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p-Phenylenediacrylic Acid Dimethyl Ester (*p*-PDAMe), a Photopolymerizable Crystal

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Abstract. $C_{14}H_{14}O_4$, M_r = 246·3, triclinic, $P\bar{1}$, a = 7·148 (3), b = 8·382 (2), c = 5·844 (2) Å, α = 94·97 (3), β = 116·85 (2), γ = 78·06 (3)°, Z = 1, D_x = 1·339, D_m = 1·330 g cm^{-3}. The molecules are nearly planar and are piled up along the a axis, displaced in the direction of the molecular long axis, to form a parallel plane-to-plane stack. In the stack, double bonds related by a centre of symmetry have a closest approach of 3·937 Å.

Introduction. *p*-PDAMe is photopolymerized in the crystalline state to give a linear polymer containing a cyclobutane ring in the main chain; its reduced viscosity is often as high as 3 m^3 kg^{-1} (Suzuki, Suzuki, Nakanishi & Hasegawa, 1969). The crystal structure analysis of *p*-PDAMe was undertaken as part of the crystallographic studies on such four-centre-type photopolymerization (Nakanishi, Ueno & Sasada, 1976).

p-PDAMe was synthesized according to Suzuki *et al.* (1969). Colourless prism-like crystals were grown from a methanol solution by slow evaporation. The specimen used was 0·20 × 0·30 × 0·40 mm. The precise lattice constants and intensity data were obtained from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. All reflexions within the range $2\theta < 60°$ were collected with the 2θ–ω scan mode and a scanning rate of 4° min^{-1}. Stationary background counts were accumulated for 15 s before and after each scan. Of 1785 reflexions, 1071 were greater than $3\sigma(|F_o|)$ and were used for the structure determination. No correction was made for absorption (μ = 1·16 cm^{-1}).

The structure was solved by conventional Patterson and Fourier techniques in space group $P\bar{1}$. The parameters were refined by the block-diagonal least-squares method using $w = 0·5$ for $|F_o| \leq 1·0$, 1·0 for $|F_o| > 1·0$. The H atoms were located in a difference Fourier map and all the parameters were then refined by the full-matrix least-squares method using the weighting scheme described above. The final R value was 0·057.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates are given in Table 1.

Table 1. *Fractional atomic coordinates* (×10^4 *for* C, O; ×10^3 *for* H)

Estimated standard deviations are in parentheses.

	x	y	z
C(1)	9145 (4)	1539 (3)	−1049 (4)
C(2)	9278 (4)	−558 (3)	1544 (5)
C(3)	8386 (3)	996 (2)	498 (4)
C(4)	6707 (3)	2087 (3)	955 (4)
C(5)	5771 (3)	1770 (3)	2336 (4)
C(6)	4133 (3)	3048 (3)	2630 (4)
O(1)	3560 (3)	2584 (2)	4312 (3)
O(2)	3395 (3)	4336 (2)	1546 (4)
C(7)	1989 (5)	3768 (4)	4769 (7)
H(C1)	857 (4)	262 (3)	−176 (4)
H(C2)	880 (4)	−98 (3)	262 (5)
H(C4)	628 (4)	314 (3)	17 (4)
H(C5)	605 (4)	63 (3)	332 (5)
H(C7)1	261 (5)	482 (4)	548 (6)
H(C7)2	182 (6)	332 (4)	601 (7)
H(C7)3	66 (6)	396 (4)	307 (7)

Discussion. The molecular structure and the numbering system used are shown in Fig. 1. The bond lengths and angles are similar to those in related compounds (Leiserowitz & Schmidt, 1965; Hanson, 1975). The benzene ring, and ethylene and carbonyl groups are planar.* The benzene ring rotates 2·2° about C(3)—C(4) from the ethylenic plane, and the carbonyl rotates 7·2° about C(5)—C(6) in the same direction. Thus, the molecular skeleton consisting of these three groups is nearly planar (to within a deviation of 0·08 Å from the mean plane).

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* Lists of structure factors, thermal parameters and deviations of atoms from some least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33376 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

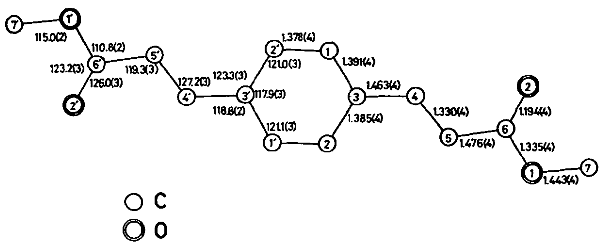

Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.

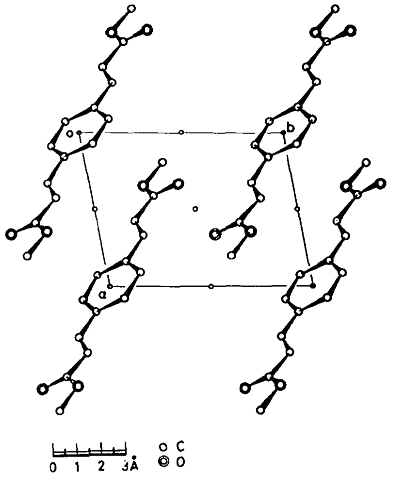

Fig. 2. The crystal structure viewed along the *c* axis.

Table 2. *Intermolecular distances* (Å) *between double bonds*

$C(4^{i})\cdots C(4'^{ii})$	4·453	$C(5^{i})\cdots C(4^{iv})$	4·763
$C(4^{i})\cdots C(5'^{ii})$	3·937	$C(4^{i})\cdots C(4'^{v})$	7·574
$C(5^{i})\cdots C(5'^{ii})$	3·834	$C(4^{i})\cdots C(5'^{v})$	6·309
$C(4^{i})\cdots C(4'^{iii})$	4·960	$C(5^{i})\cdots C(5'^{v})$	5·076
$C(4^{i})\cdots C(5'^{iii})$	5·312	$C(4^{i})\cdots C(4'^{vi})$	7·325
$C(5^{i})\cdots C(5'^{iii})$	5·947	$C(4^{i})\cdots C(5'^{vi})$	6·635
$C(4^{i})\cdots C(4'^{iv})$	5·719	$C(5^{i})\cdots C(5'^{vi})$	6·160
$C(4^{i})\cdots C(5'^{iv})$	5·541	$C(4^{i})\cdots C(4'^{vii})$	7·333
$C(5^{i})\cdots C(5'^{iv})$	5·677	$C(4^{i})\cdots C(5'^{vii})$	7·728
$C(4^{i})\cdots C(4^{iv})$	5·844	$C(5^{i})\cdots C(5'^{vii})$	8·319
$C(4^{i})\cdots C(5^{iv})$	7·011		

Symmetry code [reference molecule (i) is at the centre of symmetry (1,0,0)]

(i)	x,	y,	z	(v)	$-1+x$,	y,	$1+z$
(ii)	$-1+x$,	y,	z	(vi)	$-1+x$,	$1+y$,	$1+z$
(iii)	$-1+x$,	$1+y$,	z	(vii)	x,	$1+y$,	$1+z$
(iv)	x,	y,	$1+z$				

The crystal structure viewed along the *c* axis is shown in Fig. 2. The molecules are piled up along the *a* axis, displaced in the direction of the molecular long axis by about half a molecule, to form a parallel plane-to-plane stack. In the stack, double bonds related by a centre of symmetry approach at the shortest distance of 3·937 Å (Table 2). The second shortest distance of 5·312 Å is found between molecules in different stacks ([$\bar{1}$10] translation) and is too long for reaction to occur (Bregman, Osaki, Schmidt & Sonntag, 1964). Therefore, it is most probable that the double bonds in the stack react to form a cyclobutane ring, and consequently polymer chains should grow in the direction of the *a* axis. This has been confirmed by the investigation of the crystal change from monomer to polymer (Nakanishi, Hasegawa & Sasada, 1977). Fig. 3 shows the intermolecular contacts of reacting molecules. The ester O atom with lone-pair electrons approaches the benzene ring. A similar type of intermolecular contact between electron-rich and electron-deficient moieties has been observed in other photopolymerizable crystals (Nakanishi, Ueno & Sasada, 1978).

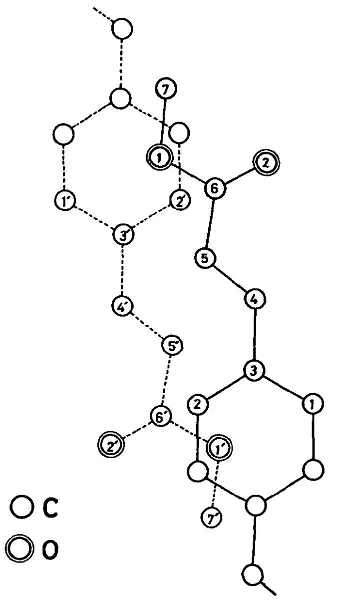

Fig. 3. The overlapping of reacting molecules viewed along the normal of the mean plane of the molecule.

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