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
$\langle \lvert E\rvert\rangle$	0·749	0·798	0·886
$\langle \lvert E^2-1\rvert\rangle$	1·051	0·968	0·736
$\lvert E\rvert > 3$	0·5 %	0·3 %	0·01 %
$\lvert E\rvert > 2$	5·6	5·0	1·8
$\lvert E\rvert > 1$	29·4	32·0	36·8

This work was supported by the National Science Foundation and the Advanced Research Projects Agency, Office of the Secretary of Defense.

References

Dijk, B. van & Visser, G. J. (1971). *Acta Cryst.* **B27**, 846.
Lee, J. D. & Bryant, M. W. R. (1969). *Acta Cryst.* **B25**, 2497.
Wilkins, M. F. H., Arnott, S., Marvin, D. A. & Hamilton, L. D., (1970). *Science*, **167**, 1693.

Acta Cryst. (1971). B27, 847

A further note on the structure of dibenzyl disulphide.

By J. D. Lee, *Department of Chemistry, University of Technology, Loughborough, Leics., England*

(*Received* 2 *December* 1970)

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.

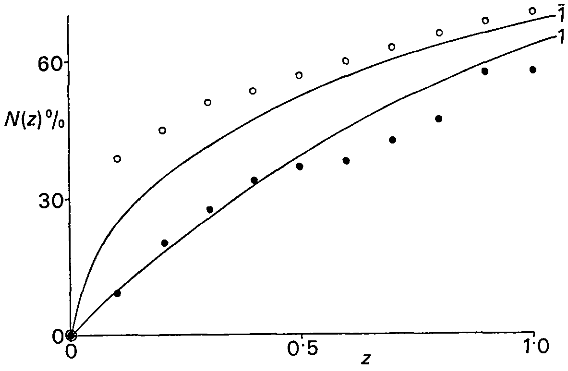

Fig. 1. $N(z)$ test. The theoretical intensity distributions for centrosymmetric and non-centrosymmetric cases are shown as solid lines. Calculated results for *hk*0 reflexions are shown as solid circles, and general *hkl* reflexions (omitting projection data) are shown as white circles. Unobserved reflexions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

The e.s.d. of position calculated from full-matrix least squares with space group *Cc* show that some of the atoms have highly significant deviations from the higher symmetry, indicating that *Cc* is correct.

In cases where the space group is not absolutely certain, from a structural point of view it is safest (and cannot be wrong) to assume the lower symmetry. It is my view that the structure of dibenzyl disulphide is adequately described by *Cc*.

References

DIJK, B. VAN & VISSER, G. J. (1971). *Acta Cryst.* **B27**, 846.

EINSPAHR, H. & DONOHUE, J. (1971). *Acta Cryst.* **B27**, 846.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

LEE, J. D. & BRYANT, M. W. R. (1969). *Acta Cryst.* **B25**, 2497.

Acta Cryst. (1971). **B27**, 848

Refinement of the structure of γ-Ca_2SiO_4.

By REINHARD CZAYA, *Mineralogisches Institut der Universität Kiel, Kiel, Olshausenstrasse, Germany (BRD)*

(*Received* 26 *May* 1970)

The crystal structure of γ-Ca_2SiO_4 has been redetermined on the basis of 1198 three-dimensional integrated Weissenberg reflexions. Single crystals of γ-Ca_2SiO_4 were obtained by thermal decomposition of the new compound $Ca_2SiO_4.CaCl_2$. The results confirm the structure reported by Smith, Majumdar & Ordway, but show that the distortion of the SiO_4 tetrahedron found by these authors is not real.

The structure determination of γ-Ca_2SiO_4 by Smith, Majumdar & Ordway (1963) showed a surprisingly irregular SiO_4 tetrahedron, which is unusual for orthosilicates. Si–O bond lengths range from 1·589 to 1·725 Å. An interpretation of this result could not be given, so that a redetermination of the structure seemed to be necessary.

Single crystals of γ-Ca_2SiO_4 were obtained by thermal decomposition of the synthetic compound $Ca_2SiO_4.CaCl_2$ (Czaya, 1970). The refined lattice constants (from 43 Guinier reflexions) are:

$$a_0 = 5·078 \pm 0·002 \text{ Å}$$
$$b_0 = 11·225 \pm 0·003$$
$$c_0 = 6·760 \pm 0·002$$

These values differ substantially from those given by Smith *et al.* (1963), but are in good agreement with the data given by Yannaquis (1955) and by Yamaguchi, Ono, Kawamura & Soda (1963). Of the possible space groups *Pbnm* and *Pna*2$_1$ the former, which is centrosymmetric, proved to be correct.

Integrating Weissenberg photographs for the *hk*0 to *hk*6 layers were obtained using Mo *Kα* radiation, and the intensities of 1198 independent reflexions were measured photometrically. No corrections were made for absorption or extinction. Six cycles of least-squares refinement (full-matrix program) with individual isotropic temperature factors gave an *R* value of 0·07.

Table 1 lists the atomic coordinates and temperature factors and Table 2 gives the interatomic distances and angles.

Table 2. *Interatomic distances and angles with standard deviations in brackets for* γ-Ca_2SiO_4

(*a*) Distances

	Multiplicity	
Ca(1) octahedron		
Ca(1)–O(1)	2	2·355 (6)
Ca(1)–O(2)	2	2·311 (6)
Ca(1)–O(3)	2	2·388 (8)
O(1)—O(2)	2	3·441 (2)
O(1)—O(2)	2	3·161 (10)
O(1)—O(3)	2	3·537 (7)
O(1)—O(3)	2	3·152 (11)
O(2)—O(3)	2	2·610 (8)
O(2)—O(3)	2	3·909 (9)
Ca(2) octahedron		
Ca(2)–O(1)	1	2·442 (8)
Ca(2)–O(2)	1	2·286 (8)
Ca(2)–O(3)	2	2·385 (6)
Ca(2)–O(3)	2	2·426 (6)
O(1)—O(3)	2	3·161 (10)
O(1)—O(3)	2	3·456 (7)
O(2)—O(3)	2	3·234 (8)
O(2)—O(3)	2	3·630 (8)
O(3)—O(3)	1	2·613 (8)
O(3)—O(3)	2	3·307 (7)
Si(1) tetrahedron		
Si(1) –O(1)	1	1·634 (9)
Si(1) –O(2)	1	1·655 (8)
Si(1) –O(3)	2	1·657 (6)

Table 1. *Atomic parameters and isotropic temperature factors with standard deviations in bracket for* γ-Ca_2SiO_4

	x	*y*	*z*	*B* (Å^3)
Ca(1)	0·0	0·0	0·0	0·44 (2)
Ca(2)	−0·0096 (5)	0·2809 (2)	0·25	0·38 (2)
Si(1)	0·4283 (6)	0·0959 (3)	0·25	0·23 (3)
O(1)	−0·2502 (16)	0·0926 (7)	0·25	0·55 (8)
O(2)	0·2981 (16)	−0·0393 (6)	0·25	0·49 (7)
O(3)	0·2954 (11)	0·1620 (4)	0·0567 (8)	0·38 (5)