

to the mean molecular planes, suggesting that the planarity is an artifact due to superposition of two non-planar forms. This situation is again rather similar to that of DHA in DHA.2TNB; both systems would appear to require further study, preferably over a range of temperatures.

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Structural Studies of the Phase Transition in *N*-Isopropylcarbazole

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Abstract

The crystal structures of *N*-isopropylcarbazole (C₁₅H₁₅N, *M_r* = 209.27) stable above and below 139.5 K were solved by direct methods using three-dimensional X-ray diffraction data. The structure at

294 K is orthorhombic, space group *Iba*2, with *a* = 16.808 (5), *b* = 17.984 (8), *c* = 7.983 Å, *V* = 2413.1 Å³, *Z* = 8, *D_x* = 1.15 Mg m⁻³, *Mo Kα*, λ = 0.7107 Å, μ = 0.036 mm⁻¹, *F*(000) = 896; the structure at 118 K is also orthorhombic, space group *Pbc*2₁,

$a = 16.842(4)$, $b = 17.463(3)$, $c = 7.863(4)$ Å, $V = 2312.2$ Å³, $Z = 8$, $D_x = 1.20$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.036$ mm⁻¹, $F(000) = 896$. The final R factors reached in a full-matrix least-squares refinement were 0.057 and 0.058 for the high- and low-temperature phases, respectively. A rigid-body thermal-motion analysis revealed a large libration of the molecule at 294 K which decreased significantly in the low-temperature phase suggesting an order-disorder type of phase transition. Group-theoretical analysis of the structural changes in the *N*-isopropylcarbazole crystal at 139.5 K were also performed to establish the symmetry properties of an excitation responsible for driving the phase transition.

Introduction

The polar crystal of *N*-isopropylcarbazole (NIPC), C₁₅H₁₅N, was recently found to exhibit a structural phase transition at 139.5 K (Nowak & Poprawski, 1984). Extensive studies performed by Nowak, Sworakowski, Kowal, Dziedzic & Poprawski (1986) revealed anomalies of the thermal expansion, spontaneous polarization and dielectric constant near the temperature of the phase transition. Other interesting properties such as triboluminescence (Nowak, Krajewska & Samo e, 1983) and pyroluminescence (Dreger, Kalinowski, Nowak & Sworakowski, 1984) were also reported and it was found that the crystals emitted light during the phase transition. However, the explanation of these properties was seriously limited owing to the unknown structures of the high- and low-temperature phases.*

In the present paper, the structures of both NIPC modifications are reported. Some interesting information about the nature of the phase transition was deduced from a thermal-motion analysis considering the NIPC molecule as a rigid body. Finally, the symmetry aspects of the transition were also analysed to determine a wavevector and polarization vectors which describe the low-temperature phase in relation to the high-temperature one.

Experimental

N-Isopropylcarbazole was synthesized according to the general method of carbazole alkylation proposed by Stevens & Tucker (1923). Crude material was carefully purified by means of repeated crystallization, liquid chromatography, sublimation and zone refining. A crystal of the high-temperature phase suitable for X-ray measurements was grown inside a Lindemann-glass capillary according to the procedure described elsewhere (Chaplot, McIntyre,

Mierzejewski & Pawley, 1981). Approximate dimensions of the sample were 0.3 × 0.5 × 0.4 mm. A single crystal of the low-temperature phase was obtained by slowly cooling the former sample below the phase transition in an open stream of nitrogen (Leybold Heraeus system).

Accurate cell dimensions and intensities of Bragg reflexions were measured by an automatic four-circle diffractometer (Philips PW 1100) in the ω - 2θ mode using Mo $K\alpha$ radiation. The scan width was 1.2° for each reflexion. A total number of 2032 Bragg intensities up to $\sin \theta/\lambda < 0.745$ Å⁻¹ ($0 < h < 23$, $0 < k < 25$, $0 < l < 11$) was recorded for the high-temperature phase at 294(2) K and 5405 up to $\sin \theta/\lambda < 0.807$ Å⁻¹ ($0 < h < 17$, $0 < k < 28$, $0 < l < 12$) were collected for the low-temperature phase at 118 ± 0.5 K. In both phases the data were corrected for the Lorentz-polarization factor, but no absorption or extinction correction was made. There was no significant variation of standard reflections.

Structure determination

The unit cell of the high-temperature phase was found to be orthorhombic. Systematic absences of the hkl reflections for $h+k+l$ odd, $h0l$ for h odd and $0kl$ for k odd implied space group $Iba2$ with molecules situated at general positions. The volume of the body-centred unit cell suggested that it contains eight molecules. The above crystal data correspond to those reported by Cherin & Burack (1966).

Additional reflexions appeared below 139.5 K, changing the space-group symmetry of the crystal. The new systematic absences: $0kl$ for k odd and $h0l$ for l odd indicated orthorhombic space group $Pbc2_1$. This space group has been chosen to facilitate the comparison between the two phases. The eight molecules in the primitive unit cell occupy two symmetry-nonrelated sets of C_1 sites.

Both structures of NIPC were solved using the *MULTAN* program based on direct methods (Germain, Main & Woolfson, 1971). Preliminary atom positions were found by taking into account 445 reflexions with normalized structure factors $E > 1.20$ for the high-temperature phase and 449 reflexions with $E > 1.56$ for the low-temperature one. A difference Fourier synthesis revealed the positions of all the H atoms except some attached to the isopropyl group in the high-temperature phase. Therefore, the positions of the missing H atoms were generated assuming a C-H distance of 1.08 Å, before the structure refinement was performed.

The structures were refined (on F) by the program *SHELX76* (Sheldrick, 1976) using all reflexions with intensity larger than $3\sigma(I)$; 683 symmetry-independent reflexions of the high-temperature phase and 3616 of the low-temperature phase entered the calculations. The small number of reflexions used for the

* A paper describing the structure of the high-temperature phase of NIPC appeared (Saravari, Kitamura, Tazuke, Takenaka & Sasada, 1984) while the present manuscript was in preparation.

high-temperature phase is due in part to a lower cut-off of the data, and in part to the important thermal agitation of the atoms in this structure. Scattering factors for C and N were taken from *International Tables for X-ray Crystallography* (1974), while the factors for H were those of Stewart, Davidson & Simpson (1965). With unit weights, final *R* factors of 5.7 and 5.8% were achieved for the high- and low-temperature phases, respectively. The absolute values of the peaks and troughs in the final difference Fourier synthesis map did not exceed $0.2 e \text{ \AA}^{-3}$; $(\Delta/\sigma)_{\max}$ are 0.52 and 0.15 for the high- and low-temperature structures respectively; the atom positions corresponding to the best *R* values are listed in Table 1.* Table 2 gives bond lengths and angles. According to *International Tables*, the origin of the coordinates system is placed on 2 for the *Iba2* structure, and on 2_1 for the *Pbc2_1*. Therefore, the origin of the latter coordinates system in Fig. 1 was shifted by the vector $[-0.25, 0.25, 0]$ to emphasize structural similarities between both phases. Fig. 2 is a projection of the structures along *a*.

The NIPC molecules form layers parallel to the *bc* plane in the crystal lattice. The two layers in each unit cell are labelled (I) and (II) (*cf.* Fig. 1). In the high-temperature phase, both layers are related to each other by a *c* glide plane, which vanishes at the phase transition breaking the mutual dependence of the layers. As a result, the volume of the primitive cell is doubled below 139.5 K. Comparison of the low- and high-temperature structures shows only minimal differences of molecular orientations. Rotational and translational shifts of the molecules during the phase transition are comparable with the amplitudes of their thermal vibrations.

The phase transition does not affect essentially the molecular conformation. The only significant change is a rotation of the isopropyl group around the C–N bond by angles of 14 and 10° for layers (I) and (II), respectively. The carbazole group is almost planar in both phases (see Table 4). In both modifications, the C–N bonds of all the molecules are placed around the *c* direction; thus spontaneous polarization of the crystal is parallel to the *c* axis. Bond lengths at 294 K are generally shorter than those at 118 K due to smearing of the atom positions in the high-temperature phase.

Thermal motions

The thermal motions of the C and N atoms were described by anisotropic parameters while isotropic

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and distances of the N atoms from the centres of mass of the molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42562 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j (\times 10^2).$$

	x	y	z	U_{eq}
High-temperature phase				
C(2)	3050 (3)	1849 (3)	5674 (9)	72 (8)
C(3)	2310 (3)	1442 (3)	5751 (10)	70 (8)
N	3093 (3)	1061 (3)	7902 (8)	93 (8)
C(12)	3340 (5)	2392 (4)	4618 (10)	100 (10)
C(13)	3311 (5)	737 (4)	9519 (12)	134 (12)
C(4)	2360 (4)	970 (3)	7143 (10)	87 (10)
C(1)	3503 (4)	1594 (3)	7005 (9)	68 (8)
C(9)	4248 (4)	1902 (4)	7302 (8)	82 (9)
C(11)	4063 (5)	2679 (4)	4940 (11)	123 (12)
C(7)	1002 (4)	995 (5)	5251 (15)	109 (18)
C(5)	1732 (6)	510 (4)	7518 (11)	130 (14)
C(8)	1612 (4)	1427 (3)	4819 (11)	96 (11)
C(10)	4508 (3)	2453 (4)	6230 (11)	103 (11)
C(15)	3216 (5)	1225 (4)	10926 (10)	183 (14)
C(14)	3967 (6)	238 (4)	9521 (11)	201 (16)
C(6)	1084 (5)	527 (5)	6529 (18)	148 (21)
Low-temperature phase				
Molecule (1)				
C(12)	5333 (2)	3865 (1)	1774 (4)	17 (2)
C(13)	4595 (2)	4265 (1)	1517 (4)	17 (2)
N(1)	4439 (1)	3441 (1)	3758 (3)	23 (2)
C(112)	6076 (2)	3895 (2)	988 (4)	21 (2)
C(113)	4183 (2)	3092 (2)	5381 (4)	22 (3)
C(14)	4061 (2)	4002 (2)	2779 (4)	18 (2)
C(111)	5212 (2)	3371 (2)	3188 (4)	17 (2)
C(19)	5820 (2)	2908 (2)	3798 (5)	23 (3)
C(111)	6680 (2)	3435 (2)	1615 (5)	23 (3)
C(17)	3602 (2)	5124 (2)	472 (5)	29 (3)
C(15)	3294 (2)	4304 (2)	2900 (4)	25 (3)
C(18)	4362 (2)	4829 (2)	365 (4)	21 (2)
C(110)	6553 (2)	2949 (2)	3004 (5)	26 (3)
C(115)	4316 (2)	3648 (2)	6846 (5)	28 (4)
C(114)	3337 (2)	2789 (2)	5319 (5)	26 (3)
C(16)	3079 (2)	4864 (2)	1731 (5)	29 (3)
Molecule (2)				
C(22)	-180 (2)	1001 (1)	10914 (4)	18 (2)
C(23)	597 (2)	654 (1)	10981 (4)	16 (2)
N(2)	485 (2)	1490 (1)	13194 (4)	21 (2)
C(212)	-825 (2)	907 (2)	9818 (5)	25 (3)
C(213)	595 (2)	1888 (2)	14835 (5)	25 (3)
C(24)	983 (2)	955 (2)	12428 (4)	19 (2)
C(21)	-225 (2)	1506 (2)	12308 (4)	24 (2)
C(29)	-924 (2)	1926 (2)	12619 (5)	35 (3)
C(211)	-1511 (2)	1314 (2)	10136 (5)	35 (3)
C(27)	1730 (2)	-130 (2)	10405 (5)	32 (5)
C(25)	1749 (2)	720 (2)	12858 (4)	22 (3)
C(28)	974 (2)	108 (2)	9970 (4)	20 (2)
C(210)	-1550 (2)	1817 (2)	11520 (6)	44 (4)
C(215)	514 (4)	1328 (3)	16299 (6)	48 (7)
C(214)	1374 (2)	2316 (2)	14923 (5)	26 (3)
C(26)	2106 (2)	174 (2)	11830 (5)	30 (3)

ones were satisfactory for H atoms. Fig. 3 shows the thermal ellipsoids of the atoms of the NIPC molecules.

With the NIPC molecule considered as a rigid body, T, L and S tensors describing its thermal motions were fitted to the U_{ij} 's of C and N atoms using the least-squares procedure proposed by Schomaker & Trueblood (1968). The elements of these tensors are given in Table 3. The r.m.s. differences between the observed U_{ij} and those calculated from the T, L and S tensors do not exceed 0.0070 \AA^2 in the low-temperature phase indicating that the molecules are reasonably rigid at 118 K.

Rigid-body thermal-motion analysis of the NIPC structure provides useful information about the librations of the whole molecule around three principal

axes, which, in this case, approximately coincide with the principal axis of inertia. Libration around the axis of the greatest moment of inertia exhibits at 294 K a surprisingly large amplitude of 7.1° , being at least two times larger than the amplitudes of the two other principal librations at the same temperature. However, the amplitude considered diminishes significantly below the phase transition and becomes more comparable with other librational amplitudes at 118 K.

The translational motions of NIPC molecules in both phases are much less anisotropic than the librational ones. It should be noted, however, that the largest translations occur almost parallel to the longest molecular axis, *i.e.* the axis of the smallest moment of inertia. There are also orientational changes of the molecules at the phase transition; the angles which the normal to the mean plane of the carbazole of the molecules makes with the cell axes are reported in Table 4.

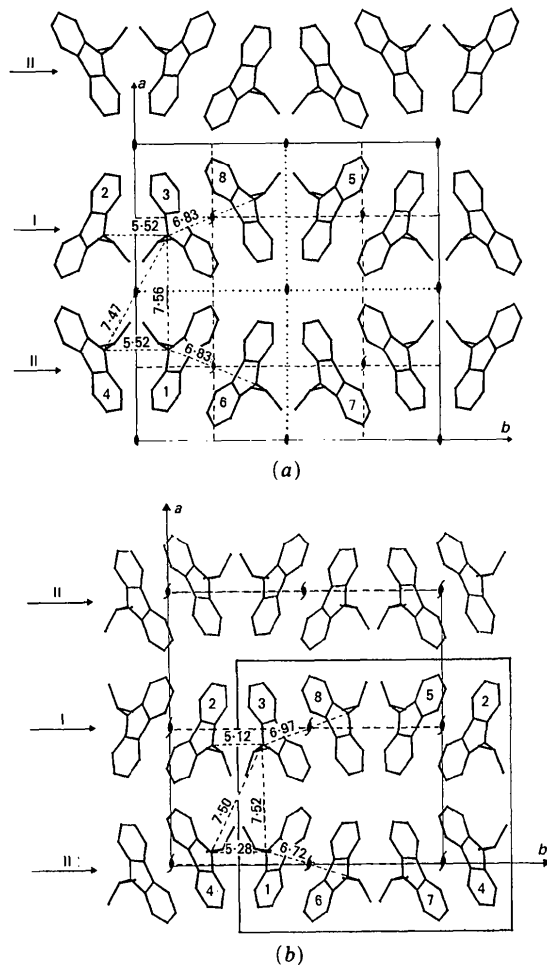


Fig. 1. Projections of the structures along *c*. Distances (\AA) between the N atoms of the molecules are shown. (a) High-temperature phase ($\bar{\sigma} = 0.017 \text{ \AA}$). (b) Low-temperature phase ($\bar{\sigma} = 0.009 \text{ \AA}$).

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

	High-temperature phase	Low-temperature phase	
		molecule (1)	molecule (2)
C(2)–C(3)	1.445 (8)	1.440 (4)	1.443 (4)
C(2)–C(12)	1.379 (10)	1.397 (4)	1.397 (4)
C(2)–C(1)	1.386 (10)	1.421 (4)	1.408 (4)
C(3)–C(4)	1.402 (10)	1.416 (4)	1.412 (4)
C(3)–C(8)	1.390 (10)	1.394 (4)	1.395 (4)
N–C(13)	1.463 (11)	1.478 (4)	1.478 (5)
N–C(4)	1.382 (9)	1.400 (4)	1.392 (4)
N–C(1)	1.381 (8)	1.381 (4)	1.385 (4)
C(12)–C(11)	1.345 (12)	1.387 (4)	1.379 (5)
C(13)–C(15)	1.434 (12)	1.523 (5)	1.517 (6)
C(13)–C(14)	1.421 (13)	1.522 (5)	1.510 (5)
C(4)–C(5)	1.374 (11)	1.399 (4)	1.395 (4)
C(1)–C(9)	1.389 (9)	1.391 (4)	1.409 (5)
C(9)–C(10)	1.380 (10)	1.387 (5)	1.376 (5)
C(11)–C(10)	1.336 (12)	1.399 (5)	1.400 (6)
C(7)–C(8)	1.331 (10)	1.383 (5)	1.382 (5)
C(7)–C(6)	1.329 (16)	1.401 (5)	1.393 (5)
C(5)–C(6)	1.345 (14)	1.390 (5)	1.386 (5)
C(3)–C(2)–C(12)	133.6 (6)	133.8 (3)	132.8 (3)
C(3)–C(2)–C(1)	105.8 (5)	106.3 (2)	106.4 (2)
C(12)–C(2)–C(1)	120.6 (6)	119.8 (3)	120.8 (3)
C(2)–C(3)–C(4)	106.8 (6)	106.9 (2)	106.9 (2)
C(2)–C(3)–C(8)	135.6 (6)	132.6 (3)	132.7 (3)
C(4)–C(3)–C(8)	117.6 (6)	120.4 (3)	120.3 (3)
C(13)–N–C(4)	124.2 (6)	129.1 (3)	128.2 (3)
C(13)–N–C(1)	127.5 (6)	121.3 (3)	122.5 (3)
C(4)–N–C(1)	107.5 (6)	108.1 (2)	108.5 (3)
C(3)–C(4)–N	109.2 (6)	108.9 (2)	108.7 (3)
C(3)–C(4)–C(5)	119.4 (7)	120.8 (3)	120.7 (3)
N–C(4)–C(5)	131.4 (7)	130.3 (3)	130.5 (3)
C(2)–C(1)–N	110.7 (6)	109.6 (3)	109.4 (3)
C(2)–C(1)–C(9)	119.6 (6)	121.1 (3)	120.4 (3)
N–C(1)–C(9)	129.6 (6)	129.2 (3)	130.2 (3)
C(1)–C(9)–C(10)	117.7 (6)	118.1 (3)	117.3 (3)
C(9)–C(10)–C(11)	121.3 (7)	121.2 (3)	122.6 (4)
C(12)–C(11)–C(10)	122.4 (8)	121.1 (3)	120.3 (3)
C(2)–C(12)–C(11)	118.3 (7)	118.6 (3)	118.6 (3)
C(4)–C(5)–C(6)	118.8 (3)	117.5 (3)	117.6 (3)
C(7)–C(6)–C(5)	123.3 (10)	122.1 (3)	122.2 (3)
C(8)–C(7)–C(6)	119.2 (9)	120.4 (3)	120.3 (3)
C(7)–C(8)–C(3)	121.5 (7)	118.9 (3)	118.9 (3)
N–C(13)–C(15)	114.8 (7)	110.3 (3)	110.3 (3)
N–C(13)–C(14)	116.5 (7)	112.9 (3)	112.4 (3)
C(15)–C(13)–C(14)	118.1 (8)	112.6 (3)	111.3 (3)

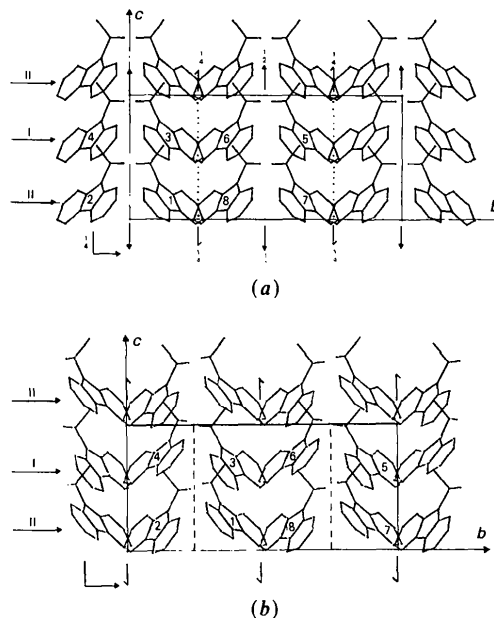


Fig. 2. Projections of the structures along *a*. (a) High-temperature phase ($\bar{\sigma} = 0.017 \text{ \AA}$). (b) Low-temperature phase ($\bar{\sigma} = 0.009 \text{ \AA}$).

Table 3. Rigid-body vibration parameters for all the heavy atoms of the molecules

	High-temperature phase			Low-temperature phase					
				molecule 1			molecule 2		
$T(\text{\AA}^2) \times 10^{-4}$	792 (40)	170 (3)	57 (37)	217 (7)	-18 (7)	5 (6)	234 (23)	-28 (23)	44 (21)
		678 (50)	47 (42)		190 (9)	-1 (8)		184 (30)	4 (25)
			527 (44)			139 (8)			111 (25)
$L(\text{rad}^2) \times 10^{-4}$	26 (12)	-37 (7)	0 (8)	9 (2)	6 (1)	-1 (1)	14 (7)	9 (4)	0 (5)
		106 (9)	58 (7)		14 (1)	3 (1)		29 (5)	-3 (4)
			78 (9)			9 (1)			14 (5)
$S(\text{\AA rad}) \times 10^{-5}$	-334 (227)	-426 (128)	-256 (140)	-16 (39)	-90 (23)	-31 (25)	211 (135)	-135 (74)	134 (83)
	656 (116)	-73 (182)	706 (103)	17 (21)	38 (31)	-11 (17)	346 (64)	-129 (102)	30 (56)
	692 (119)	-13 (99)	407 (1291)	-32 (22)	-51 (17)	-54 (231)	14 (213)	-87 (57)	-82 (756)
R.m.s.	$U^a - U^c (\text{\AA}^2)$	0.0115			0.0021			0.0067	
E.s.d.	$U_j^{\text{obs}} (\text{\AA}^2)$	0.0129			0.0023			0.0076	

T and L referred to the inertial axes of the molecule

Principal axes (\AA^2) $\times 10^{-4}$	High-temperature phase			Principal axes (deg 2)	L (rad^2) $\times 10^{-4}$	Low-temperature phase			Direction cosines			
	$T(\text{\AA}^2) \times 10^{-4}$					Inertial moments	x	y	z			
928	913	73	9	1.0	16	27	18	289	0.891	0.448	0.062	
556		562	-16	52.1		153	0	644	-0.406	0.731	0.548	
513			552	16.2			42	391	0.200	0.514	0.834	
Low-temperature phase												
Molecule (1)												
226	226	-1	-2	1.34	5	0	-3	302	0.891	-0.447	0.078	
181		168	-19	6.07		17	-4	671	0.326	0.750	0.574	
139			152	3.20			10	406	-0.316	-0.486	0.815	
Molecule (2)												
258	256	-10	13	2.9	10	0	2	303	0.925	-0.344	0.162	
177		133	40	10.9		30	8	670	0.374	0.754	-0.538	
95			141	4.5			16	405	0.063	0.559	0.826	

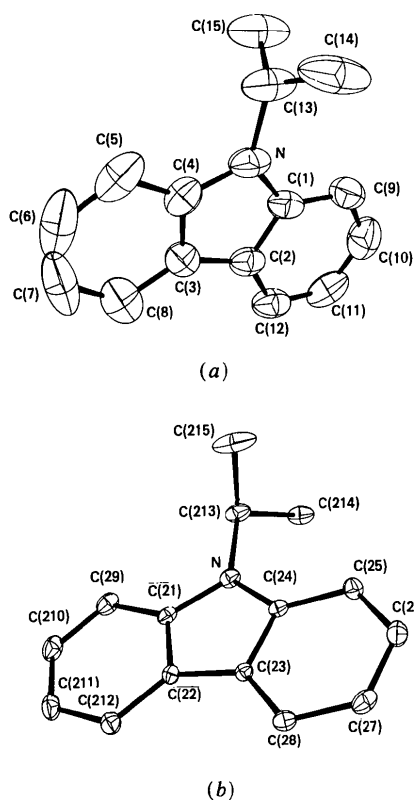


Fig. 3. Perspective view of the molecule and key to the numbering of the atoms in the molecule. (a) High-temperature phase. (b) Low-temperature phase.

Table 4. Least-squares planes and deviations (\AA) of atoms from these

	High-temperature phase		Low-temperature phase	
	(I) Lateral group N-CH(CH $_3$) $_2$		molecule (1)	molecule (2)
N	0.032 (6)		0.073 (3)	0.052 (3)
C(13)	-0.211 (18)		-0.318 (3)	-0.321 (4)
C(15)	0.067 (9)		0.157 (4)	0.240 (6)
C(14)	0.087 (10)		0.129 (3)	0.102 (4)
(II) Flat part of the molecule				
C(2)	0.023 (6)		0.033 (3)	0.026 (3)
C(3)	0.013 (7)		0.033 (3)	0.029 (3)
N	0.008 (6)		0.035 (3)	0.029 (3)
C(12)	0.020 (7)		0.007 (3)	0.005 (3)
C(4)	-0.006 (7)		0.008 (3)	-0.003 (3)
C(1)	0.023 (6)		0.012 (3)	0.014 (3)
C(9)	-0.012 (7)		-0.019 (3)	-0.019 (4)
C(11)	-0.015 (8)		-0.034 (3)	-0.039 (4)
C(7)	-0.052 (9)		-0.020 (4)	-0.018 (3)
C(5)	-0.015 (8)		-0.040 (3)	-0.028 (3)
C(8)	0.007 (7)		0.016 (3)	0.018 (3)
C(10)	-0.038 (8)		-0.049 (4)	-0.046 (4)
C(6)	-0.002 (11)		-0.052 (4)	-0.042 (4)

Equations for the least-squares planes

High-temperature phase	Angle between planes ($^\circ$)	Angles ($^\circ$) of the normal to plane (II)		
		α_x	α_y	α_z
(I) $0.774x + 0.620y - 0.127z - 4.375$	93.3	67	-45*	-54
(II) $0.394x - 0.707y - 0.587z + 3.009$				
Low-temperature phase, molecule (1)				
(I) $-0.602x + 0.787y - 0.134z + 0.239$	107.4	-72	-44	-52
(II) $-0.301x - 0.716y - 0.629z + 8.449$				
Low-temperature phase, molecule (2)				
(I) $0.719x - 0.694y - 0.018z + 1.454$	103.7	68	43	-55
(II) $0.364x + 0.732y - 0.574z + 3.789$				

* 180° has been subtracted to take account of the different sense.

Symmetry aspects of the phase transition

During the phase transition, the space group *Iba2* of the high-temperature phase changes to *Pbc2₁* of the low-temperature one, but the point group of the crystal remains the same. From the point of view of further experiments, it is important to know what kind of molecular movements can lead to the phase transition without changing the point-group symmetry of the crystal. Therefore, the group-theoretical analysis was performed in order to calculate wave and polarization vectors, which correspond to molecular movements and irreducible representation of the *Iba2* space group defining the symmetry of the low-temperature phase.

The orthorhombic unit cell of the high-temperature phase contains eight molecules, whereas there are only four molecules in the primitive cell. The basic vectors of the primitive unit cell are:

$$\begin{aligned} \mathbf{a}_1 &= (-\tau_x, \tau_y, \tau_z); & \mathbf{a}_2 &= (\tau_x, -\tau_y, \tau_z); \\ \mathbf{a}_3 &= (\tau_x, \tau_y, -\tau_z), \end{aligned} \quad (1)$$

where $2\tau_x = a$; $2\tau_y = b$; $2\tau_z = c$ are the lattice periods along the axes of the rectangular coordinate system. The basic vectors of the reciprocal lattice are thus given by:

$$\begin{aligned} \mathbf{b}_1 &= \left(0, \frac{\pi}{\tau_y}, \frac{\pi}{\tau_z}\right); & \mathbf{b}_2 &= \left(\frac{\pi}{\tau_x}, 0, \frac{\pi}{\tau_z}\right); \\ \mathbf{b}_3 &= \left(\frac{\pi}{\tau_x}, \frac{\pi}{\tau_y}, 0\right). \end{aligned} \quad (2)$$

In the Brillouin zone of the C_{2v}^{21} structure, only the line described by the vector:

$$\mathbf{k} = \mu(\mathbf{b}_1 + \mathbf{b}_2 - \mathbf{b}_3) = \left(0, 0, \frac{2\mu\pi}{\tau_z}\right); \quad -\frac{1}{2} < \mu < \frac{1}{2} \quad (3)$$

is relevant to the phase transition discussed because the point group of the wavevector group $G(\mathbf{k})$ is C_{2v} and all other points in the Brillouin zone have lower symmetry. Considering the translational symmetry of the crystal, if $\mu = \frac{1}{2}$, then the wavevector $\mathbf{k} = [0, 0, (\pi/\tau_z)]$ belongs to the boundary of the Brillouin zone and the basic vectors of the new phase can be chosen as:

$$\mathbf{a}'_1 = \mathbf{a}_2 + \mathbf{a}_3; \quad \mathbf{a}'_2 = \mathbf{a}_1 + \mathbf{a}_3; \quad \mathbf{a}'_3 = \mathbf{a}_1 + \mathbf{a}_2. \quad (4)$$

The volume of the new unit cell is then twice as great as the volume of the high-temperature primitive cell.

The wavevector \mathbf{k} defines only the translational symmetry of the low-temperature phase; the movements of molecules inside the unit cell are defined by the polarization vectors. The equivalent positions of eight molecules in the unit cell of the high-

temperature phase can be generated as follows:

$$\begin{aligned} \mathbf{w}_1 &= E \cdot \mathbf{w}; & \mathbf{w}_2 &= C_2^z \cdot \mathbf{w}; & \mathbf{w}_3 &= \sigma_x \cdot \mathbf{w} + (0, 0, \frac{1}{2}); \\ \mathbf{w}_4 &= \sigma_y \cdot \mathbf{w} + (0, 0, \frac{1}{2}); & \mathbf{w}_i &= \mathbf{w}_{i-4} + (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}); \end{aligned} \quad (5)$$

$$i = 5, 6, 7, 8,$$

where $\mathbf{w} = (x, y, z)$ stands for an atom coordinate vector. In the low-temperature phase, the molecules assigned as 1, 4, 6, 7 are no longer correlated by any symmetry operation with molecules numbered 2, 3, 5, 8 and, as a consequence, the primitive unit cell of this phase contains eight molecules. From the dynamical point of view, the movements of molecules leading to such a change of symmetry are described by the general translational-librational polarization vector, whose components correspond to the eight molecules in the high-temperature unit cell and are defined as:

$$\begin{aligned} \mathbf{P}_1 &= \begin{bmatrix} x \\ y \\ z \\ \theta \\ \varphi \\ \psi \end{bmatrix}; & \mathbf{P}_2 &= -C_2^z \cdot \mathbf{P}_1 = \begin{bmatrix} x \\ y \\ -z \\ \theta \\ \varphi \\ -\psi \end{bmatrix}; \\ \mathbf{P}_3 &= -\sigma_x \cdot \mathbf{P}_1 = \begin{bmatrix} x \\ -y \\ -z \\ -\theta \\ \varphi \\ \psi \end{bmatrix}; & \mathbf{P}_4 &= \sigma_y \cdot \mathbf{P}_1 = \begin{bmatrix} x \\ -y \\ z \\ -\theta \\ \varphi \\ -\psi \end{bmatrix}; \end{aligned} \quad (6)$$

$$\mathbf{P}_i = -\mathbf{P}_{i-4}; \quad i = 5, 6, 7, 8.$$

Such a movement associated with the structural transformation may be realized by only slight translation and or rotation of the molecules and should be related to the lowest energy excitation in the crystal.

Discussion

Structural studies of the NIPC crystal at 294 and 118 K provide interesting information about the nature of the phase transition. The most important information comes from thermal-vibration analysis. Extremely large librations of NIPC molecules around the greatest moment of inertia can be interpreted as a result of static or dynamic disorder. Static disorder is characterized by a double-well potential, while dynamic disorder can be described in terms of a flat-bottomed potential. Unfortunately, the limited accuracy of the rigid-body thermal-motion analysis does not allow the type of disorder in the NIPC crystal to be specified. Therefore, two different mechanisms of the phase transition can be suggested.

One way to approach the low-temperature phase is by freezing the orientational motions executed by

the molecules in the single-well potential. According to the group-theoretical analysis, this means that one of the six phonons described by the general polarization vector defined above would be expected to exhibit a soft-mode behaviour at the zone boundary of the high-temperature phase. This mode becomes a totally symmetric zone-centre phonon in the low-temperature phase; hence some symptoms of the soft-mode behaviour should be observed in the Raman spectra of this phase.

If static disorder is assumed for the high-temperature phase, the orientational motions should be understood as jumps of NIPC molecules between two statistically occupied potential wells. Such a system could be conveniently described by a pseudospin model in which the pseudospin operator takes values ± 1 , defining two possible molecular orientations. Then the phase transition could be interpreted as a freezing of the pseudospin-wave motion which would be described by the same polarization vector as in the case of a soft-phonon induced phase transition. From the experimental point of view, the quasielastic peak should be observed in the high-temperature phase in neutron scattering experiments. The width of this peak should decrease when the temperature of the phase transition is approached.

Usually, it is rather difficult to find examples of phase transitions in molecular crystals which would have such a 'pure' character as described above. Therefore, one should expect that the phase transition

in the NIPC crystal has a more complicated, mixed, order-disorder and displacive, nature.

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Centrosymmetric or Noncentrosymmetric?*

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Abstract

In cases where diffraction data do not provide a clear choice between a centrosymmetric and a noncentrosymmetric space group, it is better to opt for the centrosymmetric description even though disorder may result. The disorder model implies that the crystal is a composite of two or more molecular structures that cannot be distinguished from one another. On the other hand, attempts to refine a single, ordered model in the noncentrosymmetric space group (which

should lead to poor convergence because of near singularities) may lead to the erroneous conclusion that a unique structure has been found. Three examples of this latter situation are given.

One of the most troublesome problems in crystal-structure analysis is resolving the ambiguity between a centrosymmetric and a noncentrosymmetric space group when systematic absences are of no help. This ambiguity exists within many pairs of commonly occurring space groups, such as $P1-P\bar{1}$, $P2_1-P2_1/m$, $Cc-C2/c$, $Pna2_1-Pnam$, and many others. If the

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