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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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(*Received* 2 *July* 1979; *accepted* 10 *April* 1980)

## 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 [111] 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 $F(\mathbf{Q})$ 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.

0567-7408/80/112636-07$01.00

As we are dealing with cubic symmetry, we use an isotropic translational Debye–Waller factor. Then

$$F(\mathbf{Q}) = \exp[-Q^2\,\langle u^2x\rangle/2]\,F^{\mathrm{rot}}(\mathbf{Q}). \qquad (1)$$

The rotational form factor in X-ray diffraction for a molecule with atoms arranged in $s$ shells ($s = 4$ for adamantane) with $n_\mu$ equivalent atoms on the $\mu$th shell can be written as:

$$F^{\mathrm{rot}}(\mathbf{Q}) = \sum_{\mu=1}^{s} n_\mu f_\mu(Q) \int_{\mathrm{cell}} \exp(i\mathbf{Q}\mathbf{r})\, C_\mu(\mathbf{r})\,\mathrm{d}\mathbf{r}. \qquad (2)$$

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

$C_\mu(\mathbf{r})$ can be expanded into symmetry-adapted functions, which are in this case the cubic harmonics $K_{l,m}$ (Appendix $A$).

If we call $\Omega_{\mathrm{Q}}$ and $\Omega_{\mathrm{r}}$ the polar angles of respectively the scattering vector $\mathbf{Q}$ and of $\mathbf{r}$, given a coordinate system defined by the standard crystallographic axes, then one can write:

$$\begin{aligned} C_\mu(\mathbf{r}) &= \delta(r - R_\mu)/r^2\, C_\mu(\theta,\varphi) \\ &= \delta(r - R_\mu)/r^2 \sum_{l,m} C^\mu_{l,m}\, K_{l,m}(\Omega_{\mathrm{r}}). \qquad (3) \end{aligned}$$

So

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

$R_\mu$ is the radius of the $\mu$th shell with respect to the centre of mass of the average molecule, $j_l$ is the spherical Bessel function of order $l$, and $C_\mu(\theta,\varphi)$ is the orientational average density in the crystal lattice of the atoms of the $\mu$th cell. We call $f(\omega)$ the probability that a molecule is in an orientation specified by the Euler angles $(\alpha,\beta,\gamma)$ with respect to the crystal axes.

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

$$f(\omega) = \frac{1}{8\pi^2} \sum_{lmm'} (2l + 1)\, A^l_{mm'}\, U^l_{mm'}(\omega)$$

with

$$A^0_{11} = U^0_{11} = 1, \qquad (5)$$

where the $U^l_{mm'}(\omega)$ are the cubic rotator functions (Appendix $B$). If $b_\mu(\mathbf{r}')$ is the nuclear density of an atom of the $\mu$th shell with respect to a coordinate system (primed) fixed in the molecule and rotating with it;

$$\begin{aligned} b_\mu(\mathbf{r}') &= \delta(r' - R_\mu)/r'^2\, b_\mu(\theta',\varphi') \\ &= \delta(r' - R_\mu)/r'^2 \sum_{l',m'} b^\mu_{l',m'}\, K_{l',m'}(\Omega_{\mathrm{r}'}). \qquad (6) \end{aligned}$$

The atomic positions and therefore the orientational average nuclear densities $b_\mu(\theta',\varphi')$ in this primed system are known. $b^\mu_{l',m'}$ which is the $K_{l',m'}(\Omega_{\mathrm{r}'})$ value corresponding to the polar angles of an atom of the $\mu$th shell with respect to the molecular axes can then be calculated.

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

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

Then

$$\begin{aligned} F^{\mathrm{rot}}(\mathbf{Q}) &= \sum_{lmm'} i^l A^l_{mm'}\, T^l_{m'}(Q)\, K_{l,m}(\Omega_{\mathrm{Q}}) \\ &= \mathbf{R}[F^{\mathrm{rot}}(\mathbf{Q}) + i\mathbf{I}[F^{\mathrm{rot}}(\mathbf{Q})] \qquad (8) \end{aligned}$$

with

$$T^l_{m'}(Q) = 4\pi \sum_{\mu=1}^{s} j_l(QR_\mu)\, b^\mu_{l,m'}\, n_\mu f_\mu(Q). \qquad (9)$$

Owing to the symmetry invariance of the site and of the molecule, the cubic harmonics belong to the totally symmetric representation $A1$ and so only a few coefficients $A^l_{mm'}$ are different from zero.

So for a $\bar{4}3m$ or 432 molecular symmetry:

$$\begin{aligned} \mathbf{R}[F^{\mathrm{rot}}(\mathbf{Q})] &= T^0_1(Q)/\sqrt{4\pi} \\ &\quad + \sum_{p=2}^{5} (-1)^p A^{2p}_{11}.T^{2p}_1(Q).K_{2p,1}(\Omega_{\mathrm{Q}}) \\ &\quad + \sum_{m,m'=1}^{2} A^{12}_{mm'}.T^{12}_{m'}(Q).K_{12,m}(\Omega_{\mathrm{Q}}) + \ldots \\ \mathbf{I}[F^{\mathrm{rot}}(\mathbf{Q})] &= \sum_{p=1,3,4} (-1)^p A^{2p+1}_{11}.T^{2p+1}_1(Q) \\ &\quad \times K_{2p+1,1}(\Omega_{\mathrm{Q}}). \qquad (10) \end{aligned}$$

For a f.c.c. unit cell, the space group of the average structure can be $Fm3m$ in two cases:

– if the molecule is centrosymmetric (*i.e.* $m3m$ symmetry): then

$$T^3_1(Q) = T^7_1(Q) = T^9_1(Q) = 0.$$

– if the time-average positions of the molecule are centrosymmetric: then

$$A^3_{11} = A^7_{11} = A^9_{11} = 0.$$

With the use of these preceding cubic harmonics $K_{l,m}$ (Appendix $A$), as

$$K_{l,m}(h,k,l') = (-1)^l\, K_{l,m}(\bar{k},h,l'),$$

we have:

$$|F^{\mathrm{rot}}(h,k,l')| = |F^{\mathrm{rot}}(\bar{k},h,l')|.$$

To describe the space group with no fourfold axis as *Fm*3 and *F*23, we then should have to use other cubic harmonics.

## III. Structure investigation of adamantane, $C_{10}H_{16}$, at room temperature

The 90 experimental structure factors, the definition of $R_w$, the method of refinement and the five parameters defining the molecule are those described in the preceding paper (Amoureux, Bee & Damien, 1980).

For the four atomic shells of the adamantane molecule, we calculated (Appendix *A*) the $b^{\mu}_{l,m'}$ which gave us the $T^l_{m'}(Q)$ values. In order to find the correct space group (*Fm*3*m*, $F\bar{4}3m$ or *F*432), a refinement with all the nine parameters $\langle u^2x\rangle$, $A^3_{11}$, $A^4_{11}$, $A^6_{11}$, $A^7_{11}$, $A^8_{11}$, $A^9_{11}$, $A^{10}_{11}$ and a scale factor was carried out. It was found that $A^3_{11} = A^7_{11} = A^9_{11} = 0$ ($A^3_{11} = 0{\cdot}09 \pm 0{\cdot}08$, $A^7_{11} = 0{\cdot}06 \pm 0{\cdot}11$, $A^9_{11} = 0{\cdot}07 \pm 0{\cdot}13$). It follows that the space group is centrosymmetric, *Fm*3*m*.

We therefore fixed the three preceding parameters $A^{2p+1}_{11}$ to zero (space group *Fm*3*m*) for the further refinements, whose results are summarized in Table 1. The calculated structure factors obtained with the cubic harmonics up to the order 10 are listed in the paper dealing with the Frenkel model (Amoureux, Bee & Damien, 1980).

With the aim of improving the fit ($R_w = 10{\cdot}3\%$), we then introduced the coupling translation–rotation in the analysis of the Bragg intensity, following the method described by Press, Grimm & Hüller, 1979 (Appendix *D*).* However, in spite of the seven new coupling parameters, the residual $R_w$ fell by only 0·8%.

The Bragg intensities corresponding to large *Q* values are sometimes important (*i.e.* 0,0,12). Therefore the contribution of the cubic harmonics of the order 12 may not be negligible. With three more parameters, $A^{12}_{11}$, $A^{12}_{12}$, $A^{12}_{22}$ (nine in all for the space group *Fm*3*m*), $R_w$ fell from 10·3 to 2·5%, but the three new coefficients were obtained with less accuracy than the previous ones.

In Fig. 1 the orientational average of the density of the tertiary carbon atoms is represented in the $(1\bar{1}0)$ plane with respect to the crystal axes.

$$C_{\mathrm{CT}}(\theta,\varphi) = \sum_{l,m,m'} A^l_{mm'}\, b_{l,m'}(\mathrm{CT})\, K_{l,m}(\theta,\varphi). \qquad (13)$$

This average nuclear density is nearly the same before and after introduction of the $A^{12}_{mm'}$ parameters. The physical description of the structure is then obtained using only the cubic harmonics up to the order 10 (six parameters in all). The stereographic projection (Fig. 2) of $C_{\mathrm{CT}}(\mathbf{r})$ shows quasi-isotropic librations and so justifies the isotropic Debye–Waller factor (Willis & Pawley, 1970) we used in the Frenkel structure of adamantane (previous paper, Amoureux, Bee & Damien, 1980). The results obtained in the previous paper concerning the equilibrium positions and the translational and librational displacements ($\langle u^2x\rangle_{\mathrm{Frenkel}} = 0{\cdot}048 \pm 0{\cdot}003$ Å$^2$, $\langle\theta^2_{\mathrm{isotropic}}\rangle^{1/2}_{\mathrm{Frenkel}} = 9{\cdot}0 \pm 0{\cdot}2°$) are in very good agreement with those we present now.

As there are some small slightly negative regions for $C_{\mathrm{CT}}(\mathbf{r})$, we examined the method described by Hüller & Press (1979) in which positive-definite functions for $C_{\mu}(\mathbf{r})$ and $f(\omega)$ are always obtained by fitting the coefficients of the average potential to the cubic rotators $U^l_{mm'}(\omega)$. However, this method is not possible in our case as this potential development on the cubic rotators converges too slowly (Appendix *C*). We have represented in Fig. 3 the molecular orientation probability density function $f(\omega)$ *versus* $v$, the rotation angle round the [111], [110] or [001] axis. It can be seen that $f(\omega)$ remains positive within the error bars. However, if we take into account the accuracy of the results on $f(\omega)$ and then on the potential barriers, no real physical information on the reorientations can be obtained.

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* Appendices *C* and *D* and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35336 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Results for adamantane*, $C_{10}H_{16}$

$\langle\theta^2_{\mathrm{isotropic}}\rangle$ in Tables 1 and 2 is calculated for isotropic harmonic librations.

| $R_w$ (%) | $R$ (%) | $\langle u^2x\rangle$ (Å$^2$) | $\langle\theta^2_{\mathrm{isotropic}}\rangle^{1/2}$ (°) | $A^4_{11}$ | $A^6_{11}$ | $A^8_{11}$ | $A^{10}_{11}$ | $A^{12}_{11}$ | $A^{12}_{22}$ | $A^{12}_{21}$ | $A^{12}_{22}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 61·3 | 55·9 | 0·010 | | 0·534 | | | | | | | |
| 43·8 | 26·9 | 0·036 | | 0·611 | 0·468 | | | | | | |
| 12·5 | 7·3 | 0·043 | 11·4 | 0·653 | 0·551 | 0·378 | | | | | |
| 10·3 | 6·4 | 0·044<br>±0·004 | 8·6 | 0·657<br>±0·012 | 0·557<br>±0·009 | 0·379<br>±0·010 | 0·367<br>±0·061 | | | | |
| 2·5 | 2·1 | 0·046<br>±0·001 | 8·5 | 0·653<br>±0·003 | 0·565<br>±0·003 | 0·393<br>±0·003 | 0·256<br>±0·018 | 0·082<br>±0·019 | −0·357<br>±0·098 | | 0·218<br>±0·026 |
| 2·4 | 2·1 | 0·046<br>±0·001 | 8·4 | 0·653<br>±0·003 | 0·564<br>±0·002 | 0·393<br>±0·003 | 0·254<br>±0·018 | 0·087<br>±0·020 | −0·337<br>±0·099 | 0·022<br>±0·023 | 0·390<br>±0·118 |

## IV. Structure determination of 2-adamantanone, $C_{10}H_{14}O$, at room temperature

The 106 experimental structure factors and the six parameters defining the molecule we use are those described in the paper on the Frenkel structure model (Amoureux & Bee, 1980). As for adamantane, we found a f.c.c. lattice with parameter $a = 9.524\ (4)$ Å, $Z = 4$, and with only three possible space groups: $Fm3m, F\bar{4}3m, F432$. 2-Adamantanone, tricyclo[3.3.1.1]-decan-2-one, is obtained from adamantane by substituting two methylene hydrogens bonded to a secondary carbon by an oxygen (Fig. 4). If we suppose that this substitution does not change the rest of the molecule, its symmetry is $mm2$. The decomposition of $b_\mu(\theta',\varphi')$ needs many symmetry-adapted functions and so we have many different parameters $A^l_{mm'}$ to refine. The molecules of adamantane and adamantanone being very similar, in the following we shall determine the 2-adamantanone structure by using the average density of adamantane. With this approximation (7% of the electrons), we obtain again a high symmetry ($\bar{4}3m$) for $b_\mu(\theta',\varphi')$ and so only a few parameters $A^l_{11}$ to refine. Corresponding to the previous approximation, we then

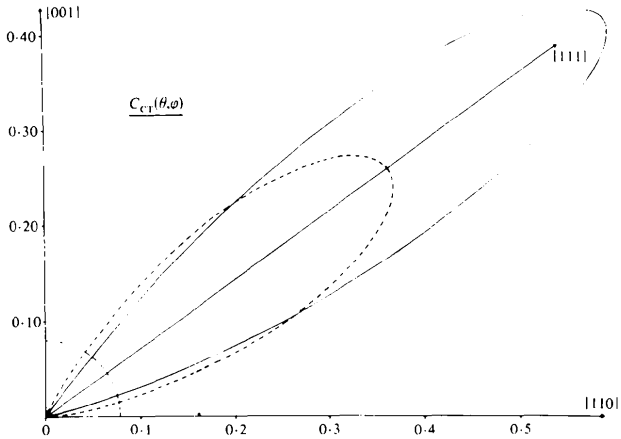

Fig. 1. The orientational average nuclear density in the (1$\bar{1}$0) plane, for the tertiary carbons of $C_{10}H_{16}$, using cubic harmonics up to the order 8 (dashed curve) or 10 (solid curve). The circle corresponds to the value $1/4\pi$ for a completely random distribution of orientations.

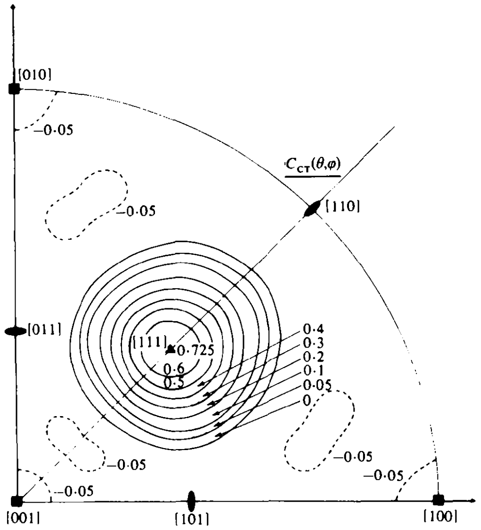

Fig. 2. Stereographic projection of the angular part of the tertiary carbon density. On Figs. 2 and 3 the description is obtained with cubic harmonics up to the order 10.

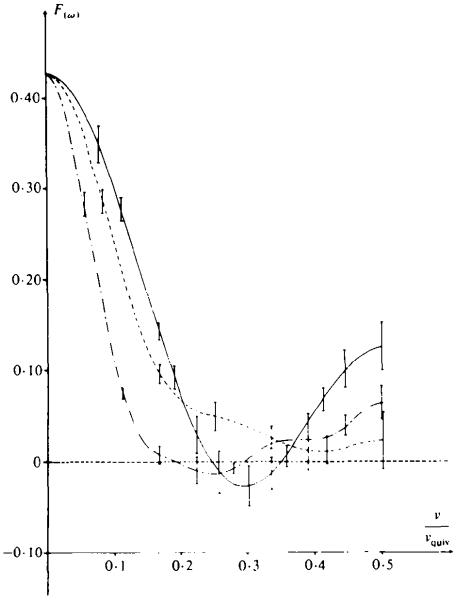

Fig. 3. Molecular orientation density function $f(\omega)$ *versus* $\nu$, the rotation angle. $\nu_{\text{quiv}}$ is equal to 90, 120, 180° respectively for rotations around the crystallographic axes [001] (solid line), [111] (dashed line), [110] (dot-dashed line).

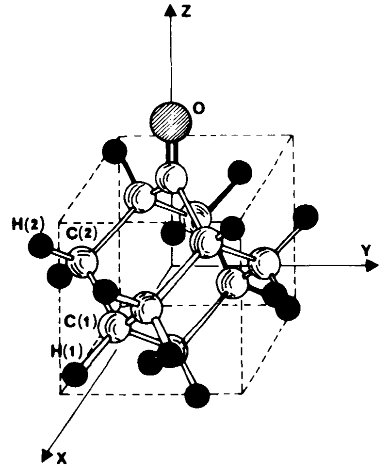

Fig. 4. Molecule of $C_{10}H_{14}O$ defined in a set of orthonormal axes attached to the centre of mass of the four tertiary carbons.

Table 2. *Results for 2-adamantanone*, $C_{10}H_{14}O$

| $R_w$ (%) | $R$ (%) | $\langle u^2x\rangle$ (Å$^2$) | $\langle\theta^2_{\text{isotropic}}\rangle^{1/2}$ (°) | $A^4_{11}$ | $A^6_{11}$ | $A^8_{11}$ |
|---|---|---|---|---|---|---|
| 65·5 | 59·8 | 0·012 | | 0·549 | | |
| 40·4 | 32·2 | 0·051 | | 0·605 | 0·472 | |
| 10·4 | 10·9 | 0·079<br>±0·004 | 11 | 0·665<br>±0·024 | 0·556<br>±0·020 | 0·539<br>±0·040 |

analysed the structure of 2-adamantanone using cubic harmonics only up to the order 8.

To find the correct space group ($Fm3m$, $F\bar{4}3m$ or $F432$) we carried out a fit with all seven parameters: $\langle u^2x\rangle$, $A^3_{11}$, $A^4_{11}$, $A^6_{11}$, $A^7_{11}$, $A^8_{11}$ and a scale factor. The values we obtained proved that the space group is centrosymmetric: $Fm3m$ ($A^3_{11} = 0{\cdot}13 \pm 0{\cdot}11$, $A^7_{11} = 0{\cdot}11 \pm 0{\cdot}13$).

The results of the further refinements performed with the space group $Fm3m$ ($A^3_{11} = A^7_{11} = 0$) (Table 2) are very similar to those of adamantane. These results are in very good agreement with the corresponding values obtained by the Frenkel model: $\langle u^2x\rangle_{\text{Frenkel}} = 0{\cdot}074 \pm 0{\cdot}004$ Å$^2$; $\langle\theta^2_{\text{isotropic}}\rangle^{1/2}_{\text{Frenkel}} = 9{\cdot}5° \pm 0{\cdot}3°$.

## Discussion

The refinement of the adamantane crystal structure (residual $R_w = 10{\cdot}3\%$, $R = 6{\cdot}4\%$) starting with 90 independent measured reflexions has been carried out with only six parameters. Owing to the preceding structural study of this compound we think that for most plastic crystals with globular molecular skeletons, the average density is very well described by cubic harmonics up to a maximum order of 12. However, for some more linear-shaped molecules (*i.e.* symmetry $\bar{3}m$ or $\bar{6}m2$) with very anisotropic librations the decomposition of $C_\mu(\theta,\varphi)$ on symmetry-adapted functions may converge too slowly and then other methods can be used (Amoureux & Bee, 1979).

Cubic-harmonics analysis always requires the molecule to have a very high symmetry ($m3m$, $\bar{4}3m$, $\bar{3}m$, $\bar{6}m2$), but we have shown for 2-adamantanone ($mm2$) that it is sometimes possible to fulfil this criterion with some simple approximations on the molecule.

We have demonstrated that the coupling between translation and rotation of the adamantane molecule has no effect on the experimental structure factors. By introducing this phenomenon in $CBr_4$ ($\langle u^2x\rangle = 0{\cdot}19$ Å$^2$, $\langle\theta^2_{\text{isotropic}}\rangle^{1/2} \simeq 20°$), Press, Grimm & Hüller (1979) reduced $R_w$ from 7·7% to 3·4% with three additional parameters.

These two studies reveal, according to the amplitudes of the displacement, the importance of the effects of this coupling on plastic crystal structures.

The authors thank G. Odou for measuring the intensities and C. Carpentier and M. Muller for growing the single crystals. We thank also W. Press, A. Hüller and J. More for their extensive friendly advice.

## APPENDIX *A*

### Normalized cubic harmonics

Cubic harmonics $K_{l,m}$ are linear combinations of spherical harmonics $Y_{l,m}$ which form the basis for an irreducible representation of the cubic symmetry group (Von der Lage & Bethe, 1947; Altmann & Cracknell, 1965),

$$K_{l,m}(\theta,\varphi) = \sum_{n=-l}^{l} Y_{l,n}(\theta,\varphi)\, S^l_{n,m}.$$

$(\theta,\varphi)$ denote the polar angles of either the positional vector **r** or the momentum transfer **Q**.

$$x = \sin\theta\cos\varphi,\quad y = \sin\theta\sin\varphi,\quad z = \cos\theta.$$

Functions in square brackets indicate the cubic harmonics with the normalization factor omitted.

*Example:* $[K_{4,1}] = x^4 + y^4 + z^4 - 0{\cdot}6$.

$$(4\pi)^{1/2}K_{0,1} = 1.$$

$$(4\pi)^{1/2}K_{3,1} = (105)^{1/2}xyz.$$

$$(4\pi)^{1/2}K_{4,1} = 1{\cdot}25\,(21)^{1/2}(x^4 + y^4 + z^4 - 0{\cdot}6).$$

$$(4\pi)^{1/2}K_{6,1} = 231\,(26)^{1/2}(x^2y^2z^2 + [K_{4,1}]/22 \\ - 1/105)/8.$$

$$(4\pi)^{1/2}K_{7,1} = 2{\cdot}75\,(1365)^{1/2}xyz\,(x^4 + y^4 + z^4 - 5/11).$$

$$(4\pi)^{1/2}K_{8,1} = 65(561)^{1/2}(x^8 + y^8 + z^8 - 5{\cdot}6[K_{6,1}] \\ - 210[K_{4,1}]/143 - 1/3)/16.$$

$$(4\pi)^{1/2}K_{9,1} = N_{9,1}\,xyz(x^2y^2z^2 + 3(x^4 + y^4 + z^4)/34 \\ - 27/442).$$

$$(4\pi)^{1/2}K_{10,1} = 11 \times 17 \times 19\,(227{\cdot}5)^{1/2} \\ \times (x^{10} + y^{10} + z^{10} - 45[K_{8,1}]/19 \\ - 126[K_{6,1}]/17 - 210[K_{4,1}]/143 \\ - 3/11)/80.$$

$$(4\pi)^{1/2}K_{12,1} = N_{12,1}(x^{12} + y^{12} + z^{12} - 66[K_{10,1}]/23 \\ - 495[K_{8,1}]/133 - 2772[K_{6,1}]/323 \\ - 315[K_{4,1}]/221 - 3/13).$$

$$K_{12,2} = 4(145/33)^{1/2}\,{}^{c}Y_{12,4}/15 - (19307/33)^{1/2} \\ \times {}^{c}Y_{12,8}/30 + (371/11)^{1/2} \\ \times {}^{c}Y_{12,12}/30$$

with $N_{9,1} = 2187{\cdot}44$, $N_{12,1} = 1582{\cdot}0556$.

Table 3. *The* $(4\pi)^{1/2} K_{l,m}$ *values in the three simplest crystallographic directions*

| $l,m$ | 3,1 | 4,1 | 6,1 | 7,1 | 8,1 | 9,1 | 10,1 | 12,1 | 12,2 |
|---|---|---|---|---|---|---|---|---|---|
| Direction | | | | | | | | | |
| \|100\| | 0 | $\sqrt{21}/2$ | $\sqrt{26}/4$ | 0 | $\sqrt{561}/8$ | 0 | $\sqrt{227\cdot5}/8$ | 3·4775 | 0 |
| \|110\| | 0 | $-\sqrt{21}/8$ | $-13\sqrt{26}/32$ | 0 | $9\sqrt{561}/128$ | 0 | $\sqrt{227\cdot5}/256$ | −0·64187 | −2·931 |
| \|111\| | $\sqrt{35}/3$ | $-\sqrt{(7/3)}$ | $4\sqrt{26}/9$ | $-\sqrt{455}/9$ | $\sqrt{561}/27$ | 2·2576 | $-16\sqrt{227\cdot5}/81$ | −0·27427 | −2·059 |

$$(4\pi)^{1/2}\,{}^{c}_{Y12,4} = 15\,(2002)^{1/2}\sin^4\theta[7429\cos^8\theta - 9044\cos^6\theta + 3230\cos^4\theta - 340\cos^2\theta + 5]\cos 4\varphi/2048.$$

$$(4\pi)^{1/2}\,{}^{c}_{Y12,8} = 5(33\times13\times17\times19)^{1/2} \times \sin^8\theta[161\cos^4\theta - 42\cos^2\theta + 1] \times \cos 8\varphi/1024.$$

$$(4\pi)^{1/2}\,{}^{c}_{Y12,12} = 5(13\times14\times17\times19\times23)^{1/2}\sin^{12}\theta \times \cos 12\varphi/2048.$$

The $(4\pi)^{1/2} K_{l,m}$ values in the three simplest crystallographic directions are listed in Table 3.

## APPENDIX *B*

### Cubic rotator functions

Here, the cubic rotator functions $U^l_{mm'}(\omega)$ are given in terms of the Wigner matrix:

$$D^l_{mm'}(\alpha,\beta,\gamma) = d^l_{mm'}(\beta)\exp[-i(m\alpha + m'\gamma)]. \quad (B1)$$

$\omega = (\alpha,\beta,\gamma)$ are the Euler angles (Rose, 1957).

$$U^l_{mm'}(\omega) = \sum_{\lambda=-l}^{l}\sum_{q=-l}^{l} D^l_{\lambda,q}(\omega)\, S^{*l}_{\lambda m}\, S^l_{qm'}. \quad (B2)$$

If we consider the $S^l_{\lambda m}$ values and the following relations:

$$S^{2p}_{\bar{m}\lambda} = S^{2p}_{m\lambda},\quad S^{2p+1}_{\bar{m}\lambda} = -S^{2p+1}_{m\lambda},\quad d^l_{\lambda q}(\beta) = (-1)^{\lambda+q}\, d^l_{q\lambda}(\beta) \quad (B3)$$

we obtain ($\delta$ is the Kronecker symbol)

$$U^{2p}_{mm'}(\omega) = \tfrac{1}{2}\sum_{j,k=0}^{p/2} S_{4j,m}\, S_{4k,m'}\, \mathbf{R}[D^{2p}_{4j,4k}(\omega) + D^{2p}_{4j,-4k}(\omega)]\,[4 - 2\delta_{jk,0} - \delta_{j+k,0}]. \quad (B4)$$

Equation ($B$4) illustrates the relation

$$U^{2p}_{mm'}(\alpha,\beta,\gamma) = U^{2p}_{m'm}(\gamma,\beta,\alpha). \quad (B5)$$

As $d^l_{\lambda,q}(-C) = d^l_{\lambda,-q}(C)$, we have only to calculate ($C = \cos\beta$):

$$d^l_{\lambda q}(\beta) = \sin^{\lambda-q}(\beta)[1 + C]^q P^l_{\lambda q}(C), \quad \text{for } l \ge \lambda \ge q \ge 0. \quad (B6)$$

$P^4_{00} = (3 - 30C^2 + 35C^4)/8,\quad P^4_{40} = \sqrt{70}/16.$

$P^4_{44} = 1/16.$

$P^6_{00} = (-5 + 105C^2 - 315C^4 + 231C^6)/16.$

$P^6_{40} = 3\sqrt{14}\,(11C^2 - 1)/32,$

$P^6_{44} = (13 - 44C + 33C^2)/32.$

$P^8_{00} = 35(1 - 36C^2 + 198C^4 - 1716C^6/5 + 1287C^8/7)/128.$

$P^8_{88} = 1/256.$

$P^8_{44} = (-9 - 78C + 546C^2 - 910C^3 + 455C^4)/64.$

$P^8_{40} = 3(154)^{1/2}(1 - 26C^2 + 65C^4)/128.$

$P^8_{80} = 3(1430)^{1/2}/256.$

$P^8_{84} = (455)^{1/2}/128.$

$P^{10}_{00} = (-63 + 3465C^2 - 30030C^4 + 90090C^6 - 109395C^8 + 46189C^{10})/256.$

$P^{10}_{44} = (1 + 300C - 1245C^2 - 680C^3 + 8415C^4 - 11628C^5 + 4845C^6)/128.$

$P^{10}_{88} = (59 - 152C + 95C^2)/512.$

$P^{10}_{40} = (4290)^{1/2}(-1 + 45C^2 - 255C^4 + 323C^6)/256.$

$P^{10}_{80} = (24310)^{1/2}(-1 + 19C^2)/512.$

$P^{10}_{84} = (51)^{1/2}(11 - 76C + 95C^2)/512.$

$P^{12}_{00} = 231(1 - 78C^2 + 975C^4 - 4420C^6 + 62985C^8/7 - 8398C^{10} + 96577C^{12}/33)/1024.$

$P^{12}_{40} = 3(77\times13)^{1/2}(5 - 340C^2 + 3230C^4 - 9044C^6 + 7429C^8)/2048.$

$P^{12}_{44} = (239 - 11560C + 29988C^2 + 162792C^3 - 610470C^4 + 162792C^5 + 1492260C^6 - 1961256C^7 + 735471C^8)/4096.$

$P^{12}_{80} = (66\times13\times17\times19)^{1/2}(1 - 42C^2 + 161C^4).$

$P^{12}_{84} = (6\times7\times17\times19)^{1/2}(-9 + 12C + 330C^2 - 1012C^3 + 759C^4)/4096.$

$$P^{12}_{88} = (673 - 5208C + 13398C^2 - 14168C^3 + 5313C^4)/2048.$$

$$P^{12}_{12,0} = (7 \times 13 \times 17 \times 19 \times 23)^{1/2}/2048.$$

$$P^{12}_{12,4} = 3(11 \times 17 \times 19 \times 23)^{1/2}/4096.$$

$$P^{12}_{12,8} = (21 \times 22 \times 23)^{1/2}/4096.$$

$$P^{12}_{12,12} = 1/4096.$$

The single terms $S^l_{\lambda m}$ not equal to zero are the following:

$$S^3_{21} = -i/\sqrt{2}, \quad S^7_{21} = -i\sqrt{39}/12,$$

$$S^7_{61} = -i\sqrt{33}/12, \quad S^9_{21} = -0{\cdot}43301i/\sqrt{2},$$

$$S^9_{61} = 0{\cdot}90139i/\sqrt{2},$$

$$S^4_{01} = (7/12)^{1/2}, \quad S^4_{41} = (5/24)^{1/2},$$

$$S^6_{01} = 1/(2\sqrt{2}), \quad S^6_{41} = -(7)^{1/2}/4,$$

$$S^8_{01} = (33)^{1/2}/8, \quad S^8_{41} = (7/6)^{1/2}/4,$$

$$S^8_{81} = (65/6)^{1/2}/8,$$

$$S^{10}_{01} = (65/6)^{1/2}/8, \quad S^{10}_{41} = -(11)^{1/2}/8,$$

$$S^{10}_{81} = -(11 \times 17/3)^{1/2}/16,$$

$$S^{12}_{01} = 0{\cdot}69550266, \quad S^{12}_{41} = 0{\cdot}22212032,$$

$$S^{12}_{81} = 0{\cdot}24639103, \quad S^{12}_{12,1} = 0{\cdot}3848273,$$

$$S^{12}_{42} = 4(5 \times 29/66)^{1/2}/15,$$

$$S^{12}_{82} = -(43 \times 449/66)^{1/2}/30,$$

$$S^{12}_{12,2} = (7 \times 53/22)^{1/2}/30.$$

If we want to carry out a $\nu$ angle rotation around a simple crystallographic axis, the corresponding Euler angles are obtained with the following formulae:

$$R(\nu)[001]: \beta = 0, \quad \alpha + \gamma = \nu,$$

$$R(\nu)[110]: \alpha = 225°, \quad \beta = \nu, \quad \gamma = 135°,$$
$$\text{or } \alpha = 45°, \quad \beta = -\nu, \quad \gamma = -45°,$$

$$R(\nu)[111]: \alpha = -\arccos\left[\frac{1 - \cos\nu + \sqrt{3}\sin\nu}{2\sqrt{(2 - \cos^2\nu - \cos\nu)}}\right],$$

$$\beta = \arccos\left[\frac{1 + 2\cos\nu}{3}\right],$$

$$\gamma = \alpha + \frac{\pi}{2}.$$

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*Acta Cryst.* (1980). B**36**, 2642–2645

# On the Polymorphism of Barbituric Acid Derivatives

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(*Received* 4 *March* 1980; *accepted* 30 *May* 1980)

## Abstract

The barbituric acid derivative 5-ethyl-5-isopentylbarbituric acid (known as amobarbital or Amytal) has two polymorphic forms in which the hydrogen-bond systems are identical but the space group is different. Another derivative, 5,5-diethylbarbituric acid (known as barbital or Veronal), has three polymorphs with

0567-7408/80/112642-04$01.00