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Structure of *p*-Methacryloyloxybenzoic acid at 140 K

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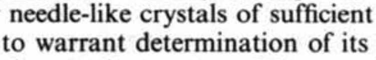
Abstract. $C_{11}H_{10}O_4$, $M_r = 206{\cdot}2$, monoclinic, $P2_1/n$, $a = 3{\cdot}769\,(2)$, $b = 35{\cdot}673\,(9)$, $c = 7{\cdot}376\,(1)$ Å, $\beta = 103{\cdot}47\,(1)^\circ$, $V = 964{\cdot}4\,(0{\cdot}9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}420$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}02$ cm^{-1}, $F(000) = 432$, $T = 140$ K, $R = 0{\cdot}059$ for 1583 reflections with $I > 3\sigma(I)$. The molecules are linked through their carboxyl groups into hydrogen-bonded dimers. The terminal C—CH_3 and C=CH_2 groups are disordered.

Introduction. The title compound (1) was synthesized to investigate the kinetics of its polymerization under various conditions. During attempts to purify it, layered or needle-like crystals of sufficient size could be grown to warrant determination of its previously undescribed crystal structure. Measurements were made at a temperature of 140 K in order to discern the adjacent C=CH_2 and C—CH_3 bonds more clearly (Viersen, Menge, Tan & van Bolhuis, 1988).



(I)

Experimental. To a stirred solution of 45 g (0·326 mol) purified *p*-hydroxybenzoic acid (m.p. 487–488 K) in 600 ml 5% NaOH aqueous solution under a nitrogen blanket and cooled with ice, 37·5 g (0·359 mol) of predistilled methacroyl chloride was added dropwise within about 1 h. After 30 min the clear solution was acidified with *ca* 30 ml concentrated HCl to pH 5. The precipitated (1) was filtered off, washed thoroughly with water, added to 600 ml of methanol with stirring, cooled to 255 K, isolated, and finally dried in a vacuum oven at 323 K. The yield was 56·5 g (84%). Purification by recrystallization was achieved by preparing a saturated solution of (1) in lukewarm methanol to which water was added dropwise until incipient turbidity, and keeping it at 255 K. The product thus recovered had an m.p. of 455 K in agreement with Amerik, Konstantinov & Krentsel (1968). Larger crystals could be obtained by very slow crystallization or solvent evaporation of a saturated methanol solution at room temperature. Sublimation at 433 K under vacuum was also possible but the method was not optimized further. The crystal had a platelet or needle-like habit (Fig. 1).

A crystal of (1), having dimensions 0·30 × 0·35 × 0·20 mm, was mounted in a random position on a glass fibre. The data were collected at 140 K on a Nonius CAD-4F diffractometer equipped with a single-crystal graphite monochromator, using the ω–2θ scan technique. For measuring lattice parameters 25 reflections were used in the range $8{\cdot}06 \le \theta \le 21{\cdot}27^\circ$. The intensities of three standard reflections, 172, 103 and $1,13,\bar{2}$, which were measured every three hours, were used to control drift in the primary beam and mounting system as well as possible decrease of the crystal quality. $0 \le h \le 4$, $0 \le k \le 45$, $-9 \le l \le 9$. In the interval $1 \le \theta \le 27^\circ$, 2099 reflections were found, of which 1583 had intensities greater than 3·0 times their standard deviations;

Fig. 1. Scanning electron micrograph of the title compound. Magnification 680 ×.

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these were used in the refinement. Scaling factors based on the fluctuation (2·3% on I) of the standard reflections, Lorentz and polarization corrections were applied to the data. No absorption corrections were made. The structure was solved by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The positions of the remaining atoms were revealed from successive difference syntheses. Scattering factors were taken from Cromer & Waber (1974). The values for f' and f'' were those of Cromer (1974). Full-matrix least-squares refinement of F, with unit weights, converged to a final $R = 0{\cdot}059$ and $wR = 0{\cdot}076$ using anisotropic temperature factors for the non H-atoms only $[(\Delta/\sigma)_{\max} = 0{\cdot}08$ and $(\Delta/\sigma)_{\text{ave}} = 0{\cdot}03]$. Max. and min. heights in final difference synthesis 0·38 and $-0{\cdot}15\ \text{e}\ \text{Å}^{-3}$, goodness of fit is 1·3. In the final refinement C—H and O—H bond lengths were constrained to a distance of 0·96 Å and fixed isotropic ($B = 5{\cdot}0\ \text{Å}^2$) temperature factors were used for H atoms. All calculations were performed on a PDP-11/23 computer using the *SDP*/*PDP* programs (Frenz, 1978).

Table 1. *Positional parameters* ($\times 10^4$) *of* O *and* C *atoms and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	2430 (4)	1891 (3)	6131 (5)	1·94 (5)
O(2)	0232 (7)	1418 (1)	7610 (4)	1·54 (5)
O(3)	−1958 (8)	0435 (1)	0277 (4)	1·93 (5)
O(4)	1781 (7)	0062 (1)	2317 (4)	1·78 (5)
C(1)	0423 (6)	1831 (1)	10702 (3)	2·15 (8)
C(2)	1040 (10)	2008 (1)	9093 (5)	1·63 (7)
C(3)	1470 (10)	2402 (1)	8915 (6)	2·06 (8)
C(4)	1340 (10)	1777 (1)	7441 (5)	1·41 (7)
C(5)	0184 (9)	1168 (1)	6138 (5)	1·22 (6)
C(6)	1980 (10)	0831 (1)	6603 (5)	1·40 (7)
C(7)	1864 (9)	0565 (1)	5223 (5)	1·29 (6)
C(8)	−0071 (9)	0639 (1)	3399 (5)	1·12 (6)
C(9)	−1920 (10)	0979 (1)	2975 (5)	1·28 (6)
C(10)	−1810 (10)	1246 (1)	4345 (5)	1·36 (6)
C(11)	−0070 (10)	0360 (1)	1919 (5)	1·30 (6)

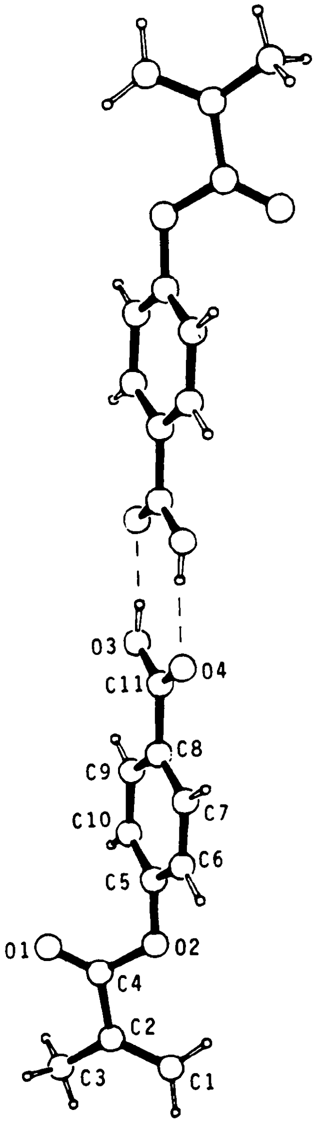

Fig. 2. Molecular structure of the title compound in the dimer form with numbering scheme.

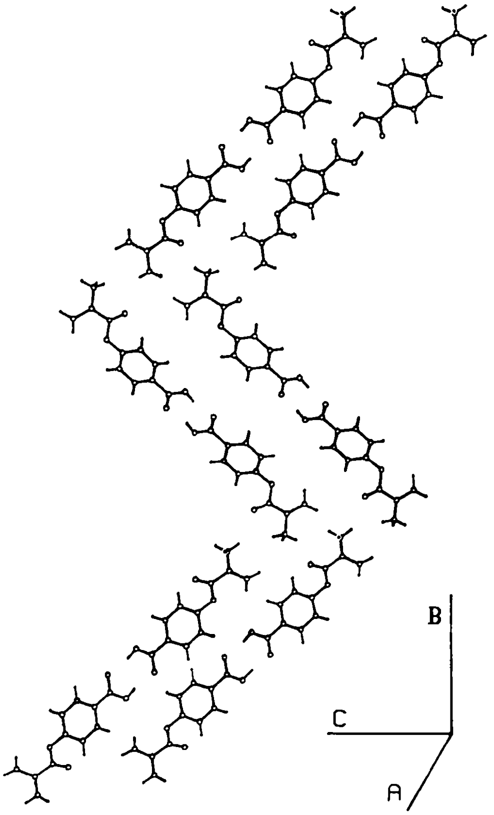

Fig. 3. Arrangement of dimers of the title compound in the lattice. Crystal stucture along the a axis.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(4)	1·206 (4)	C(5)—C(6)	1·383 (5)
O(2)—C(4)	1·361 (4)	C(5)—C(10)	1·389 (5)
O(2)—C(5)	1·401 (4)	C(6)—C(7)	1·386 (5)
O(3)—C(11)	1·282 (4)	C(7)—C(8)	1·399 (5)
O(4)—C(11)	1·267 (4)	C(8)—C(9)	1·398 (5)
C(1)—C(2)	1·411 (5)	C(8)—C(11)	1·477 (5)
C(2)—C(3)	1·424 (6)	C(9)—C(10)	1·382 (5)
C(2)—C(4)	1·497 (6)	O(3)—H(O3)	0·950 (2)
		O(3)—O(4′)	2·620 (3)
		H(O3)—O(4′)	1·683 (2)
C(4)—O(2)—C(5)	118·4 (3)	C(5)—C(6)—C(7)	119·0 (3)
C(1)—C(2)—C(3)	124·3 (3)	C(6)—C(7)—C(8)	119·8 (3)
C(1)—C(2)—C(4)	119·7 (3)	C(7)—C(8)—C(9)	120·0 (3)
C(3)—C(2)—C(4)	116·0 (4)	C(7)—C(8)—C(11)	119·6 (3)
O(1)—C(4)—O(2)	124·1 (3)	C(9)—C(8)—C(11)	120·3 (3)
O(1)—C(4)—C(2)	124·7 (3)	C(8)—C(9)—C(10)	120·4 (3)
O(2)—C(4)—C(2)	111·2 (3)	C(5)—C(10)—C(9)	118·4 (3)
O(2)—C(5)—C(6)	116·3 (3)	O(3)—C(11)—O(4)	123·3 (3)
O(2)—C(5)—C(10)	121·1 (3)	O(3)—C(11)—C(8)	117·5 (3)
C(6)—C(5)—C(10)	122·4 (3)	O(4)—C(11)—C(8)	119·2 (3)

Primed atoms are derived from those in Table 1 by the operations $\bar{x}, \bar{y}, \bar{z}$.

Discussion. The molecular structure with the atomic numbering scheme is shown in Fig. 2 in the form of a dimer, consisting of two molecules held together by the carboxyl groups through hydrogen bonding. Such a tendency is quite common for molecules carrying carboxyl groups, even in solutions of non-polar or weakly polar solvents.

The positional parameters of the C and O atoms are listed in Table 1.* Selected distances and angles are given in Table 2.

The arrangement of the molecules in the crystal is depicted in Fig. 3 showing alternating polar and non-polar layers owing to dimer formation. This explains the platelet-like or flat needle-like structure of the grown crystals (Fig. 1). It is possible that the layered nature of the crystals (Fig. 1) causes a small disorder. This disorder probably partly averages the single and double C—C bonds at the non-polar ends of the dimers, because the C(2)—C(3) and C(1)—C(2) bond distances are similar despite the low measurement temperature. Moreover, the difference between these two bonds hardly increased on lowering the temperature from ambient to 140 K which contrasts with previous findings concerning the compound (2,6-diphenyl)phenyl methacrylate (Viersen, Menge, Tan & van Bolhuis, 1988).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52486 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acetylsaturejol, an *endo*-Peroxide Menthane Derivative from *Satureja gilliessi*

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Abstract. $\mathrm{C_{12}H_{18}O_5}$, $M_r = 242·27$, monoclinic, $P2_1$, $a = 8·187\,(3)$, $b = 11·536\,(6)$, $c = 7·698\,(3)$ Å, $\beta = 115·17\,(3)$°, $V = 658·0\,(5)$ Å^3, $Z = 2$, $D_x = 1·223$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0·71069$ Å, $\mu = 0·08$ mm^{-1}, $F(000) = 236$, $T = 293$ K, $R = 0·060$, $wR = 0·045$ for 894 unique observed reflections [$F >$

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