ethylene group. The absolute configuration was not determined in the present study.

Related literature. The detailed synthetic method and spectral data of the enone derivatives will be published by Shigemasa (1989).

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References

Ashida, T. (1973). *HBLS-V. The Universal Crystallographic Computing System, Osaka*, pp. 55–61. Computing Center, Osaka Univ., Japan.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A27, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Shigemasa, Y. (1989). In preparation.

Takenaka, A. (1977). *DCM-3*. Program for drawing crystal and molecular structures. Tokyo Institute of Technology, Japan.

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Structure of Hexa-2,4-diyne-1,6-diyl Bis(4-methoxybenzoate)

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Abstract. $C_{22}H_{18}O_6$, $M_r = 378·4$, monoclinic, $C2/c$, $a = 23·084\ (4)$, $b = 4·269\ (11)$, $c = 19·071\ (3)$ Å, $\beta = 97·82\ (1)°$, $V = 1861·9$ Å^3, $Z = 4$, $D_x = 1·35$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·092$ mm^{-1}, $F(000) = 792$, room temperature, $R = 0·030$ and $wR = 0·032$ for 981 diffractometer reflections with $F_o > 6\sigma(F_o)$. Only one crystal form was obtained from a variety of solvents. The crystal surfaces become red on exposure to X-rays, but the bulk crystal does not undergo polymerization even after prolonged exposure to heat or X- or γ-radiation. The monomer molecules form a regular inclined stack along the crystal y direction.The distance between reactive 1···4′ acetylenic C atoms in adjacent molecules is 4·00 Å, the angle between the diacetylene chain and the stacking direction is 59·4°.

Experimental. The title compound was prepared at room temperature by the dropwise addition of 4-methoxybenzoyl chloride in tetrahydrofuran to a stirred mixture of hexa-2,4-diyne-1,6-diol and triethylamine in tetrahydrofuran. Recrystallization from ethanol gave pale-yellow crystals; yield 77%, m.p. 387–388 K, found C = 69·8, H = 4·8%; $C_{22}H_{18}O_6$ requires C = 69·8, H = 4·8%. Further recrystallization by room-temperature evaporation of acetone, methanol, chloroform, diethyl ether or dichloromethane solutions gave colourless needles. These were examined optically but all specimens appeared to have the same crystal form. Differential scanning calorimetry (Mettler TA 3000) over the range 303–453 K in a nitrogen atmosphere showed no reaction exotherm before or after the melting point; samples started to decompose at 453 K. There was no obvious polymerization when samples were subjected to pressure in a KBr disc press. When crystals were exposed to X-rays they developed red surfaces suggesting some polymerization or other surface reaction, but there were no detectable changes to the diffraction angles or intensities of X-ray reflections. A sample of single crystals was also exposed to γ-radiation (50 Mrads over 7 d) at the Scottish Universities Reactor, East Kilbride. The surfaces of these crystals became black but again oscillation and Weissenberg X-ray photography showed no change to the space group, nor any detectable changes to cell parameters or relative intensities of reflections.

Two crystals grown from acetone solution (and not previously subjected to X- or γ-radiation) were used for X-ray measurements. Crystal (1) had dimensions 0·48 × 0·40 × 0·08 mm and was mounted along the b axis. Crystal (2) had dimensions 0·40 × 0·38 × 0·10 mm and was mounted along the $[1\bar{1}0]$ face diagonal. The space group and approximate cell parameters were calculated from oscillation and Weissenberg photographs (Cu $K\alpha$ radiation). Accurate cell parameters and intensity data were measured using a Stoe Stadi-2 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell parameters determined from ω and 2θ angles of 20 $h0l$ reflections ($21 < 2\theta < 29°$) from crystal (1) and 14 nnl reflections ($19 < 2\theta < 35°$) from crystal (2). Intensity data were measured for the layers h, $0 \rightarrow 5$, l from crystal (1), and $m + n$, n, l for $m = 0,2,4,6$ from crystal (2). (Diagonal layers with m = odd are systematically

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Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters* (U_{eq}) *with e.s.d.'s in parentheses*

$U_{eq} = (U_1U_2U_3)^{1/3}$ where U_i are the diagonal elements of the diagonalized orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
O1	0·43888 (5)	−0·2187 (3)	0·29191 (6)	0·0534 (8)
O2	0·35578 (6)	−0·1316 (5)	0·33598 (7)	0·0706 (11)
O3	0·30140 (6)	0·5371 (4)	0·03902 (7)	0·0677 (10)
C1	0·49119 (8)	−0·0822 (5)	0·46936 (10)	0·0512 (11)
C2	0·47554 (8)	−0·2236 (5)	0·41659 (10)	0·0535 (12)
C3	0·45727 (11)	−0·4106 (6)	0·35310 (11)	0·0611 (14)
C4	0·38437 (8)	−0·0985 (5)	0·28842 (9)	0·0493 (11)
C5	0·36620 (7)	0·0709 (5)	0·22237 (9)	0·0444 (10)
C6	0·40055 (8)	0·0965 (5)	0·16910(9)	0·0484 (11)
C7	0·38073 (8)	0·2513 (5)	0·10668 (10)	0·0531 (12)
C8	0·32560 (8)	0·3819 (5)	0·09735 (9)	0·0502 (11)
C9	0·29086 (9)	0·3575 (6)	0·15092 (10)	0·0598 (13)
C10	0·31076 (8)	0·2059 (6)	0·21214 (10)	0·0566 (13)
C11	0·33303 (16)	0·5581 (11)	−0·01962 (14)	0·0808 (21)

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

C1	C1^i	1·376 (4)	C1	C2	1·187 (3)
C2	C3	1·464 (3)	C3	O1	1·442 (3)
C3	H3	1·02 (2)	C3	H4	1·01 (2)
C4	C5	1·464 (3)	C4	O1	1·352 (2)
C4	O2	1·200 (2)	C5	C6	1·376 (2)
C5	C10	1·393 (3)	C6	C7	1·384 (3)
C6	H6	0·95 (2)	C7	C8	1·379 (3)
C7	H7	0·93 (2)	C8	C9	1·386 (3)
C8	O3	1·349 (2)	C9	C10	1·359 (3)
C9	H9	0·97 (2)	C10	H10	0·99 (2)
O3	C11	1·419 (3)	C11	H11	1·00 (3)
C11	H12	0·94 (4)	C11	H13	0·96 (3)

C1^i	C1	C2	179·5 (2)	C1	C2	C3	177·4 (2)
C2	C3	O1	112·3 (2)	C2	C3	H3	109 (1)
C2	C3	H4	109 (1)	O1	C3	H3	109 (1)
O1	C3	H4	103 (1)	C3	O1	C4	115·2 (1)
H3	C3	H4	115 (2)	C5	C4	O1	112·7 (1)
C5	C4	O2	125·9 (2)	C4	C5	C6	123·3 (2)
C4	C5	C10	118·4 (2)	O1	C4	O2	121·5 (2)
C6	C5	C10	118·3 (2)	C5	C6	C7	121·1 (2)
C5	C6	H6	118 (1)	C5	C10	C9	120·9 (2)
C5	C10	H10	117 (1)	C7	C6	H6	121 (1)
C6	C7	C8	119·7 (2)	C6	C7	H7	118 (1)
C8	C7	H7	122 (1)	C7	C8	C9	119·4 (2)
C7	C8	O3	125·2 (2)	C9	C8	O3	115·4 (2)
C8	C9	C10	120·5 (2)	C8	C9	H9	119 (1)
C8	O3	C11	118·8 (2)	C10	C9	H9	120 (1)
C9	C10	H10	122 (1)	O3	C11	H11	104 (2)
O3	C11	H12	107 (2)	O3	C11	H13	112 (2)
H11	C11	H12	113 (3)	H11	C11	H13	113 (2)
H12	C11	H13	108 (3)				

Symmetry code: (i) = $1 - x, -y, 1 - z$.

absent for a *C*-centred unit cell.) Data were measured for $\theta < 25{\cdot}5°$, using equi-inclination geometry and variable-width ω step scans. Two check reflections on each layer showed no decay. Corrections were applied for Lorentz and polarization effects, but not for absorption. 1720 reflections were measured from crystal (1) and 701 reflections from crystal (2), yielding 1705 unique reflections of which 981 with $F_o > 6\sigma(F_o)$ were used for final structure refinement. Interlayer scale factors were determined using *SHELX76* (Sheldrick, 1976) and using only reflections with $F_o > 4\sigma(F_o)$, the merging R factor for equivalent reflections was 0·012.

For a monomeric species in $C2/c$ with $Z = 4$, the molecules must lie across special positions and exhibit C_2 or C_i symmetry. Either possibility would be consistent with the chemical formula. The non-H atoms were located by direct methods using *SHELXS86* (Sheldrick, 1986) to show molecules lying across centres of symmetry. All H atoms were located from difference Fourier syntheses. Least-squares refinements using *SHELX76* were to minimize $\sum w(|F_o| - |F_c|)^2$ with isotropic thermal parameters for H atoms and anisotropic thermal parameters for O and C atoms. $R = 0{\cdot}030$, $wR = 0{\cdot}032$. Final weighting scheme was $w^{-1} = 1 + 0{\cdot}12(9 - F_o)^2$ for $F_o < 9$ and $w^{-1} = 1 + 0{\cdot}0019(F_o - 9)^2$ for $F_o > 9$. Final value of isotropic extinction parameter was $g = 2{\cdot}0\,(2) \times 10^{-7}$ where $F_c' = F_c(1 - gF_c/\sin\theta)$. Final Δ/σ (max.) = 0·01, residual electron density within ±0·12 e Å^{-3}. Atomic scattering factors as imbedded in *SHELX76*. Calculations performed

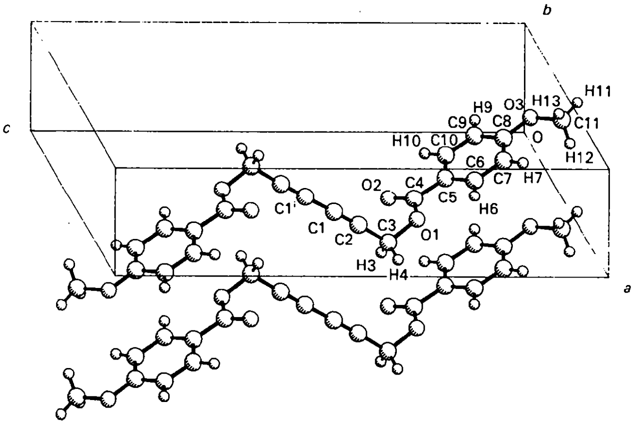


Fig. 1. View to show atom labels and stacking of molecules in the y direction.

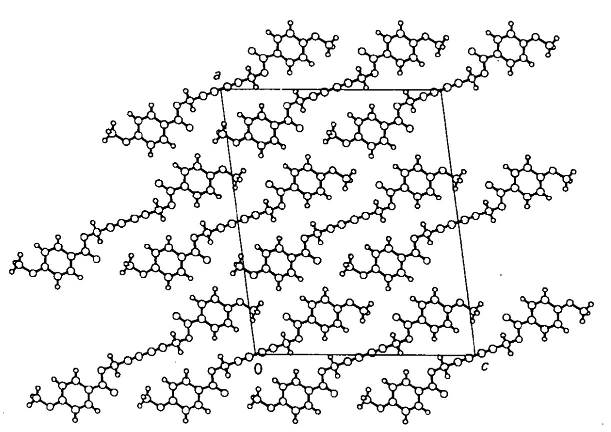
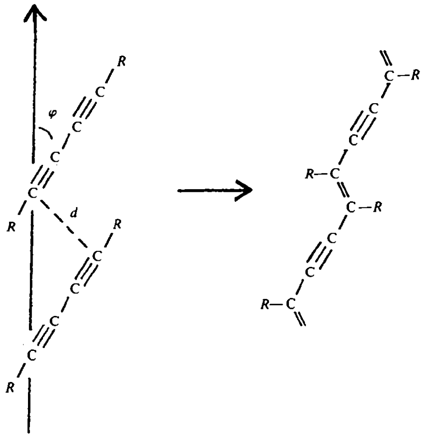


Fig. 2. Unit-cell contents in projection down the b axis.

using an Acorn Workstation ACW443. Final atomic parameters are listed in Table 1 and bond lengths and angles in Table 2.* Fig. 1 shows the atomic labelling scheme and illustrates the packing of molecules in the y direction. Fig. 2 shows the unit-cell contents viewed in projection down the b axis.

Related literature. The molecules are arranged in the y direction to form a close, inclined stack. The stack repeat distance is the length of the b axis, 4·269 Å. The intermolecular separation d between the diacetylene C atoms C2 and C2(at $1-x$, $-1-y$, $1-z$) is 4·00 Å; these are the C atoms which are potentially reactive in respect of solid-state *trans*-1,4′-polymerization (see scheme). The stacking angle, φ, is defined by the intermolecular angle C1—C2···C2(at x, $1+y$, z) and is 59·4°. These distance and angle parameters are at the limit of the range of values considered appropriate for crystal-state polymerization reactivity (Schmidt, 1967; Baughman, 1974; Wegner, 1977).



The only other 4-alkoxybenzoate diester whose crystal structure has been reported is hexa-2,4-diyne-1,6-diyl bis(4-hexyloxybenzoate), determined at room temperature by Shklover, Struchkov, Bagirov, Konstantinov & Amerik (1985) and at 185 K by Barrow, Lough, Milburn, Hardy, Nyitrai & Horvath (1989). The crystal structure of a sulfonate diester analogue, hexa-2,4-diyne-1,6-diyl bis(4-methoxybenzenesulfonate), has been determined by Fisher, Ando, Bloor & Hursthouse (1979). Both the above compounds exhibit polymerization activity but not in the crystal forms whose structures were determined.

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References

Barrow, M. J., Lough, A. J., Milburn, G. H. W., Hardy, G., Nyitrai, K. & Horvath, J. (1989). *Acta Cryst.* **C45**, 609–611.

Baughman, R. H. (1974). *J. Polym. Sci. Polym. Phys. Ed.* **12**, 1511–1535.

Fisher, D. A., Ando, D. J., Bloor, D. & Hursthouse, M. B. (1979). *Acta Cryst.* **B35**, 2075–2079.

Schmidt, G. M. J. (1967). *Reactivity of Photoexcited Organic Molecules*, p. 227. New York: John Wiley.

Sheldrick, G.M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Shklover, V. E., Struchkov, Yu, T., Bagirov, I. A., Konstantinov, I. I. & Amerik, Yu. B. (1985). *Z. Kristallogr.* **173**, 25–31.

Wegner, G. (1977). *Chemistry and Physics of One-dimensional Metals*, edited by H. J. Keller, pp. 297–314. New York: Plenum.

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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 51918 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of *anti*-2-(2-Cyano-3-methoxy-6-methylphenyl)-1,2-diphenyl-1-ethanol

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Abstract. $C_{23}H_{21}NO_2$, $M_r = 343·4$, monoclinic, $P2_1/c$, $a = 10·873\,(5)$, $b = 9·131\,(5)$, $c = 19·009\,(7)$ Å, $\beta = 104·54\,(4)°$, $V = 1826\,(1)$ Å^3, $Z = 4$, $D_x = 1·25$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·74$ cm^{-1}, $F(000) = 728$, $T = 295$ K. Final $R = 0·046$ for 1597 observed reflections. The bond distances are C—CN = 1·433 (5), C≡N = 1·146 (5), O—C(benz.) = 1·360 (4), O—CH$_3$ = 1·428 (4), C—C(benz., av.) =

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