Acta Cryst. (1981). A**37**, 97–104

A Symmetry-Adapted-Function Analysis of Plastic Crystals. Application to 1-Cyanoadamantane at Room Temperature

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(*Received* 28 *February* 1980; *accepted* 1 *August* 1980)

Abstract

X-ray diffraction of plastic crystals is investigated by using the decomposition of the orientational average density of the atoms on symmetry-adapted functions. For a cubic lattice, the molecular librational amplitude is related to the order of the cubic harmonics to be used. For a rigid molecule with $3m$ symmetry in a cubic lattice, the symmetry-adapted functions and the rotator functions are given up to order 12. The plastic phase structure of 1-cyanoadamantane, $C_{11}H_{15}N$, which is f.c.c., $Z = 4$ and $a = 9{\cdot}813\ (3)$ Å, has been studied in the $Fm3m$ space group. The orientational average density of the cyano group has a very sharp maximum in the [001] directions not completely describable ($R_w = 15{\cdot}4\%$) with cubic harmonics of order only up to 12. All the results obtained with this method agree very well with the corresponding ones from the Frenkel model structure of this compound.

I. Introduction

Plastic-crystal structures are usually studied with a Frenkel model, in which the molecules perform small librations around the 'equilibrium positions'. However, when large molecular amplitude librations occur in these plastic crystals this notion of 'equilibrium positions' becomes meaningless.

For this reason, a new method, which analyses the orientational structure of plastic crystals with rigid molecules, was proposed some years ago (Press & Hüller, 1973). This method, which calculates the molecular orientational probability with respect to the lattice, has only been used for cubic lattices with the corresponding molecular symmetries ($m3m$, $\bar{4}3m$, 432) or for a hexagonal lattice with a dumb-bell molecule (Press & Hüller, 1978).

Therefore, in this paper we study the X-ray diffraction results of plastic crystals with different lattice and molecule symmetries.

We have applied these general calculations to the particular case of a molecule of $3m$ symmetry in a cubic lattice.

II. Symmetry-adapted-function analysis of plastic-crystal structure

(1) *General case*

In this paper we use a general method for structural investigations given by Seymour & Pryor (1970), Press & Hüller (1973) and Yvinec (1977).

In the following we use the notation of Press & Hüller (1973). According to this paper, if the coupling between translational and rotational motions is neglected, the structure factor $F(\mathbf{Q})$ can be written as a product of two terms: the first one corresponds to the librations and the second to the centre-of-mass translations.

The first term (rotational form factor), for a molecule with atoms arranged in s shells with n_μ equivalent atoms in the μth shell, can be written in X-ray diffraction as

$$F^{\rm rot}(\mathbf{Q}) = \sum_{\mu=1}^{s} n_\mu f_\mu(Q) \int_{\rm cell} \exp(i\mathbf{Qr})\, C_\mu(\mathbf{r})\, d\mathbf{r}; \qquad (1)$$

$\mathbf{Q}$ is the momentum transfer, $f_\mu(Q)$ and $C_\mu(\mathbf{r})$ are respectively the atomic X-ray scattering factor (in electrons) and the positional probability of an atom of the μth shell with respect to the crystal structure built up with the centres of gravity of the average molecules.

$C_\mu(\mathbf{r})$ may be expanded into functions $L_{l,m}$ adapted to the symmetry of the lattice. If we call Ω_Q and Ω_r the polar angles of the scattering vector $\mathbf{Q}$ and of $\mathbf{r}$ respectively, given a coordinate system defined by the standard crystallographic axes, then one can write

$$\begin{aligned} C_\mu(\mathbf{r}) &= \delta(r - R_\mu)/r^2\, C_\mu(\theta,\varphi) \\ &= \delta(r - R_\mu)/r^2 \sum_{l,m} C^\mu_{l,m} L_{l,m}(\Omega_r). \qquad (2) \end{aligned}$$

So

$$F^{\rm rot}(\mathbf{Q}) = 4\pi \sum_{\mu=1}^{s} n_\mu f_\mu(Q) \sum_{l,m} i^l j_l(QR_\mu) C^\mu_{l,m}(\Omega_Q). \qquad (3)$$

j_l is the spherical Bessel function of order l, $C_\mu(\theta,\varphi)$ is the orientational average density in the crystal lattice of an atom of the μth shell, and δ is the Kronecker symbol. R_μ is the radius of the μth shell with respect to the centre of mass of the average molecule, which is at the origin of the crystal lattice.

If the molecule is centred, or if it possesses several high-symmetry elements ($m3m$, $\bar{4}3m$, 432, $\bar{6}m2$), the centre of gravity of the average molecule O is identical to that of the individual molecule G. In other cases, these two mass centres are not *a priori* identical and it will be necessary to introduce an eccentricity parameter $\mathbf{e} = \mathbf{OG}$ in the fitting procedure.

We call $f(\omega)$ the probability that a molecule is in an orientation specified by the Euler angles $\omega = (\alpha,\beta,\gamma)$ with respect to the crystal axes.

If we take into account both site and molecule symmetries, we have

$$f(\omega) = \frac{1}{8\pi^2} \sum_{l,m,m'} (2l+1)\, A^l_{mm'}\, R^l_{mm'}(\omega) \qquad (4)$$

with $A^0_{11} = R^0_{11}(\omega) = 1$; where $R^l_{mm'}(\omega)$ are the rotator functions which allow the passage from molecular to lattice symmetry (Appendix *B*).

One of the interesting properties of the molecular orientational probability is that $f(\omega)$ allows the calculation of the rotational potential (Amoureux & Bee, 1980).

If $b_\mu(\boldsymbol{\Omega}_{\mathbf{r}'})$ is the nuclear density of atoms of the μth shell with respect to a coordinate system (primed) fixed in the molecule and rotating with it,

$$\begin{aligned} b_\mu(\mathbf{r}') &= \delta(r' - R_\mu)/r'^2\, b_\mu(\theta',\varphi') \\ &= \delta(r' - R_\mu)/r'^2 \sum_{l',m'} b^\mu_{l',m'}\, M_{l',m'}(\Omega_{\mathbf{r}'}). \qquad (5) \end{aligned}$$

$M_{l',m'}(\boldsymbol{\Omega}_{\mathbf{r}'})$ are the functions adapted to the molecular symmetry in this primed system. The atomic positions and therefore the orientational average nuclear densities, $b_\mu(\theta',\varphi')$, for this rigid molecule are known in this molecular rotating system. $b^\mu_{l',m'}$ which is the particular $M^*_{l',m'}(\Omega_{\mathbf{r}'})$ value corresponding to the polar angles of an atom of the μth shell with respect to the molecular axes can then be calculated.

As $C_\mu(\mathbf{r}) = \int f(\omega)\, b_\mu(\mathbf{r}')\, \mathrm{d}\omega$ (6), Press & Hüller (1973) have demonstrated that

$$C^\mu_{l,m} = \sum_{m'} A^l_{mm'}\, b^\mu_{l,m'}. \qquad (7)$$

The orientational average density of the μth shell can then be written as

$$C_\mu(\theta,\varphi) = \sum_{l,m,m'} A^l_{mm'}\, b^\mu_{l,m'}\, L_{l,m}(\theta,\varphi). \qquad (8)$$

Then

$$\begin{aligned} F^{\mathrm{rot}}(\mathbf{Q}) &= \sum_{l,m,m'} i^l A^l_{mm'}\, T^l_{m'}(Q) L_{l,m}(\Omega_{\mathbf{Q}}) \\ &= \mathrm{R}[F^{\mathrm{rot}}(\mathbf{Q})] + i\,\mathrm{I}[F^{\mathrm{rot}}(\mathbf{Q})] \qquad (9) \end{aligned}$$

with

$$T^l_{m'}(Q) = 4\pi \sum_{\mu=1}^{s} j_l(QR_\mu)\, b^\mu_{l,m'}\, n_\mu f_\mu(Q). \qquad (10)$$

In (9) the lattice symmetry gives the $L_{l,m}$ functions; the molecular symmetry influences the $T^l_{m'}(Q)$ terms by means of the $b^\mu_{l,m'}$, the $A^l_{mm'}$ terms being coupled to the molecular and lattice symmetries.

(2) $A^l_{mm'}$ *values corresponding to a fixed molecule*

The analysis of a plastic-crystal structure is carried out by refining the $A^l_{mm'}$ parameters in order to reduce the weighted reliability factor R_w. The signs and the values of these $A^l_{mm'}$ terms vary considerably according to the molecular 'equilibrium positions'.

It is therefore very important for the least-squares procedure to introduce 'good' initial $A^l_{mm'}$ values not too far from their final values. An easy way to solve this problem is to introduce the $A^l_{mm'}$ values corresponding to the 'equilibrium positions' obtained with a first preliminary Frenkel model refinement.

We then have to know what the relations are for the $A^l_{mm'}$ terms corresponding to a direction or to a molecule fixed with respect to the crystal lattice.

By using the orthonormalization of the functions $L_{l,m}(\theta,\varphi)$, it can be shown that the orientational average density $C(\theta,\varphi)$ of a direction fixed with respect to the crystal lattice (θ_1,φ_1 and equivalent polar angles), can be mathematically described as

$$\begin{aligned} C(\theta,\varphi) &= \delta(\cos\theta - \cos\theta_1)\, \delta(\varphi - \varphi_1) \\ &= \sum_{l,m} L^*_{l,m}(\theta_1,\varphi_1)\, L_{l,m}(\theta,\varphi). \qquad (11) \end{aligned}$$

For the same reason, the orientational probability $f(\omega)$ for the molecule fixed with respect to the crystal lattice (ω_1 and equivalent Euler angles), is written as

$$\begin{aligned} f(\omega) &= \delta(\alpha - \alpha_1)\, \delta(\cos\beta - \cos\beta_1)\, \delta(\gamma - \gamma_1) \\ &= \frac{1}{8\pi^2} \sum_{l,m,m'} (2l+1)\, R^{*l}_{mm'}(\omega_1)\, R^l_{mm'}(\omega). \qquad (12) \end{aligned}$$

These two equations [(11) and (12)] correspond respectively [(8), (4)] to the following relations:

$$L^*_{l,m}(\theta_1,\varphi_1) = \sum_{m'} A^l_{mm'}\, b^\mu_{l,m'} \qquad (13)$$

$$R^{*l}_{mm'}(\omega_1) = A^l_{mm'}. \qquad (13')$$

μ in (13) is related to the direction in the molecular system which is fixed after rotation at θ_1,φ_1 (with respect to the lattice).

When the same symmetry-adapted functions can describe both molecular and lattice symmetry ($B4$), then the molecule fixed at $\omega_1 = (0,0,0)$ (and equivalent Euler angles) corresponds to

$$A^{l}_{mm'} = \delta_{mm'}. \qquad (14)$$

For a molecule of $3m$ symmetry fixed at $\omega_1 = (0,0,0)$ with respect to the cubic lattice, whether the factor group is centred ($m3m$) or not ($\bar{4}3m$ or 432), all the $A^{l}_{mm'}$ equal zero ($B6$) except

$$A^{2p}_{m,4q+1} = (2-\delta q,0)^{1/2}\, \mathrm{S}^{2p}_{12q,m}(L), \quad q = 0, 1,2 \ldots. \qquad (15)$$

$\mathrm{S}^{2p}_{12q,m}(L)$ is defined in Appendix B.

(3) *Cubic lattice*

If the crystal lattice is cubic, then the $L_{l,m}$ symmetry-adapted functions are the cubic harmonics $K_{l,m}$ (Bradley & Cracknell, 1972).

In this lattice symmetry, it has been demonstrated (Amoureux & Bee, 1980) that the rotational form factor can be written, up to order 12, as

$$\begin{aligned} \mathrm{R}[F^{\mathrm{rot}}(\mathbf{Q})] = {} & T^{0}_{1}/\sqrt{4\pi} \\ & + \sum_{m'} \sum_{p=2}^{5} (-1)^{p} A^{2p}_{1m'}\, T^{2p}_{m'}(Q)\, K_{2p,1}(\boldsymbol{\Omega}_{\mathrm{Q}}) \\ & + \sum_{m'} \sum_{m=1,2} A^{12}_{mm'}\, T^{12}_{m'}(Q) K_{12,m}(\Omega_{\mathrm{Q}}) + \ldots, \end{aligned} \qquad (16)$$

$$\begin{aligned} \mathrm{I}[F^{\mathrm{rot}}(\mathbf{Q})] = {} & \sum_{m'} \sum_{p=1,3,4,5} (-)^{p} A^{2p+1}_{1m'}\, T^{2p+1}_{m'}(Q) \\ & \times K_{2p+1,1}(\Omega_{\mathrm{Q}}) + \ldots. \end{aligned} \qquad (17)$$

The factor group of the average structure is centred ($m3m$) if the imaginary part of $F(\mathbf{Q})$ is equal to zero; that is to say, only in two cases:

(*a*) if the molecule is centrosymmetric then $T^{2p+1}_{m'}(Q) = 0$;

(*b*) if the time-average orientational probability of the molecule is centrosymmetric, then $A^{2p+1}_{mm'} = 0$.

When the site group is 432, only the cubic harmonic (up to order 12) of odd order $K_{9,1}$ exists (Bradley & Cracknell, 1972).

As we deal with cubic symmetry, we use an isotropic translational Debye–Waller factor:

$$F(\mathbf{Q}) = \exp[-Q^2 \langle u^2 x\rangle/2] F^{\mathrm{rot}}(\mathbf{Q}). \qquad (18)$$

$\langle u^2 x\rangle = \langle u^2\rangle/3$ is the mean-square amplitude along any axis of the translational motions of the whole molecule.

If we use a Frenkel model in which the molecule carries out isotropic librations (r.m.s. amplitude $\langle\theta^2_{\mathrm{isotropic}}\rangle^{1/2}$) with a Gaussian orientational average density $C(\theta,\varphi)$, its maximum value (along the N equivalent equilibrium positions) is

$$C_{\max} = [2\pi N \langle\theta^2_{\mathrm{isotropic}}\rangle]^{-1}. \qquad (19)$$

Table 1. *Maximum orientational average density $C_{max}(\theta_1,\varphi_1)$ and the corresponding minimum libration amplitude for the cubic harmonics up to order* 12 *describing a direction fixed in (θ_1,φ_1)*

θ_1,φ_1	[001]	[110]	[111]	$[111]_{m3m}$
$C_{\max}$	2·57	1·38	2·95	1·79
$\langle\theta^2_{\mathrm{isotropic}}\rangle^{1/2}_{\min}$	5·8°	5·6°	4·7°	6·1°

We can calculate up to order 12 (equation 11) the maximum orientational average density $C_{\max}(\theta_1,\varphi_1)$ along the symmetry axes of the lattice (Table 1).

These results (Table 1) point out that the cubic harmonics up to order 12 cannot correctly describe plastic crystals carrying out librations with r.m.s. amplitude smaller than 6°.

(4) *Molecule of* 3*m symmetry in a cubic lattice*

For the molecular threefold axis (denoted in the following as Δ), the only $b^{\Delta}_{l,m'}$ values different from zero (equation $A5$) are those with $m' = 1$:

$$b^{\Delta}_{l,m'} = [(2l+1)/4\pi]^{1/2}, \delta m', 1. \qquad (20)$$

Therefore, the orientational average density of the molecular threefold axis (Δ) is fixed by the terms A^{l}_{m1} alone:

$$C_{\Delta}(\theta,\varphi) = \sum_{l,m} A^{l}_{m1} [(2l+1)/4\pi]^{1/2} K_{l,m}(\theta,\varphi). \qquad (21)$$

Since for $\theta = \varphi = 0$ the only non-vanishing cubic harmonics are $K_{2p,1}$, the above orientational average density has the same value along the [001] directions whether the factor group is centred ($m3m$) or not ($\bar{4}3m$ or 432):

$$\begin{aligned} C_{\Delta}([001]) = {} & \frac{1}{4\pi} \\ & + \sum_{p=2}^{\infty} A^{2p}_{11} [(4p+1)/4\pi]^{1/2} K_{2p,1}([001]). \end{aligned} \qquad (22)$$

Therefore, if the 'equilibrium positions' for the molecular threefold axis (Δ) are along the [001] axes:

(i) it will then be very difficult to know if the factor group is centred or not (equations 22, $B7$);

(ii) moreover, these [001] axes being twelvefold ($m3m$) or sixfold ($\bar{4}3m$,432) axes for the orientational probability of the molecule, $f(\alpha,0,\gamma)$ (equation $B7$), it will often be very useful to consider only the free uniaxial rotation (Fig. 4) for the molecule.

The other terms $A^{l}_{mm'}$ ($m' \neq 1$) which determine the molecular position around the threefold axis (Δ) are all

Table 2. *The $A^l_{m,1}$ values corresponding to the orientation of the molecular threefold axis Δ fixed with respect to the cubic lattice (θ_1,φ_1 and equivalent polar angles)*

These $A^l_{m,1}$ values correspond to the site group $\bar{4}3m$ or $m3m$ (l even).

l,m θ_1,φ_1	3,1	4,1	6,1	7,1	8,1	9,1	10,1	12,1	12,2
100	0	$\frac{\sqrt{21}}{6}$	$\frac{\sqrt{2}}{4}$	0	$\frac{\sqrt{33}}{8}$	0	$\frac{\sqrt{65}}{8\sqrt{6}}$	0·6955	0
110	0	$\frac{\sqrt{21}}{24}$	$-\frac{13\sqrt{2}}{32}$	0	$\frac{9\sqrt{33}}{128}$	0	$\frac{-\sqrt{65}}{256\sqrt{6}}$	−0·12837	−0·5862
111	$\frac{\sqrt{5}}{3}$	$-\frac{\sqrt{21}}{9}$	$\frac{4\sqrt{2}}{9}$	$-\frac{\sqrt{91}}{9\sqrt{3}}$	$\frac{\sqrt{33}}{27}$	0·518	$\frac{-16\sqrt{65}}{81\sqrt{6}}$	0·05485	−0·4118

equal to zero for a free uniaxial rotation (equation $A6$).

In order to describe the free uniaxial rotation for a molecule with any symmetry around one of its axes, one has only to fix this axis along OZ' in the molecular rotating system. In the same way as for the $3m$ symmetry, the free uniaxial rotation around OZ' removes the influence of all the $M_{l,m}$ functions except the spherical harmonics $Y_{l,0} = M_{l,1}$. In the refinement, this free uniaxial rotation is then obtained easily by setting all the $A^l_{mm'}$ ($m' \neq 1$) to zero.

The orientation of the molecular threefold axis (Δ) fixed with respect to the lattice (θ_1,φ_1 and equivalent polar angles), corresponds to (equations 11, 21):

$$A^l_{m1}(\theta_1,\varphi_1) = [4\pi/(2l+1)]^{1/2} K_{l,m}(\theta_1,\varphi_1). \quad (23)$$

These $A^l_{m1}(\theta_1,\varphi_1)$ values which are given in Table 2 for the three crystallographic directions [001], [011], [111] are identical to those obtained from (13).

III. Structure determination of 1-cyanoadamantane, $C_{10}H_{15}CN$, at room temperature

The 112 independent experimental structure factors, the seven parameters defining the molecule, and the weighted reliability factor R_w are those described in the paper on the Frenkel model (Amoureux & Bee, 1979).

We found a f.c.c. lattice with a parameter a = 9·813 (3) Å, Z = 4, and only three possible space groups: $Fm3m$, $F\bar{4}3m$, $F432$. 1-Cyanoadamantane or adamantane carbonitrile ($C_{10}H_{15}CN$), formally known as tricyclo[3.3.1.1^{3,7}]decane-1-carbonitrile is obtained from adamantane ($C_{10}H_{16}$) by substituting a $-C{\equiv}N$ radical for one methyl hydrogen (Fig. 1). This substitution brings about no change in the rest of the molecule (Chadwick, Legon & Millen, 1972); the symmetry is $3m$. In the molecular rotating coordinate system (primed), the eccentricity vector $\mathbf{e}$ = $\mathbf{OG}$ between the origin O and the the mass centre G of the molecule is along the molecular threefold axis (Δ) for symmetry reasons.

Let us call $\mathbf{e}_1$ the $\mathbf{e}$ value when O is at the centre of gravity O' of the four tertiary carbon atoms. In the general case (Appendix C, Table 4), for the calculation of the $T^l_{m'}$ (Q) values, there are ten different sorts of atoms on ten different shells with respect to the origin of the lattice. In the particular case $\mathbf{e} = \mathbf{e}_1$, there are only nine different sorts of atoms on six different shells.

In the paper on the Frenkel model structure (Amoureux & Bee, 1979), we have shown that for the 'equilibrium positions', the molecular threefold axis (Δ) is along the lattice fourfold axis [001], and $\mathbf{e} = \mathbf{e}_1$.

Moreover, in this Frenkel model, the refinement carried out with a free uniaxial rotation around Δ gave a fair agreement between observed and calculated

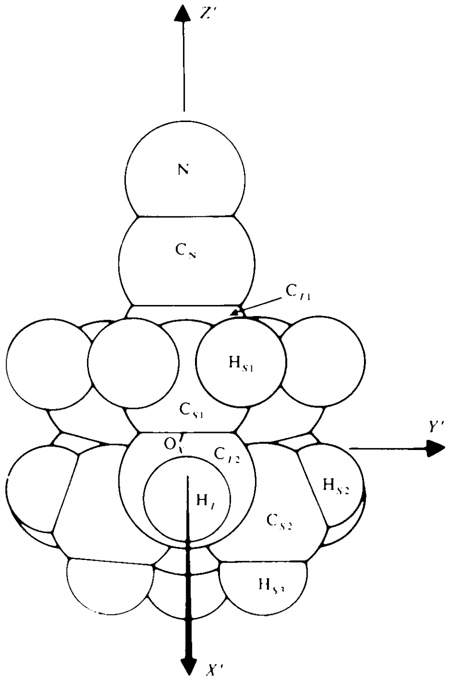

Fig. 1. A molecule of 1-cyanoadamantane $C_{10}H_{15}CN$ in the molecular rotating system for $\mathbf{e} = \mathbf{e}_1$. The definition of the different sorts of atoms corresponds to that given in Table 4.

Table 3. *Results for* 1-*cyanoadamantane* $C_{10}H_{15}CN$

$\langle\theta^2_{\text{isotropic}}\rangle_\Delta$ is calculated for isotropic harmonic librations.

R_w (%)	$\langle u^2\rangle$ (Å^2)	$\langle\theta^2_{\text{isotropic}}\rangle^{1/2}_\Delta$ (°)	A^4_{11}	A^6_{11}	A^8_{11}	A^{10}_{11}	A^{12}_{11}	A^{12}_{21}
34·1	0·24 ±0·05	9·4	0·64 ±0·06	0·26 ±0·05	0·55 ±0·08			
27·4	0·26 ±0·03	8·7	0·67 ±0·06	0·27 ±0·04	0·51 ±0·07	0·26 ±0·07		
15·4	0·22 ±0·02	7·0	0·57 ±0·06	0·24 ±0·03	0·54 ±0·05	0·23 ±0·05	0·48 ±0·05	−0·08 ±0·04

structure factors ($R_w = 8\%$) with only three adjustable parameters.

In this compound the coupling between translations and rotations has a very small influence on experimental results: the C≡N reorientations being very scarce at room temperature (400 kHz).

Taking into account the preceding results and following the corresponding conclusions of §II.4, we decided to carry out the refinement in the $Fm3m$ space group for a free uniaxial molecule rotating around Δ (only $A^{2p}_{m1} \neq 0$).

The results* (Table 3) obtained by fixing $\mathbf{e} = \mathbf{e}_1$ incite three comments:

(i) The isotropic translational mean-square amplitude is the same as the one found in the Frenkel model structure: $\langle u^2\rangle_{\text{Frenkel}} = (0{\cdot}207 \pm 0{\cdot}006)$ Å^2.

(ii) The fitted A^{2p}_{m1} values are close to those of Table 2 corresponding to the molecular threefold axis (Δ) fixed along [001].

(iii) The r.m.s. amplitude (7°) (Fig. 2) for the isotropic librations of Δ is much larger than the value (3·5°) deduced from the Frenkel model structure.

This very small value (3·5°), which would have needed a higher-order development for the symmetry-adapted functions, is certainly the reason why the refinement is not as good as we would like. We then introduced in the refinement the terms $A^{2p}_{mm'}$ ($m' \neq 1$), but as was foreseeable these inaccurate fitted values did not significantly change the residual factor R_w (13·7%).

We then refined the eccentricity vector $\mathbf{e}$ and verified that the centre of gravity of the average molecule O is (Fig. 3) at O', the centre of gravity of the four tertiary carbon atoms.

IV. Discussion

We have calculated the rotational form factor $F^{\text{rot}}(\mathbf{Q})$ for X-ray diffraction of plastic crystals using two different symmetry-adapted functions: one for the molecule and one for the lattice.

We have demonstrated that, for a cubic lattice, the use of the cubic harmonics up to order 12 can only describe molecules with r.m.s. librational amplitudes larger than 6°.

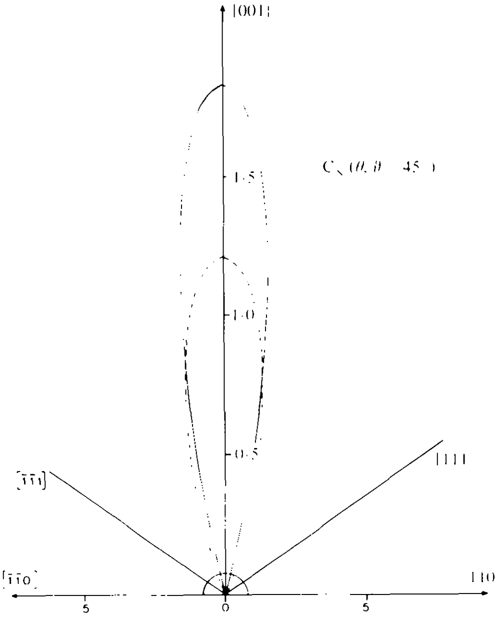

Fig. 2. The orientational average nuclear density in the (1$\bar{1}$0) plane for the cyano group of $C_{10}H_{15}CN$ calculated with cubic harmonics up to order ten (dashed curve) or 12 (solid curve). The circle corresponds to the value $1/4\pi$ for a completely random distribution of orientations.

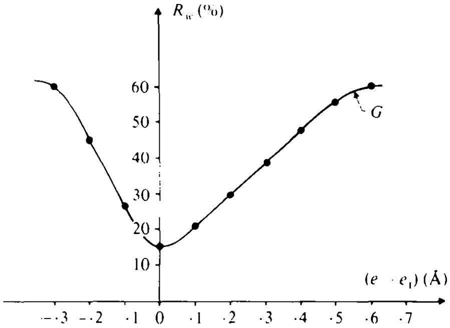

Fig. 3. Minimum R_w value *versus* the eccentricity parameter $e - e_1$.

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* Lists of structure factors and $F_{l,q}$ and $D^l_{m,n}$ values necessary to calculate $M_{l,q}(\theta', \varphi')$ in Appendix *A* and $R^{2p}_{\tau q}(\alpha,\beta,\gamma)$ in Appendix *B* have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35569 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

We have applied these calculations to the particular case of a molecule with $3m$ symmetry in a cubic lattice, and we have given the $A^l_{mm'}$ values according to the 'equilibrium positions'. For cyanoadamantane $C_{10}H_{15}CN$, the translational r.m.s. amplitude $\langle u^2\rangle$, the orientational average density for the cyano group $C_\Delta(\theta,\varphi)$ and the position for the mass centre of the individual molecule ($\mathbf{e} = \mathbf{e}_1$) correspond exactly to those found by the Frenkel model (Amoureux & Bee, 1979).

The refinement, not as good as we would like ($R_w = 15{\cdot}4\%$), is the result of a very small librational amplitude (r.m.s. = 3·5°) for the cyano group, not describable with cubic harmonics with order only up to 12.

The authors thank G. Odou for measuring the intensities and C. Carpentier and M. Muller for growing the single crystals. They also thank W. Press and A. Hüller for their friendly advice, and Professor Fouret for his constant interest in this work.

APPENDIX *A*
3*m* molecular symmetry-adapted functions

The molecular symmetry being $3m$, we choose its primed rotating system such that OZ' is along the threefold axis Δ and $X'OZ'$ is one of the three mirrors of the molecule.

The $3m$ molecular symmetry-adapted functions $\mathsf{M}_{l,q}(\theta',\varphi')$ are defined according to the polar angles θ',φ' with respect to this molecular system:

$$\mathsf{M}_{l,q}(\theta',\varphi') = \mathsf{M}_{l,q}(\theta',-\varphi') = \mathsf{M}_{l,q}(\theta',\varphi' + 2\pi/3). \qquad (A1)$$

With respect to normalized spherical harmonics (Bradley & Cracknell, 1972) we have

$$\mathsf{M}_{l,q}(\theta',\varphi') = [\mathsf{Y}_{l,3(1-q)}(\theta',\varphi') - (-1)^q\,\mathsf{Y}_{l,3(q-1)}(\theta',\varphi')] \times [2(1+\delta_{q,1})]^{-1/2} \quad q \geq 1, \qquad (A2)$$

$$\mathsf{M}_{l,q}(\theta',\varphi') = \cos[3(q-1)\,\varphi']\,\sin^{3(q-1)}(\theta') \times \mathsf{E}_{l,q}(\theta')\mathsf{F}_{l,q}(\theta')/(4\pi)^{1/2}, \qquad (A3)$$

where

$$\left.\begin{aligned} \mathsf{E}_{l,q}(\theta') &= 1 \text{ if } l+q \text{ is odd,} \\ \mathsf{E}_{l,q}(\theta') &= \cos(\theta') \text{ if } l+q \text{ is even,} \end{aligned}\right\} \qquad (A4)$$

$\mathsf{F}_{l,q}(\theta')$ is a polynomial in $u^2 = \cos^2(\theta')$ such that

$$\mathsf{F}_{l,1}(0) = (2l+1)^{1/2}. \qquad (A5)$$

The sum over all the identical atoms resulting from the symmetry elements of the $\mathsf{M}_{l,q}$ values is equal to zero:

(i) for $l + q$ even, if there is a mirror perpendicular to the molecular threefold axis Δ ($\bar{6}m2$);

(ii) for l odd, if the molecule is centrosymmetric ($\bar{3}m$).

When the molecule carries out a free uniaxial rotation around its threefold axis (Δ) which is along OZ', then the only symmetry-adapted functions to be used are $\mathsf{M}_{l,1}$, in which φ' does not occur. This corresponds in the structure refinement to fixing

$$\mathsf{A}^l_{mm'} = 0 \text{ if } m' \neq 1. \qquad (A6)$$

APPENDIX *B*
Molecular-lattice rotator functions R(ω)

I. *General case*

In the general case we have two types of symmetry-adapted functions: one for the molecule $\mathsf{M}_{l,q}(\theta,\varphi)$ and one for the lattice $\mathsf{L}_{l,\tau}(\theta,\varphi)$.

The molecular $\mathsf{M}_{l,q}$ and lattice $\mathsf{L}_{l,\tau}$ symmetry-adapted functions are linear combinations (James & Keenan, 1959) of spherical harmonics:

$$\left.\begin{aligned} \mathsf{M}_{l,q}(\theta,\varphi) &= \sum_{n=-l}^{l} \mathsf{S}^l_{nq}(M)\,\mathsf{Y}_{l,n}(\theta,\varphi); \\ \mathsf{L}_{l,\tau}(\theta,\varphi) &= \sum_{m=-l}^{l} \mathsf{S}^l_{m\tau}(L)\,\mathsf{Y}_{l,m}(\theta,\varphi). \end{aligned}\right\} \qquad (B1)$$

The spherical harmonics and symmetry-adapted functions being orthonormalized, the matrices of order $2l + 1$, with coefficients $\mathsf{S}^l_{n,q}(M)$ and $\mathsf{S}^l_{m,\tau}(L)$, are unitary.

The symmetry-adapted functions $\mathsf{M}_{l,q}$ and $\mathsf{L}_{l,\tau}$ can be related to each other by means of molecular-lattice rotator functions $\mathsf{R}(\omega)$ in which $\omega = (\alpha,\beta,\gamma)$ are the Euler angles (Rose, 1957):

$$\mathsf{M}_{l,q}(\theta',\varphi') = \sum_{\tau=1}^{2l+1} \mathsf{L}_{l,\tau}(\theta,\varphi)\,\mathsf{R}^l_{\tau q}(\omega), \qquad (B2)$$

then

$$\mathsf{R}^l_{\tau q}(\omega) = \sum_{n,m=-l}^{l} \mathsf{S}^l_{nq}(M)\,\mathsf{S}^{l*}_{m\tau}(L)\,\mathsf{D}^l_{mn}(\omega). \qquad (B3)$$

When molecular and lattice symmetry-adapted functions are identical, from ($B3$) we deduce that

$$\mathsf{R}^l_{\tau q}(0) = \delta_{\tau,q}. \qquad (B4)$$

II. *Molecule of* 3*m symmetry in a cubic lattice*

For a molecule of $3m$ symmetry, the only terms $\mathsf{S}^l_{nq}(M)$ not equal to zero (Appendix A), are the following:

$$\left.\begin{aligned} \mathsf{S}^l_{01}(M) = 1, \quad \mathsf{S}^l_{3(q-1),q}(M) = (-1)^{q+1}/\sqrt{2}, \\ \mathsf{S}^l_{3(1-q),q}(M) = 1/\sqrt{2} \text{ with } l \geq 3(q-1) > 0. \end{aligned}\right\} \qquad (B5)$$

By using these $\mathsf{S}^l_{nq}(M)$ values [equation ($B5$)], ($B3$) and the $\mathsf{S}^l_{m\tau}(L)$ values (Bradley & Cracknell, 1972; Amoureux & Bee, 1980), it can be shown that the only $\mathsf{R}^l_{\tau q}(\alpha,0,\gamma)$ values not equal to zero are the following:

$$\mathsf{R}^{2p}_{\tau,4q+1}(\alpha,0,\gamma) = \sqrt{(2-\delta_{q,0})}\,\mathsf{S}^{2p}_{12q,\tau}(L) \times \cos[12q(\alpha+\gamma)] \quad 2p \geq 12q \geq 0; \tag{B6}$$

$$\mathsf{R}^{2p+1}_{\tau,2q+1}(\alpha,0,\gamma) = -i\sqrt{2}\,\mathsf{S}^{*2p+1}_{6q,\tau}(L)\sin[6q(\alpha+\gamma)] \quad 2p+1 > 6q > 0.$$

The Euler angles $(\alpha,0,\gamma)$ correspond to a rotation $\alpha + \gamma$ around the [001] axis.

So, from ($B6$) when the molecular threefold axis Δ is along the [001] axes, these are then 12-fold axes ($m3m$) or sixfold axes ($\bar{4}3m$,432) for the molecular orientation probability around these axes [001].

For example, up to order 12, we can write:

$$\begin{aligned} 8\pi^2 f(\alpha,0,\gamma) = 1 &+ \sum_{p=2}^{6}(4p+1)\,\mathsf{A}^{2p}_{11}.\mathsf{S}^{2p}_{01}(L) \\ &+ 25\sqrt{2}\cos[12(\alpha+\gamma)] \\ &\times \sum_{m=1}^{2}\mathsf{A}^{12}_{m5}\,\mathsf{S}^{12}_{12,m}(L) \\ &-i\sqrt{2}\sin[6(\alpha+\gamma)] \\ &\times \sum_{p=3,4,5}(4p+3)\,\mathsf{A}^{2p+1}_{13}\,\mathsf{S}^{*2p+1}_{6,1}(L) \\ &+ \ldots \end{aligned} \tag{B7}$$

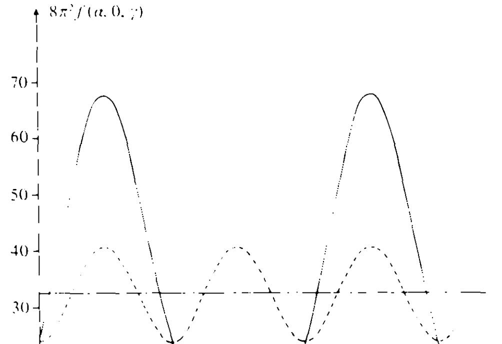

Fig. 4. For $K_{l,m}$ up to order 12 (equation 12), $8\pi^2 f(\alpha,0,\gamma)$ *versus* $\alpha + \gamma$ (the rotation angle around the [001] axis) is represented by a dashed curve ($Fm3m$) and by a solid curve ($F\bar{4}3m$) for a fixed molecule ($\alpha + \gamma = 15°$, $\beta = 0$), and by a dot-dashed curve for a free uniaxial rotational model. In the $Fm3m$ space group, if the cubic harmonics are not used up to order 12, $f(\alpha,0,\gamma)$ has the same constant value whether the molecule is fixed or carrying out a free uniaxial rotation.

For this particular 'equilibrium position', with Δ along the [001] axes:

(i) it will be very difficult to show that the factor group is not centred: only A^7_{13}, A^9_{13} and A^{11}_{13} influence $f(\alpha,0,\gamma)$;

(ii) in the $m3m$ factor group, A^{12}_{15} and A^{12}_{25} are the first two $A^{2p}_{mm'}$ terms which modulate $f(\alpha,0,\gamma)$ *versus* $(\alpha + \gamma)$, but only to a small extent (Fig. 4). So it will be very useful in this case to utilize a free uniaxial rotational model ($\mathsf{A}^l_{mm'} = 0$ if $m' \neq 1$).

When the 'equilibrium positions' for Δ are not close to the [001] axes, then the influence of these terms $\mathsf{A}^l_{mm'}$ ($m' \neq 1$) may be very great (Fig. 5).

In the general case for $\omega = (\alpha,\beta,\gamma)$, we obtain for the $Fm3m$ space group:

$$\mathsf{R}^{2p}_{\tau q}(\alpha,\beta,\gamma) = \frac{(2-\delta q,1)^{1/2}}{2}\sum_{J=0}^{p/2}(2-\delta_{J,0})\,\mathsf{S}^{2p}_{4J,\tau}(L) \times \mathbb{R}[\mathsf{D}^{2p}_{4J,3(1-q)}(\omega) - (-1)^q\,\mathsf{D}^{2p}_{4J,3(q-1)}(\omega)]. \tag{B8}$$

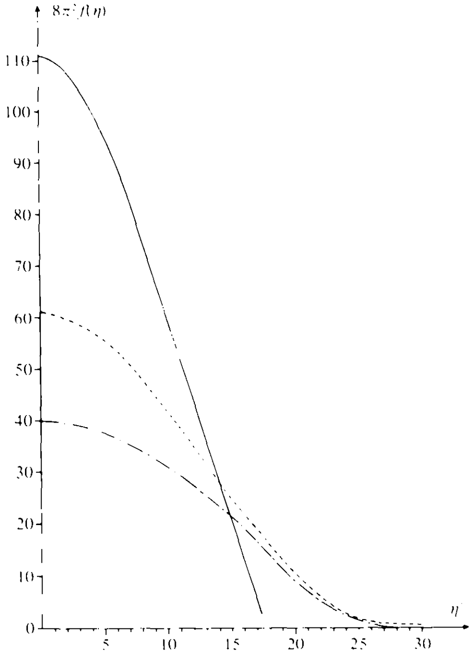

Fig. 5. The molecular orientational probability $f(\eta)$ *versus* η, the rotation angle around the [111] axis, for a fixed molecule in the $m3m$ factor group. In this fixed position the molecule has its threefold axis Δ along [111] and its three mirrors in the $(1\bar{1}0)$ planes. $8\pi^2 f(\eta)$ is represented according to the order of the cubic harmonic development: solid curve for order 12; dashed curve for order ten; dot-dashed curve for order eight. If the molecular librations perpendicular to Δ are supposed to be harmonic, we find for their r.m.s. amplitudes: 7·5; 9·5; 11·5° respectively. For the same-order development, in the free uniaxial rotational model, $8\pi^2 f(\eta)$ is constant and equal to 22·4; 18·4; 9·2 respectively.

Table 4. *Description of the atoms with respect to the molecular rotating system*

The number of atoms belonging to each of the ten different shells is given in parentheses.

For each sort of atom, the three values X', Y' and $Z' + e_1 - e$ have to be multiplied by the corresponding radius R, the values of which have been published (Amoureux & Bee, 1979).

Quantity ( )	(1) N	(1) C_N	(1) C_{T1}	(3) C_{T2}	(3) H_T	(3) C_{S1} (+) (3) C_{S2} (−)	(6) H_{S1}	(3) H_{S2} (+) (3) H_{S3} (−)
Multiplication factor	$\times R_{NT}$	$\times R_{CNT}$	$\times R_{CT}$	$\times R_{CT}$	$\times R_{HT}$	$\times R_{CS}$	$\times R_{HS}$	$\times R_{HS}$
X'	0	0	0	$\frac{2\sqrt{2}}{3}$	$\frac{2\sqrt{2}}{3}$	$\pm\frac{\sqrt{6}}{3}$	$\frac{\sqrt{6}}{3}\cos\eta'$	$\frac{\sqrt{6}}{3}\left(\pm\frac{\sin\eta'}{\sqrt{2}}-\cos\eta'\right)$
Y'	0	0	0	0	0	0	$\sin\eta'$	0
$Z' + e_1 - e$	1	1	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\pm\frac{1}{\sqrt{3}}$	$\frac{\cos\eta'}{\sqrt{3}}$	$\frac{\pm\sqrt{2}\sin\eta'-\cos\eta'}{\sqrt{3}}$

In ($B8$), we can use the relations:

$$\mathrm{D}^l_{m,n}(\alpha,\beta,\gamma) = d^l_{m,n}(\beta)\exp[-i(m\alpha + n\gamma)],$$

$$d^l_{n,m}(\beta) = (-1)^{m+n}\, d^l_{m,n}(\beta) = d^l_{-m,-n}(\beta),$$

$$d^l_{m,-n}(\beta) = d^l_{m,n}(\pi - \beta). \qquad (B9)$$

So, if we call $C = \cos\beta$, we have only to calculate

$$d^l_{m,n}(\beta) = \sin^{m-n}(\beta)(1 + C)^n\, \mathrm{P}^l_{m,n}(C)$$
$$\text{for } l \geq m \geq n \geq 0. \qquad (B10)$$

All the $\mathrm{P}^l_{m,n}(C)$ values necessary to calculate ($B8$) up to order 12 have been published (Amoureux & Bee, 1980).

APPENDIX *C*
Description of the molecule

Let us call η' the angle between two next-nearest methylene hydrogens and O' the mass centre of the four tertiary carbons. In the general case, we have ten different sorts of atoms (Table 4) on ten different radii (with respect to the origin of the lattice O). In the particular case $\mathbf{e} = \mathbf{e}_1$ (O is on O'), there are only nine different sorts of atoms ($C_{S1} \equiv C_{S2}$) on six different radii.

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