1)	5.8 (2)	4.9 (1)	-0.6 (1)	-0.1 (1)	0.5 (1)

Table 3. Positional and thermal parameters of the hydrogen atoms

Positional parameters are $\times 10^3$. Thermal parameters (\AA^2) have been multiplied by 10^2 . E.s.d.'s are in parentheses. The isotropic temperature factor is of the form

$$\exp(-8\pi^2 U \sin^2 \theta / \lambda^2).$$

	x/a	y/b	z/c	U
H(2)	363 (1)	-297 (4)	-89 (5)	4.8 (8)
H(3)	374 (2)	-570 (5)	-40 (7)	8.4 (12)
H(4)	340 (1)	-695 (5)	326 (6)	7.0 (9)
H(5)	291 (1)	-535 (4)	597 (6)	6.5 (9)
H(6)	278 (2)	-259 (5)	516 (7)	8.5 (12)
H(8)	426 (1)	200 (4)	-381 (6)	6.3 (9)
H(9)	521 (1)	248 (4)	-301 (6)	6.9 (10)
H(10)	572 (2)	143 (5)	26 (6)	9.3 (12)
H(11)	518 (1)	-5 (4)	312 (6)	7.4 (10)
H(12)	423 (1)	-50 (4)	257 (5)	6.3 (9)

Table 4. Bond distances (\AA)

E.s.d.'s are shown in parentheses.

S(1)-S(2)	2.023 (1)	C(6)-C(1)	1.391 (4)
S(1)-C(1)	1.789 (3)	C(7)-C(8)	1.391 (4)
S(2)-C(7)	1.788 (2)	C(8)-C(9)	1.388 (4)
C(1)-C(2)	1.382 (4)	C(9)-C(10)	1.373 (5)
C(2)-C(3)	1.377 (4)	C(10)-C(11)	1.375 (5)
C(3)-C(4)	1.379 (5)	C(11)-C(12)	1.389 (4)
C(4)-C(5)	1.380 (5)	C(12)-C(7)	1.372 (4)
C(5)-C(6)	1.382 (4)		

Table 5. Bond angles ($^\circ$)

E.s.d.'s are shown in parentheses.

C(1)-S(1)-S(2)	106.5 (1)	C(5)-C(6)-C(1)	119.4 (3)
C(7)-S(2)-S(1)	105.2 (1)	S(2)-C(7)-C(8)	115.4 (2)
S(1)-C(1)-C(2)	124.4 (2)	S(2)-C(7)-C(12)	124.4 (2)
S(1)-C(1)-C(6)	115.4 (2)	C(8)-C(7)-C(12)	120.2 (2)
C(2)-C(1)-C(6)	120.1 (2)	C(7)-C(8)-C(9)	119.2 (3)
C(1)-C(2)-C(3)	119.7 (3)	C(8)-C(9)-C(10)	120.7 (3)
C(2)-C(3)-C(4)	120.5 (3)	C(9)-C(10)-C(11)	119.8 (3)
C(3)-C(4)-C(5)	119.7 (3)	C(10)-C(11)-C(12)	120.2 (3)
C(4)-C(5)-C(6)	120.4 (3)	C(11)-C(12)-C(7)	120.0 (3)

hams & Keve, 1971), which provide useful information on the presence of systematic errors and on the correct assignment of the standard-deviation values. The HNP plots for all the fractional coordinates, the U_{IJ} values of the C atoms, and the U_{IJ} values of the S atoms are shown in Fig. 1(a), (b) and (c) respectively. The e.s.d.'s of the U_{IJ} values were not reported by LB and were assumed to be 4.2 times our e.s.d.'s. The number 4.2 was obtained by comparing the e.s.d.'s of the positional parameters. For Fig. 1(c) the values of expected Δp , corrected for the small dimensions of

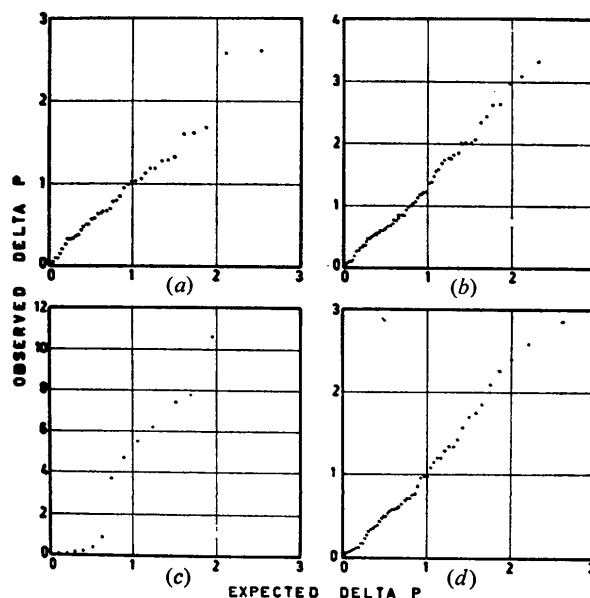


Fig. 1. Half-normal probability plots. The numbers given below in parentheses for the plots (a), (b) and (d) are: number of included values, slope and intercept of the least-squares line through all the points of the plot. (a) (42, 0.03, 0.98) comparison of the atomic positional parameters; (b) (72, -0.04, 1.42) comparison of the U_{IJ} values of the C atoms; (c) comparison of the U_{IJ} values of the S atoms; (d) (55, -0.08, 1.10) comparison of the intramolecular distances ≤ 4.65 \AA .

the sample, were taken from Hamilton & Abrahams (1972). The comparison of the molecular geometries [Fig. 1(d)] was with all the intramolecular distances ≤ 4.65 Å instead of bond distances and angles (De Camp, 1973).

The HNP plot for all the positional parameters [Fig. 1(a)] is reasonably linear, with nearly zero intercept, suggesting that no systematic error is present. The slope of the plot indicates that the standard deviations are correctly estimated. These results are confirmed by the HNP plot for the intramolecular distances [Fig. 1(d)].

The HNP plot for the U_{ij} 's of all the atoms (not reported here) was markedly non-linear. However, elimination of all the U_{ij} 's of the S atoms resulted in the plot of Fig. 1(b), which is linear with zero intercept. It shows that systematic errors are absent but the standard deviations are underestimated by a factor of 1.4.

A systematic error in one or both structure determinations is clearly shown by the HNP plot for the U_{ij} 's of the S atoms [Fig. 1(c)]. All the observed $\Delta p \geq 3.7$ are relative to the U_{ii} terms, whose correlation coefficient with the overall

scale factor is about 0.4. This suggests that the systematic error is caused by the procedure, used by LB, of changing the interlayer scaling factors during the isotropic refinement.

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An improved method for intensity data collection with a computer-controlled diffractometer. By I. J. TICKLE,
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A method for calculation of the integrated peak intensities of reflexions measured with a computer-controlled four-circle diffractometer is described. This is put forward as an alternative to the commonly used 'ordinate analysis' method for installations where the memory capacity of the computer is severely limited and external storage devices are not available. It is demonstrated by computer simulation that 'ordinate analysis' systematically overestimates weak reflexions whereas this effect is not significant for the method described.

This paper will be of interest mainly to users of a single-crystal X-ray diffractometer controlled by a computer with limited program storage. The method to be described has been programmed for a PDP-8I with neither 'extended memory' nor magnetic storage devices, and is currently in routine use on a Hilger and Watts Y290 four-circle diffractometer. The particular problem of concern here is that of deriving the integrated peak intensity from the measured step-scan reflexion profile. If the peak is consistently centred in the scan the usual 'background-peak-background' method will suffice. Protein crystals, however, when mounted in the usual way (*i.e.* in a capillary adhering by surface tension to the wall) are often subject to small movements which must be allowed for if frequent realignment is to be avoided.

One method in current popular use is 'ordinate analysis' (Watson, Shotton, Cox & Muirhead, 1970) in which a reflexion is scanned in $2n$ steps, starting n steps before the predicted peak position. The peak is taken as the consecutive n steps with the greatest sum. The background intensity is then taken as the sum of the counts for the remaining n steps. Net positive intensity will always be found by this procedure, and a statistical analysis will show that weak reflexions are systematically overestimated.

Alternative methods have been proposed: Diamond (1969) has suggested that the measured profile should be fitted to a stored peak profile which varies over reciprocal space. Vandlen & Tulinsky (1971) describe a scheme in which a realignment subroutine is automatically entered if the intensities of monitor reflexions fall below pre-designated values, indicative of crystal motion. Lehmann & Larsen (1974) have shown that the peak can be defined as the set of consecutive steps for which $\sigma(I)/I$ is a minimum (I is the net integrated intensity for the assumed peak); the portion of the scan taken as peak is thus a characteristic of the scan profile, and not, as is common practice, a function only of the Bragg angle. Unfortunately these methods, although superior to 'ordinate analysis' in coping with crystal motion are either too sophisticated for a computer with limited memory capacity, or demand storage of the profiles for subsequent off-line processing, and many diffractometer users will not have the facilities to implement them.

The procedure proposed here can be envisaged in three stages: (i) the reflexion is scanned in $2n$ steps centred on the predicted position and the profile is stored in the computer; (ii) the actual peak position is computed, and (iii) the peak is taken as the n steps centred on the actual position, the