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Structure and Packing Arrangement of Molecular Compounds. VIII. Orientational Disorder in a Complex of TCNQ with *o*-Phenanthroline

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Calculated energy profiles of *o*-phenanthroline in its crystalline complex with TCNQ, followed by a constrained refinement of the structure, indicate that the thermal parameters of *o*-phenanthroline represent a minor orientational disorder. The disordered model considered consists of two *o*-phenanthroline molecules with respective occupancies of 0·72 and 0·28. The molecule with the higher occupancy is close to the conventionally refined one, and confirms the indication obtained from the energy profile; the lower occupancy appears to correspond to a less well defined species. The disorder is believed to be dynamic. Packing restrictions which act on *o*-phenanthroline and which favour its disordered state are illustrated and discussed. The structural information obtained is presented in detail.

Introduction

As is well known, large thermal parameters, in addition to representing average atomic motion, may well camouflage effects of minor disorder. Such ambiguities have been reported for several molecular compounds (*e.g.* Williams & Wallwork, 1967; Kumakura, Iwasaki & Saito, 1967; Tsuchiya, Marumo & Saito, 1972), and attempts at their resolution were made *via* difference density maps (Kumakura *et al.*, 1967; Herbstein, 1971) and by consideration of approximate energy profiles (Shmueli & Goldberg, 1973). Any of the above diagnostic techniques may lead to a proposal for a disordered model, but the usual poor quality of such electron density difference maps and the approximate character of atom–atom potential calculations call for a more reliable specification of the model. This can be done by fitting the postulated disordered structure to the experimental data, and the constrained refinement technique (Pawley, 1971) appears to be suitable for this.

The first application of constrained refinement, in the above context, was made by Shmueli & Goldberg (1974), who determined the orientational disorder of naphthalene in its crystalline complex with tetracyanoethylene (TCNE). In the present article we present a similar application of constrained refinement to the structure of (1:1) *o*-phenanthroline (PHT)–7,7,8,8-tetracyanoquinodimethane (TCNQ) which has been studied in this laboratory (Goldberg & Shmueli, 1973*a*). As will be shown, this is a much less obvious instance of a disorder–motion ambiguity than the naphthalene–TCNE case, mentioned above. We also take this opportunity to describe the details of the PHT–TCNQ structure, as these were only briefly summarized previously. Such a description is of interest in connexion with the somewhat unusual packing arrangement observed in this molecular compound and with its electronic structure (Goldberg, 1975).

Experimental

Rapid cooling, below room temperature, of an equimolar mixture of TCNQ and PHT solutions in acetonitrile, yielded red elongated crystals suitable for study.

Crystal data

$(C_{12}H_8N_2)(C_{14}H_4N_4)$, $M_r = 384\cdot4$, m.p. about 210°C;* $a = 7\cdot417$ (1), $b = 19\cdot904$ (3), $c = 13\cdot079$ (4) Å, $\beta = 92\cdot47$ (5)°, $V = 1929$ Å^3; $D_m = 1\cdot30$, $Z = 4$, $D_c = 1\cdot323$ g cm^{-3}. Space group $P2_1/n$, μ(Mo $K\alpha$) = 0·9 cm^{-1}, λ(Mo $K\alpha$) = 0·7107 Å.

The unit-cell dimensions were obtained from their least-squares fit to 28 measurements on Weissenberg and precession photographs. In order to keep the monoclinic angle as close as possible to 90°, the space group $P2_1/n$ was chosen, rather than the conventional $P2_1/c$. Density measurements were performed by the flotation method with toluene–CCl$_4$ mixtures.

Intensity data were collected, from a crystal with approximate dimensions of 0·3 × 0·4 × 0·6 mm, by the integrating precession method. The intensities of 3084 reflexions, from 11 layers (0*kl* through 4*kl*, and *h*0*l* through *h*5*l*), were measured with the aid of a Joyce–Loebl III CS recording microdensitometer. Structure amplitudes were evaluated without correcting

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* The crystals change colour at about 115°C, which may indicate a possible transition to a high-temperature phase.

for absorption or extinction, and were brought to a common scale. The cross-scaling was based on 347 reflexions which appeared on more than one layer. After averaging out symmetry-related reflexions, 2412 independent structure amplitudes, including 1201 'unobserveds', were available for study. The intensities of the 'unobserveds' were taken as $I_{\text{min}}/3$, where I_{min} is the weakest observed intensity.

Most of the computer programs used in this work were briefly described elsewhere (Goldberg & Shmueli, 1971), and a more detailed description of the constrained refinement routine employed is given by Shmueli & Goldberg (1974). The calculations were carried out on a CDC 6600 computer at the Tel-Aviv University Computation Centre.

Determination of the structure

Attempts at solving the structure by direct methods were unsuccessful. An inspection of the three-dimensional Patterson synthesis, based on all the observed reflexions, indicated that both TCNQ and PHT have their planes nearly parallel to the *ab* plane. In addition, only one high peak was found in each of the asymmetric units of the $P(\frac{1}{2},v,\frac{1}{2})$ and $P(u,\frac{1}{2},w)$ sections. On the assumption that these were true Harker peaks, approximate positions of the molecular centres for a usual TCNQ–donor separation were derived. A trial structure in which (*a*) the molecular centres of the TCNQ and an adjacent PHT overlap each other [for PHT the midpoint of C(13)–C(14) was

Table 1. *Atomic positional* ($\times 10^4$) *and thermal* ($\times 10^3$) *parameters*

The e.s.d.'s are given in parentheses in units of the last decimal place. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(h_ia^i)(h_ja^j)U^{ij}]$ where h_i and a^i ($i = 1, 2, 3$) are reflexion indices and reciprocal unit-cell edges respectively. The parameters of PHT result from the conventional refinement while those of TCNQ are derived from the refinement of the disordered model (see text).

	x	*y*	*z*	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
PHT									
N(1)	1136 (8)	2647 (2)	3796 (3)	100 (5)	44 (3)	76 (3)	−10 (3)	−2 (3)	−28 (3)
C(2)	880 (12)	3332 (3)	3787 (5)	165 (9)	48 (4)	77 (4)	−36 (5)	2 (3)	−30 (5)
C(3)	−811 (17)	3642 (4)	3701 (6)	267 (16)	56 (5)	75 (5)	52 (7)	−15 (4)	−49 (7)
C(4)	−2253 (12)	3254 (4)	3632 (5)	149 (9)	91 (6)	53 (4)	58 (6)	−19 (4)	0 (4)
C(5)	−2145 (11)	2548 (3)	3631 (4)	87 (6)	66 (4)	46 (3)	33 (5)	−9 (3)	−4 (4)
C(6)	−3713 (10)	2132 (4)	3567 (4)	50 (5)	153 (7)	58 (4)	36 (6)	0 (5)	3 (3)
C(7)	−3454 (10)	1456 (4)	3587 (4)	58 (6)	107 (6)	64 (4)	−21 (5)	5 (4)	1 (4)
C(8)	−1742 (11)	1154 (3)	3659 (4)	83 (6)	57 (4)	40 (3)	−8 (5)	2 (3)	1 (3)
C(9)	−1524 (11)	441 (3)	3653 (4)	103 (7)	76 (5)	61 (4)	−47 (5)	12 (4)	−2 (4)
C(10)	171 (13)	189 (3)	3744 (4)	153 (9)	42 (4)	68 (4)	6 (5)	−2 (3)	4 (5)
C(11)	1603 (10)	633 (3)	3836 (4)	100 (7)	70 (4)	66 (4)	31 (5)	6 (4)	8 (4)
N(12)	1487 (8)	1289 (2)	3828 (3)	77 (5)	39 (3)	64 (3)	7 (3)	−1 (2)	10 (3)
C(13)	−198 (9)	1556 (3)	3738 (3)	57 (5)	41 (3)	40 (3)	−1 (4)	−5 (2)	0 (3)
C(14)	−391 (10)	2281 (3)	3731 (3)	72 (5)	45 (3)	40 (3)	−1 (4)	−7 (3)	−5 (3)
TCNQ									
C(1′)	2353 (8)	1893 (3)	1215 (4)	41 (5)	49 (4)	69 (4)	−17 (5)	−2 (4)	−4 (3)
C(2′)	1554 (9)	2494 (3)	1166 (4)	30 (5)	52 (4)	64 (4)	−17 (4)	5 (3)	1 (3)
C(3′)	−388 (9)	2551 (3)	1121 (4)	43 (5)	46 (4)	40 (4)	−7 (4)	5 (3)	1 (3)
C(4′)	−1206 (9)	3175 (3)	1099 (4)	33 (6)	52 (4)	54 (4)	−17 (5)	6 (3)	10 (3)
C(5′)	−248 (10)	3781 (3)	1094 (5)	43 (6)	49 (4)	100 (5)	2 (4)	4 (4)	12 (4)
N(6′)	513 (9)	4282 (3)	1075 (5)	75 (6)	56 (4)	175 (6)	−11 (4)	−1 (4)	24 (4)
C(7′)	−3140 (10)	3241 (3)	1148 (4)	60 (5)	45 (4)	47 (4)	−12 (6)	5 (3)	15 (4)
N(8′)	−4662 (8)	3302 (3)	1239 (4)	54 (4)	83 (4)	81 (4)	−12 (5)	−4 (3)	9 (3)
C(9′)	−1440 (8)	1940 (3)	1108 (4)	32 (4)	54 (4)	51 (3)	−13 (4)	−8 (3)	4 (3)
C(10′)	−619 (9)	1334 (3)	1136 (4)	31 (5)	45 (4)	58 (4)	−16 (4)	−3 (3)	4 (3)
C(11′)	1313 (9)	1285 (3)	1186 (4)	39 (6)	47 (4)	43 (3)	−8 (4)	−3 (3)	1 (3)
C(12′)	2122 (9)	670 (3)	1201 (4)	25 (6)	48 (4)	64 (4)	−10 (5)	−2 (3)	−1 (3)
C(13′)	1127 (9)	49 (3)	1175 (4)	50 (6)	53 (4)	49 (4)	8 (4)	1 (3)	1 (3)
N(14′)	356 (8)	−448 (2)	1159 (4)	91 (6)	46 (4)	106 (4)	−18 (4)	−7 (3)	7 (3)
C(15′)	4034 (12)	579 (3)	1212 (5)	65 (6)	35 (4)	83 (4)	−14 (6)	−5 (3)	−12 (5)
N(16′)	5570 (9)	513 (4)	1206 (5)	51 (5)	70 (4)	165 (6)	−15 (6)	0 (4)	1 (5)

	x	*y*	*z*		*x*	*y*	*z*
H(2)	2049	3643	3847	H(7)	−4595	1145	3527
H(3)	−958	4158	3685	H(9)	−2623	106	3585
H(4)	−3557	3486	3569	H(10)	356	−338	3734
H(6)	−5062	2333	3499	H(11)	2970	434	3908
H(1′)	3786	1882	1255	H(9′)	−2903	1957	1064
H(2′)	2386	2934	1185	H(10′)	−1462	900	1125

taken as the centre], (*b*) the long molecular axes of TCNQ and PHT are parallel and (*c*) there are four molecules stacked along **c**, led to $R = 0\cdot40$. Further packing considerations and preliminary refinement runs indicated that TCNQ and PHT had to be rotated through 25 and 5° about the [001] and [010] directions, respectively, in order to relieve some close approaches. An overall isotropic refinement of the adjusted trial structure, including 323 reflexions with $\sin\theta/\lambda \leq 0\cdot3$, led to $R = 0\cdot15$; a further few cycles of individual isotropic refinement, based on 1210 observed reflexions, reduced R to 0·138. The 004 reflexion, the intensity of which could not be reliably measured, was excluded from the calculation at this stage.

Refinement

Conventional refinement

Further calculations dealt with the refinement of 271 parameters: three positional and six thermal parameters for each of the heavy atoms and an overall scale factor. Since the observations-to-parameters ratio was <5 at this stage, the positional and thermal parameters of the H atoms were not refined but were included in the structure-factor calculation towards the end of the refinement. The H positions were derived from chemical considerations (C—H = 1·07 Å), while their isotropic vibration parameters were set equal to those of the C atoms to which they are bonded. The parameters of TCNQ and PHT were kept in two separate blocks of the matrix of normal equations. Only the 1210 observed reflexions participated in the first stages of the refinement, but towards the end of the calculation those unobserved reflexions for which $|F_c| \geq F_o/K$ were also included. The final unweighted and weighted discrepancy indices were $R = 0\cdot071$ (0·085) and $r = 0\cdot068$ (0·073) respectively, the figures in parentheses referring to 1496 reflexions including the 'unobserveds'. The final value of $\langle w(\Delta F)^2\rangle^{1/2}_{n-m}$, with $n = 1496$ and $m = 271$, is 1·19. The final average shift-to-standard deviation ratio was 0·3.*

Atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964) for C and N, and from Stewart, Davidson & Simpson (1965) for H. The final atomic parameters, obtained from the conventional refinement for the PHT molecule, are listed in Table 1 along with their estimated standard deviations. The final parameters of TCNQ shown in Table 1 result from the constrained refinement described below. They differ very little from those obtained from the conventional refinement (see Goldberg & Shmueli, 1973*a*).

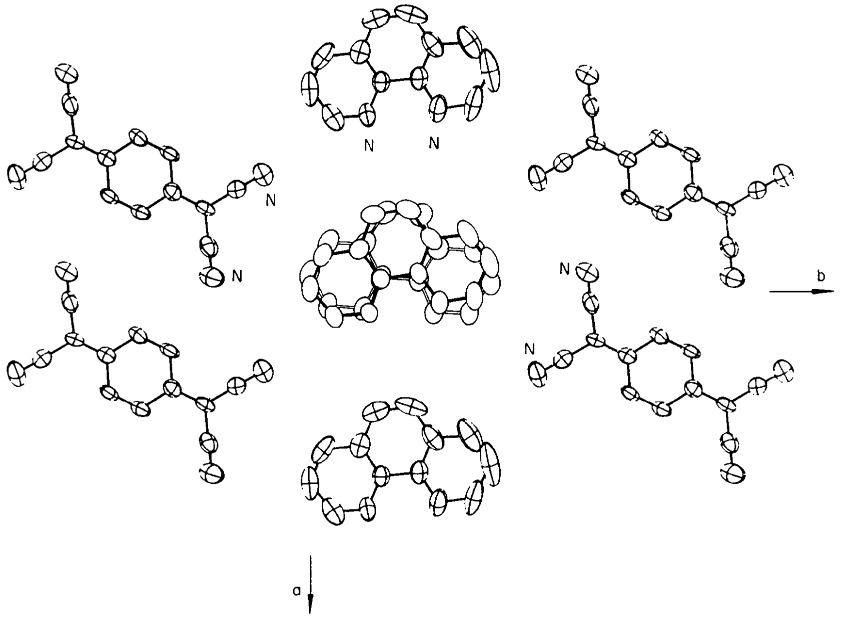

Fig. 1. Projection of a single layer of PHT and TCNQ molecules onto the *ab* plane. The central PHT molecule has been replaced by the result of the constrained refinement, where heavily lined bonds belong to the molecule with greater occupancy factor (major site; see text and Table 3). Thermal parameters are displayed by 50% probability ellipsoids.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32534 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Constrained refinement

Thermal-ellipsoid plots of PHT and TCNQ (Fig. 1) and rigid-body motion analyses based on the results of the conventional refinement (Goldberg, 1973), show that the thermal parameters of PHT are unusually large and that the molecule appears to librate mainly about a direction close to its plane normal. Such situations were previously encountered in other molecular compounds (*e.g.* Williams & Wallwork, 1968; Goldberg & Shmueli, 1973*b*), and were often correlated with orientational disorder or with a possibly anharmonic type of motion. In order to clarify the situation in this structure, an energy profile corresponding to the rotation of PHT about its plane normal was constructed. The profile (Fig. 2), calculated as explained elsewhere (Shmueli & Goldberg, 1973), shows two rather shallow minima, the deeper one being close to the observed structure. Presence of two energy minima separated by a very low barrier (less than kT, as viewed from either side) indicates that we may be dealing with a borderline case in which both genuine motion and a tendency towards disorder may be responsible for the thermal motion of PHT. Of course, the energy-profile calculations are approximate and can only be used in generating hypotheses which still need to be confronted with experiment. However, since charge-transfer interactions are known to be fairly isotropic with respect to the small motion considered (Kuroda, Amano, Ikemoto & Akamatu, 1967), van der Waals interactions are thought to be mainly responsible for the above observation and, hence, semi-empirical pairwise energy functions on which the profile in Fig. 2 is based are likely to give qualitatively correct indications. A relevant hypothesis, which can be handled by a constrained-refinement routine, is that PHT represents an average of two energetically preferred molecular orientations. For this purpose it was decided to insert into the unit cell a PHT molecular model of *mm* symmetry with correspondingly averaged dimensions based on Frenz & Ibers (1972) and Table 1, and to bring its molecular axes into coincidence with those of the motion and/or disorder affected one. We shall refer to this model, given in Table 2, as the average PHT. Accordingly, a disordered model was constructed containing an unmodified TCNQ molecule and two PHT molecules generated by rotating the average PHT about its plane normal through +7° and −7°, with their occupancy factors each being set equal to 0·5.

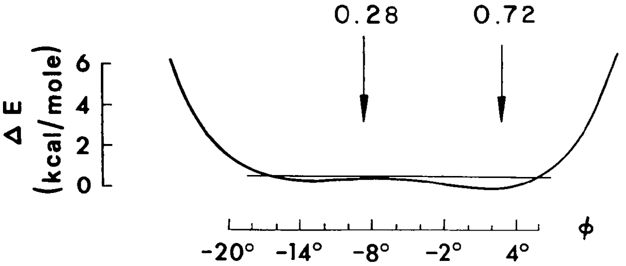

Fig. 2. Energy profile obtained by rotating an idealized PHT molecule about its plane normal, in the conventionally refined crystal structure of PHT–TCNQ. The zero on the energy scale corresponds to the deepest minimum, and the horizontal line above the φ axis has been drawn at the height of kT. The energy ΔE at $\varphi = 0°$ corresponds to the conventionally refined structure while the vertical arrows indicate the molecular orientations of PHT, resulting from the constrained refinement. The relative occupancies of PHT, in this model, are indicated above the arrows (see Table 3).

This model was subjected to a constrained refinement in which positional and thermal parameters of both PHT molecules were simultaneously adjusted. These included three angular parameters, taken as rotations about the principal axes of the molecular tensor of inertia of the average PHT, three positional parameters, taken as displacements from the centre of gravity of the latter, and 20 components of the rigid-body tensors **T**, **L**, **S** for each PHT molecule. Hence, including *one* properly constrained occupancy factor and an overall scale factor, the model was defined by 54 adjustable parameters.* The isotropic vibration

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* Since the **TLS** tensors reflect intermolecular interactions, and the environments of the two PHT molecules in the disordered model are not the same, these thermal parameters were varied independently for each molecule.

Table 2. *Fractional coordinates* (× 10^4) *of the PHT molecule input to the constrained-refinement calculations*

	x_o	y_o	z_o		x_o	y_o	z_o
N(1)	1121	2655	3801	N(12)	1494	1297	3820
C(2)	873	3327	3788	C(13)	−192	1553	3736
C(3)	−803	3642	3705	C(14)	−391	2278	3726
C(4)	−2293	3254	3631	H(2)	2042	3642	3846
C(5)	−2132	2548	3639	H(3)	−950	4177	3698
C(6)	−3653	2132	3564	H(4)	−3609	3174	3566
C(7)	−3465	1450	3573	H(6)	−4969	2352	3498
C(8)	−1750	1156	3658	H(7)	−4634	1135	3515
C(9)	−1523	453	3670	H(9)	−2693	138	3612
C(10)	147	185	3753	H(10)	294	−350	3760
C(11)	1616	620	3826	H(11)	2932	400	3891

Table 3. *Summary of the constrained refinement*

All the parameters refined in this calculation (**φ**, **Δρ**, **T**, **L**, **S**) were referred to the principal axes of the inertia tensor of the idealized PHT molecule (Table 2). The angles φ_l, φ_m and φ_n (components of **φ**) denote rotations of the input molecule about its (principal) axes **l**(X), **m**(Y) and **n**(Z) respectively; a positive φ corresponds to a rotation in the anticlockwise sense while looking from the origin towards the negative end of the axis. The vector **Δρ** denotes a shift of the centre of gravity, resulting from the refinement. The PHT molecules in the major and the minor sites are denoted by A and B respectively.

(*a*) Input
PHT

(1) Idealized model given in Table 2
(2) Positional parameters $\varphi_l^{A,B} = \varphi_m^{A,B} = 0$; $\varphi_n^A = +7°$, $\varphi_n^B = -7°$
(3) Thermal parameters $T_{ij}^{A,B} = \delta_{ij} \times 0{\cdot}05$ Å^2, $L_{ij}^{A,B} = 0{\cdot}001$ rad^2, $S_{ij}^{A,B} = 0$
(4) Isotropic u_o's of H atoms – not refined

TCNQ

Initially, all parameters were fixed at values resulting from the last cycle of the conventional refinement. They were conventionally refined during the final stage.

(*b*) Final discrepancy indices (m = number of parameters)

Conventional	$R = 0{\cdot}071$,	$r = 0{\cdot}068$,	$m = 271$
Constrained (TCNQ fixed)	$R = 0{\cdot}073$,	$r = 0{\cdot}075$,	$m = 54$
Constrained (TCNQ readjusted)	$R = 0{\cdot}070$,	$r = 0{\cdot}068$,	$m = 197$
Number of reflexions	$n = 1210$	(throughout)	

(*c*) Results
PHT(A) (occupancy: 0·72)

(1) Positional parameters

	l	**m**	**n**
φ	−0·5 (3)°	−0·3 (2)°	2·1 (4)°
Δρ	−0·020 (7) Å	0·017 (6) Å	0·014 (7) Å

The output fractional coordinates can be obtained from Table 2 by the following transformation:*

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_A = \begin{pmatrix} 0{\cdot}99962 & -0{\cdot}10095 & -0{\cdot}01496 \\ 0{\cdot}01405 & 0{\cdot}99928 & -0{\cdot}00311 \\ 0{\cdot}00489 & 0{\cdot}00426 & 0{\cdot}99959 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_o + \begin{pmatrix} 0{\cdot}0226 \\ 0{\cdot}0012 \\ 0{\cdot}0007 \end{pmatrix}.$$

(2) Thermal parameters (×10⁴)

T_{11}	414 (19) Å^2	L_{11}	68 (15) rad^2	S_{11}	29 (14) rad Å
T_{22}	477 (25)	L_{22}	25 (6)	S_{12}	−56 (14)
T_{33}	355 (51)	L_{33}	56 (8)	S_{13}	−25 (8)
T_{12}	−39 (13)	L_{12}	21 (4)	S_{21}	38 (7)
T_{23}	52 (22)	L_{23}	−6 (5)	S_{22}	−35 (12)
T_{31}	−36 (16)	L_{31}	−9 (8)	S_{23}	−16 (5)
				S_{31}	−41 (9)
				S_{32}	32 (8)
				S_{33}	6

Principal values and axes of **L**, referred to the inertial system of PHT at this site

Eigenvalues	Eigenvectors		
26·5(°)^2	−0·8696	0·0602	0·4901
17·0	−0·0716	0·9667	−0·2457
5·6	0·4885	−0·2487	−0·8363

Table 3 *cont.*

PHT(B) [occupancy: 0·28 (5)]

(1) Positional parameters

	l	**m**	**n**
φ	2·3 (9)°	0·6 (4)°	−8·9 (9)°
Δρ	0·068 (17) Å	−0·021 (15) Å	−0·039 (20) Å

The output fractional coordinates can be obtained from Table 2 by the following transformation:*

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_B = \begin{pmatrix} 0{\cdot}98563 & 0{\cdot}41536 & 0{\cdot}06644 \\ -0{\cdot}05781 & 0{\cdot}98789 & 0{\cdot}00452 \\ -0{\cdot}02080 & -0{\cdot}00907 & 1{\cdot}00089 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_o + \begin{pmatrix} -0{\cdot}1025 \\ -0{\cdot}0001 \\ -0{\cdot}0030 \end{pmatrix}.$$

(2) Thermal parameters (×10⁴)

T_{11}	593 (60) Å^2	L_{11}	95 (46) rad^2	S_{11}	7 (41) rad Å
T_{22}	740 (80)	L_{22}	51 (18)	S_{12}	117 (40)
T_{33}	413 (145)	L_{33}	14 (20)	S_{13}	−25 (27)
T_{12}	98 (38)	L_{12}	−21 (15)	S_{21}	29 (21)
T_{23}	−8 (64)	L_{23}	−2 (15)	S_{22}	−17 (31)
T_{31}	−151 (53)	L_{31}	−80 (23)	S_{23}	29 (16)
				S_{31}	−22 (24)
				S_{32}	−17 (19)
				S_{33}	10

Principal values and axes of **L**, referred to the final inertial system of PHT at this site

Eigenvalues	Eigenvectors		
48·3 (°)^2	0·8568	−0·3287	0·3973
16·4	0·3920	−0·0854	−0·9160
−12·2	0·3350	0·9406	0·0556

TCNQ – see Table 1.

* The transformation is given by

$$\mathbf{r}_{\text{final}} = B^{-1}MB\mathbf{r}_{\text{input}} + \boldsymbol{\rho}_{\text{final}} - B^{-1}MB\boldsymbol{\rho}_{\text{input}},$$

where $B^{-1}MB$ is the rotation matrix $M(\boldsymbol{\varphi})$ transformed to the crystal system, $\boldsymbol{\rho}_{\text{final}}$ and $\boldsymbol{\rho}_{\text{input}}$ are final and initial centres of gravity of the molecule, and **r** denotes an atomic position vector. All four vectors are referred, in this expression, to the crystal system.

parameters of the H atoms of PHT were taken as one-third of the trace of **U**, where **U** is the vibration tensor of the C atom to which the H is bonded, as evaluated from the **TLS** tensors of the molecule to which the H belongs.

The constrained-refinement calculation was carried out with the aid of the same routine that had been employed in our study of the TCNE–naphthalene complex (Shmueli & Goldberg, 1974). During the first stage of the calculation only the above 54 parameters were refined. The convergence was smooth and the discrepancy indices reached, for the 1210 observed reflexions, were $R = 0{\cdot}073$ and $r = 0{\cdot}075$. This stage was followed by one cycle of a conventional refinement of the TCNQ molecule, the PHT's being kept fixed. The final values of the discrepancy indices, based on 1210 observed reflexions and 197 parameters, are $R = 0{\cdot}070$ and $r = 0{\cdot}068$. In view of the considerable reduction in the number of adjustable parameters it is evident that the disordered model is favoured by the experimental results, although to a lesser extent than was found in the case of TCNE–naphthalene. The results of the constrained refinement of the disordered PHT–TCNQ model are shown in Table 3.

It should be pointed out that the orientation of PHT in its major site appears to be more reliable than that obtained for the minor site. The negative eigenvalue of L_{33} for PHT(minor), its awkward location on the plateau of the energy profile and, last but not least, the packing considerations given in the next section, indicate that the minor site of PHT may represent a range of equally probable molecular orientations. The disordered model of PHT, supported by the above constrained refinement, thus leads to a tentative conclusion that the disorder in this compound is mainly of a dynamic nature.

Discussion

Packing arrangement

The spatial arrangement of TCNQ and PHT in the crystal can be conveniently discussed in terms of partially disordered molecular layers, parallel to the (001) plane, and the stacking of these layers which leads to a rather unusual pairing of donor and acceptor molecules. Fig. 1 shows a projection of a PHT–TCNQ layer down **c***. The layer is centred at about $z = 0{\cdot}125$, and the maximum separation along **c** between two atoms within a layer is close to 0·55 Å. The layer consists of alternating rows of TCNQ and PHT molecules, running along **a**. TCNQ molecules along these rows are rather tightly packed [H(2′)···N(8′) = 2·31 Å, H(10′)···N(14′) = 2·34 Å, Fig. 3], while the phenathroline moieties seem, at least in the conventionally refined structure, to be more loosely bound.

Regarding the disorder of PHT, which has mainly an intralayer character, it is interesting to compare Figs. 1, 2 and 4 with respect to the packing restrictions acting on a PHT molecule. The orientation of the major site correlates well with the deepest trough in the approximate energy profile, as should be expected. The presence of the minor site, or a *range of such sites*, may be partly because, while the PHT molecules are rotated away from the major site, in the direction of decreasing φ, the most repulsive PHT···PHT interactions become relaxed. On the other hand, the PHT···TCNQ contacts are much less affected by this rotation. This description can be illustrated by a consideration of specific contacts, *e.g.* the H(7)···H(11) distances between nearest neighbours in a row are 2·24, 2·89 and 3·14 Å in major···major, major···minor and minor···minor site interactions respectively. On the other hand, the H(2)···N(14′) distance (Fig. 4) decreases from 2·73 to 2·53 Å and H(11)···N(6′) decreases from 2·54 to 2·51 Å, for PHT(major)···TCNQ and PHT(minor)···TCNQ interactions respectively.

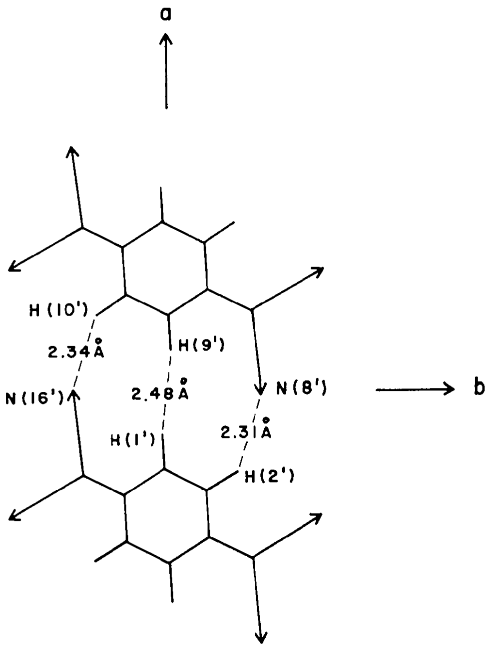


Fig. 3. Schematic illustration of the closely packed arrangement of TCNQ molecules along **a**.

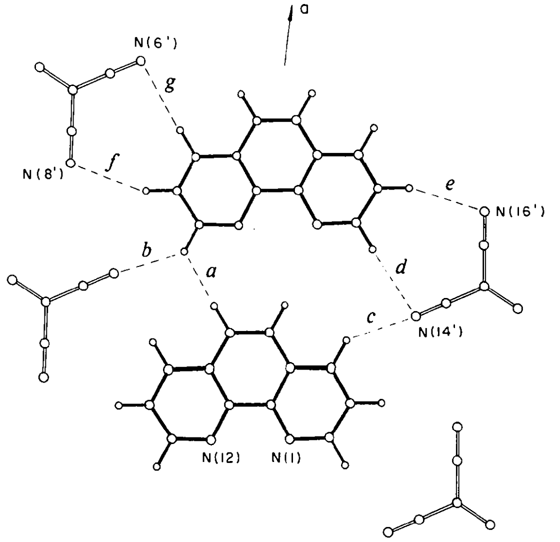


Fig. 4. Non-bonded contact distances within a PHT–TCNQ layer, involving the major site of PHT. The contacts shown are: *a*[H(11)···H(7)] = 2·24, *b*[H(11)···N(6′)] = 2·54, *c*[H(4)···N(14′)] = 2·56, *d*[H(2)···N(14′)] = 2·73, *e*[H(3)···N(16′)] = 2·73, *f*[H(10)···N(8′)] = 2·76, *g*[H(9)···N(6′)] = 2·79 Å.

It might be interesting to extend the above description to a more profound analysis of the dynamics of PHT in this crystal. However, in view of the probably significant anharmonicity, indicated by Fig. 2, this does not seem to be an easy task.

The unit cell of PHT–TCNQ is crossed by two pairs of layers, such as that discussed above, the pairs being centred at $z = 0{\cdot}25$ and $z = 0{\cdot}75$. Within each pair, the donor and acceptor molecules overlap each other as shown in Fig. 5, while the corresponding overlap of molecules belonging to adjacent pairs of layers is minimal (see Fig. 2, Goldberg & Shmueli, 1973*a*). This is why, effectively, only donor–acceptor pairs appear in the crystal rather than the usual infinite column arrangement. For example, the components of the distance between centres of gravity of two closest non-overlapping PHT(major) and TCNQ molecules, in the (001) projection, are $ax = 4{\cdot}59$ Å and $by = 2{\cdot}36$ Å. The overall packing arrangement, present in this crystal, can be readily visualized if Fig. 1 in this paper is compared with Fig. 2 of Goldberg & Shmueli (1973*a*). The best-plane data for PHT and TCNQ are presented in Table 4. The approximate mean interplanar donor–acceptor separation, within an overlapping PHT–TCNQ pair, is 3·41 Å for the conventionally refined structure.

Molecular geometry

Bond lengths and valency angles within the TCNQ and PHT molecules, which result from the conventional refinement, are listed elsewhere (Goldberg & Shmueli, 1973*a*); for PHT, the geometrical parameters are also shown in Fig. 6. Fig. 7 illustrates the molecular geometry of TCNQ obtained from the final refinement. The interatomic separations within the TCNQ molecule are close to previously observed values in essentially neutral TCNQ species found in mixed-stack charge-transfer complexes with planar aromatic donors. Although some of the chemically equivalent molecular dimensions of TCNQ in the present structure are not

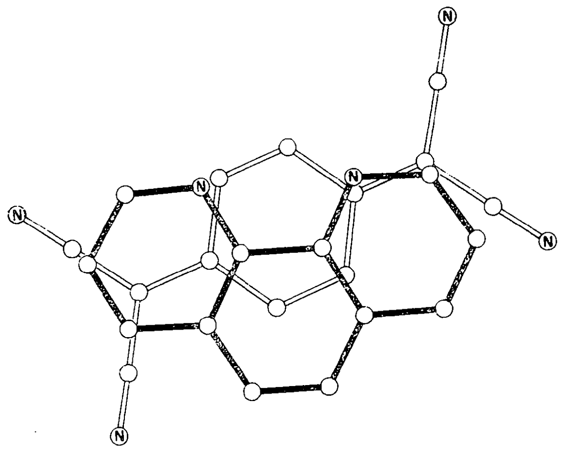


Fig. 5. Overlap diagram of the PHT–TCNQ complex. The PHT molecule was taken from the conventional-refinement results.

Table 4. *Best planes of PHT and TCNQ*

(*a*) Equations of best planes

(1) PHT at the principal site
$-0{\cdot}711x - 0{\cdot}125y + 13{\cdot}060z = 4{\cdot}887$ Å

(2) PHT at the minor site
$-0{\cdot}366x + 0{\cdot}276y + 13{\cdot}078z = 4{\cdot}892$ Å

(3) TCNQ (quinonoid part)
$-0{\cdot}329x + 0{\cdot}144y + 13{\cdot}079z = 1{\cdot}522$ Å

(4) PHT from conventional refinement
$-0{\cdot}648x + 0{\cdot}0023y + 13{\cdot}066z = 4{\cdot}894$ Å

(*b*) Deviations (Å) from the best planes

(3) C(2′)–C(4′), C(9′)–C(12′) $\leq \pm 0{\cdot}01$; C(1′) 0·02; C(5′) −0·03; N(6′) −0·07; C(7′) 0·13; N(8′) 0·30; C(13′) −0·02; N(14′) −0·02; C(15′) −0·06; N(16′) −0·12.

(4) N(1)–C(6), C(8), C(10)–C(14) $\leq \pm 0{\cdot}01$; C(7) 0·02; C(9) −0·02.

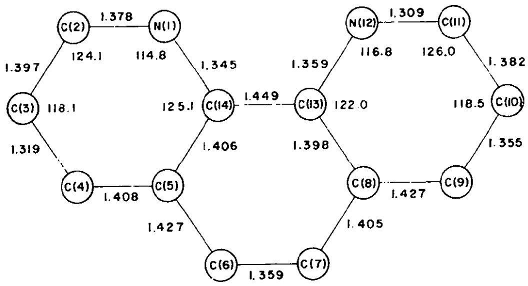


Fig. 6. Molecular geometry of PHT resulting from the conventional refinement. The average e.s.d. of an interatomic distance is 0·010 Å.

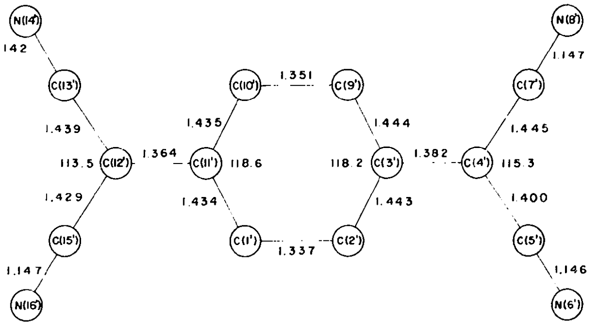
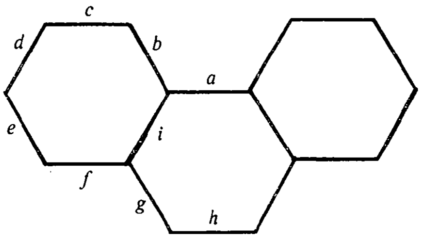


Fig. 7. Molecular geometry of TCNQ after the constrained refinement. The average e.s.d. of an interatomic distance is 0·008 Å.

Table 5. *Averaged bond distances of 1,10-phenanthroline and corresponding bond orders*

The π bond order, relating atoms i and j, is defined as $P_{ij} = \Sigma_k n_k c_{ik} c_{jk}$, where c_{pq} are the coefficients of atomic orbitals in the corresponding molecular orbitals (MO), and n_q is the number of electrons occupying the qth MO. The MO's were calculated by the iterative extended Huckel method (Rein, Clarke & Harris, 1970).



Bond	Present work	Frenz & Ibers (1972)*	Frenz & Ibers (1972)	Veal, Hatfield & Hodgson (1973)	Bond order
a	1·45 Å	1·42 Å	1·41 Å	1·42 Å	0·31
b	1·35	1·37	1·35	1·36	0·42
c	1·34	1·34	1·33	1·34	0·54
d	1·39	1·42	1·41	1·41	0·45
e	1·34	1·36	1·34	1·35	0·52
f	1·42	1·41	1·39	1·39	0·40
g	1·43	1·44	1·43	1·43	0·33
h	1·36	1·34	1·32	1·32	0·59
i	1·40	1·43	1·42	1·40	0·40

* Averaged data from Table 7.

equal, within the limits of the statistical error, the average bond distances of TCNQ agree well with the relevant dimensions in other TCNQ compounds (*e.g.* Shaanan, Shmueli & Rabinovich, 1976; Lisensky, Johnson & Levy, 1976). It is reasonable to assume that the observed deviations in chemically equivalent bond lengths, *e.g.* C(3′)–C(4′), C(11′)–C(12′) and C(4′)–C(5′), C(4′)–C(7′) of this structure, originate mainly from the lack of a precise structural model of the complex (because of the dynamic disorder), as well as from the somewhat limited observed intensity data.

The dimensions of the conventionally refined PHT molecule are of low accuracy, which is probably in part a result of the unaccounted for orientational disorder of PHT. Thus, some chemically equivalent distances in PHT [*e.g.* N(1)–C(2) and C(11)–N(12)] differ from their mean by more than three times the estimated standard deviations. Nevertheless, the distribution of mean bond distances in the PHT molecule is similar to that observed in a large number of PHT complexes (Table 5). In particular, the C(3)–C(4), C(6)–C(7) and C(9)–C(10) bonds are usually much shorter than the other C–C bonds within the molecular framework. This distribution of bond lengths also compares reasonably well with relative bond-order values evaluated from iterative extended Huckel MO calculations on a molecular model of PHT (Table 5, Goldberg, 1973).

As mentioned above, the molecular donor–acceptor units in the crystal structure of PHT–TCNQ are arranged as separate entities rather than in the form of continuous stacks. Semi-empirical calculations (Goldberg, 1975), indicate that the observed overlap mode between PHT at its major site and TCNQ (Fig. 5) closely corresponds to a relative configuration of a donor–acceptor pair obeying Mulliken's (1956) 'overlap and orientation principle'. This indicates that a relative arrangement of PHT and TCNQ, which is favoured by Mulliken's model of charge-transfer interactions, is also accommodated by the much more powerful pattern of London–van der Waals interactions. Similar encouraging correlations between observed overlap modes and calculated donor–acceptor overlap integrals were also obtained for several other TCNQ mixed-stack compounds (Goldberg, 1975).

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Die Kristallstruktur von Tetramethylammonium-hexaisothiocyanatoferrat(III), $[N(CH_3)_4]_3[Fe(NCS)_6]$

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$[N(CH_3)_4]_3[Fe(NCS)_6]$ cristallizes in the monoclinic space group $C2/c$; the lattice parameters are $a = 24\cdot95$, $b = 9\cdot30$, $c = 34\cdot43$ Å and $\beta = 125\cdot22°$; $Z = 8$. With X-ray diffraction data collected on a four-circle diffractometer, the crystal structure was solved with the combined information of a three-dimensional Patterson synthesis and of structure factor signs determined by the 'direct' method; light atoms, including 20 H atoms, were found by difference Fourier syntheses. Refinement by the method of least squares led to an agreement index of $R = 8\cdot0\%$ for the 1265 observed reflexions. In the structure, two crystallographically independent $[Fe(NCS)_6]^{3-}$ ions are present; they differ in their geometry, having point symmetry 1 and 2, respectively. All the NCS groups are bonded to Fe *via* their N atoms, with Fe—N—C bond angles between 145 and 179°. Of the three crystallographically independent $N(CH_3)_4^+$ ions, one is either disordered or rotates in the crystal.

Nach Fung & Drickamer (1969) soll das $[Fe(NCS)_6]^{3-}$-Ion bei Normalbedingungen als Thiocyanato-Komplex mit Fe—S-Bindungen vorliegen, welcher sich unter Druck irreversibel zum Isothiocyanatoferrat(III) umlagert. Die druckabhängige Isomerisierung konnte von Hellner, Ahsbahs, Dehnicke & Dehnicke (1974) nicht bestätigt werden, und schwingungsspektroskopische Befunde sprechen dafür, dass der Komplex nur als Isothiocyanatoferrat mit Fe—N-Bindungen existiert (Bailey, Kozak, Michelsen & Mills, 1971; Clark & Goodwin, 1970; Forster & Goodgame, 1965). Um eine sichere Aussage über die Struktur bei Normaldruck zu erhalten, wurde die vorliegende Strukturbestimmung durchgeführt.

Messmethodik und Kristalldaten

Einkristalle von $[N(CH_3)_4]_3[Fe(NCS)_6]$ wurden nach der Methode von Forster & Goodgame (1965) erhalten. Ein Exemplar davon, das etwa 0,135 × 0,17 × 0,23 mm gross war, diente für alle Messungen.

Zur Ermittlung der Elementarzelle und Raumgruppe wurden zunächst mehrere Präzessionsdiagramme angefertigt. Die Berechnung genauerer Gitterkonstanten erfolgte dann mit den Werten der Beugungswinkel von 15 ausgewählten Reflexen, die am Einkristalldiffraktometer mit Mo $K\alpha$-Strahlung vermessen wurden. Die erhaltenen Werte sind nachstehend mit einigen weiteren Angaben aufgeführt.

Gitterkonstanten: $a = 24{,}95 \pm 0{,}05$; $b = 9{,}30 \pm 0{.}03$; $c = 34{,}43 \pm 0{,}06$ Å; $\beta = 125{,}22 \pm 0{,}06°$; $V = 6567$ Å^3. Ausgelöschte Reflexe: hkl wenn $h + k = 2n + 1$; $h0l$ wenn $l = 2n + 1$. Raumgruppe: $C2/c$ (Nr. 15) (die nach den Auslöschungen ebenfalls mögliche Raumgruppe Cc konnte später ausgeschlossen werden). Formeleinheiten pro Elementarzelle: $Z = 8$ (aus der Volumenbeanspruchung der Atome abgeschätzt). Berechnete Dichte: 1,28 g cm^{-3}. $F(000) = 2632$.

Die Interferenzintensitäten wurden bei Zimmertemperatur an einem automatischen Vierkreisdiffraktometer der Firma Enraf–Nonius (Kappa-Geometrie) mit monochromatischer Mo $K\alpha$-Strahlung gemessen (50 kV, 20 mA; Graphit-Monochromator; ω–$\frac{1}{3}\theta$-scan). Von symmetrieäquivalenten Reflexen wurde jeweils nur einer gemessen, und zwar alle theoretisch möglichen im Messbereich bis $\theta = 14{,}2°$, von $\theta = 14{.}2$ bis 24° jedoch nur, nachdem eine schnelle Vorausmessung eine nennenswerte Intensität erwarten liess. Bei schwachen Reflexen wurde die Messzeit auf

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* Gegenwärtige Anschrift.