The Crystal Structure of the 2:1 Complex of Pyromellitic Dianhydride with *trans*-4-Methylstilbene

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(Received December 26, 1973)

The 2:1 complex of pyromellitic dianhydride with *trans*-4-methylstilbene crystallizes in the Cc space group with four pyromellitic dianhydride molecules and two *trans*-4-methylstilbene molecules in a unit cell with dimensions of $a=12.780$, $b=7.446$, $c=15.050$ Å, and $\beta=91.09°$. In addition to the clearly-defined Laue spots, diffuse streaks elongated perpendicular to the molecular layers were observed with a half period of the b^* axis of the reciprocal lattice. The structure was solved from a three-dimensional $|E|^2$ Patterson synthesis and was refined by a block-diagonal least-squares method to the final R value of 0.13 for the visually-estimated 703 reflections. Refinement was difficult, however, because of the large correlation between parameters caused by the disorder. The crystal is built up of molecular layers stacked parallel to the $(10\bar{2})$ plane and is disordered in the stacking arrangement of the molecular layers. The pyromellitic dianhydride molecule and one of the benzene rings of the *trans*-4-methylstilbene molecule are alternately stacked plane-to-plane in infinite columns along $[10\bar{2}]$. The ethylene group of the *trans*-4-methylstilbene molecule joins the two columns. The molecular arrangement of the component molecules resembles those observed in the anthracene, pyrene, and perylene complexes with pyromellitic dianhydride and presents a striking contrast to that of the *trans*-stilbene complex. The interplanar distances range from 3.25 to 3.56 Å, smaller than that of the *trans*-stilbene complex.

The crystal structure of the equimolar charge transfer (CT) complex between pyromellitic dianhydride (PMDA) and *trans*-stilbene (STB) has been determined.[1] The crystal-structure analysis of the 2:1 pyromellitic dianhydride-*trans*-4-methylstilbene (ME-STB) complex was undertaken in order to study the CT interaction by comparing the molecular arrangement of the donor and acceptor molecules with those of a series of complexes of PMDA.[1-3]

Experimental

Red crystals of the complex grown from an ethyl acetate solution were kindly supplied by Professor Taku Matsuo of Kyushu University. The crystals cleave easily into thin plates and are sensitive to atmospheric moisture. The crystals are monoclinic, and the systematic absences, hkl (when $h+k$ is odd) and $h0l$ (when l is odd), are consistent with the C2/c or Cc space group (Cc was proved to be the true space group at a stage of the refinement). The lattice parameters were determined from zero-layer back-reflection Weissenberg photographs around the b and c axes. The crystal density was determined by flotation in trichloroethylene-chloroform mixture. The crystal data are:

$C_{15}H_{14}\cdot 2C_{10}H_2O_6$ F.W. = 630.5
Monoclinic
$a = 12.780 \pm 0.008$ Å
$b = 7.446 \pm 0.005$ Å
$c = 15.050 \pm 0.004$ Å
$\beta = 91.09 \pm 0.04°$
$U = 1432$ Å^3
$D_m = 1.48\ \mathrm{g\cdot cm^{-3}}$
$z = 2$
$D_x = 1.48\ \mathrm{g\cdot cm^{-3}}$
Space group: Cc

On oscillation photographs around the b axis, well-defined sharp spots appeared in the k th layer lines ($k=0, 1, 2, \cdots$), whereas diffuse spots drawn out into streaks perpendicular to the b^* axis appeared in the $k+1/2$th layer lines, as is shown in Fig. 1. From Weissenberg photographs around the b axis (Fig. 2), the streaks were found to be elongated along $[10\bar{2}]$ in the reciprocal space.

The specimens with dimensions of $0.15\times0.23\times0.11$ mm and $0.17\times0.21\times0.13$ mm were used for the intensity measurements around the b and c axes respectively. The intensity data were recorded on multiple-film equi-inclination Weissenberg photographs around the b axis up to the 5th layer and around the c axis up to the 10th layer using Cu$K\alpha$ radiation. The intensities were estimated visually by a comparison with a time-calibrated intensity strip prepared from a well-defined sharp spot. 703 independent reflections were collected. The usual Lorentz, polarization, and spot shape correc-

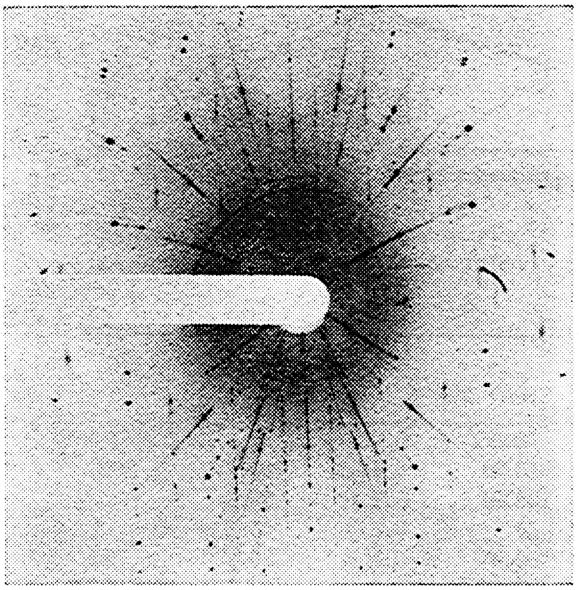

Fig. 1. Oscillation photograph around the b axis taken by Cu$K\alpha$ radiation

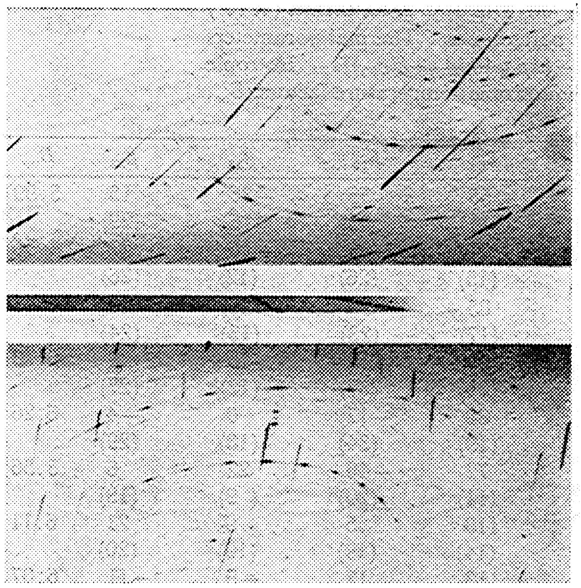

Fig. 2. Weissenberg photograph of the 3/2th layer around the *b* axis taken by the equi-inclination method using Cu$K\alpha$ radiation

tions were applied, but the absorption correction was neglected in view of the small size of the specimens.

Structure Determination

The layer structure of molecules parallel to $(10\bar{2})$ was indicated by the characteristic features that the cleavage plane is $(10\bar{2})$ and that the $20\bar{4}$ reflection and its higher-order reflections give strong X-ray intensities with thermal diffuse scattering and fall off uniformly in intensity. An $N(z)$ test based on the $h0l$ reflections indicated the crystal structure to be hypercentric. Therefore, the C2/c space group was assumed. Since only four PMDA molecules and two ME–STB molecules exist in a unit cell, they must be located at some kind of special positions.

A three-dimensional Patterson synthesis using $|E|^2$ as the coefficient was calculated using the complete set of observed data. The structure of the PMDA molecule was found to have a center of symmetry, thus accounting for the predominant peaks. The atomic coordinates of the PMDA molecule thus determined, combined with appropriate individual isotropic temperature factors, gave an *R* value of 0.45 for all the reflections.

A Fourier synthesis showed the ME–STB molecule to be located along the two-fold axis parallel to the *b* axis and to extend over a range of twice the *b* length-that is, over the twice repetition unit $b'=2b$ along the *b* axis; in other words, the two benzene rings of the ME–STB molecule were found to be overlapped at the same area in a scale of *b* units. It is necessary to measure the intensities of the diffuse reflections in order to determine the structure of the true unit cell of the crystal, but we did not undertake to do so because of the many atomic parameters in comparison with the small number of diffuse reflections and because of the poor quality of the crystals. Therefore, the average structure in the scale of *b* units along the *b* axis was determined in the present work. Assigning the C2/c space group to the crystal, the asymmetric unit of the structure consists of one-half of a PMDA molecule and a quarter of a ME–STB molecule. In the ME–STB molecule there is only one methyl group attached to the C(4) or the C(4′) position, so a quarter of a ME–STB molecule is a quasi-asymmetric unit.

After another Fourier synthesis, the atomic coordinates were refined by means of the block-diagonal least-squares procedure using a program written by Dr. Ashida. The structure data based on the C2/c space group gave an *R* value of 0.23. The difference synthesis showed several extra peaks around the benzene ring of the ME–STB molecule. Therefore, refinement based on the Cc space group, starting from a model with two independent benzene rings, was carried out; an *R* value of 0.15 was thus obtained. Since the *R* value was significantly lower, and since only simple patterns with low peak heights appeared on the difference synthesis, Cc was found to be the correct space group. Because of the parameter interaction, the positional and thermal parameters of one benzene ring of the ME–STB molecule were fixed, while those of the other were refined at each stage of the refinement. After three cycles of refinement using anisotropic temperature factors, the *R* value was lowered to 0.118, but there were several absurd bond lengths, from 1.1 to 1.6 Å, in the benzene rings of the ME–STB molecule. At each stage of the refinement, the *R* value shifted up and down. Therefore, refinement was done again by adjusting the positional parameters so as to give plausible bond lengths before each cycle of refinement. The *R* value gradually fell to 0.13. The weighting scheme for the least-squares procedure was: 0.5 for $|F_o|<5.0$ and 1.0 for $|F_o|\geq 5.0$. The topography of the final difference synthesis is flat within the range of ± 0.7 eÅ^{-3}. The final atomic and thermal parameters are listed in Table 1. A complete list of the observed and calculated structure factors is deposited at the Chemical Society of Japan.[4] The atomic scattering curves were taken from the International Tables for X-ray Crystallography.

Description and Discussion of the Structure

Crystal Structure. The projection of the structure viewed along the *a* axis is shown in Fig. 3. One of the possible positions of the methyl carbon atom is indicated by dotted lines. In view of the stacking disorder to be described later, it seemed that the position is on either the C(7) or the C(7′) position. The crystal is built up of molecular layers stacked parallel to $(10\bar{2})$. The component molecules are alternately stacked plane to plane in infinite columns along $[10\bar{2}]$. Each unit of the structure, namely, a PMDA molecule or one half of a ME–STB molecule, is surrounded by six others in a quasi-hexagonally close-packed array.

The molecular arrangement and intermolecular contacts of the component molecules in the column are shown in Figs. 4 and 5. The arrangement is quite

TABLE 1. FINAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^4$) (Estimated standard deviations are shown in parentheses. Thermal parameters are in the form of $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. Isotropic temperature factors equivalent to the given anisotropic temperature factors, B_{eq}, are also shown in the last column.)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{ep}
C (11)	−350	−1857	63	125	217	55	56	−36	15	5.99
	(23)	(35)	(19)	(36)	(72)	(14)	(36)	(16)	(29)	
C (12)	−946	−380	365	56	162	71	−65	−10	22	4.56
	(17)	(33)	(17)	(15)	(58)	(15)	(26)	(12)	(26)	
C (13)	−547	1433	255	64	63	85	−25	−26	−20	4.43
	(17)	(30)	(17)	(16)	(46)	(17)	(23)	(13)	(24)	
C (14)	−1960	−274	829	52	299	59	−15	−5	−8	5.13
	(17)	(40)	(16)	(16)	(76)	(14)	(37)	(12)	(27)	
C (15)	−1356	2616	665	130	105	88	−17	0	−4	6.26
	(26)	(34)	(22)	(27)	(59)	(19)	(34)	(18)	(29)	
O (11)	−2588	−1448	961	81	220	72	−46	22	6	5.56
	(13)	(24)	(12)	(13)	(45)	(11)	(20)	(9)	(19)	
O (12)	−2250	1516	940	77	150	110	5	9	21	6.11
	(13)	(24)	(14)	(13)	(24)	(14)	(19)	(10)	(20)	
O (13)	−1387	4142	721	53	203	113	17	−9	−11	6.07
	(12)	(23)	(14)	(10)	(43)	(14)	(18)	(10)	(21)	
C (11′)	411	1752	−100	43	143	45	−59	1	18	3.35
	(14)	(29)	(13)	(13)	(55)	(12)	(21)	(10)	(20)	
C (12′)	963	283	−369	46	120	41	−31	−5	1	3.12
	(15)	(29)	(14)	(12)	(47)	(10)	(22)	(10)	(20)	
C (13′)	601	−1384	−313	65	176	38	−6	−13	39	3.86
	(17)	(33)	(15)	(15)	(58)	(10)	(24)	(10)	(21)	
C (14′)	1982	215	−732	70	292	55	−16	−9	11	5.34
	(18)	(38)	(17)	(19)	(76)	(14)	(31)	(13)	(30)	
C (15′)	1404	−2600	−626	66	156	41	−2	−15	−15	3.83
	(17)	(31)	(15)	(16)	(55)	(11)	(24)	(11)	(23)	
O (11′)	2592	1374	−956	65	215	121	−8	−14	64	6.66
	(12)	(25)	(14)	(12)	(49)	(16)	(21)	(11)	(23)	
O (12′)	2222	−1632	−911	77	190	66	2	−23	−41	5.08
	(12)	(23)	(11)	(12)	(42)	(10)	(19)	(9)	(18)	
O (13′)	1470	−4189	−735	143	263	49	21	−2	−12	6.54
	(16)	(25)	(12)	(19)	(50)	(10)	(26)	(11)	(18)	
C (1)	11	7591	2513	85	290	26	−26	−5	−29	4.78
	(54)	(51)	(54)	(31)	(120)	(17)	(106)	(19)	(80)	
C (2)	−753	8956	2809	26	324	16	3	−46	32	3.45
	(33)	(68)	(30)	(21)	(131)	(16)	(39)	(17)	(36)	
C (3)	−552	602	2731	52	257	65	−52	−11	19	5.00
	(36)	(74)	(33)	(30)	(140)	(28)	(54)	(24)	(50)	
C (4)	373	1401	2380	123	115	57	73	−29	0	5.25
	(28)	(59)	(30)	(50)	(110)	(28)	(56)	(32)	(50)	
C (5)	1076	269	2111	91	121	48	−12	32	51	4.33
	(32)	(62)	(28)	(39)	(114)	(24)	(53)	(25)	(45)	
C (6)	962	8274	2135	83	571	16	−47	16	−91	6.52
	(36)	(71)	(32)	(34)	(201)	(18)	(72)	(20)	(52)	
C (7)	−78	5751	2734	358	697	73	9	−72	−48	15.15
	(36)	(55)	(30)	(48)	(143)	(13)	(54)	(20)	(27)	
C (1′)	106	2346	2373	135	208	26	15	−25	24	5.27
	(39)	(66)	(52)	(52)	(113)	(30)	(90)	(31)	(50)	
C (2′)	−783	1681	2664	106	162	37	−89	−5	−2	4.62
	(38)	(66)	(29)	(43)	(125)	(23)	(58)	(25)	(43)	
C (3′)	−963	−123	2686	61	256	28	20	−19	32	4.07
	(32)	(70)	(25)	(30)	(131)	(19)	(51)	(20)	(43)	
C (4′)	−130	−1389	2489	158	279	44	47	−28	−32	6.83
	(80)	(72)	(60)	(68)	(134)	(23)	(109)	(33)	(86)	
C (5′)	882	−675	2271	81	300	32	−40	25	−66	4.95
	(35)	(72)	(29)	(39)	(157)	(21)	(61)	(24)	(46)	
C (6′)	999	1169	2236	13	89	55	53	11	−79	2.60
	(24)	(54)	(27)	(18)	(97)	(22)	(33)	(16)	(38)	
C (7′)	399	4409	2316	217	634	53	−142	−27	−6	11.01
	(39)	(66)	(37)	(27)	(115)	(13)	(40)	(17)	(28)	

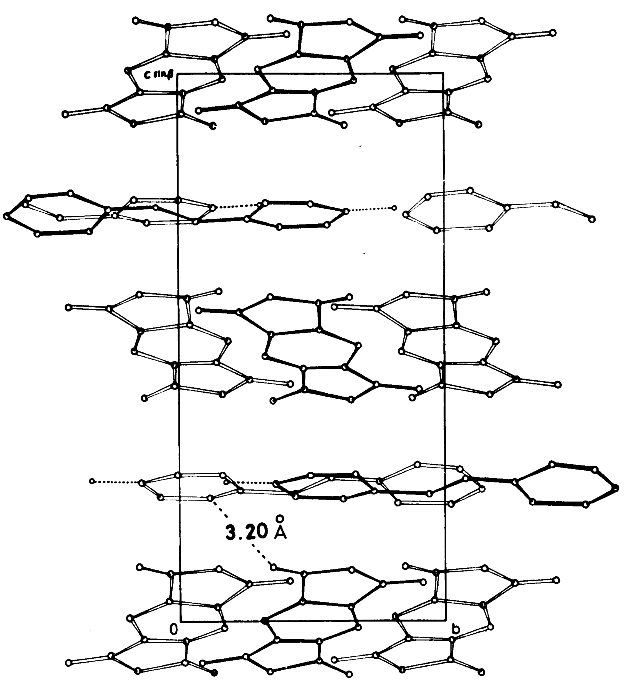

Fig. 3. The projection of the crystal structure viewed along the *a* axis. The molecules in thick lines are related to those in thin lines by the symmetry operation of C-face center.

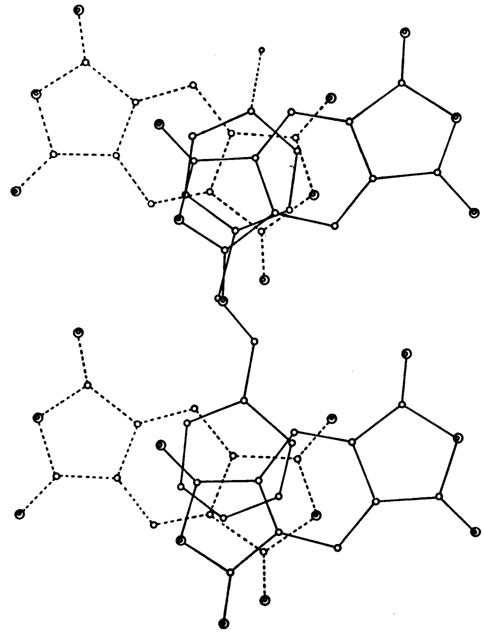

Fig. 4. The molecular arrangement of the component molecules of the PMDA-ME-STB complex projected perpendicular to the plane $(10\bar{2})$. The benzene ring planes of the ME-STB molecule contact the PMDA molecules in solid and dotted lines on both sides.

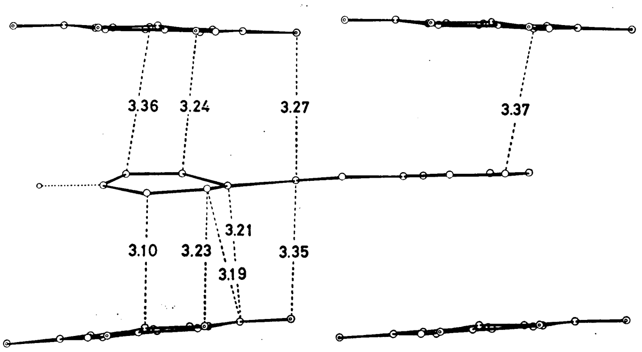

Fig. 5. Intermolecular contacts between PMDA and ME-STB with intermolecular distances shorter than 3.40 Å in Å units.

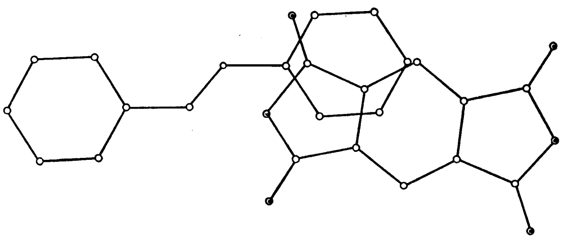

Fig. 6. The molecular arrangement of the component molecules of the PMDA-STB complex.

different from that of the STB complex,[1] which is shown in Fig. 6. The long axes of the component molecules are perpendicular to each other in the ME-STB complex, whereas they are parallel in the STB complex. Thus, the molecular arrangement of the component molecules was shown to be easily changed in the crystalline state by the slight geometrical difference between the ME-STB and the STB molecules. The difference in the molecular ratio of the component molecules between the 2:1 PMDA-ME-STB complex and the equimolar PMDA-STB complex corresponds to the difference in the molecular stacking; in the ME-STB complex both sides of the benzene ring planes of the ME-STB molecule are in contact with PMDA molecules, whereas in the STB complex only one side of the ring is in contact with a PMDA molecule. Because of the distinct difference in the overlapping geometry, the stacking axis of the component molecules is approximately perpendicular to the PMDA plane in the ME-STB complex, but is inclined about 39° against the PMDA plane in the STB complex. The ethylene group of the ME-STB molecule

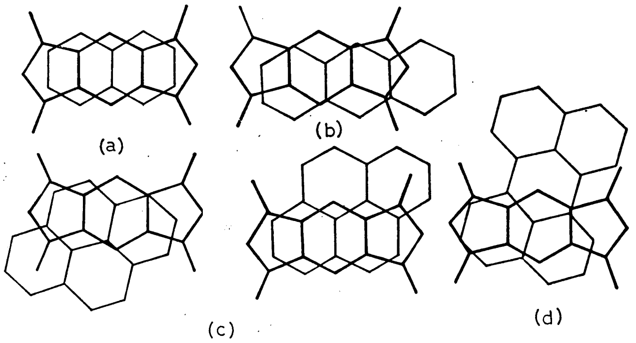

Fig. 7. The molecular arrangements of the component molecules of the complexes of PMDA with (a) naphthalene,[6] (b) anthracene,[2] (c) pyrene,[3] and (d) perylene.[2] Two independent molecular arrangements exist in PMDA-pyrene complex as shown in the figure.

of the ME–STB complex lies halfway between two columns and joins them, but that of the STB molecule of the STB complex lies within a column.

No theoretical consideration of the molecular arrangement of the component molecules of a series of CT complexes containing PMDA as an acceptor has hitherto been reported, but considerations of complexes containing maleic anhydride as an acceptor have been reported by Kobayashi *et al.*[5] The most stable molecular arrangements predicted in view of the CT interaction are consistent with those experimentally found in complexes of PMDA with perylene[2] and pyrene[3] (as is shown in Fig. 7). In view of the CT interaction, the molecular arrangement of the ME–STB complex seems to be more stable than that of the STB complex.

The PMDA molecule is planar within the maximum deviation of 0.007 Å of the atoms from the mean molecular plane. Moreover the benzene ring plane formed by C(1),⋯C(6) and that formed by C(1′),⋯C(6′) of the ME–STB molecule are planar within the maximum deviations of 0.01 and 0.06 Å respectively. The three molecular planes are expressed by the following equations, in the order mentioned above:

$$0.416x - 0.071y + 0.907z = 0.024 \qquad (1)$$

$$0.41x - 0.01y + 0.91z = 3.39 \qquad (2)$$

$$0.27x + 0.03y + 0.96z = -3.56 \qquad (3)$$

where x, y, and z are coordinates (in Å) with respect to the a, b, and c crystal axes respectively. The (2) plane makes angles of 4.1 and 4.4° with the planes of the PMDA molecules within a column, with the average interplanar distances of 3.42 and 3.41 Å. The (3) plane makes angles of 10.7 and 9.7° with the planes of the PMDA molecules within a column, with the average interplanar distances of 3.52 and 3.56 Å.

The average intermolecular distances, the angles between the overlapping planes, and the C=O bond lengths of the CT complexes containing PMDA as an acceptor are shown in Table 2. The average intermolecular distance between the component molecules of the STB complex is the longest. The C=O bond lengths of a series of the complexes containing PMDA as an acceptor seem to tend to be shorter as the average intermolecular distances between the component molecules become longer.

The bond lengths and angles of the component molecules are shown in Figs. 8 and 9; they are also listed, along with the standard deviations, in Table 3. The ME–STB molecule is not planar, and the two benzene rings of the ME–STB molecule are twisted with an angle of 9°. A detailed structural discussion of the component molecules cannot be done because of the large standard deviations.

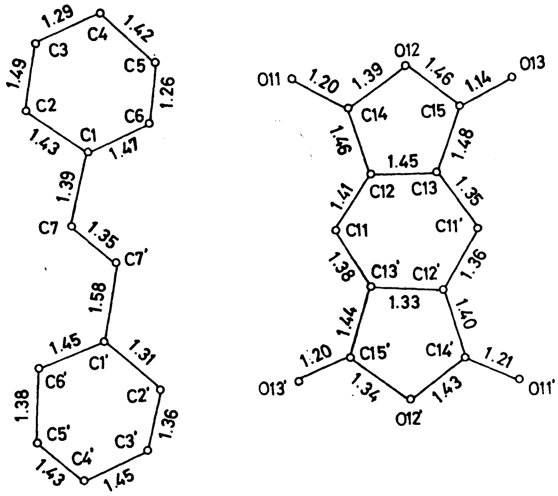

Fig. 8. Bond lengths (Å).

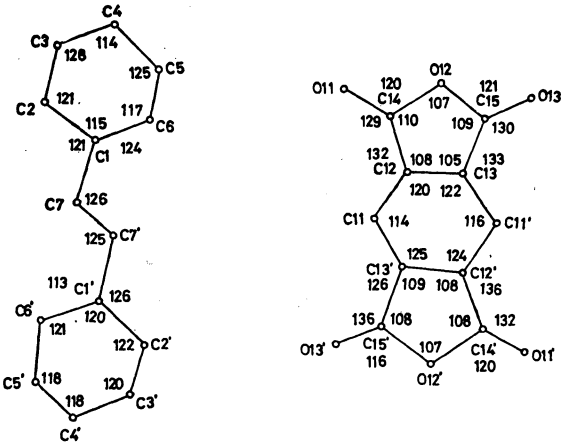

Fig. 9. Bond angles (degrees).

Description of the Disordered Crystal Structure. The observed diffuse reflections with indices of $k+1/2$ are elongated along $[10\bar{2}]$; that is, they are perpendicular to the molecular layers. Therefore, they can be explained if we assume that the stacking sequence of the molecular layers contains such mistaken layers that are shifted from the normal positions by half the $b'(b'=2b)$ axis. One of the models of the disordered crystal structure of this complex is shown schematically in Fig. 10. Although the inter-layer arrangement of the component molecules remains practically unchanged,

Table 2. The average intermolecular distances, the angles between the overlapping planes and the C=O bond lengths of the charge transfer complexes containing PMDA as an acceptor

Donor	STB	ME-STB		Pyrene (110 K)		Perylene
Average interplanar spacing (Å)	3.58	3.41	3.42	3.33	3.30	3.33
		3.56	3.25			
Angle between the molecular planes (°)	4.8	4.4	4.0	1.34	1.18	0.82
		9.7	10.7			
C=O Bond length (Å)	1.181	1.20	1.14	1.197	1.195	1.23
	1.188	1.20	1.12	1.191	1.190	1.18
	±0.009	±0.04		±0.006		±0.01

Table 3. Bond lengths and angles and their standard deviations

PMDA			
C(11)–C(12)	1.41(0.04)Å	C(13′)–C(11)–C(12)	114(1)°
C(11)–C(13′)	1.38(0.04)	C(11)–C(12)–C(13)	120(2)
C(12)–C(13)	1.45(0.04)	C(11)–C(12)–C(14)	132(2)
C(12)–C(14)	1.46(0.04)	C(13)–C(12)–C(14)	108(2)
C(13)–C(15)	1.48(0.05)	C(12)–C(13)–C(11′)	122(1)
C(13)–C(11′)	1.35(0.03)	C(12)–C(13)–C(15)	105(2)
C(14)–O(11)	1.20(0.04)	C(15)–C(13)–C(11′)	133(2)
C(14)–O(12)	1.39(0.04)	C(12)–C(14)–O(11)	129(2)
C(15)–O(12)	1.46(0.04)	C(12)–C(14)–O(12)	110(2)
C(15)–O(13)	1.14(0.04)	O(11)–C(14)–O(12)	120(2)
C(11′)–C(12′)	1.36(0.04)	C(13)–C(15)–O(12)	109(1)
C(12′)–C(13′)	1.33(0.04)	C(13)–C(15)–O(13)	130(3)
C(12′)–C(14′)	1.40(0.04)	O(12)–C(15)–O(13)	121(3)
C(13′)–C(15′)	1.44(0.04)	C(14)–O(12)–C(15)	107(2)
C(14′)–O(11′)	1.21(0.04)	C(13)–C(11′)–C(12′)	116(1)
C(14′)–O(12′)	1.43(0.04)	C(11′)–C(12′)–C(13′)	124(2)
C(15′)–O(12′)	1.34(0.03)	C(11′)–C(12′)–C(14′)	136(1)
C(15′)–O(13′)	1.20(0.04)	C(13′)–C(12′)–C(14′)	108(2)
		C(11)–C(13′)–C(12′)	125(2)
		C(11)–C(13′)–C(15′)	126(2)
		C(12′)–C(13′)–C(15′)	109(2)
		C(12′)–C(14′)–O(11′)	132(2)
		C(12′)–C(14′)–O(12′)	108(2)
		O(11′)–C(14′)–O(12′)	120(2)
		C(13′)–C(15′)–O(12′)	108(1)
		C(13′)–C(15′)–O(13′)	136(2)
		O(12′)–C(15′)–O(13′)	116(2)
		C(14′)–O(12′)–C(15′)	107(2)
ME-STB			
C(1)–C(2)	1.43(0.11)	C(2)–C(1)–C(6)	115(3)
C(1)–C(6)	1.47(0.09)	C(7)–C(1)–C(2)	121(4)
C(1)–C(7)	1.39(0.13)	C(7)–C(1)–C(6)	124(6)
C(2)–C(3)	1.49(0.10)	C(1)–C(2)–C(3)	121(7)
C(3)–C(4)	1.29(0.08)	C(2)–C(3)–C(4)	128(4)
C(5)–C(6)	1.26(0.09)	C(3)–C(4)–C(5)	114(3)
C(4)–C(5)	1.42(0.08)	C(4)–C(5)–C(6)	125(4)
C(7)–C(7′)	1.35(0.18)	C(1)–C(6)–C(5)	117(5)
C(1′)–C(7′)	1.58(0.12)	C(1)–C(7)–C(7′)	126(14)
C(1′)–C(2′)	1.31(0.11)	C(7)–C(7′)–C(1)	125(9)
C(1′)–C(6′)	1.45(0.10)	C(2′)–C(1′)–C(6′)	120(3)
C(2′)–C(3′)	1.36(0.09)	C(7′)–C(1′)–C(2′)	126(5)
C(3′)–C(4′)	1.45(0.12)	C(7′)–C(1′)–C(6′)	113(6)
C(4′)–C(5′)	1.43(0.13)	C(1′)–C(2′)–C(3′)	122(5)
C(5′)–C(6′)	1.38(0.08)	C(2′)–C(3′)–C(4′)	120(4)
		C(3′)–C(4′)–C(5′)	118(3)

and although, moreover, the PMDA molecules are stacked regularly, the ethylene groups of the ME–STB molecules are randomly exchanged by the methyl groups and the hydrogens attached to C(4) of the neighboring ME–STB molecules. Since approximately equal electron densities were observed at the C(7) and C(7′) positions, the –CH=CH– ethylene groups are probably exchanged not only by the $-CH_3\cdots H-$ atomic groups, but also by the $-H\cdots CH_3-$ atomic groups which correspond to the upside-down arrangement of the ME–STB molecules. Such a random arrangement is probable because the forces between the layers are weaker than the forces within each layer and because the sizes of the –CH=CH– and $-CH_3\cdots H-$ atomic groups are similar. Such a geometric resemblance is considered to play an important role in the present type of disorder. No similar type of disorder was observed in the crystal of the PMDA–STB complex, which possesses no methyl group.

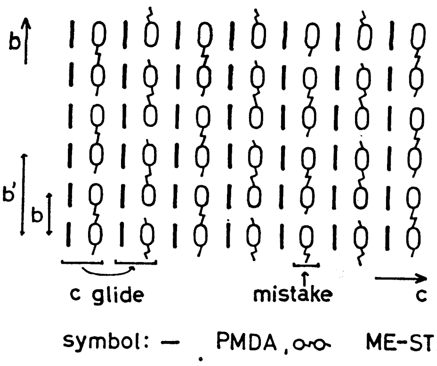

Fig. 10. Diagram showing the arrangement of molecules parallel to (100) described one of the models of the disordered structure.

The calculations were carried out on the HITAC 5020E computer at the Computer Centre of the University of Tokyo. The authors wish to express their thanks to Professor Yoshihiko Saito, the University of Tokyo, and Professor Fumiyuki Marumo, Tokyo Institute of Technology, for their helpful discussions.

References and Notes

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