The Crystal Structure of the 1:1 Complex of Pyromellitic Dianhydride with *trans*-Stilbene

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The 1: 1 complex of pyromellitic dianhydride with *trans*-stilbene crystallizes in the space group $P2_1/c$ with two pairs of the component molecules in a unit cell with dimensions of $a=12.48$, $b=6.33$, $c=13.17$ Å, and $\beta=111.6°$. The structure was solved from a three-dimensional $|E|^2$ Patterson synthesis and refined by a block-diagonal least-squares method to a final R value of 0.12 for 1635 reflections. In the *trans*-stilbene molecule, the plane containing the central ethylene group makes an angle of 11.5° with the phenyl plane. The non-planarity of the *trans*-stilbene molecule seems to be largely due to a steric repulsion between the hydrogen atom attached to the ethylene moiety and that at the 6 and 6′ position in the phenyl group. The pyromellitic dianhydride molecule is approximately planar. The component molecules are stacked alternately in infinite columns along the a axis. The average spacing between the phenyl plane of *trans*-stilbene and the molecular plane of pyromellitic dianhydride is 3.59 Å, and these palnes make an angle of 4.8° with each other. The relative arrangement of the component molecules in the crystal differs from that observed in the crystal of the anthracene, pyrene, or perylene complex with pyromellitic dianhydride. The van der Waals forces are considered to be more important than the charge transfer force in determining the relative arrangement of the component molecules in this crystal.

The charge transfer (CT) complex of *trans*-stilbene (STB) with pyromellitic dianhydride (PMDA) crystallizes with a 1: 1 molecular ratio, whereas the CT complex of *trans*-4-methylstilbene crystallizes with a 2: 1 molecular ratio.[1] The crystal structure analysis of the former complex was carried out in order to study the molecular interaction between the donor and acceptor molecules.

Experimental

Crystals of the complex were kindly supplied by Professor Matsuo of Kyushu University. They were in the form of bright red thin plates. The cell constants were determined from zero-layer back-reflection Weissenberg photographs around the b and c axes. The crystal data are listed in Table 1. The specimens used for the intensity measurements had dimensions of 0.24×0.24×0.05 mm and 0.23×0.21×0.05 mm. Multiple film equi-inclination Weissenberg photographs were taken around the b axis up to the fifth layer and around the c axis up to the tenth layer. The intensities of 1635 independent reflections were estimated visually by comparison with a standard scale. The usual Lorentz, polarization, and spot-shape corrections were applied; however, no correction was made for the absorption in view of the small size of the specimens.

Table 1. Crystal data

Chemical formula: $C_{10}H_2O_6 \cdot C_{14}H_{12}$
M.W.=398.4
Crystal system: Monoclinic
$a=12.48\pm0.01$Å
$b=6.33\pm0.01$Å
$c=13.17\pm0.02$Å
$\beta=111.56\pm0.07°$
$V=967.6$Å^3
Space group: $P2_1/c$
$D_x=1.37$ g·cm^{-3}
$D_m=1.38$ g·cm^{-3}
$Z=2$

Structure Determination

A Patterson synthesis sharpened by the $\exp(B\sin^2\theta/\lambda^2)$ factor was calculated using the complete set of observed data, but it could not be interpreted satisfactorily because of the severe overlapping of peaks. The structure was, however, solved by an $|E|^2$ Patterson synthesis. From the peaks around the point of origin, the orientations of the benzene rings in the component molecules could be fixed. The molecular orientations and the relative arrangement of the component molecules were assumed so as to account for the characteristic distribution of the prominent peaks. The structure factors were calculated on the basis of the trial model thus obtained by assuming the isotropic temperature factors of all the atoms. The R value was 0.46. The atomic coordinates and isotropic temperature factors were refined by means of the block-diagonal least-squares procedures using a program written by Dr. Ashida. After five cycles of refinement, anisotropic temperature factors were introduced. The positions of the hydrogen atoms were supplied by calculation; they were not refined. The temperature factors of the hydrogen atoms were assumed to be isotropic and were given the same values as those of the atoms to which the hydrogen atoms were attached. The following weighting scheme was employed for the least squares refinement:

$$1.0 \text{ for } |F_o| \geq 5.0$$

and:

$$0.7 \text{ for } |F_o| < 5.0$$

The final R value was 0.12. The topography of the final differential synthesis was flat within the range of ±0.3eÅ^{-3}. The final atomic and thermal parameters are listed in Table 2. A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan.[2] Atomic scattering curves taken from the International Tables for X-ray Crystallography were used throughout.

TABLE 2. FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS
(Estimated standard deviations are shown in parentheses ($\times 10^4$). Thermal parameters are in the form of $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.)

Atom	$x/a\times10^4$	$y/b\times10^4$	$z/c\times10^4$	$\beta_{11}\times10^4$	$\beta_{22}\times10^4$	$\beta_{33}\times10^4$	$\beta_{12}\times10^4$	$\beta_{13}\times10^4$	$\beta_{23}\times10^4$
STB									
C (1)	4056 (6)	1914 (14)	1659 (6)	0056	0242	0070	−0007	0078	−0032
C (2)	3477 (7)	1612 (15)	2362 (7)	0069	0309	0077	0006	0099	−0065
C (3)	2913 (7)	−0322 (14)	2335 (6)	0063	0296	0065	−0002	0087	−0016
C (4)	2929 (6)	−1893 (14)	1604 (6)	0061	0236	0070	−0043	0075	−0023
C (5)	3521 (6)	−1594 (14)	0903 (6)	0056	0250	0058	−0021	0057	−0023
C (6)	4121 (6)	0336 (13)	0944 (6)	0050	0248	0057	0011	0065	0009
C (7)	4847 (6)	0693 (14)	0286 (6)	0050	0264	0056	−0026	0065	0005
PMDA									
C (11)	0338 (6)	1972 (11)	0646 (5)	0054	0114	0046	−0032	0068	−0017
C (12)	−0674 (5)	−1496 (11)	0216 (5)	0042	0147	0042	−0016	0053	0001
C (13)	−0386 (5)	0384 (11)	0825 (5)	0047	0160	0035	0012	0060	0004
C (14)	−1380 (6)	−2754 (12)	0669 (6)	0052	0184	0056	−0027	0075	0015
C (15)	−0902 (6)	0329 (12)	1670 (5)	0051	0216	0047	0019	0069	0006
O (11)	−1769 (5)	−4469 (10)	0454 (5)	0090	0246	0088	−0113	0114	−0003
O (12)	−1533 (4)	−1566 (09)	1505 (4)	0060	0244	0056	−0052	0093	−0014
O (13)	−0851 (4)	1514 (10)	2385 (4)	0066	0340	0051	−0005	0083	−0057

Description and Discussion of the Structure

The bond lengths and angles of the PMDA and STB molecules are shown in Fig. 1 and are listed in Table 3. The standard deviations are also included in the Table. Both PMDA and STB molecules have a center of symmetry. The phenyl plane of the PMDA molecule is given by this equation:

$$0.621x - 0.452y + 0.640z = 0.000, \qquad (1)$$

where x, y, and z are the coordinates in Å units referred to the a, b, and c crystal axes. The maximum deviation of the atoms from this plane is 0.010 Å. The carbonyl oxygen atoms in this molecule are significantly deviated outwards by 0.061 and 0.128 Å from this plane. The plane through C(14), O(11), C(15), and O(13) is expressed as;

$$0.723x - 0.395y + 0.567z = -0.322 \qquad (2)$$

and makes an angle of 7.9° with the plane given by Eq. (1). The maximum deviation of the atoms from this plane given by Eq. (2) is 0.003 Å. Similar deviations of the carbonyl groups in the PMDA molecules were observed by Herbstein *et al.* in the complexes of PMDA with perylene[3] and pyrene.[4]

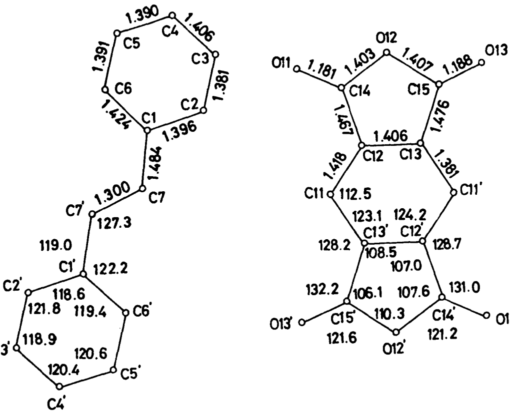

Fig. 1. Bond lengths and angles.

The C–C bond lengths in the benzene ring of PMDA agree with the normal value within 2σ. All the bond angles of the benzene ring deviate significantly from

TABLE 3. BOND LENGTHS AND ANGLES WITH THEIR STANDARD DEVIATIONS

STB				PMDA			
C(1)–C(2)	1.396(0.012)Å	C(2)–C(1)–C(6)	118.7(0.7)°	C(11)–C(12)	1.418(0.010)Å	C(13)–C(11)–C(12)	112.6(0.4)°
C(1)–C(6)	1.424(0.012)	C(2)–C(1)–C(7)	119.0(0.5)	C(11)–C(13′)	1.381(0.011)	C(11)–C(12)–C(13)	124.2(0.5)
C(2)–C(3)	1.381(0.014)	C(6)–C(1)–C(7)	122.3(0.6)	C(12)–C(13)	1.406(0.009)	C(11)–C(12)–C(14)	128.7(0.5)
C(3)–C(4)	1.406(0.013)	C(1)–C(2)–C(3)	121.9(0.6)	C(12)–C(14)	1.467(0.011)	C(13)–C(12)–C(14)	107.1(0.6)
C(4)–C(5)	1.390(0.013)	C(2)–C(3)–C(4)	119.0(0.6)	C(13)–C(15)	1.476(0.011)	C(12)–C(13)–C(11′)	123.1(0.6)
C(5)–C(6)	1.391(0.013)	C(3)–C(4)–C(5)	120.4(0.7)	C(14)–O(11)	1.181(0.009)	C(12)–C(13)–C(15)	108.6(0.5)
C(1)–C(7)	1.484(0.012)	C(4)–C(5)–C(6)	120.6(0.6)	C(14)–O(12)	1.403(0.011)	C(11′)–C(13)–C(15)	128.2(0.5)
C(7)–C(7′)	1.300(0.012)	C(1)–C(6)–C(5)	119.5(0.6)	C(15)–O(12)	1.407(0.009)	C(12)–C(14)–O(11)	131.0(0.7)
		C(1)–C(7)–C(7′)	127.4(0.5)	C(15)–O(13)	1.188(0.009)	C(12)–C(14)–O(12)	107.7(0.4)
						O(11)–C(14)–O(12)	121.3(0.7)
						C(13)–C(15)–O(12)	106.2(0.5)
						C(13)–C(15)–O(13)	132.2(0.6)
						O(12)–C(15)–O(13)	121.6(0.7)
						C(14)–O(12)–C(15)	110.4(0.5)

the normal value of 120.0°, as in the complexes with pyrene and perylene. Such strong deviations that cause the benzene ring to destroy the six-fold symmetry were not observed even in the TCNQ and the TCNB CT complexes, but are comparable with those of the *p*-nitroaniline molecule. The bond lengths and angles in the five-membered ring of this molecule are also in accordance with those of the related complexes. The STB molecule is non-planar. The ethylene reference plane and the benzene ring plane are given by the following equations:

$$0.564x - 0.213y + 0.798z = 3.521 \qquad (3)$$

and:

$$0.616x - 0.375y + 0.693z = 3.591 \qquad (4)$$

respectively. The maximum deviation of the atoms from the (4) plane is 0.018 Å. The planes given by Eqs. (3) and (4) make an angle of 11.5° with each other. Robertson *et al.*[5] found that the crystal of *trans*-stilbene is composed of two kinds of STB molecules, with torsional angles of about 3° and 10° formed between the ethylene and the benzene-ring planes. The torsional angle of 11.5° observed in the STB molecule in the present complex agrees with the latter value. The H(6)···H(7′) distance of 2.1 Å coincides with the usual van der Waals contact (2.2 Å). The C(6)–C(1)–C(7) angle is significantly larger than the C(2)–C(1)–C(7) angle. This might indicate that the repulsion between hydrogen atoms plays an important role in determining the torsional angle of the molecule. The C–C bond lengths in the benzene ring of STB except for C(1)–C(6) agree with the normal value within 2σ.

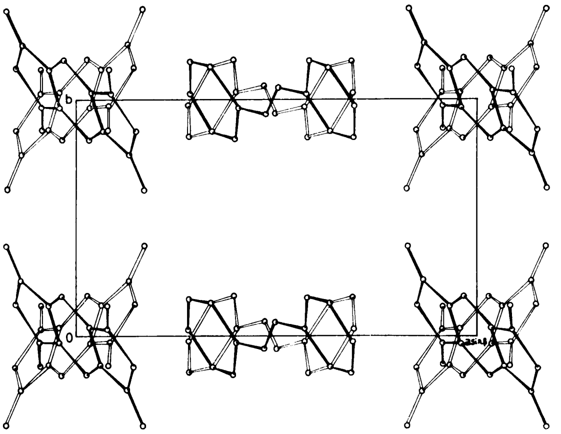

Fig. 2. The structure viewed along the c axis.

The projection of the structure viewed along the c axis is shown in Fig. 2. The crystal is composed of infinite columns in which the component molecules are alternately stacked, plane to plane, along the a axis. Each molecule is surrounded by six others in a quasi-hexagonally close-packed array. The shortest C···C, C···O, and O···O approaches between stacks are 3.64, 3.05, and 3.05 Å respectively, indicating that there are only van der Waals contacts between the stacks. In the column, one of the benzene rings of the STB molecule overlaps with the PMDA molecule related to the first by a unit translation along the *a* axis. The intermolecular contacts in the column are shown in Fig. 3. The mean plane of the PMDA molecule is given by the equation:

$$0.633x - 0.438y + 0.639z = 0.000, \qquad (5)$$

and is inclined to the stack axis at an angle of 39.3°. The dihedral angle between the phenyl plane of STB and the molecular plane of PMDA is 4.8°. The average interplanar distance of 3.59 Å agrees with that observed in the crystal of the TCNB–hexamethylbenzene complex (3.54 Å)[6] and is longer than that in the crystal of graphite (3.35 Å). The shortest intermolecular contact of 3.49 Å in the stack occurs between C(4) and C(11′).

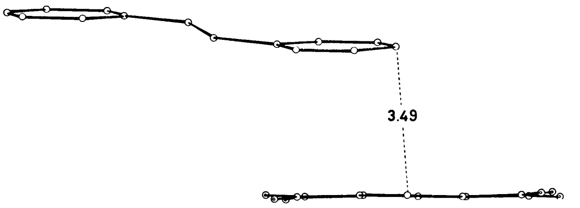

Fig. 3. Intermolecular contacts between PMDA and STB.

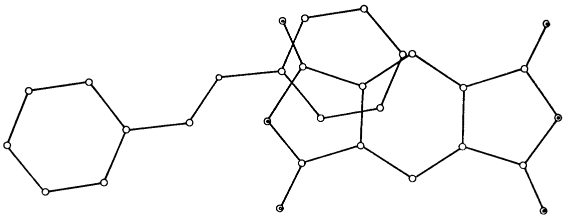

Fig. 4. The projection of STB on the molecular plane of PMDA.

A projection of the STB molecule on the molecular plane of PMDA is shown in Fig. 4. The center of the C(12′)–C(13′) bond in PMDA is superimposed on one of the C–C bonds in the phenyl group of STB adjacent to it in the stack. This relative arrangement is an interesting contrast to that observed in the crystal of the anthracene, pyrene, or perylene complexes with PMDA, in which the center of the C(12′)–C(13′) bond in PMDA is approximately superimposed on the center of the phenyl ring in the aromatic donor. The arrangements of the component molecules in these complexes seem to favor the π-π interaction between the molecules in support of the theoretical study with regard to the related complexes involving maleic anhydride as an accepter.[7] The relative arrangement observed in the present complex seems to be unfavorable for the CT interaction between the STB and the PMDA molecules. Accordingly, it may be concluded that the relative arrangment of the STB and the PMDA molecules in the crystal is mainly determined by the van der Waals interaction rather than by the CT interaction.

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The calculations were carried out on a FACOM 202 computer at the Institute for Solid State Physics and on a HITAC 5020 computer at the Computer Center of the University of Tokyo.

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