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## Characterization of an Orientational Disorder in Two Charge-Transfer Complexes: Anthracene–Tetracyanobenzene (A–TCNB) and Naphthalene–Tetracyanobenzene (N–TCNB)

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#### Abstract

A problem of an orientational disorder in mixed-stack charge-transfer crystals has been addressed. New X-ray diffraction data, collected at several temperatures for A–TCNB and N–TCNB complexes, are reported. The data were analysed using conventional structure-refinement procedures and utilizing symmetry-adapted functions. The orientational probability functions allowed the disorder of donor sublattices to be characterized as dynamic in A–TCNB and static in N–TCNB crystals. Conclusions concerning the mechanisms of the orientational phase transitions in both crystals are supported by intensity measurements of some superlattice reflections. The structure of the low-temperature phase of the N–TCNB complex has been determined for the first time, the structure of pure TCNB has been redetermined at 294 K. In addition to observations

concerning characterization and mechanisms of the orientational disorder and instabilities, a general conclusion is drawn that the architecture of the mixed-stack charge-transfer crystals is governed by the close-packing principle. Crystal data at 294 K: A–TCNB, anthracene–1,2,4,5-benzenetetracarbonitrile (1/1),  $C_{14}H_{10}C_{10}H_2N_4$ ,  $M_r = 356.4$ ,  $C2/m$ ,  $a = 9.526$  (2),  $b = 12.780$  (3),  $c = 7.440$  (2) Å,  $\beta = 92.36$  (1)°,  $V = 905.0$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.307$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.74$  cm<sup>-1</sup>,  $R = 0.049$  for 916 observed reflections; N–TCNB, naphthalene–1,2,4,5-benzenetetracarbonitrile (1/1),  $C_{10}H_8C_{10}H_2N_4$ ,  $M_r = 306.3$ ,  $C2/m$ ,  $a = 9.420$  (2),  $b = 12.684$  (2),  $c = 6.880$  (1) Å,  $\beta = 107.46$  (3)°,  $V = 784.2$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.297$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.75$  cm<sup>-1</sup>,  $R = 0.040$  for 594 observed reflections; TCNB, 1,2,4,5-benzenetetracarbonitrile,  $C_{10}H_2N_4$ ,  $M_r = 178.2$ ,  $P2_1/a$ ,  $a = 13.698$  (3),  $b = 10.329$  (2),  $c = 6.577$  (2) Å,

$\beta = 112.10 (1)^\circ$ ,  $V = 862.2 (7) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.372 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$ ,  $\mu = 0.84 \text{ cm}^{-1}$ ,  $R = 0.046$  for 821 observed reflections.

### Introduction

Organic charge-transfer (CT) crystals, composed of planar aromatic electron-donor and electron-acceptor molecules, form columnar structures. The crystals with a predominantly neutral ground state (called weak CT complexes) crystallize in mixed stacks with uniformly spaced donor and acceptor molecules. The columnar architecture, being a compromise between close packing and CT interactions, is essential to the highly anisotropic nature of the crystals and allows a substantial orientational freedom of the molecules around plane normals. There is agreement about the orientational disorder in one (usually donor) or rarely two sublattices, but no adequate characterization of the disorder has been made. The need to characterize the disorder relates to the renewed interest in mixed-stack CT complexes mostly as a result of their intriguing phase transitions (Torrance, Vazques, Mayerle & Lee, 1981; Luty & Kuchta, 1986, 1987; Fyfe, Smith & Ripmeester, 1976), physical properties (ferromagnets, for example: Chittipeddi, Cromack, Miller & Epstein, 1987) and potential applications as memory devices (Stolarczyk & Piela, 1984). A precise characterization of the orientational disorder is essential to an understanding of the microscopic mechanisms of the phase transformations; slight orientational disorder may have a critical effect on optical, magnetic and transport properties.

The problem of the orientational disorder in mixed-stack CT crystals has been addressed in many papers and is still unresolved. The disorder is generally characterized by either of two extremes, statistical 'static' disorder which is describable as a double-well potential with the barrier much higher than  $kT$  or as dynamic disorder for which the energy diagram displays a flat-bottomed well. The phase transitions, which are initiated by the disorder, are then classified as order-disorder or displacive type, respectively. Studies of the phase transitions by resonant methods help to determine the disorder. However, one would expect that structure determinations provide the most direct information about the type of the disorder. The attempts depend on the analysis of difference Fourier maps or on rigid-body thermal-motion analysis. The conventional assessment of diffraction data can lead to chemically suspect results as the anisotropic thermal vibrations can effectively mask a substantial degree of the disorder. The thermal parameters may be artificial and camouflage an orientational disorder, as was shown in Fig. 3 of Boeyens & Levendis (1984). A definite characterization of the disorder from crystallographic analysis critically depends on the structural model and

variables used to describe rotational motions. The single-particle orientational potential can help us in both aspects of the problem.

It is important to stress that crystal structure analysis using the diffraction method determines a molecule in its effective, single-particle potential, as does every method which averages out a crystal over the reciprocal space. Thus, the shape of the orientational potential suggests whether angles (for strong, single-minimum potentials) or symmetry-adapted functions (for weak potentials with low energy barriers) should be used as variables to describe orientational probability functions. The proper choice of dynamical variables is also essential for analysis of the lattice dynamics of the crystals. The probability functions can be determined from a crystal structure analysis and compared with those calculated for a given single-particle orientational potential. The comparison allows the orientational disorder to be characterized.

The CT complexes of tetracyanobenzene (acceptor) with anthracene (A-TCNB) and naphthalene (N-TCNB) can serve as model systems to study the orientational disorder and, related to it, phase transitions. The characterization of the orientational disorder of anthracene molecules in A-TCNB has been addressed in recent papers (Fyfe *et al.*, 1976; Luty & Kuchta, 1986; Boeyens & Levendis, 1984; Stezowski, 1980), but the structural analyses (Boeyens & Levendis, 1984; Stezowski, 1980) gave controversial results. The analysis performed by Stezowski (1980) was based on conventional assessment of diffraction data in terms of the numerical agreement between the observed electron density and a dynamic molecular model with standard thermal parameters. Although it was difficult to draw any definite conclusions about the type of orientational disorder in the anthracene sublattice, the author suggested that it was dynamic. Boeyens & Levendis (1984) did not agree with the conclusions, reanalysed the diffraction data in terms of a structural model of disorder based on numerical calculations of an orientational potential, and finally concluded a static disorder of the anthracene molecules in the high-temperature (HT) phase of the A-TCNB crystal. This also contradicts recent studies of the phase transition in the A-TCNB crystal (Luty & Kuchta, 1986; Mierzejewski, Ecolivet, Pawley, Luty, Lemée & Girard, 1988), where a displacive transformation and dynamic disorder were found. The reason why the conclusion reached by Boeyens & Levendis (1984) is incorrect is that instead of constructing a model of disorder based on the single-particle orientational potential, the authors used the so-called concerted motion model based on a crystal potential for particular, correlated motions of the anthracene molecules. This is actually an important inconsistency as the authors in their calculations simulated the librational phonon mode (the critical one from the Brillouin zone boundary, with respect to which

the crystal is unstable and thus the crystal potential has a double minimum), which obviously cannot be observed by X-ray diffraction. The problem of orientational disorder in A-TCNB, as well as in N-TCNB, still requires careful experimental studies.

In the present paper, new X-ray diffraction data, collected at various temperatures for A-TCNB and N-TCNB, are reported with the aim of characterizing the orientational disorder in the crystals. The data were analysed using a conventional structure refinement procedure (*SHELX76*; Sheldrick, 1976) and a procedure utilizing symmetry-adapted functions (Press & Hüller, 1973; Lefebvre, Fouret & Zeyen, 1984). The orientational probability functions were compared with those calculated for the known single-particle orientational potentials (Luty & Kuchta, 1986). The comparison provided information on the nature of the disorder in the donor sublattice of the crystals as well as on the mechanisms of the orientational phase transitions. The choice of the crystals, A-TCNB and N-TCNB, was very fortunate as it has been found that these crystals correspond to two extreme cases: dynamic and static disorder, respectively. Conclusions concerning the mechanisms of the phase transitions in the both crystals are supported by intensity measurements of superlattice reflections as a function of temperature and precise thermal-expansion measurements in a large temperature range for the A-TCNB crystal. Furthermore, the structure of the pure TCNB crystal was redetermined with the aim of obtaining precise information about the molecular geometry. It could be useful in an analysis of possible molecular distortions caused by charge transfer in the complex crystal.

### Experimental

TCNB was prepared according to the method described by Bailey, Henn & Langdon (1963). The final product was identified by checking its melting point and lattice parameters. A single crystal,  $0.3 \times 0.3 \times 0.4$  mm, was used for data collection. The experiment was performed at one temperature (294 K) only.

Stoichiometric mixtures of TCNB and anthracene (or naphthalene) were dissolved in pure acetone. Red A-TCNB crystals and yellow N-TCNB crystals were grown from the solutions by slow evaporation. Two A-TCNB crystals were used in the diffraction experiments; dimensions of the crystal measured at 294 K were  $0.4 \times 0.5 \times 0.6$  mm, while the dimensions of the crystal measured at 225 and 65 K were  $0.3 \times 0.4 \times 0.4$  mm. Only one N-TCNB sample, dimensions  $0.3 \times 0.4 \times 0.4$  mm, was used in all experiments. In contrast to Kumakura, Iwasaki & Saito (1967), our N-TCNB sample was a single crystal.

Intensity measurements were performed with the automatic X-ray diffractometer recently built in our

laboratory by Odou & More (1989). The incident X-ray beam [ $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ ] was monochromatized with a pyrolytic graphite crystal. Unit-cell dimensions of each sample were refined from the positions of 25 selected reflections. The  $\omega$ -scan mode was utilized with  $2 < \omega < 30^\circ$  ( $0.05 < (\sin\omega)/\lambda < 0.70 \text{ \AA}^{-1}$ ). In all experiments, the total scan width was kept constant ( $\Delta\omega = 1.5^\circ$ ) and the scan speed was  $0.015^\circ \text{ s}^{-1}$ .

Different data-collection procedures were followed for the HT and LT phases. For the HT phases, the reflection intensity was first integrated, then the background intensity was counted on each side of the Bragg peak for half of the total scan time. The step-scanning method was employed for measurements of the LT phases where superlattice reflections usually have low intensity. The procedure started from a fast prescan to exclude reflections of negligible intensity. Each reflection was then scanned in 100 steps with a counting time of 1 s per measured point. The scan could be repeated up to three times as the total number of counts reached 800. Intensity changes of three standard reflections were checked every 2 h at room temperature and at 1 h intervals at low temperatures. Any significant variation was observed.

Crystal data and details of the structure refinement are given in Table 1. The intensity data were corrected for Lorentz-polarization factors, but no extinction or absorption corrections were made. In all the experiments the maximum value of  $\mu R$  was around 0.03. The scattering factors of C, N and H atoms were approximated using the analytical expression with  $a_i$ ,  $b_i$  and  $c$  coefficients from *International Tables for X-ray Crystallography* (1974). For all seven studied structures, the maximum shift in the last cycle was lower than  $0.1\sigma$ .

All the three crystals, pure TCNB, A-TCNB and N-TCNB, crystallize in the monoclinic system. In the TCNB crystal, systematic absences of  $0k0$  reflections with  $k = 2n + 1$  and  $h0l$  reflections with  $h = 2n + 1$  suggested space group  $P2_1/a$ . The four molecules occupy general positions in the primitive cell.

Analysis of the systematic absences in diffraction patterns of the A-TCNB and N-TCNB crystals at 65 K showed that the LT phases of both crystals are isostructural. The absences of the  $0k0$  reflections with  $k$  odd and  $h0l$  with  $h$  odd again indicated space group  $P2_1/a$ . The primitive cell contains two complex units with molecules situated at  $C_i$  positions. Assuming that the donor molecules are at  $2(a)$  positions  $(0,0,0$  and  $\frac{1}{2}, \frac{1}{2}, 0)$ , the TCNB molecules have to occupy  $2(b)$  positions  $(0,0, \frac{1}{2}$  and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  to preserve the mixed-stack structure of the complex.

The HT phases of both crystals are also isostructural. The systematic absences of the  $hkl$  reflections with  $h + k$  odd correspond to a  $C$ -face-centred unit cell which can be described by one of three possible space

Table 1. Data-collection and refinement parameters

Formula	TCNB		A-TCNB			N-TCNB		
	$C_{10}H_8N_4$ 178.2		$C_{14}H_{10}C_{10}H_2N_4$ 356.4			$C_{10}H_8C_{10}H_2N_4$ 306.3		
$T$ (K)	294		294	225	65	294	95	65
Space group	$P2_1/a$		$C2/m$	$C2/m$	$P2_1/a$	$C2/m$	$C2/m$	$P2_1/a$
$Z$	2		2	2	2	2	2	2
$a$ (Å)	13.698 (3)		9.526 (2)	9.509 (2)	9.441 (2)	9.420 (2)	9.335 (3)	9.337 (3)
$b$ (Å)	10.329 (2)		12.780 (3)	12.724 (4)	12.650 (4)	12.684 (2)	12.611 (6)	12.554 (6)
$c$ (Å)	6.577 (2)		7.440 (2)	7.384 (2)	7.299 (1)	6.880 (1)	6.748 (3)	6.738 (2)
$\beta$ (°)	112.10 (1)		92.36 (1)	92.66 (2)	93.11 (2)	107.46 (3)	107.50 (3)	107.40 (2)
$V$ (Å <sup>3</sup> )	862.2 (7)		905.0 (7)	892.4 (7)	870.4 (6)	784.2 (4)	757.6 (9)	753.7 (8)
$D_x$ (g cm <sup>-3</sup> )	1.372		1.307	1.326	1.359	1.297	1.342	1.349
$\mu$ (cm <sup>-1</sup> )	0.84		0.74	0.76	0.77	0.75	0.77	0.78
No. of measured reflections	2634		1467	2905	1584	1594	2293	2833
No. of observed reflections [ $I > 3\sigma(I)$ ]	821		916	676	1414	594	794	1270
$g^*$	$2 \times 10^{-4}$		$1 \times 10^{-4}$	$1 \times 10^{-4}$	$2 \times 10^{-4}$	$3 \times 10^{-4}$	$1.5 \times 10^{-4}$	$7 \times 10^{-4}$
$R$	0.046		0.049	0.049	0.036	0.040	0.037	0.035
$wR$	0.039		0.054	0.044	0.044	0.037	0.036	0.038
No. of parameters	135		77	77	151	96	91	131
$h, k, l$ range	$-17 \leq h \leq 17, 0 \leq k \leq 14,$ $0 \leq l \leq 8$		$-13 \leq h \leq 13, 0 \leq k \leq 17, 0 \leq l \leq 10$	$\dagger$	$\dagger$	$-13 \leq h \leq 13, 0 \leq k \leq 17, 0 \leq l \leq 9$	$\dagger$	$\dagger$
$\Delta\rho$ (e Å <sup>-3</sup> )	+0.16 -0.16		+0.20 -0.17	+0.17 -0.19	+0.35 -0.25	+0.16 -0.19	+0.38 -0.23	+0.39 -0.20
$S$	0.49		0.43	0.55	0.45	0.41	0.49	0.38

\* The weighting scheme is  $w = [\sigma^2(F) + gF^2]^{-1}$ .

† Friedel reflections measured.

‡ Reflections of layers  $l = 5, 6$  and  $7$  repeated.

groups:  $C2/m$ ,  $Cm$  or  $C2$ . The problem of a proper symmetry choice will be discussed below. The primitive cell is two times smaller than that in the LT phase and contains only one complex unit.

### Conventional structure determination

#### Refinement procedure

The crystal structure of pure TCNB was refined by *SHELX76* (Sheldrick, 1976) starting from the atom positions published by Prout & Tickle (1973). Thermal motions of the C and N atoms were described by anisotropic parameters, while the H-atom motions were assumed to be isotropic. In the refinement procedure, final residual factors  $R = 0.046$  and  $wR = 0.039$  were achieved. The atom positions corresponding to the best  $R$  values are listed in Table 2.\*

The HT structure of the A-TCNB crystals was previously determined by Tsuchiya, Marumo & Saito (1972) and Stezowski (1980) assuming  $Cm$  symmetry. Such a space-group choice was strongly criticized by Boeyens & Levendis (1984) who argued for  $C2/m$  symmetry. We agree with the latter opinion and  $C2/m$  symmetry was adopted for the A-TCNB crystals in the present studies. An initial set of parameters used in *SHELX76* was obtained by averaging coordinates of two equivalent C (or N) atoms reported by Stezowski. A Fourier synthesis map calculated after a few cycles of

the refinement allowed us to localize H atoms. Anisotropic temperature factors for C and N atoms and isotropic ones for H atoms were then introduced. The final residual factors  $R$  and  $wR$  were 0.049 and 0.054, respectively. The A-TCNB structure at 225 K was refined in the same way starting from an initial parameter set, which consisted of the best atom coordinates found at 294 K. In this case, the final  $R$  and  $wR$  residual factors were 0.049 and 0.044, respectively.

The LT phase structure of the A-TCNB complex was determined at 65 K. The refinement started from the parameters of the C and N atoms obtained by Stezowski (1980) at 119 K. The positions of the H atoms were found from the Fourier synthesis map. Thermal motions of the C and N atoms were described by anisotropic temperature factors. Attempts were also made to introduce anisotropic factors for the H atoms but convergence was not improved significantly. Therefore, isotropic factors were again used in the final stages of this refinement, which converged to  $R = 0.036$  and  $wR = 0.044$ .

The structure of the N-TCNB crystal at room temperature was solved for the first time by Kumakura *et al.* (1967) using a set of structure factors obtained with a twinned crystal. In this paper attempts were made to refine the structure with well-oriented naphthalene molecules at  $(0,0,\frac{1}{2})$  sites but the residual factor was very poor:  $R = 0.28$ . The refinement procedure was repeated assuming orientational disorder of the naphthalene molecules and the  $R$  factor decreased to a value of 0.165. The above structure-determination procedure was used in our studies to elaborate diffraction data for the N-TCNB crystals measured at 294 K. Positions of the C and N atoms published by Kumakura *et al.* (1967) formed the initial

\* Lists of structure factors, anisotropic thermal parameters, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51652 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

$U_{\text{eq}} = \frac{1}{3} \text{trace}(U)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>					
<b>(a) TCNB, 294 K</b>					<b>(e) N-TCNB, 294 K</b>									
C(1)	2910 (2)	5458 (2)	4193 (4)	39 (4)	C(1)	-187 (27)	537 (3)	-194 (31)	42 (14)					
C(2)	1838 (2)	5533 (2)	3816 (4)	45 (3)	C(2)	882 (6)	1323 (5)	333 (6)	65 (6)					
C(3)	1147 (2)	6174 (3)	1986 (4)	50 (4)	C(3)	2354 (11)	1068 (9)	1018 (10)	57 (11)					
C(4)	1536 (2)	6736 (2)	529 (4)	43 (3)	C(12)	-1753 (9)	777 (7)	-782 (9)	71 (8)					
C(5)	2612 (2)	6662 (2)	919 (4)	44 (4)	C(13)	-2780 (5)	-61 (24)	-1216 (6)	57 (14)					
C(6)	3298 (2)	6023 (3)	2758 (4)	46 (4)	H(2)	516 (41)	2064 (32)	127 (73)	84 (15)					
C(7)	3615 (2)	4767 (3)	6084 (4)	53 (4)	H(3)	3055 (54)	1593 (37)	1252 (62)	73 (14)					
C(8)	1457 (2)	4932 (3)	5368 (5)	57 (4)	H(12)	-2086 (132)	1469 (71)	-989 (145)	153 (58)					
C(9)	859 (2)	7411 (3)	-1414 (4)	60 (4)	H(13)	-3867 (34)	269 (31)	-1705 (43)	55 (10)					
C(10)	3000 (2)	7264 (3)	-604 (4)	60 (4)	C(5)	0	1104 (2)	5000	45 (2)					
N(7)	4167 (2)	4207 (3)	7559 (4)	74 (3)	C(6)	1330 (2)	554 (1)	5560 (2)	39 (1)					
N(8)	1200 (2)	4468 (3)	6658 (4)	93 (4)	C(7)	2718 (2)	1120 (1)	6144 (3)	49 (2)					
N(9)	378 (2)	7950 (3)	-2979 (4)	89 (4)	N(8)	3818 (2)	1567 (1)	6619 (3)	65 (2)					
N(10)	3280 (2)	7747 (2)	-1835 (4)	107 (4)	H(5)	0	1870 (20)	5000	51 (6)					
H(3)	434 (17)	6220 (20)	1719 (33)	51 (6)	<b>(f) N-TCNB, 95 K</b>									
H(6)	4041 (18)	5989 (22)	3019 (34)	59 (7)	C(1)	-242 (4)	543 (2)	-118 (17)	19 (5)					
<b>(b) A-TCNB, 294 K</b>					<b>(g) N-TCNB, 65 K</b>									
C(1)	0	1079 (2)	0	64 (2)	C(2)	840 (3)	1359 (2)	313 (4)	20 (2)					
C(2)	1176 (1)	555 (1)	-548 (2)	55 (1)	C(3)	2346 (4)	1132 (3)	995 (4)	19 (3)					
C(3)	2406 (2)	1084 (1)	-1136 (3)	88 (3)	C(12)	-1819 (3)	754 (2)	-829 (4)	23 (2)					
C(4)	3517 (2)	536 (3)	-1649 (2)	147 (7)	C(13)	-2834 (2)	-106 (3)	-1252 (3)	17 (1)					
H(1)	0	1829 (22)	0	86 (6)	H(2)	477 (27)	2079 (19)	90 (49)	22 (7)					
H(3)	2175 (23)	1863 (20)	-1138 (33)	146 (8)	H(3)	3079 (38)	1692 (22)	1275 (44)	22 (7)					
H(4)	4360 (26)	922 (22)	-2053 (28)	167 (7)	H(12)	-2163 (63)	1491 (33)	-1112 (73)	43 (18)					
C(5)	0	1096 (2)	5000	48 (1)	H(13)	-3958 (22)	151 (31)	-1770 (30)	15 (7)					
C(6)	1178 (1)	548 (1)	4504 (1)	42 (1)	C(5)	0	1119 (1)	5000	16 (1)					
C(7)	2412 (1)	1111 (1)	3987 (2)	52 (1)	C(6)	1345 (1)	558 (1)	5569 (2)	15 (1)					
N(8)	3375 (1)	1566 (1)	3583 (2)	74 (1)	C(7)	2750 (1)	1129 (1)	6164 (2)	19 (1)					
H(5)	0	1846 (17)	5000	55 (5)	N(7)	3870 (1)	1579 (1)	6648 (2)	25 (1)					
<b>(c) A-TCNB, 225 K</b>					<b>(g) N-TCNB, 65 K</b>									
C(1)	0	1085 (3)	0	51 (4)	C(1)	-237 (2)	541 (1)	-140 (2)	13 (1)					
C(2)	1181 (2)	557 (2)	-549 (2)	45 (2)	C(2)	859 (2)	1362 (1)	286 (2)	14 (1)					
C(3)	2406 (3)	1091 (3)	-1134 (3)	70 (4)	C(3)	2359 (2)	1118 (1)	975 (2)	15 (1)					
C(4)	3522 (3)	543 (3)	-1646 (3)	114 (7)	C(12)	-1801 (2)	767 (1)	-843 (2)	16 (1)					
H(1)	0	1825 (25)	0	63 (9)	C(13)	-2837 (2)	-39 (1)	-1247 (2)	17 (1)					
H(3)	2258 (26)	1875 (22)	-1130 (34)	112 (10)	H(2)	493 (19)	2085 (13)	59 (23)	16 (3)					
H(4)	4340 (27)	968 (22)	-2058 (30)	136 (9)	H(3)	3084 (20)	1689 (14)	1286 (26)	23 (4)					
C(5)	0	1101 (2)	5000	38 (3)	H(12)	-2163 (20)	1532 (13)	-1088 (25)	19 (4)					
C(6)	1181 (2)	549 (1)	4506 (2)	33 (2)	H(13)	-3946 (24)	119 (13)	-1772 (29)	26 (4)					
C(7)	2418 (2)	1119 (1)	3995 (2)	40 (2)	C(5)	-24 (1)	1124 (1)	4977 (2)	12 (1)					
N(8)	3384 (2)	1573 (1)	3586 (2)	57 (2)	C(6)	1336 (1)	576 (1)	5556 (2)	11 (1)					
H(5)	0	1867 (21)	5000	45 (7)	C(7)	2725 (1)	1163 (1)	6157 (2)	14 (1)					
<b>(d) A-TCNB, 65 K</b>					<b>(g) N-TCNB, 65 K</b>									
C(1)	-177 (2)	1098 (1)	108 (2)	17 (1)	N(8)	3840 (1)	1625 (1)	6668 (2)	18 (1)					
C(2)	1095 (1)	690 (1)	-491 (2)	14 (1)	C(16)	-1357 (1)	547 (1)	4426 (2)	11 (1)					
C(3)	2219 (2)	1362 (1)	-1015 (2)	18 (1)	C(17)	-2770 (1)	1100 (1)	3842 (2)	12 (1)					
C(4)	3448 (2)	952 (1)	-1593 (2)	21 (1)	N(18)	-3906 (1)	1540 (1)	3388 (2)	18 (1)					
C(12)	-1281 (1)	434 (1)	603 (2)	15 (1)	H(5)	-38 (17)	1884 (15)	4970 (22)	16 (3)					
C(13)	-2586 (2)	831 (1)	1239 (2)	22 (1)	<p>naphthalene molecules then had to occupy two equilibrium positions generated by the mirror plane to preserve <math>2/m</math> site symmetry. Each of the equilibrium positions possessed a site-occupation factor of 0.5. Molecules in the TCNB sublattice were kept ordered. The same refinement procedure as for TCNB and A-TCNB was used leading to low residual factors: <math>R = 0.040</math> and <math>wR = 0.037</math>. The N-TCNB structure at 95 K was solved in the same way using coordinates of the C and N atoms found at 294 K to create the initial set of parameters. At this temperature, the C(3') atom of the disordered naphthalene molecule is close to the mirror plane. Therefore, attempts to fit its anisotropic temperature factor failed owing to strong correlations between variable parameters. Despite of this limitation, final residual factors <math>R = 0.037</math> and <math>wR = 0.036</math> were achieved.</p> <p>The structure of the N-TCNB complex in its LT phase (at 65 K) was solved for the first time. As a</p>									
C(14)	-3635 (2)	161 (1)	1708 (2)	24 (1)										
C(5)	-41 (2)	1113 (1)	4986 (2)	14 (1)										
C(6)	1170 (1)	582 (1)	4497 (2)	12 (1)										
C(7)	2388 (2)	1173 (1)	3952 (2)	15 (1)										
N(8)	3339 (1)	1648 (1)	3503 (2)	19 (1)										
C(16)	-1213 (1)	534 (1)	5485 (2)	13 (1)										
C(17)	-2483 (2)	1077 (1)	5964 (2)	16 (1)										
N(18)	-3488 (1)	1518 (1)	6326 (2)	22 (1)										
H(1)	-331 (16)	1859 (13)	202 (20)	15 (3)										
H(3)	2068 (19)	2136 (14)	-996 (24)	34 (4)										
H(4)	4212 (21)	1406 (14)	-2003 (24)	31 (4)										
H(13)	-2568 (19)	1602 (13)	1369 (22)	28 (4)										
H(14)	-4574 (19)	450 (14)	2183 (23)	27 (4)										
H(5)	-98 (17)	1851 (13)	4955 (21)	19 (3)										

set of parameters for *SHELX76*. The structure refinement with the assumption of well-ordered naphthalene molecules at the 2(a) sites again gave a very poor result: the  $R$  factor was 0.20. Following Kumakura *et al.* (1967), orientational disorder was introduced in the naphthalene sublattice. The molecular symmetry was relaxed to  $C_1$ ; the molecular center of inversion coincided with the inversion center of the 2(a) site. The

Table 3. Selected bond lengths (Å) and bond angles (°)

(a) TCNB molecule	TCNB		A-TCNB		N-TCNB		
	294 K	294 K	225 K	65 K	294 K	95 K	65 K
C(5)-C(6)	1.385 (4)	1.386 (2)	1.388 (2)	1.390 (3)	1.384 (2)	1.391 (1)	1.392 (2)
C(6)-C(7)	1.445 (5)	1.444 (1)	1.446 (2)	1.444 (3)	1.440 (2)	1.444 (1)	1.439 (2)
C(6)-C(6')	1.398 (4)	1.400 (2)	1.398 (3)	1.412 (2)	1.404 (3)	1.408 (2)	1.410 (2)
C(7)-N(8)	1.136 (4)	1.137 (2)	1.138 (2)	1.144 (2)	1.140 (2)	1.147 (2)	1.152 (2)
C(5)-H(5)	0.947 (26)	0.958 (21)	0.974 (26)	0.935 (17)	0.972 (24)	0.983 (18)	0.954 (19)
C(6)-C(5)-C(6'')	119.1 (3)	119.3 (2)	119.2 (1)	119.3 (1)	119.4 (1)	118.8 (1)	119.0 (1)
C(6)-C(5)-H(5)	120.4 (14)	120.4 (8)	120.4 (9)	120.4 (14)	120.3 (9)	120.6 (6)	120.5 (12)
C(5)-C(6)-C(7)	120.6 (3)	119.7 (1)	119.5 (1)	119.8 (2)	119.8 (1)	119.5 (1)	119.7 (1)
C(5)-C(6)-C(6')	120.4 (3)	120.4 (1)	120.4 (1)	120.3 (1)	120.3 (1)	120.6 (1)	120.5 (1)
C(7)-C(6)-C(6')	119.0 (3)	119.9 (1)	120.1 (1)	119.8 (1)	119.9 (1)	119.9 (1)	119.8 (1)
C(6)-C(7)-N(8)	177.6 (4)	179.1 (1)	179.5 (2)	179.0 (2)	179.6 (2)	179.6 (1)	179.2 (2)

(b) Anthracene molecule	Anthracene*		A-TCNB		(c) Naphthalene molecule				
	294 K	294 K	225 K	65 K	Naphthalene†		N-TCNB		
					294 K	294 K	95 K	65 K	
C(1)-C(2)	1.399 (3)	1.381 (2)	1.385 (2)	1.400 (3)	C(1)-C(2)	1.425 (3)	1.414 (23)	1.419 (7)	1.421 (3)
C(2)-C(3)	1.433 (3)	1.437 (2)	1.432 (3)	1.430 (2)	C(1)-C(1')	1.410 (6)	1.412 (10)	1.436 (4)	1.424 (2)
C(2)-C(2')	1.436 (4)	1.418 (3)	1.419 (4)	1.435 (2)	C(2)-C(3)	1.361 (4)	1.385 (19)	1.392 (5)	1.371 (3)
C(3)-C(4)	1.366 (4)	1.337 (4)	1.339 (4)	1.361 (3)	C(3)-C(3')	1.421 (6)	1.333 (31)	1.365 (5)	1.421 (2)
C(4)-C(4')	1.419 (6)	1.371 (8)	1.382 (5)	1.422 (2)	C(2)-H(2)	—	0.962 (72)	0.975 (35)	0.990 (19)
C(1)-H(1)	—	0.959 (28)	0.942 (30)	0.977 (16)	C(3)-H(3)	—	0.990 (44)	1.007 (28)	0.988 (24)
C(3)-H(3)	—	1.020 (25)	1.008 (26)	0.986 (20)	C(2)-C(1)-C(1')	119.2 (2)	118.7 (16)	118.8 (6)	119.0 (1)
C(4)-H(4)	—	1.000 (27)	1.006 (26)	1.008 (21)	C(2)-C(1)-C(2')	121.5 (3)	121.6 (14)	122.4 (5)	121.9 (1)
C(2)-C(1)-C(2'')	121.0 (4)	122.0 (1)	122.0 (2)	121.5 (1)	C(1)-C(2)-C(3)	120.2 (3)	119.5 (11)	120.0 (5)	120.6 (1)
C(2)-C(1)-H(1)	—	119.0 (10)	119.0 (11)	119.2 (9)	C(1)-C(2)-H(2)	—	118.8 (47)	118.1 (24)	118.5 (11)
C(1)-C(2)-C(3)	121.8 (4)	122.9 (1)	122.7 (2)	122.2 (1)	C(3)-C(2)-H(2)	—	121.6 (46)	121.8 (23)	120.8 (11)
C(1)-C(2)-C(2')	119.5 (2)	119.0 (1)	119.0 (2)	119.2 (1)	C(2)-C(3)-C(3')	120.5 (2)	121.4 (13)	121.2 (3)	120.3 (1)
C(3)-C(2)-C(2')	118.7 (2)	118.1 (1)	118.3 (2)	118.6 (1)	C(2)-C(3)-H(3)	—	113.7 (27)	116.3 (17)	120.0 (13)
C(2)-C(3)-C(4)	120.6 (3)	120.4 (2)	120.3 (3)	121.0 (1)	C(3')-C(3)-H(3)	—	124.9 (28)	122.6 (18)	119.7 (13)
C(2)-C(3)-H(3)	—	106.3 (14)	110.7 (15)	117.7 (11)					
C(4)-C(3)-H(3)	—	133.2 (14)	129.0 (15)	121.3 (11)					
C(3)-C(4)-C(4')	120.7 (2)	121.6 (2)	121.4 (3)	120.5 (1)					
C(3)-C(4)-H(4)	—	118.8 (14)	116.1 (15)	121.4 (11)					
C(4')-C(4)-H(4)	—	119.6 (14)	122.5 (15)	118.3 (11)					

\* Cruickshank (1956).

† Cruickshank (1957).

starting point, an assumption was made that the lattice was well ordered at this temperature. In terms of  $P2_1/a$  symmetry requirements, this means that the naphthalene molecules are frozen in one of the two possible equilibrium orientations existing in the HT phase. The refinement procedure started with atomic parameters obtained at 95 K. After several cycles, residual factors  $R = 0.043$  and  $wR = 0.045$  were achieved by fitting the anisotropic temperature factors for the C and N atoms and the isotropic ones for the H atoms. A Fourier synthesis map was prepared at this stage of the refinement. It revealed several peaks with heights of about  $0.5 e \text{ \AA}^{-3}$  close to the second naphthalene equilibrium position in the HT phase and the conclusion was drawn that the lattice was not completely ordered. There was a small number of the naphthalene molecules persisting in the second orientation. The disorder was taken into account in the further steps of the refinement by introducing a new parameter describing the probability of the naphthalene molecule being in the first ( $P^+$ ) or in the second ( $P^- = 1 - P^+$ ) orientation. The procedure started with atomic coordinates of the naphthalene molecule in the second orientation generated from those in the first orientation by the mirror plane in the HT phase. To decrease the number of the fitted parameters, a common isotropic

temperature factor was introduced for all the heavy atoms with the probability  $P^-$ . The H atoms were neglected. This was justified because the probability of finding the naphthalene molecule in the first orientation ( $P^+ = 0.952_4$ ) was much larger than in the second one. Finally, the residual factors  $R = 0.035$  and  $wR = 0.038$  were achieved. The common isotropic temperature factor was  $0.020_4 \text{ \AA}^2$ .

### Results and discussion

The final atomic coordinates and equivalent isotropic temperature factors for the seven studied structures are presented in Table 2. Bond lengths and bond angles are given in Table 3. The symmetry of the naphthalene and anthracene molecules at 65 K is lower than  $2/m$  but the distortions are very small. Therefore, the corresponding entries in Table 3 are mean values of the equivalent bonds and angles, respectively. Numbering of the atoms is shown in Fig. 1.

Projections of the both complex structures along **b** are presented in Fig. 2, drawn using ORTEPII (Johnson, 1976). It is evident from the figure that the TCNB, anthracene and naphthalene molecules are planar in these lattices. Therefore, equations of the least-square planes passing through the heavy atoms

were calculated and are reported in Table 4. Standard deviations of the atoms from the best planes are small enough to justify the approximation of the planar molecules. As can be seen in Fig. 2, mixed stacks of donor and acceptor molecules are formed along the  $c$  axis in A-TCNB and N-TCNB crystals. However, the inclination  $\nu_0$  of the molecular planes with respect to the  $a$  axis is different in both structures (see Table 4). In N-TCNB, normals to the TCNB and naphthalene planes are parallel and coincide with  $c$  axis. In A-TCNB, the normals to the TCNB and anthracene planes make an angle of about  $2^\circ$  and are inclined at  $22^\circ$ , on average, to the  $c$  axis. As a consequence, the mass centers of both molecules do not lie on the normal connecting the donor and acceptor planes in the complex unit. The relative departure of both the mass centers from normal, called overlap, is about  $1.34 \text{ \AA}$  in

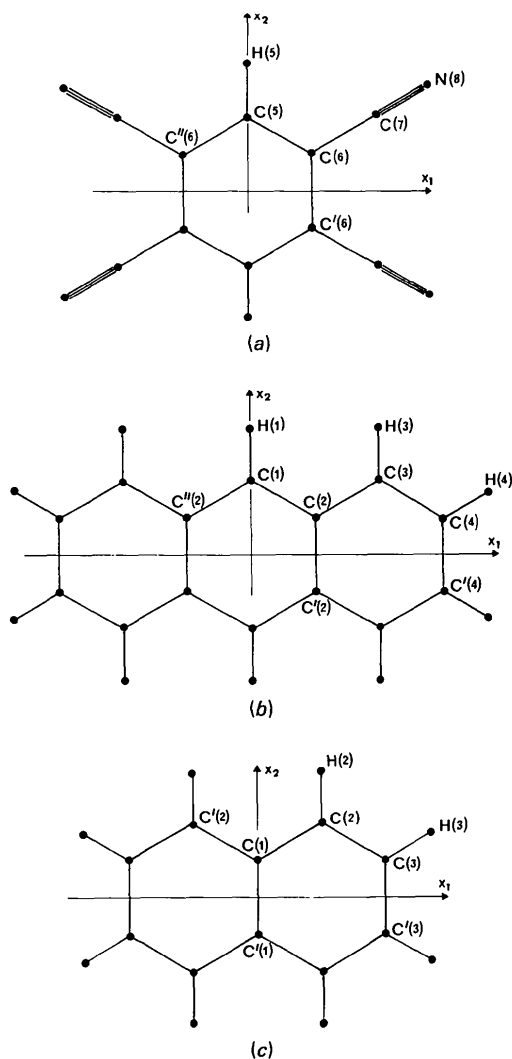


Fig. 1. Numbering of atoms in (a) TCNB, (b) anthracene and (c) naphthalene molecules. Molecular axes are marked.

this case. The value corresponds roughly to the radius of the benzene ring. In the N-TCNB complex, the overlap is about zero. In the both cases, the overlaps are almost temperature independent (see Table 5). Such an arrangement of donor and acceptor molecules is a simple consequence of the close-packing principle. It is best seen in Fig. 3, which shows a projection of the complex units along the normal to the molecular planes. The distance between successive molecules in the stacks is almost the same for the N-TCNB and A-TCNB complexes. Roughly, it corresponds to the thickness of an aromatic molecule [ $3.40 \text{ \AA}$  according to Pauling (1960)]. When the temperature is lowered, the distance decreases markedly leading to considerable changes in the overlap of the  $\pi$  orbitals of the donor and acceptor molecules. As a result, the CT absorption band is considerably shifted towards higher energies (Steudle, Von Schütz & Möhwald, 1978). It is important to note that TCNB at the  $(0,0,\frac{1}{2})$  site and anthracene at the  $(1,0,0)$  site, for example, lie on the same  $(102)$  plane. The long axes of both the molecules tend to be coaxial along the  $[20\bar{1}]$  direction. However, such an arrangement is frustrated by the steric hindrance of the cyano

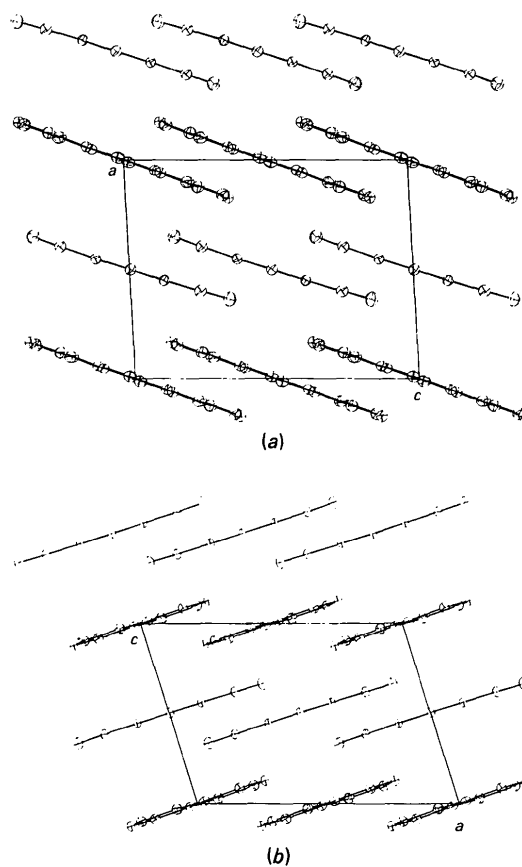


Fig. 2. Packing projection along the  $b$  axis at 65 K for (a) A-TCNB and (b) N-TCNB.

Table 4. *Least-squares planes for A-TCNB and N-TCNB*

Normals of the least-squares planes are given in the form  $px + qy + rz = s$ .  $\sigma$  is the standard deviation. The axes of the orthogonal coordinate system are along **a**, **b** and **c\***. For definitions of  $\nu_0$  and  $\psi_0$  see text.

TCNB	A-TCNB			N-TCNB		
	294 K	225 K	65 K	294 K	95 K	65 K
<i>P</i>	0.3074	0.3041	0.2983	-0.3088	-0.3071	-0.3048
<i>q</i>	0	0	0.0325	0	0	-0.0075
<i>r</i>	0.9516	0.9526	0.9539	0.9511	0.9517	0.9524
<i>s</i> (Å)	3.490	3.461	3.417	3.440	3.374	3.369
$\sigma$ (Å)	0.001	0.002	0.014	0.003	0.002	0.012
$\nu_0$ (°)	72.1	72.3	72.6	108.0	107.9	107.7
$\psi_0$ (°)	0	0	1.4	0	0	0.8
A or N						
<i>P</i>	0.3390	0.3357	0.3343	-0.3203	-0.3194	-0.3183
<i>q</i>	0	0	-0.0119	0.0191	0.0212	0.0344
<i>r</i>	0.9408	0.9420	0.9424	0.9471	0.9474	0.9474
<i>s</i> (Å)	0	0	0	0	0	0
$\sigma$ (Å)	0.003	0.003	0.004	0.030	0.004	0.003
$\nu_0$ (°)	70.2	70.4	70.5	108.7	108.6	108.6
$\psi_0$ (°)	0	0	7.8	16.8	18.4	17.4

Table 5. *Distance and overlap between two consecutive molecules on a stack*

	A-TCNB			N-TCNB		
	294 K	225 K	65 K	294 K	95 K	65 K
Distance <i>d</i> (Å)	3.468	3.439	3.394	3.440	3.374	3.369
Overlap $\delta$ (Å)	1.346	1.342	1.341	0.052	0.044	0.045

groups in the TCNB molecule. For example, an average H-N distance for A-TCNB at 225 K is 2.602 Å (see Fig. 4), slightly smaller than the sum of the corresponding van der Waals radii:  $r_H + r_N = 2.66$  Å. Therefore, interactions between the H atoms of the donor molecule and the N atoms of the acceptor molecule are some of the strongest in the lattices. It suggests that the A-TCNB crystal should be considered as a layer structure built up of (102) sheets of TCNB and anthracene molecules. The same situation exists in the N-TCNB crystal. The TCNB and naphthalene molecules form (10 $\bar{2}$ ) planes inside which the specific competition between an orienting field of the naphthalene molecules and the steric hindrance of the TCNB molecules takes place. However, the H-N distance is 2.32 Å at 95 K when the naphthalene molecule is coaxial with the TCNB molecule and is shorter than the sum of the hydrogen and nitrogen van der Waals radii. Therefore, the naphthalene molecule has to turn right or left with respect to the TCNB long axis to reach minimum-energy positions. In such positions, the H-N distance is elongated to 2.682 Å as can be seen in Fig. 4.

The molecular packing in the TCNB crystal is completely different to that in the complex structures. One can suppose that the orientation of the TCNB molecules inside the unit cell depends essentially on dipole-dipole interactions between cyano groups. An exchange of alternate TCNB molecules by anthracene

or naphthalene molecules separates the cyano groups so much that their mutual interactions are no longer a dominating influence on the molecular packing in the complex structures.

In the final stage of the N-TCNB and A-TCNB structure refinements at 65 K, precise Fourier synthesis maps were made and a careful comparison of the conformation of the TCNB, naphthalene and anthracene molecules in crystals of the complexes and of the pure compounds was performed. The aim of the analysis was to search for possible distortions of the electron density distribution and molecular conformation which could be related to charge transfer in the complexes. The bond lengths and angles of the donors are almost identical to those observed in pure

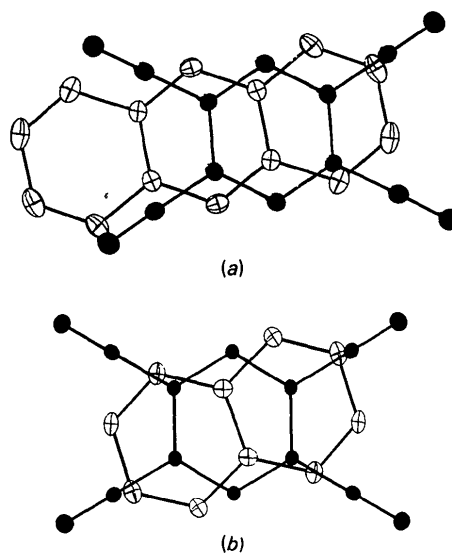


Fig. 3. Projection along the normal to the molecular planes of (a) A-TCNB at 225 K and (b) N-TCNB at 95 K (with only one equilibrium position for the naphthalene molecule). Atoms of the TCNB molecule are drawn in black.

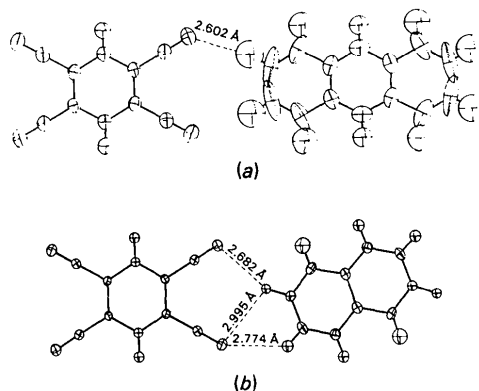


Fig. 4. Packing of the donor and acceptor molecules in neighbouring stacks for (a) A-TCNB and (b) N-TCNB. Distances in Å.



naphthalene and anthracene crystals. In the TCNB molecule, an elongation of the C(7)≡N(8) bond (1.152 Å) in N-TCNB with respect to that (1.136 Å) in pure TCNB was observed.

A careful analysis of the Fourier synthesis maps did not reveal any significant changes of the electron density distributions as could be expected for a weak CT complex. In the donor molecules, electron density peaks of about  $0.25 \text{ e \AA}^{-3}$  are found in the middle of each C-C bond. The height of the corresponding peaks in the benzene ring of the TCNB molecule is  $0.34 \text{ e \AA}^{-3}$ , while a peak of  $0.24 \text{ e \AA}^{-3}$  appears in the middle of the C(6)-C(7) bond. The electron density around the C(7)≡N(8) bond does not exceed  $0.17 \text{ e \AA}^{-3}$ . Outside the bonds, the electron density varies between  $+0.12$  and  $-0.23 \text{ e \AA}^{-3}$ .

Finally, a rigid-body thermal analysis was performed to study the anthracene and TCNB motions at 294 and 225 K. Elements of the **T** and **L** tensors were calculated using the least-squares procedure proposed by Schomaker & Trueblood (1968) and are presented in Table 6. The principal axes of the **L** tensor coincide well with the principal axes of inertia. The largest amplitude  $(L_3)^{1/2} = 9.1^\circ$  at 294 K belongs to a libration of the anthracene molecule around the axis perpendicular to the molecular plane. Such a large amplitude of the libration indicates orientational disorder of the anthracene molecules in the (102) plane. To characterize the type of the disorder, orientational probability functions of the donor molecules were calculated using structural data for the A-TCNB and N-TCNB complexes. The detailed procedure and results are presented below.

### Characterization of the disorder

#### Theory

The donor and acceptor molecules are planar as has been shown above. The molecular planes are exactly perpendicular to the crystallographic mirror plane (see Table 4) except for the naphthalene plane which makes an angle of  $\sim 1^\circ$  with the normal to the mirror plane. However, we neglect this small deviation to simplify the further considerations. Keeping in mind that the flat molecules occupy sites of  $2/m$  symmetry, one can conclude that the molecular symmetry is described by point group  $D_{2h}$ . Finally, a molecular coordinate system is defined in the following way:  $Y'$  is parallel to the crystallographic  $b$  axis;  $Z'$  is perpendicular to the molecular plane; and  $X'$  is perpendicular to  $Z'$  and  $Y'$ .

The site symmetry contains a center of inversion which removes coupling between the **T** and **L** tensors. Therefore, an orientational probability function for an  $i$ th atom in the molecule can be written in the following form:

$$F^i(\mathbf{r}') = \int F_T(\mathbf{R}') F_R^i(\mathbf{r}' - \mathbf{R}') d\mathbf{R}' \quad (1)$$

Table 6. Rigid-body analysis of A and TCNB molecules of the A-TCNB complex

$T_i$  values are given in  $10^{-4} \text{ \AA}^2$ ,  $L_i$  values in  $\text{deg}^2$ . The orthogonal coordinate system is **a**, **b**, **c\***.

	294 K				225 K			
	Eigen-values	Eigenvectors			Eigen-values	Eigenvectors		
TCNB molecule								
$T_1$	377	0.7882	0	-0.6154	304	0.8151	0	-0.5793
$T_2$	490	0	1.0000	0	380	0	1.0000	0
$T_3$	305	0.6154	0	0.7882	219	0.5793	0	0.8151
$L_1$	38.5	0.9248	0	-0.3811	31.4	0.9249	0	-0.3802
$L_2$	4.8	0	1.0000	0	2.2	0	1.0000	0
$L_3$	6.5	0.3811	0	0.9246	4.6	0.3802	0	0.9249
R.m.s.		0.0022 Å <sup>2</sup>				0.0018 Å <sup>2</sup>		
E.s.d.		0.0023 Å <sup>2</sup>				0.0020 Å <sup>2</sup>		
A molecules								
$T_1$	409	0.9038	0	-0.4280	324	0.9105	0	-0.4135
$T_2$	498	0	1.0000	0	415	0	1.0000	0
$T_3$	330	0.4280	0	0.9038	254	0.4135	0	0.9105
$L_1$	26.7	0.9840	0	-0.1780	15.6	0.9784	0	-0.2069
$L_2$	5.4	0	1.0000	0	4.1	0	1.0000	0
$L_3$	83.1	0.1780	0	0.9840	65.3	0.2069	0	0.9784
R.m.s.		0.0086 Å <sup>2</sup>				0.0053 Å <sup>2</sup>		
E.s.d.		0.0092 Å <sup>2</sup>				0.0057 Å <sup>2</sup>		

where  $\mathbf{R}'$  is an instantaneous mass-center position of the molecule and  $\mathbf{r} = \mathbf{r}' - \mathbf{R}'$  is a position of the  $i$ th atom with respect to the mass center.

A probability function of the mass center,  $F_T(\mathbf{R}')$ , is taken in a Gaussian form and for  $D_{2h}$  molecular symmetry can be expressed as:

$$F_T(\mathbf{R}') = G \exp \left[ - \left( \frac{X^2}{2T_1} + \frac{Y^2}{2T_2} + \frac{Z^2}{2T_3} \right) \right] \quad (2)$$

where  $\mathbf{R} = \mathbf{R}' - \mathbf{R}_0 = (X, Y, Z)$  describes a displacement of the mass center from its equilibrium position,  $T_i$  stands for the translational temperature factors and  $G$  is a normalization factor.

The librational motions of the donor molecules are strongly anisotropic as was shown previously. Thermal motions around the  $Z'$  axis have extremely large amplitudes of libration and are entirely responsible for the orientational disorder in the donor sublattice. Therefore, the rotational probability function  $F_R^i(\mathbf{r})$  should consist of two terms. One of them should represent the probability function of the small-amplitude librations around the  $X'$  and  $Y'$  axes and can be approximated by the Gaussian function. The second term should contain a one-dimensional probability function which describes properly the orientational disorder around the  $Z'$  axis. Thus, the appropriate  $F_R^i(\mathbf{r})$  function can be written as follows:

$$F_R^i(\mathbf{r}) = \frac{G'}{r} \exp \left[ - \left( \frac{x^2}{2L_1} + \frac{y^2}{2L_2} \right) \right] \times \delta(r - r_i) \delta(z) P^i(\psi) \quad (3)$$

where  $G'$  is normalization factor and the last term is expressed in a cylindrical coordinate system  $[\mathbf{r} = (r, \psi, z)]$ . The angle is counted from the crystallographic mirror plane. The position of the  $i$ th atom belonging to

a given molecule is described by the vector  $\mathbf{r}_i = (r_i, \psi_i, z_i = 0)$ ;  $z_i = 0$  because the molecules are planar. Elements of the  $\mathbf{L}$  tensor,  $L_1$  and  $L_2$ , describe the librations of the molecule around its  $X'$  and  $Y'$  axes, respectively.  $P^i(\psi)$  represents the orientational probability function of the  $i$ th atom around the  $Z'$  axis. Taking into account the  $2/m$  site symmetry, the  $P^i(\psi)$  function can be written in a form of a cosine series:

$$P^i(\psi) = (1/2\pi) \left[ 1 + \sum_{n=1}^{\infty} a_{2n}^i \cos(2n\psi) \right]. \quad (4)$$

If the molecule can be regarded as a rigid body, there are relations between the  $a_{2n}^i$  coefficients corresponding to the different atoms in the molecule. A general form of the relations was given by Press & Hüller (1973):

$$a_m^i = b_m^i c_m \quad (5)$$

where  $c_m$  are coefficients in a cosine series used to determine the orientational probability function of the whole molecule at the  $2/m$  site:

$$P(\psi) = (1/2\pi) \left[ 1 + \sum_{n=1}^{\infty} c_{2n} \cos(2n\psi) \right]. \quad (6)$$

The  $b_m^i$  coefficients correspond to the equilibrium position of atom  $i$  in the molecular coordinate system and can be expressed in this case as cosine functions:

$$b_{2n}^i = \cos(2n\psi_i). \quad (7)$$

Thus,  $P^i(\psi)$  can now be rewritten in the following form:

$$P^i(\psi) = (1/2\pi) \left[ 1 + \sum_{n=1}^{\infty} c_{2n} \cos(2n\psi_i) \cos(2n\psi) \right]. \quad (8)$$

It must be stressed that equivalent atoms have the same orientational probability function  $P^i(\psi)$ .

The molecular structure factor for a scattering vector  $\mathbf{Q}$  is:

$$F(\mathbf{Q}) = \sum_i n_i f_i(\mathbf{Q}) \int F^i(\mathbf{r}) \exp(i\mathbf{Q}\mathbf{r}) d\mathbf{r} \quad (9)$$

where  $n_i$  is the number of equivalent atoms and the summation runs over all the nonequivalent atoms in the molecule;  $f_i(\mathbf{Q})$  is the scattering factor of the  $i$ th atom. Using the relation:

$$\exp\{i\mathbf{Q}\mathbf{r}\} = \exp\{iQ_z z\} \left\{ J_0(Q_r r) + 2 \sum_{m=1}^{\infty} (i)^m J_m(Q_r r) \times \cos[m(\psi_Q - \psi)] \right\},$$

where the  $\mathbf{Q}$  vector is expressed in the same cylindrical coordinates as  $\mathbf{r}$  [ $\mathbf{Q} = (Q_r, \psi_Q, Q_z)$ ] and  $J_m(Q_r r)$  is the cylindrical Bessel function of order  $m$ , the structure factor of the disordered donor molecule is given by:

$$F(\mathbf{Q}) = F_{hkl} = [1 + (-1)^{h+k}] \left\{ \sum_i n_i f_i(\mathbf{Q}) \times \exp[-W_i(\mathbf{Q})] \left[ J_0(Q_r r_i) + \sum_{n=1}^{\infty} (-1)^n c_{2n} \times \cos(2n\psi_i) \cos(2n\psi_Q) J_{2n}(Q_r r_i) \right] \right\} \quad (10)$$

where  $W_i(\mathbf{Q})$  are the Debye-Waller factors which take into account the translation motions and the librations around the  $X'$  and  $Y'$  axes of the molecule in the following form:

$$W_i(\mathbf{Q}) = \frac{1}{2} \left[ \sum_{j=1}^3 T_j Q_j^2 + (r_{1j}^2 L_2 + r_{2j}^2 L_1) Q_j^2 \right]. \quad (11)$$

In the above relations, the components of  $\mathbf{Q}$  and  $\mathbf{r}_i$  are expressed in the same coordinates as the  $\mathbf{T}$  and  $\mathbf{L}$  tensors.

### Results and discussion

A computer program was written by the authors to fit the structure factors calculated from the proposed model to the measured  $F_{hkl}$ . In the refinement, the TCNB molecule was also treated as the rigid body and a coincidence of principal axes of the  $L$  and  $T$  tensors with those of the inertia tensor was assumed. Moreover, the  $r_i$  and  $\psi_i$  coordinates of the  $i$ th atom were calculated by averaging the corresponding coordinates at 65 K of all the equivalent atoms to the given one. The cosine series in the orientational probability function had a limited number of terms. It consisted only of terms for which standard deviations of the  $c_{2n}$  coefficients were smaller than the coefficients themselves. Generally, the number of adjustable parameters in the model presented is four to five times smaller than the number of the parameters fitted with *SHELX76*. The refinement procedure was performed several times assuming different inclinations of the molecular planes to the  $\mathbf{a}$  axis. The residual factor  $R$  was used to monitor the best choice of the inclination angle  $\nu$ . The structures of the A-TCNB complex at 294 and 225 K, as well as the structures of N-TCNB at 294 and 95 K, were studied in this way. In all cases, the smallest  $R$  factor was obtained for  $\nu$  angles equal to the inclinations of the best molecular planes found in the conventional refinement procedure. Final results are given in Table 7. The orientational probability functions obtained for the anthracene and naphthalene molecules are shown in Fig. 5.

The quality of the refinements for the A-TCNB crystal is almost as good as that achieved in the conventional way despite the smaller number of adjustable parameters. In the N-TCNB case, the results are inferior – the  $R$  value is about 0.11. The poorer refinement is mostly caused by the fact that the naphthalene plane is not exactly perpendicular to the crystallographic mirror plane as was assumed in this model.

The eigenvalues of the  $\mathbf{T}$  and  $\mathbf{L}$  tensors also compare well with those presented in Table 6. Differences appear only for  $T_2$  and  $L_1$  elements describing the rigid-body motions of the anthracene molecules.

The orientational probability function of the anthracene molecule exhibits a broad single peak

Table 7. Structural parameters obtained with the adapted symmetry functions

$T_i$  values are given in  $10^{-4} \text{ \AA}^2$ ,  $L_i$  in  $\text{deg}^2$ .

	A-TCNB		N-TCNB	
	294 K	225 K	294 K	95 K
$R$	0.064	0.058	0.118	0.111
$wR^*$	0.056	0.056	0.123	0.118
No. of parameters	19	20	19	20
<b>TNCB molecule</b>				
$\psi_{\text{TNCB}}$	72.1°	72.3°	118.0°	118.0°
$T_1$	373 (5)	299 (6)	413 (12)	221 (9)
$T_2$	504 (7)	405 (8)	324 (15)	142 (10)
$T_3$	336 (9)	236 (11)	237 (26)	86 (14)
$L_1$	35.4 (28)	29.3 (35)	34.0 (83)	10.4 (42)
$L_2$	6.0 (9)	3.5 (11)	5.7 (25)	2.3 (13)
$L_3$	6.3 (3)	4.2 (3)	5.9 (7)	1.9 (4)
<b>Donor molecule</b>				
$\psi_D$	70.2°	70.4°	118.7°	118.6°
$T_1$	450 (7)	348 (8)	496 (38)	217 (20)
$T_2$	614 (12)	481 (14)	588 (42)	228 (20)
$T_3$	322 (13)	257 (16)	278 (55)	95 (30)
$L_1$	39.6 (28)	27.5 (33)	15.0 (118)	5.9 (59)
$L_2$	5.6 (4)	3.6 (5)	9.6 (38)	2.6 (18)
$C_2$	1.95 (1)	1.97 (2)	1.67 (4)	1.56 (4)
$C_4$	1.67 (2)	1.70 (3)	0.81 (4)	0.62 (3)
$C_6$	1.42 (2)	1.51 (2)	-0.30 (15)	0.60 (10)
$C_8$	1.15 (4)	1.27 (5)	-0.94 (7)	1.52 (5)
$C_{10}$	0.67 (5)	0.81 (6)	-1.21 (8)	1.78 (6)
$C_{12}$	0.39 (3)	0.58 (3)	-1.00 (10)	-1.40 (7)
$C_{14}$	0.13 (3)	0.29 (4)	-0.57 (22)	-0.57 (10)
$C_{16}$	—	0.09 (5)	—	0.89 (46)

\* Unit weights.

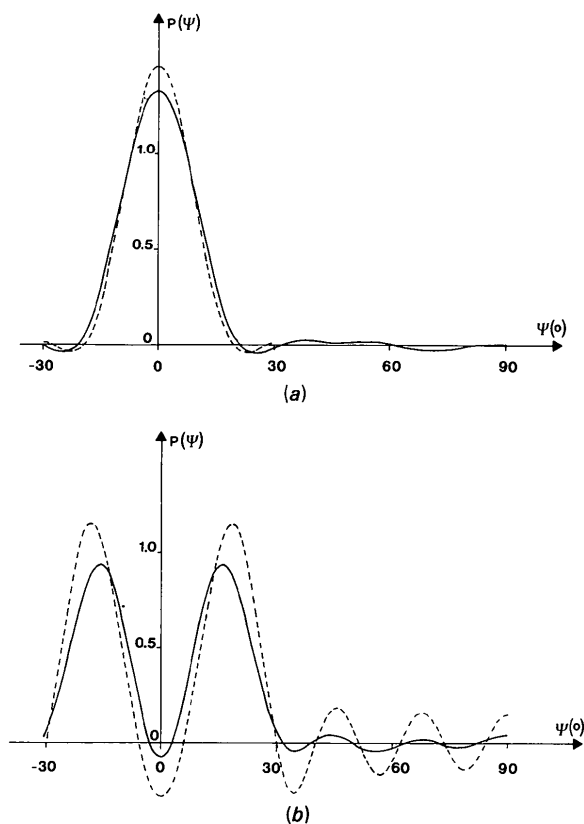


Fig. 5. Orientational probability function for the donor molecule in (a) A-TCNB (full line 294 K, dashed line 225 K) and (b) N-TCNB (full line 294 K, dashed line 95 K).

centered at  $\psi_0 = 0^\circ$  (see Fig. 5). The peak shape is close to a Gaussian profile. The full width at half maximum is  $22^\circ$  at 294 K and  $20^\circ$  at 225 K. The shape of the orientational probability function reproduces the shape of the single-particle potential at the site occupied by the donor molecule. Therefore, one can conclude that the anthracene molecules are in the single-well potential and so exhibit large-amplitude librations around the  $Z'$  axis. This means that the orientational disorder in the HT phase of the A-TCNB crystals can be classified as dynamic.

On the other hand, the orientational probability function for the donor molecules in the N-TCNB crystal has two maxima at  $\psi_0 = \pm 16^\circ$  (294 K) and at  $\psi_0 = \pm 18.5^\circ$  (95 K). The probability maxima correspond well to the two orientations of the naphthalene molecule in the HT unit cell as was found in the conventional structure determination (see Table 4) and recently by incoherent neutron-scattering studies (Czarniecka, Janik, Janik, Krawczyk, Natkaniec, Wasicki, Kowal, Pigon & Otnes, 1986). Outside the region of the probability peaks, the function exhibits evident oscillations, as  $P^i(\psi)$  is determined by a cosine series that is too short. However, the series length depends on the number of measured structure factors used in the refinement and cannot be enlarged freely. Both maxima of the probability function are well separated. Thus, the corresponding single-particle potentials have two deep wells characteristic of static orientational disorder.

The above results are in an excellent agreement with recent calculations of single-particle orientational potentials in A-TCNB and N-TCNB crystals performed by Luty & Kuchta (1986).

### Intensities of superlattice reflections

The dynamic disorder in A-TCNB and the static disorder in N-TCNB can initiate displacive and order-disorder phase transitions, respectively. Therefore, intensity changes of some superlattice reflections were measured as a function of temperature to confirm the different types of phase transition in the crystals. The (1,4,0) reflection for A-TCNB and the (3,2,3) reflection for N-TCNB were chosen. The temperature dependence of the measured intensities is presented in Fig. 6.

The phase transitions were observed at  $T_c = 213.5$  K in the A-TCNB crystal and at  $T_c = 73.5$  K in the N-TCNB crystal. The transformation temperatures are close to those determined by DSC and NMR methods (Ecolivet, Bertault, Mierzejewski & Collet, 1987; Dalal, Ripmeester, Reddoch & Williams, 1978).

For A-TCNB, the intensity of the (1,4,0) reflection changes gradually over the whole temperature range. The dependence becomes linear between 207 K and  $T_c$ , and is described by the simple formula  $I(T) = I_0(T_c - T)$ . Above  $T_c$ , diffuse scattering appears, which is a

phenomenon characteristic of displacive phase transitions. There is no evidence of another phase transition below  $T_c$  (213.5 K), which was observed in the DSC experiment (Ecolivet *et al.*, 1987).

The intensity of the (3,2,3) reflection in N-TCNB changes in a different way. It decreases only a little when the temperature is increased up to the vicinity of  $T_c$ . Then, it falls rapidly on approaching  $T_c$ . Such a behavior is characteristic of order-disorder phase transitions (Terauchi & Yamada, 1972). In systems passing such phase transitions, the intensity of the superlattice reflections is proportional to a square of the order parameter. The last quantity can be easily defined in the following way (Lefebvre *et al.*, 1984):

$$\eta = (P^+ - P^-)/(P^+ + P^-) \quad (12)$$

where  $P^+$  ( $P^-$ ) is the probability of finding a given molecule in one (or other) orientation at its site. The N-TCNB structure refinement revealed that the donor sublattice was not completely ordered at 65 K and the corresponding probability of finding a disordered molecule was  $P^- = 0.048_4$ . Then, the order parameter

$\eta = 0.904_8$ , allowing us to recalculate the temperature dependence of the (3,2,3) reflection intensity on the  $\eta(T)$  function. Eventually, an analysis of the  $\eta(T)$  function shows that the number of the disordered molecules becomes important just below  $T_c$ .

### Thermal expansion of the A-TCNB lattice

The thermal expansion of the A-TCNB unit-cell parameters was measured around  $T_c$  in order to complete the results of Stezowski (1980). The lattice parameters at each temperature were determined from positions of 25 selected Bragg reflections. It should be noted that different samples were used in this study and the structure determination experiments. Thus, the absolute values of the lattice parameters can vary slightly from one crystal to another, but the character of their temperature dependence should remain unchanged. The measurements were performed in a wide temperature range and the results are shown in Fig. 7.

Looking at Fig. 7, one can conclude that all the unit-cell parameters change continuously (within experimental error) at  $T_c = 213.5$  K. Then, the unit-cell volume does not change at all at the phase-transition temperature. This indicates that the phase transition is second order.

Remarkable thermal expansion anomalies are observed along the *a* axis only. The temperature variation of the *a* period can be explained by the fact that the most important ordering processes in the lattice take place along this direction, as was discussed above.

Principal coefficients of the thermal-expansion tensor at various temperatures are presented in Table 8. The tensor is strongly anisotropic far from  $T_c$  and reflects the strength of intermolecular forces inside the lattice. In both the phases, the 'softest' direction (the largest  $\alpha_i$ ) coincides roughly with a normal to the molecular planes along which intermolecular interactions are weakest. On the other hand, the lattice is stiffest along the [102] direction where the interactions between the anthracene and TCNB molecules are strongest.

### Concluding remarks

The problem of characterization of orientational disorder in mixed-stack CT complexes has been addressed. The careful analysis of the X-ray diffraction data for A-TCNB and N-TCNB crystals allows the following conclusions to be drawn. Dynamic orientational disorder of the anthracene molecules in A-TCNB has been found, documented and confirmed. The single-particle orientational potential for the anthracene molecule has been found to be a single minimum in agreement with the predictions of calculations (Luty & Kuchta, 1986). For the N-TCNB crystal, static orientational disorder of the naphthalene molecules has been found. The orientational probability density function, extracted

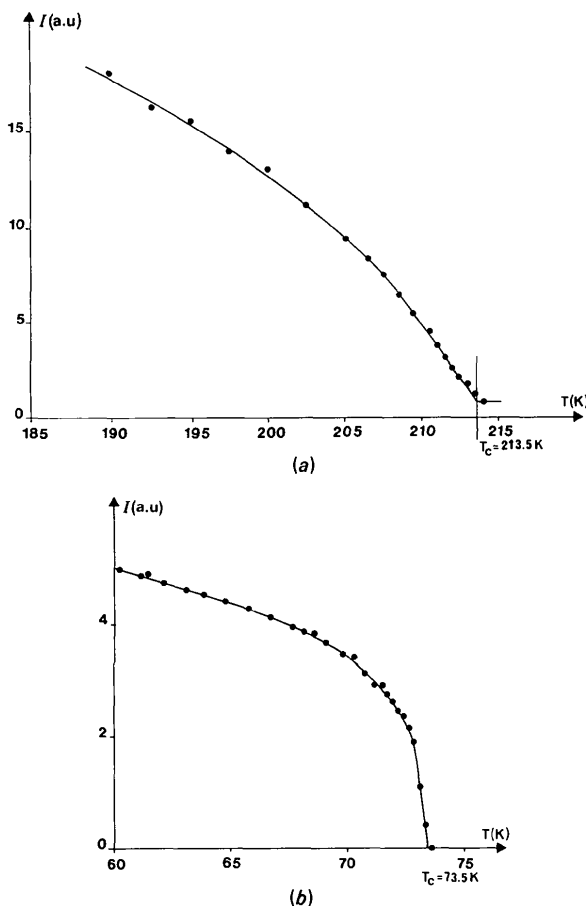


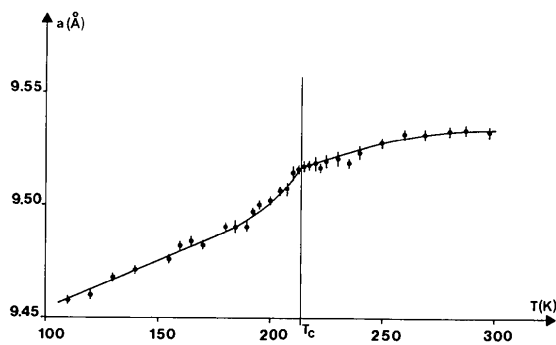
Fig. 6. Intensity of superlattice reflections *versus* temperature: (a) A-TCNB, 140 reflection; (b) N-TCNB, 323 reflection.

from the X-ray diffraction data analysis, indicated a double-minima potential for the naphthalene molecules. As the analysis of the diffraction data was performed using both a conventional structure-refinement procedure and a procedure utilizing symmetry-adapted functions, we can conclude that the orientational disorder in the A-TCNB and N-TCNB crystals has been completely characterized, as stated

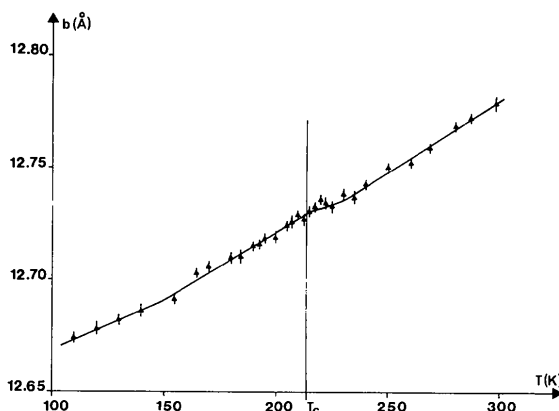
Table 8. *Eigenvalues* ( $\times 10^6 \text{ K}^{-1}$ ) of the thermal-expansion tensor of A-TCNB

Orthogonal axes are along  $a$ ,  $b$  and  $c^*$ ;  $\alpha_1$  is along  $b$  by symmetry arguments. The angle between the eigenvector of  $\alpha_1$  and  $a$  is  $\gamma$ .

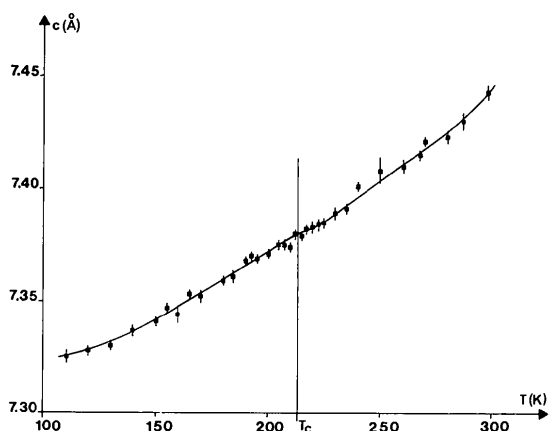
$T$ (K)	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\gamma$
170	100	47	35	$62^\circ$
210	146	47	71	$27^\circ$
250	120	50	14	$66^\circ$



(a)



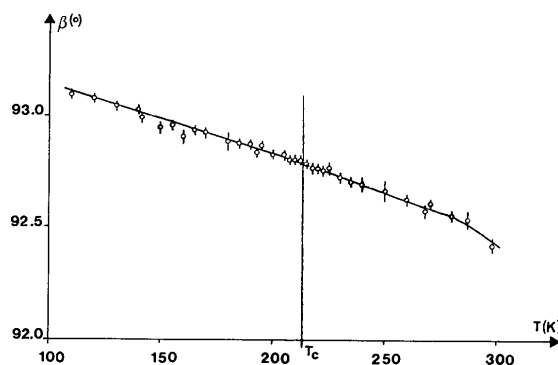
(b)



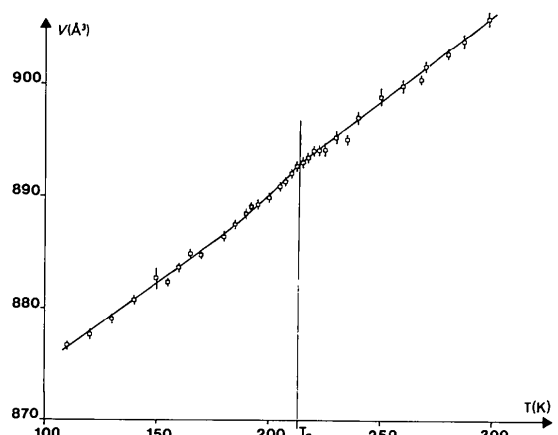
(c)

above. In particular, the controversy about the type of disorder in the A-TCNB crystal has been solved. From a comparison of the results of the crystal structure analysis using both of the above procedures we can conclude that for orientationally well-localized molecules the methods give equally good results.

The mechanisms of the orientational phase transitions have been studied by measurements of temperature dependencies of the intensities of superlattice reflections. The results clearly indicate displacive mechanisms for A-TCNB crystal [in agreement with Raman studies (Mierzejewski *et al.*, 1988)] and an order-disorder mechanism for the N-TCNB system.



(d)



(e)

Fig. 7. Lattice parameters of A-TCNB versus temperature: (a) the  $a$  period, (b) the  $b$  period, (c) the  $c$  period, (d) the  $\beta$  angle, (e) volume of the monoclinic cell.

The structure of the low-temperature phase of N-TCNB has been determined for the first time. The structure refinement at 65 K revealed that the donor sublattice was not completely ordered, the probability of finding the disordered molecule being 0.048.

Finally, it should be stressed that the characterization of the orientational disorder and mechanisms of the phase transitions (in particular, the agreement between experimental results and theoretical predictions) for both systems studied strongly supports the conclusion that the architecture of the mixed-stack CT crystals is governed by the close-packing principle. This seems to be an essential and general conclusion.

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