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Crystal Structure of 1-Cyanoadamantane, $C_{10}H_{15}CN$, in Its Plastic Phase

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Abstract

Single-crystal X-ray diffraction data were collected and interpreted for the plastic phase of 1-cyano-adamantane, $C_{11}H_{15}N$, at 293 K. The unit cell is face-centred cubic with $a = 9.813$ (3) Å, space group $Fm3m$, $Z = 4$. On the assumption of a rigid molecular skeleton, several types of orientational disorder were investigated: isotropic rotation of the molecules about their centre of mass, hindered re-orientations between equally weighted orientations and free uniaxial rotations of the molecule about the C—C≡N axis. For the second and third model, fair agreement is found between observed and calculated structure factors (residual $R_w = 8\%$), but the third is thought to be the best. The C—C≡N axis has six possible orientations along the fourfold axes of the crystal. The molecule performs free uniaxial rotations around these six equilibrium positions of the cyano group.

I. Introduction

1-Cyanoadamantane or adamantanecarbonitrile, $C_{10}H_{15}CN$, formally known as tricyclo[3.3.1.1^{3,7}]-decane-1-carbonitrile, is a globular molecule of C_{3v} symmetry, obtained from adamantane ($C_{10}H_{16}$) by substitution of one methyl H by a —C≡N radical.

Like adamantane, it is a plastic crystal. A specially interesting point is the existence of a very high dipolar momentum for this molecule. This compound is studied here as a test for determining plastic-crystal structures for molecules with a rigid skeleton when numerous independent Bragg reflexions are observed, allowing a Frenkel model to be used.

II. Structure of a plastic crystal made of rigid molecules

(1) The molecule

The molecule is defined in a set of orthonormal axes referred to the centre of mass of the four tertiary C atoms (Fig. 1). In the following, we will assume that the

Table 1. *Parameters defining the molecule*

R_j: distance between the atom j and the origin of the crystal lattice.
θ: angle between a secondary carbon and its two bonded hydrogen atoms.

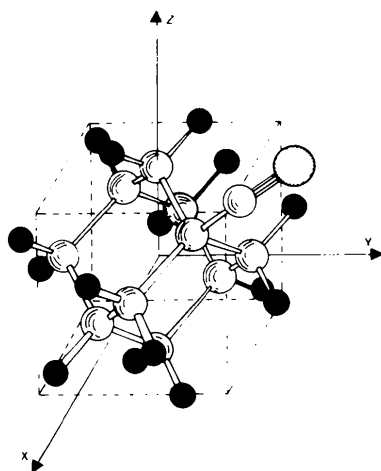| Parameter	Atoms	Value
R_{CT}	4 tertiary C	1·52 Å
R_{CS}	6 secondary C	1·77
R_{HT}	3 tertiary H	2·60
R_{HS}	12 secondary H	2·55
R_{CNT}	C bonded to the N	2·98
R_{NT}	N	4·14
θ	12 secondary H	109·47°

Fig. 1. Molecule of $C_{10}H_{15}CN$ defined in a set of orthonormal axes referred to the centre of mass of the tertiary C atoms.

substitution of one H atom of adamantane by a $-C\equiv N$ group does not distort the rest of the molecule. Therefore the molecule can be totally defined in the above set of axes by seven parameters which take their usual values (Table 1) (Chadwick, Legon & Millen, 1972).

(2) General position for the molecule

The molecule has been related to the molecular axes. Two different operations are needed to obtain the general position of the molecule in the crystal lattice.

First we need to relate the origin of the crystal lattice to the molecular axes. Symmetry considerations impose placing this origin on the $C-C\equiv N$ axis of the molecule. Let us call $\mathbf{e}$ the vector between this origin and the centre of mass of the tertiary C atoms. Then we need to rotate the molecular axes with respect to the crystal axes by the so-called α, β and γ Euler angles. We then define the rotation $R(\alpha,\beta,\gamma)$, so that $\mathbf{M} = R(\alpha,\beta,\gamma)\mathbf{m}$, where $\mathbf{M}$ and $\mathbf{m}$ are the position vectors for atoms, respectively, about the crystal axes when the rotation R has been made and about the crystal axes after translation by $\mathbf{e}$. We call $\mathbf{M_G}$ the $\mathbf{M}$ value when the origin of the crystal lattice is on the centre of mass G of the molecule. If (α,β,γ) is an equilibrium position for the molecule, the others will be obtained by application of the symmetry operations of the factor group for the average crystal. Therefore we obtain 48 equilibrium positions for a particular molecule in a general position if the factor group is $m3m$, only 24 if this group is $\bar{4}3m$ or 432.

(3) Temperature factors exp $(-w)$

One can define a Debye–Waller factor for isotropic translation by $\langle u_x^2 \rangle = \langle u^2 \rangle / 3$. This factor is related to

the translational motions of the whole molecule and so is identical for all 27 atoms.

With the shape of the molecule taken into account, two different anisotropic rotational Debye–Waller factors can be defined: (i) the first, $\langle \theta_{uniaxial}^2 \rangle$, taking account of the librations of the molecule around its long $C-C\equiv N$ axis, (ii) the second, $\langle \theta_{\perp}^2 \rangle$, taking account of librations perpendicular to this long axis with respect to the centre of mass G of the molecule.

The external product $(\mathbf{X} \wedge \mathbf{M_G})$ of the two vectors $\mathbf{M_G}$ and $\mathbf{X}$ (vector of diffusion) can be separated into two parts: $(\mathbf{X} \wedge \mathbf{M_G})_{\parallel}$ parallel to the $C-C\equiv N$ axis and $(\mathbf{X} \wedge \mathbf{M_G})_{\perp}$ perpendicular to it.

It can be seen that to a first-order approximation we have:

$$W = 2\Pi^2 X^2 \langle u_x^2 \rangle + 2\Pi^2 (\mathbf{X} \wedge \mathbf{M_G})_{\parallel}^2 \langle \theta_{uniaxial}^2 \rangle$$
$$+ 2\Pi^2 (\mathbf{X} \wedge \mathbf{M_G})_{\perp}^2 \langle \theta_{\perp}^2 \rangle.$$

When molecular librations are supposed to be isotropic (Willis & Pawley, 1969), the last two factors of the previous formula are replaced by an isotropic librational Debye–Waller factor $\langle \theta_{isotropic}^2 \rangle$.

(4) Refinement

For each of the N independent Bragg reflexions hkl, experiment gives the observed structure factor $F_o(hkl)$ as well as the estimated standard deviation $\sigma(hkl)$.

Let us define the weighted reliability factor R_w by

$$R_w^2 = \sum_{l=1}^{N} \{[F_o(l) - F_c(l)]/\sigma(l)\}^2 \Big/ \sum_{l=1}^{N} [F_o(l)/\sigma(l)]^2.$$

When the refinement is carried out with the classical R factor (unweighted), only the reflexions with $F_o/\sigma \geq 3$ are generally used; when R_w is used, all the reflexions are taken into account.

For a plastic crystal, where the number of independent reflexions is always very small (112 for cyanoadamantane, only 42 of them corresponding to $F_o/\sigma \geq 3$), improvement in the accuracy of results requires the use of R_w.

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 a 0.8 mm ø collimator. To avoid free sublimation, the single crystal (size $\simeq 0.3$ mm) was sealed in a glass capillary tube. A $\theta-2\theta$ scan with a minimum speed of $0.6°$ min^{-1} and unvarying scan width of $1.2°$ was used.

The system is f.c.c. with $a = 9.813$ (3) Å, $Z = 4$ and $V = 944$ Å^3. A comparison of strong reflexions for two single crystals very different in size showed that

secondary extinction did not occur. For the 112 independent reflexions collected, no absorption or extinction corrections were therefore applied.

The condition $F_o(hkl) = F_o(\bar{k}hl)$ was verified either by diffractometer measurements or by Laue patterns. This allowed us to reject the space groups $Fm3$ and $F23$ leaving only three possibilities: $Fm3m$, $F\bar{4}3m$ and $F432$.

IV. Structure determination

First of all we tried an isotropic free-rotation model (Press & Hüller, 1973)

$$F_c(X) = \exp[-2\Pi^2 X^2 \langle u_x^2 \rangle] \sum_{j=1}^{27} f_j(X)$$

$$\times \sin 2\Pi X R j / 2 \Pi X R j.$$

The agreement was so poor ($R_w \geq 65\%$) that we decided to make a new attempt with the Frenkel model described in § II. To refine this model we used our own computer program particularly suitable for cubic lattices.

(1) The Frenkel model with an isotropic thermal factor

The molecule was first oriented in a 'classical' way as it is in adamantane (Amoureux & Bee, 1979a; Amoureux, Bee & Damien, 1979) or adamantanone (Amoureux & Bee, 1979b), with the C—C≡N group placed along the crystalline [111] axis. The least-squares fit was very poor ($R_w \geq 65\%$). To find the real equilibrium positions, a new refinement was made with all seven parameters: one scale factor, two isotropic Debye–Waller factors $\langle u_x^2 \rangle$ and $\langle \theta_{isotropic}^2 \rangle$, three Euler angles α, β, γ, the eccentricity parameter e.

Whatever the space group, agreement was always obtained for values close to $\alpha_0 = 45°$; $\beta_0 = -54.74°$; $\gamma_0 = -45°$; $e_0 = 0$. These values correspond to a $54.74°$ rotation of the molecular axes around the [1$\bar{1}$0] axis of the crystal. The C—C≡N group is then aligned along the [001] direction.

For this special position, the $m3m$ factor group gives 24 distinct equilibrium positions, and the $\bar{4}3m$ and 432 groups give the same 12. The refinement was done with the three free parameters (α, β, γ and e being fixed at the previous values α_0, β_0, γ_0, e_0) and gave the following results, $Fm3m$: $R_w = 9.9\%$, $\langle u_x^2 \rangle = (0.067 \pm 0.009)$ Å^2, $\langle \theta_{isotropic}^2 \rangle^{1/2} = 3.0 \pm 0.2°$; $F\bar{4}3m$; $R_w = 11.8\%$, $\langle u_x^2 \rangle = (0.073 \pm 0.009)$ Å^2, $\langle \theta_{isotropic}^2 \rangle^{1/2} = 3.0 \pm 0.2°$. When the parameters α, β and γ are left free to vary about the special position (α_0, β_0, γ_0) we then obtain our best fit for: $Fm3m$: $R_w = 8.2\%$, $\alpha = 52.8 \pm 1.6°$, $\beta = -56.0 \pm 0.7°$, $\gamma = -44.3 \pm 1.0°$. This would correspond to molecules with a —C≡N group $1.4°$ away from the fourfold axes of the crystal. We

think that this result has no real physical meaning. Improvement in R_w is obtained only because three new fitting parameters (α, β and γ) are used.

We have made a test on the accuracy of equilibrium-position determinations. In Fig. 2 we report, for the $Fm3m$ space group, the minimum R_w value versus φ (rotation of the molecular axes around the [1$\bar{1}$0] axis). The C—C≡N group is aligned along the [110], [111] and [001] axes respectively for $\varphi = -35$, 0 and 55°. For a change of $2.8°$ from the [001] equilibrium position, R_w changes from 9.9 to 18%. This result clearly indicates how sensitive the localization is to the C—C≡N groups along the fourfold axes of the crystal.

In Fig. 3 we show, for the $Fm3m$ and $F\bar{4}3m$ groups, the minimum R_w value versus φ' (rotation of the molecule around the C—C≡N axis from its equilibrium position). This rotation has only a small influence on R_w indicating that the molecule is poorly localized around the C—C≡N axis.

We have seen that the refinement has located the origin of the crystal lattice at the centre of mass of the tertiary C atoms ($e_0 = 0$) and not at the centre of
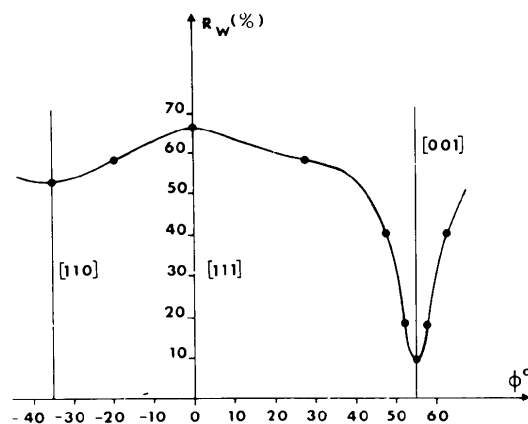
Fig. 2. Minimum R_w value versus φ (rotation of the molecular axes around the [1$\bar{1}$0] axis) for the space group $Fm3m$.
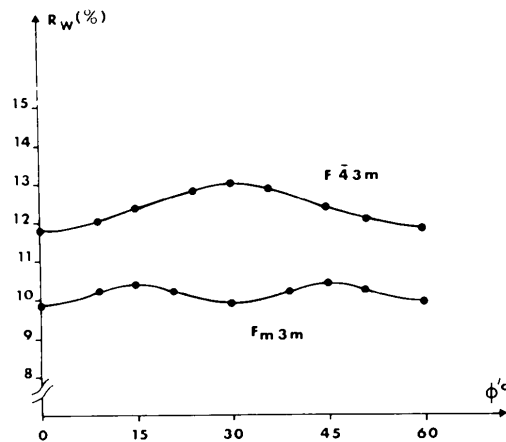
Fig. 3. Minimum R_w value versus φ' (rotation of the molecule around the C—C≡N axis) for the space groups $Fm3m$ and $F\bar{4}3m$.

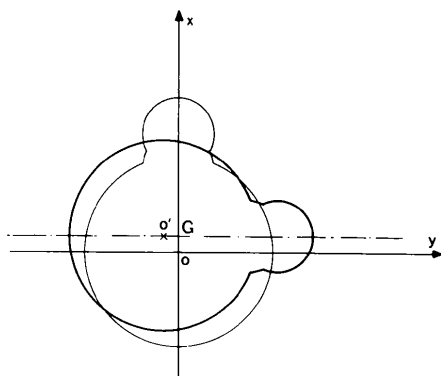Fig. 4. An example of a molecule before and just after its reorientation around G.

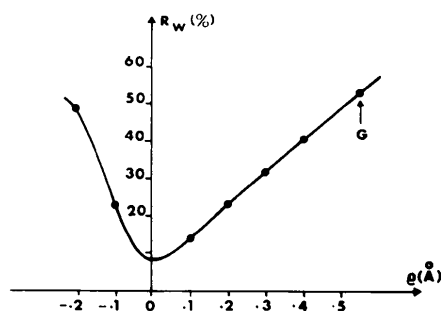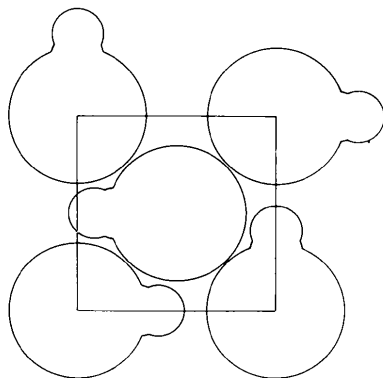Fig. 5. Minimum R_w value *versus* the eccentricity parameter e (Å).

Fig. 6. Example of suitable packing in the (001) plane.

mass G of the molecule ($e = +0.55$ Å) (Fig. 4). Fig. 5 shows the minimum R_w *versus* e for a few values of this parameter. Fig. 6 shows the packing and explains quite well the zero value of the eccentricity parameter e. Indeed we can see that the spheres, on which H atoms are located, are all in contact, therefore fixing the e parameter at zero.

(2) *The Frenkel model with an anisotropic thermal factor*

The average square amplitude for isotropic rotation $\langle \theta^2_{\text{isotropic}} \rangle = (3°)^2$ is very small compared to the values $(9°)^2$ for adamantane and $(9.5°)^2$ for adamantanone though these plastic crystals are very similar to the one studied here. This small value and the results shown in Fig. 2 led us to assume that the molecular librations are not isotropic and that reorientations of the $C-C\equiv N$ group do not occur very often. This hypothesis has been confirmed by measurements of dielectric relaxation (Amoureux, Bee & Castelain, 1979a) and wideband NMR (Amoureux, Bee & Castelain, 1979b). Returning to the two anisotropic rotational Debye–Waller factors defined in § II(3), we then made a new refinement (with the previous values of a_0, β_0, γ_0, e_0) and found the following results, $Fm3m$: $R_w = 7.9\%$, $\langle u_x^2 \rangle = 0.069 \pm 0.002$ Å^2, $\langle \theta^2_{\text{uniaxial}} \rangle^{1/2} = 9.6 \pm 1.5°$, $\langle \theta^2_\perp \rangle^{1/2} = 2.8 \pm 0.2°$. We note that $\langle \theta^2_{\text{uniaxial}} \rangle$ is far greater than $\langle \theta^2_\perp \rangle$. This difference is a confirmation of the existence of preferred reorientations.

(3) *Uniaxial free rotation*

We have shown that the $-C\equiv N$ groups are directed along the fourfold axes of the crystal. Thus they have six distinct equilibrium positions. With the Frenkel model, 24 equilibrium positions for a particular molecule are obtained for $Fm3m$ and 12 for $F\bar{4}3m$. For a $-C\equiv N$ group attached to a fourfold axis, this corresponds to four distinct equilibrium positions for $Fm3m$ and two positions for $F\bar{4}3m$.

Figs. 7 and 8 give, for one $-C\equiv N$ group along the [001] axis, a projection of the three other tertiary C atoms on the XOY plane. On these drawings the three C atoms corresponding to the same equilibrium position are represented by the same symbol. Their size is only 0.4 times that given by the van der Waals radius.
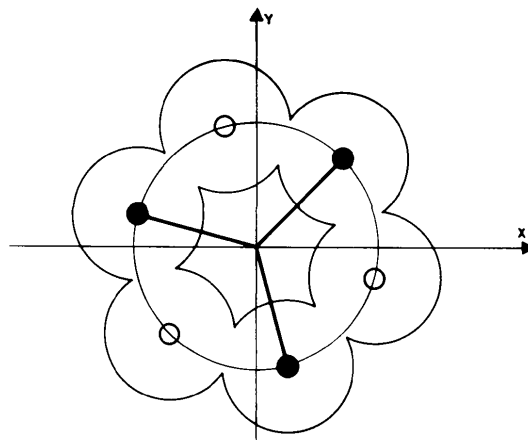

Fig. 7. Projection of the other three tertiary C atoms on the XOY plane for a $-C\equiv N$ group along the [001] axis for space group $F\bar{4}3m$.

We note that passing from one equilibrium position to another needs a 60° rotation around the $-C\equiv N$ axis for $F\bar{4}3m$ and one of 30° for $Fm3m$. In the Frenkel model, $\langle \theta^2_{uniaxial} \rangle$ has been found to be $\simeq (10°)^2$. This high value plus the overlap between the volumes occupied by C atoms of neighbouring equilibrium positions clearly indicate that the notion of equilibrium position is meaningless for this particular re-orientational motion of the molecule around the $-C\equiv N$ axis. Thus we have studied a model of uniaxial free rotation around this $C-C\equiv N$ axis. For such a model, the scattering function is $\exp(-w)f(x) \times \exp[2i\Pi M_0 X]J_0(2\Pi tr)$ (International Tables for X-
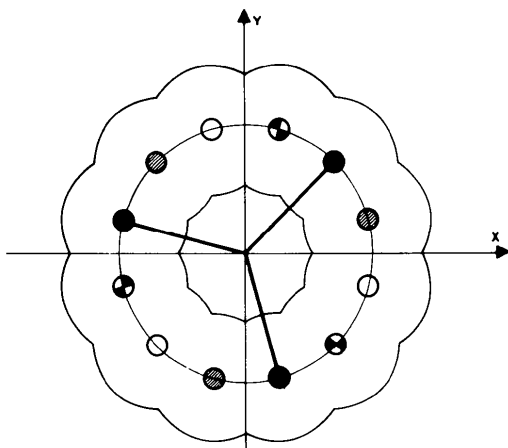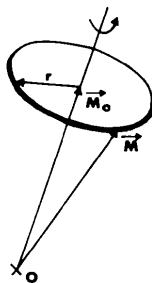

Fig. 8. As Fig. 7, for space group $Fm3m$.

Fig. 9. Definition of M, M_0, and r for a free uniaxial rotation.

ray crystallography, 1959) where t in reciprocal space is the distance from the diffusion vector $X(hkl)$ to an axis parallel to the axis of rotation and passing through the origin, M_0 is the projection of the M vector on the axis of free uniaxial rotation (Fig. 9), J_0 is the zero-order cylindrical Bessel function, and r is the distance between the atom and the axis of rotation.

By symmetry considerations, one can see that free uniaxial rotation is consistent only with the space group $Fm3m$. Only three parameters are then left: $\langle u^2_x \rangle$, $\langle \theta^2_\perp \rangle$ and the scale factor. The refinement gives the values: $Fm3m$: $R_w = 8\cdot1\%$, $R = 10\cdot4\%$,[*] $\langle u^2_x \rangle = 0\cdot063 \pm 0\cdot002$ Å^2, $\langle \theta^2_\perp \rangle^{1/2} = 3\cdot5 \pm 0\cdot2°$. The small value of R_w obtained by a fit of only three parameters is a strong argument in favour of the free uniaxial rotation. This is in fair agreement with measurements by NMR (Amoureux, Bee, Castelain, Arnaud & Schouteeten, 1979) showing that the motion of the molecule around the $-C\equiv N$ axis which appears above $T = 120$ K is very fast at room temperature: $\tau = 2 \times 10^{-12}$ s.

Table 2 shows the atomic coordinates of the molecule.

V. Discussion

A good fit has been obtained using only three adjustable parameters and starting with 112 measured reflexions. Coupling between translations and rotations has not been taken into account. Indeed Schomaker & Trueblood (1968) have shown that these couplings do not modify experimental results if the space group is centrosymmetric and our crystal is precisely that.

In this crystal we have found two types of very different motions. The molecule can perform a uniaxial free rotation around the $C-C\equiv N$ axis and no steric hindrance then occurs. The molecular dipolar momen-

Table 2. *Atomic coordinates of a molecule with its* $C-C\equiv N$ *bond along the* [001] *axis*

The other five molecules are obtained with first a 120° rotation around the [111] axis, and second inversion about the origin. These six molecules are then freely rotating around their $C-C\equiv N$ bond.

Atom	N	C_N	$C_{T1(N)}$	C_{T2}	C_{T3}	C_{T4}	C_{SA}	C_{SB}	C_{SC}	C_{SD}	C_{SE}	C_{SF}
X(Å)	0	0	0	−1·01	−0·37	1·38	1·39	−1·39	−0·37	0·37	−1·02	1·02
Y(Å)	0	0	0	−1·01	1·38	−0·37	−0·37	0·37	1·39	−1·39	−1·02	1·02
Z(Å)	4·12	2·98	1·52	−0·51	−0·51	−0·51	1·02	−1·02	1·02	−1·02	1·02	−1·02

Atom	H_{T2}	H_{T3}	H_{T4}	H_{SA1}	H_{SA2}	H_{SB1}	H_{SB2}	H_{SC1}	H_{SC2}	H_{SD1}	H_{SD2}	H_{SE1}	H_{SE2}	H_{SF1}	H_{SF2}
X(Å)	−1·73	−0·64	2·37	1·63	2·12	−2·40	−1·35	−1·41	0·40	0·65	0·36	−0·71	−2·03	1·76	0·98
Y(Å)	−1·73	2·37	−0·64	−1·41	0·40	0·65	0·36	1·63	2·12	−2·40	−1·35	−2·03	−0·71	1·76	0·98
Z(Å)	−0·87	−0·87	−0·87	1·36	1·36	−0·60	−2·14	1·36	1·36	−0·60	−2·14	1·36	1·36	−0·60	−2·14

tum stays fixed (Fig. 6). This motion does not affect the average space-group symmetry. Therefore there is no reason to expect coupling between translation and uniaxial rotation to exist and affect the observed Bragg reflexions. On the contrary, by looking at Fig. 6, one can see that —C≡N reorientations cannot occur without a huge local distortion of the crystal lattice. Fig. 4 shows a molecule aligned in the [010] direction and the same one after such a reorientation around G. If we want to put this molecule in an equilibrium position again, we must translate it by $OO' = 0.78$ Å. These two reasons clearly indicate that a strong coupling exists between translations and reorientations of the C≡N group. The influence of this strong coupling on experimental results remains small only because its frequency is very small, of the order of 400 kHz at room temperature (Amoureux, Bee & Castelain, 1979a).

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Dimethylglyoxime: a Restricted X-ray Charge-Density Refinement

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Abstract

Crystals of dimethylglyoxime ($C_4H_8N_2O_2$) are triclinic, space group $P\bar{1}$ with $a = 6.075$ (3), $b = 6.314$ (3), $c = 4.484$ (2) Å, $\alpha = 122.50$ (3), $\beta = 91.66$ (4), $\gamma = 77.75$ (3)° with one molecule per cell. The structure has been redetermined from 521 X-ray intensities measured with Cu $K\alpha$ radiation (sin $\theta/\lambda \leq 0.60$ Å^{-1}). After a conventional least-squares refinement ($R = 0.034$), population parameters were introduced for octapole deformations of spherical Hartree–Fock C, N and O atoms in order to fit apparent residual bonding charge density. The agreement improved significantly ($R = 0.025$). Charge deformations in the oxime group were found to be trigonal for N and tetrahedral for O.

Introduction

McCrone (1949) reported morphological and optical properties for dimethylglyoxime (Fig. 1) and measured

the X-ray cell data. Merritt & Lanterman (1952) determined the crystal structure (Fig. 2) from X-ray photographic intensity data. Hamilton (1961) used neutron $hk0$ and $0kl$ data to show that the molecules in the structure existed in the hydroxyimino tautomeric form.
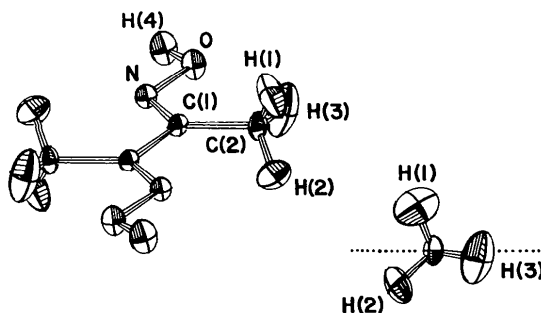

Fig. 1. Molecular structure and atomic nomenclature for dimethylglyoxime. Thermal parameters are represented as 25% probability ellipsoids. In the view of the methyl group down the C(1)–C(2) bond, the trace of the molecular plane is shown as a dotted line.