Structure of Adamantane, $C_{10}H_{16}$, in the Disordered Phase

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Abstract

Single-crystal X-ray diffraction data have been collected for disordered adamantane at room temperature (T = 293 K). The crystal structure is face-centred cubic with a = 9·445 (4) Å, Z = 4 and space group $Fm3m$. On the assumption of a rigid molecular skeleton, two kinds of orientational disorder have been investigated: isotropic free rotation of molecules around their centre of mass and hindered reorientations between equally weighted orientations. The second model gives the best fit and good agreement is found between observed and calculated structure factors (R_w = 14·0%, R = 11·0%). The molecular packing then shows tertiary carbon atoms aligned in the |111| directions.

I. Introduction

Adamantane, tricyclo[3.3.1.1]decane, is a globular molecule and crystallizes in a plastic phase above T_c = 208·6 K. The structure investigation of this crystal has already been carried out three times but the results are generally not satisfactory. The first two studies by Nowacki (1945) and Giacomello & Illuminati (1945) were made by X-ray diffraction of polycrystalline samples. Their conclusions led to an ordered structure in space group $F\bar{4}3m$. In 1960, evidence for a phase transition was given by Chang & Westrum (1960) with thermodynamic measurements. Nordman & Schmitkons (1965) returned to the structure problem using Weissenberg and precession photographs of small single crystals below and above the transition point. In the disordered phase they could measure only 39 independent reflexions with a poor accuracy and therefore their paper, though credible, is not conclusive: a disordered structure exists in space group $Fm3m$, with a very small r.m.s. translational amplitude of about 0·06 Å. Reynolds (1978) reported that adamantane exists as an ordered crystal at room temperature in space group $F\bar{4}3m$, but this last study was carried out on very special single crystals obtained after long annealing at high temperature.

We have been working for a long time on orientationally disordered crystals and particularly on adamantane, and have found it necessary to study carefully this controversial structure. As orientational disorder might occur, classical structure methods could no longer be used and the refinement was carried out with the method (Amoureux & Bee, 1979) which is briefly summarized in §II for this very symmetrical molecule.

II. Disordered phase of adamantane

The molecule has a highly symmetrical skeleton ($\bar{4}3m$) which can be described by five parameters (Table 1). Then, let us attach to the centre of mass of this skeleton (Fig. 1) a set of orthonormal axes corresponding to the three fourfold directions (molecular axes). In a second step, we need to give to the molecule a general orientation with respect to the lattice which we can build up with the centres of mass of average molecules (crystal lattice). So we rotate the previous molecular axes about the centre of mass by three angles α, β and γ, the so-called Euler angles. If a set of three angles (α,β,γ) corresponds to an equilibrium position of a particular molecule, all the others will be found by applying symmetry operations of the factor group for the average crystal structure. This gives 48 equilibrium positions for a particular molecule in a general position if the factor group is $m3m$ and only 24 positions if it is $\bar{4}3m$ or 432. As for any plastic crystal, the number of

Table 1. *Description of molecular skeleton*

$R[C(1)]$: distance between the atom C(1) and the origin of the crystal lattice.

η: angle between a secondary carbon and its two bonded H atoms.

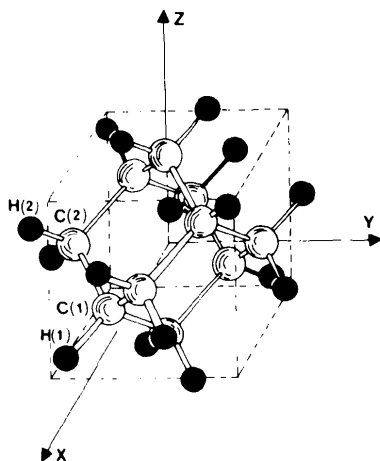| Parameter	Atoms	Value
$R[C(1)]$	4 tertiary carbons	1·52 Å
$R[C(2)]$	6 secondary carbons	1·77
$R[H(1)]$	4 methyl hydrogens	2·60
$R[H(2)]$	12 methylene hydrogens	2·55
η	12 methylene hydrogens	109·47°

Fig. 1. Molecule of $C_{10}H_{16}$ defined in a set of orthonormal axes attached to the centre of mass of this molecule. In order to clarify this figure, we have represented only one atom of each sort.

independent Bragg reflexions is very small. Among the 90 independent measured reflexions, only 66 correspond to a ratio $F_o/\sigma \geq 3$ (σ is obtained from counter statistics). This is a high number for a plastic crystal, but not for a brittle one. In order to improve the accuracy of this work by including all reflections in the calculation, we have used a weighted reliability factor R_w: $R_w^2 = \sum [F_o - |F_c|]^2 \sigma^{-2}/\sum F_o^2 \sigma^{-2}$. We have calculated R_w *versus* all the parameters and sought its minimum value (we have not considered correlations) with a local least-squares computer program.

III. Experiment

Measurements were made at room temperature on an automatic X-ray diffractometer (Philips PW 1100) with Mo $K\bar{\alpha}$ radiation ($\lambda = 0.7107$ Å) and 0.8 mm diameter collimator. To prevent free sublimation, the single crystals were placed in sealed glass capillary tubes. $\theta-2\theta$ scans at a minimum speed of $0.6°$ min^{-1} and a constant scan width of $1.6°$ were made for $\sin \theta/\lambda \leq 0.7035$ Å^{-1}. We found a f.c.c. system with $a = 9.445$ (4) Å, $Z = 4$ and $V = 843$ Å^3. To ensure against occurrence of secondary extinction, we made measurements at room temperature of strong reflexions on three crystals of different sizes. As the same ratios were found for the intensities, no absorption or extinction corrections were applied.

IV. Structure determination

The condition $F_o(h,k,l) = F_o(\bar{k},h,l)$ has always been verified by diffractometer measurements. Of the five possible space groups, we have therefore rejected $Fm3$ and $F23$. There remain only the three space groups $Fm3m$, $F\bar{4}3m$ and $F432$.

We first attempted a free-rotation model (Press & Hüller, 1973), which failed ($R_w \geq 65\%$). The second model used was the Frenkel model described in §II. Equilibrium positions of the molecules were found by making a refinement on six parameters: one scale factor, two uncoupled isotropic Debye–Waller factors (Willis & Pawley, 1970) $\langle u^2x \rangle = \langle u^2 \rangle/3$ for translations and $\langle \theta^2_{\text{isotropic}} \rangle$ for librations, and three Euler angles (α,β,γ). Independently of the space group, the lowest R_w values were found for a set of Euler angles equal to zero (Fig. 2). We therefore fixed α,β,γ to zero leaving only three free fitting parameters. This is a special position for all molecules. It corresponds to two equilibrium positions in space group $Fm3m$ (Table 2) and a completely ordered arrangement in space group $F\bar{4}3m$ and $F432$. The results obtained are shown in Table 3.*

A comparison of the two R_w values (Table 3) allows us to conclude definitively that adamantane crystallizes in $Fm3m$ with two equilibrium positions for a particular molecule with occupation probability $\frac{1}{2}$. The r.m.s. translational vibration amplitude $\langle u^2 \rangle^{1/2}$ found here is six times that found by Nordman & Schmitkons (1965).

The previous results can be compared to the general Debye–Waller factor obtained in incoherent quasi-elastic neutron scattering (IQNS). In this technique, the fast motions (translations and librations) which are assumed to be uncoupled with the slow ones (reorientations) are restored in a Debye–Waller factor. The incoherent cross section for hydrogen is so strong that only the average value for these atoms is observed. This Debye–Waller factor for hydrogen in IQNS is assumed isotropic. So the corresponding mean-square

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35335 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final structure parameters for the four different sorts of atoms in the space group Fm3m*

	Wyckoff notation	Coordinates (Å)	Occupation probability
C(1)	f	0.878, 0.878, 0.878	0.5
H(1)	f	1.501, 1.501, 1.501	0.5
C(2)	e	1.77, 0, 0	1.0
H(2)	k	0.623, 0.623, 2.393	0.5

Table 3. *Final R values*

	R_w (%)	R (%)	$\langle u^2x \rangle$ (Å^2)	$\langle \theta^2_{\text{isotropic}} \rangle^{1/2}$ (°)
$Fm3m$	14.0	11.0	0.048 ± 0.003	9.0 ± 0.2
$F\bar{4}3m$–$F432$	27.0	23.0	0.043 ± 0.004	8.6 ± 0.3

amplitude $\langle \overline{u_H^2} \rangle$ is equal to the average for the hydrogens of one third of the trace of the Debye–Waller tensor obtained with the structure,

$$\langle \overline{u_H^2} \rangle = \langle u^2 x \rangle + \tfrac{1}{6}\langle \theta_{\text{isotropic}}^2 \rangle \{R^2[H(1)] + 3R^2[H(2)]\}$$
$$= 0\cdot 15 \text{ Å}^2.$$

The value of $0\cdot 15$ Å^2 obtained by the structure determination is in excellent agreement with that given by IQNS: $\langle \overline{u_H^2} \rangle = 0\cdot 15$ Å^2 (Bee, Amoureux & Lechner, 1980; Lechner & Heidemann, 1976). The values of $\langle u^2 x \rangle$ and $\langle \theta_{\text{isotropic}}^2 \rangle$ are also very close to those obtained when the structure of adamantane is determined by a completely different method (Amoureux & Bee, 1980). It should also be noted that taking the experimental values $V_L \simeq 2600$ ms^{-1} and $V_T \simeq 1600$ ms^{-1} (Damien, 1978) for mean sound velocities in adamantane and assuming a Debye approximation, one obtains the value

$$\langle u^2 x \rangle = \frac{3kT}{M}\left[\frac{a^3}{72\pi^2}\left(\frac{1}{V_L^3} + \frac{2}{V_T^3}\right)\right]^{2/3}$$
$$= 0\cdot 041 \text{ Å}^2,$$

which agrees quite well with our previous value: $\langle u^2 x \rangle = 0\cdot 048 \pm 0\cdot 003$ Å^2 (M = mass of a molecule, $a = 9\cdot 445$ Å is the lattice parameter).

V. Coupling between translations and rotations

Here we would like to analyse the reasons why the fit ($R_w = 14\%$, $R = 11\%$) is perhaps not as good as expected.

The coupling between translations and rotations, often important in plastic crystals, has no influence on the Bragg intensities of our Frenkel structure carried out with the average molecule whose factor group is
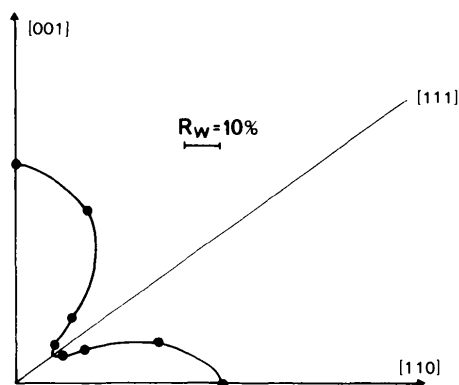

Fig. 2. Minimum R_w value *versus* the position of a tertiary carbon, for different mean orientations of the molecule corresponding to a rotation around the $[1\bar{1}0]$ axis. These results are to be related to $\langle \theta_{\text{isotropic}}^2 \rangle^{1/2} = 9\cdot 0°$. The R_w value is proportional to the distance of one of the points on the curves to the origin. The length corresponding to $R_w = 10\%$ is marked.

centrosymmetric: $m3m$ (Schomaker & Trueblood, 1968). With a more detailed mathematical development on particular molecules (Press, Grimm & Hüller, 1979), we have found (Amoureux & Bee, 1980) the influence of this coupling on Bragg intensities to be negligible.

In a structure determination assuming a Frenkel model and an isotropic Debye–Waller rotational factor the residual R_w for plastic crystals is usually of the order 10 to 15% for a σ^{-2} weighting scheme. However, the use of an isotropic librational Debye–Waller factor allows one to determine equilibrium positions and displacement amplitudes of the molecule with only three parameters. Nevertheless, when these librations are too large, as they are in orientationally disordered crystals, then it is not totally convenient. These assumptions are verified in a study of the adamantane structure we made using the same data but a very different method (Amoureux & Bee, 1980). Using the σ^{-2} weighting scheme we find with this method a minimum value of $2\cdot 5\%$ for R_w. This indicates the inadequacy of the isotropic librational Debye–Waller factor.

Discussion

Starting from 90 independent measured reflexions, the refinement has been made using only three adjustable parameters and has given $R_w = 14\%$ and $R = 11\%$. Equilibrium positions and Debye–Waller factors are in excellent agreement with all the results obtained by other experiments on adamantane (quasi-elastic incoherent scattering, nuclear magnetic resonance, inelastic scattering on the deuterated compound).

The crystal structure is face-centred cubic with space group $Fm3m$ and is obviously orientationally disordered.

The single crystal studied by Reynolds (1978) was certainly in an unstable phase resulting from its very special growth.

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A Cubic Harmonic Analysis of the Plastic Crystal Structures of Adamantane, $C_{10}H_{16}$, and Adamantanone, $C_{10}H_{14}O$, at Room Temperature

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Abstract

The plastic phases of single crystals of adamantane ($C_{10}H_{16}$) and 2-adamantanone ($C_{10}H_{14}O$) have been investigated by X-ray diffraction at room temperature. The structure factors were calculated by a cubic harmonic analysis. The plastic phases of these two compounds are both cubic, space group $Fm3m$, $Z = 4$, with $a = 9 \cdot 455$ (4) Å for $C_{10}H_{16}$ and $a = 9 \cdot 524$ (4) Å for $C_{10}H_{14}O$. The average density of the tertiary carbon atoms which have a very sharp maximum in the $\lfloor 111 \rfloor$ directions necessitated the use of cubic harmonics and rotator functions up to the order 12. The translational and librational displacements are so small that the coupling between orientation and position of a molecule does not change the experimental structure factors. All the results obtained with this method agree very well with those resulting from the Frenkel-model structures of these compounds.

I. Introduction

The normal structure investigations of these two plastic crystals at room temperature have already been reported: $C_{10}H_{14}O$ (Amoureux & Bee, 1980), $C_{10}H_{16}$ (Amoureux, Bee & Damien, 1980). In these Frenkel models we used two uncoupled isotropic Debye–Waller factors; the first one for the librations and the second for the translations. However, the librational temperature factor gave only rough information about the molecular librations.

We have studied the molecular reorientations of these two compounds with two different techniques: pulsed and wide-band NMR (Amoureux, Bee & Virlet, 1980) and incoherent quasi-elastic neutron scattering on single crystals (Bee, Amoureux & Lechner, 1980). In these techniques the theoretical calculations were always carried out with the classical Frenkel model and we wanted to examine the validity of this hypothesis for these two crystals. We also hoped to obtain some information on these reorientations by way of the molecular orientation function $f(\omega)$.

II. Cubic harmonic analysis of plastic crystal structures

In this paper we use a general method for structure investigation given by Seymour & Pryor (1970) and Press & Hüller (1973). We assume that the lattice is cubic and that the molecule has the symmetry $m3m$, $\bar{4}3m$ or 432. The structure investigations of plastic crystals published up to now and using this cubic harmonic analysis have always been carried out with neutron diffraction data and for molecules with only one kind of atom. Therefore we derive, in the following, equations for cubic harmonic analysis of X-ray diffraction data and for molecules with these particular symmetries ($m3m$, $\bar{4}3m$ or 432) having several different kinds of atoms. In the following we use the notation of Press & Hüller (1973). The structure factor $F(Q)$ can be written as a product of two terms (if the coupling between translational and rotational motion is neglected): the first corresponds to the librations and the second to the centre-of-mass motions.