The Crystal and Molecular Structure of Dimethyl
m-Phenylenediacrylate

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Photooligomerizable crystals of dimethyl m-phenylenediacrylate are orthorhombic, $Pmn2_1$, with $a=26.419(8)$, $b=3.960(1)$, $c=5.935(2)$ Å, and $Z=2$. The structure was solved by the direct method and refined by the block-diagonal least-squares calculation to the R value of 0.042 for 617 observed reflections. The molecule is nearly planar and V-shaped with a mirror symmetry. A parallel plane-to-plane stack is found along the short b-axis. The molecules in the stack overlap completely, in contrast with the half-molecule overlap in the photopolymerizable crystals of this kind. The length of the b-axis is just the shortest intermolecular distance between reactive double bonds, indicating that the double bonds related by the b-translation would react to form a cyclobutane ring with a mirror symmetry.

Many diolefinic compounds undergo the four-center type photopolymerization in the crystalline state.[1] In the serial studies on the photopolymerizable crystals,[2] we have shown that all the photopolymerizable diolefins with p-phenylene moiety change, under the strict control of monomer crystal lattice, into crystalline polymers containing cyclobutane rings with the center of symmetry.

In contrast, dimethyl m-phenylenediacrylate (m-PDAMe) has been found to give amorphous oligomer having more than two kinds of cyclobutane rings with respect to steric configuration, by prolonged irradiation. At the lower reaction temperature, the dimer with a regular conformation of cyclobutane ring is formed in better yield.[3] From such results, a two-step reaction mechanism, i.e., topochemical dimer formation in a regular crystal lattice and subsequent random cycloaddition in a disordered crystal lattice, was proposed previously.[3] The present crystal structure analysis has been undertaken in order to clarify the mechanism of such characteristic oligomer formation.

Experimental

m-PDAMe was synthesized according to the method described in the previous paper.[4] Plate-shaped crystals were grown from a methanol solution by slow evaporation. The specimen used was a fragment of a plate, $0.15 \times 0.15 \times 0.10$ mm in size. The space group was determined from photographs. The precise lattice constants and intensity data were obtained from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromatized Cu $K\alpha$ radiation. All reflections within the range of $2\theta < 150°$ were collected by use of 2θ-ω scan mode with the scanning rate of $4°$ min^{-1}. Stationary background counts were accumulated for 10 s before and after each scan. Out of 681 reflections, 617 were greater than $3\sigma(|F_o|)$ and were used for structure determination. No correction was made for absorption. Crystallographic data of m-PDAMe are: $C_{14}H_{14}O_4$, M. W. 246.3. Orthorhombic, $Pmn2_1$, $a=26.419(8)$, $b=3.960(1)$, $c=5.935(2)$ Å, $U=620.9$ Å^3. $Z=2$, $Dx=1.318$, $Dm=1.320$ g cm^{-3}. μ(Cu $K\alpha$)$=9.30$ cm^{-1}.

Determination and Refinement
of the Structure

The space group and Z indicated that the molecule has a mirror symmetry. The structure was solved by the direct method with MULTAN.[5] All the non-hydrogen atoms were clearly located in the E map computed with the best set of phases. The parameters were refined by the block-diagonal least-squares method using $\omega=0.5$ for $|F_o| \leq 1.0$, 1.0 for $|F_o| > 1.0$. Isotropic hydrogen atoms were first located geometrically and then refined. The final R value was 0.042.* Atomic scattering factors were taken from International Tables for X-Ray Crystallography (1962). Final atomic coordinates and thermal parameters are given in Table 1.

Results and Discussion

Bond Lengths and Angles. The molecular structure and the numbering system used are shown in Fig. 1. The structure is compared with those of related compounds[6-10] in Table 2, where abbreviations of the compounds are also given.

Close resemblance is found among the molecular dimensions of m-PDAMe, p-phenylenediacrylic acid (p-PDA) derivatives and the corresponding half of
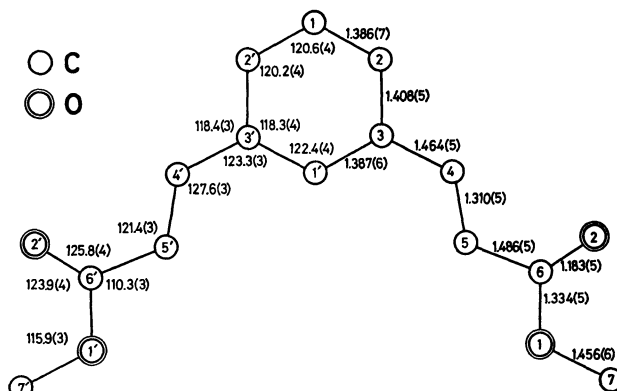

Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.

TABLE 1. ATOMIC PARAMETERS

(a) Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms.

	x	y	z		x	y	z
C(1')	0(0)	4733(11)	5694(8)	C(5)	1034(1)	6243(9)	3736(6)
C(1)	0(0)	1446(14)	9801(9)	C(6)	1557(1)	6958(9)	2944(6)
C(2)	456(1)	2293(8)	8791(6)	O(1)	1547(1)	8239(7)	865(5)
C(3)	460(1)	3937(8)	6687(6)	O(2)	1933(1)	6437(8)	3968(6)
C(4)	950(1)	4812(9)	5691(6)	C(7)	2036(2)	9125(11)	−98(8)

(b) Thermal parameters for non-hydrogen atoms ($\times 10^3$). The anisotropic thermal parameters are described by $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1')	1.33(6)	47(3)	21.0(13)	−0.0(0)	−0.0(0)	5(4)
C(1)	1.66(8)	70(4)	25.1(15)	−0.0(0)	−0.0(0)	17(5)
C(2)	1.67(5)	55(2)	24.5(10)	1.0(6)	−2.2(4)	6(3)
C(3)	1.26(4)	47(2)	22.2(9)	0.3(5)	−0.2(4)	0(3)
C(4)	1.11(4)	63(2)	28.5(11)	1.4(6)	−1.4(4)	1(3)
C(5)	1.08(4)	69(2)	25.8(10)	0.7(6)	−0.9(4)	1(3)
C(6)	1.19(4)	67(2)	30.6(11)	0.4(6)	0.6(4)	−0(3)
O(1)	1.13(3)	112(2)	29.6(8)	−0.9(5)	1.5(3)	20(3)
O(2)	1.09(3)	147(3)	42.2(10)	−0.6(6)	−1.9(3)	34(4)
C(7)	1.53(6)	113(4)	40.9(15)	−2.5(9)	4.8(5)	27(5)

(c) Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms. The bond lengths to the attached carbons are also given.

	x	y	z	B (Å^2)	C–H (Å)
H(C1')	0(0)	622(13)	442(10)	3.2(13)	0.96(6)
H(C1)	0(0)	−22(16)	1118(11)	4.5(15)	1.05(6)
H(C2)	80(1)	173(8)	951(5)	1.3(7)	1.03(3)
H(C4)	124(1)	431(10)	654(7)	4.1(10)	0.93(4)
H(C5)	77(1)	670(10)	271(7)	3.6(10)	0.95(4)
H(C7)1	198(2)	1038(12)	−149(8)	6.8(13)	0.98(5)
H(C7)2	227(1)	709(9)	−15(7)	2.8(8)	1.02(4)
H(C7)3	219(1)	1114(11)	113(7)	5.4(12)	1.16(4)

TABLE 2. BOND LENGTHS (Å) AND ANGLES (°) OF m-PDAMe AND RELATED COMPOUNDS

	p-PDAMe[a]	p-PDAEt[b]	p-PDAPh[c]	HNCMe[d]	CVCCMe[e]	m-PDAMe[f]
C1'–C3	1.385(4)	1.388(3)	1.399(9)	1.386(3)	1.397(8)	1.387(6)
C2–C3	1.391(4)	1.388(3)	1.387(9)	1.398(3)	1.419(9)	1.408(5)
C3–C4	1.463(4)	1.466(3)	1.468(9)	1.468(3)	1.478(8)	1.464(5)
C4–C5	1.330(4)	1.316(3)	1.325(3)	1.308(4)	1.306(9)	1.310(5)
C5–C6	1.476(4)	1.479(3)	1.468(9)	1.471(3)	1.476(9)	1.486(5)
C6–O2	1.194(4)	1.197(3)	1.182(8)	1.188(3)	1.207(8)	1.183(5)
C6–O1	1.335(4)	1.332(3)	1.368(8)	1.341(3)	1.329(8)	1.334(5)
O1–C7	1.443(4)	1.461(3)	1.412(8)	1.442(4)	1.443(9)	1.456(6)
C1'–C3–C2	117.9(3)	118.0(2)	117.4(6)	117.6(2)	118.0(5)	118.3(4)
C2–C3–C4	118.8(2)	118.7(2)	119.7(6)	119.6(2)	119.1(5)	118.4(3)
C1'–C3–C4	123.3(3)	123.3(2)	122.9(6)	122.8(2)	122.9(5)	123.3(3)
C3–C4–C5	127.2(3)	127.2(2)	125.9(6)	126.4(2)	127.5(6)	127.6(3)
C4–C5–C6	119.3(3)	120.4(2)	119.6(6)	121.6(2)	120.0(6)	121.4(3)
C5–C6–O1	110.8(2)	110.9(2)	108.8(5)	111.0(2)	110.9(5)	110.3(3)
C5–C6–O2	126.0(3)	125.2(2)	127.3(6)	126.4(2)	125.7(6)	125.8(4)
O1–C6–O2	123.2(3)	123.9(2)	123.9(6)	122.6(2)	123.4(6)	123.9(4)
C6–O1–C7	115.0(2)	115.5(2)	117.6(5)	116.4(2)	116.6(5)	115.9(3)
θ_1[g]	2.2	6.0	−15.9	1.4	5.1	3.4
θ_2[h]	7.2	10.9	10.8	1.5	3.3	3.5
θ_3[i]	1.0	5.0	65.0	0.9	2.0	1.3
Ref.	6	7	8	9	10	This work

a) p-Phenylenediacrylic acid dimethyl ester. b) p-Phenylenediacrylic acid diethyl ester. c) p-Phenylenediacrylic acid diphenyl ester. d) Methyl 4-hydroxy-3-nitrocinnamate. e) 4-(β-Carboxyvinyl)-α-cyanocinnamic acid dimethyl ester. f) m-Phenylenediacrylic acid dimethyl ester. g) The internal rotation (°) around the bond C(3)–C(4). h) The internal rotation around C(5)–C(6). i) The rotation around C(6)–O(1).

TABLE 3. DEVIATIONS (Å, ×10³) OF ATOMS FROM SOME LEAST-SQUARES PLANES

The equation of the plane is expressed in the form of $AX+BY+CZ+D=0$, where X, Y, and Z are in Å referred to orthogonal axes, a, b, and c*.

	P(I)[a]	P(II)	P(III)	P(IV)[a]	P(V)[a]
A	0	40	52	0	0
B	−884	−900	−921	−888	−890
C	−468	−433	−386	−460	−456
D	3238	3077	2991	3252	3215
C(1′)	−0	−74[b]		8	6
C(1)	9	42[b]		43	52
C(2)	−7			21	27
C(3)	2			16	17
C(4)		−2	65[b]	−19	−21
C(5)		−2	2	11	4
C(6)		2	−5	−25	−34
O(1)		79[b]	2	92	78
O(2)		−36[b]	2	−121	−127
C(7)			−33[b]		26

a) For these planes, the equivalent atoms which are related by the mirror symmetry have also been included in the plane evaluation. b) The atoms are not included in the plane evaluation.

CVCCMe: all the bond lengths and angles other than the double bond lengths of six esters in Table 2 are nearly identical within 3σ.

Planarity and Conformation. The equations of mean planes and the displacements of atoms from each plane are given in Table 3. The benzene ring, ethylene and carbonyl groups are planar. Referring to the benzene ring, the ethylenic plane rotates by 3.4° (θ_1 in Table 2) about C(3)–C(4), and the carbonyl by 3.5° (θ_2) about C(5)–C(6) in the same direction. The methyl group rotates by only 1.5° (θ_3) about O(1)–C(7). Thus, the molecule as a whole is nearly planar within the deviation of 0.127 Å from the mean plane; the maximum deviation is found at O(2).

The carbonyl oxygen atom with lone pair electrons is situated at the same side as the ethylenic double bond with respect to the intervening single bond C(5)–C(6), so that the lone pair electrons extend parallel to the double bond. This is also the case of photopolymerizable diolefins,[7] and suggests that the electronic interaction between lone pair and π electrons (especially of ethylenic double bond) is operative for taking the present conformation in preference to the alternative one where the carbonyl group is at the opposite side.

According to the discussion in the previous paper,[7] the internal rotation (θ_2) around C(5)–C(6) should be near 10° in this type of conjugated system. However, θ_2 of *m*-PDAMe is considerably small compared with those of the photopolymerizable diolefins. Such small θ_2 is also found in CVCCMe and HNCMe (Table 2). This may be due to intermolecular repulsion, since molecules in these three crystals are piled up along the short crystal axis as will be described below.

Crystal Structure and Reaction Mechanism. The crystal structure viewed along the b-axis is shown in Fig. 2. The molecules are piled up along the shortest
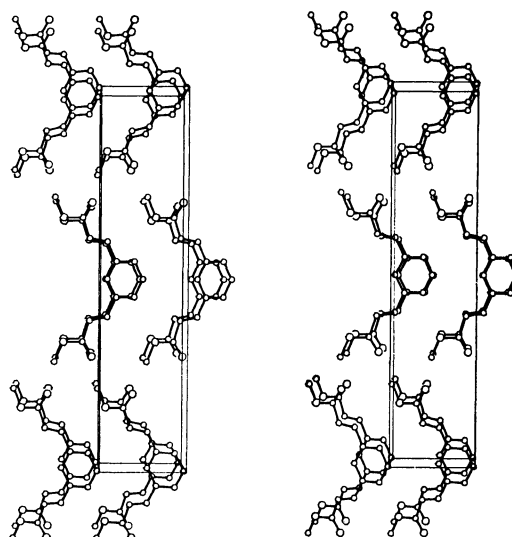

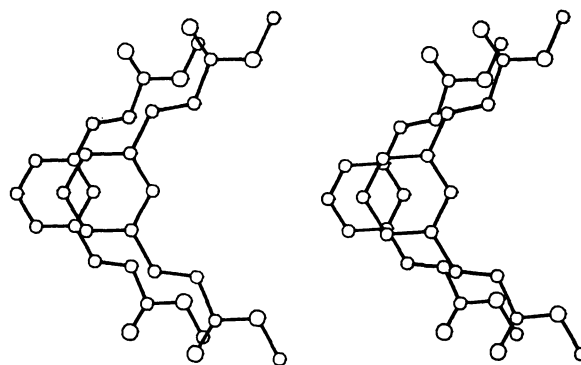Fig. 2. A stereoview of the crystal structure viewed along the b-axis.

Fig. 3. A stereoview of the overlapping of molecules to react, viewed along the normal of the mean plane of the molecule.

crystal axis (b-axis) to form a parallel plane-to-plane stack. As seen from Fig. 3, the adjacent molecules in the stack overlap completely to each other. The same type of stack is also found in CVCCMe, another photo-oligomerizable crystal having the shortest crystal axis of 3.956 Å.[10] This stack is quite different from that in the photopolymerizable crystals where molecules are piled up along about 7 Å axis, displaced by half a molecule in the direction of the molecular long axis,[7] and also from the layer-type packing of the photostable modification of 2,5-distyrylpyrazine where molecules in the adjacent layers do not overlap at all.[11]

The length of the b-axis is just the shortest inter-molecular distance between reactive double bonds, which is very close to those found in the photopoly-merizable crystals (3.94 Å on the average). The second shortest distance, longer than 5 Å, is found between the molecules in different stacks (related by the two-fold screw axis) (Table 4).

The most plausible explanation for the reaction behavior,[3] on the basis of the crystal structure, is as follows. At the initial stage of photoirradiation, the molecules related by the b-translation react topo-

TABLE 4.   INTERMOLECULAR DISTANCE (Å)
BETWEEN DOUBLE BONDS

$C(4^i) \cdots C(4^{ii})$	3.960	$C(5^i) \cdots C(4'^{iv})$	9.986
$C(4^i) \cdots C(5^{ii})$	4.679	$C(5^i) \cdots C(5'^{iv})$	9.657
$C(5^i) \cdots C(4^{ii})$	3.593	$C(4^i) \cdots C(4'^{v})$	9.510
$C(5^i) \cdots C(5^{ii})$	3.960	$C(4^i) \cdots C(5'^{v})$	9.986
$C(4^i) \cdots C(4'^{ii})$	6.392	$C(5^i) \cdots C(4'^{v})$	9.270
$C(4^i) \cdots C(5'^{ii})$	7.021	$C(5^i) \cdots C(5'^{v})$	9.657
$C(5^i) \cdots C(4'^{ii})$	6.350	$C(4^i) \cdots C(4'^{vi})$	8.714
$C(5^i) \cdots C(5'^{ii})$	6.747	$C(4^i) \cdots C(5'^{vi})$	8.182
$C(4^i) \cdots C(4^{iii})$	7.135	$C(5^i) \cdots C(4'^{vi})$	8.984
$C(4^i) \cdots C(5^{iii})$	8.419	$C(5^i) \cdots C(5'^{vi})$	8.354
$C(5^i) \cdots C(4^{iii})$	5.862	$C(4^i) \cdots C(4'^{vii})$	8.714
$C(5^i) \cdots C(5^{iii})$	7.135	$C(4^i) \cdots C(5'^{vii})$	8.984
$C(4^i) \cdots C(4'^{iv})$	9.510	$C(5^i) \cdots C(4'^{vii})$	8.182
$C(4^i) \cdots C(5'^{iv})$	9.270	$C(5^i) \cdots C(5'^{vii})$	8.354

Symmetry code:
Superscript

i	x	y	z
ii	x	$1+y$	z
iii	x	y	$-1+z$
iv	$1/2-x$	$-y$	$1/2+z$
v	$1/2-x$	$-y$	$-1/2+z$
vi	$1/2-x$	$1-y$	$1/2+z$
vii	$1/2-x$	$1-y$	$-1/2+z$

chemically to form the dimer having a cyclobutane ring with a mirror symmetry. The cyclobutane ring formation in one wing of the molecular pair makes large the distance between the double bonds in the other wing. The dimerization of this type probably destroys the regular arrangement of surrounding monomers. The subsequent reaction between the dimer and its neighbor in the disordered crystal lattice results in amorphous oligomer having more than two kinds of cyclobutane rings. The rate of the reaction should be smaller than

that of the initial dimerization with topochemical assistance. Such reaction in the disordered lattice will be more favorable at higher temperature. Thus, the reaction mechanism proposed previously[3] is supported by the present structural study.

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