Short Communications

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Note on the space group of dibenzyl disulphide.

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The space group of dibenzyl disulphide is *C*2/*c*.

The difficulties encountered by Lee & Bryant (1969) when refining the structure of dibenzyl disulphide in space group *C*2/*c* are due to the fact that the molecules have been placed on the line [0*y*0] rather than on the line [0*y*¼] which coincides with the twofold axis in *C*2/*c*. After we had changed the *z* coordinates by $\Delta z = +0{\cdot}25$, rapid convergence was obtained in a least-squares refinement for space group *C*2/*c* on the TR4 computer in Groningen. Use was made of a program working in block diagonal approximation, in the final cycles Lee & Bryant's (1969) weighting scheme was used. The index *R* decreased to 0·086 ($R=0{\cdot}104$ for a structure factor calculation on the TR4 based on the parameters and scattering factors from Lee & Bryant's paper, space group *Cc*). The final coordinates of the non-hydrogen atoms are given in Table 1. The hydrogen atoms were fixed at a distance of 1·08 Å from their respective carbon atoms and were given an isotropic temperature factor

$$\exp\left(-5{\cdot}0 \sin^2 \theta/\lambda^2\right).$$

Table 1. *Final coordinates and standard deviations as calculated by the least-squares program*

	x	*y*	*z*
S(1)	0·0041 (1)	0·0111 (2)	0·3399 (1)
C(1)	0·1030 (3)	0·1625 (6)	0·3902 (4)
C(2)	0·2065 (3)	0·1038 (4)	0·3819 (4)
C(3)	0·2541 (3)	−0·0152 (5)	0·4611 (3)
C(4)	0·3500 (3)	−0·0646 (6)	0·4539 (4)
C(5)	0·4034 (3)	0·0058 (5)	0·3722 (4)
C(6)	0·3575 (3)	0·1214 (7)	0·2975 (4)
C(7)	0·2595 (3)	0·1724 (5)	0·3030 (3)

The lengths of the C–C bonds in the benzene ring vary from 1·351 to 1·407 Å. The variation in these bond lengths is three times as large as expected from the standard deviations calculated by the least-squares program used in Groningen. Therefore all standard deviations calculated by this least-squares program have been multiplied by three. The lengths of the bonds not belonging to the benzene rings are (for numbering see Lee & Bryant, 1969): S(1)–S(2) = 2·015 (±0·003), S(1)–C(1) = 1·844 (±0·012), C(1)–C(2) = 1·491 (±0·015) Å. These values are almost identical with the average values given by Lee & Bryant (1969).

In view of the discussion given above we think that the space group of dibenzyl disulphide is *C*2/*c*. Also in an early paper by Egartner, Halla & Schacherl (1932) this space group has been adopted, as according to these authors dibenzyl disulphide does not show a piezoelectric effect.

The authors wish to thank Professor Aafje Vos for valuable discussions.

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A further note on the space group of dibenzyl disulfide.

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In agreement with van Dijk & Visser we find that the space group of dibenzyl disulfide is *C*2/*c*, and not *Cc*, as reported by Lee & Bryant.

On the basis of a least-squares refinement in *C*2/*c*, van Dijk & Visser (1971) concluded that it is the correct space group of dibenzyl disulfide, rather than *Cc* reported by Lee & Bryant (1969). Our own work on this problem was completed before we learned of the work of van Dijk & Visser, and we wish to report here the results of some calculations not made by them. Our least-squares results differ only negligibly from theirs, the small discrepancies probably

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arising from different treatment of the hydrogen atoms and from the fact that we used average F values for 30 reflections for which two values were contained in the data table of Lee & Bryant.

The positions of the hydrogen atoms were assumed by van Dijk & Visser; we located them in a difference Fourier map, the power of which had been recently brought to our attention (Wilkins, Arnott, Marvin & Hamilton, 1970). This map contained peaks corresponding to the hydrogen atoms at positions close to those assumed by van Dijk & Visser, and no spurious peaks.

Lee & Bryant stated that space group *Cc* was 'confirmed by the pyroelectric test, the statistical test, and by the structure refinement'. Neither we nor van Dijk & Visser confirmed this conclusion by structure refinement, nor did we carry out a pyroelectric test, a notoriously fickle experiment. We did, however, make statistical tests.

The data were converted to E values in the usual manner. Reflections missing from the data set which were not space group extinctions were assumed to be unobservable and assigned a vanishingly small F_o. The $\sin \theta/\lambda$ cut-off was set at 0·55 Å^{-1}. The total number of input data was 773, of which 140 were unobserved. The resulting E statistics, shown in Table 1, clearly favor the centric alternative, and we believe that there is no doubt that the true space group is *C*2/*c*. Although we have not tested this possibility, the inclusion by Lee & Bryant of the 30 redundant reflections may have upset the results of their statistical test, the details of which were not described by them.

Table 1. *E statistics for dibenzyl disulfide*

	Observed	Centric	Acentric
$\langle E^2 \rangle$	1·012	1·000	1·000
$\langle \|E\| \rangle$	0·749	0·798	0·886
$\langle \|E^2-1\| \rangle$	1·051	0·968	0·736
$\|E\| > 3$	0·5 %	0·3 %	0·01 %
$\|E\| > 2$	5·6	5·0	1·8
$\|E\| > 1$	29·4	32·0	36·8

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A further note on the structure of dibenzyl disulphide.

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Evidence is produced that the space group of dibenzyl disulphide is *Cc*, not *C*2/*c* as suggested by van Dijk & Visser and Einspahr & Donohue.

The original paper on the crystal and molecular structure of dibenzyl disulphide (Lee & Bryant, 1969) reported the space group as *Cc* or *C*2/*c*, and described refinement in the former (non-centrosymmetric) space group. Other workers, van Dijk & Visser (1971), and Einspahr & Donohue (1971) have used the same data to refine the structure in the centrosymmetric space group. The results of all three analyses are very similar, but the analysis in the *Cc* space group indicates that the molecule *almost* has a twofold axis and the structure may be described as *nearly* centrosymmetric, whilst *C*2/*c* requires exact symmetry.

Since the two models are so similar, statistical tests such as E statistics or $N(z)$ test (Howells, Phillips & Rogers, 1950) are unlikely to resolve the problem. It is interesting that an $N(z)$ test performed on *hk*0 data originally reported has since been repeated, and indicates the absence of a centre, whilst the same test on general *hkl* reflexions is close to the centrosymmetric case (Fig. 1).

The R index is not necessarily an infallible guide, but the value of 7·9 % for *Cc* (with 144 atomic parameters) is lower than 8·6 % and 8·9 % for *C*2/*c* (with 72 parameters), although the difference is not sufficient to resolve the ambiguity.

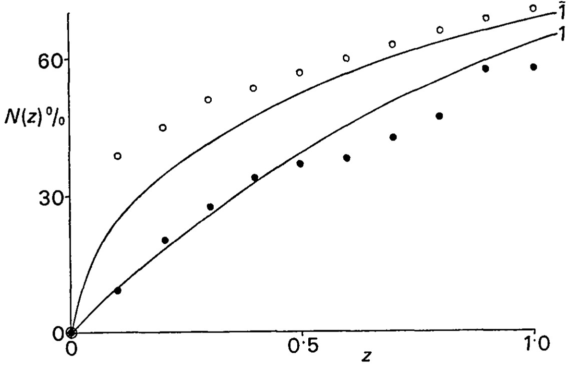

Fig. 1. $N(z)$ test. The theoretical intensity distributions for centrosymmetric and non-centrosymmetric cases are shown as solid lines. Calculated results for *hk*0 reflexions are shown as solid circles, and general *hkl* reflexions (omitting projection data) are shown as white circles. Unobserved reflexions were included with a value of $F_o = 0·3$. The Wilson ratios were calculated as 0·78 for *hk*0 data and 0·51 for general *hkl* reflexions (theoretical values for curve $\bar{1} = 0·64$, for curve $1 = 0·79$).