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The Crystal Structure of the 1 : 1 Complex of Naphthalene with 1, 2, 4, 5-Tetracyanobenzene

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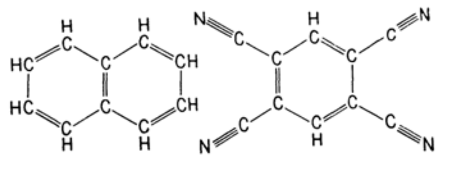
The crystal of the equimolar complex between 1, 2, 4, 5-tetracyanobenzene and naphthalene is monoclinic, with space group $C2/m$, a=9.39, b=12.66, c=6.87 Å, β=107.2° and Z=2. The structure was deduced from the $hk0$ weighted reciprocal lattice and a packing consideration, and refined by the three-dimensional difference synthesis and the block-diagonal least-squares method. The constituent molecules are approximately planar and overlap each other with an average interplanar spacing of 3.43 Å. They are stacked alternately in infinite columns along the c axis. The structure is disordered, with the naphthalene molecules adopting one of alternative orientations with equal probability. The determined structure is consistent with the electronic spectra of the cyrstal.

1, 2, 4, 5 - Tetracyanobenzene(TCNB) - naphthalene complex is one of the series of charge transfer complexes containing TCNB as an electron acceptor, whose crystal sturctures have been determined in this laboratory.[1,2]



Naphthalene 1, 2, 4, 5-Tetracyanobenzene

The crystal structure analysis of the present complex, which is considered as a weak charge transfer complex in the series, was undertaken to investigate the molecular interaction between

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1) Y. Ohashi, H. Iwasaki and Y. Saito, This Bulletin, **40**, 1789 (1967).

2) N. Niimura, Y. Ohashi, F. F. Iwasaki and Y. Saito, Presented at the Symposium on Molecular Structure held at Osaka, in October, 1966.

the donor and the acceptor and also to facilitate the interpretation of the electronic spectra of the crystal. Measurement of absorption and luminescence spectra of the complex as well as their theoretical study was already made by Iwata, Tanaka and Nagakura.3)

Experimental

Light yellow crystals of the molecular complex of TCNB and naphthalene grown from ethanol solution are monoclinic prisms elongated along the *c* axis, with well developed {110} planes. These crystals are always twinned on (100). All attempts to obtain the individual single crystals failed.

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 ($\lambda=1.542$ Å). They are listed in Table 1, together with other crystal data. $C2/m$ is consistent with the structure.

TABLE 1. CRYSTAL DATA

Monoclinic
$a=9.39\pm0.01$Å
$b=12.66\pm0.02$Å
$c=6.87\pm0.02$Å
$\beta=107.2\pm0.3°$
$V=780.2$Å^3
Formula $C_{10}H_2N_4\cdot C_{10}H_8$, F. W.$=612.7$
$D_x=1.31$ g/cm^3
$D_m=1.30$ g/cm^3
$Z=2$
$\mu=7.66$ cm^{-1} (Cu$K\alpha$)

Possible space group: $C2$, Cm or $C2/m$
(Absent spectra: *hkl* when $h+k$ is odd.)

The specimens with dimensions $0.25\times0.11\times0.10$ mm and $0.11\times0.08\times0.70$ mm were used for the collections of the intensity data around the *b* and *c* axes respectively. Intensity data were recorded on the equi-inclination Weissenberg photographs taken around the *b* axis up to the ninth layer and around the *c* axis up to the fifth layer using multiple film technique. Of the 939 independent reflections within the effective copper sphere ($\sin\theta\leqq0.999$), 822 non-zero reflections were observed. The range of the observed intensities is about 1 to 10000. The usual Lorentz-polarization and the spot shape corrections were applied, but the absorption correction was neglected in view of the small size of the specimen and the small value of the linear absorption coefficient. On Weissenberg photographs taken around the *b* axis *hk*0 reflections from the twinning individuals perfectly overlapped. Therefore it was necessary to divide the observed intensity according to the intensity ratio obtained from resolved *hkl* reflections. This procedure may limit the accuracy of the structure analysis to some extent. Details of the twinning will be described in the Appendix.

Structure Analysis

Since Wilson's statistics indicated the presence of a center of symmetry, the space group $C2/m$ was assumed. There are only two pairs of component molecules in a unit cell; therefore, the centers of gravity of the molecules must lie on twofold special positions, and the molecules are required to have a symmetry $2/m$. In order to obtain the familiar mixed stacks, the TCNB and naphthalene molecules must be centered at positions 2 *a*: (000) and (1/2, 1/2, 0); and 2 *c*: (0, 0, 1/2) and (1/2, 1/2, 1/2), respecitvely. The orientations of the molecules were deduced from a packing consideration and a study of the *hk*0 weighted reciprocal lattice. A trial structure thus deduced is such that the molecules of naphthalene and TCNB are aranged with their planes perpendicular to the *c* axis and are stacked alternately along this axis. Calculated structure amplitudes $F(hk0)$ and $F(h0l)$ based on this model (hereafter called Structure I) showed fairly good agreement with those observed. Then the atomic coordinates except those of hydrogen were refined by the three-dimensional difference synthesis and the diagonal-approximated least-squares procedure using the program due to Y. Iitaka, the temperature factors being assumed isotropic. The *R*-factor reduced to 28% for 822 independent non-zero reflections.

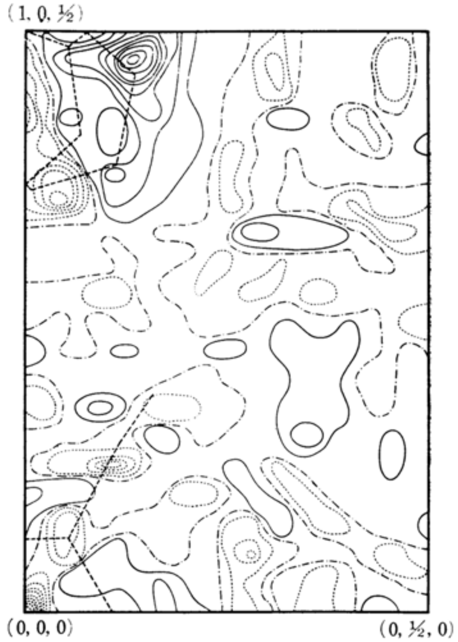

Fig. 1. A section of difference synthesis through the plane (10$\bar{2}$). Contours are at intervals of 0.2 e.Å^{-3}; solid contours are positive, dotted contours are negative, chain contour is zero. The centers of TCNB and naphthalene molecules are placed on the positions (0,0,0) and (1,0,1/2) respectively.

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3) S. Iwata, J. Tanaka and S. Nagakura, *J. Am. Chem. Soc.,* in press.

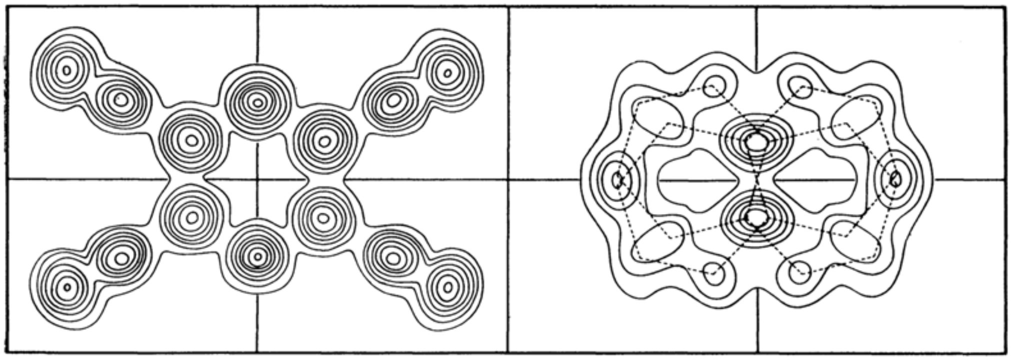

Fig. 2. A section of F_o synthesis through the plane $(10\bar{2})$. Contours are at intervals of 1 e.Å^{-3}, the lowest contour being 1e.Å^{-3}.

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/a $\times10^4$	$\sigma(x/a)$ $\times10^4$	y/b $\times10^4$	$\sigma(y/b)$ $\times10^4$	z/c $\times10^4$	$\sigma(z/c)$ $\times10^4$	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												
C(1)	0	0	1121	0005	0	0	0095	0049	0213	0	0037	0
C(2)	1321	0005	0563	0004	0564	0007	0116	0060	0216	−0014	0126	0009
C(3)	2727	0006	1125	0004	1163	0008	0137	0045	0290	0042	0163	0066
N(4)	3810	0005	1574	0004	1584	0009	0109	0085	0456	−0062	0116	−0002
Naphthalene												
C(5)	0214	0013	0543	0005	5134	0021	0157	0055	0143	0054	0	−0044
C(6)	1783	0014	0801	0010	5822	0017	0164	0082	0211	0034	0010	0028
C(7)	0898	0014	1363	0010	5323	0015	0251	0078	0165	−0090	0107	0038
C(8)	2382	0013	1102	0015	5977	0020	0119	0204	0350	−0098	0104	0065
C(9)	2796	0011	0058	0027	6240	0015	0163	0157	0265	−0100	0149	0156

At this stage a three-dimensioal difference synthesis was computed. The section of this synthesis through the plane $(10\bar{2})$, which is approximately parallel to the planes of the constituent molecules, is shown in Fig. 1. Anomalous peaks, about 2.0 eÅ^{-3} in heights, are found on this map. Furthermore, the temperature factors of the α- and β-carbon atoms of naphthalene were unusually large. Consequently a disordered model (called Structure II) was constructed. This is also illustrated in Fig. 1. In this model the naphthalene molecule adopts one of alternative orientations to maintain the site symmetry. The atomic coordinates and isotropic temperature factors of Structure II were refined by means of the block diagonal least-squares procedure using the program due to T. Ashida. The anisotropic temperature factors were introduced at a later stage of this refinement. The weighting scheme for the least-squares procedure was: 0.5 for $F_o<3.0$ and 1.0 for $F_o\geqq3.0$. After three cycles the R-factor reduced to 18%. However, the shape of naphthalene molecules thus determined was largely distorted and the standard deviations of atomic coordinates of the carbon atoms C(5) and C(9) were unusually large. These anomalies were considered as being caused by parameter interactions.4) To overcome these difficulties, the refinement was carried out as follows: at first the positional parameters of C(5) and C(9) were fixed in such a way as to give normal bond distances and angles found in a naphthalene molecule, and the rest of the parameters were refined in three cycles; then the temperature factors thus obtained for C(5) and C(9) were fixed and all other parameters were refined in additional three cycles. After these refinements the R-factor reduced to 16.5%. The comparatively high value of the R-factor may have resulted from the existence of disorder in the structure. A section of three-dimensional Fourier synthesis is shown in Fig. 2. The topography of the final difference synthesis is flat, within the range of ±0.8 eÅ^{-3}. The final atomic and thermal parameters are listed in Table 2. A comparison of the observed and calculated structure factors is given in Table 3. Atomic scattering

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4) S. Geller, *Acta Cryst.*, **14**, 1026 (1961).

TABLE 3. STRUCTURE FACTORS

h	k	l	Fo	Fc
2	0	0	-39.2	-38.6
6	0	0	-4.1	-3.8
8	0	0	22.0	22.8
1	1	0	57.6	56.0
3	1	0	16.6	14.6
5	1	0	5.0	3.6
7	1	0	17.4	16.8
9	1	0	-4.6	-3.0
11	1	0	2.4	2.0
0	2	0	66.6	70.8
2	2	0	-21.2	-17.2
4	2	0	11.2	13.8
6	2	0	4.6	4.8
8	2	0	4.6	3.8
10	2	0	-0.8	-1.2
1	3	0	24.2	29.0
3	3	0	-29.6	-27.6
5	3	0	-18.8	-16.4
7	3	0	11.2	10.2
9	3	0	5.0	4.0
11	3	0	-3.8	-3.4
0	4	0	-78.0	-81.2
2	4	0	10.4	8.8
4	4	0	-5.0	-4.6
6	4	0	8.0	8.4
8	4	0	-7.6	-8.8
10	4	0	-3.2	-3.0
1	5	0	-27.0	-27.4
3	5	0	4.4	3.4
5	5	0	-3.0	-2.2
7	5	0	-6.8	-8.4
9	5	0	-4.0	-1.4
11	5	0	-1.4	-1.2
0	6	0	-9,2	-9.0
2	6	0	5.6	6.0
4	6	0	-16.0	-16.8
6	6	0	-5.6	-5.0
8	6	0	-3.2	-0.4
10	6	0	2.8	2.2
1	7	0	-24.8	-22.2
3	7	0	19.6	20.4
5	7	0	4.2	1.2
7	7	0	-6.2	-4.2
9	7	0	-4.8	-4.6
0	8	0	4.2	4.6
2	8	0	-9.8	-9.2
4	8	0	18.0	17.8
6	8	0	-10.8	-8.8
8	8	0	-4.0	-1.2
10	8	0	3.2	4.0
1	9	0	-1.2	-2.2
3	9	0	8.4	7.2
5	9	0	-5.8	-5.6
7	9	0	4.4	4.8
9	9	0	3.0	0.0
0	10	0	-7.4	-8.0
2	10	0	-9.0	-11.4
4	10	0	19.2	18.2
8	10	0	-3.0	-2.4
1	11	0	-6.8	-6.6
3	11	0	4.2	0.6
7	11	0	-4.0	-3.4
0	12	0	-4.2	-6.0
2	12	0	-4.2	-1.4
4	12	0	-4.4	-5.4
1	13	0	-5.8	-4.6
3	13	0	-4.6	-3.8
5	13	0	4.6	2.8
0	14	0	-5.2	-2.8
2	14	0	3.4	2.8
4	14	0	-10.2	-7.4
3	15	0	-4.4	-2.8
0	16	0	2.4	3.4
-10	0	1	-5.2	-2.8
-8	0	1	20.4	22.2
-6	0	1	7.0	8.0
-4	0	1	-22.8	-24.4
-2	0	1	-33.2	-36.2
0	0	1	20.0	26.4
2	0	1	40.4	36.6
4	0	1	-23.6	-24.2
8	0	1	7.2	8.4
-11	1	1	2.6	1.8
-9	1	1	4.2	3.6
-7	1	1	4.2	3.8
-5	1	1	-14.2	-14.4
-3	1	1	18.4	19.2
1	1	1	-18.2	-20.0
3	1	1	-17.0	-16.0
5	1	1	2.2	2.6
7	1	1	13.2	15.4
11	1	1	-1.2	-1.8
-10	2	1	2.4	1.8
-8	2	1	3.8	1.4
-6	2	1	-6.6	-6.8
-4	2	1	-21.4	-20.2
-2	2	1	28.2	25.8
0	2	1	-12.6	-11.4
2	2	1	-20.6	-17.0
4	2	1	-16.2	-12.4
6	2	1	4.8	4.0
8	2	1	3.2	3.6
10	2	1	-4.2	-3.8
-11	3	1	-9.2	-8.6
-9	3	1	4.6	4.6
-7	3	1	3.4	2.4
-5	3	1	-15.4	-11.0
-3	3	1	-46.0	-46.2
-1	3	1	-9.6	-10.8
1	3	1	54.8	54.2
3	3	1	-31.8	-31.2
5	3	1	-12.4	-13.6
7	3	1	-10.6	-10.2
9	3	1	5.6	5.2
-10	4	1	3.2	1.4
-8	4	1	-13.6	-15.2
-6	4	1	-2.6	-0.8
-4	4	1	-29.2	-27.8
-2	4	1	33.2	33.4
0	4	1	-25.8	-27.2
2	4	1	-29.8	-26.8
4	4	1	-10.0	-7.8
6	4	1	-3.2	-3.8
8	4	1	2.6	0.4
10	4	1	-7.6	-7.6
-11	5	1	-4.0	-3.2
-9	5	1	4.0	1.4
-7	5	1	-9.8	-11.8
-3	5	1	-7.2	-6.2
-1	5	1	-12.0	-12.8
1	5	1	6.6	4.2
3	5	1	-27.6	-26.4
5	5	1	11.8	12.0
7	5	1	-10.8	-13.0
9	5	1	-3.4	-0.8
-10	6	1	-2.8	-2.8
-8	6	1	-3.8	-3.2
-6	6	1	14.4	16.2
-4	6	1	-14.6	-15.2
-2	6	1	-9.6	-11.8
0	6	1	-3.6	-3.6
2	6	1	14.8	14.6
4	6	1	-1.4	-0.2
6	6	1	-7.8	-8.2
8	6	1	-3.6	-1.4
10	6	1	2.0	1.6
-9	7	1	-1.4	-4.6
-7	7	1	-4.2	-3.6
-5	7	1	12.8	13.2
-3	7	1	17.6	18.2
-1	7	1	-4.8	-3.2
1	7	1	-14.0	-14.6
3	7	1	6.0	7.0
5	7	1	14.0	15.4
7	7	1	3.4	0.4
9	7	1	-3.6	-2.6
-10	8	1	2.2	0.8
-8	8	1	1.8	1.6
-6	8	1	4.4	3.0
-4	8	1	19.0	21.0
0	8	1	1.2	2.2
2	8	1	7.2	8.8
4	8	1	15.8	17.4
6	8	1	3.4	4.4
-9	9	1	-3.2	-2.2
-7	9	1	5.2	6.6
-5	9	1	11.2	13.4
-3	9	1	4.4	4.8
-1	9	1	3.6	4.4
1	9	1	8.4	9.0
3	9	1	22.0	23.8
5	9	1	-4.8	-2.0
7	9	1	4.4	1.8
9	9	1	2.0	1.6
-6	10	1	-4.2	-2.4
-4	10	1	17.6	19.6
-2	10	1	8.2	8.6
0	10	1	4.2	1.6
2	10	1	4.4	3.0
4	10	1	10.6	12.0
6	10	1	4.0	2.6
-5	11	1	4.2	3.0
-3	11	1	5.8	5.8
1	11	1	4.4	5.2
3	11	1	8.0	7.0
-6	12	1	3.6	3.2
-4	12	1	-4.2	-3.4
-2	12	1	4.4	1.6
2	12	1	7.2	6.6
4	12	1	-4.0	-1.2
6	12	1	-5.6	-5.4
-7	13	1	-5.0	-5.0
-5	13	1	-4.2	-0.8
-3	13	1	4.0	3.8
3	13	1	-5.4	-6.6
5	13	1	3.0	3.6
-4	14	1	-6.6	-6.6
0	14	1	-5.4	-6.6
4	14	1	-2.8	-2.8
-3	15	1	-3.6	-2.0
3	15	1	-3.8	-2.8
-10	0	2	-7.2	-6.0
-8	0	2	22.0	19.8
-6	0	2	6.4	5.2
-4	0	2	18.6	17.0
-2	0	2	15.0	11.2
0	0	2	79.0	73.2
2	0	2	25.8	21.6
4	0	2	7.4	7.4
6	0	2	10.8	10.0
8	0	2	-3.0	-1.8
10	0	2	4.6	4.4
-11	1	2	2.4	1.4
-9	1	2	11.4	12.4
-5	1	2	2.6	2.4
-3	1	2	-18.6	-17.4
-1	1	2	143.0	149.0
1	1	2	-27.8	-24.6
3	1	2	5.6	6.0
5	1	2	2.4	0.6
7	1	2	13.4	16.0
-10	2	2	1.4	1.0
-8	2	2	13.2	13.2
-6	2	2	-7.6	-9.4
-4	2	2	-5.6	-4.2
-2	2	2	29.8	29.4
0	2	2	39.6	40.4
2	2	2	-16.2	-14.2
4	2	2	-5.6	-4.2
6	2	2	11.8	14.4
8	2	2	3.2	1.0
10	2	2	-2.0	-1.0
-11	3	2	-4,0	-4.0
-9	3	2	-4.2	-4.4
-7	3	2	10.8	11.8
-5	3	2	4.0	5.4
-3	3	2	-11.6	-10.8
-1	3	2	-34.4	-31.6
1	3	2	7.6	8.8
3	3	2	5.6	7.2
5	3	2	3.2	3.2
7	3	2	-4.0	-5.0
9	3	2	-2.6	-1.2
-10	4	2	3.4	2.6
-8	4	2	-4.0	-3.4
-6	4	2	-7.0	-7.4
-4	4	2	-11.8	-10.8
-2	4	2	6.4	6.4
0	4	2	-15.6	-15.0
2	4	2	-13.6	-15.0
4	4	2	-9.4	-9.8
6	4	2	3.4	3.0
8	4	2	3.6	0.8
10	4	2	-3.2	-3.8
-9	5	2	-4.6	-3.8
-7	5	2	3.8	0.8
-5	5	2	-12.6	-13.8
-3	5	2	11.6	9.8
-1	5	2	-37.8	-36.8
1	5	2	6.4	4.8
3	5	2	-14.0	-14.8
5	5	2	4.0	1.8
7	5	2	-5.4	-5.0
9	5	2	-2.6	-1.2
-10	6	2	-3.6	-3.8
-8	6	2	-6.6	-7.0
-6	6	2	4.0	5.2
-4	6	2	7.4	8.2
-2	6	2	-26.8	-24.6
0	6	2	-25,8	-24.2
2	6	2	19.2	19.4
4	6	2	-3.4	-2.4
6	6	2	-8.0	-9.4
8	6	2	-3.2	-3.6
-9	7	2	-3.8	-1.0
-7	7	2	-10.0	-9.2
-5	7	2	4.2	1.2
-3	7	2	2.8	3.0
-1	7	2	4.4	4.6
1	7	2	-9.4	-7.6
3	7	2	3.6	1.4
5	7	2	-7.4	-7.0
7	7	2	4.8	0.8
9	7	2	2.2	2.6
-8	8	2	4.0	2.8
-6	8	2	-5.4	-5.2
-4	8	2	12.6	13.6
-2	8	2	-9.6	-9.6
0	8	2	-6.0	-5.0
2	8	2	9.4	10.6
4	8	2	-2.0	-1.2
6	8	2	3.2	0.8
8	8	2	-2.4	-2.0
-9	9	2	-4.8	-2.8
-7	9	2	-4.8	-2.4
-5	9	2	17.6	19.0
-3	9	2	-9.6	-11.8
-1	9	2	-4.0	-2.6
1	9	2	-8.4	-9.6
3	9	2	21.4	22.0
5	9	2	-5.2	-6.8
7	9	2	-3.8	-1.2
-8	10	2	3.4	0.8
-6	10	2	-5.8	-5.0
-4	10	2	7.6	7.8
-2	10	2	-4.2	-4.4
0	10	2	-4.4	-3.4
2	10	2	-4.4	-1.4
4	10	2	4.2	1.0
-5	11	2	5.8	3.8
-3	11	2	-10.0	-5.0
-1	11	2	-6.8	-7.0
1	11	2	-5.4	-6.4
3	11	2	6.8	5.0
-8	12	2	-4.0	-5.2
-6	12	2	3.4	3.2
-4	12	2	-4.2	-1.6
-2	12	2	-7.0	-6.6
0	12	2	-7.8	-6.2
2	12	2	-5.0	-2.0
4	12	2	3.6	3.0
-5	13	2	-7.0	-7.2
-3	13	2	3.8	2.8
-1	13	2	-5.0	-4.4
3	13	2	-7.8	-8.8
-4	14	2	-5.6	-5.4
-2	14	2	4.2	0.8
0	14	2	-3.4	-0.8
4	14	2	-1.8	-1.0
-3	15	2	2.8	0.6
-1	15	2	2.8	0.4
-8	0	3	5.2	5.4
-6	0	3	-4.6	-5.0
-4	0	3	19.0	18.4
-2	0	3	-5.8	-5.4
0	0	3	-21.6	-23.4
2	0	3	-2.2	-0.8
4	0	3	4.0	4.0
6	0	3	13.4	14.4
8	0	3	-2.6	-2.4
-11	1	3	-2.6	-0.2
-9	1	3	11.6	11.8
-7	1	3	1.2	1.0
-5	1	3	-15.0	-16.0
-3	1	3	-4.0	-4.2
-1	1	3	7.6	10.8
1	1	3	6.4	6.0
3	1	3	-15.4	-15.8
5	1	3	2.6	1.6
7	1	3	7.2	8.2
9	1	3	2.0	0.8
-12	2	3	-2.8	-3.4
-10	2	3	4.0	3.8
-8	2	3	4.6	4.0
-6	2	3	-10.6	- 9.2
-4	2	3	-17.0	-15.2
-2	2	3	2.2	2.6
0	2	3	16.6	15.2
2	2	3	-18.4	-17.2
4	2	3	-7.8	-8.2
6	2	3	3.4	2.4
8	2	3	2.8	2.6
-11	3	3	2.4	0.4
-9	3	3	-8.8	-7.6
-7	3	3	-3.0	-2.4
-5	3	3	-14.4	-13.2
-3	3	3	18.2	18.8
-1	3	3	-21.8	-21.4
1	3	3	-14.6	-11.8
3	3	3	-8.6	-6.0
5	3	3	-2.8	-1.0
7	3	3	-3.2	-1.0
9	3	3	-4.2	-5.4
-10	4	3	5.2	5.0
-8	4	3	-6.6	-6.4
-6	4	3	-5.8	-5.8
-4	4	3	-26.0	-24.0
-2	4	3	-2.0	-0.4
0	4	3	20.8	21.6
2	4	3	-26.2	-26.2
4	4	3	-3.4	-2.6
6	4	3	-10.8	-12.0
8	4	3	3.6	3.2
-11	5	3	-2.2	-1.6
-9	5	3	-7.8	-6.6
-7	5	3	6.0	6.6
-5	5	3	-17.8	-18.8
-3	5	3	6.0	4.4
-1	5	3	-10.0	-11.2
1	5	3	2.6	1.2
3	5	3	-7.0	-7.8
5	5	3	-4.2	-4.2
7	5	3	-3.6	-2.0
9	5	3	-1.8	-2.2
-10	6	3	-3.4	-2.0
-8	6	3	-9.2	-9.0
-6	6	3	8.0	8.6
-4	6	3	6.8	6.8
-2	6	3	-7.8	-9.0
0	6	3	-10.4	-10.6
2	6	3	-5.6	-3.6
4	6	3	14.4	15.2
6	6	3	-6.6	-6.6
8	6	3	-2.8	-2.6
-9	7	3	3.8	0.4
-7	7	3	5.6	5.8
-5	7	3	4.4	3.4
-3	7	3	-3.0	-2.2
-1	7	3	3.4	1.4
1	7	3	6.8	8.0
3	7	3	6.6	6.4
5	7	3	3.6	1.2
7	7	3	-3.4	-2.2
-10	8	3	-2.4	-3.6
-8	8	3	4.2	3.0
-6	8	3	11.2	11.2

TABLE 3. (Continued)

h	k	l	Fo	Fc
-4	8	3	9.6	10.0
-2	8	3	1.8	0.6
0	8	3	-3.4	-1.4
2	8	3	13.6	15.4
4	8	3	6.4	6.2
6	8	3	3.6	3.0
8	8	3	-1.8	-0.8
-9	9	3	-3.0	-1.6
-7	9	3	-4.4	-1.0
-5	9	3	19.8	21.2
-3	9	3	4.6	5.0
1	9	3	4.0	3.0
3	9	3	16.0	16.6
5	9	3	4.2	3.8
7	9	3	-2.8	-1.8
-8	10	3	2.6	1.2
-6	10	3	4.4	4.0
-4	10	3	5.0	5.8
-2	10	3	5.0	4.2
0	10	3	7.0	7.6
2	10	3	13.2	11.8
4	10	3	-4.2	-1.2
-7	11	3	2.8	0.6
-5	11	3	6.0	5.2
-3	11	3	4.0	4.0
1	11	3	5.0	4.6
3	11	3	4.6	4.4
5	11	3	-3.2	-2.0
-8	12	3	-3.4	-5.0
-6	12	3	2.6	1.2
-4	12	3	3.6	4.0
-2	12	3	-4.2	-3.8
0	12	3	3.4	0.6
2	12	3	-3.8	-0.6
-3	13	3	2.8	2.2
-1	13	3	-3.8	-6.0
1	13	3	3.8	3.8
3	13	3	-4.6	-4.0
-4	14	3	-3.6	-1.0
-2	14	3	-4.2	-4.0
0	14	3	-2.4	-1.2
2	14	3	-4.4	-4.0
-1	15	3	-2.6	-3.4
1	15	3	-1.4	-0.4
-10	0	4	8.8	8.4
-8	0	4	-3.2	-0.6
-6	0	4	-1.4	-0.4
-4	0	4	-4.4	-4.4
-2	0	4	78.8	79.4
0	0	4	-16.2	-13.0
2	0	4	5.6	5.6
4	0	4	3.0	2.0
6	0	4	15.0	13.8
-11	1	4	-2.8	-2.6
-9	1	4	15.4	14.8
-7	1	4	-3.0	-2.6
-5	1	4	4.4	4.4
-3	1	4	3.4	3.6
-1	1	4	45.0	42.0
1	1	4	2.6	2.2
3	1	4	3.2	2.0
5	1	4	5.2	7.2
7	1	4	3.2	1.0
-10	2	4	2.8	2.2
-8	2	4	6.4	6.4
-6	2	4	3.2	1.6
-4	2	4	-10.0	-9.4
-2	2	4	27.2	24.8
0	2	4	2.2	0.6
2	2	4	3.4	4.6
4	2	4	2.6	0.4
6	2	4	4.4	4.6
8	2	4	2.2	0.0
-11	3	4	2.6	2.0
-9	3	4	4.0	1.4
-7	3	4	-5.4	-5.6
-5	3	4	-4.4	-3.6
-3	3	4	11.8	11.2
-1	3	4	-2.4	-0.6
1	3	4	-12.8	-12.6
3	3	4	-4.8	-3.0
5	3	4	7.6	8.2
7	3	4	3.2	0.2
-10	4	4	-3.0	-2.6
-8	4	4	4.2	5.4
-6	4	4	-4.0	-4.4
-4	4	4	-2.6	-1.6
-2	4	4	-24.0	-24.2
0	4	4	6.2	5.4
2	4	4	-4.4	-5.0
4	4	4	3.2	0.6
6	4	4	-4.4	-4.4
8	4	4	-1.6	-1.0
-11	5	4	-2.4	-0.4
-9	5	4	-6.0	-6.0
-7	5	4	3.4	2.4
-5	5	4	-3.4	-2.6
-3	5	4	-5.4	-5.6
-1	5	4	-16.4	-17.4
1	5	4	5.0	4.0
3	5	4	-4.0	-6.2
5	5	4	-4.4	-3.2
7	5	4	-2.8	-1.4
-10	6	4	-2.6	-2.0
-8	6	4	-7.4	-5.6
-6	6	4	-4.6	-3.8
-4	6	4	7.6	7.0
-2	6	4	-8.8	-7.6
0	6	4	-4.6	-5.4
2	6	4	-5.0	-4.6
4	6	4	-4.0	-2.2
6	6	4	-2.8	-1.6
-9	7	4	-3.4	-0.4
-7	7	4	-4.2	-0.8
-5	7	4	6.8	6.8
-3	7	4	-11.2	-11.0
-1	7	4	-6.4	-6.0
1	7	4	9.4	11.4
3	7	4	-3.8	-3.0
5	7	4	-5.0	-4.6
7	7	4	-2.4	-2.0
-10	8	4	-2.0	-2.4
-8	8	4	-6.0	-3.6
-6	8	4	-7.8	-8.8
-4	8	4	-3.8	-3.4
-2	8	4	-3.2	-1.2
0	8	4	-6.0	-7.0
2	8	4	11.8	12.0
4	8	4	-6.4	-6.6
6	8	4	2.8	0.4
-9	9	4	2.8	2.0
-7	9	4	-5.8	-6.6
-5	9	4	11.4	11.4
-3	9	4	-4.4	-5.6
-1	9	4	-3.4	-1.6
1	9	4	3.6	0.0
3	9	4	4.0	2.4
5	9	4	3.4	1.6
-8	10	4	3.0	0.4
-6	10	4	8.6	7.4
-4	10	4	-5.2	-6.2
-2	10	4	-3.6	-4.2
0	10	4	-5.2	-6.0
2	10	4	11.6	10.6
4	10	4	-3.4	-2.6
-7	11	4	-2.8	-0.4
-5	11	4	4.6	3.8
-3	11	4	-5.0	-5.8
-1	11	4	-5.0	-4.4
1	11	4	-4.4	-3.2
3	11	4	2.6	3.4
5	11	4	-1.8	-2.0
-6	12	4	-2.8	-2.2
-4	12	4	3.6	1.0
-2	12	4	-4.6	-5.2
0	12	4	-3.6	-2.8
2	12	4	-2.8	-3.4
4	12	4	1.8	1.6
-5	13	4	-3.6	-4.4
-3	13	4	-3.2	-1.0
-1	13	4	-4.4	-3.0
1	13	4	-2.8	-1.6
3	13	4	1.2	0.0
-4	14	4	2.0	1.2
-2	14	4	-2.4	-1.4
-10	0	5	9.2	9.2
-8	0	5	2.4	0.8
-6	0	5	-7.4	-8.8
-4	0	5	-1.0	-2.0
-2	0	5	8.0	8.0
0	0	5	1.2	0.0
2	0	5	-6.2	-9.6
6	0	5	7.6	8.6
-11	1	5	1.8	0.2
-9	1	5	5.0	5.2
-7	1	5	-3.2	-3.0
-5	1	5	2.4	0.2
-3	1	5	-2.8	-2.0
-1	1	5	-2.8	-2.8
1	1	5	-3.2	-2.6
3	1	5	-3.4	-2.2
5	1	5	5.2	6.6
7	1	5	1.8	0.4
-10	2	5	2.2	1.4
-8	2	5	2.6	0.0
-6	2	5	-6.6	-7.8
-4	2	5	2.6	2.6
-2	2	5	-3.8	-3.0
0	2	5	-2.4	-0.6
2	2	5	-7.2	-6.8
4	2	5	-2.6	-0.8
6	2	5	-3.6	-2.4
-11	3	5	3.0	4.0
-9	3	5	-3.2	-1.8
-7	3	5	-4.6	-5.4
-5	3	5	-12.2	-13.8
-3	3	5	4.0	4.8
-1	3	5	11.0	10.9
1	3	5	-15.2	-15.0
3	3	5	-3.8	-5.4
5	3	5	-4.2	-3.8
7	3	5	2.4	2.6
-10	4	5	-4.4	-4.6
-8	4	5	3.6	1.6
-6	4	5	-8.0	-10.8
-4	4	5	3.6	4.6
-2	4	5	-10.2	-10.2
0	4	5	4.4	1.0
2	4	5	-7.2	-6.4
4	4	5	-3.2	-2.8
6	4	5	-2.6	-3.2
-9	5	5	-7.0	-7.2
-7	5	5	3.2	2.6
-5	5	5	-4.8	-6.2
-3	5	5	-3.0	-2.6
-1	5	5	1.2	0.8
1	5	5	-8.6	-8.4
3	5	5	4.2	4.6
5	5	5	-5.8	-7.8
-10	6	5	-2.0	-1.2
-8	6	5	3.4	3.0
-6	6	5	-4.0	-4.8
-4	6	5	3.0	1.4
-2	6	5	-3.4	-3.2
0	6	5	3.0	2.8
2	6	5	-3.8	-1.6
4	6	5	3.4	1.4
6	6	5	-2.4	-2.0
-9	7	5	-2.8	-1.6
-7	7	5	7.4	8.2
-5	7	5	5.0	5.8
-3	7	5	-4.6	-3.6
-1	7	5	-4.6	-4.8
1	7	5	4.8	6.4
3	7	5	8.0	8.8
5	7	5	-3.4	-0.4
-8	8	5	3.2	0.8
-6	8	5	10.6	11.2
-4	8	5	3.4	2.2
-2	8	5	3.2	0.6
0	8	5	3.6	2.2
2	8	5	11.6	10.2
4	8	5	3.2	3.4
-9	9	5	2.0	1.6
-7	9	5	3.8	3.8
-5	9	5	7.4	7.4
-3	9	5	4.2	3.4
-1	9	5	3.4	3.0
1	9	5	8.4	9.2
3	9	5	3.8	2.2
5	9	5	1.8	2.6
-8	10	5	1.8	0.0
-6	10	5	9.8	9.4
-4	10	5	4.0	3.2
-2	10	5	3.0	1.0
0	10	5	3.2	3.2
2	10	5	9.4	8.6
-7	11	5	1.6	1.2
-5	11	5	4.4	4.2
-3	11	5	3.0	0.4
-1	11	5	2.6	3.0
1	11	5	5.2	3.2
3	11	5	1.6	0.8
-6	12	5	-1.6	-2.2
-4	12	5	2.4	2.8
-2	12	5	-3.4	-2.8
0	12	5	2.8	3.4
2	12	5	-1.4	-1.0
-3	13	5	-2.0	-3.0
-1	13	5	-1.6	-1.0
-10	0	6	9.2	10.8
2	0	6	27.6	29.2
0	0	6	1.4	1.4
2	0	6	1.4	1.4
-9	1	6	4.6	3.0
-7	1	6	-3.2	-0.2
-5	1	6	-2.8	-2.6
-3	1	6	23.2	26.0
1	1	6	2.6	3.8
3	1	6	3.2	1.0
5	1	6	4.6	6.2
-10	2	6	3.6	5.0
-8	2	6	-3.0	-2.2
-6	2	6	-3.2	0.6
-4	2	6	2.8	2.6
-2	2	6	10.6	11.4
0	2	6	-3.4	-3.2
2	2	6	2.6	0.6
4	2	6	4.6	5.0
-9	3	6	3.8	4.4
-7	3	6	-2.6	-1.6
-5	3	6	-3.4	-3.6
-3	3	6	-3.4	-1.6
-1	3	6	3.4	2.2
1	3	6	-2.8	-1.4
3	3	6	3.0	0.2
5	3	6	2.0	0.4
-10	4	6	-1.8	-2.6
-8	4	6	3.2	0.8
-6	4	6	-3.2	-2.2
-4	4	6	3.4	1.2
-2	4	6	-8.2	-9.2
0	4	6	-2.8	-2.4
2	4	6	-3.2	-2.8
4	4	6	2.4	1.6
-9	5	6	-2.6	-1.0
-7	5	6	-2.8	-2.0
-5	5	6	3.2	1.8
-3	5	6	-8.2	-9.0
1	5	6	-3.8	-3.6
3	5	6	-2.6	-1.0
5	5	6	-1.8	-2.2
-8	6	6	3.2	0.6
-6	6	6	4.2	0.2
-4	6	6	-5.2	-4.0
-2	6	6	-6.0	-6.4
0	6	6	5.4	4.8
2	6	6	-3.6	-4.4
4	6	6	-2.6	-3.4
-9	7	6	-3.0	-3.2
-7	7	6	4.0	2.0
-5	7	6	4.6	1.2
-3	7	6	-4.8	-1.2
-1	7	6	-4.8	-4.6
1	7	6	4.4	3.8
3	7	6	-3.0	-3.8
-8	8	6	-2.4	-3.8
-6	8	6	7.6	7.0
-4	8	6	-3.8	-5.4
-2	8	6	-3.8	-0.6
0	8	6	3.6	2.4
2	8	6	3.4	0.4
-7	9	6	3.0	4.2
-5	9	6	-5.4	-2.8
-3	9	6	-4.2	-1.2
-1	9	6	-4.0	-4.0
1	9	6	8.8	8.0
3	9	6	-2.0	-3.2
-9	1	7	2.2	0.6
-7	1	7	-2.8	-3.8
-1	1	7	-3.2	-1.4
1	1	7	-4.8	-4.2
3	1	7	2.8	0.4
-8	2	7	-2.0	-2.2
-6	2	7	-4.8	-4.4
-4	2	7	3.2	1.4
-2	2	7	2.6	2.0
0	2	7	-4.2	-5.0
2	2	7	-2.4	-3.0
-9	3	7	2.0	0.4
-7	3	7	-5.0	-5.8
-5	3	7	3.2	0.8
-3	3	7	-3.2	-3.0
-1	3	7	3.2	1.8
1	3	7	-2.8	-5.0
-8	4	7	-2.2	-0.2
-6	4	7	-5.2	-6.8
-4	4	7	3.6	1.4
-2	4	7	3.6	2.8
0	4	7	-5.4	-6.4
2	4	7	-2.2	-0.8
-7	5	7	-4.0	-4.8
-5	5	7	2.8	1.4
-3	5	7	-3.4	-4.2
-1	5	7	4.0	2.2
1	5	7	-3.0	-3.4
3	5	7	2.0	0.0
-8	6	7	2.4	4.0
-6	6	7	-2.8	-0.6
-4	6	7	-3.4	-2.0
-2	6	7	-4.0	-2.0
0	6	7	3.0	0.4
-7	7	7	2.8	3.2
-5	7	7	3.2	1.6
-3	7	7	-3.4	-1.6
-1	7	7	3.2	0.6
1	7	7	2.6	3.4
-6	8	7	5.4	5.0
-4	8	7	2.8	0.4
-2	8	7	-2.8	-0.6
0	8	7	4.0	5.0
-4	0	8	11.6	13.2
-2	0	8	1.0	2.8
0	0	8	0.8	2.6
-3	1	8	11.2	12.8
-1	1	8	1.8	0.0
1	1	8	2.4	0.8
-8	2	8	-1.2	-0.8
-6	2	8	-2.2	-1.4
-4	2	8	5.6	5.6
-2	2	8	2.0	1.4
0	2	8	2.0	0.4
-7	3	8	-2.0	-0.6
-5	3	8	2.2	0.4
-3	3	8	-2.4	-0.6
-1	3	8	-2.2	-1.6
1	3	8	-1.4	-0.2
-6	4	8	-2.0	-0.4
-4	4	8	-2.2	-3.2
-2	4	8	-2.2	-1.2
0	4	8	-1.6	-2.0
-5	5	8	-2.2	-0.4
-3	5	8	-4.8	-5.0
-1	5	8	2.0	0.2
-4	5	8	-2.6	-2.4
-2	5	8	-4.0	-2.4

curves taken from the International Tables[5] were used throughout.

Discussion of the Structure

The structure of naphthalene and TCNB complex is composed of columns in which the component molecules are alternately stacked along the *c* axis plane to plane. The naphthalene and TCNB molecules are planar and their mean planes are:

$$-0.322x-0.031y+0.999z=3.431$$

and $-0.307x+1.000z=0$

respectively, where *x*, *y*, *z* are coordinates in Å with respect to the crystal axes *a*, *b* and *c*. The maximum deviation of atoms from the planes is 0.012 Å for both carbon and nitrogen atoms. The molecular planes are very nearly perpendicular to the *c* axis. The molecules overlap each other with an average interplanar spacing of 3.43 Å, as shown in Fig. 3. This value may be compared with those obtained for other TCNB complexes.[1,2] The planes of the component molecules make an angle of 1.1° with each other. The orientation of naphthalene is disordered. The napthalene molecules adopt two alternative orientations with equal probability, as illustrated in Fig. 2. The relative orientations of the molecules are shown in Fig. 4. The molecular centers are approximately superimposed but the aromatic rings are different in orientation by about 18°. Such an arrangement might imply π-π interaction and this was indeed verified by the spectroscopic observation.[3] This is an interesting contrast to the structure of the tetracyanobenzene-tetramethyl-*p*-phenylenediamine complex, where the molecular centers are shifted sideways and n-π interaction is expected. Interatomic distances between the molecules arranged on $(10\bar{2})$ are shown in Fig. 4. The positions of hydrogen atoms which were deduced by assuming the C-H bond length of 1.1 Å are also indicated. The atomic separations of H(4′)⋯N(4) and H(3)⋯N(4) are 2.76 and 2.73 Å, being close to the normal van der Waals separation. It is to be noted here that H(3)⋯N(4) decreases to an abnormally short distance of 2.36 Å if Structure I is assumed. Theoretical estimation of the charge-transfer energies based on the molecular arrangements corresponding to Structures I and II revealed that Structure I is more stable by 0.2 kcal/mol

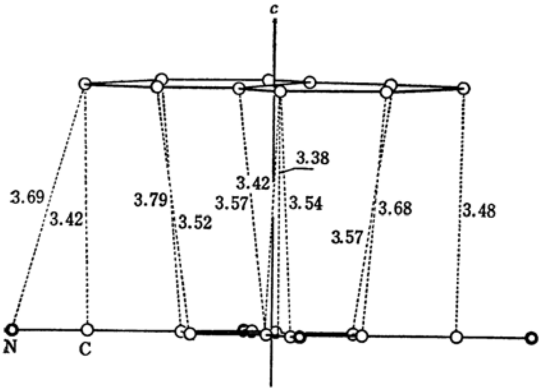

Fig. 3. Intermolecular contacts between TCNB and naphthalene.

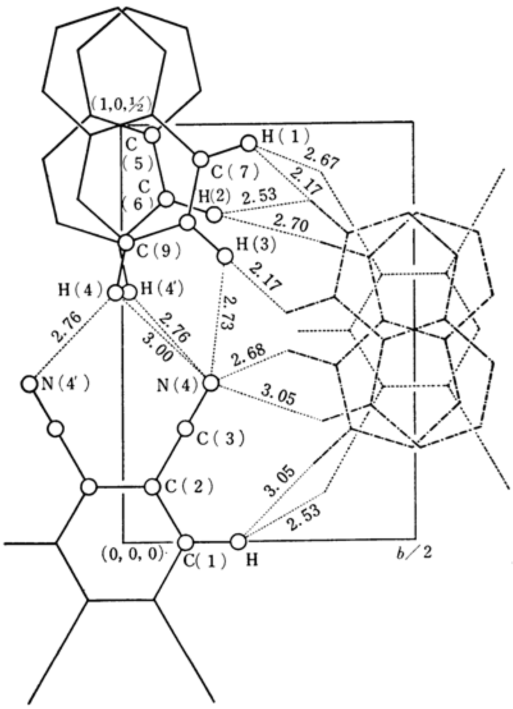

Fig. 4. Interatomic distances between the molecules arranged on $(10\bar{2})$. The centers of molecules drawn by dotted and chain lines are placed on the positions (1/2,1/2,0) and (1/2, 1/2,1/2) respectively.

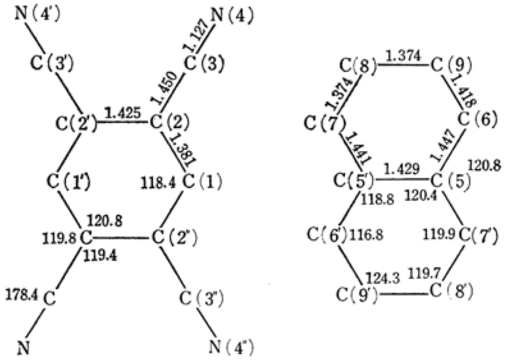

Fig. 5. Bond lengths and angles in the component molecules.

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[5] "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

TABLE 4. BOND LENGTHS AND ANGLES

Bond	Length (Å)	σ(Å × 1000)
TCNB		
C(1) C(2)	1.381	6
C(2) C(3)	1.450	7
C(2) C(2′)	1.425	7
C(3) N(4)	1.127	7
Naphthalene		
C(5) C(6)	1.447	17
C(6) C(9)	1.418	29
C(7) C(8)	1.374	18
C(8) C(9)	1.374	37
C(5) C(5′)	1.429	9
C(7) C(5′)	1.441	15

Atoms	Angle	σ
TCNB		
C(1)-C(2)-C(3)	119.8°	0.4°
C(2′)-C(2)-C(3)	119.4	0.4
C(1)-C(2)-C(2′)	120.8	0.4
C(2)-C(3)-N(4)	178.4	0.5
C(2)-C(1)-C(2″)	118.4	0.6
Naphthalene		
C(5′)-C(5)-C(6)	118.8	0.8
C(5)-C(6)-C(9)	116.8	1.4
C(6)-C(9)-C(8)	124.3	1.2
C(7)-C(8)-C(9)	119.7	1.8
C(5′)-C(7)-C(8)	119.9	1.1
C(6)-C(5)-C(7′)	120.8	0.8
C(7)-C(5′)-C(5)	120.4	1.0

than Structure II.3) Accordingly the repulsion between hydrogen and nitrogen atoms may be more important and seems to have the determining influence on the molecular orientation. Bond lengths and angles in the component molecules are shown in Table 3 and in Fig. 5. The C(2)-C(2′) distance of 1.425 Å found in TCNB molecule is significantly different from a value, 1.39 Å usually found in benzene. This distance varies from complex to complex as shown below:

Donor		Ionization potential
Naphthalene	1.425Å	8.12 eV
Hexamethylbenzene	1.414Å	7.85 eV
N, *N*, *N′*, *N′*-tetramethyl-*p*-phenylenediamine	1.390Å	6.75 eV

It is interesting that this distance decreases in the order of decreasing ionization potential of the donor molecules.

The bond lengths in the aromatic system found in the TCNB molecule are compared with the results of theoretical calculations6,7) as follows:

Bond length	Observed	Calculated
C(2)-C(2′)	1.425±0.007Å	1.43Å
C(1)-C(2)	1.381±0.006Å	1.40Å

The agreement between the calculated bond lengths and those found in naphthalene complex is fairly good.

Iwata, Tanaka and Nagakura3) measured the visible and near ultraviolet absorption spectra of the single crystal at room temperature. The spectra have two peaks polarized parallel to the *c* axis at 25000 cm^{-1} and at 33000—29000 cm^{-1} and one peak at 33000—29000 cm^{-1} polarized perpendicular to it. Comparing them with the solution spectra of the component molecules and the complex, these authors concluded that those polarized parallel to the *c* axis are the charge transfer bands. The large value of the absorption intensity ratio $(A_{\parallel}/A_{\perp}>25)$ of the first band at 25000 cm^{-1}, combined with the result of the crystal structure analysis, strongly suggests that the direction of the transition moment of this band is nearly perpendicular to the planes of the component molecules. The local symmetry of the relative arrangement of the donor and acceptor molecules in crystals, C_2, is consistent with the observation that there exist two peaks polarized along the *c* axis. If the local symmetry were C_{2v} corresponding to Structure I, only one peak polarized parallel to the *c* axis could be expected in the region 25000—33000 cm^{-1}.

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

The authors wish to express their appreciation to Professor Saburo Nagakura and Dr. Suehiro Iwata of this Institute for their helpful discussion and for supplying them with the crystals of the complex. Part of the cost of this investigation has been defrayed by a Scientific Research Grant of the Ministry of Education, to which the authors' thanks are due.

Appendix

Description of the Twinning

The symmetry of oscillation and *hk*0 Weissenberg photographs showed an apparent orthorhombic symmetry. However, *h*0*l* reciprocal lattice deduced from the Weissenberg photograph, illustrated in Fig. 6, indicated that the crystals are reflection-twinned by pseudo-merohedry of Friedel's classification, (100) being the reflection plane. The obliquity is 17.2°. Friedel and Mallard8) empirically found that the

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6) C. A. Coulson, R. Daudel and J. M. Robertson, *Proc. Roy. Soc.*, **207**, 306 (1951).

7) S. Iwata, J. Tanaka and S. Nagakura, *J. Am. Chem. Soc.*, **88**, 894 (1966).

8) R. W. Cahn, *Advan. Phys.*, **3**, 363 (1954).

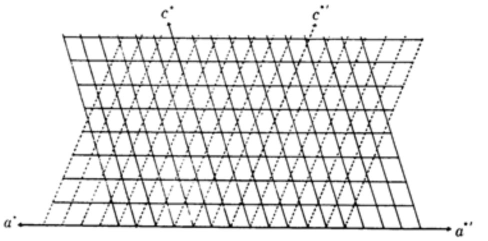

Fig. 6. Twinned zero-layer a^*c^* nets deduced from the Weissenberg photograph.

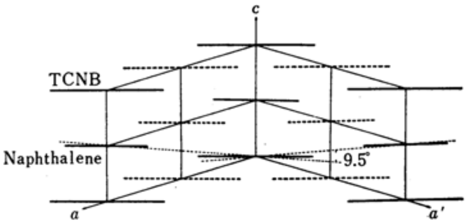

Fig. 7. The view along the *b* axis, showing the molecular orientation in the boundary region of the twinned individuals. The dashed lines indicate the molecules shifted (1/2)*b* along the *b* axis.

obliquity of this type of twinning is usually smaller than 5°. Thus, the obliquity in the present case is exceptionally large. In Fig. 7 is shown the molecular arrangement in the boundary region of the twinned individuals. The difference in molecular orientation in one individual and in the other is so small that the energy of adding more molecules in the one or the other orientation during crystal growth would be nearly equal.