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(2,6-Diphenyl)phenyl Methacrylate.* 1. Synthesis and Crystal Structure

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Abstract. $C_{22}H_{18}O_2$, $M_r = 314.4$, monoclinic, $P2_1/c$, $a = 14.214$ (2), $b = 7.259$ (3), $c = 16.369$ (2) Å, $\beta = 96.80$ (1)°, $V = 1677.1$ (1.1) Å^3, $Z = 4$, $D_x = 1.245$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0.7107$ Å, $\mu(\text{Mo }K\alpha) = 0.73$ cm^{-1}, $F(000) = 664$, $T = 140$ K, $R = 0.047$ for 2241 reflections with $I \geq 3\sigma(I)$. Prepared by reaction of *m*-terphenyl-2′-ol or its K salt with methacryloyl chloride in ether or in tetrahydrofuran. The monomer (m.p. 374.6–375.6 K) was not polymerizable owing to steric hindrance of the bulky ester group.

Introduction. In the search for methacrylate monomers that on polymerization produce as little shrinkage as possible, the title compound (1) seems a most attractive candidate. This monomer has not been described before. It can be readily synthesized by reacting methacryloyl chloride with the appropriate phenol, either as such or as its K salt.

Besides characterization by IR and NMR, its crystal structure has been determined. When this was done at room temperature it was difficult to assign unambiguously the two adjacent bonds C=CH$_2$ and C–CH$_3$, since they gave approximately identical bond-distance values, *viz.* 1.433 and 1.442 Å. The same problem was encountered in determining the structure of 4-(α,α-dimethylbenzyl)phenyl methacrylate at room tem-

perature (Viersen, Tan, van Bolhuis & Zwiers, 1985). Two explanations were forwarded: one was rapid rotation around the C–C ester bond, the other was a 50–50 disorder placement of C=CH$_2$ and C–CH$_3$ bonds. In order to establish the true reason, measurements were made at 140 K.
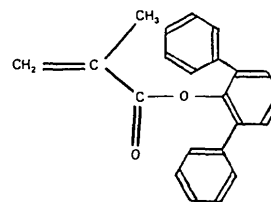
(1)

Experimental. *Synthesis.* To a 200 ml ether solution of 12.8 g (0.052 mol) of *m*-terphenyl-2′-ol and 51.3 g (0.052 mol) of triethylamine under a N$_2$ blanket, 6.3 g (0.061 mol) of methacryloyl chloride was added dropwise. After 24 h the reaction mixture was filtered, washed with water, *etc.* On cooling the concentrated ether solution to 253 K pure crystals of (1) were obtained. Yield: 4.0 g (22%). Alternatively (1) could be synthesized in a much better yield as follows. To a solution of 24.6 g (0.1 mol) of *m*-terphenyl-2′-ol in 100 ml absolute ethanol 5.8 g (0.1 mol) of powdered KOH was added. After 15 min stirring the yellowish

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* IUPAC name: *m*-terphenyl-2′-yl methacrylate.

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solution was concentrated by evaporation. The residual ethanol was stripped with THF and twice with ether. The K salt was collected as a light yellow powder (yield: 95%). This was dissolved in 200 ml dry tetrahydrofuran (THF) with 5 g of triethylamine and put under a N_2 blanket. Then 11·0 g (0·105 mol) of methacryloyl chloride was added slowly under cooling and stirred for 4 h at 313 K. Subsequently the reaction mixture was washed with successively 100 ml of 5% HCl, 100 ml of H_2O and 100 ml of 5% $NaHCO_3$, and dried with $MgSO_4$. After evaporation of THF, the solid residue was dissolved in hot 2-propanol and kept at 277 K for one night, after which 21 g (67%) of crystalline material could be collected. By repeated crystallizations (thrice) in 2-propanol a product was obtained with m.p. 374·6–375·6 K.

Spectroscopic data. ^1H NMR ($CDCl_3$, TMS as reference): $\delta = 1·66$ (s; 3-H), $\delta_t = 5·38$ (m; 1-H) (calc. 5·58). $\delta_c = 5·90$ (m; 1-H) (calc. 6·15). $\delta = 7·4$ (m; 13-H). Calculated values are according to Hesse, Meyer & Zeeh (1979). IR (KBr): 3030–3090 (w; C—H aromatic, vinylic), 2930–3010, 1468, 1460, 1383 (all w; CH aliphatic), 1638, 1425, 958 (w, m, m; C=C), 1600, 1575, 1500 (all w, phenyl), 811, 804 (m, m) and 769, 759 (both m/s; phenyl), 704 (s; monosubstituted phenyl), 1195, 1130, (s, s; O=C—O—), 1323, 1300 (m, m; C—O). For the complete spectrum, see Fig. 1.

Crystal structure. The data were collected on a Nonius CAD-4–SDP23M diffractometer, interfaced to a PDP-11/23 computer, using Mo $K\alpha$ radiation monochromated by a single graphite crystal. The intensity measurements were carried out by the ω–2θ scan technique at 140 K ($\theta \leq 25°$). In total, 2241 unique reflections with intensity $I \geq 3\sigma(I)$ were found. A crystal with dimensions 0·32 × 0·20 × 0·17 mm was used. Unit cell: 16 reflections in the interval $8 < \theta < 17°$. Max. $(\sin\theta)/\lambda = 0·59$ Å^{-1}, $0 \leq h \leq 17$, $0 \leq k \leq 8$, $-19 \leq l \leq 19$. Three standard reflections: $\bar{6}14$, $\bar{5}08$ and $\bar{9}40$. The structure was solved by *MULTAN*82 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). All the H atoms were revealed in successive difference maps. Full-matrix least-squares refinement on F converged to a final $R = 0·047$, using anisotropic temperature factors only for the non-hydrogen atoms. $(\Delta/\sigma)_{max} = 0·07$ and $(\Delta/\sigma)_{ave} = 0·02$. Max. and min.

heights in final difference Fourier synthesis 0·2 and $-0·11$ e Å^{-3}. Goodness of fit = 1·3. The positions of the H atoms were constrained to those of the corresponding C atoms at a distance of 0·96 Å using isotropic temperature factors. No absorption corrections were applied. All computations were performed using CAD-4 *SDP* programs (Enraf–Nonius, 1979). For recording of spectra and determination of melting point, see Viersen *et al.* (1985).

Discussion. The molecular structure with the atom-numbering scheme is shown in Fig. 2. As anticipated the three phenyl rings do not lie in the same plane. If we denote plane C(5)—C(10) by X, plane C(11)—C(16) by Y, and plane C(17)—C(22) by Z, then the dihedral angles are $\angle XY = 130·7$ or 49·3, $\angle ZY = 63·9$ and $\angle ZX = 83·6°$. With respect to the central ring Y the outer rings X and Z are tilted in opposite directions, but not to the same degree, giving the three rings the impression of an imperfect semi-helix. This may also be deduced if we denote the plane defined by the C atoms C(1)—C(4) and the O atoms O(1) and O(2) by P, and calculate the dihedral angles between the respective rings and P, these being $\angle XP = 62$, $\angle YP = 102$ and $\angle ZP = 120°$.

The positional parameters of the C and O atoms are listed in Table 1.* Bond lengths and bond angles were calculated from these data, but only those between C and O atoms are given (Table 2).

As is seen from Table 2 the bond distances C(2)—C(1) and C(2)—C(3) are different, *viz.* 1·337 and

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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 44358 (15 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
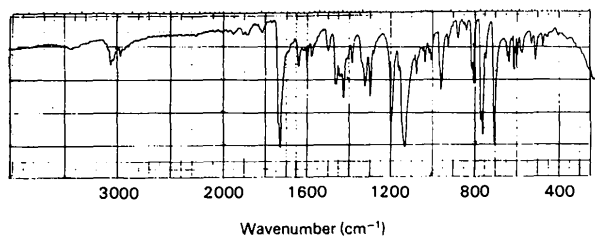

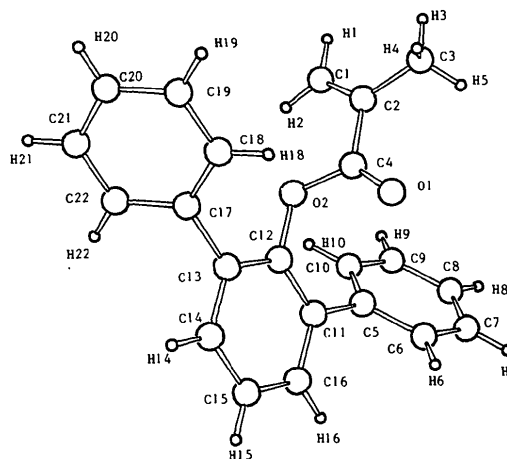Fig. 1. IR spectrum of the title compound (KBr disk).

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

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*

$$B_{eq} = \tfrac{4}{3}\Sigma_i \Sigma_j \beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$$

	x	y	z	B_{eq}
O(1)	6127 (1)	3398 (2)	6563 (2)	1·69 (4)
O(2)	7514 (1)	1948 (3)	6971 (1)	1·21 (4)
C(1)	6756 (3)	−0070 (5)	8102 (2)	2·76 (7)
C(2)	6208 (2)	1277 (4)	7689 (2)	1·54 (6)
C(3)	5265 (2)	1768 (5)	7858 (2)	1·93 (6)
C(4)	6577 (2)	2325 (4)	7016 (2)	1·31 (5)
C(5)	7082 (2)	0547 (4)	5324 (2)	1·27 (5)
C(6)	6367 (1)	0669 (3)	4662 (1)	1·68 (6)
C(7)	5780 (2)	−0814 (5)	4447 (2)	2·05 (6)
C(8)	5898 (2)	−2454 (5)	4877 (2)	2·03 (6)
C(9)	6613 (2)	−2609 (5)	5532 (2)	1·85 (6)
C(10)	7195 (2)	−1111 (4)	5751 (2)	1·54 (6)
C(11)	7719 (2)	2146 (4)	5528 (2)	1·21 (5)
C(12)	7922 (2)	2819 (4)	6329 (2)	1·21 (5)
C(13)	8557 (2)	4246 (4)	6543 (2)	1·29 (5)
C(14)	8994 (2)	5060 (4)	5909 (2)	1·56 (6)
C(15)	8783 (2)	4476 (4)	5103 (2)	1·61 (6)
C(16)	8156 (2)	3025 (4)	4913 (2)	1·46 (6)
C(17)	8794 (2)	4846 (4)	7409 (2)	1·36 (5)
C(18)	8111 (2)	5623 (4)	7856 (2)	1·57 (6)
C(19)	8351 (2)	6189 (5)	8664 (2)	1·85 (6)
C(20)	9272 (2)	5996 (5)	9039 (2)	1·96 (6)
C(21)	9955 (2)	5227 (5)	8601 (2)	1·96 (6)
C(22)	9723 (2)	4670 (5)	7792 (2)	1·70 (6)

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

O(1)–O(4)	1·204 (3)	C(11)–C(12)	1·397 (4)
O(2)–C(4)	1·370 (3)	C(11)–C(16)	1·398 (4)
O(2)–C(12)	1·410 (4)	C(12)–C(13)	1·391 (4)
C(1)–C(2)	1·377 (5)	C(13)–C(14)	1·401 (4)
C(2)–C(3)	1·444 (4)	C(13)–C(17)	1·484 (4)
C(2)–C(4)	1·486 (4)	C(14)–C(15)	1·384 (4)
C(5)–C(6)	1·398 (3)	C(15)–C(16)	1·391 (4)
C(5)–C(10)	1·392 (4)	C(17)–C(18)	1·400 (4)
C(5)–C(11)	1·486 (4)	C(17)–C(22)	1·399 (4)
C(6)–C(7)	1·382 (4)	C(18)–C(19)	1·389 (4)
C(7)–C(8)	1·382 (5)	C(19)–C(20)	1·386 (4)
C(8)–C(9)	1·391 (4)	C(20)–C(21)	1·390 (5)
C(9)–C(10)	1·388 (4)	C(21)–C(22)	1·386 (4)

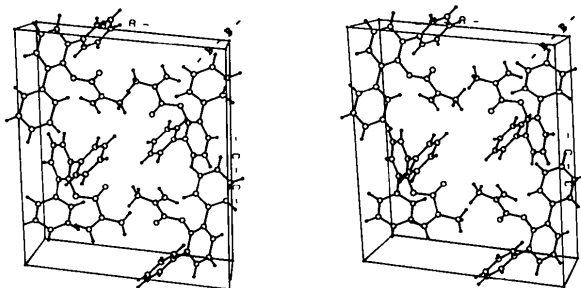|			
C(4)–O(2)–C(12)	116·0 (2)	C(8)–C(9)–C(10)	119·6 (3)
C(1)–C(2)–C(3)	124·4 (3)	C(5)–C(10)–C(9)	121·2 (3)
C(1)–C(2)–C(4)	119·9 (3)	C(5)–C(11)–C(12)	122·4 (3)
C(3)–C(2)–C(4)	115·6 (3)	C(5)–C(11)–C(16)	120·4 (3)
O(1)–C(4)–O(2)	123·0 (3)	C(12)–C(11)–C(16)	117·2 (3)
O(1)–C(4)–C(2)	125·4 (3)	O(2)–C(12)–C(11)	119·1 (3)
O(2)–C(4)–C(2)	111·6 (2)	O(2)–C(12)–C(13)	117·3 (2)
C(6)–C(5)–C(10)	118·3 (3)	C(11)–C(12)–C(13)	123·5 (3)
C(6)–C(5)–C(11)	119·5 (2)	C(12)–C(13)–C(14)	117·3 (3)
C(10)–C(5)–C(11)	122·1 (2)	C(12)–C(13)–C(17)	121·7 (3)
C(5)–C(6)–C(7)	120·6 (2)	C(14)–C(13)–C(17)	120·9 (3)
C(6)–C(7)–C(8)	120·6 (3)	C(13)–C(14)–C(15)	120·8 (3)
C(7)–C(8)–C(9)	119·7 (3)	C(14)–C(15)–C(16)	120·4 (3)
C(11)–C(16)–C(15)	120·7 (3)	C(13)–C(17)–C(18)	121·6 (3)
C(13)–C(17)–C(22)	119·7 (3)	C(18)–C(17)–C(22)	118·6 (3)
C(17)–C(18)–C(19)	120·7 (3)	C(18)–C(19)–C(20)	120·2 (3)
C(19)–C(20)–C(21)	119·5 (3)	C(20)–C(21)–C(22)	120·6 (3)
C(17)–C(22)–C(21)	120·4 (3)		

Fig. 3. Three-dimensional picture of a crystal cell of the title compound.

1·444 Å respectively, in contrast to the findings at room temperature mentioned in the *Introduction*. Also, from the final difference map based on all the atoms except H(1) to H(5), the positions of the latter atoms could be revealed. Therefore we may assign C(2)–C(1) to the C=CH$_2$ bond and C(2)–C(3) to the C–CH$_3$ bond. From these results we may also conclude that the equality in distance of the two bonds at room temperature is not caused by disorder but by a rapid rotation around the C(2)–C(4) bond axis. It should be noted, however, that the distance of 1·444 Å is rather short compared with 1·54 Å of a single bond on the one hand and the distance of 1·377 Å is somewhat longer than 1·34 Å for a double bond on the other hand. It is probable that these discrepancies are caused by a slight delocalization of the π electrons over the two bonds. If this suggestion is justified, then such a situation should

also exist at room temperature in an enhanced state, though masked by the rapid rotation.

The monomer forms monoclinic crystals (a stereoscopic view is given in Fig. 3) in which the intermolecular distance between two adjacent double bonds is somewhat larger than 4·5 Å. This is shorter than that of 4-(α,α-dimethylbenzyl)phenyl methacrylate (5·4 Å). Nevertheless, no polymerization of (1) could be induced by γ-irradiation. The reason for this may be steric hindrance by the bulky side group since (1) could not be polymerized in solution using radical or anionic initiators, but was able to copolymerize with methyl methacrylate. This will be the subject of the next paper.

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