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The Crystal Structure of the 1 : 1 Complex of 1, 2, 4, 5-Tetracyanobenzene and Hexamethylbenzene

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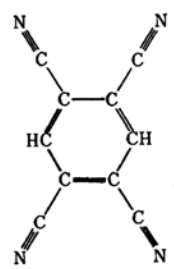
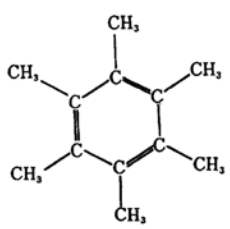
The crystal structure of the 1 : 1 complex formed between hexamethylbenzene and 1, 2, 4, 5-tetracyanobenzene has been determined by X-rays. The crystal is monoclinic, with two formula units of the complex in a cell of dimensions ; $a=15.07$, $b=8.92$, $c=7.41$ Å and $\beta=104.9°$. The space group is $P2_1/n$. The structure was deduced from a three-dimensional Patterson synthesis, and refined by block-diagonal least-squares method. The constituent molecules are stacked alternately in infinite columns along the c-axis. The relative configuration of the donor and acceptor molecules is consistent with the theoretical calculation.

The complex between 1, 2, 4, 5-tetracyanobenzene (TCNB) and hexamethylbenzene (HMB) is the third member of the series of charge transfer complexes containing TCNB as an electron acceptor, of which the crystal structures have been determined in this laboratory. The structure of the complex between





TCNB and N, N, N', N'-tetramethyl-p-phenylenediamine (TMPD)[1] indicated specific interaction localized between the nitrogen atoms of the donor and the cyano groups of the acceptor, whereas the structure of the TCNB-naphthalene complex[2] was found to exhibit π-π interaction between the donor and the acceptor, and was consistent with the result of the theoretical calculation and the electronic spectra.[3] It is expected that in the crystals of the complex between TCNB and typical π-donor such as benzene or hexa-

1) Y. Ohashi, H. Iwasaki and Y. Saito, *This Bulletin*, **40**, 1789 (1967).
2) S. Kumakura, F. Iwasaki and Y. Saito, *ibid.*, **40**, 1826 (1967).
3) S. Iwata, J. Tanaka and S. Nagakura, *J. Am. Chem. Soc.*, **89**, 2813 (1967).

methylbenzene, the relative arrangement of the donor and acceptor molecules may be consistent with the result of theoretical calculation involving the π-π interaction only. In the present paper, haxametylbenzene was selected as a donor. The relative configuration of the donor and the acceptor of this complex has been presumed theoretically.[4] It may be of interest to see whether this presumption is correct or not and to compare the crystal structure with those of the related molecular complexes.

Experimental

The molecular complex of TCNB and HMB crystallizes as yellow needles. They decompose easily when exposed to X-rays in the air. Specimens had to be sealed in thin-walled borosilicate glass capillaries. The crystals are monoclinic and the cell dimensions and the space group were determined from oscillation and Weissenberg photographs taken around the b- and c-axes using Cu$K\alpha$ radiation (λ=1.542 Å). They are listed in Table 1.

TABLE 1. CRYSTAL DATA

TCNB-HMB
Monoclinic
a=15.07±0.01 Å
b= 8.92±0.01 Å
c= 7.41±0.04 Å
β=104.9±0.4°
Z=2
$P2_1/n$
μ=5.6 cm^{-1} (Cu $K\alpha$)

Intensity data were recorded on the equi-inclination Weissenberg photographs taken around the b- and c-axis up to the fourth layer, respectively, using multiple film technique. The relative intensities, estimated visually with a set of standard scales, were corrected for Lorentz and polarization factors, and spot shape, and were put on a common scale. The absorption correction was neglected in view of the small size of the specimen and the small value of the linear absorption coefficient. 587 independent reflections were observed.

Structure Determination

From the systematic absences the space group was uniquely determined to be $P2_1/n$. Since there are only two pairs of component molecules in the unit cell, the centers of gravity of each molecule must lie on a set of special positions. In order to obtain familiar mixed stacks, the TCNB and HMB molecules must be centered at positions, (000), (1/2 1/2 1/2) and (0 0 1/2), (12/ 1/2 0) respectively.

The trial structure was readily deduced from the three-dimensional Patterson synthesis. The structure thus obtained was refined by difference syntheses projected along the b- and c-axes, and later by a three-dimensional block-diagonal least-squares method with HBLS program written by Ashida. After a few cycles of this refinemet, anisotropic temperature factors were introduced. A weighting scheme,

$$w=1 \quad \text{if} \quad F_o \geq 2.0$$
$$\text{otherwise} \quad w=0.2$$

was employed.

The final discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$ became 0.154 for all the observed reflections. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[5] Final atomic parame-

TABLE 2. ATOMIC PARAMETERS

The expression of the temperature factor is $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$

Atom	$x\times10^4$	$y\times10^4$	$z\times10^4$	$\sigma(x)$ $\times10^4$	$\sigma(y)$ $\times10^4$	$\sigma(z)$ $\times10^4$	B_{11} $\times10^4$	B_{22} $\times10^4$	B_{33} $\times10^4$	B_{12} $\times10^4$	B_{13} $\times10^4$	B_{23} $\times10^4$
TCNB												
N 1	788	4064	−960	12	18	28	95	177	506	−47	132	144
N 2	1908	−2847	2645	10	20	22	59	263	356	87	19	1
C 1	547	2925	−734	11	22	25	45	233	294	−16	50	34
C 2	1349	−2055	1905	12	21	24	64	178	253	−22	69	−2
C 3	924	457	596	11	19	21	57	159	132	14	2	103
C 4	675	−984	949	11	20	25	35	176	323	20	39	22
C 5	255	1431	−396	12	19	22	71	146	158	0	81	58
HMB												
C 6	1062	2738	4706	16	24	35	110	171	692	−173	175	−36
C 7	1006	−2719	6672	17	23	33	132	128	571	142	29	214
C 8	2020	32	6394	13	36	34	28	543	602	16	2	−96
C 9	512	1298	4879	11	21	25	50	172	306	−31	45	−7
C 10	461	−1291	5787	13	21	24	81	160	226	53	36	38
C 11	953	1	5655	11	22	26	39	229	285	17	15	−7

4) S. Iwata, J. Tanaka and S. Nagakura, *ibid.*, **88**, 894 (1966).
5) "International Tables for X-Ray Crystallography" Vol. III, Kynoch Press, Birmingham (1962), p. 202.

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	Fo	Fc
l=0			
2	0	83.1	86.4
4	0	-47.3	-45.3
6	0	-51.2	-46.2
8	0	-40.6	-34.6
10	0	8.6	6.2
12	0	-8.6	-7.1
1	1	90.2	72.8
2	1	-10.9	-2.2
3	1	5.2	0.9
4	1	-54.6	-46.2
6	1	-11.5	-8.9
7	1	-21.4	-16.7
0	2	-43.7	-33.9
1	2	10.0	5.6
2	2	-7.8	-2.2
3	2	35.0	32.8
4	2	12.1	10.2
5	2	12.9	11.8
6	2	-22.6	-18.4
7	2	-7.7	-7.2
8	2	-7.4	-6.5
9	2	-3.5	-4.7
10	2	11.9	11.3
11	2	-10.0	-9.9
12	2	8.4	7.9
13	2	-6.8	-6.8
1	3	11.6	5.2
2	3	-35.4	-26.9
3	3	-35.2	-29.3
4	3	10.4	9.3
5	3	-20.4	-15.4
6	3	5.4	3.1
7	3	-23.5	-20.9
8	3	5.6	6.8
9	3	7.2	8.3
11	3	15.8	17.1
12	3	-5.8	-6.8
0	4	3.6	3.3
2	4	-40.0	-30.9
3	4	-7.6	-6.9
4	4	-34.0	-26.5
5	4	9.4	6.1
6	4	-3.7	-1.3
7	4	8.8	9.1
8	4	9.9	10.0
9	4	-5.3	-6.1
10	4	16.9	17.6
1	5	-16.8	-14.2
2	5	-4.9	-1.1
3	5	-15.1	-10.5
4	5	-5.3	-4.5
5	5	-6.8	-4.6
6	5	6.3	6.2
7	5	11.5	11.0
8	5	4.9	5.0
9	5	12.3	11.4
10	5	5.7	2.9
0	6	-7.1	-6.9
4	6	6.9	8.7
6	6	7.8	7.4
9	6	8.7	9.7
1	7	17.9	17.8
3	7	8.3	6.8
4	7	-4.8	-4.3
7	7	-6.8	-8.7
0	8	5.6	6.9
1	8	-4.2	-3.6
2	8	5.0	4.2
3	8	-10.1	-9.7
5	8	-5.7	-4.7
l=1			
-5	0	-33.7	-35.5
-3	0	9.6	12.4
1	0	3.8	0.3
3	0	38.3	40.1
5	0	21.5	20.4
7	0	-5.3	-2.3
9	0	-8.7	-9.5
13	0	7.8	8.3
-8	1	13.2	11.8
-7	1	12.3	9.1
-6	1	-5.6	-3.6
-5	1	38.0	40.6
-4	1	22.0	22.1
-3	1	-8.6	-13.1
-2	1	8.6	7.2
-1	1	12.5	14.0
0	1	-25.8	-23.9
1	1	13.0	20.9
3	1	-26.3	-28.1
4	1	-30.3	-27.4
5	1	-4.4	-2.6
6	1	18.7	17.1
7	1	-13.2	-12.8
8	1	8.4	8.8
9	1	-5.5	-5.1
11	1	-4.5	-3.1
12	1	9.8	11.3
13	1	-4.4	-4.1
-14	2	9.2	9.4
-12	2	8.2	10.0
-10	2	9.3	9.1
-9	2	8.8	9.2
-8	2	14.0	15.3
-7	2	-7.8	-6.6
-6	2	-5.2	-5.2
-5	2	-9.0	-6.9
-4	2	-16.9	-15.6
-3	2	16.2	12.1
-2	2	-16.6	-17.4
-1	2	-20.3	-17.7
0	2	-9.7	-7.9
1	2	43.7	39.9
2	2	17.1	12.1
3	2	-23.2	-22.6
4	2	9.3	9.4
5	2	-29.3	-30.5
6	2	6.0	5.1
7	2	5.4	8.6
9	2	-3.9	-3.2
10	2	-9.0	-9.4
11	2	7.8	9.3
12	2	-7.8	-9.3
13	2	2.2	0.4
-13	3	8.3	10.7
-11	3	8.3	8.7
-10	3	-10.8	-13.7
-7	3	-14.9	-15.9
-6	3	3.7	3.2
-5	3	-24.2	-25.4
-3	3	25.2	26.6
-2	3	-4.0	-4.3
-1	3	18.6	15.8
0	3	-10.9	-9.5
1	3	-5.9	-6.1
2	3	21.7	19.9
4	3	11.9	11.5
5	3	-8.0	-6.5
6	3	-7.3	-8.5
7	3	5.5	4.9
8	3	-10.3	-11.6
10	3	-8.4	-9.3
12	3	-4.7	-5.0
-11	4	-7.0	-7.9
-9	4	-8.0	-9.1
-8	4	-8.1	-7.3
-7	4	3.2	4.4
-5	4	7.7	8.9
-4	4	7.0	7.7
-3	4	8.0	6.7
-2	4	-4.6	-4.6
-1	4	-8.5	-9.1
0	4	-8.9	-7.3
1	4	-13.0	-13.5
2	4	-11.9	-9.1
3	4	16.1	14.2
4	4	14.5	13.6
5	4	7.8	8.4
6	4	10.9	9.8
8	4	-6.4	-7.6
9	4	-11.3	-13.4
11	4	-9.8	-9.0
-11	5	-6.3	-7.4
-9	5	-9.4	-11.3
-8	5	6.4	6.7
-7	5	-6.9	-6.3
-6	5	-8.8	-10.3
-5	5	9.2	9.5
-3	5	7.4	5.3
0	5	3.7	6.5
2	5	7.2	5.8
4	5	-8.0	-7.2
5	5	2.7	5.1
6	5	2.0	2.9
8	5	-4.0	-3.6
9	5	4.9	2.8
10	5	-5.9	-5.5
-10	6	-6.9	-6.2
-8	6	-4.0	-4.0
-7	6	6.6	6.5
-6	6	-7.5	-6.6
-2	6	5.9	6.2
-1	6	-6.9	-7.1
0	6	5.4	2.4
1	6	-6.6	-5.6
3	6	-3.8	-3.1
4	6	-6.5	-8.6
5	6	7.1	6.7
7	6	8.5	10.0
8	6	11.1	12.0
-7	7	5.0	4.2
-6	7	4.9	7.7
-3	7	2.1	0.7
-2	7	-6.9	-8.7
0	7	-7.2	-8.5
1	7	-2.1	-1.7
2	7	4.9	6.2
3	7	-6.0	-5.5
4	7	11.8	14.1
6	7	4.5	4.9
7	7	2.2	4.7
-7	8	2.2	3.6
-6	8	6.0	5.4
-5	8	6.5	5.5
-4	8	10.3	9.7
-2	8	6.2	4.8
-1	8	-9.5	-9.9
1	8	-5.2	-2.7
2	8	-7.7	-7.8
l=2			
-10	0	-10.0	-7.1
-8	0	-21.7	-21.7
-6	0	-40.4	-43.6
-2	0	98.2	117.2
0	0	51.8	65.8
2	0	25.6	31.5
4	0	2.5	1.4
6	0	-20.1	-19.9
8	0	3.8	6.4
-10	1	-3.5	-5.4
-9	1	-20.4	-21.5
-8	1	-6.4	-5.2
-7	1	-12.5	-13.1
-6	1	-9.0	-12.1
-5	1	11.1	13.7
-3	1	45.2	53.9
-2	1	81.0	105.2
-1	1	68.4	81.8
0	1	56.2	64.3
1	1	-4.5	-6.3
2	1	-12.5	-17.0
3	1	-19.9	-24.0
4	1	-11.5	-13.6
5	1	-20.6	-21.4
6	1	-16.4	-16.9
7	1	-5.8	-4.1
8	1	-4.9	-6.9
9	1	11.3	12.3
10	1	-7.1	-8.3
12	1	-3.1	-4.8
-12	2	6.6	7.7
-9	2	6.2	5.4
-8	2	-11.2	-13.4
-7	2	8.1	8.6
-6	2	8.7	11.9
-5	2	11.2	13.0
-4	2	-10.7	-8.6
-3	2	11.0	15.3
-2	2	5.2	5.3
-1	2	4.7	3.0
0	2	24.2	24.1
1	2	6.1	8.0
2	2	-19.8	-23.0
3	2	4.8	6.5
4	2	-18.2	-19.2
5	2	7.5	9.1
6	2	-16.2	-17.0
8	2	4.9	6.2
9	2	-10.5	-12.6
10	2	10.7	12.5
11	2	-5.8	-7.8
-14	3	4.6	6.8
-13	3	10.8	9.8
-11	3	10.0	10.6
-10	3	-4.1	-4.5
-9	3	2.7	1.2
-8	3	-9.4	-11.1
-7	3	-6.0	-6.2
-5	3	-25.7	-27.8
-4	3	20.1	22.3
-3	3	-16.0	-17.6
-2	3	-2.6	-4.3
0	3	2.4	2.1
1	3	-9.4	-5.8
2	3	21.7	24.5
3	3	-10.1	-7.1
4	3	3.0	2.7
5	3	-18.3	-18.3
6	3	-2.6	-3.4
7	3	2.7	5.8
8	3	-8.5	-10.0
9	3	12.3	13.9
-13	4	2.9	3.6
-12	4	11.7	11.7
-10	4	7.3	8.2
-9	4	-13.9	-13.9
-7	4	-4.8	-5.8
-6	4	-13.2	-14.5
-5	4	2.2	1.9
-4	4	-15.1	-13.4
-3	4	8.7	8.7
-1	4	4.4	4.6
0	4	-17.2	-20.0
1	4	-5.7	-8.2
2	4	-17.8	-17.0
3	4	3.7	3.9
4	4	-8.2	-8.6
7	4	-3.8	-5.0
8	4	10.6	13.1
9	4	3.1	3.1
-11	5	10.7	13.4
-9	5	6.9	8.2
-8	5	-6.9	-7.5
-6	5	-7.9	-8.3
-5	5	-5.4	-4.4
-4	5	-5.9	-7.1
-3	5	-11.0	-12.6
-2	5	3.7	4.3
-1	5	-5.4	-6.8
0	5	-4.0	-4.8
1	5	-9.8	-8.7
2	5	-11.8	-15.0
4	5	-2.7	-3.8
5	5	7.8	8.6
6	5	2.9	5.5
8	5	8.1	9.5
-9	6	2.9	5.1
-5	6	-2.7	-2.9
-4	6	2.6	3.4
-3	6	-7.7	-9.6
-2	6	2.9	3.8
-1	6	-13.0	-14.7
1	6	-10.1	-10.3
3	6	-6.1	-6.3
4	6	2.9	3.6
5	6	6.1	9.0
7	6	10.6	12.2
-6	7	6.2	7.2
-4	7	2.9	5.1
-3	7	2.8	2.9
-2	7	-2.8	-4.3
-1	7	7.2	9.1
0	7	-6.7	-9.0
1	7	10.4	11.8
2	7	-4.6	-5.4
3	7	7.3	7.4
-5	8	3.0	3.5
-4	8	3.0	2.3
-3	8	4.9	7.6
-2	8	3.8	3.5
-1	8	3.9	6.8
0	8	4.0	4.0
l=3			
-7	0	-23.3	-24.6
-5	0	5.6	8.5
-3	0	-10.9	-5.9
-1	0	-29.1	-32.0
1	0	20.4	16.6
3	0	7.6	6.4
5	0	21.2	19.8
7	0	8.1	8.1
9	0	4.4	5.6

TABLE 3. (Continued)

h	k	Fo	Fc
11	0	11.3	11.3
-13	1	3.3	3.8
-12	1	-4.5	-6.3
-9	1	5.9	3.5
-8	1	-7.0	-5.0
-6	1	3.9	1.9
-5	1	-13.8	-8.8
-4	1	18.1	16.6
-3	1	14.7	13.0
-2	1	4.5	3.5
-1	1	-4.6	-3.5
0	1	2.1	3.4
1	1	7.2	7.7
2	1	-14.7	-13.4
3	1	24.4	22.4
4	1	-2.1	-3.4
6	1	3.3	3.4
7	1	-2.0	-4.8
9	1	-6.5	-7.9
10	1	10.7	12.1
-14	2	3.5	4.4
-13	2	-3.9	-5.1
-12	2	4.8	5.0
-10	2	7.4	6.3
-9	2	5.6	5.1
-7	2	16.2	15.9
-6	2	7.2	6.8
-5	2	2.6	0.7
-4	2	7.7	9.2
-3	2	-13.0	-10.2
-1	2	9.5	11.7
0	2	-8.8	-9.8
1	2	-7.0	-5.3
2	2	-17.2	-18.1
3	2	-10.7	-10.1
5	2	-7.4	-1.6
6	2	7.7	9.2
7	2	-4.9	-5.2
-15	3	3.9	4.5
-14	3	3.5	4.4
-13	3	4.9	5.6
-11	3	8.0	8.0
-10	3	2.5	3.9
-9	3	-2.1	-1.9
-7	3	-11.6	-9.5
-6	3	-2.4	-2.5
-5	3	-3.5	-3.8
-2	3	-11.1	-8.6
-1	3	11.0	10.6
0	3	13.9	10.4
2	3	5.3	1.5
3	3	-10.7	-9.2
4	3	-8.3	-8.1
8	3	-8.7	-8.5
9	3	4.2	3.8
10	3	-5.4	-5.7
-13	4	3.4	3.3
-12	4	-4.7	-6.0
-10	4	-10.1	-11.0
-7	4	-10.5	-9.9
-6	4	4.9	6.1
-5	4	1.3	2.2
-4	4	7.6	5.9
-3	4	4.4	4.5
0	4	-7.6	-8.6
1	4	9.8	9.0
2	4	7.1	7.4
7	4	-8.3	-8.3
9	4	-8.7	-8.0
10	4	-1.8	-4.3
-11	5	-7.6	-8.3
-10	5	1.9	3.5
-9	5	-8.2	-8.5
-8	5	3.7	4.1
-6	5	5.4	5.4
-5	5	2.1	2.1
-3	5	1.4	4.0
-2	5	-6.1	-5.9
-1	5	-2.9	-2.9
0	5	-3.0	-4.2
2	5	4.2	6.6
3	5	3.5	2.9
4	5	8.9	8.9
6	5	-4.3	-6.6
8	5	-8.1	-8.2
9	5	-1.8	-2.4
-8	6	-3.8	-4.2
-4	6	3.1	2.9
-3	6	-1.5	-3.0
1	6	2.9	3.3
2	6	-10.0	-11.3
3	6	7.2	7.1
6	6	1.9	4.9
7	6	-3.1	-1.6
-6	7	-3.8	-3.7
-5	7	4.0	5.0
-4	7	-6.1	-7.3
-3	7	5.4	5.7
-2	7	-7.8	-7.4
1	7	-7.5	-7.7
2	7	6.0	7.1
3	7	-1.8	-4.3
4	7	3.7	4.7
5	7	1.7	4.2
7	7	6.2	4.3
-1	9	-4.1	-2.8

l=4

h	k	Fo	Fc
-10	0	-8.2	-9.4
-8	0	-8.0	-6.7
-6	0	10.9	10.4
-4	0	1.7	2.3
0	0	2.2	2.0
6	0	5.6	8.5
8	0	10.1	10.5
-13	1	2.5	2.6
-12	1	-3.4	-3.5
-11	1	-7.6	-6.7
-9	1	-12.9	-13.1
-8	1	-11.4	-9.4
-7	1	-9.0	-7.3
-6	1	-2.6	-4.7
-5	1	8.1	5.7
-4	1	34.9	31.1
-3	1	34.1	32.3
-2	1	22.3	20.4
-1	1	13.8	13.2
0	1	14.0	14.1
1	1	-7.5	-6.2
2	1	10.2	10.3
3	1	-12.6	-13.5
5	1	-11.8	-10.4
7	1	9.1	9.5
8	1	-10.0	-11.4
9	1	7.8	6.9
10	1	-7.1	-5.3
-14	2	2.5	0.9
-13	2	-3.6	-3.6
-11	2	-6.5	-6.5
-10	2	-4.2	-3.8
-9	2	-5.3	-4.7
-7	2	9.6	10.1
-6	2	-10.0	-10.8
-5	2	26.2	25.1
-4	2	16.3	17.6
-3	2	26.8	29.6
-2	2	26.5	28.1
-1	2	14.3	11.0
0	2	-11.8	-12.8
2	2	-16.1	-15.2
4	2	-14.8	-14.5
5	2	-4.4	-3.4
7	2	-8.2	-7.9
8	2	7.3	8.3
-15	3	3.3	2.7
-13	3	6.3	6.2
-12	3	-4.2	-2.7
-11	3	6.5	7.4
-10	3	-6.1	-6.7
-8	3	4.4	4.2
-7	3	-6.8	-5.1
-6	3	11.1	10.8
-5	3	-7.6	-6.5
-4	3	2.0	2.4
-2	3	9.6	8.8
0	3	7.3	7.5
1	3	-11.3	-10.4
2	3	2.3	2.8
3	3	-10.2	-8.7
4	3	-2.5	-1.7
5	3	2.6	3.8
6	3	-7.9	-7.0
7	3	4.8	6.2
-15	4	4.0	4.5
-14	4	7.0	6.1
-12	4	6.4	8.1
-11	4	-8.2	-8.0
-10	4	5.8	2.9
-9	4	-6.7	-6.5
-8	4	-3.3	-4.1
-7	4	-3.3	-3.8
-6	4	-4.9	-3.3
-5	4	3.3	3.0
-4	4	-6.9	-4.5
-3	4	2.9	1.9
-2	4	-5.5	-4.3
3	4	-6.7	-7.0
5	4	2.8	0.8
7	4	3.8	5.4
-14	5	2.6	3.1
-13	5	4.5	5.0
-9	5	-2.6	-2.3
-8	5	-5.8	-4.8
-6	5	-7.5	-7.0
-4	5	-3.9	-3.8
-3	5	4.1	4.0
-2	5	-8.0	-9.6
0	5	-10.1	-11.6
2	5	-5.8	-5.3
5	5	-4.9	-6.2
6	5	6.1	7.3
-12	6	3.1	2.9
-8	6	-6.1	-5.4
-6	6	-5.0	-5.6
-5	6	-2.7	-3.2
-3	6	-8.7	-9.6
-2	6	7.1	7.3
-1	6	-13.0	-14.6
0	6	2.7	4.5
1	6	-10.8	-11.4
3	6	2.8	4.4
5	6	6.4	6.1
-2	7	-3.9	-2.9
-1	7	2.5	2.1
0	7	-4.6	-5.1
5	7	5.1	4.8
-6	9	3.4	4.0

l=5

h	k	Fo	Fc
-7	0	11.2	6.5
-3	0	-9.2	-7.0
1	0	-12.3	-11.7
7	0	12.9	9.9
9	0	9.3	10.6
-3	1	-10.1	-8.8
1	1	8.1	7.3
3	1	7.7	8.0

l=6

h	k	Fo	Fc
0	0	-12.3	-10.2
6	0	13.0	12.2
8	0	8.5	8.4
-6	1	11.7	8.0
-8	2	-9.4	-7.3
-7	2	10.5	8.2
-6	2	9.5	5.6
-5	2	16.2	14.7
-4	2	14.1	11.0
-3	2	13.5	9.5
-6	3	9.1	7.2
-5	3	12.5	7.2
-4	3	6.4	10.1

l=8

h	k	Fo	Fc
-2	0	-8.2	-5.3
0	0	-8.4	-6.6

ters and their standard deviations are listed in Table 2. The observed and calculated structure factors are tabulated in Table 3.

Description of the Structure and Discussion

The component molecules are stacked alternately in infinite columns along the *c*-axis. Both the TCNB and HMB molecules are planar within the experimental errors and the mean planes are expressed by:

$$-0.3747x + 0.3132y + 0.9400z = 0$$

and

$$-0.3221x + 0.2903y + 0.9538z = 3.5435$$

respectively, where x, y and z are coordinates (in Å) with respect to the crystal axes a, b and c.

Bond distances and angles in each molecule are listed in Table 4 and they are also shown in Fig. 1. The C(5)-C(4′) distance of 1.41 Å found in TCNB molecule is longer than the C(3)-C(4) distance of 1.38 Å or C(3)-C(5) distance of 1.39 Å. This deformation of the aromatic ring in the TCNB molecule is also found in the complex between TCNB and naphthalene, and is consistent with the result of theoretical calculation.[2)]

Intermolecular atomic distances less than 3.6 Å are indicated in Fig. 2 and listed in Table 5. These distances are of the same order as generally accepted van der Waals distances.

The nature of the anisotropic thermal motion is illustrated in Fig. 3. For HMB molecule, the motion appears to be simply

TABLE 4. BOND DISTANCES AND ANGLES AND THEIR STANDARD DEVIATIONS

TCNB					
N(1)-C(1)	1.11	(0.02) Å	N(2)-C(2)-C(4)	176.7	(1.9)°
C(1)-C(5)	1.44	(0.02)	C(2)-C(4)-C(5′)	118.5	(1.6)
C(5)-C(4′)	1.41	(0.02)	C(2)-C(4)-C(3)	121.2	(1.5)
C(5)-C(3)	1.39	(0.02)	C(3)-C(4)-C(5′)	120.3	(1.5)
C(3)-C(4)	1.38	(0.02)	C(4)-C(3)-C(5)	119.2	(1.5)
C(4)-C(2)	1.44	(0.02)	C(3)-C(5)-C(4′)	121.0	(1.5)
C(2)-N(2)	1.13	(0.02)	C(3)-C(5)-C(1)	117.3	(1.6)
			C(1)-C(5)-C(4′)	122.2	(1.5)
			N(1)-C(1)-C(5)	178.4	(2.1)
HMB					
C(6)-C(9)	1.55	(0.02) Å	C(6)-C(9)-C(10′)	120.0	(1.7)°
C(9)-C(11)	1.38	(0.02)	C(6)-C(9)-C(11)	121.1	(1.6)
C(11)-C(8)	1.56	(0.02)	C(10′)-C(9)-C(11)	118.8	(1.7)
C(11)-C(10)	1.39	(0.02)	C(9)-C(11)-C(8)	118.2	(1.6)
C(10)-C(7)	1.57	(0.02)	C(8)-C(11)-C(10)	120.7	(1.6)
C(10)-C(9′)	1.42	(0.02)	C(9)-C(11)-C(10)	121.1	(1.6)
			C(11)-C(10)-C(7)	118.2	(1.7)
			C(7)-C(10)-C(9′)	121.7	(1.6)
			C(11)-C(10)-C(9′)	120.1	(1.6)

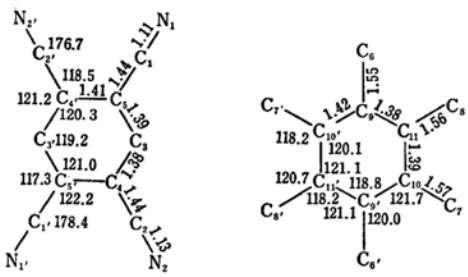


Fig. 1. Bond distances and angles.

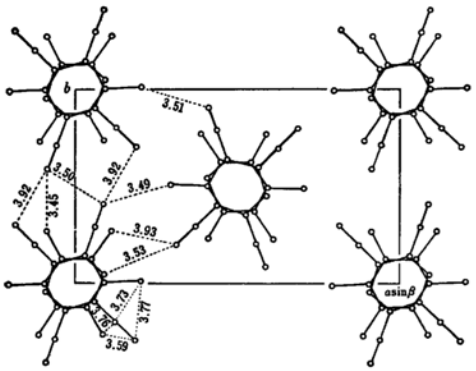
rigid-body libration about the center of gravity, chiefly in the molecular plane. The thermal motion of the less rigid TCNB molecule is more complex and defies rigorous analysis. However, it is at least certain that the out-of-plane vibration of the cyano groups is appreciable.

The molecules overlap each other as shown in Fig. 4, with interplanar spacing of 3.54 Å. The molecular plane of TCNB makes an angle of about 2° with that of HMB. This spacing is about 0.11 Å larger than that found in TCNB-naphthalene complex.[2] This difference is clearly due to the difference in the thickness of the donor molecules.

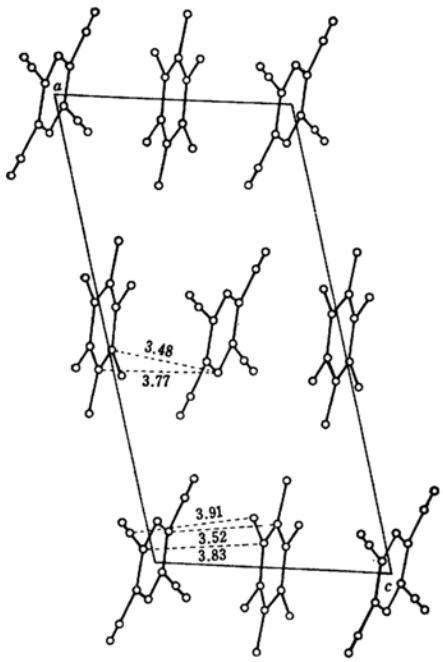
Iwata, Tanaka and Nagakura[4] calculated the electronic structures of this molecular complex only by considering the interaction between π-electrons of the donor and the acceptor. They concluded that the center of the donor molecule should lie above the carbon atom or the C-C bond of the benzene ring of the acceptor molecule in the stable configuration. As shown in Fig. 4, their conclusion agrees well with the determined structure. It is particularly noteworthy that the relative arrangement of the donor and acceptor molecules in the crystal agrees with the result of the theoretical calculation based on the π-π interaction only. It is certain that the relative arrangement of the donor and the acceptor molecules will be affected by various interactions other than the charge tranfer interaction, such as van der Waals, repulsive interactions etc. Actually the packing of the molecular stacks along the *c*-axis seems to be determined mainly by van der Waals interactions. But, as for the relative arrangement of the component molecules, the following conditions seem to enable the theoretical conclusion to be consistent with the result of the structure analysis. Firstly both the acceptor and the donor molecules are planar. Especially, the donor molecule which is surrounded by six methyl groups is disc-shaped. The relative translation of one component molecule with respect to another does not result in any particular stable molecular packing. Secondly the donor molecules contain neither nitrogen nor oxygen atom having lone pair electrons. Consequently any localized interaction between the component molecules

TABLE 5. CLOSEST INTERMOLECULAR CONTACTS

C(7)-N(2′)	3.51 Å
N(1)-N(1′)	3.50
N(1)-C(7′)	3.49
N(1′)-C(6)	3.45
C(3)-N(1′)	3.53
C(6′)-N(2)	3.59
C(5)-C(10)	3.52
C(11)-C(3)	3.48



(a) viewed along [001]



(b) viewed along [010]

Fig. 2. Closest intermolecular contacts between TCNB and HMB.

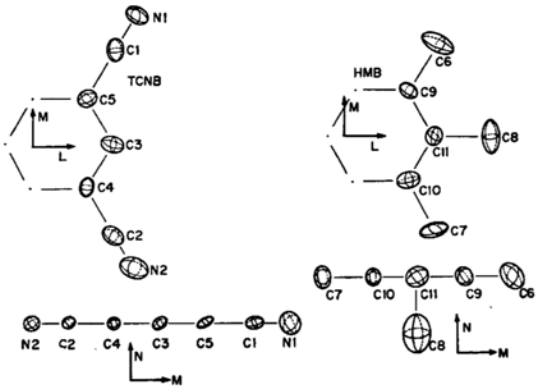


Fig. 3. The thermal motion ellipsoids.

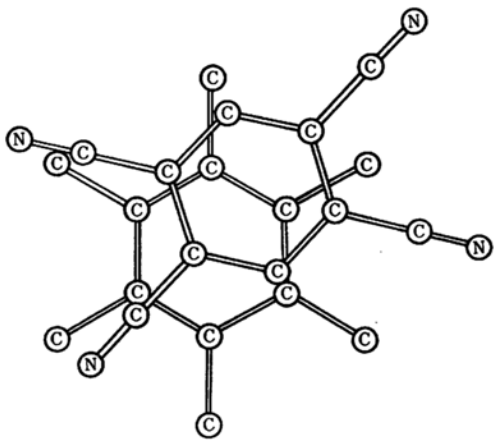


Fig. 4. Overlapping molecules, viewed approximately normal to their plane.

cannot be expected. Therefore the relative arrangement of the donor and the acceptor molecules in the molecular stack is mainly determined by the π-π interaction. The same situation will also be found in the case of the TCNB-naphthalene,[2] TCNE-naphthalene,[6,7] TCNE-pyrene[6,8] and TCNE-perylene[9] complexes.

Calculations were carried out on FACOM 202 computer at this institute and on HITAC 5020 at the Computer Center of the University.

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