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Structure and Packing Arrangement of Molecular Compounds. I. (1:1) 7,7,8,8-Tetracyanoquinodimethane*N*–,*N'*-Dimethyldihydrophenazine

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The 1:1 modification of the molecular complex of 7,7,8,8-tetracyanoquinodimethane (TCNQ) with *N,N'*-dimethyldihydrophenazine (DMPH) crystallizes in the *C*-centred monoclinic Bravais lattice with two units of the complex in a unit cell of dimensions: $a=11{\cdot}166$ (8), $b=13{\cdot}583$ (6), $c=6{\cdot}799$ (3) Å and $\beta=92{\cdot}39$ (5)°. The structure was solved from three-dimensional integrated precession data with the aid of a Patterson synthesis and other considerations. The space group *Cm* was confirmed by the structure determination. Least-squares refinement, based on precession and diffractometer data, led to conventional *R* indices of 0·049 and 0·056 and to weighted *r* indices of 0·045 and 0·020 for the film and counter data respectively. The structure consists of stacks in which TCNQ and DMPH alternate along the *c* axis. DMPH is folded about the central N---N line while TCNQ is bowed significantly, so that short (< 3·3 Å) intermolecular approaches can be maintained throughout the stack. Intrastack contacts and molecular geometry of TCNQ suggest the presence of rather strong charge transfer interactions. The overall tight packing is reflected in a similar description of motion of the two molecules. The dihedral angle between the two halves of DMPH is about 165°. The methyl carbon atoms are quasi-equatorially attached to the central ring of DMPH. The C–N(ring) bond distances average 1·391 Å indicating, in comparison with other structures, partially sp^3 hybridized nitrogen atoms in DMPH.

Introduction

The present paper is part of a study of mixed-stack charge-transfer complexes involving 7,7,8,8-tetracyanoquinodimethane (TCNQ) as the acceptor. Specifically, it is desired to produce in this study reasonably accurate structural information on a series of complexes involving donors of comparable shapes but differing in their electronic structures, and to attempt, where feasible, a theoretical explanation of the observed packing arrangements.

A preliminary note on the structure of the (1:1) TCNQ–phenazine complex was presented elsewhere (Goldberg & Shmueli, 1971*b*), the (1:1) TCNQ–*N,N'*-dimethyldihydrophenazine (DMPH) complex is the subject of the present paper and the (1:1) TCNQ complexes with phenazine and dibenzo-*p*-dioxin are described after this paper (Goldberg & Shmueli, 1973*a,b*).

Prior to this study, the structures of (1:1) TCNQ–*N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Hanson, 1965), of (1:1) TCNQ–anthracene (Williams & Wallwork, 1968) and of (1:1) TCNQ–hexamethylbenzene (Colton & Henn, 1970) complexes were described. Anthracene-like donors are readily available in modifications corresponding to the above set criteria and hence these donors, supplemented by the known anthracene, were chosen to be studied.

The purpose of this paper is to describe the crystal and molecular structure of the TCNQ–DMPH complex as determined from three-dimensional intensity data collected by photographic and counter methods.

Experimental

Crystals of the TCNQ–DMPH complex were kindly supplied by Dr L. R. Melby. Symmetry information and approximate cell constants were deduced from Weissenberg and precession photographs of these crystals. Further recrystallization, necessary in order to obtain large enough specimens, was performed by a (prolonged) slow cooling of a saturated solution of the complex in acetonitrile. Black prisms, elongated in the [001] direction were obtained.

Crystal data

$(C_{14}H_{14}H_2)(C_{12}H_4H_4)$, M. W. 414·5
Monoclinic
$a=11{\cdot}166\pm0{\cdot}008$, $b=13{\cdot}583\pm0{\cdot}006$, $c=6{\cdot}799\pm003$Å
$\beta=92{\cdot}39\pm0{\cdot}05°$, $V_{cell}=1030{\cdot}3$ Å^3
$D_m=1{\cdot}32$ g cm^{-3} (by flotation), $Z=2$,
$D_c=1{\cdot}336$ g cm^{-3}

Systematic absences: *hkl* with $h+k=2n+1$
Possible space groups: *C*2, *Cm* and *C*2/*m* (*Cm* confirmed by the structure determination)
μ(Mo $K\alpha$) = 0·9 cm^{-1}.

The unit-cell dimensions were derived from their least-squares fit to 21 observations on copper-calibrated Weissenberg [λ(Cu $K\alpha_1$) = 1·54051, λ(Cu $K\alpha_2$) = 1·54433 Å] and on precession [λCu $K\alpha$) = 1·5418 Å] photographs. The intensity data were collected first by photographic techniques and at a later stage by counter methods.

Precession data

Integrated precession intensity data were obtained using Mo $K\alpha$ radiation. 2367 reflexions were recorded on twelve layers ($0kl$–$5kl$, $h0l$–$h5l$) and their intensities were measured with a Joyce–Loebl microdensitometer. 869 reflexions, too weak to be reliably measured, were classified as unobserved and their intensities were taken as $\frac{1}{2}I_{\min}$. Data reduction consisted of evaluating weighting parameters, application of Lorentz and polarization corrections and cross-scaling of the reflexions on different layers. 287 reflexions which appeared on more than one layer were used in the least-squares scaling procedure. The resulting data set, which was subsequently used in the structure determination, consists of 1080 independent F_o values including 398 F_o's that correspond to the unobserved reflexions. Absorption corrections were not applied.

Diffractometer data

The counter data on TCNQ–DMPH were collected at the Laboratory of Structural Chemistry and processed at the Computation Centre of the University of Groningen. A crystal of approximate dimensions $0{\cdot}15\times0{\cdot}15\times0{\cdot}30$ mm was mounted rigidly onto a thin glass needle and was aligned with **c*** parallel to the φ axis of an Eulerian cradle. A three-circle automatic diffractometer of Nonius (Mark AD-3) with Mo $K\alpha$ radiation were employed. The cell dimensions, used previously for the film work, were rechecked and the angular settings were computed from them. Two sets of data, $I(hkl)$ and $I(h\bar{k}l)$, each comprising all the independent reflexions with $\sin\theta/\lambda\le0{\cdot}65$ Å^{-1}, were measured with the θ–2θ scanning technique. 1093 and 1083 non-zero intensities were obtained from the $I(hkl)$ and $I(h\bar{k}l)$ sets respectively, out of the 1242 reflexions within the scanning range. The maximum deviations of the intensities of standard reflexions amounted to about 2% (*ca.* two standard deviations) of their average values. The intensity of a standard reflexion was recorded after each group of 47 measurements. Structure amplitudes were obtained in the usual manner, without applying absorption or extinction corrections. Each reflexion was assigned a weight $w(F_o)=1/\sigma^2(F_o)$ where $\sigma(F_o)$ is the standard deviation of F_o based on counting statistics and on estimates of error in attenuation-filter factors. The two data sets were scaled together and averaged. The unified set contains 996 non-zero reflexions common to both sets, including 153 reflexions for which $F_o\le3\sigma(F_o)$. These weak reflexions were excluded from the refinement of the structure.

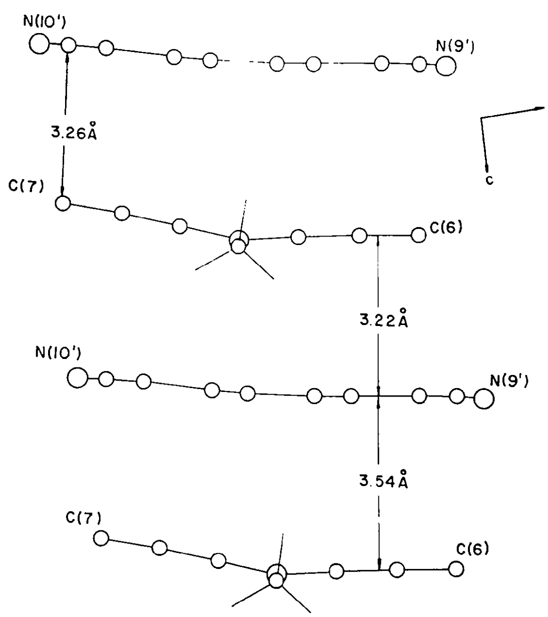


Fig. 1. Projection of the stack down the b axis.

Most of the computations were performed on the CDC-6600 computer at the Tel-Aviv University with programs described elsewhere (Goldberg & Shmueli, 1971*a*). Thermal ellipsoid and some packing illustrations were drawn with the aid of the *ORTEP* program (Johnson, 1965).

Structure determination and refinement

The molecular orientation deduced from a three-dimensional Patterson synthesis and supported by packing and intensity considerations led to a trial structure in which nearly planar molecules of DMPH and TCNQ are stacked along the c axis with their mean planes parallel to the $(10\bar{2})$ plane. The available symmetry information and unit-cell contents ($Z=2$) also indicated that DMPH and TCNQ form mixed rather than segregated stacks.

Intensity statistics indicated, through the $N(z)$ (Howells, Phillips & Rogers, 1950) and intensity moment (Foster & Hargreaves, 1963) tests, a centric intensity distribution. Accordingly, a model with planar molecules and disordered methyl groups of DMPH, based on the space group $C2/m$, was assumed. However, this assumption was indicated to be inadequate by the failure of R to decrease below 0·33 in the isotropic refinement of the $C2/m$ trial structure. Re-examination of the assumptions in view of the chemistry of the TCNQ–DMPH complex in solution (Melby, 1965) showed that the postulated planar skeleton of DMPH was probably a weak link. On the other hand, hypersymmetry could be suspected in this highly ordered arrangement and in fact (centric) hypersymmetry was found previously in the related arrangement of the 1:1 TCNQ–phenazine complex (Goldberg & Shmueli, 1973*a*). Since only a minor change of configuration of DMPH was possible, the same trial structure was refined in the space group Cm, as the space group $C2$ was ruled out on the basis of packing considerations. After several cycles of isotropic refinement the R index dropped to 0·15 and the calculation proceeded smoothly from this point on.

The photographic data used for the determination of the structure and the later available diffractometer data were employed in two separate least-squares refinements of the structure. In order to economize on this process, each molecule was kept in a separate block in the matrix of normal equations. As a starting point for the refinement with counter data the output of the last isotropic cycle with film data was taken.

Some details on the refinement and final reliability indices are presented for both sets of data in Table 1. The weights for the counter data set were taken as $w=1/\sigma^2(F_o)$ without modifications, since the distribution of $\langle w\Delta^2\rangle$ with increasing $\sin\theta/\lambda$ appeared reasonably constant (Table 2).

The initial coordinates of all the hydrogen atoms were derived, in both cases, from difference maps computed in planes parallel to the relevant planes of DMPH and of TCNQ and in planes perpendicular to the N–C(methyl) bond in DMPH. Difference maps based on the counter data set had a lower background and

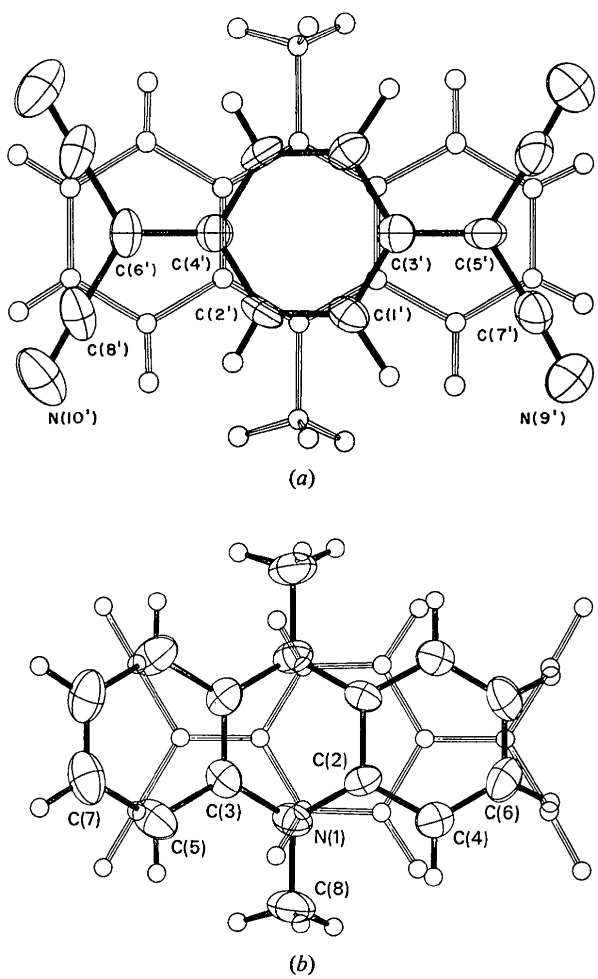


Fig. 2. Molecular overlap in projection on the best plane of TCNQ; (*a*) the symmetrically superimposed pair, (*b*) the staggered pair. This figure, with 50% probability thermal ellipsoids, was produced with the aid of the program *ORTEP* (Johnson, 1965).

Table 1. *Some details on the refinement*

	Precession data	Diffractometer data
Number of reflexions in the final stage	679 (observed) 124 (unobserved with $\|F_c\|>F_o/K$)	841 (with $F_o>3\sigma(F_o)$)
Weighting function	*$w=4w_o/F_o^2$	$w=1/\sigma^2(F_o)$
Conventional R	†0·049 (observed only) †0·060 (including unobserved)	‡0·056
Weighted r§	†0·045 (including unobserved)	‡0·020
$[\sum w(F_o-K\|F_c\|)^2/(n-m)]^{1/2}$ with $m=186$	1·04 ($n=803$)	1·21 ($n=841$)

* The experimental weighting parameter w_o is given, for a single measurement, by $w_o=I^2/\sigma^2(I)$ where I is the relative intensity and $\sigma(I)$ is the corresponding error estimate.

† The reflexions 002, 020 and $11\bar{2}$ were excluded because of probable extinction.

‡ The reflexion $11\bar{2}$ was excluded because of probable extinction, and the 003 reflexion, which was affected by white radiation due to 002, was also omitted.

§ $r=[\sum w(F_o-K|F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. *Distribution of* $\langle w\Delta^2\rangle$ *in the diffractometer data set, as a function of* $\sin\theta/\lambda$

Group*	$\langle F_o\rangle$	$\langle w\Delta^2\rangle$	$\langle\sin\theta/\lambda\rangle$
1	53·0	3·74	0·175
2	35·3	2·42	0·265
3	26·2	1·99	0·318
4	19·1	1·52	0·363
5	20·3	1·31	0·398
6	21·0	1·08	0·427
7	19·7	1·03	0·454
8	18·5	1·08	0·477
9	14·0	0·81	0·501
10	14·3	1·16	0·525
11	12·0	1·25	0·552
12	12·0	1·26	0·584
13	11·1	0·98	0·609
14	11·0	1·57	0·635

* Each group contains 60 reflexions ordered on increasing $\sin\theta/\lambda$.

gave more reasonable positions for several hydrogen atoms.

The discrepancies between both sets of data are reflected in the agreement factors. The somewhat higher unweighted R for counter data is due to poorer agreement between F_o and $K|F_c|$ for the very weak reflexions while the lower r reflects the superiority of the weighting scheme based on counting statistics. The values of $F_o-K|F_c|$ for moderate and strong reflexions are smaller for the counter data set, which is consistent with the cleaner difference maps. These differences affect mainly the comparison of the thermal parameters. The t-test ratio

$$t=\frac{|p_F-p_D|}{[\sigma^2(p_F)+\sigma^2(p_D)]^{1/2}}\ ,$$

where the subscripts F and D stand for film and diffractometer respectively, exceeds 3 for seven parameters while $2 \leq t < 3$ for sixteen parameters, most of these being components of anisotropic vibration tensors. These discrepancies are seen in the results of rigid-body motion analyses. The positional parameters, on the other hand, agree much better as can also be appreciated from the description of the structure, given below.

The final atomic parameters obtained from the two sets of intensity data are given in Tables 3 and 4. A list of observed and calculated structure amplitudes is given in Table 5 for precession and the diffractometer data sets.

The atomic scattering factors used in this study were taken from Hanson, Herman, Lea & Skillman (1964) for carbon and nitrogen, and from Stewart, Davidson & Simpson (1968) for hydrogen.

Description of the structure

Packing and thermal motion

The DMPH and TCNQ molecules form mixed stacks along the c axis. An edge-on view of the molecules (Fig. 1) shows several features of interest regarding the molecular configurations and packing.

It is not possible to define interplanar spacings in the stack since the DMPH molecule is folded along the N---N line, the mean dihedral angle being about 165°, while TCNQ has its central part slightly but significantly bowed.* It is seen, however, that a range of rather short (< 3·3 Å) contacts is maintained throughout the stack, suggesting the presence of a relatively strong charge transfer interaction. Distortions of TCNQ from planarity have also been observed in other structures where strong attractive interactions are known to be present [*e.g.* $TCNQ^-Rb^+$; Hoekstra, Spoelder & Vos, 1972; $(TCNQ)_2^-$-tetraphenylphosphonium; Goldstein, Seff & Trueblood, 1968]. These examples, however, refer to structures in which TCNQ forms segregated stacks.

The two different modes of superposition of the stacked molecules are shown in Fig. 2. In projection, the symmetric superposition [Fig. 2(*a*)] is similar to that observed in the TCNQ–anthracene complex (Williams & Wallwork, 1968). In the other superposition, which corresponds to the more tightly packed pair, the molecules are staggered so that the C(4′)–C(6′) quinonoid bond of the TCNQ partially overlaps the central ring of DMPH.

A projection of part of the structure on the ab plane (Fig. 3) shows that the sideways packing of the stacks is stabilized to a considerable extent by the H(meth-

* It is noted that this picture rests on the two sets of intensity data. The drawings, however, were prepared from the atomic parameters based on the diffractometer data set.

Table 3. *Fractional atomic coordinates* (×10⁴)

E.s.d.'s, in parentheses, are given in units of the last decimal place.

	Precession data			Diffractometer data		
	x	*y*	*z*	*x*	*y*	*z*
DMPH						
N(1)	−909	1007 (3)	365	−898	1010 (2)	377
C(2)	195 (5)	520 (3)	539 (6)	183 (3)	523 (2)	560 (5)
C(3)	−1922 (5)	516 (3)	−309 (6)	−1921 (4)	510 (3)	−295 (5)
C(4)	1286 (6)	1009 (5)	781 (7)	1281 (4)	1004 (4)	796 (7)
C(5)	−2966 (6)	1016 (5)	−939 (7)	−2951 (4)	1018 (4)	−949 (7)
C(6)	2335 (6)	503 (5)	1047 (7)	2342 (4)	503 (3)	1053 (7)
C(7)	−3986 (6)	516 (5)	−1508 (7)	−3983 (4)	510 (4)	−1513 (7)
C(8)	−941 (8)	2093 (4)	559 (9)	−924 (5)	2094 (3)	557 (8)
H(8–1)	−40 (5)	229 (4)	158 (7)	−34 (3)	234 (3)	167 (5)
H(8–2)	−96 (5)	239 (4)	−78 (7)	−68 (3)	231 (3)	−82 (5)
H(8–3)	−183 (7)	224 (6)	98 (9)	−180 (3)	229 (3)	110 (5)
H(4)	131 (5)	170 (4)	88 (6)	126 (3)	171 (3)	96 (5)
H(5)	−284 (4)	169 (4)	−102 (5)	−293 (3)	168 (3)	−92 (5)
H(6)	298 (5)	83 (4)	129 (7)	304 (3)	79 (3)	127 (5)
H(7)	−474 (5)	86 (4)	−193 (6)	−470 (3)	88 (3)	−179 (5)
TCNQ						
C(1′)	131 (6)	903 (4)	5275 (6)	151 (4)	913 (3)	5284 (5)
C(2′)	−1055 (5)	897 (4)	4904 (6)	−1046 (4)	890 (3)	4905 (5)
C(3′)	796 (7)	0	5423 (7)	806 (5)	0	5453 (7)
C(4′)	−1696 (7)	0	4651 (8)	−1697 (5)	0	4652 (8)
C(5′)	2029 (7)	0	5750 (9)	2037 (5)	0	5762 (9)
C(6′)	−2906 (7)	0	4100 (8)	−2903 (5)	0	4094 (8)
C(7′)	2685 (5)	888 (5)	5943 (7)	2709 (4)	888 (4)	5959 (6)
C(8′)	−3567 (6)	900 (5)	3819 (7)	−3567 (4)	910 (4)	3839 (6)
N(9′)	3211 (5)	1617 (4)	6135 (7)	3202 (3)	1625 (3)	6149 (6)
N(10′)	−4068 (6)	1634 (5)	3657 (7)	−4075 (4)	1616 (4)	3665 (6)
H(1′)	63 (5)	150 (5)	554 (7)	70 (3)	161 (3)	554 (5)
H(2′)	−150 (4)	149 (4)	484 (6)	−146 (2)	146 (2)	489 (4)

yl)···N(cyano) short contact of about 2·4 Å. The only other interstack contact shorter than the sum of the van der Waals radii (Pauling, 1960) involved is C(methyl)···N(cyano) = 3·38 Å. Adjacent stacks in a sheet parallel to the *ac* plane are staggered along the *c* axis so that the *zc* coordinates of N(9′) and N(10′) in adjacent stacks differ by 1·7 Å.

The anisotropic vibration parameters of TCNQ and DMPH are consistent with the packing just described. Thus, the unequal vibration of the cyanomethylene groups in TCNQ [Fig. 2(*a*), Table 4] is compatible with the C(5′) and C(7′) atoms being located in the region of closest approach with DMPH, where C(5′) exactly overlaps the centre of the C(6)–C(14) bond in

Table 4. *Anisotropic vibration components* $U^{ij} \times 10^4$ (Å^2)

E.s.d.'s, in parentheses, are given in units of the last decimal place. The 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.

(*a*) From diffractometer data

	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
			DMPH			
N(1)	526 (22)	316 (19)	377 (21)	77 (19)	−64 (18)	−118 (17)
C(2)	425 (24)	288 (22)	259 (18)	−67 (21)	5 (20)	3 (16)
C(3)	414 (23)	435 (27)	240 (19)	63 (22)	−39 (22)	−92 (16)
C(4)	461 (32)	366 (31)	529 (27)	−26 (28)	−7 (27)	−29 (21)
C(5)	648 (36)	467 (41)	414 (26)	175 (30)	−84 (28)	−116 (23)
C(6)	371 (28)	586 (35)	583 (28)	−138 (26)	−7 (26)	91 (23)
C(7)	448 (28)	846 (42)	433 (25)	120 (24)	−52 (25)	−115 (21)
C(8)	755 (37)	295 (24)	700 (39)	78 (26)	−81 (26)	−159 (31)
			TCNQ			
C(1′)	418 (28)	328 (24)	336 (25)	92 (30)	−49 (24)	17 (19)
C(2′)	443 (34)	257 (23)	384 (25)	173 (28)	−7 (22)	−34 (21)
C(3′)	382 (39)	361 (46)	258 (33)	0	0	−46 (27)
C(4′)	350 (42)	341 (45)	306 (32)	0	0	−20 (28)
C(5′)	479 (48)	232 (40)	435 (40)	0	0	−49 (32)
C(6′)	267 (39)	581 (50)	349 (34)	0	0	−57 (27)
C(7′)	389 (29)	457 (32)	489 (26)	68 (26)	−21 (24)	−105 (21)
C(8′)	320 (28)	702 (40)	436 (27)	124 (27)	127 (26)	7 (20)
N(9′)	599 (27)	573 (32)	899 (34)	−111 (22)	−49 (25)	−131 (24)
N(10′)	640 (29)	795 (38)	829 (33)	324 (25)	185 (27)	−33 (23)

Isotropic vibration parameters of the hydrogen atoms

H(8–1)	3·9 (0·9)	H(4)	3·0 (0·9)	H(7)	6·7 (1·3)
H(8–2)	4·9 (1·1)	H(5)	2·6 (0·9)	H(1′)	7·0 (1·3)
H(8–3)	6·0 (1·1)	H(6)	2·9 (1·0)	H(2′)	0·9 (0·8)

(*b*) From precession data

	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
			DMPH			
N(1)	481 (29)	203 (20)	393 (20)	36 (30)	−40 (18)	−93 (18)
C(2)	378 (30)	230 (25)	291 (18)	26 (36)	50 (22)	20 (17)
C(3)	445 (29)	425 (29)	221 (17)	143 (37)	−37 (22)	−93 (17)
C(4)	436 (38)	328 (34)	497 (27)	−137 (47)	30 (28)	−34 (22)
C(5)	590 (45)	464 (45)	380 (24)	41 (46)	−108 (29)	−148 (24)
C(6)	352 (35)	487 (41)	549 (30)	−62 (41)	46 (27)	95(26)
C(7)	440 (35)	866 (54)	368 (24)	165 (40)	−2 (26)	−70 (23)
C(8)	840 (59)	252 (28)	673 (38)	1 (41)	10 (28)	−347 (36)
			TCNQ			
C(1′)	388 (36)	282 (28)	309 (22)	−16 (50)	−17 (24)	−4 (20)
C(2′)	319 (39)	250 (28)	345 (22)	62 (47)	4 (23)	17 (20)
C(3′)	234 (46)	381 (50)	198 (28)	0	0	−55 (26)
C(4′)	304 (53)	326 (47)	204 (26)	0	0	−74 (27)
C(5′)	360 (61)	338 (53)	411 (38)	0	0	−40 (33)
C(6′)	245 (51)	328 (48)	322 (31)	0	0	−31 (29)
C(7′)	241 (38)	508 (41)	513 (28)	72 (39)	−52 (28)	−48 (23)
C(8′)	410 (42)	565 (44)	419 (25)	−48 (42)	73 (29)	−11 (22)
N(9′)	425 (35)	575 (37)	838 (32)	−131 (30)	−40 (27)	−58 (26)
N(10′)	639 (43)	709 (45)	812 (34)	211 (38)	160 (28)	4 (28)

Isotropic vibration parameters of the hydrogen atoms:

H(8–1)	5·3 (1·4)	H(4)	3·7 (1·2)	H(7)	4·8 (1·4)
H(8–2)	6·6 (1·2)	H(5)	1·3 (0·9)	H(1′)	5·1 (1·6)
H(8–3)	10·1 (2·4)	H(6)	4·7 (1·6)	H(2′)	3·3 (1·3)

DMPH. The other, 'free', cyanomethylene group appears to have a larger libration component in its plane. A corresponding feature of DMPH are smaller vibration components of C(2), C(4) and C(6) than those of C(3), C(5) and C(7) respectively [Fig. 2(*b*), Table 4].

Rigid-body motion analysis of the heavy atom vibration parameters was performed by the method of Schomaker & Trueblood (1968) and is summarized briefly

Table 5. *Observed and calculated structure amplitudes* (×5)

The reflexions excluded from the refinement are denoted by two asterisks, and those treated as unobserved by one asterisk.

(*a*) Film data

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

(*b*) Diffractometer data

H	K	L	FO	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

in Table 6. The discrepancies between the two data sets are reflected here in the systematically smaller librational and larger translational motion indicated by the diffractometer data set. The fit of TCNQ to the rigid-body model is rather poor and improves somewhat when the cyano groups are excluded from the analysis. However, the main features of the rigid-body motion of the whole TCNQ molecule and of its quinonoid fragment are very similar. The agreement of DMPH with the rigid-body model appears to be, on the average, more satisfactory.

In spite of the rather serious discrepancies between the two analyses, they agree in their physically reasonable description of the motion. Thus, the directions of largest libration and largest translation are close to the long axes of the molecules, the motion in the remaining two directions being more restricted (in particular the libration) in agreement with the restrictions imposed by the packing arrangement. Another indication of these analyses is the general similarity of the motions of the two molecules, as far as the amplitudes are concerned. This too seems reasonable in view of the similar packing restrictions on the freedom of motion of DMPH and TCNQ.

Molecular structure

The bond distances in DMPH and TCNQ (Table 7 and Fig. 4) do not differ significantly between the diffractometer and precession data sets. The t-test ratio

$$t=\frac{l_D-l_F}{[\sigma^2(l_D)+\sigma^2(l_F)]^{1/2}},$$

does not exceed 2 for any but three bonds [N(1)–C(2), and C(3)–C(11) in DMPH and C(8′)–N(10′) in TCNQ with t values of 3·1, 2·1 and 2·4 respectively]. As far as the internal consistency of chemically equivalent bonds is concerned, there are some discrepancies but their trend is similar for the two sets of data. The formal possibility of a fortuitously similar accumulation of errors in the diffractometer and precession data sets cannot, of course, be excluded. However, since these chemically equivalent bonds have considerably

Table 6. *Results of rigid-body motion analysis*

The eigenvectors of **L** and **T** are referred (in terms of the corresponding direction cosines $\times 10^4$) to the molecular systems defined by the eigenvectors of the molecular tensors of intertia **I**. The eigenvectors of **I** are referred to the reciprocal base vectors **a***, **b*** and **c***. Calculation is referred to the origin which symmetrizes **S** and reduces the trace of **T** (Schomaker & Trueblood, 1968). Components of the origin shifts, referred to the molecular centroids are given below, in Å units, as $\boldsymbol{\varrho}(\varrho_1,\varrho_2,\varrho_3)$. The r.m.s. discrepancies $\langle \Delta U^2\rangle^{1/2}$, corrected for the number of the degrees of freedom, are calculated in the crystal system to which the U^{ij}'s of Table 4 are referred.

(*a*) DMPH (all heavy atoms)

Precession data: Eigenvalues		Eigenvectors			Diffractometer data: Eigenvalues		Eigenvectors		
391 (at.wt. Å^2)		10·836	0	1·364	391 (at.wt. Å^2)		10·832	0	1·376
977	**I**	0	−13·583	0	978	**I**	0	−13·583	0
1355		2·694	0	−6·660	1355		2·713	0	−6·658
(5·6°)* 94×10^{-4} rad^2		8685	0	−4957	(5·0°) 75×10^{-4} rad^2		9079	0	−4191
(2·1°) 14	**L**	4957	0	8685	(2·9°) 26	**L**	4191	0	9079
(2·0°) 12		0	−1	0	(2·3°) 17		0	−1	0
398×10^{-4} Å^2		9531	0	3026	421×10^{-4} Å^2		9391	0	3436
253	**T**	3026	0	−9531	274	**T**	0	−1	0
234		0	1	0	249		3436	0	9391
		$\boldsymbol{\varrho}$(1·05, 0, −0·80)					$\boldsymbol{\varrho}$(0·34, 0, −0·05)		
		$\langle \Delta U^2\rangle^{1/2}$=0·0058 Å^2					$\langle \Delta U^2\rangle^{1/2}$=0·0046 Å^2		

(*b*) TCNQ (hydrogen atoms and C≡N groups excluded)

Precession data: Eigenvalues		Eigenvectors			Diffractometer data: Eigenvalues		Eigenvectors		
72 (at.wt. Å^2)		10·947	0	1·062	72 (at.wt. Å^2)		10·941	0	1·080
256	**I**	0	−13·583	0	257	**I**	0	−13·583	0
327		2·203	0	−6·715	329		2·233	0	−6·712
(5·6°) 97×10^{-4} rad^2		9738	0	2275	(4·8°) 70×10^{-4} rad^2		9362	0	3514
(2·9°) 26	**L**	0	−1	0	(2·5°) 19	**L**	0	−1	0
(1·5°) 7		2275	0	−9738	(2·0°) 12		3514	0	−9362
318×10^{-4} Å^2		9391	0	3436	$401\times10^{4-}$ Å^2		9055	0	4244
273	**T**	0	−1	0	285	**T**	0	−1	0
163		3436	0	−9391	238		4244	0	−9055
		$\boldsymbol{\varrho}$(−0·17, 0, 0·06)					$\boldsymbol{\varrho}$(0·97, 0, 0·78)		
		$\langle \Delta U^2\rangle^{1/2}$=0·0054 Å^2					$\langle \Delta U^2\rangle^{1/2}$=0·0089 Å^2		

* The corresponding r.m.s. amplitudes are given in parentheses.

different surroudings, some of the discrepancies may also be due in part to different environmental effects.

The bond distances in TCNQ, especially the charge-sensitive quinonoid bonds (averaging 1·386 Å), suggest, when compared with the compilation of Hoekstra *et al.* (1972), that TCNQ in this complex is partially charged. This barely significant indication is nevertheless consistent with the fact that in solution there is an equilibrium between the (TCNQ) (DMPH) and $(TCNQ)^-(DMPH)^+$ species (Melby, 1965) and which might reflect itself in the crystal as delocalization of charge throughout the stack. Another and probably better indication of strong charge transfer is provided by the rather short intermolecular distances along the stack, as mentioned above. A clear proof is, however, still missing since if ion–radical pairs exist in the crystal they are probably not in the triplet state as e.s.r. absorption is obtained only when the crystals are powdered. It is of interest to note here that no e.s.r. absorption was obtained from either powdered or crystalline TCNQ–phenazine (Goldberg & Shmueli, 1973*a*) and TCNQ–dibenzo-*p*-dioxin (Goldberg & Shmueli, 1973*b*) complexes, which probably have a mainly no-bond ground state.

The folded configuration of DMPH and the slight but significant bowing of its folded halves are further displayed by the deviations from some planes shown in Table 8. While folding of the molecule is probably a consequence of, at least partially, sp^3-hybridized nitrogen atoms in DMPH, the bowing of each half (planes III and IV in Table 8) is consistent with the packing forces operating in this system. This appears to be logical for the more distorted odd-numbered half of DMPH (Plane III) as the C(7) and C(15) carbon atoms are bowed away from the C(6′) cyanomethylene group of TCNQ so as to attain a 3·26 Å intermolecular separation (Fig. 1) from this group.

The C–N bond distances in the central ring, averaging 1·391 Å, are considerably longer than those observed in phenazine (1·345 Å; Herbstein & Schmidt, 1955) and somewhat shorter than those found in phenothiazine (1·406 Å; Bell, Blount, Briscoe & Freeman, 1968) and in *N*-substituted phenothiazine derivatives (*e.g.* diethazine, 1·41 and 1·42 Å; Marsau, 1971). This is consistent with DMPH having partially sp^3-hybridised nitrogen atoms.

The substitution of the methyl groups in DMPH is quasi-equatorial with respect to the central ring, similarly to the situation observed in phenothiazine (Bell *et al.*, 1968) and diethazine (Marsau, 1971).

Discussion

The description of DMPH–TCNQ presented above places this complex among mixed-stack structures commonly observed in π-molecular compounds (Prout &

Table 7. *Bond distances* (Å)

E.s.d.'s in parentheses are given in units of the last decimal place.

DMPH	(*a*)*	(*b*)*		(*a*)	(*b*)
N(1)–C(2)	1·378 (4)	1·400 (6)	C(5)–C(7)	1·384 (7)	1·369 (9)
	1·383	*1·404*		*1·389*	*1·372*
N(1)–C(3)	1·390 (4)	1·376 (6)	C(2)–C(10)	1·420 (5)	1·412 (6)
	1·394	*1·380*		*1·427*	*1·420*
N(1)–C(8)	1·480 (5)	1·481 (7)	C(3)–C(11)	1·385 (5)	1·403 (7)
	1·485	*1·489*		*1·392*	*1·411*
C(2)–C(4)	1·393 (6)	1·374 (8)	C(6)–C(14)	1·368 (7)	1·366 (9)
	1·397	*1·379*		*1·375*	*1·373*
C(3)–C(5)	1·397 (6)	1·400 (8)	C(7)–C(15)	1·384 (7)	1·402 (9)
	1·401	*1·404*		*1·391*	*1·410*
C(4)–C(6)	1·371 (7)	1·382 (9)			
	1·376	*1·386*			
C(4)–H(4)	0·97 (5)	0·94 (7)	C(8)–H(8–1)	1·04 (4)	0·94 (6)
C(5)–H(5)	0·90 (6)	0·93 (8)	C(8)–H(8–2)	1·02 (4)	0·99 (6)
C(6)–H(6)	0·88 (5)	0·86 (7)	C(8)–H(8–3)	1·09 (6)	1·06 (7)
C(7)–H(7)	0·96 (4)	1·00 (7)			
TCNQ					
C(1′)–C(2′)	1·351 (6)	1·338 (8)	C(5′)–C(7′)†	1·424 (6)	1·415 (8)
	1·354	*1·340*		*1·424*	*1·415*
C(1′)–C(3′)	1·442 (5)	1·435 (7)	C(6′)–C(8′)†	1·448 (6)	1·437 (9)
	1·447	*1·441*		*1·457*	*1·446*
C(2′)–C(4′)	1·417 (5)	1·420 (7)	C(8′)–N(10′)†	1·118 (7)	1·146 (9)
	1·422	*1·427*		*1·156*	*1·182*
C(3′)–C(5′)	1·382 (9)	1·385 (11)	C(7′)–N(9′)†	1·147 (7)	1·156 (9)
	1.384	*1·388*		*1·180*	*1·184*
C(4′)–C(6′)	1·384 (8)	1·386 (11)			
	1·387	*1·389*			
C(1′)–H(1′)	1·14 (5)	1·00 (7)	C(2′)–H(2′)	0·90 (5)	0·94 (7)

* Columns (*a*) and (*b*) refer to diffractometer and precession data sets respectively. Italicized values denote bond lengths corrected for libration [equation (21); Schomaker & Trueblood, 1968).

† Corrected for 'riding motion' by the method of Busing & Levy (1964).

Wright, 1968; Herbstein, 1971). The relatively short intrastack distances and the molecular geometry of TCNQ, described above, indicate that the 1:1 DMPH–TCNQ complex has a markedly dative (ionic) ground state. In this respect it is similar to 1:1 TCNQ–*N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (Hanson, 1965) and differs from other TCNQ mixed-stack complexes whose structures were described to date (with

Table 8. *Equations of some best planes with atomic deviations, based on the atomic parameters from the diffractometer data set*

The equation of a plane is given as $Ax+By+Cz=D$ where x,y,z are fractional coordinates of any point in the plane and D is its distance from the unit-cell origin. Only pertinent deviations (Å $\times 10^3$) are shown.

(*a*) DMPH

	I	II	III	IV	V
N(1)	0	−77	−33	−15	−213
C(2)	0	0	0		−41
C(3)	0	0		0	−43
C(4)			0		99
C(5)			−20	0	113
C(6)					216
C(7)				−59	208
C(8)	240	0			−340

Plane	defining atoms	*A*	*B*	*C*	*D* (Å)
I	N(1) C(2) C(3)	−2·604	−3·353	6·456	0·139
II	C(2) C(3) C(8)	−2·671	−1·869	6·597	0·223
III	C(2) C(4) C(10) C(12)	−1·455	0	6·772	0·353
IV	C(3) C(5) C(11) C(13)	−4·079	0	6·427	0·594
V	all heavy atoms	−2·713	0	6·658	0·282

(*b*) TCNQ

C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(7′)	C(8′)	N(9′)	N(10′)
0	0	26	31	81	149	92	179	69	189

Defining atoms: C(1′) C(2′) C(11′) C(12′)
Equation of the plane: $-2{\cdot}131x+6{\cdot}722z=3{\cdot}520$ Å

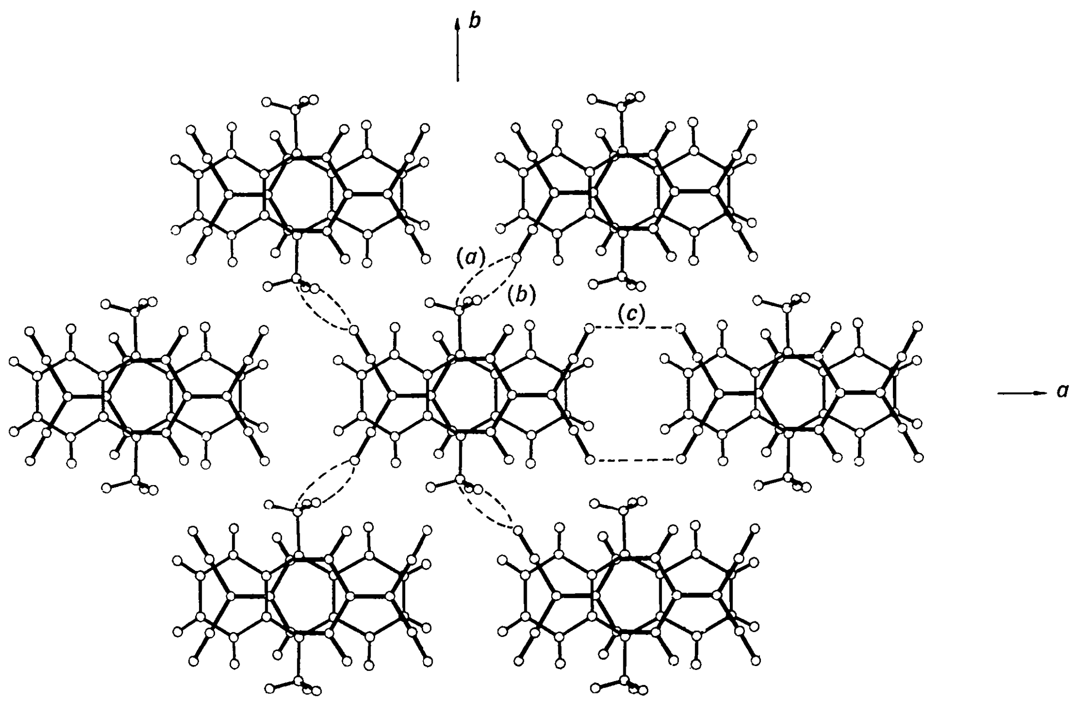
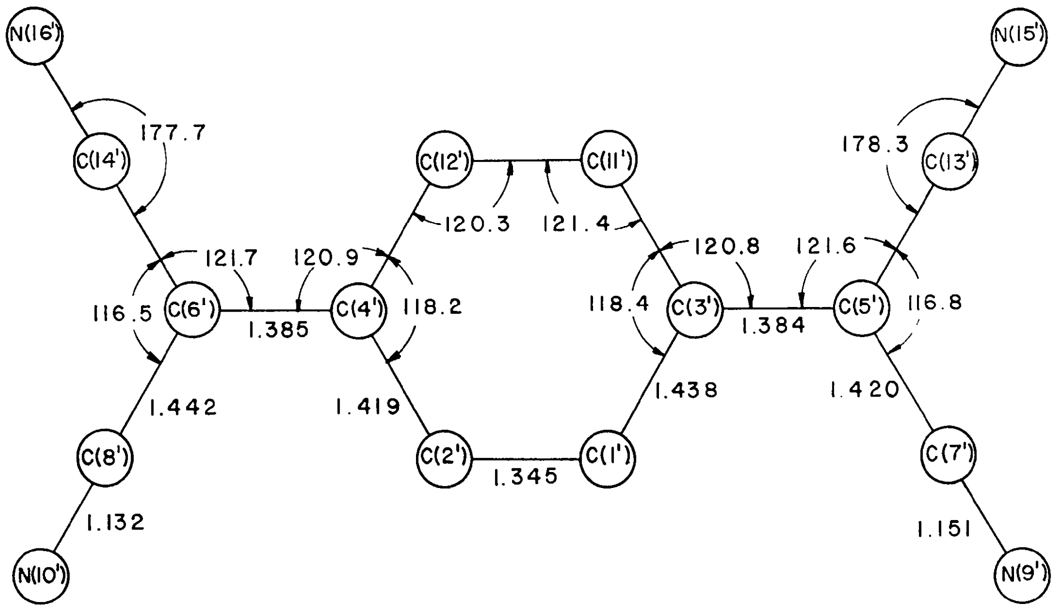
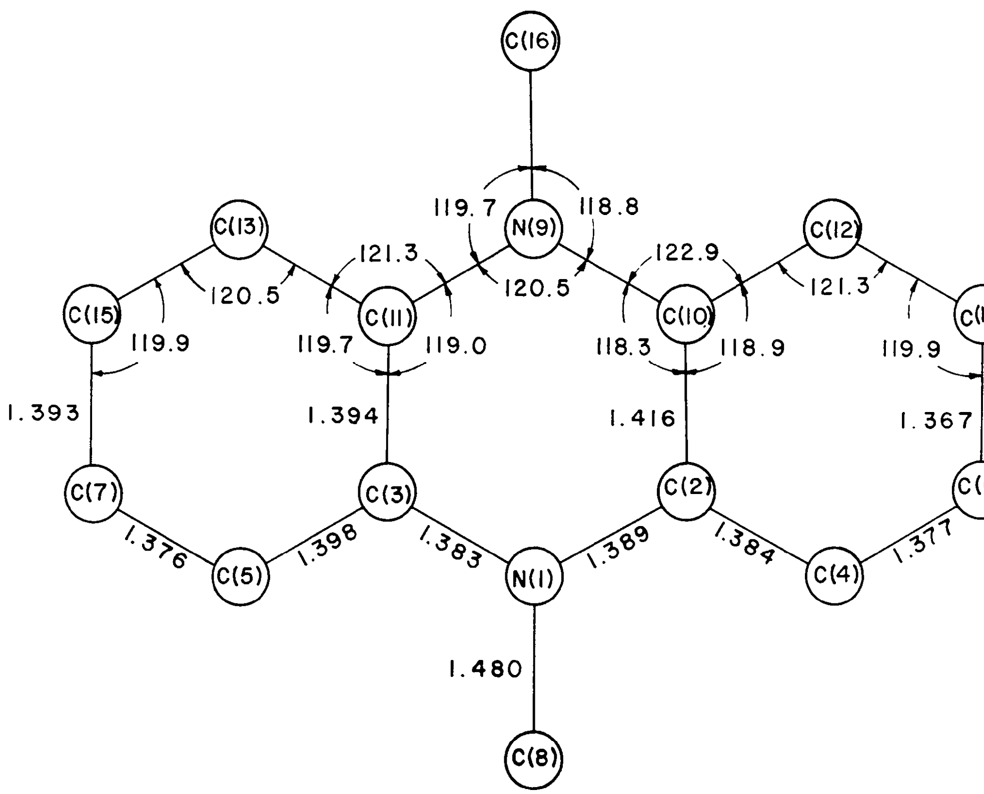


Fig. 3. Projection of part of the structure on the *ab* plane. The contacts marked are: $a=3{\cdot}38$ Å, between C(8) at x,y,z and N(10′) at $\frac{1}{2}+x, \frac{1}{2}+y, z$; $b=2{\cdot}38$ Å, between H(8–1) at x,y,z and N(10′) at $\frac{1}{2}+x,\frac{1}{2}+y,z$; $c=3{\cdot}54$ Å between N(9′) at x,y,z and N(10′) at $1+x,y,z$.



(*a*)



(*b*)

Fig. 4. Molecular geometry. (*a*) TCNQ, (*b*) DMPH. The bond distances and angles shown in the figure are averages from both sets of data, uncorrected for libration.

anthracene, by Williams & Wallwork, 1968; with phenazine, by Goldberg & Shmueli, 1973*a*; with dibenzo-*p*-dioxin, by Goldberg & Shmueli, 1973*b*; with hexamethylbenzene, by Colton & Henn, 1970) and which have a mainly no-bond ground state. DMPH–TCNQ presents a relatively rare instance of a complex in which a folded, non-centrosymmetric donor is found to be ordered in a mixed-stack structure. These deviations from planarity and centrosymmetry are reflected in two different modes of molecular overlap (Fig. 2). Whereas in structures containing planar, anthracene-like donors, the Mulliken orientation and overlap principle (Mulliken, 1956; Prout & Wright, 1968), as applied to a single donor–acceptor pair, can account rather well for the mode of *physical* overlap observed in the crystal (Goldberg & Shmueli, 1973*c*), the situation in DMPH–TCNQ is probably somewhat more difficult. This is due primarily to the attractive dispersion interactions involving the methyl groups and their inter- and intra-stack environment. A possible qualitative explanation of the observed mode of molecular overlap is the tendency to achieve short intermolecular distances on both sides of the folded DMPH molecule, as would be expected to occur in a charged system.

The only other structural study of *N*,*N*′-dimethyldihydrophenazine is the measurement of the dipole moment by Campbell, Le Fèvre, Le Fèvre & Turner (1938). These authors propose several configurations which, according to them, might account for the observed dipole moment of 0·4 D. Their models are based on a fully folded phenazine nucleus and three different substitution modes of the methyl groups: axial, equatorial and mixed. The present structure is close to the equatorial model, however, it is much less distorted from planarity than suggested by Campbell *et al.* (1938) for the uncomplexed neutral molecule in solution.

The abnormally large out-of-plane vibration of the methyl group in *N*-methylphenazinium (NMPH) was ascribed to a possible disorder or to a genuine thermal motion (Fritchie, 1966). It appears, on the basis of Fritchie's and present findings, that disordered methyl groups, attached to slightly pyramidal nitrogens can account for this feature of NMPH. In fact, the total average displacement of the methyl group in DMPH from the C(2)N(1)C(3) plane is about 0·52 Å while the r.m.s. amplitude of the out-of-plane vibration of the methyl group in NMPH is 0·43 Å.

It would be interesting to see whether an equally abnormal thermal motion of the methyl group also exists in the structure of (1:1) TCNQ–*N*-methylphenothiazine in which the donor was reported, in a preliminary communication, to be disordered (Kobayashi & Saito, 1971).

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