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

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The crystal structure of the 1 : 1 complex formed between *N*, *N*, *N'*, *N'*-tetramethyl-*p*-phenylenediamine and 1, 2, 4, 5-tetracyanobenzene has been determined by X-rays at room temperature. The crystals are triclinic with one formula unit of the complex in a cell of dimensions: $a=7.654$ Å, $b=8.041$ Å, $c=7.462$ Å, $\alpha=96.7°$, $\beta=85.9°$ and $\gamma=101.3°$. The space group is $P\bar{1}$. The structure has been solved by three-dimensional Fourier and least-squares methods. The component molecules are stacked alternately in infinite columns along the *c*-axis. The structure does not seem to show the usual π-π interaction between the two aromatic rings, but indicates the n-π interaction localized between the nitrogen atoms of the donor and the cyano groups of the acceptor. From the direct integration of the electron density, the quantity of the charge transfer from the donor to the acceptor has been estimated to be 0.24 in electron units.

The complex between *N*, *N*, *N'*, *N'*-tetramethyl-*p*-phenylenediamine (TMPD) and 1, 2, 4, 5-tetracyanobenzene (TCNB) is one of the following

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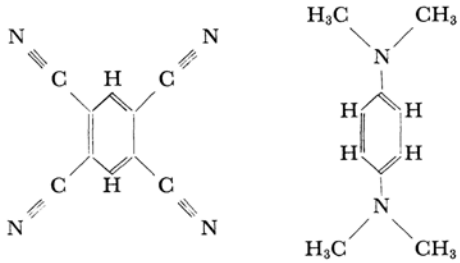
series of the TCNB complexes whose structures have been determined: TCNB-TMPD;[1] TCNB-naphthalene;[2] and TCNB-hexamethylbenzene.[3]



The dark color of this crystal suggests that there is a certain amount of charge transfer. Since this complex is one of the more highly colored and the ionization potential of the donor molecule is the lowest among the series investigated, it was felt that a detailed crystallographic examination would be of interest.

Experimental

Crystals were deposited as black needles with metallic lustre when the solutions of the components in benzene had been mixed. They are very stable in air. Equi-inclination Weissenberg photographs were taken around the c-axis (needle axis) up to the fourth layer and the a-axis up to the fifth layer with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). Multiple film technique was used. 1233 independent reflections were observed, corresponding to about two thirds of those within the copper sphere. The intensities were estimated visually with a standard film strip and were converted to $|F_o(hkl)|^2$ and $|F_o(hkl)|$ by applying the usual Lorentz, polarization and shape correction. No correction was made for either absorption or extinction, since the crystal used had a maximum dimension of 0.15 mm (c-axis) and 0.2 mm (a-axis). The crystal data are shown in Table 1.

Table 1. Crystal data

$C_6H_2(CN)_4\cdot C_6H_4N_2(CH_3)_4$
Triclinic
$a=7.654\pm0.012$ Å
$b=8.041\pm0.010$ Å
$c=7.462\pm0.013$ Å
$\alpha=96.7°\pm0.1°$
$\beta=85.9°\pm0.1°$
$\gamma=101.3°\pm0.1°$
$D_x=1.27$ g·cm^{-3}
$D_m=1.26$ g·cm^{-3}
$Z=1$
Space group $P\bar{1}$ or $P1$
Linear absorption coefficient for Cu$K\alpha$, $\mu=7.12$ cm^{-1}

Wilson's test indicated the presence of a center of symmetry; hence the space group $P\bar{1}$ was adopted and this was confirmed by refinement of the structure.

Structure Analysis

Each component molecule is required to occupy a center of symmetry, since a unit cell contains only

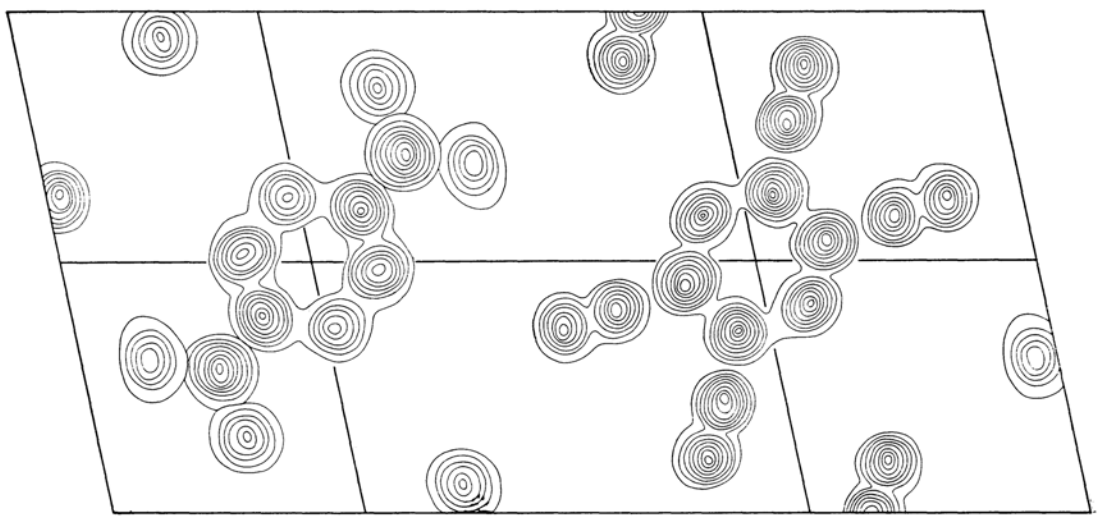


Fig. 1. Composite Fourier three-dimensional diagram of sections parallel to $(10\bar{2})$. Contours are at intervals of 1 e. Å^{-3}, the lowest contour being 1 e. Å^{-3}.

1) Y. Ohashi, H. Iwasaki and Y. Saito, Presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

2) S. Kumakura, F. F. Iwasaki and Y. Saito, Presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966; This Bulletin, **40**, 1826 (1967).

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

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 $\times10^4$	$\sigma(x)$ $\times10^4$	y $\times10^4$	$\sigma(y)$ $\times10^4$	z $\times10^4$	$\sigma(z)$ $\times10^4$	B_{11} $\times10^5$	B_{22} $\times10^5$	B_{33} $\times10^5$	B_{12} $\times10^5$	B_{13} $\times10^5$	B_{23} $\times10^5$
TMPD												
C(1)	1238	0013	1386	0011	0773	0011	1740	1295	0941	−0399	−0421	0355
C(2)	1577	0012	−0242	0011	0555	0012	1273	1685	1459	0629	−1513	0722
C(3)	0371	0013	−1607	0011	−0180	0012	1909	1219	1487	0794	−1078	0474
N(1)	2472	0011	2775	0010	1617	0011	2018	1401	1754	−0821	−1504	0277
C(4)	4310	0015	2477	0016	1846	0016	1712	2881	2602	−1325	−2653	0937
C(5)	2273	0016	4503	0012	1284	0016	2900	1165	2977	−1930	−1947	0519
H(1)	2375	0139	−0657	0132	0999	0140	3.55 (Å²)					
H(2)	0727	0139	−2794	0133	−0153	0140	3.55 (Å²)					
TCNB												
C(6)	0689	0011	1725	0009	5358	0010	1264	0827	1064	−0338	−0886	−0107
C(7)	1669	0010	0517	0010	5662	0010	0753	1241	0968	−0309	−0873	0458
C(8)	1006	0011	−1179	0009	5317	0011	1384	0957	1444	0586	−1248	0389
C(9)	1375	0012	3522	0010	5747	0012	1479	1020	1731	0487	−1673	0014
C(10)	3454	0012	1105	0010	6353	0012	1552	1181	1437	0199	−1308	−0039
N(2)	1913	0012	4911	0009	6101	0012	2191	0996	2813	−0397	−2596	−0314
N(3)	4815	0011	1585	0011	6893	0011	1611	2010	2158	−0235	−2489	−0241
H(3)	1706	0139	−2177	0121	5536	0143	3.55 (Å²)					

one formula unit of the complex. The intensities of reflections $10\bar{2}$ and $20\bar{4}$ are the strongest by far from the rest, which suggest that most of the atoms might be on the plane $(10\bar{2})$. The orientation of each molecule in the plane $(10\bar{2})$ was easily deduced from three-dimensional Patterson synthesis.

The structure thus obtained was refined by difference synthesis projected along the *a*- and *c*-axes, later by a block diagonal least-squares method with HBLS program written by Dr. T. Ashida. After four cycles of this refinement, anisotropic temperature factors were introduced. Hydrogen atoms attached to the benzene rings were found in the three-dimensional difference Fourier map at this stage. Those of the methyl groups, however, could not be identified, probably due to the rotation of the methyl groups. The final refinement including these hydrogen atoms was performed with HBLS, the temperature factors of hydrogen atoms being fixed. A weighting scheme,

$$w = 1 \quad \text{if} \quad F_o \geqq F_{\text{minimum}} \quad (= 1)$$

otherwise

$$w = 0$$

was employed.

The final discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$ became 0.159 for all the observed reflections. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[4] Figure 1 is a composite electron density

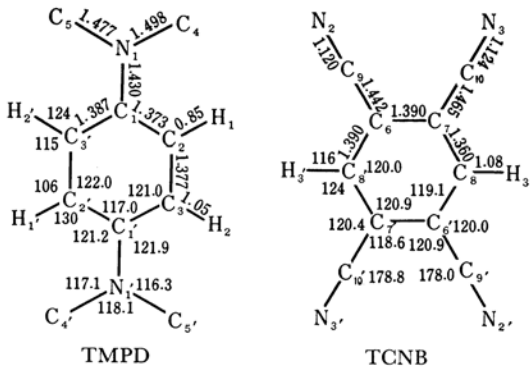


Fig. 2. Bond distances and angles.

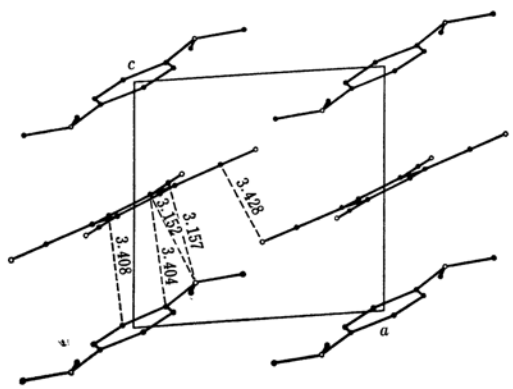


Fig. 3. Closest intermolecular contacts between TMPD and TCNB.

diagram from the sections of atomic peaks parallel to $(10\bar{2})$, on which most of the atoms are

4) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

approximately found to lie. Final atomic parameters and their standard deviations are summarized in Table 2. The observed and calculated structure factors are listed in Table 3.

Description of the Structure and Discussion The component molecules are stacked alternately in infinite columns along the *c*-axis. Both molecules lie approximately in the plane $(10\bar{2})$. Bond distances and angles in each molecule are listed in Table 4 and Fig. 2. As shown in Fig. 2, the distance C(1)–N(1) in TMPD (1.43 Å) is evidently longer than the corresponding distance found in

Table 3. Observed and calculated structure factors

H	Fo	Fc
K,L = 0, 0		
1	377	361
2	87	-77
3	382	-318
4	64	-59
5	39	-15
6	37	29
K,L = 1, 0		
0	269	328
1	303	-249
-1	482	456
2	287	218
-2	214	174
3	62	-40
-3	26	20
4	30	-29
-4	221	-185
5	104	-92
-5	59	-56
6	91	85
9	34	-35
K,L = 2, 0		
0	8	-14
1	181	154
-1	89	67
2	132	-94
-2	462	-385
3	198	-177
-3	63	-76
4	83	-66
-4	88	-65
5	104	91
-5	32	36
6	84	91
-6	96	82
7	43	-35
-7	50	43
-8	40	-34
9	21	-17
K,L = 3, 0		
0	305	-272
1	105	-86
2	198	-161
-2	139	-135
-3	76	-58
4	39	-32
-4	72	-69
5	130	113
-5	49	-48
-6	46	43
-7	114	107
K,L = 4, 0		
0	50	-48
1	53	-50
-1	66	-60
2	139	-111
-2	215	-172
3	26	-28
-3	102	-88
4	83	74
-4	80	74
5	142	144
-5	84	72
-7	47	34
8	43	-58
K,L = 5, 0		
0	92	-85
1	37	-35
-1	49	32
2	109	105
-2	66	56
3	81	78
-3	82	-59
4	58	53
5	61	-55
-5	72	57
6	39	-39
-6	55	54
-9	43	-39
K,L = 6, 0		
0	83	87
1	131	133
-1	16	26
2	25	14
-2	108	95
3	98	-102
4	27	-23
-4	19	16
6	36	33
K,L = 7, 0		
0	50	45
2	46	-46
-2	97	92
3	17	17
-3	59	42
4	47	34
-4	32	20
5	44	-43
-5	20	-11
-6	24	-34
K,L = 8, 0		
0	33	33
-2	10	-13
-3	17	-17
4	50	-45
-4	37	-30
-5	16	10
K,L = 9, 0		
0	28	-23
1	33	-39
2	17	-23
-3	17	5
-4	68	-52
-5	46	-32
K,L = 10, 0		
0	29	-26
-1	43	-40
-2	40	-39
-3	15	9
K,L = 0, 1		
0	64	-121
1	111	-69
-1	19	7
2	32	18
-2	64	-60
3	168	171
-3	17	-7
4	148	138
-4	76	71
5	31	-26
-5	84	104
6	16	-29
-6	27	-36
7	84	97
-8	27	33
K,L = 1, 1		
0	104	-56
1	116	101
-1	34	20
2	22	27
-2	112	128
3	9	-17
-3	140	-155
4	54	38
-4	136	-115
5	17	10
-5	27	-23
6	113	151
-6	34	38
7	55	73
-7	37	-41
-9	16	-22
K,L = -1, 1		
0	58	55
1	163	178
-1	47	98
2	236	-280
-2	51	34
3	156	-148
-3	29	36
4	19	-19
-4	28	24
5	102	124
-5	36	27
6	59	-73
7	20	20
-7	82	99
8	25	-34
-8	26	39
K,L = 2, 1		
0	71	70
1	12	11
-1	248	-288
2	123	-96
-2	151	162
3	65	-57
-3	74	66
4	25	24
-4	58	55
5	36	31
-5	104	-105
6	83	94
-6	47	-59
-7	72	-86
8	16	27
K,L = -2, 1		
0	197	-235
1	214	242
-1	103	86
2	100	128
-2	46	-22
3	40	23
-3	29	-29
4	171	-174
-4	11	-13
5	76	-85
-5	12	2
6	76	-104
-6	28	41
7	29	-37
-7	69	74
K,L = 3, 1		
0	184	219
1	71	-85
-1	124	-134
2	59	-42
-2	30	-43
3	38	-41
-3	30	-33
4	53	53
-4	46	-57
5	56	59
-5	18	-16
7	18	-54
-7	43	-58
-8	33	
K,L = -3, 1		
0	84	-87
1	86	-121
-1	154	166
2	80	73
-2	48	-53
3	30	25
-3	54	-37
4	81	86
-4	49	-40
5	24	-25
-5	24	-34
6	40	-56
7	97	-122
8	23	-29
K,L = 4, 1		
0	114	102
1	29	21
-1	17	30
2	47	44
-2	134	-119
3	64	-62
-3	53	49
4	137	-138
-4	9	-3
5	114	-124
-5	59	69
8	15	31
K,L = -4, 1		
0	91	89
1	208	-211
-1	74	65
2	73	75
-2	22	18
3	11	-4
-3	25	-15
4	81	80
-4	52	-60
-5	96	-96
6	17	21
-6	42	-62
7	20	-22
K,L = 5, 1		
0	15	-21
1	35	45
-1	70	100
2	10	9
-2	69	-68
3	22	-20
4	99	-104
-4	37	-26
5	19	-17
-5	49	44
6	17	19
-6	50	65
-7	25	26
K,L = -5, 1		
0	119	137
1	59	-65
-1	23	-38
2	56	-46
-2	23	19
3	26	-29
-3	19	-12
4	68	57
-4	32	-24
5	96	104
-5	96	-86
6	26	34
7	20	-18
9	19	28
K,L = 6, 1		
0	10	19
1	140	163
-1	50	-58
2	70	77
-2	118	-125
-3	22	-29
4	70	-61
-4	32	28
5	36	31
6	15	-17
-6	33	41
-7	31	36
K,L = -6, 1		
0	63	-76
1	66	-85
-1	12	16
2	45	-49
-2	119	139
3	39	43
-3	74	71
4	22	-14
-4	21	-24
5	51	67
-5	50	-48
6	53	70
K,L = 7, 1		
0	100	106
1	30	39
-1	50	62
2	16	14
-2	63	-64
-3	134	-140
4	22	16
-4	31	-35
5	32	27
K,L = -7, 1		
0	43	60
1	40	-57
-1	105	136
2	157	-177
-2	44	51
3	33	-41
-3	12	12
-4	38	-21
5	31	33
-5	38	23
6	22	38
K,L = 8, 1		
0	23	-25
-1	15	-19
2	52	57
-2	18	16
3	17	-15
-3	26	-27
4	17	7
-5	21	-13
K,L = -8, 1		
1	19	26
2	25	-33
3	21	-26
-3	29	40
4	29	-17
5	29	-23
K,L = 9, 1		
2	27	-27
-2	8	-8
-3	27	-26
-4	20	10
-5	32	33
K,L = -9, 1		
2	29	-34
-2	10	10
4	52	45
5	31	22
K,L = 10, 1		
-2	21	24
K,L = -10, 1		
0	10	-15
1	19	23
2	28	31
4	17	11
K,L = 0, 2		
0	274	326
1	126	-120
-1	970	1028
2	210	-208
-2	171	204
3	83	-80
-3	39	-28
4	17	-16
-4	209	-205
5	13	18
-5	49	-52
6	43	46
9	27	-44
K,L = 1, 2		
0	204	-216
1	299	281
-1	156	188
2	59	-58
-2	66	73
3	69	-72
-3	102	111
4	137	-145
-4	22	-12
5	130	141
-5	93	-83
6	35	37
-6	20	-26
-7	18	18
8	29	-41
9	10	-25
K,L = -1, 2		
0	553	636
1	121	135
-1	205	231
2	88	77
-2	99	-94
3	236	-250
-3	17	25
4	59	-75
-4	34	-28
5	26	-25
-5	22	-18
6	26	38
-6	20	-26
-7	24	29
9	18	-32
K,L = 2, 2		
0	24	33
1	66	-79
-1	40	47
2	280	-261
-2	80	-70
3	33	-30
-3	210	-203
4	66	79
-4	35	-34
5	130	138
6	68	-87
-7	62	62
K,L = -2, 2		
0	173	192
1	281	-301
-1	29	-39
2	114	-114
-2	128	130
3	78	-81
-3	71	-65
4	26	38
-4	53	-66
5	68	80
-5	51	-50
6	48	55
-6	62	65
7	44	-48
-7	28	39
-8	18	-3
9	10	-29
K,L = 3, 2		
0	91	-100
1	132	-135
-1	144	-160
-2	23	-17
3	24	-40
-3	126	-118
4	76	82
-4	24	-20
5	15	23
7	33	49
-7	24	39
8	36	-54
K,L = -3, 2		
0	5	4
1	8	-28
-1	194	-193
2	128	-125
-2	70	-60
3	131	-133
-3	100	-97
4	107	-109
-4	16	-7
5	30	46
6	132	156
7	25	35
K,L = 4, 2		
0	44	-45
1	89	-93
-1	46	-52
2	18	10
-2	7	5
3	38	47
-3	119	-108
4	150	176
-4	32	-38
5	24	-18
-5	38	42
-6	45	50
7	47	-75
-8	30	21
K,L = -4, 2		
0	120	-130
1	150	-144
-1	35	-31
2	92	-109
-2	55	-48
3	84	86
-3	83	-69
4	52	54
-4	32	-36
5	17	-10
-5	89	81
6	26	36
-6	76	85
-7	19	3
K,L = 5, 2		
0	18	25
1	104	131
-1	50	-68
2	69	82
-2	37	37
-3	22	25
4	36	-43
-4	22	-18
5	59	-59
6	25	33
-6	25	28
7	18	-29
K,L = -5, 2		
0	12	12
1	42	45
-1	53	-56
2	101	-99
-2	49	-60
-3	45	45
4	70	79
-4	55	57
5	72	82
-5	74	66
-6	38	-37
8	49	-58
K,L = 6, 2		
0	104	125
1	6	-2
-1	59	85
2	94	-119
-2	40	52
3	17	-14
-3	70	59
4	25	24
5	26	28
K,L = -6, 2		
0	8	5
1	87	99
-1	46	50
2	9	26
-2	88	91
3	11	11
-3	19	17
4	12	11
-4	52	-47
5	46	34
-5	32	-24
-6	16	-14
8	28	-32
K,L = 7, 2		
0	6	-21
1	22	-34
-1	19	21
2	11	17
-2	39	41
-3	68	67
4	52	-65
-4	13	13
5	38	-52
-5	28	12
-6	26	-12
K,L = -7, 2		
0	12	27
1	81	87
-1	40	50
2	74	75
3	25	22
-3	32	-41
5	30	-31
7	33	-16
K,L = 8, 2		
0	12	3
2	19	-33
-2	21	-17
3	37	-42
-4	28	-24
-5	19	-22
K,L = -8, 2		
0	13	2
1	17	-21
-1	33	35
2	8	5
-2	13	10
3	20	-24
4	22	15
5	18	-12
K,L = 9, 2		
0	30	-35
1	11	-22
-1	25	-25
2	22	13
-2	15	-16
K,L = -9, 2		
0	13	10
-1	12	-12
-2	29	-32
3	55	-58
-3	9	-17
4	50	-45
5	26	-19
K,L = -10, 2		
0	30	-36
-1	13	-30
4	17	-16
K,L = 0, 3		
0	50	-52
1	45	37
-1	164	-146
2	201	170
-2	31	32
3	113	89
-3	52	-27
4	20	14
5	27	-32
6	138	166
-6	50	47
-7	27	-25
9	27	-37
K,L = 1, 3		
0	98	89
1	24	-14
-1	120	-115
2	62	-59
3	26	17
-3	44	35
4	60	59
-4	49	-40
5	153	147
6	102	107
-6	17	-15
K,L = -1, 3		
0	66	66
1	194	-202
-1	53	49
2	96	-91
-2	112	101
3	23	17
-4	154	160
-4	17	14
5	74	-73
-5	30	25
-8	53	44
K,L = 2, 3		
0	49	40
1	124	-114
-1	11	5
2	86	-59
-2	157	-137
3	34	33
-3	61	53
4	15	9
-4	31	30
5	77	66
-5	38	37
-6	46	-37
7	19	34
-7	43	-41
-8	50	-49
K,L = -2, 3		
0	233	155
1	132	135
-1	34	-40
2	44	-45
-2	39	41
3	169	-151
-3	30	-17
4	112	-103
5	70	-78
-5	19	8

TABLE 3 (Continued)

H	Fo	Fc
6	54	-74
7	22	32
-7	40	31
8	27	-38
-8	47	40
9	20	27
K,L = 3, 3		
0	30	-45
1	24	-15
-1	125	121
2	6	-6
-2	94	-85
3	33	-28
4	112	-114
5	47	-43
-5	35	44
6	29	-29
-6	34	36
-8	30	-36
K,L = -3, 3		
0	110	-100
1	111	115
2	11	-10
-2	54	55
3	86	75
-3	18	-13
4	54	-49
-4	24	-12
5	49	-44
-5	24	-25
6	152	-182
-6	83	-23
7	36	-50
-7	23	13
9	31	46
K,L = 4, 3		
0	36	29
1	89	84
-1	85	92
2	50	-53
-2	28	-20
3	151	-141
-3	39	-29
4	162	-166
-4	32	19
5	13	-8
-6	34	42
7	24	38
-7	12	24
K,L = -4, 3		
0	173	-164
1	48	48
-1	80	73
2	36	21
-2	31	30
3	42	41
-3	13	12
4	12	-15
-4	43	-31
5	17	22
-5	58	-50
-6	48	-49
K,L = 5, 3		
0	45	43
1	36	30
-1	11	13
2	11	-16
-2	24	26
3	71	-77
-3	48	-44
4	24	-21
-4	19	21
5	34	30
6	22	-20
-6	34	26
-7	42	32
K,L = -5, 3		
0	32	-33
1	116	-102
-1	93	95
2	6	-4
-2	54	48
3	10	-8
-3	117	118
4	29	-20
-4	16	22
5	38	-26
-5	47	-47
8	33	49
K,L = 6, 3		
0	124	122
1	57	66
2	22	32
-2	40	-38
3	58	-51
-3	123	-110
4	22	24
-4	24	-21
5	17	-17
6	7	13
K,L = -6, 3		
0	21	-30
1	62	-69
-1	54	-65
2	19	25
-2	9	12
3	20	-21
-3	76	82
4	71	83
-4	63	46
5	96	98
-5	35	-29
6	29	36
-6	24	-28
7	19	-26
K,L = 7, 3		
0	19	23
1	8	12
-1	61	51
2	9	20
-2	38	40
-3	59	-55
4	49	38
-4	83	-78
-5	18	-25
K,L = -7, 3		
0	42	-42
1	131	-152
-1	31	42
2	47	-51
-2	139	115
3	12	12
-3	61	51
4	37	37
5	49	62
-5	35	-24
6	22	32
7	18	-18
K,L = 8, 3		
1	37	47
-1	31	-31
2	18	-15
K,L = -8, 3		
0	20	24
1	16	-26
-1	24	21
2	50	-47
-2	16	18
3	17	-16
-3	20	22
4	30	-26
7	22	-24
K,L = -9, 3		
1	23	-30
-1	7	12
2	17	-21
3	50	44
4	24	25
5	17	-12
K,L = -10, 3		
0	17	21
1	10	29
2	10	-12
K,L = 0, 4		
0	68	-78
1	60	-35
-1	178	175
2	119	-91
-2	380	337
3	30	-18
-3	103	91
4	19	-11
5	115	101
-5	94	-97
-6	39	-39
8	54	-56
K,L = 1, 4		
0	105	122
1	80	-48
-1	52	-67
2	140	-103
-2	51	57
3	125	-106
-3	18	-23
4	142	132
-4	31	42
5	82	65
6	49	-36
-6	27	-31
8	36	-40
K,L = -1, 4		
0	73	71
1	63	65
-1	424	372
2	189	-160
-2	128	108
3	101	-75
-3	18	-8
4	54	-45
-4	44	-35
5	75	71
-5	33	-31
8	49	-41
K,L = 2, 4		
0	57	-52
1	212	-185
-1	21	-29
-2	23	39
3	43	34
-3	64	-73
4	128	123
-4	65	-82
5	126	-108
-8	24	35
K,L = -2, 4		
0	73	-73
1	106	-96
-1	153	143
2	43	-37
-2	8	-6
3	11	11
-3	57	47
4	64	51
-4	47	-38
5	60	46
-5	18	-27
6	45	-30
-6	21	-20
-7	29	31
K,L = 3, 4		
0	83	-62
-1	63	-82
-2	26	-49
3	16	21
-3	16	-25
4	60	59
-4	24	-63
6	81	78
7	97	-83
K,L = -3, 4		
0	48	53
1	138	-126
2	168	-132
-2	83	-76
3	146	-121
-3	48	-44
4	32	44
-4	40	-44
5	170	155
-5	12	-14
6	76	56
-7	50	47
9	31	-38
K,L = 4, 4		
0	32	-28
1	36	33
-1	66	-36
2	26	30
-2	50	-31
3	162	144
5	21	-13
K,L = -4, 4		
0	69	-64
1	65	-65
-1	117	-114
2	47	41
-2	38	-31
-3	44	-38
4	45	-33
-4	35	-33
5	17	28
-5	28	-16
6	77	56
-6	70	61
7	50	-27
-7	37	42
K,L = 5, 4		
0	123	105
1	59	57
-1	62	50
2	17	-26
-2	43	-23
3	9	-13
4	68	-57
5	51	41
K,L = -5, 4		
0	6	2
1	79	-83
-2	26	-30
3	84	74
-3	40	-42
4	82	76
-5	49	40
6	47	33
-6	49	48
7	86	-60
8	43	-33
K,L = 6, 4		
1	82	-86
-1	128	78
-2	81	57
3	35	40
-3	92	54
-4	36	27
K,L = -6, 4		
0	68	67
1	12	29
-2	17	14
3	21	25
-3	50	39
4	68	49
8	40	-35
K,L = 7, 4		
0	19	-21
1	8	7
2	22	22
3	69	-64
-4	53	36
K,L = -7, 4		
0	60	59
1	71	82
-1	10	21
2	13	20
-2	38	33
4	13	-13
-4	26	-22
K,L = 8, 4		
1	27	-38
2	26	-29
K,L = -8, 4		
0	21	-15
1	22	23
-2	31	25
3	17	12
-3	12	5
5	18	-18
K,L = -9, 4		
0	12	-9
-1	16	22
2	35	-42
3	51	-47
4	27	-20
5	11	-12
K,L = 0, 5		
0	31	30
1	55	75
-1	33	-43
2	27	31
3	38	39
5	158	169
K,L = 1, 5		
0	20	-22
1	45	-57
-1	35	40
3	111	75
4	85	89
5	98	108
K,L = -1, 5		
0	66	-75
1	29	-35
-1	11	-14
2	42	35
-2	28	24
3	106	108
-3	53	53
4	23	-24
K,L = 2, 5		
0	62	-74
1	21	-24
-1	28	29
2	17	26
4	12	5
5	21	29
K,L = -2, 5		
0	81	77
1	33	-47
-1	51	63
2	71	-73
-2	31	33
3	97	-82
-3	22	24
4	38	-34
-4	16	18
5	83	-88
K,L = 3, 5		
0	6	10
1	23	27
2	26	-29
3	118	-126
4	66	-68
5	28	-27
K,L = -3, 5		
0	74	82
-1	22	-31
2	29	31
-2	22	19
3	46	-40
-3	7	11
4	60	-41
5	178	-184
K,L = 4, 5		
0	60	70
1	18	-30
2	85	-105
3	134	-149
4	7	-5
5	15	9
6	60	31
K,L = -4, 5		
0	11	13
1	31	39
-1	59	-75
-2	33	35
-3	13	14
-5	40	-22
K,L = 5, 5		
0	33	33
2	19	-32
3	31	-27
4	39	29
5	38	-32
K,L = -5, 5		
0	91	-96
1	12	14
2	32	31
-2	49	43
3	87	84
-4	32	-14
-5	37	-18
K,L = 6, 5		
0	39	47
1	23	37
2	25	-28
K,L = -6, 5		
0	54	-66
1	7	-10
-2	43	-37
3	63	72
4	94	100
-4	58	35
5	38	41
-5	30	19
K,L = 7, 5		
1	15	22
2	16	-15
K,L = -7, 5		
0	85	-94
1	49	-59
-1	26	-27
2	11	12
-2	25	25
3	26	32
-3	86	69
4	89	75
5	58	48
K,L = -8, 5		
0	9	-16
1	38	-51
-1	12	15
2	17	-16
-2	35	29
3	17	-17
5	26	20
K,L = -9, 5		
0	13	-19
2	31	28
3	20	22
4	24	-13
K,L = 0, 6		
0	9	3
1	61	-75
-1	19	-27
2	29	-29
4	92	110
K,L = 1, 6		
0	23	-33
1	60	-84
-1	16	18
2	30	-42
3	65	74
4	59	66
5	66	-61
K,L = -1, 6		
0	17	28
1	37	-64
-1	37	54
2	54	-67
3	26	-34
4	64	73
5	36	43
K,L = 2, 6		
0	59	-84
1	5	6
-1	25	-41
3	47	63
4	63	-71
K,L = -2, 6		
0	43	-55
-1	17	24
-2	74	82
3	13	20
4	35	29
5	7	12
K,L = 3, 6		
3	57	72
5	61	66
K,L = -3, 6		
0	69	-79
1	60	-94
-1	37	58
2	56	-81
3	23	27
-3	30	-25
4	94	106
-4	43	-29
5	55	63
K,L = 4, 6		
0	25	32
1	12	24
2	57	82
3	28	27
4	42	-32
5	33	-34
K,L = -4, 6		
0	9	-20
1	5	-9
-1	10	-17
2	25	-29
-2	59	-65
3	37	-40
-3	35	-29
-4	35	-25
5	74	65
-5	16	-16
K,L = 5, 6		
0	22	27
1	16	-25
3	28	-33
4	27	22
K,L = -5, 6		
0	33	-42
-1	16	-19
2	32	45
-2	18	-18
3	32	41
-3	19	-19
-4	31	-22
5	24	33
K,L = 6, 6		
0	35	-45
2	25	31
3	10	-19
K,L = -6, 6		
0	12	21
1	7	-13
-1	30	31
2	24	24
3	38	43
K,L = -7, 6		
0	55	60
1	9	17
-1	29	32
2	10	14
5	18	-21
K,L = -8, 6		
0	21	25
1	7	10
-1	6	-5
K,L = 0, 7		
0	10	16
-1	10	14
2	25	38
3	20	27
4	114	109
5	57	47
K,L = 1, 7		
0	37	-38
2	35	54
3	39	34
4	69	71
K,L = -1, 7		
0	8	-14
1	11	21
-1	17	-26
2	39	52
3	13	18
4	8	11
5	76	63
K,L = 2, 7		
1	10	20
-1	20	-30
2	16	-12
3	32	-34
4	19	24
K,L = -2, 7		
0	13	-21
1	17	-29
-1	20	32
2	36	-46
3	11	-13
4	64	-62
5	52	49
K,L = 3, 7		
0	29	32
1	16	-22
2	92	-95
3	83	-74
4	19	-18
5	11	-16
K,L = -3, 7		
0	9	13
-1	35	43
2	12	-21
3	45	-41
4	138	-131
5	92	-79
K,L = 4, 7		
1	46	-60
2	88	-96
3	18	-13
K,L = -4, 7		
0	30	35
1	8	-14
-2	25	-20
5	96	-81
K,L = 5, 7		
2	23	-25
K,L = -5, 7		
0	15	12
1	12	21
-1	56	-58
2	34	37
K,L = -6, 7		
0	22	-27
-1	40	-47
2	43	47
3	59	74
4	42	32
5	12	-11
K,L = -7, 7		
0	49	-53
-1	36	-48
2	21	25
3	59	66
4	54	50
K,L = 0, 8		
0	29	-47
1	21	-31
3	66	76
5	11	-6
K,L = 1, 8		
0	34	-47
-1	15	-23
2	22	27
3	39	41
4	66	-54
K,L = -1, 8		
0	11	-22
1	35	-51
3	47	53
4	57	54
K,L = 2, 8		
2	10	18
3	25	-22
4	12	-2
K,L = -2, 8		
1	5	-16
-1	17	-20
3	21	21
4	45	40
K,L = 3, 8		
2	46	54
3	7	13
K,L = -3, 8		
0	43	-56
1	21	-42
-1	27	-31
3	52	55
4	58	55
K,L = 4, 8		
1	24	36
K,L = -4, 8		
0	17	-25
1	23	-33
2	27	-33
4	53	48
K,L = -5, 8		
1	8	14
-1	9	-12
4	15	21
K,L = -6, 8		
1	7	13
2	19	26
K,L = 0, 9		
1	16	27
2	20	29
3	38	48
K,L = 1, 9		
1	17	28
K,L = -1, 9		
1	13	22
2	23	28
3	9	14
K,L = 2, 9		
0	8	15
1	6	-10
K,L = -2, 9		
1	12	-19
3	20	-25
K,L = -3, 9		
2	25	-30

Table 4. Bond distances and angles and their standard deviations

TMPD			
C(1)-C(2)	1.373±0.13 Å	C(2)-C(1)-C(3′)	117.0°±0.8°
C(2)-C(3)	1.377±0.012	C(1)-C(2)-C(3)	122.0±0.9
C(1)-C(3′)	1.387±0.015	C(2)-C(3)-C(1′)	121.0±0.9
C(1)-N(1)	1.430±0.011	C(2)-C(1)-N(1)	121.2±0.9
N(1)-C(4)	1.498±0.015	C(3′)-C(1)-N(1)	121.9±0.8
N(1)-C(5)	1.477±0.013	C(1)-N(1)-C(4)	117.1±0.8
C(2)-H(1)	0.85 ±0.11	C(1)-N(1)-C(5)	116.3±0.8
C(3)-H(2)	1.05 ±0.11	C(4)-N(1)-C(5)	118.1±0.8
		C(1)-C(2)-H(1)	130 ±8
		C(3)-C(2)-H(1)	106 ±8
		C(2)-C(3)-H(2)	115 ±6
		C(1′)-C(3)-H(2)	124 ±6
TCNB			
C(6)-C(7)	1.390±0.012 Å	C(6)-C(7)-C(8)	120.9°±0.7°
C(7)-C(8)	1.360±0.010	C(7)-C(6)-C(8′)	119.1±0.7
C(6)-C(8′)	1.390±0.012	C(7)-C(8)-C(6′)	120.0±0.8
C(6)-C(9)	1.442±0.010	C(9)-C(6)-C(7)	120.9±0.7
C(7)-C(10)	1.465±0.012	C(9)-C(6)-C(8′)	120.0±0.8
C(9)-N(2)	1.120±0.010	C(10)-C(7)-C(6)	118.6±0.7
C(10)-N(3)	1.124±0.012	C(10)-C(7)-C(8)	120.4±0.8
		C(6)-C(9)-N(2)	178.0±0.8
		C(7)-C(10)-N(3)	178.8±1.0
		C(7)-C(8)-H(3)	124 ±6
		C(6′)-C(8)-H(3)	116 ±6

Table 5. Closest intermolecular contacts between TMPD and TCNB

N(1)-C(6)	3.152±0.012 Å
N(1)-C(9)	3.157±0.013
C(1)-C(6)	3.404±0.013
C(3′)-C(8′)	3.408±0.014
C(10)-C(10′)	3.428±0.013
H(3)-C(10′)	3.10 ±0.10
H(1)-C(10′)	3.10 ±0.10

TMPD-TCNQ*2 complex[5] (1.36 Å), and is closer to a single-bond separation. The distance C(7)–C(8) in TCNB is shorter by 0.03 Å than the distances C(6)–C(7) and C(6)–C(8′). C(6)–C(9) is shorter by 0.025 Å than C(7)–C(10).

Intermolecular atomic distances less than 3.5 Å are indicated in Fig. 3 and Table 5. These distances are of the same order as generally accepted van der Waals distances except for the short ones between N(1) and C(9), and between N(1) and C(6). They seem to indicate the existence of some specific interactions between these atoms.

The TCNB molecule is planar within the experimental errors and the mean plane is expressed by

$$-0.3313x - 0.0623y + 0.9171z = 3.4215,$$

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

The TMPD molecule as a whole is not planar. But, apart from the carbon atoms of the methyl groups, the rest of the atoms are coplanar, the mean plane of the atoms in TMPD being expressed by

$$-0.3492x - 0.1816y + 0.8962z = 0.$$

The carbon atoms of the methyl groups are bent and twisted from this plane, as shown in Fig. 4. Thus it seems likely that the electronic orbital of the nitrogen atom, N(1), exhibits tetrahedral character and the lone pair electrons of

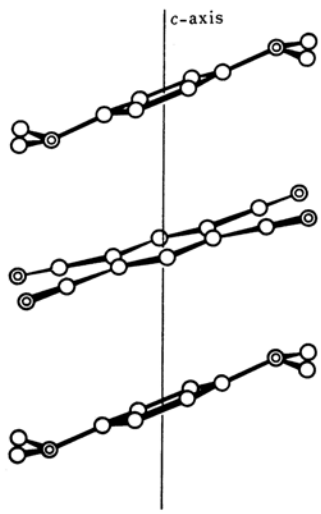


Fig. 4. The structure, viewed along [1$\bar{1}$0].

*2 TCNQ: 7, 7, 8, 8-Tetracyanoquinodimethane.

5) A. W. Hanson, *Acta Cryst.*, **19**, 610 (1965).

Fig. 5. Overlapping molecules, viewed approximately normal to their mean plane.

the nitrogen atom do not seem to be perfectly delocalized with π-electrons of the benzene ring.

The molecules overlap each other as shown in Fig. 5, with an interplanar spacing of 3.40 Å, though the molecular plane of TCNB makes an angle of 7° with that of TMPD except the methyl groups.

Two rings of TCNB and TMPD overlap to a small extent in spite of Mulliken's prediction that the extent of overlap of benzene rings should be large.[6]

As seen in Fig. 5, the component molecules are tightly packed, namely, the methyl groups of TMPD lie between the two cyano groups of TCNB, thus the TCNB molecule being fixed by the methyl groups.

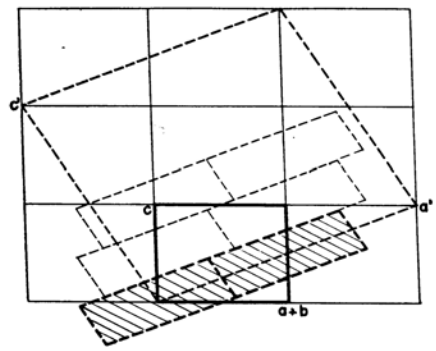
On the other hand, the carbon atoms of the TCNB molecule lie between the two methyl groups attached to the nitrogen atom at 3.502 and 3.620 Å from them.

These facts indicate that the relative orientation of the two component molecule is mainly determined by the packing of the molecules, especially by those of the methyl groups. The methyl groups hinder the approach and overlap of the benzene rings of the two component molecules, thus preventing the charge transfer between π-electrons of the benzene rings of the two components to some extent.

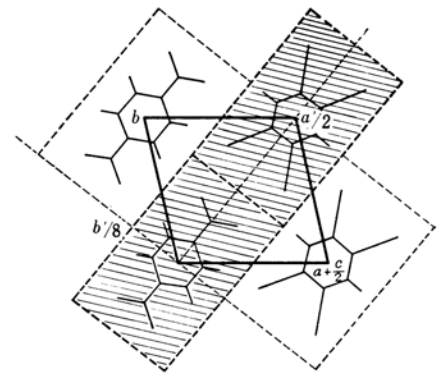
Nitrogen atoms of TMPD come near the cyano groups of TCNB in this orientation. The short distances between N(1)–C(9) and N(1)–C(6), strongly suggest that the lone pair electrons that are partially located on these nitrogen atoms are transferred to the cyano groups. This local charge transfer is further supported by the conclusion drawn from molecular orbital calculation that the carbon atoms of the cyano groups in a free molecule of TCNB is deficient in electron density.[7] The charge transfer force seems to make the bond distance C(6)–C(9) shorter than C(7)–C(10) and make C(7)–C(8) shorter than C(6)–C(7) and C(6)–C(8′), thus the benzene ring of TCNB assuming quinoide structure. On the other hand in TMPD molecule, the bond distance C(1)–N(1) appears to be elongated by this interaction. In TMPD-TCNQ complex,[5] however, the methyl groups do not affect the relative orientation, because of the geometry of TCNQ molecule. Since the electron affinity of TCNQ is much larger than that of TCNB, the π–π interaction is much stronger than that in this complex. Consequently no local specific interaction occurs and the charge transfer force should result in small molecular separation.

The Quantity of the Charge Transfer

A most interesting point to be pursued will be the problem of the quantity of the charge transfer which may take place between the donor molecule



6(a)



6(b)

Fig. 6(a) and 6(b). The relation between crystallographic axes a', $b,'$ c' and a, b, c. The range of integration is shown by the shaded area, (a) viewed along $[1\bar{1}0]$, (b) viewed along $[10\bar{2}]$.

6) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); *ibid.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

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

and the acceptor molecule. In the case of quinhydrone,[8] this quantity was estimated to be 0.21 in electron units from the direct integration of the charge density. In the present case, the following favorable conditions will enable us to estimate the amount of the charge transfer by the same method:

(1) Each of the bulk of the space occupied by the two component molecules is equal.

(2) The molecules lie in the plane having simple Miller index.

(3) The total number of electrons of the two molecules are equal.

In order to integrate the electron density over a molecule, it is convenient to transform the crystal axes into a new set a', b' and c' as shown in Fig. 6(a) and (b). The relations between these two coordinate systems are expressed by $a'=2a+2b+c$, $b'=-2a+2b-c$ and $c'=-a+2c$. In this case, a' and b' are nearly on the molecular plane. a' nearly coincides with the long axes of the two component molecules. b' is nearly perpendicular to a'. c' is almost perpendicular to the molecular plane. Referring to this new coordinate system, the Miller indices are expressed by $h'=2h+2k+l$, $k'=-2h+2k-l$ and $l'=-h+2l$. The charge of TMPD molecule and TCNB molecule is given by:

$$Q_{\mathrm{TMPD}} = \int_{-1/4a'}^{1/4a'} \int_{-1/8b'}^{1/8b'} \int_{-1/10c'}^{1/10c'} \rho \mathrm{d}\tau \qquad (1)$$

and

$$Q_{\mathrm{TCNB}} = \int_{-1/4a'}^{3/4a'} \int_{-1/8b'}^{1/8b'} \int_{-1/10c'}^{1/10c'} \rho \mathrm{d}\tau \qquad (2)$$

respectively, where

$$\rho = \frac{1}{V'} \sum_{h'} \sum_{k'} \sum_{l'} F(h'k'l') \cos 2\pi(h'x'+k'y'+l'z') \qquad (3)$$

The range of integration is shown by the shaded area in Fig. 6. After integration, (1) and (2) become

$$Q_{\mathrm{TMPD}} = \frac{1}{2} F(000) - \Delta Q \qquad (4)$$

$$Q_{\mathrm{TCNB}} = \frac{1}{2} F(000) + \Delta Q \qquad (5)$$

where

$$\Delta Q = -\frac{2}{5\pi^2} \sum_{h'} \sum_{k'} \frac{F(h'k'0)}{h'k'} \sin\frac{\pi h'}{2} \sin\frac{\pi k'}{4} - \frac{2}{\pi^3} \sum_{h'} \sum_{k'} \sum_{l'} \frac{F(h'k'l')}{h'k'l'} \frac{\pi h'}{2} \sin\frac{\pi k'}{4} \sin\frac{\pi l'}{5} \qquad (6)$$

Only 515 reflections out of the total of 1233 reflections are necessary for this calculation, because of the presence of the sine terms.

The characteristic features of the molecular arrangement make the intensities of all these reflections weak or medium. Consequently the extinction effect for these reflections are negligible. Because of the presence of h', k' and l' in the denominators of each term, the higher order terms are less important. Moreover, all of the most important terms were incidentally obtained on first layer photographs of c-axis rotation. By virtue of those favorable circumstances mentioned above the errors accompanying the calculations of total charge in a molecule are conceived to be fairly small.

In order to check the validity of the choice of the region occupied by the two component molecules, ΔQ given by Eqs. (4) and (5) was calculated using F_c instead of F_o. Since the scattering factors used for the calculation of the structure factors are those for neutral atoms, the value ΔQ_c thus obtained should be zero. If it is not zero, ΔQ_c should be used as a correction to be applied to ΔQ. The result of calculation indicated that 0.04 in electron units protruded beyond the region of integration from the acceptor to the donor. This small value, however, appears to be the upper limit of the correction, because the hydrogen atoms of the methyl groups were excluded from the calculation of the structure factors. Consequently this correction was negligible.

The results of calculation showed that

$$Q_{\mathrm{TMPD}} = \frac{1}{2} F(000) - 0.24$$

$$Q_{\mathrm{TCNB}} = \frac{1}{2} F(000) + 0.24$$

Thus it can be concluded that the quantity of the charge transfer is 0.24 in electron units, that is 0.12 electron units of charge per one pair of C≡N and N. From the optical absorption spectrum of the quinhydrone crystal,[9] Suzuki calculated that the amount of charge transfer is 0.04 e.[10] The fact that more charge is transferred in n-σ interaction than in the case of π-σ interaction[11] suggests that the amount of charge transfer in n-π interaction will be much larger than that in π-π interaction. Consequently the value of 0.12 e obtained in this investigation seems to be plausible. Calculations were carried out on FACOM 202 computer at this Institute and on HITAC 5020 at the Computer Center of this University.

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