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The Crystal Structure of the Pyrene-Tetracyanoethylene Complex

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The crystal structure of the pyrene-tetracyanoethylene (TCNE) complex has been determined by the two-dimensional Fourier method. The monoclinic unit cell dimensions are: $a=14.58$, $b=7.34$, $c=8.09$ Å and $\beta=92.4°$. The space group is $P2_1/a$. Two pyrene and two TCNE molecules are contained in a unit cell. Pyrene and TCNE molecules are stacked alternately along the c-axis direction, making their molecular planes parallel to each other. The center of a TCNE molecule is not directly above that of the neighboring pyrene molecule, but is displaced considerably along the long axis of pyrene. The mean separation of the molecular plane is 3.32 Å.

The crystal of the charge-transfer complex involving pyrene as the electron donor and tetracyanoethylene (TCNE) as the electron acceptor is an organic semiconductor, the resistivity of

which is about $10^{12}\Omega\cdot$cm. at room temperature with an energy gap of 1.6 eV.[1] Interestingly, this complex exhibits a relatively high photoconductivity, which enables us to determine the drift mobilities of charge carriers.[2] Further investigation is going on in our laboratory in order to elucidate the nature of the electronic conduction. The determination of the crystal structure was undertaken, in the first place, in connection with these studies. There is, however, another point of interest in its crystal structure. The pyrene and the TCNE molecules are nonpolar and planar molecules, similar in shape and size to each other. In this case, the intermolecular forces other than the charge-transfer one do not seem to depend strongly on the relative orientation of the symmetry axes of the pyrene molecule to those of TCNE in so far as they are stacked face-to-face. One may, therefore, presume that the relative orientation is mainly determined by the charge-transfer interaction. It would be interesting to see if the orientation of the molecules in the crystal is the one expected from the charge-transfer theory.

Experimental

The dark purple crystals of a lath shape elongated in the c-axis direction, or of a square, thin plate with a (100) face, were obtained by slowly evaporating the solvent from the chloroform solution containing equimolar amounts of pyrene and TCNE. The mole ratio of pyrene and TCNE in the crystal was determined to be 1 : 1 by chemical analysis. The crystal is stable if it is kept in an atmosphere saturated with vapors of pyrene and TCNE, but it decomposes gradually in air. Thus, the crystal was sealed in a glass capillary with a very thin wall during the X-ray experiments.

The crystal data are as follows:

Pyrene-TCNE complex: $C_{16}H_{10}\cdot C_6N_4$

Monoclinic

$a=14.58\pm0.05$ Å

$b=7.34\pm0.03$ Å

$c=8.09\pm0.03$ Å

$\beta=92.4°$

Volume of the unit cell: 864.4 Å^3

Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd.

Space group: $P2_1/a$ (C_{2h}^5)

Assuming that two molecules of pyrene and two molecules of TCNE are in a unit cell, the density is calculated to be 1.28 g.cm^{-3} (the density observed by the floatation method is 1.3 ± 0.02 g.cm^{-3}).

The intensities of $h0l$ and $hk0$ reflexions were measured visually from multiple-film Weissenberg photographs with Cu$K\alpha$ radiation. The number of the measured reflexions is 80 for $h0l$ and 92 for $hk0$. No correction was made for the absorption, while the corrections for the Lorentz and polarization factors were made in the usual way.

The Determination of the Crystal Structure

The crystal shows a marked dichroism.[3] It is known that the strong band at 830 mμ in the absorption spectrum of the crystal is the charge-transfer band, which is distinctly polarized in the c-axis direction. This fact indicates that the donor and the acceptor molecules are stacked alternately along the c-axis making their molecular planes parallel to each other, so as to give a large overlap between their molecular orbitals. From the consideration of the symmetry of the molecules and the space group of the crystal structure, one can fix the positions of the centers of two pyrene and two TCNE molecules in the unit cell as follows:

Pyrene: 0, 0, 0; 1/2, 1/2, 0

TCNE: 0, 0, 1/2; 1/2, 1/2, 1/2

Assuming the known bond distances from the crystal structures of pyrene[4] and TCNE[5] respectively, several trial structures were deduced; then the structure factors were calculated on each trial structure. The one that gives the best agreement between the calculated and the observed structure factors was chosen and refined by means of two-dimensional Fourier syntheses on $(h0l)$ and $(hk0)$. The calculation of the structure factors and the Fourier syntheses were repeated several times, and then the (F_o-F_c) syntheses were applied to correct the atomic coordinates. The temperature factors were assumed to be the same for all atoms, the values being 4.00 for $(h0l)$ and 4.79 for $(hk0)$.

The electron density projection along the b-axis and that along the c-axis are shown in Fig. 1 and Fig. 2 respectively. The atomic coordinates of the final structure are given in Table I, for

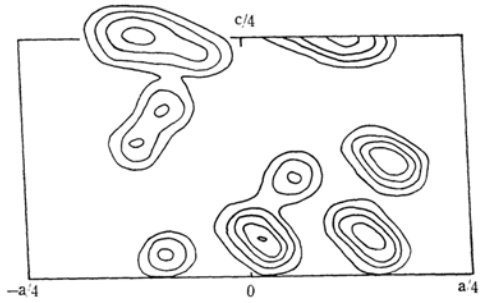

Fig. 1. Electron-density projection along [010]. Contours at intervals of 1.5 e.Å^{-2}, with the lowest solid contour of 4 e.Å^{-2}.

1) H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, *J. Chem. Phys.*, **36**, 457 (1962).

2) H. Kuroda, K. Yoshihara and H. Akamatu, This Bulletin, **36**, 1365 (1963).

3) H. Kuroda and H. Akamatu, *J. Chem. Phys.*, **40**, 3748 (1964).

4) J. M. Robertson and J. G. White, *J. Chem. Soc.*, **1947**, 358.

5) D. A. Bekoe and K. N. Trueblood, *Zeit. Krist.*, **113**, 1 (1960).

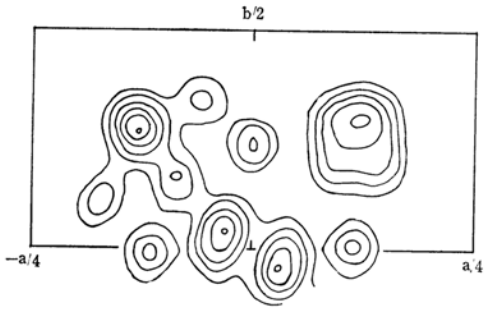

Fig. 2. Electron-density projection along [001]. Contours at intervals of 1.5 e.Å^{-2}, with the lowest solid contour of 4 e.Å^{-2}.

which the discrepancy index, $R=\sum||F_o|-|F_c||/\sum|F_o|$, is 19% for both ($hk0$) and ($h0l$). The observed and the calculated structure factors are given in Table II.

Table I. Atomic coordinates of pyrene-TCNE complex

		X	Y	Z
Pyrene				
C	1	0.146	−0.285	0.266
	2	0.176	−0.103	0.213
	3	0.119	0.007	0.106
	4	0.029	−0.057	0.053
	5	−0.002	−0.238	0.106
	6	0.055	−0.349	0.213
	7	0.149	0.189	0.053
	8	0.094	0.298	−0.053
TCNE				
C	9	0.042	0.009	0.530
	10	0.086	−0.133	0.630
	11	0.097	0.173	0.507
N	1	0.121	−0.247	0.710
	2	0.139	0.301	0.489

Description and Discussion of the Structure

The arrangement of molecules in the crystal is shown in Fig. 3. The donor and the acceptor molecules are stacked alternately along the c-axis. The molecules can be considered planar. The equations of the mean planes of pyrene and TCNE are:

$$-1.3361x+0.6639y+1.4371z=0$$

and

$$-1.6990x+0.8630y+2.0000z=1$$

respectively.

The departures of the atoms from the mean planes are less than 0.02 Å. The molecular planes of pyrene and TCNE are almost parallel to each other, the deviation from parallelism being about 2°. The average separation between the planes is 3.32 Å, which is smaller than the usual van der

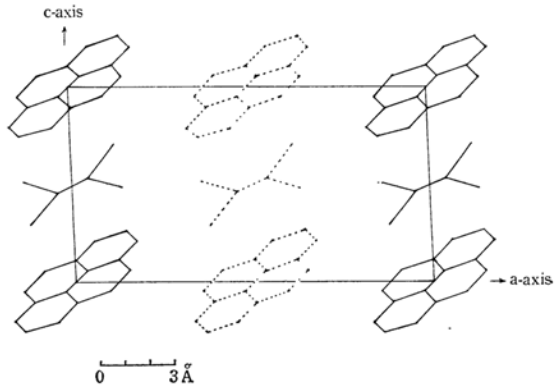

Fig. 3. Projection of the molecular arrangement on the (010) plane.

Waals separation. The distances between the atoms of the nearest neighbor pyrene and TCNE molecules are shown in Fig. 4, where the shortest one is 3.30 Å. Such close contact between the donor and the acceptor molecules suggests the presence of a strong intermolecular interaction between them.

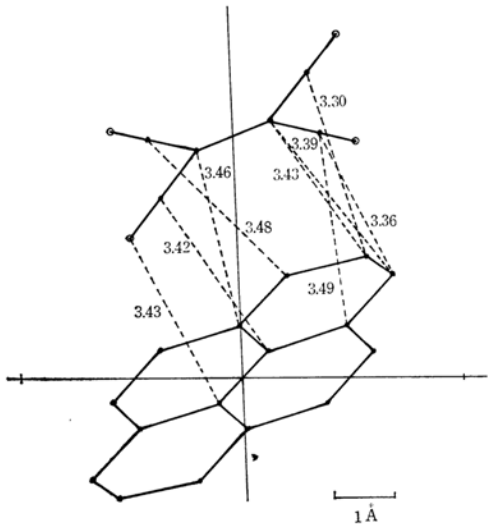

Fig. 4. Distances between atoms of the nearest neighbor pyrene and TCNE.

It is known that TCNE behaves as a very strong electron acceptor. There is reason to believe that nearly half of the binding energy between pyrene and TCNE is associated with the charge-transfer interaction in the case of the 1 : 1 complex formed in the solution. According to the charge-transfer theory, the donor molecule is supposed to take an orientation relative to the acceptor molecule, so as to give the largest overlap between the highest occupied orbital of the donor and the lowest vacant orbital of the acceptor, provided that the former is the donating orbital and the latter is the accepting one. This rule, known as

TABLE II. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 0 1	22.36	14.08	−10 0 5	6.26	− 5.38	16 0 0	2.25	− 1.82	1 4 0	9.54	6.62
2	31.88	37.96	8	4.78	4.97	1 1 0	53.36	65.96	2	11.15	10.70
3	24.33	−23.01	−12 0 1	3.52	− 4.23	4	5.10	4.58	3	3.78	2.45
4	40.25	33.22	3	3.60	4.29	5	4.44	1.50	4	4.87	− 5.12
5	34.51	−26.49	4	5.51	− 9.21	6	21.07	17.21	5	4.69	2.65
6	11.32	− 6.34	−14 0 2	2.05	− 3.71	7	5.47	2.96	6	7.00	9.96
7	24.95	−21.54	−16 0 2	8.46	− 9.44	8	10.53	5.99	7	9.35	12.22
8	2.89	2.67	2 0 1	17.90	−15.17	9	0.94	1.71	8	22.26	20.13
9	3.54	− 4.50	2	20.42	−20.42	10	1.01	0.90	9	3.90	4.80
−2 0 0	48.68	76.89	5	21.91	−20.27	11	1.07	1.75	12	7.70	− 5.26
1	35.66	36.60	6	9.11	− 5.95	13	5.30	− 5.81	13	1.07	2.76
2	64.34	88.15	8	2.86	4.42	14	5.12	− 6.25	2 5 0	3.79	7.34
3	19.09	−16.55	9	3.85	3.32	15	5.78	− 5.30	3	7.14	9.10
4	14.43	−12.50	4 0 1	43.92	46.05	16	0.99	− 3.35	4	5.57	− 2.92
6	3.85	2.55	2	17.38	−17.70	0 2 0	65.94	−62.32	5	2.15	1.51
7	15.66	−11.07	3	8.30	6.10	1	13.17	10.31	6	5.96	− 6.64
8	4.57	− 2.58	4	21.45	−18.21	2	3.96	2.96	7	2.77	1.50
−4 0 0	59.50	−84.42	5	24.14	20.55	4	48.10	44.76	8	4.88	3.31
1	6.64	− 2.13	7	6.60	7.33	5	5.21	− 2.78	9	3.65	3.03
2	14.27	14.76	8	9.03	− 3.71	6	5.07	− 6.14	10	6.69	7.01
3	17.97	−15.50	9	11.73	11.42	7	0.85	1.82	11	4.16	− 1.63
4	26.96	−21.95	6 0 1	6.56	11.11	8	18.82	−21.42	12	1.05	3.11
5	7.31	5.94	2	5.50	− 5.96	9	3.71	− 3.50	13	0.96	− 1.21
−6 0 0	10.82	10.32	3	9.31	9.64	10	3.17	− 5.17	14	0.84	0.87
1	33.62	35.93	5	5.48	− 4.30	11	1.11	3.78	0 6 0	5.60	3.74
2	5.00	− 7.03	6	22.67	−20.38	12	11.48	− 8.87	1	1.94	− 1.91
3	26.28	−22.88	8	7.17	− 3.75	13	8.01	5.57	2	3.19	− 0.03
4	11.17	9.40	8 0 1	14.29	−16.88	14	12.61	−10.67	4	6.38	− 8.60
6	6.46	6.23	4	19.53	−17.89	1 3 0	26.67	24.89	5	4.00	4.92
7	7.21	5.54	5	29.61	−33.88	2	15.22	14.72	6	9.75	− 9.10
−8 0 0	22.64	20.58	6	24.23	−17.64	3	7.60	6.80	7	1.63	− 0.09
1	36.34	35.21	10 0 1	5.82	7.53	4	5.25	5.92	8	4.54	− 4.23
2	16.60	18.57	3	14.65	−12.13	5	5.60	− 2.77	9	1.10	2.39
3	6.96	9.48	4	25.00	−22.81	6	17.46	13.42	10	4.35	− 3.62
4	10.96	9.48	12 0 1	6.47	11.18	7	0.94	3.53	11	1.70	3.30
5	9.23	− 9.58	14 0 3	5.53	4.22	8	2.24	4.68	12	1.77	− 1.44
6	12.00	11.00	16 0 2	4.48	− 5.98	9	1.06	− 3.25	1 7 0	2.30	2.32
7	12.15	8.56	3	4.64	− 6.02	10	5.65	− 5.17	2	7.79	−12.73
8	7.75	6.32	2 0 0	73.96	77.64	11	15.40	−12.86	3	7.04	− 7.50
−10 0 0	2.56	− 3.96	4	83.05	−82.56	12	6.94	3.09	4	3.20	1.40
1	2.57	2.21	6	15.14	9.85	13	11.62	− 6.84	5	8.92	− 8.92
2	9.37	7.92	8	27.27	23.28	14	7.35	6.29	6	7.15	8.07
3	20.11	19.84	10	3.48	− 0.53	0 4 0	28.75	23.42			

the orientation and overlap principle, leads to the following structural model for the 1 : 1 complex of pyrene and TCNE: pyrene and TCNE molecules are stacked face-to-face, so that their molecular centers are directly over each other and the central double bond of TCNE is parallel to the short axis of pyrene. The relative orientation of pyrene to TCNE found in the crystal is, however, considerably different from the model described above, as is shown in Fig. 5. Naturally there can be several factors affecting the relative orientation of molecules in the crystal other than the charge-transfer interaction between the donor and the acceptor which are the nearest neighbors. Therefore, it is possible that the orientation in the crystal is not identical with the stable orientation for the 1: 1 complex. It seems worthwhile, however, to examine the theoretical bases of the model for the 1 : 1 complex described previously.

According to the charge-transfer theory, the ground state of the complex is expressed by the resonance hybrid between the no-bond structure and the dative structure, or the charge-transfer state. Usually it is regarded enough for the first approximation to take as the dative structure merely the lowest charge-transfer state where

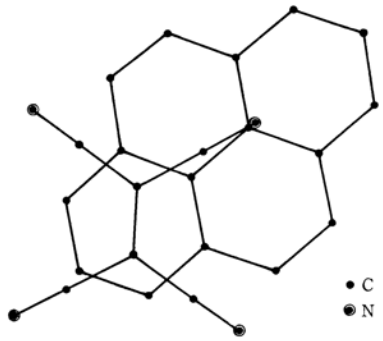

Fig. 5. Relative orientation of pyrene to TCNE found in the crystal.

an electron has been transferred from the highest occupied orbital of the donor to the acceptor. We have found, however, that the pyrene-TCNE complex shows two charge-transfer bands in the crystalline state as well as in the solution. The charge-transfer bands of the crystal are at 830 mμ and 510 mμ, and both of them are polarized in the c-axis direction. The first band is associated with the charge-transfer from the highest occupied orbital of pyrene to the lowest vacant orbital of TCNE, while the second one is associated with the charge transfer from the second highest occupied orbital of pyrene. The intensities of the two charge-transfer bands are comparable to each other. This can not be explained unless the charge-transfer state associated with the second band is as important a resonance structure as that of the lowest charge-transfer state. These facts suggest that the approximation neglecting the interactions of the charge-transfer states other than the lowest one is not satisfactory for the pyrene-TCNE complex. If such is the case, the orientation deduced from this approximation may not be the most stable structure, even for the 1 : 1 complex, since the overlap between the second highest occupied orbital of pyrene and the lowest vacant orbital of TCNE is largest when the central double bond of TCNE is parallel to the long axis, not the short axis, of pyrene. It is likely that the interactions of other charge-transfer states also make significant contributions to the binding energy. Further theoretical investigation seems to be necessary in this respect. Presumably the stable orientation for the 1 : 1 complex in solution will be similar, if not identical, to the one found in the crystal. Since there is a strong intermolecular interaction between pyrene and TCNE, we could expect deformations in the molecular structures. The bond distances determined at the present stage are, however, not accurate enough for us to determine conclusively if the molecules have been deformed by the complex formation or not. In order to solve this problem, refinements of the atomic coordinates as well as of the temperature factors are now in progress by means of three-dimensional analysis.

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