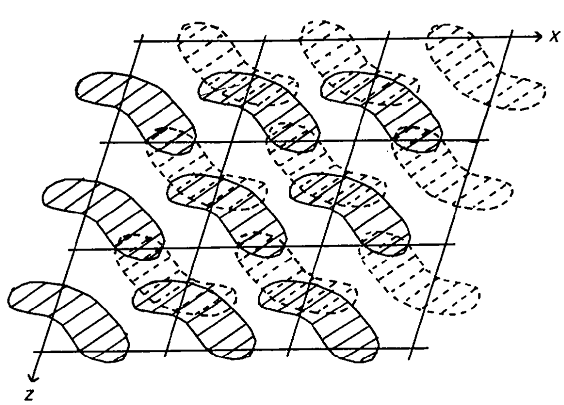

Fig. 6. Disposition schématique des molécules dans le réseau cristallin.

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The Crystal Structure of the 1:1 Complex of *N*,*N*-Dimethyl-*p*-phenylenediamine and 1,2,4,5-Tetracyanobenzene

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The crystal structure of the 1:1 complex formed between *N*,*N*-dimethyl-*p*-phenylenediamine (DMPD; $C_8H_{12}N_2$) and 1,2,4,5-tetracyanobenzene (TCNB; $C_{10}H_2N_4$) has been determined by X-ray diffraction techniques. The crystal is monoclinic, with four formula units of the complex in a cell of dimensions a = 29·117 (11), b = 7·785 (2), c = 7·250 (4) Å and β = 95·30 (5)°. The space group is $P2_1/a$. The intensity data were collected on a linear diffractometer. The structure was deduced from a three-dimensional Patterson synthesis and refined by block-diagonal least-squares methods. The final R was 0·075 for 1711 observed reflexions. The constituent molecules are stacked alternately in infinite columns along the c axis. The structure indicates the n–π interaction between the nitrogen atoms of the DMPD molecule and the ring carbon atoms to which the cyano groups of the acceptor are attached. This n–π interaction was observed in the complexes between TCNB and *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine, and between TCNB and *p*-phenylenediamine. The strength of the n–π interaction corresponds with that of the electron-donating power of the donor molecule.

Introduction

Recently the crystal structures of the charge-transfer complexes formed by 1,2,4,5-tetracyanobenzene (TCNB) as an acceptor have been reported (Ohashi, Iwasaki & Saito, 1967; Kumakura, Iwasaki & Saito, 1967; Niimura, Ohashi & Saito, 1968; Tsuchiya, Marumo & Saito, 1972; Tsuchiya, Marumo & Saito, 1973). The structures of naphthalene, anthracene and hexamethylbenzene complexes exhibited usual π–π interaction and were consistent with the structure predicted by the theoretical calculation involving π–π

interaction only (Iwata, Tanaka & Nagakura, 1966, 1967). The structure of the N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) complex, however, could not be explained by π–π interaction and n–π interaction was observed, which was localized between the nitrogen atoms of the donor molecule and the cyano groups of the acceptor molecule. In the complex containing p-phenylenediamine (PD) as a donor, the n–π interaction was observed but to a small extent. The crystal structure analysis of the molecular complex between N,N-dimethyl-p-phenylenediamine (DMPD) and TCNB was undertaken to examine this n–π interaction more precisely.

Experimental

Black needle-like crystals with metallic lustre, elongated along the c axis, were deposited when solutions of the components in methylene chloride had been mixed. The cell dimensions were determined from zero-level Weissenberg photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) about the b and c axes. Powder diffraction lines of copper were superimposed on the films for calibration.

The crystallographic data are: $C_8H_{12}N_2.C_{10}H_2N_4$, F.W. 314·2, monoclinic, space group $P2_1/a$, $a = 29{\cdot}117$ (11), $b = 7{\cdot}785$ (2), $c = 7{\cdot}250$ (4) Å, $\beta = 95{\cdot}30$ (5)°, $U = 1636{\cdot}5$ Å^3, $D_m = 1{\cdot}26$ g cm^{-3}, by flotation, $Z = 4$, $D_x = 1{\cdot}27$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) $= 0{\cdot}99$ cm^{-1}.

A crystal of approximate dimensions $0{\cdot}6 \times 0{\cdot}5 \times 0{\cdot}5$ mm was selected for the collection of intensity data. The intensities for layers $h0l$ to $h9l$ were collected on a Hilger–Watts linear diffractometer using Zr-filtered Mo $K\alpha$ radiation. In each layer, the intensities for which $8° \leq 2\theta \leq 60°$ were recorded. All reflexions were measured three times. 3895 accessible reflexions were collected, those reflexions of which the intensities were less than three times their standard deviations being regarded as unobserved. The reflexions $h00$ and $00l$ were also excluded, because they were smeared by white radiation. The remaining 1716 reflexions were used for the structure determination. The usual Lorentz and polarization, but no absorption, corrections were made.

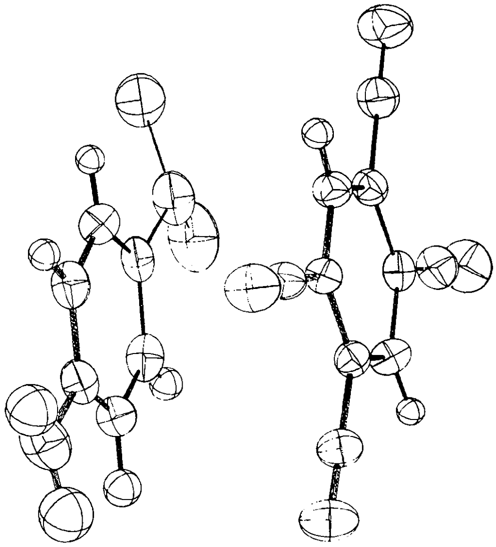

Fig. 1. Thermal ellipsoids at the 30% probability level, the methyl hydrogen atoms being omitted for clarity.

Table 1. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (× 10^5) *for the non-hydrogen atoms*

The anisotropic thermal parameters are of the form: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$.

Estimated standard deviations are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1507 (1)	5437 (5)	0917 (6)	108 (6)	1353 (75)	1785 (92)	−21 (34)	58 (35)	−45 (142)
C(2)	1207 (1)	2277 (6)	−0408 (6)	129 (6)	1546 (80)	1393 (82)	−76 (37)	110 (34)	−253 (143)
C(3)	1818 (1)	4106 (6)	0789 (6)	99 (5)	1625 (84)	1686 (94)	−84 (34)	127 (34)	157 (146)
C(4)	0893 (1)	3602 (6)	−0268 (6)	103 (6)	1781 (87)	1558 (91)	−87 (36)	42 (35)	−33 (146)
C(5)	1667 (1)	2511 (6)	0120 (6)	107 (6)	1573 (87)	2342 (110)	61 (36)	224 (38)	31 (158)
C(6)	1044 (1)	5195 (6)	0386 (6)	115 (6)	1567 (85)	2048 (100)	72 (37)	69 (37)	−178 (158)
C(7)	1675 (1)	7072 (6)	1625 (7)	115 (6)	1813 (95)	2563 (120)	18 (40)	−32 (42)	−262 (177)
C(8)	1043 (2)	0622 (6)	−1085 (6)	156 (7)	1663 (93)	2212 (113)	−65 (43)	43 (44)	−324 (165)
C(9)	2294 (2)	4346 (6)	1402 (7)	126 (6)	1583 (88)	2750 (124)	38 (39)	123 (43)	252 (171)
C(10)	0411 (2)	3334 (6)	−0798 (7)	141 (7)	1904 (100)	2263 (113)	−25 (43)	−19 (43)	−754 (176)
C(11)	1782 (2)	4688 (7)	6008 (6)	142 (7)	2157 (102)	1714 (97)	−273 (43)	36 (40)	135 (170)
C(12)	1004 (2)	2892 (6)	4436 (6)	155 (7)	2104 (98)	1372 (88)	−221 (43)	111 (38)	−37 (161)
C(13)	1809 (2)	2994 (7)	5525 (6)	146 (7)	2227 (108)	2117 (110)	100 (45)	125 (43)	235 (184)
C(14)	0975 (2)	4610 (7)	4951 (7)	139 (7)	2248 (107)	2292 (118)	113 (45)	180 (44)	−297 (188)
C(15)	1437 (2)	2110 (6)	4754 (6)	188 (8)	1608 (88)	1965 (104)	−63 (44)	252 (44)	−105 (168)
C(16)	1358 (2)	5467 (6)	5732 (6)	195 (8)	1404 (82)	1966 (106)	−98 (43)	143 (46)	−310 (156)
C(17)	0645 (3)	0173 (9)	3374 (9)	323 (14)	3266 (164)	3328 (169)	−1075 (80)	134 (76)	−1533 (275)
C(18)	0168 (2)	2689 (11)	3697 (8)	134 (8)	5876 (159)	3202 (159)	−678 (74)	164 (54)	−676 (338)
N(1)	2163 (2)	5576 (7)	6888 (7)	212 (8)	3148 (125)	3161 (124)	−519 (53)	−195 (50)	−308 (208)
N(2)	0625 (1)	2017 (6)	3518 (6)	178 (7)	3173 (114)	2203 (99)	−607 (47)	140 (39)	−317 (177)
N(3)	1820 (2)	8328 (6)	2210 (7)	184 (7)	1870 (89)	4125 (142)	−168 (42)	−30 (49)	−1296 (186)
N(4)	0920 (2)	−0700 (6)	−1589 (7)	226 (8)	1892 (93)	3512 (132)	−148 (45)	5 (51)	−1032 (182)
N(5)	2676 (1)	4538 (6)	1911 (7)	137 (6)	2267 (99)	4491 (149)	−49 (41)	30 (47)	636 (204)
N(6)	0029 (1)	3116 (6)	−1233 (7)	144 (7)	2725 (110)	3833 (134)	−81 (44)	−182 (45)	−1551 (205)

Table 2. *Fractional atomic coordinates* (×10^3) *and the isotropic thermal parameters for hydrogen atoms*

The thermal parameters are in Å^2. Estimated standard deviations are in parentheses.

	x	*y*	*z*	*B*
H(C5)	188 (1)	172 (5)	000 (6)	2·1 (0·9)
H(C6)	084 (1)	606 (6)	040 (6)	2·6 (1·0)
H(C13)	212 (2)	244 (6)	575 (6)	3·8 (1·2)
H(C14)	069 (1)	512 (5)	483 (5)	2·2 (1·0)
H(C15)	147 (2)	101 (6)	451 (6)	3·0 (1·1)
H(C16)	130 (1)	660 (6)	605 (6)	2·8 (1·0)
H(N1)	211 (2)	680 (8)	697 (9)	7·4 (1·7)
H′(N1)	249 (2)	499 (9)	684 (9)	8·1 (1·8)
H(C17)	075	−033	450	7·0
H′(C17)	032	−007	283	7·0
H″(C17)	090	−033	250	7·0
H(C18)	−008	167	300	7·0
H′(C18)	021	400	300	7·0
H″(C18)	004	283	467	7·0

Structure determination

The strongest intensity of $\bar{4}02$ suggested that most of the atoms might be on the ($\bar{4}02$) plane. The orientation and position of each molecule were deduced from the three-dimensional Patterson synthesis.

The structure thus obtained was refined by a block-diagonal least-squares method. After four cycles of refinement, five strong reflexions were excluded because they seemed to be affected by extinction. Refinement was continued with anisotropic temperature factors. All the hydrogen atoms were found in the three-dimensional difference-Fourier maps at this stage. Including these hydrogen atoms with isotropic temperature factors, the final refinement was performed, the parameters of methyl hydrogen atoms not being refined because the peaks of these atoms were too broad.

Table 3. *Observed and calculated structure factors* (×2·5)

A weighting scheme, $w=23{\cdot}0/|F_o|$ if $|F_o|>23{\cdot}0$, $w=1{\cdot}0$ if $23{\cdot}0\geq|F_o|\geq3{\cdot}8$, $w=0{\cdot}2$ if $|F_o|<3{\cdot}8$, was employed. The final R value became 0·075 for 1711 observed reflexions. At the final stage, no peaks larger than 0·02 e Å^{-3} were observed in the difference-Fourier synthesis. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final atomic parameters and their standard deviations are given in Table 1 for non-hydrogen atoms and in Table 2 for hydrogen atoms. The observed and calculated structure factors are listed in Table 3.

Description of the structure

Thermal motion

The thermal ellipsoids of the individual atoms are illustrated in Fig. 1, which was drawn using the program *DEAM* written by Takenaka (1972). The molecular motion has been analysed in terms of the rigid-body vibration (Cruickshank, 1956*a*). Tensors, **T** and **ω**, are given in Table 4. In each molecule, the first principal axis of the molecule corresponds to the long axis of the molecule, the second axis to the short axis in the molecular plane and the third to the axis perpendicular to the plane. The **U** tensors calculated from **T** and **ω** are not significantly different from those observed, though the differences are greater in the DMPD molecule than in the TCNB molecule. The smallest amplitude of translational vibration is parallel to the third axis, along which the molecules are closest packed. The greatest amplitude of libration is approximately about the first axis, which has the smallest moment of inertia in each molecule. The bond distances have been corrected for libration (Cruickshank, 1965*b*, 1961).

Crystal structure

The arrangement of the molecules viewed along the *b* axis is shown in Fig. 2. The component molecules are

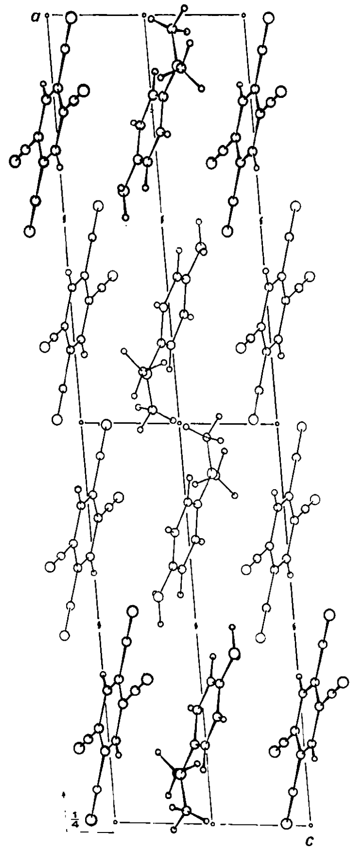

Fig. 2. Projection of the structure along the *b* axis.

Table 4. *Rigid-body thermal parameters*

Centre of vibration

TCNB

$x=0{\cdot}1358$ $y=0{\cdot}3841$ $z=0{\cdot}0286$

Principal axes of the molecule in the form: $La+Mb+Nc$

Axis	Moment of inertia (At. wt. Å^2)			
1	380·1	0·0258	0·0763	0·0505
2	1013·9	−0·0223	0·0967	0·0087
3	1393·8	0·0052	0·0365	−0·1287

Molecular vibration tensors

$$\mathbf{T}(\times 10^4)\quad \begin{pmatrix} 481\ (17) & -22\ (16) & -1\ (18) \\ & 464\ (21) & 14\ (21) \\ & & 310\ (32) \end{pmatrix}\ \text{Å}^2$$

$$\boldsymbol{\omega}(\times 10)\quad \begin{pmatrix} 431\ (90) & 5\ (6) & 3\ (12) \\ & 79\ (25) & 13\ (8) \\ & & 78\ (8) \end{pmatrix}\ \text{deg}^2$$

DMPD

$x=0{\cdot}1203$ $y=0{\cdot}3337$ $z=0{\cdot}4899$

Axis	Moment of inertia (At. wt. Å^2)			
1	103·2	0·0277	0·0650	0·0540
2	533·6	−0·0195	0·1048	0·0101
3	634·6	0·0067	0·0359	−0·1272

$$\mathbf{T}(\times 10^4)\quad \begin{pmatrix} 528\ (40) & -58\ (40) & -19\ (43) \\ & 613\ (56) & 40\ (56) \\ & & 325\ (83) \end{pmatrix}\ \text{Å}^2$$

$$\boldsymbol{\omega}(\times 10)\quad \begin{pmatrix} 444\ (192) & -7\ (39) & -133\ (70) \\ & 157\ (34) & -3\ (30) \\ & & 288\ (30) \end{pmatrix}\ \text{deg}^2$$

Principal axes of the **T** and **ω** tensors relative to the molecular axes.

TCNB

R.m.s. amplitude	Direction cosines		
0·176 Å	−0·0046	−0·0924	0·9957
0·213	−0·5775	−0·8126	−0·0781
0·229	0·8163	−0·5754	−0·0497
2·5°	0·0033	−0·6314	0·7755
2·99	0·0176	−0·7753	−0·6313
6·56	0·9998	0·0157	0·0085

DMPD

R.m.s. amplitude	Direction cosines		
0·179 Å	0·0563	−0·1250	0·9906
0·223	−0·8933	−0·4496	−0·0059
0·255	−0·4460	0·8845	0·1369
3·96°	0·0693	0·9931	0·0949
4·61	−0·4912	0·1168	−0·8632
7·21	0·8683	−0·0132	−0·4959

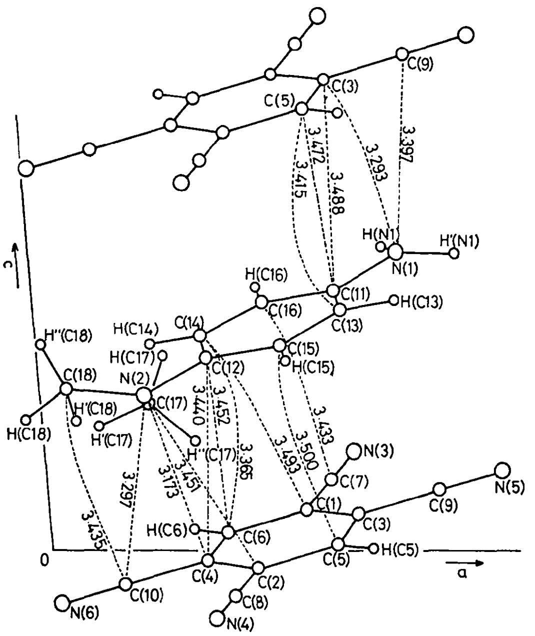

Fig. 3. Intermolecular contacts within the overlapping molecules, viewed along the *b* axis. The threshold values are 3·50 Å for contacts between non-hydrogen atoms and 2·70 Å for those involving hydrogen atoms.

stacked alternately in infinite columns along the *c* axis. Intermolecular contacts within the stacking column are shown in Fig. 3 (contacts longer than 3·50 Å for C···C, C···N and N···N, and 2·70 Å for C···H and N···H are omitted). The closest contacts occur between C(4) and N(2), and C(3) and N(1), the distances being 3·172 and 3·293 Å, respectively. Such short contacts are also observed in the TMPD and PD complexes. They indicate the existence of a specific interaction between these atoms. Fig. 4 shows the intermolecular contacts between adjacent columns of molecules. The shortest is observed between the amino group in the unit at x,y,z and the cyano group in the unit at $\frac{1}{2}-x,\frac{1}{2}+y,1-z$. The N(1)···N(5) distance is 3·227 Å and the H(N1)···N(5) distance 2·34 Å. The N–H···N angle is 152°. This suggests weak hydrogen bonding, as observed in the PD complex. Another hydrogen atom of the amino group, H'(N1), lies close to the nitrogen atom, N(3), in the unit at $\frac{1}{2}-x,\frac{1}{2}+y,1-z$, the N(1)···N(3) and H'(N1)···N(3) distances being 3·449 2·45 Å, respectively. These three atoms are approximately on a straight line. This contact might also be a very weak hydrogen bond. There are no other unusually short intermolecular contacts.

Molecular structure

Bond distances and angles in each component mole-

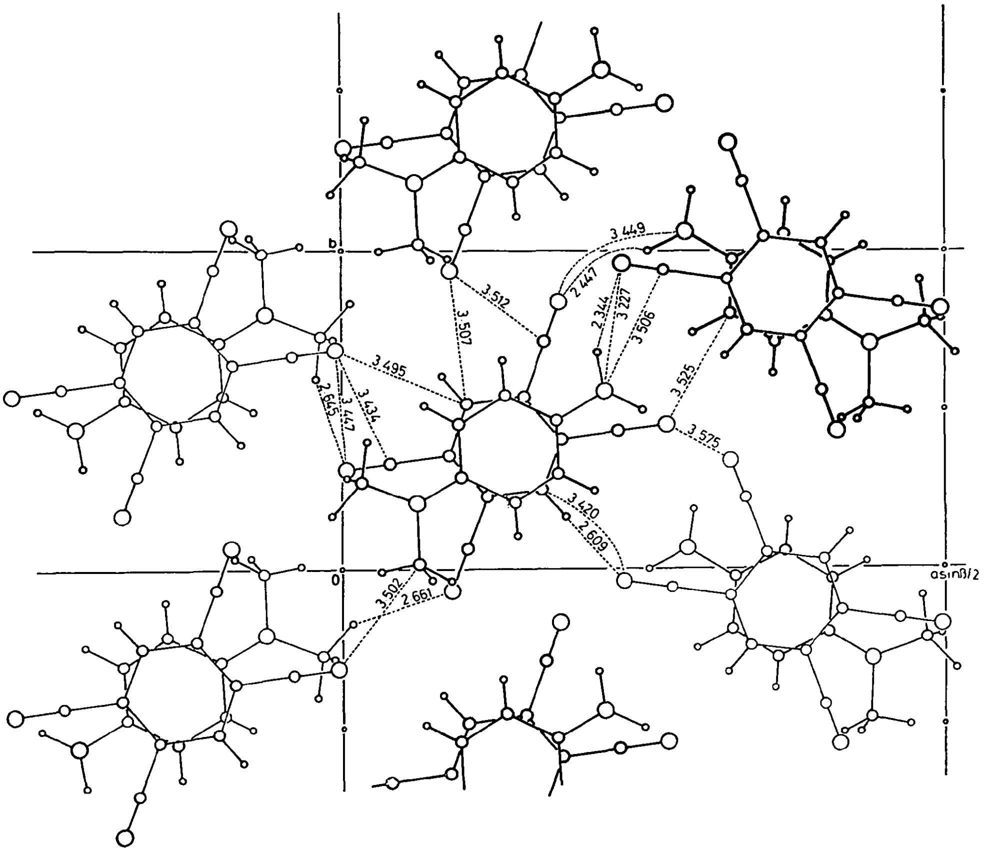

Fig. 4. Intermolecular contacts between adjacent columns of molecules, viewed along the *c* axis.

cule are listed in Tables 5 and 6, and are shown in Fig. 5. The TCNB molecule as a whole is not planar. One of the cyano groups, which is hydrogen-bonded to the neighbouring amino group of the DMPD molecule, is out of the plane of the benzene ring. Other cyano groups are slightly shifted from the plane on the same side. The TCNB molecule, therefore, exhibits the boat form to some extent. The equation of the mean plane of the benzene ring is given by

$$-0{\cdot}2287X-0{\cdot}2874Y+0{\cdot}9301Z+1{\cdot}5895=0\,,$$

where X, Y and Z are the coordinates in Å referred to the a, b and c^* axes. The deviation of each atom from the mean plane is shown in Fig. 6(*a*). The cyano group which is out of the plane makes an angle of 3·1° with the plane.

The DMPD molecule is not planar, but the aromatic ring atoms are coplanar and the mean plane is given by:

$$-0{\cdot}3021X-0{\cdot}2779Y+0{\cdot}9119Z-1{\cdot}5045=0\,.$$

This plane makes an angle of 4·4° with the ring plane of TCNB. The deviation of each atom from the mean plane is shown in Fig. 6(*b*). N(2) is above this plane, whereas C(17) and C(18) are situated below the plane. On the other hand N(1) is below the plane and H(N1) and H′(N1) are above the plane. The bond C(12)–N(2) is inclined at an angle of 4·0° with respect to this plane, whereas the bond C(11)–N(1) makes an angle of 2·8° with the plane. In the benzene ring, C(12)–C(14) and

Table 5. *Bond distances and angles with their standard deviations for the TCNB molecule*

	Uncorrected	Corrected
C(1)-C(3)	1·385 (6) Å	1·394 Å
C(1)-C(6)	1·381 (6)	1·384
C(1)-C(7)	1·441 (6)	1·443
C(2)-C(4)	1·387 (6)	1·396
C(2)-C(5)	1·372 (6)	1·376
C(2)-C(8)	1·444 (6)	1·446
C(3)-C(5)	1·390 (6)	1·393
C(3)-C(9)	1·427 (6)	1·429
C(4)-C(6)	1·385 (6)	1·388
C(4)-C(10)	1·436 (6)	1·438
C(7)-N(3)	1·132 (7)	1·133
C(8)-N(4)	1·139 (7)	1·140
C(9)-N(5)	1·149 (7)	1·150
C(10)N(6)	1·141 (7)	1·141
C(5)-H(C5)	0·89 (4)	
C(6)-H(C6)	0·91 (4)	

C(3)-C(1)—C(6)	120·5 (4)°
C(3)—C(1)-C(7)	118·8 (4)
C(6)-C(1)—C(7)	120·7 (4)
C(4)-C(2)—C(5)	120·9 (4)
C(4)-C(2)—C(8)	119·4 (4)
C(5)-C(2)—C(8)	119·7 (4)
C(1)-C(3)—C(5)	120·3 (4)
C(1)-C(3)—C(9)	120·2 (4)
C(5)-C(3)—C(9)	119·5 (4)
C(2)-C(4)—C(6)	120·1 (4)
C(2)-C(4)—C(10)	120·4 (4)
C(6)-C(4)—C(10)	119·4 (4)
C(2)-C(5)—C(3)	119·0 (4)
C(1)-C(6)—C(4)	119·2 (4)
C(1)-C(7)—N(3)	177·6 (5)
C(2)-C(8)—N(4)	178·6 (5)
C(3)-C(9)—N(5)	179·4 (5)
C(4)-C(10)-N(6)	179·5 (5)
C(2)-C(5)—H(C5)	124 (3)
C(3)-C(5)—H(C5)	117 (3)
C(1)-C(6)—H(C6)	122 (3)
C(4)-C(6)—H(C6)	119 (3)

Table 6. *Bond distances and angles with their standard deviations for the DMPD molecule*

	Uncorrected	Corrected
C(11)-C(13)	1·369 (7) Å	1·378 Å
C(11)-C(16)	1·373 (7)	1·382
C(11)-N(1)	1·409 (7)	1·410
C(12)-C(14)	1·393 (7)	1·404
C(12)-C(15)	1·399 (7)	1·410
C(12)-N(2)	1·412 (6)	1·417
C(13)-C(15)	1·358 (7)	1·364
C(14)-C(16)	1·376 (7)	1·382
C(17)-N(2)	1·441 (8)	1·446
C(18)-N(2)	1·445 (7)	1·450
C(13)-H(C13)	1·01 (5)	
C(14)-H(C14)	0·92 (4)	
C(15)-H(C15)	0·88 (4)	
C(16)-H(C16)	0·93 (4)	
N(1)—H(N1)	0·97 (6)	
N(1)—H′(N1)	1·05 (6)	
C(17)-H(C17)	0·93	
C(17)-H′(C17)	1·02	
C(17)-H″(C17)	1·09	
C(18)-H(C18)	1·17	
C(18)-H′(C18)	1·15	
C(18)-H″(C18)	0·83	

C(13)—C(11)-C(16)	117·4 (4)°
C(13)—C(11)-N(1)	121·9 (4)
C(16)—C(11)-N(1)	120·6 (4)
C(14)—C(12)-C(15)	116·8 (4)
C(14)—C(12)-N(2)	121·7 (4)
C(15)—C(12)-N(2)	121·4 (4)
C(11)—C(13)-C(15)	122·1 (4)
C(12)—C(14)-C(16)	120·6 (4)
C(12)—C(15)-C(13)	121·2 (4)
C(11)—C(16)-C(14)	121·9 (4)
C(12)—N(2)—C(17)	118·6 (5)
C(12)—N(2)—C(18)	118·0 (5)
C(17)—N(2)—C(18)	114·4 (5)
C(11)—C(13)-H(C13)	116 (3)
C(15)—C(13)-H(C13)	122 (3)
C(12)—C(14)-H(C14)	118 (3)
C(16)—C(14)-H(C14)	122 (3)
C(12)—C(15)-H(C15)	120 (3)
C(13)—C(15)-H(C15)	118 (3)
C(11)—C(16)-H(C16)	125 (3)
C(14)—C(16)-H(C16)	114 (3)
C(11)—N(1)—H(N1)	113 (4)
C(11)—N(1)—H′(N1)	116 (3)
H(N1)—N(1)—H′(N1)	125 (5)
N(2)—C(17)-H(C17)	112
N(2)—C(17)-H′(C17)	100
N(2)—C(17)-H″(C17)	116
H(C17) -C(17)-H′(C17)	119
H(C17) -C(17)-H″(C17)	100
H′(C17)-C(17)-H″(C17)	112
N(2)—C(18)-H(C18)	105
N(2)—C(18)-H′(C18)	99
N(2)—C(18)-H″(C18)	127
H(C18)-C(18)-H′(C18)	120
H(C18)-C(18)-H″(C18)	99
H′(C18)-C(18)-H″(C18)	109

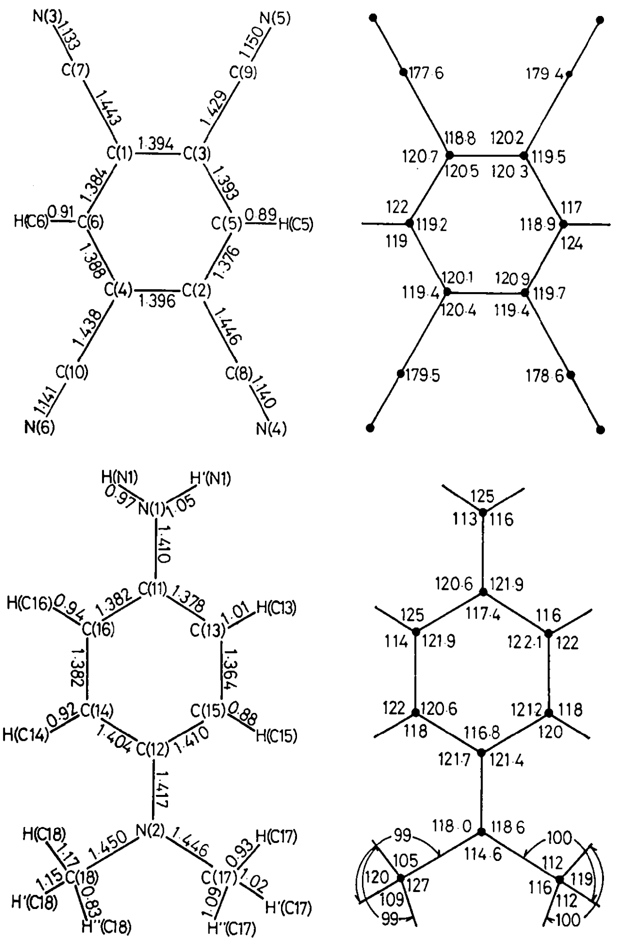

Fig. 5. Bond distances (Å) and angles (°).

C(12)–C(15) are longer than the other bond distances. This might be due to the bulky substituents.

Discussion

The structural characteristics which indicate the specific interaction in the three TCNB complexes are summarized in Table 7. Fig. 7 shows each donor molecule projected on to the least-squares plane of the TCNB molecule in each complex. [Hereafter DMPD(*a*) complex and DMPD(*b*) complex stand for the mode of the overlapping of Fig. 7(*a*) and (*b*), respectively.] The mean interplanar distances are 3·38 Å for the DMPD(*a*) complex, 3·50 Å for the DMPD(*b*) complex, 3·40 Å for the TMPD complex and 3·37 Å for the PD complex.

The overlapping modes of the donor and acceptor molecules in these complexes should be the same, if only π–π interaction is considered. However, as discerned from Fig. 7, each complex shows a different mode of overlapping. Moreover, the extent of overlap of the benzene rings in each complex is small. Accordingly, the π–π interaction seems to be very weak in the crystals of these complexes. On the other hand, these complexes would differ from each other in view of other intermolecular forces, for example the repulsion between the bulky substituents or the hydrogen bonding. Nevertheless, it is commonly seen that the nitrogen atoms of the donor molecule come close to the ring carbon atoms to which the cyano groups of the TCNB are attached. These distances are 3·152 Å for the TMPD complex, 3·173 Å for the DMPD(*a*) complex, 3·293 Å for the DMPD(*b*) complex and 3·164 Å for the PD complex. This fact suggests that fairly strong inter-

Table 7. *Interplanar distances, intermolecular atomic distances and molecular geometries related to the specific interaction in the TMPD, DMPD, PD complexes*

	TMPD	DMPD(*a*)	DMPD(*b*)	PD
Interplanar distances	3·40 Å	3·38 Å	3·50 Å	3·37 Å
N···C distances*	3·152	3·173	3·293	3·164
Angles around the nitrogen atoms of the donor molecule	117·1°	118·5°	116°	116°
	116·3	117·9	113	117
	118·1	114·6	125	113
Total	321·5	351·0	354	346
Δθ†	2·1°	4·0°	2·8°	3·7°
Δd†	0·06 Å	0·10	0·06	0·09
N–C distances	1·430 Å	1·417	1·410	1·402

Bond distances of TCNB‡

	TMPD	DMPD	PD	Average§
bond (1)	1·390 Å	1·395 Å	1·405 Å	1·403 Å
bond (2)	1·390	1·391	1·386	1·392
bond (3)	1·360	1·380	1·396	
bond (4)	1·442	1·434	1·450	1·446
bond (5)	1·465	1·445	1·449	

* The N···C distance is the intermolecular atomic distance between the nitrogen atom of the donor and the ring carbon to which the cyano group of the TCNB is attached.

† Δθ and Δd are shown in Fig. 8.

‡ The numbering of each bond is shown in Fig. 8. In the DMPD complex, the TCNB molecule is assumed to have the centre of symmetry and the corresponding bonds are averaged.

§ The average bonds are derived from the TCNB molecules in other complexes, the molecular symmetry *mmm* being assumed.

action exists between the nitrogen atom of the donor molecule and the ring carbon atom of the TCNB molecule. A slightly longer distance, 3·293 Å, in the DMPD (*b*) complex is due to the weak hydrogen bonding between the amino group and the cyano group of the neighbouring TCNB molecule.

This specific interaction has an effect on the structures of the component molecules. In donor molecules, the nitrogen atoms of the amino group lie out of the plane of the benzene rings by 0·06–0·09 Å and come close to the ring carbon atoms of TCNB. The bonds between the nitrogen atom of the amino group and the ring carbon atom make angles of 2·1–4·0° with the benzene rings. On the other hand, the methyl groups or hydrogen atoms of the amino groups are shifted on opposite sides. Accordingly, these nitrogen atoms exhibit tetrahedral character. If tetrahedral character is expressed by the sum of the three bond angles around the nitrogen atom, these values are 351·5° for the TMPD, 351·0° for the DMPD(*a*), 354° for the DMPD(*b*) and 346° for the PD molecule.

The bond distances between the ring carbon atoms and nitrogen atoms of the amino groups are 1·430 Å for the TMPD, 1·417 Å for the DMPD(*a*), 1·410 Å for the DMPD(*b*) and 1·402 Å for the PD molecule. No crystal structure of these donor molecules in the neutral state has yet been reported, but the C–N distances in other neutral aromatic amines range from 1·37 to 1·40 Å (Trueblood, Goldish & Donohue, 1961; Brown, 1951; Bertinotti, Giacomello & Liquori, 1954). From the molecular-orbital calculation (Monkhorst & Kommandeur, 1967) and the relation between bond order and bond distance (Nishimoto & Forster, 1966), the C–N distance is estimated to be 1·39 Å for the neutral TMPD molecule. Therefore, it may be adequate that the C–N distances in these donor molecules are 1·39 Å in the neutral state. The distances observed in the TMPD, DMPD and PD complexes are longer than this estimated distance. These facts may indicate that the lone-pair electrons in these complexes are localized on the nitrogen atom to a greater extent than those in the neutral state. The lone-pair electrons turn approximately toward the ring carbon atom of the TCNB molecule.

The molecular distortions are also observed in acceptor molecules. Tsuchiya, Marumo & Saito (1973) pointed out that the skeleton of the TCNB molecule did not differ significantly in hexamethylbenzene, naphthalene, anthracene and PD complexes, where the TCNB molecules were assumed to have the symmetry *mmm*. The average distances in these complexes are also included in Table 7. In the TMPD and DMPD complexes, on the other hand, two exocyclic C–C bonds are not equivalent, that is, bond (4) (Fig. 8) to which the nitrogen atom of the donor molecule comes close is shorter than bond (5). In the benzene ring, bond (3) is shorter than bonds (1) and (2). Moreover, bonds (1) and (2) are approximately the same. Therefore, the TCNB molecules in the TMPD and the DMPD complexes do not exhibit the *mmm* symmetry but possess the quinoid structure. Multivariate significance tests for five degrees of freedom (Cruickshank & Robertson, 1953) indicate that the dimensions of the TCNB molecule in the TMPD and the DMPD complexes are 'significantly' different from the average dimensions in the series. The values of T^2 are 16·01 for

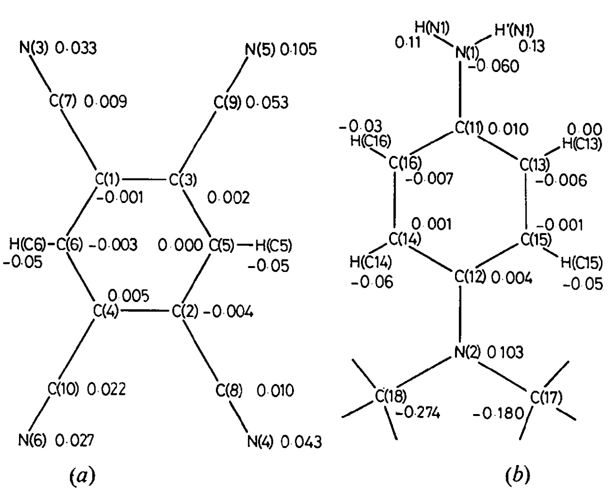

Fig. 6. The deviation (Å) of each atom from the mean plane, (*a*) in the TCNB molecule, (*b*) in the TMPD molecule.

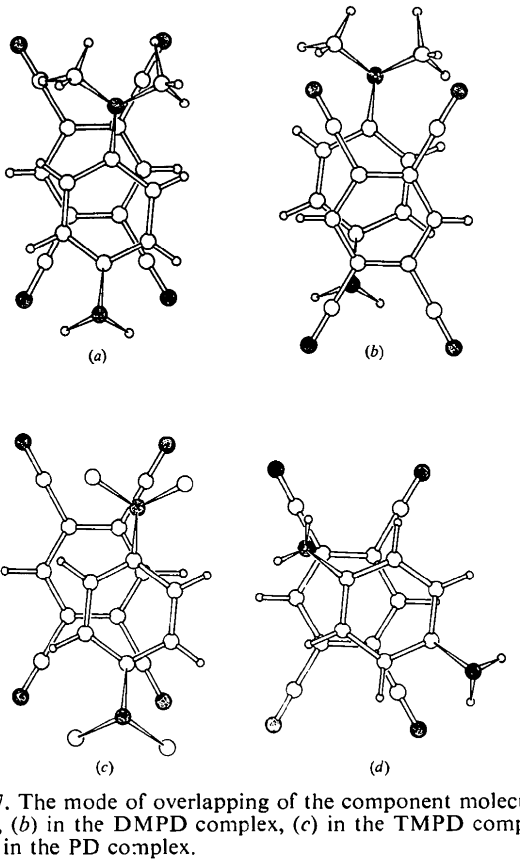

Fig. 7. The mode of overlapping of the component molecules, (*a*), (*b*) in the DMPD complex, (*c*) in the TMPD complex, (*d*) in the PD complex.

the TMPD complex and 18·82 for the DMPD complex. The quinoid structure could be explained by the fact that the lone-pair electrons of the nitrogen atoms of the donor molecule are transferred to the ring carbon atoms of the acceptor.

These results indicate n–π interaction, that is the lone-pair electrons localized on the nitrogen atoms of the donor interact with the π electrons of the ring carbon atoms to which the cyano groups of the acceptor are attached, and this n–π interaction is dominant in the crystals of these complexes. This interaction is strong for the TMPD complex and very weak for the PD complex, depending on the electron-donating power of the donor.

Nogami, Yoshihara & Nagakura (1971*a*, *b*) showed that in solutions of the TMPD–chloranil complex, both a π–π complex and a σ complex, in which the nitrogen atom of the donor molecule forms chemical bonding to the ring carbon atom of the acceptor, were found at the same temperature, and that the σ-complex was formed *via* the π–π complex by lowering the temperature.

In the present complexes, TCNB has weaker electron-accepting power than chloranil. The values of electron affinity are 2·21 eV for TCNB and 2·46 eV for chloranil (Farragher & Page, 1967). The n–π interaction observed here would be the intermediate state from π–π interaction to chemical bonding.

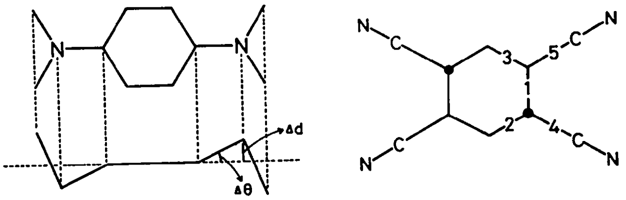

Fig. 8. The notation of $\Delta\theta$ and Δd in the DMPD, and the numbering of the bonds in the TCNB. Black circles indicate the atoms to which the nitrogen atoms of the donor molecule come close.

The computations were carried out on a HITAC 5020E computer in the University of Tokyo and on a HITAC 8700 computer in Tokyo Institute of Technology. The programs in the UNICS Program System (1967) were used with some modification.

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