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The Crystal Structure of 1,4-Diiodobicyclo[2,2,2]octane

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1,4-Diiodobicyclo[2,2,2]octane is tetragonal, probable space group $P4_12_12_1$, with $a=6{\cdot}653$ and $c=23{\cdot}311$ Å, $Z=4$. The structure, determined from Fourier maps and partial least-squares refinement, gave a final conventional R value of 0·045 for a disordered model with assumed tetrahedral bond angles and normal C–C bond lengths. The disorder arises from the molecules being rotated ±20° about the threefold molecular axis (*i.e.* the I···I axis) away from an orientation appropriate to the space-group symmetry. A less probable alternative structure requiring twinned crystals with space group $P4_1$ fits the data equally well.

Introduction

The packing of diiodoacetylene (Dunitz, Gehrer & Britton, 1972) shows unusual features, and it was thought that diiodobicyclooctane, which is another diiodide molecule with approximately cylindrical symmetry, would be worth examining. Accordingly, its structure is reported here.

Experimental

A sample of the compound, which had previously been provided for another purpose by Dr J. C. Kauer of the Central Research Department of E. I. du Pont de Nemours and Co., Inc. (*Chem. Eng. News*, 1970), was recrystallized from carbon tetrachloride. The crystals, mostly thin, square plates with no extinction perpendicular to the plate direction, were not well enough formed for any useful conclusions to be drawn about the crystallographic point group. Precession photographs showed the crystals to be tetragonal with Laue symmetry $4/mmm$. Systematic extinctions ($h00$, $h\neq 2n$; $00l$, $l\neq 4n$) indicate the space group to be $P4_12_12$ (No. 92) or its enantiomorph. The cell constants, determined from a least-squares fit of the diffractometer positions of 20 peaks (Mo $K\alpha$ radiation, $\lambda=0{\cdot}71069$ Å), are $a=6{\cdot}653$, $c=23{\cdot}311$ Å; the estimated error is less than 0·1%. For $Z=4$ the molecular volume is 258 Å^3 and the calculated density is 2·329 g cm^{-3}. The linear absorption coefficient is 61·0 cm^{-1} (Mo $K\alpha$).

A crystal 0·10 × 0·15 × 0·20 mm was used for intensity measurements. It was mounted on the end of a fine glass fibre, which was then sealed in a thin-walled glass capillary. Data were collected at room temperature using a 4-circle Hilger and Watts Y290 diffractometer with monochromatic Mo $K\alpha$ radiation. One complete octant of data (1295 reflexions) was collected for θ between 0 and 26°. Reflexions between 0 and 20° were scanned in 80 steps of 0·01° in θ and ω with 1 s counting times per step and 10 s background counts at each end of the scan; for 20–26° 100 such steps were used and the background counting time was increased to 25 s at each end. The 50 most intense reflexions were also scanned using reduced intensity to test for saturation of the counter and the seven most intense reflexions were corrected for this effect. The intensities of two check reflexions were measured every 25 reflexions; although the crystal turned dark yellow with use, there was no variation with time of the intensities of the check reflexions and the average deviation from the mean was 1·1%.

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The data were processed in the manner described by Corfield, Doedens & Ibers (1967); the value of 0·03 was used for p in the $\sigma(I)$ equation. For the 260 *hkl*-*khl* pairs of reflexions of measurable intensity for $\theta < 20^\circ$ 174 pairs had a difference in intensity, ΔI, less than the estimated standard deviation, $\sigma(I)$, for either intensity alone, 67 had $\sigma(I) < \Delta I < 2\sigma(I)$, and only 19 had $\Delta I > 2\sigma(I)$. From this we conclude that the Laue group is indeed $P4/mmm$, that absorption errors are not large, and that Bijvoet differences arising from the acentricity of the space group are not large. As an estimate of the quality of the data, $\sum\sigma(F_{\rm obs})/\sum F_{\rm obs}$ was 0·053. Lorentz and polarization corrections were made and the *hkl*-*khl* pairs combined to give 665 independent reflexions of which the 490 with $F_{\rm obs} > 2\cdot4\sigma(F_{\rm obs})$ were used in the structure determination.

Solution and refinement*

Since the data showed no significant deviations from $4/mmm$ Laue symmetry, no attempt was made to distinguish between the two enantiomorphic space groups. $P4_12_12$ was chosen arbitrarily and only the real part of the anomalous dispersion correction was used for the iodine atoms. The iodine atom positions were found from a three-dimensional Patterson map. A Fourier map phased on the iodine atoms showed the bridgehead carbon atoms clearly but did not show the other carbon atoms well resolved. After several false starts a Fourier map was prepared phased on the iodine atoms, the bridgehead carbon atoms, and 24 evenly spaced fractional carbon atoms on the ring that would be swept out by a freely rotating molecule. The section of the Fourier map through the ring of fractional atoms is shown in Fig. 1.

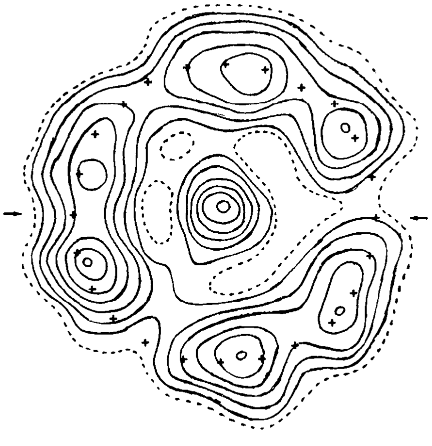

Fig. 1. Fourier map of diiodobicyclooctane: cross section through the bridging carbon atom positions. The crosses show the positions of the fractional atoms that were used to determine the phases. The contour intervals are arbitrary with the first contour above zero dotted. The peak at the centre is the edge of the peak from the bridgehead carbon atom 0·5 Å out of the plane of this map. The arrows are parallel to the crystallographic twofold axis.

This map shows clearly that the molecules are disordered, being rotated in either direction 20 ± 2° away from the nearest ordered position. An ordered structure based on twisted molecules with point symmetry 32 (D_3) was ruled out since this would require C–C bonds 1·8 Å long to match the peaks on the Fourier map. Using the iodine atom positional and anisotropic thermal parameters and the bridgehead atom thermal parameter from an earlier cycle with $R = 0\cdot058$, and carbon atom positions calculated for a molecule with tetrahedral bond angles, 1·54 Å C–C bond lengths, and exact $\bar{6}m2$ (D_{3h}) symmetry, with isotropic thermal parameters of 6·0 for the bridging atoms, the calculated value of R was 0·045 without any refinement. Since this is about the limit we would expect from the preliminary analysis of the data, and since the disorder precludes the possibility of determining light-atom positions significantly different from the idealized model, further refinement seems pointless and we report these positional and thermal parameters in Table 1.†

Table 1. *Positional and thermal parameters*

The anisotropic temperature factor is of the form exp$[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)]$. The positional parameters are multiplied by 10^4.

	x	y	z	B
I	71	6343	−764	–
C(1)	2039	4375	−284	4·2
C(21)	3176	5602	172	6·0
C(31)	3560	3391	−696	6·0
C(41)	784	2730	12	6·0
C(22)	4201	4577	−513	6·0
C(32)	1329	2185	−353	6·0
C(42)	1990	4960	355	6·0

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	6·35	5·67	6·67	1·04	−1·29	1·62

The one other possibility it seems necessary to consider is that the space group is actually $P4_1$ with ordered molecules. Since the data show $4/mmm$ symmetry, this would mean that if the crystal were ordered it would have to be twinned. Accordingly structure factors were calculated according to $|F_{hkl-{\rm twin}}| = (|F_{hkl}|^2 + |F_{khl}|^2)^{1/2}$ and an R value of 0·046 determined. The change in R value from 0·045 (disordered) to 0·046 (twinned) is inconclusive; a detailed comparison of the structure factors was equally inconclusive. Therefore, while we report the structure as if it were disordered, we cannot rule out the possibility that it is ordered and twinned. However, this seems less likely than the disorder since

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* All calculations were made using programs in the crystallographic computing library of this laboratory.

† A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30357 (11pp.). Copies may be obtained either through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England, or from the author.

it requires the iodine atom positions to be accidentally very close to the more symmetric arrangement in order to produce such good agreement with the data.

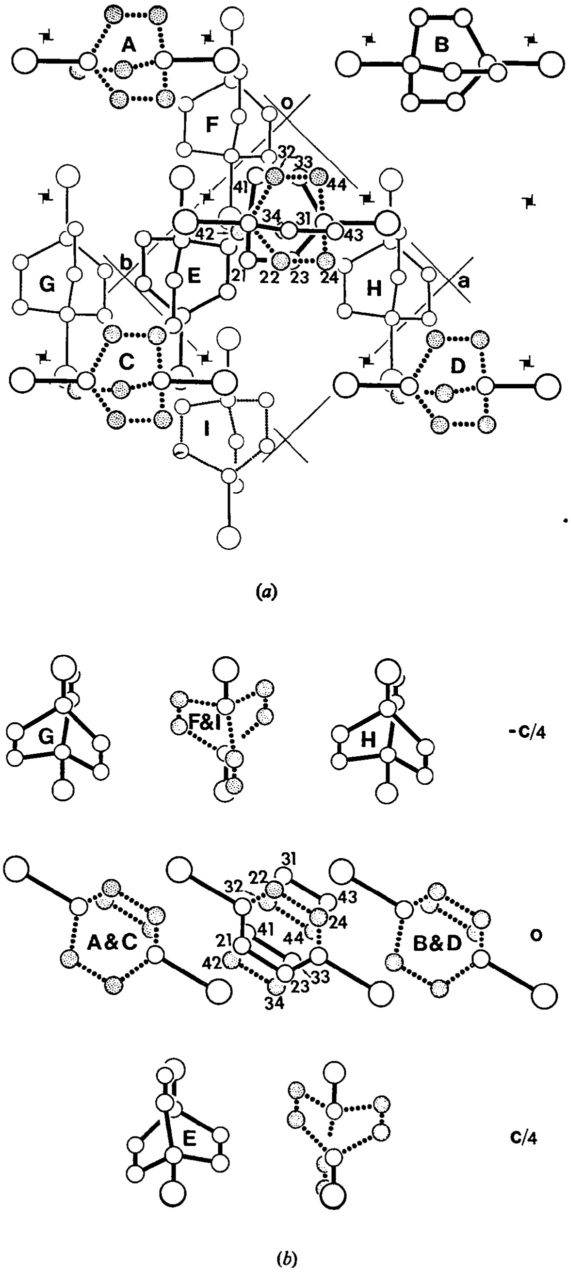

Fig. 2. The packing of diiodobicyclooctane. (*a*) View along **c**. (*b*) View along [101]. The central molecule is shown in both orientations; the remaining molecules are randomly in one or the other orientation; in the second orientation the bridging atoms are shaded and the bonds dotted to show the two alternatives more clearly. Only the molecules that make contact with the central molecule are shown. The molecules at $-c/4$ in (*b*) are shown at $3c/4$ in (*a*). The atom numberings and molecule letterings are used in Table 2 to identify intermolecular distances. Hydrogen atoms are omitted for clarity.

Discussion

The intramolecular geometry is determined by the assumptions made, except for the I–C distance, which is determined by the intramolecular I···I distance plus the assumptions made. The value found, 2·165 Å, is normal for a bond between an aliphatic carbon atom and an iodine atom. The conformation of the bicyclo[2,2,2]octane system is that found by Ermer & Dunitz (1969).

Table 2. *Intermolecular contacts*

All contacts less than 4·32 Å involving atoms in Table 1 are listed. The first atom is in the central molecule, the second in the molecule designated by the capital letter (see Fig. 2). From the symmetry each distance occurs twice; both pairs of atoms are listed.

I——I (G)	4·31 Å	I——I (I)
I——C(44) (C)	3·87	C(41)–I (A)
I——C(24) (A)	3·89	C(21)–I (C)
I——C(42) (F)	3·91	C(42)–I (E)
I——C(23) (G)	3·98	C(22)–I (I)
I——C(32) (C)	4·09	C(32)–I (B)
I——C(34) (F)	4·10	C(31)–I (H)
I——C(22) (A)	4·11	C(22)–I (D)
C(21)–C(44) (C)	3·49	C(41)–C(24) (A)
C(31)–C(33) (H)	3·87	C(32)–C(34) (F)
C(21)–C(33) (C)	3·89	C(32)–C(24) (A)
C(41)–C(43) (A)	4·00	C(42)–C(44) (C)
C(31)–C(42) (F)	4·15	C(42)–C(31) (E)
C(22)–C(33) (H)	4·23	C(32)–C(23) (F)
C(32)–C(43) (A)	4·24	C(42)–C(33) (C)
C(32)–C(42) (F)	4·31	C(42)–C(32) (E)

The packing in the crystal is shown in Fig. 2. The intermolecular distances less than 4·32 Å are given in Table 2.

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