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## 2-Azanoradamantane *N*-Oxyl: The Phase Transition and the Crystallographic Structure of the Plastic Phase

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2-Azanoradamantane *N*-oxyl is an organic free radical nitroxide which is diamagnetic at room temperature. At 343 K it undergoes a reversible endothermic transition to a paramagnetic plastic phase; twinned face-centred cubic single crystals were obtained [ $a = 9.31(1) \text{ \AA}$ ,  $Z = 4$ ]. The crystallographic structure of this plastic phase was solved with the room-temperature molecular model and the relations between the low and the high-temperature cells. A molecular block-refinement program was used; the final  $R$  value is 0.085 (31 observed structure factors and 3 variable parameters).

### Introduction

2-Azanoradamantane *N*-oxyl [which we shall henceforth call ANAO (Fig. 1)] is a nitroxide free radical which was synthesized at the Laboratoire de Chimie Organique Physique of the Centre d'Etudes Nucléaires de Grenoble (Dupeyre & Rassat, 1975). It crystallizes at room temperature in the form of pale-yellow volatile crystals of orthorhombic symmetry. In nitroxides the pale-yellow colour is characteristic of the existence of dimers due to the pairing of the electron spin localized on the N–O bonds. The pairing is confirmed by electron paramagnetic resonance studies (Decors, Genoud & Dupeyre, 1977) (the difference between the fundamental singlet and the triplet is of the order of 4000 K) and by the study of the crystallographic structure (Dupeyre & Capiomont, 1977).

At 343 K ANAO crystals undergo a reversible endothermic transition producing a plastic phase. The melting point cannot be observed as the product decomposes at about 423 K. It is the study of this

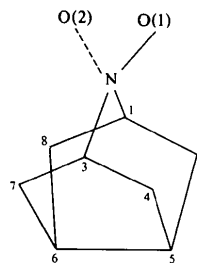


Fig. 1. Molecule of 2-azanoradamantane *N*-oxyl.

transition from crystal to plastic crystal and also the structure of the plastic phase that we shall describe here.

### I. Study of the transition

The transition occurring at 343 K was studied in a number of ways: (1) by optical observations, (2) by X-ray studies, at different temperatures, of powders and of monocrystals, (3) by measurements of the specific heat.

#### 1. Optical observations

A monocrystal, observed under a microscope, abruptly changes colour at 343 K; it becomes red and isotropic, while still remaining apparently monocrystalline; on cooling, it becomes pale yellow again and fragments; going through the transition several times produces a powder.

A crystal placed in a capillary tube and observed during the high-temperature phase flows slightly along the tube.

#### 2. X-ray studies

X-ray diffraction photographs were taken of the monocrystal at above 343 K. They allowed us to determine the cell parameters and the symmetry of the phase existing above 343 K: face-centred cubic, with  $a = 9.31 \text{ \AA}$ ,  $Z = 4$  (at 353 K). The only reflexions appearing are those at very low  $\theta$  angles, and they are broad. No diffusion is observed.

By means of superposition of photographs of the same crystal in the two phases, we were able to show the relative orientation of the two cells.

#### 3. Measurements of the specific heat

Measurements of the enthalpy increment at the transition were taken on samples of the order of 3 mg, with a differential scanning calorimeter – the reference chosen is the melting point of indium. The results are as follows: temperature of transition 343.2 K, enthalpy of transition  $\Delta H = 18\,649 \text{ J mol}^{-1}$ , entropy of transition  $\Delta S = 34 \text{ J mol}^{-1} \text{ K}^{-1}$ .

#### 4. Conclusion

The large degree of symmetry in the high-temperature phase, the high value of the entropy increment at the transition and also inspection of the diffraction photographs allow us to conclude that there is an orientational disorder of the molecules in this phase.

ANAO thus behaves in a manner analogous to that of compounds of similar spherical shape (globular

molecules) (Nordman & Schmitkons, 1965; Wulff & Westrum, 1964; Westrum & Wong, 1970). The change of colour indicates that the electron spins become unpaired at the transition.

### II. The crystallographic structure of the plastic phase

#### 1. The collection of the intensities

A monocrystal sample is enclosed in a capillary glass tube sealed so as to avoid too great a sublimation. The intensities of 31 independent reflexions were recorded at 353 K on a Siemens automatic single-crystal diffractometer (equipped with a variable-temperature device functioning with a nitrogen-gas jet) installed at the Institut Laue–Langevin at Grenoble. The features of this collection are as follows: Cu  $K\alpha$  radiation,  $\omega$  scan, five-points method (Troughton, 1969).

During the course of the experiment the intensity of the reference reflexion regularly decreases (sublimation of the crystal). A renormalization of the intensities is consequently performed.

#### 2. The search for the structure

Given the small amount of experimental data and the existence of an orientational disorder of the molecules around their centre of mass, we can only envisage refinement through a rigid molecular block.

We shall now recall the results of the structure of the low-temperature phase, analyse the cell relations between the low and the high-temperature phases and consider the most likely structure hypotheses and test them.

(a) *The structure of the orthorhombic phase* (Dupeyre & Capiomont, 1977). The crystallographic parameters are as follows:  $a = 13.43$ ,  $b = 11.47$ ,  $c = 9.22 \text{ \AA}$ , space group:  $Pbca$ ,  $Z = 8$ . Table 1 gives the crystallographic coordinates of the atoms in the cell. The plane containing the N, O, C(5), C(6) atoms is, within the margins of error, a plane of symmetry for the molecule. This plane is parallel to the  $c$  axis and almost parallel to the plane (120).

(b) *The relations between the cells of the low- and high-temperature phases.* An examination of the X-ray diffraction photographs, superposed on the same film, of a crystal before and after transition, leads one to the following observations. (1) The orthorhombic  $c_{\text{orth}}$  axis remains a crystallographic axis of the cubic phase  $c_{\text{cub}}$ . (2) Two cubic systems (indicated by subscripts  $\text{cub}_1$  and  $\text{cub}_2$ ) appear; they are symmetric in relation to the  $(100)_{\text{orth}}$  plane, and form between them an angle of  $30^\circ$  [thus  $(a_{\text{cub}_1}, a_{\text{orth}}) = -15^\circ$  and  $(a_{\text{cub}_2}, a_{\text{orth}}) = +15^\circ$ ] (Fig. 2). (This twinning was also observed when the

Table 1. *Fractional atomic coordinates in the orthorhombic cell* ( $\times 10^4$ ; for H  $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	476 (2)	8431 (2)	3464 (2)
C(9)	1456 (2)	7810 (2)	3107 (3)
C(5)	1935 (2)	8722 (2)	2116 (2)
C(4)	2350 (2)	9682 (2)	3115 (3)
C(3)	1390 (2)	10344 (2)	3451 (3)
C(7)	996 (2)	10559 (2)	1934 (3)
C(6)	1028 (2)	9311 (2)	1320 (2)
C(8)	111 (2)	8692 (2)	1948 (2)
N	714 (1)	9536 (1)	4219 (2)
O	768 (1)	9502 (1)	5608 (2)
H(1)	152	1116	406
H(2)	-4	786	408
H(3)	108	926	13
H(4)	249	834	138
H(5)	22	1087	198
H(6)	152	1112	133
H(7)	-51	928	198
H(8)	-1	786	134
H(9)	264	929	411
H(10)	286	1023	250
H(11)	190	771	411
H(12)	131	700	251

intensities were measured on the single-crystal diffractometer; we measured only those reflexions not affected by this phenomenon because of the range of the equivalent reflexions.) (3) The reciprocal  $[120]_{\text{orth}}^*$  and  $[120]_{\text{cub}_1}^*$  rows coincide in direction with the  $[110]_{\text{cub}_1}^*$  and  $[110]_{\text{cub}_2}^*$  rows (Fig. 2). We have seen (§II.2a) that the planes  $(120)_{\text{orth}}$  are virtually planes of

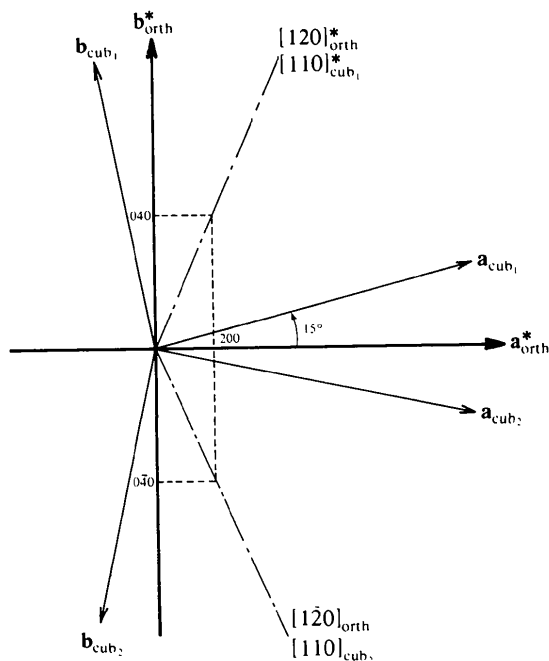


Fig. 2. Orthorhombic (orth) and cubic (cub) cell relations; the two cubic systems are indicated by subscripts  $\text{cub}_1$  and  $\text{cub}_2$ .

symmetry for the molecules; the coincidence of these planes with the  $(110)_{\text{cub}}$  planes suggests that these planes of symmetry are conserved for the molecules in the plastic phase; the formation of twins in the high-temperature phase would thus be justified.

We should point out that the variation in volume between the orthorhombic phase (at room temperature) and the cubic phase (at 353 K) is great:  $\Delta V/V = 0.13$ ; the distribution of molecules is considerably altered: in the cubic phase each molecule has 12 neighbouring molecules at 6.6 Å; in the orthorhombic phase each molecule has one neighbouring molecule at 4.8 Å (the dimer) and 11 neighbouring molecules between 6.1 and 6.8 Å.

We measured the relative variation in volume of the plastic phase in the range between 353 and 383 K. It is  $4.3 \times 10^{-4} \text{ K}^{-1}$ ; this is a value very close to that of adamantane (Mirskaya, 1963).

(c) *First structure hypothesis: Frenkel (1935) model.* One accepts that each molecule has, around its centre of mass, a number  $N$  of possible orientations, linked by the elements of symmetry of the group. In view of the high value of the entropy increment at the transition we chose the cubic face-centred space group  $Fm\bar{3}m$ , which possesses special positions of point symmetry 4, diagonal mirrors  $(110)$ , and leads to the largest possible number of orientations for the molecule. There are thus 24 orientations for the molecule around its centre of mass.

We took as molecular model that of the orthorhombic phase and imposed on it the NO—C(5)—C(6) plane exactly as a plane of symmetry.

Since the ANAO molecule is rapidly inverted at the nitroxide group in solution (Dupeyre & Capiomont, 1977), we hypothesize that this is also the case in the plastic phase. We thus have two positions for the O atom, both symmetric in relation to the C(1)—N—C(3) plane and each having an occupation rate of  $\frac{1}{2}$  (Fig. 1).

The coordinates (Å) of this model (in an  $X, Y, Z$  coordinate system related to the molecule) are indicated in Table 2.

The orientation of the molecule is noted by the three Euler angles  $\theta_1, \theta_2, \theta_3$  of the molecular coordinate system (Table 2) in relation to the crystallographic coordinate system (André, Fourme & Renaud, 1971). In the orthorhombic phase, these three angles are 178.9, -58.6 and 149.7° respectively. Having decided to start from a neighbouring orientation compatible with the cubic symmetry, we refine this orientation from the values for the Euler angles of 180, -58.6, 135° (we again find the 15° difference mentioned previously).

For the refinement we use the *ORION* program with a molecular block (André *et al.*, 1971). The available parameters are: the scale factor, the angle of orientation  $\theta_2$  [as  $\theta_1$  and  $\theta_3$  are fixed with the molecule retaining the

Table 2. Atomic coordinates ( $\text{\AA} \times 10^3$ ) chosen for the refinement of the plastic phase

The origin is at the centre of mass. The coordinate system is as follows: **Y** parallel to C(1)–C(3), **Z** normal to the N–C(1)–C(3) plane, **X** = **Y**  $\times$  **Z**. [Only half a molecule is indicated because of the mirror plane (**X**, **Z**).]

	X	Y	Z
C(1)	393	-1255	75
C(9)	-667	-1227	-1032
C(5)	-1462	0	-603
C(7)	-503	1221	1292
C(6)	-1365	0	968
N	1176	0	0
O(1)	2227	0	-737
O(2)	2227	0	737
H(1)	1034	2167	35
H(3)	-2345	0	1468
H(4)	-2495	0	-994
H(5)	77	1032	2184
H(6)	-1109	2140	1331
H(9)	-175	1043	-2006
H(10)	-1299	2121	-994

Table 3. Observed and calculated structure factors for the two refinement models of the plastic phase

Subscript 1 indicates the Frenkel model, subscript 2 the Pauling–Fowler model.

hkl	$F_{o1}$	$F_{c1}$	$F_{o2}$	$F_{c2}$
111	90.8	92.1	67.7	68.1
200	63.3	63.1	47.1	46.8
220	5.1	1.3	3.8	2.1
311	10.3	-10.2	7.7	-8.7
222	29.2	-24.6	21.8	-9.9
400	4.6	-3.8	3.4	-11.0
331	9.7	-8.4	7.3	-9.0
420	5.5	-3.3	4.1	-8.0
422	10.5	-9.2	7.8	-5.2
333	11.4	-12.3	8.5	-3.3
511	4.6	-0.4	3.4	-3.3
440	2.4	4.6	1.7	-1.2
531	0.6	-0.1	0.5	-0.4
600	0.0	4.3	0.0	-0.2
442	2.3	-1.3	1.7	-0.2
602	0.0	-0.2	0.0	0.4
533	1.2	-1.2	0.9	0.7
622	0.6	-2.0	0.4	0.7
444	1.0	0.4	0.7	0.9
711	0.2	0.8	0.2	0.9
551	3.0	3.9	2.3	0.9
640	2.7	1.9	2.0	0.9
642	1.1	0.3	0.9	0.8
731	1.7	-1.3	1.3	0.7
553	1.8	1.3	1.3	0.7
733	1.4	-1.5	1.0	0.4
644	0.0	0.7	0.0	0.4
660	1.9	2.9	1.4	0.3
751	0.9	0.9	0.7	0.2
080	0.0	1.4	0.0	0.5
082	0.0	-0.1	0.0	0.4

(110) plane as a plane of symmetry], the global isotropic temperature factor  $B$ ; i.e. three variables for 31 reflexions. The results are as follows (the standard errors are in brackets):  $\theta_2 = -54(2)^\circ$ ,  $B = 11(1) \text{\AA}^2$ ,  $R = 0.143$ ,  $R_w = 0.085$ ,  $\sigma_1 = [\Sigma(F_o - sF_c)^2 / (N_{\text{obs}} - N_{\text{var}})]^{1/2} = 1.87$ .

In Table 3 we give the values of the observed and calculated structure factors ( $F_{o1}$  and  $F_{c1}$ ). These results are quite satisfactory; the analysis of the structure (§II.3) will confirm that they are valid.

(d) *Second structure hypothesis: Pauling–Fowler model* (Pauling, 1930; Fowler, 1935). This model is that of isotropic, continuous rotation of the molecule around its centre of mass. In this case the structure factor of the reflexion  $hkl$  is given by:

$$F_{hkl} = S \exp\left(-B \frac{\sin^2 \theta_{hkl}}{\lambda^2}\right) \sum_i f_i(hkl) \frac{\sin \varphi_i}{\varphi_i}$$

[ $\varphi_i = 4\pi r_i(\sin \theta_{hkl}/\lambda)$ ,  $r_i$  is the distance from atom  $i$  to the centre of mass of the molecule]. This gives two variable parameters: the global isotropic temperature factor  $B$  and the scale factor. We wrote a least-squares refinement program incorporating these two parameters. It leads to the values  $R = 0.24$  and  $R_w = 0.19$  with  $B = 4.4 \text{\AA}^2$ . Table 3 gives the values of  $F_{o2}$  and  $F_{c2}$  for this model. These results are less satisfactory than the preceding ones.

### 3. Results

The analysis of the interatomic distances between neighbouring molecules shows that the hypothesis of the 24 orientations of the  $Fm3m$  space group leads to correct values, except for a certain number concerning the distance between C(7) and C(8), of the order of 3  $\text{\AA}$ , and distances involving O(2)(O(1)···O(2) = 2.6 and C(8)···O(2) = 2.9  $\text{\AA}$ ).

Table 4. Fractional atomic coordinates ( $\times 10^3$ ) in the cubic cell

	x	y	z
C(1)	-118	-73	29
C(9)	-0	-187	7
C(5)	102	-102	89
C(7)	36	150	-125
C(6)	2	-2	-180
N	-53	53	102
O(1)	-54	54	240
O(2)	-145	145	147
H(1)	116	213	88
H(3)	15	-15	-297
H(4)	173	-173	-154
H(5)	-59	216	-131
H(6)	130	195	-181
H(9)	210	-52	112
H(10)	280	42	-50

The hypothesis of continuous rotation can only apply if we suppose that there exist strong correlations between the orientations of the neighbouring molecules, a case which the total absence of diffusion on the photographs allows us to exclude.

So as to confirm the hypothesis of the molecule with a special position [mirror (110)], we checked that neighbouring orientations corresponding to variations in angles ( $5^\circ$  on  $\theta_1$  and on  $\theta_3$ ) lead in a fairly systematic fashion to certain interatomic distances which are too short.

Table 4 gives the crystallographic coordinates of the atoms in the cubic cell.

### III. Thermodynamic aspects of the transition

Each molecule possesses 24 possible orientations around its centre of mass; the possibility of inverting the group  $\begin{matrix} C(1) \\ C(3) \end{matrix} \rangle N-O$ , leads to 48 degrees of freedom and so to a contribution to the entropy of  $R \log 48$ . The transition occurs from a diamagnetic state (where the number of pairs in the triplet state is negligible) to a paramagnetic state, that is a contribution to the entropy of  $R \log (2S + 1) = R \log 2$  per molecule. (In Fig. 3 we have illustrated the conformation of the two nitroxide groups in a dimer, a conformation which disappears in the plastic phase.)

As a total then:  $\Delta S_{\text{calc}} = R \log 96 = 38 \text{ J mol}^{-1} \text{ K}^{-1}$ , the experimental value being  $\Delta S_{\text{exp}} = 54 \text{ J mol}^{-1} \text{ K}^{-1}$ . The excess entropy is  $16 \text{ J mol}^{-1} \text{ K}^{-1}$  (if one were to renounce the hypothesis of the inversion of the nitroxide group, this last result would be  $22 \text{ J mol}^{-1} \text{ K}^{-1}$ ). This excess entropy at transition has been studied for a large number of plastic crystals (Clark, McKervey, Mackle & Rooney, 1974); its value has been related to the nature of the molecule, to its shape

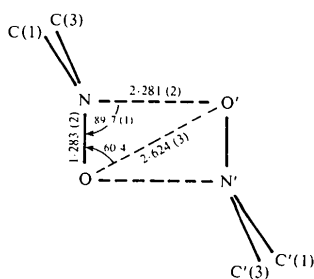


Fig. 3. The conformation of a dimer (near the N-O bonds) in the orthorhombic phase.

and to the domain of temperature in which the plastic phase exists. The value that we find for ANAO is perfectly comparable with those proposed for adamantane ( $10.4 \text{ J mol}^{-1} \text{ K}^{-1}$ ), diadamantane ( $16 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and diadamantan-1-ol ( $19.6 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

### Conclusion

In view of the poor amount of information provided by the X-ray diffraction of a plastic crystal, it is only through the crystallographic study of the low-temperature phase of ANAO that we were able to obtain information about the high-temperature phase of this compound from the conformation of the molecule, the relation between the cells and the orientation of the molecule in the cell.

It would be desirable for one to complete this study by experiments concerning the dynamic aspects of the transition and of the plastic phase: resonance, inelastic diffusion of neutrons *etc.*

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