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The Crystal Structure of the Perylene-Tetracyanoethylene Complex

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The crystal structure of the perylene-tetracyanoethylene (TCNE) complex has been determined by the two-dimensional Fourier synthesis and by difference synthesis. The monoclinic unit cell dimensions are: $a=15.79$, $b=8.28$, $c=7.31$ Å, and $\beta=96.1°$. Two perylene and two TCNE molecules are in a unit cell. The space group is $P2_1/a$. Perylene and TCNE molecules are stacked alternately along the b-axis, making their molecular planes parallel to each other. The center of a TCNE molecule is not directly above that of the neighboring perylene molecule. The mean separation of the molecular planes is 3.23 Å.

Crystal structure analysis has been performed on a number of charge-transfer complexes.¹⁾ There are two common features in the crystal structures of the complexes which involve π-donors and π-acceptors; the donor and acceptor molecules are always alternately stacked, plane-to-plane, along some crystal axis, and the separation between the molecular planes is considerably smaller than the usual van der Waals separation. This is associated with the charge-transfer interaction between donor and acceptor molecules. According to the charge-transfer theory,²⁾ the interaction between donor and acceptor is strongly dependent on their relative orientation. Thus, it is particularly interesting to examine the relative orientation of donor and acceptor molecules in the crystal structure on a series of molecular complexes composed of a π-donor and a π-acceptor and to see if the orientation is predictable from the charge-transfer theory. We considered that the tetracyanoethylene (TCNE) complexes of naphthalene, pyrene, and perylene are most suitable for this purpose. We have determined the crystal structure of the pyrene-TCNE complex,³⁾ and theoretically studied the interaction between pyrene and TCNE molecules.⁴⁾ The polarized absorption spectra of the pyrene-TCNE and perylene-TCNE complexes have been also investigated.⁵⁾ In the present paper, we shall describe the results obtained by the preliminary analysis of the crystal structure of the perylene-TCNE complex.

Experimental

Dark green, needle-shaped crystals elongated along the b-axis were obtained by slowly evaporating the solvent from a chloroform solution containing equimolar amounts of perylene and TCNE. The mole ratio of perylene and TCNE in the crystal was determined by chemical analysis to be 1 : 1. The crystal is stable if it is kept in equilibrium with the vapors of perylene and TCNE, but it decomposes gradually in air. Thus the crystal was sealed in a quartz capillary with a very thin wall during the X-ray experiments. Oscillation and Weissenberg photographs were prepared with Cu$K\alpha$ radiation.

The crystal data are as follows:
Perylene-TCNE complex, $C_{20}H_{12}\cdot C_6N_4$.
Monoclinic:

$$a=15.70\text{ Å},$$
$$b=8.28\text{ Å},$$
$$c=7.31\text{ Å},$$
$$\beta=96.1°.$$

Volume of the unit cell: 949.5 Å³.
Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd.
Space group: $P2_{1/a}$ (C_{2h}^5).
The density observed by the floating method is 1.3 g cm^{-3}.
The cell contains two formula units of the complex; the calculated density is 1.37 g cm^{-3}.

The intensity data for $hk0$ and $h0l$ reflections were recorded on zero layer Weissenberg films about the c-axis and the b-axis by the multiple-film method. The intensities were measured visually. The number of the measured reflections is 115 for $h0l$ and 120 for $hk0$. No correction was made for the absorption, but the corrections for the Lorentz and polarization factors were made in the usual way.

The Determination of the Crystal Structure

A close relation can be found between the lattice constants of the perylene-TCNE complex and those of the pyrene-TCNE complex; the b- and c-axes

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1) See, for example, L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco (1964).

2) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

3) H. Kuroda, I. Ikemoto and H. Akamatu, This Bulletin, **39**, 547 (1966).

4) H. Kuroda, I. Ikemoto and H. Akamatu, *ibid.*, **39**, 1842 (1966).

5) H. Kuroda, T. Kunii, S. Hiroma and H. Akamatu, *J. Mol. Spectry.*, **22**, 60 (1967).

of the perylene-TCNE complex seem to correspond, respectively, to the c- and b-axes of the pyrene-TCNE complex. It is known that a crystal of a charge-transfer complex usually grows along the axis which corresponds to the direction of the alternate stacking of the donor and acceptor molecules. In the case of the perylene-TCNE complex, the crystal always grows as a needle elongated along the b-axis. It exhibits a marked dichroism; in its absorption spectrum, the charge-transfer band with the maximum at 950 mμ is exclusively polarized in the direction of the b-axis. All these facts suggest that perylene and TCNE molecules are alternately stacked along the b-axis, making their molecular planes parallel to each other.

There are two molecules of perylene and two molecules of TCNE in a unit cell; hence, their centers of gravity must lie on a set of twofold special positions. Therefore, the centers of perylene and TCNE molecules can be fixed as follows:

perylene:	0, 0, 0;	½, ½, 0
TCNE :	0, ½, 0;	½, 0, 0

A computer-search technique was used in finding possible trial structures.[6] The following assumptions were made for the molecular structures: In a perylene molecule, the atoms are coplanar, and all the C–C bond distances are 1.45 Å, and the bond angles, 120°. In a TCNE molecule, the distances of the C–C, C=C, and C≡N bonds are, respectively, 1.45, 1.32, and 1.20 Å; the bond angles at the carbon atoms of the central double bond are 120°, C–C≡N is linear, and all the atoms are coplanar. Hydrogen atoms are ignored. The molecular planes of perylene and TCNE are kept parallel to each other, and the long axis of a perylene molecule is kept parallel to the C=C double bond of a TCNE molecule. A TCNE molecule is rotated about its center in its molecular plane in steps of 10° from 0° to 90°, and then perylene and TCNE molecules are rotated together about the x-axis, the y-axis, and the z-axis successively in steps of 10° from 0° to 40° and from 140° to 180°.

With an electronic computer, the atomic coor-

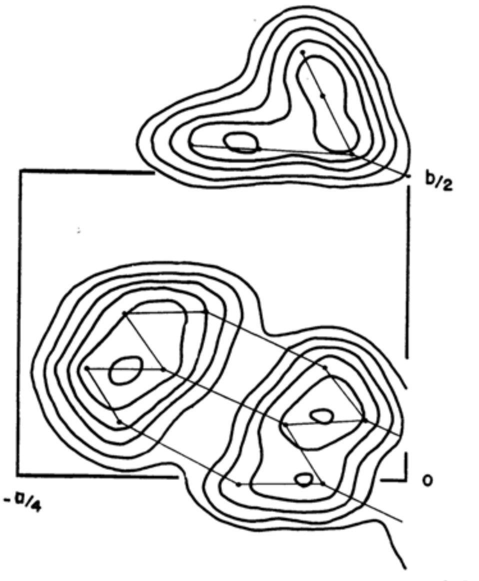

Fig. 1. Electron-density projection along [001]. Contours at intervals of 1.0 e.Å^{-2}, with the lowest solid contours of 3 e.Å^{-2}.

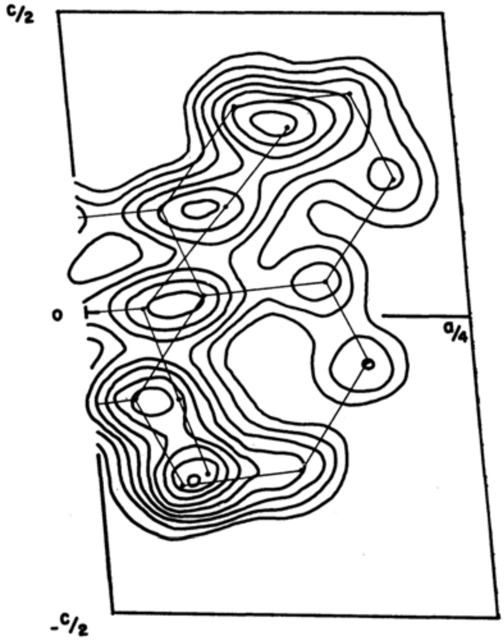

Fig. 2. Electron-density projection along [010]. Contours at intervals of 1.0 e.Å^{-2}, with the lowest solid contours of 3 e.Å^{-2}.

TABLE 1. ATOMIC PARAMETERS OF PERYLENE-TCNE COMPLEX

	x	y	z	B
Perylene				
C 1	−0.182	0.275	0.088	7.1
C 2	−0.130	0.281	0.261	5.7
C 3	−0.052	0.187	0.288	4.1
C 4	−0.026	0.100	0.146	5.7
C 5	−0.078	0.094	−0.026	5.5
C 6	−0.054	−0.005	−0.172	6.3
C 7	−0.108	−0.009	−0.344	6.3
C 8	−0.185	0.091	−0.368	8.2
C 9	−0.207	0.179	−0.225	7.4
C 10	−0.157	0.181	−0.056	6.4
TCNE				
C 11	−0.037	0.542	−0.009	4.5
C 12	−0.056	0.637	0.145	6.8
C 13	−0.097	0.547	−0.177	5.3
N 1	−0.070	0.708	0.270	9.2
N 2	−0.142	0.550	−0.304	7.1

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[6] R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Cryst.*, **18**, 932 (1965).

dinates and the intermolecular distances were calculated on about 10000 structure models associated with different orientations of molecules; models in which no intermolecular distances were less than 3.0 Å were selected. By this method, 41 possible structure models were obtained, on which models the structure factors for *h0l* and *hk0* were computed and the *R*-factors were examined. Only four models gave *R*-factors of less than 40%. All of them have the same type of structure. Thus, the model that gave the lowest *R*-factor value was taken as the starting model, and was refined by two-dimensional Fourier synthesis. The calculation of the structure factors and the Fourier synthesis were repeated several times, and then the difference synthesis was applied to correct the atomic parameters.

The electron density projections along the b-axis and the c-axis are shown in Fig. 1 and Fig. 2 respectively. The atomic parameters of the final structure are given in Table 1, for which the *R*-factors are 18.4% for (*h0l*) and 19.7% for (*hk0*).

Description and Discussion of the Structure

The accuracy of the present analysis is not sufficient to discuss the details of the structure fully; we have used only the method of two-dimensional analysis, and the overlap of atoms in the electron density projection is quite large, as Fig. 1 and Fig. 2 show. However, several important features of the crystal structure of the perylene-TCNE complex have been made clear by the present analysis.

The crystal structure projection onto (001) is shown in Fig. 3. The donor and acceptor molecules are stacked alternately along the b-axis, making their molecular planes almost parallel to each other. The molecules are almost planar.

The average separation between the planes is 3.23 Å. This seems to suggest the presence of a relatively strong interaction between perylene and TCNE. The distances between the atoms of the neighboring perylene and TCNE molecules are shown in Fig. 4. The relative orientation of perylene to TCNE, in which we are most interested, is shown in Fig. 5. Their molecular centers are not directly over each other; rather, the center of the TCNE molecule is shifted to a point above one of the peripheral benzene rings of the perylene molecule. The central double bond of a TCNE molecule is almost parallel to the long axis of a perylene molecule.

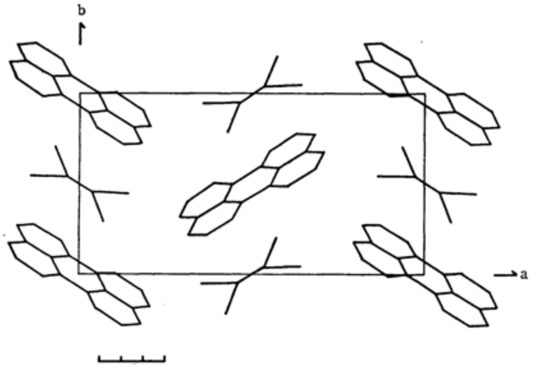

Fig. 3. Crystal structure projection onto (001).

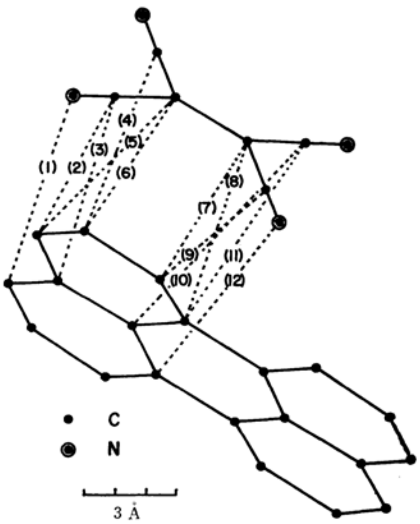

Fig. 4. Distances between atoms of perylene and TCNE in the nearest neighbor.

(1)	3.30	(2)	3.34	(3)	3.31	(4)	3.31
(5)	3.31	(6)	3.36	(7)	3.43	(8)	3.31
(9)	3.38	(10)	3.26	(11)	3.50	(12)	3.27

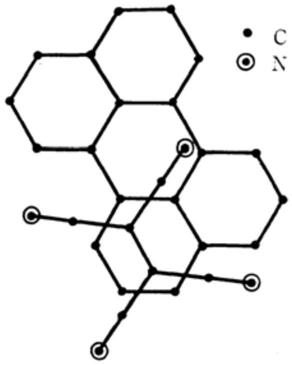

Fig. 5. Relative orientation of perylene to TCNE found in the crystal.

The bond distances determined at the present stage are not accurate enough, as has been mentioned above, but they seem to be plausible when compared with the values given by Camerman and Trotter,⁷⁾ Boeyens and Herbstein,⁸⁾ Hanson,⁹⁾

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7) A. Camerman and J. Trotter, *Proc. Roy. Soc. (London)*, **A279**, 129 (1964).

8) A. W. Hanson, *Acta Cryst.*, **16**, 1147 (1963).

9) J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem.*, **69**, 2160 (1965).

Bekoe and Trueblood,⁽¹⁰⁾ and by the present authors.⁽³⁾ Refinements of the atomic parameters are now in progress by means of three-dimensional analysis.

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The computers used in this work were the PC-2 in University of Tokyo Data Processing Centre and the HITAC 5020E in Computer Centre, The University of Tokyo.

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