carbonyl, *i.e.* that of the smallest substituent group. The new chiral centre, C(15), makes a torsion angle C(3)—C(2)—C(15)—O(15) of 14·1 (3)° with the rigid planar quinizarin and 64·3 (3)° with the sugar C(16)—C(17) (made more rigid by the isopropylidene blocking group). Within the quinizarin, there is intramolecular chelate hydrogen bonding [2·537 (4) and 2·559 (4) Å] between the hydroxyls [C—OH shortened to 1·350 (4) Å] and ketonic O atoms [C=O lengthened to 1·239 (4) Å]. These bond-length consequences of chelation have been noted elsewhere (Courseille, Busetta, Geoffre & Hospital, 1979); they also occur in anthracyclinone antibiotics such as steffimycin B (Arora, 1985). Ring bond lengths are close to those in 1,4-dihydroxyanthraquinone (Nigam & Deppisch, 1980), with high aromaticity in ring *A* [C(5) to C(8)] and some alternation in lengths in ring *C* [C(2)—C(3) is as short as 1·367 (4) Å].

Within the lyxose, the *gauche–gauche* orientation of O(15) with respect to O(17) facilitates a 2·701 (4) Å intramolecular hydrogen bond between these atoms. The blocking group causes O(17) and O(18) to be almost eclipsed and the furanose ring adopts an envelope conformation in which O(16) is displaced 0·51 (5) Å above the C(16)—C(17)—C(18)—C(19) plane [C(17) and C(18) correspond to carbohydrate C(3') and C(2'), respectively]. The dihedral angle of 63·7 (3)° between lyxose C(16)—C(17)—C(18)—C(19) and blocking-group plane O(17)—C(17)—C(18)—O(18) is almost identical to that in 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (Sheldrick, Mackie & Akrigg, 1985).

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

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Abstract. $C_{22}H_{18}O_4$, $M_r = 346·4$, monoclinic, $P2_1/c$, $a = 10·556$ (4), $b = 12·129$ (8), $c = 14·991$ (5) Å, $\beta = 108·12$ (3)°, $U = 1824·2$ Å^3, $Z = 4$, $D_x = 1·25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·081$ mm^{-1}, $F(000) = 728$, room temperature, $R = 0·062$, $wR = 0·056$ for 1059 reflections with $F_o > 4\sigma(F_o)$. Only one crystal form was obtained from a variety of solvents and these crystals do not undergo heat- or radiation-induced polymerization. The main feature of the crystal structure is an alignment of all the 4-methylbenzoate rings perpendicular to the z direction. The shortest *trans* separations between reactive acetylenic C atoms in neighbouring molecules are alternately 4·25 and 6·43 Å.

Introduction. Hexa-2,4-diyne-1,6-diyl bis(benzenesulfonate) (I) (Ando, Bloor, Hursthouse & Motevalli, 1985) and hexa-2,4-diyne-1,6-diyl bis(4-methylbenzenesulfonate) (II) (Enkelmann, Leyrer & Wegner, 1979) both crystallize with molecules arranged in an inclined stack, and both compounds undergo solid-state *trans*-1,4 polymerization according to Scheme

(*a*). The rate of polymerization is much faster for (II) than for (I). The solid-state polymerization of these and other diacetylenes is initiated by heat, pressure, light, X- or γ-radiation and appears to be mediated by the geometric arrangement of the monomer molecules in the initial crystal (Schmidt, 1967; Baughman, 1974). Usually, crystals are only reactive if the 1···4 distance, *d*, is about 4 Å and the stacking angle, φ, is about 45°. Hexa-2,4-diyne-1,6-diyl bis(benzoate) (III), which is the carboxylate analogue of (I), can also undergo polymerization at high pressure. However, (III) crystallizes in two different forms (Hanson, 1975). One form has the close-stacking arrangement as in Scheme (*a*) and is reactive. The other crystal form does not have close stacking and is inactive. We have now prepared crystals of (IV), the 4-methylcarboxylate compound, in order to investigate its polymerization activity and crystal structure.

(I)

(II)

(III)

(IV)

Scheme (*a*)
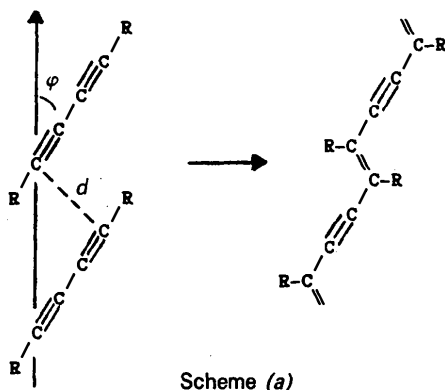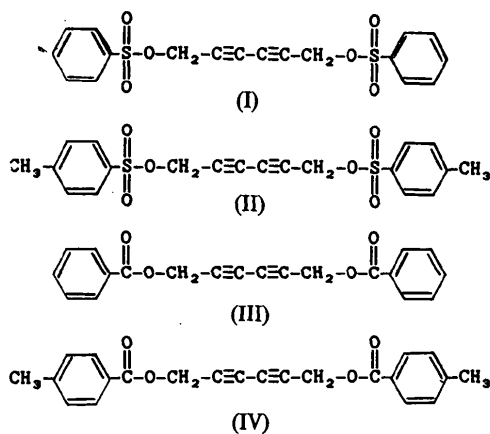
Experimental. Title compound prepared at room temperature by the dropwise addition of 4-methylbenzoyl chloride in tetrahydrofuran to a stirred mixture of hexa-2,4-diyne-1,6-diol in tetrahydrofuran and aqueous sodium hydroxide. Product precipitated from iced water and recrystallized from ethanol. Yield 68%, m.p. 379–380 K, found: C 76·0, H 5·3%; $C_{22}H_{18}O_4$ requires C 76·3, H 5·2%. Further recrys-

tallization samples by room-temperature evaporation of methanol, ethanol, acetone, diethyl ether, toluene, dichloromethane and chloroform solutions were examined optically but all samples appeared to have the same crystal form. Differential scanning calorimetry (Mettler TA 3000) over the range 303–423 K in a nitrogen atmosphere showed no reaction exotherm before or after the melting point (379–380 K); samples started to decompose at 423 K. No polymerization was observed from the action of light or X-rays, nor when samples were subjected to pressure in a KBr disc press.

The crystal used for X-ray measurements was a colourless plate, 0·4 × 0·6 × 0·2 mm, obtained by evaporation of acetone solution at room temperature and mounted along the *b* axis. Space group and approximate cell parameters from oscillation and Weissenberg photographs (Cu *Kα* radiation). Accurate cell parameters and intensity data measured using a Stoe Stadi-2 diffractometer with graphite-monochromated Mo *Kα* radiation. Cell parameters *a*, *c* and β refined from ω and 2θ values of 16 *h*0*l* reflections ($11 < 2\theta < 23°$), while *b* was determined from 18 0*kl* reflections ($13 < 2\theta < 23°$) using a second crystal mounted along the *a* axis. All intensity measurements were from the first crystal for the layers *h*, 0→12, *l* with $\theta < 25°$ and using equi-inclination geometry and variable-width ω step scans. Two check reflections on each layer showed no decay. 3238 measured reflections, 3066 unique, 1059 with $F_o > 4\sigma(F_o)$; Lorentz and polarization corrections, but not absorption. No crystallographic restrictions on molecular symmetry with $Z = 4$ in $P2_1/c$. All non-H atoms located by direct methods using *SHELXS*86 (Sheldrick, 1986), all H atoms located from difference Fourier syntheses. Least-squares refinements using *SHELX*76 (Sheldrick, 1976) to minimize $\sum w(|F_o| - |F_c|)^2$ with isotropic thermal parameters for H atoms and anisotropic thermal parameters for all other atoms. Final weighting scheme was $w^{-1} = 1 + 0·068 (14 - F_o)^2$ for $F_o < 14$ and $w^{-1} = 1 + 0·0027(F_o - 14)^2$ for $F_o > 14$. Final value of isotropic extinction parameter was $g = 8·8 (51) \times 10^{-8}$ where $F_c' = F_c(1 - gF_c/\sin\theta)$. $\Delta/\sigma(\text{max.}) = 0·07$, residual electron density within $\pm 0·23$ e Å^{-3}. Atomic scattering factors as imbedded in *SHELX*76. Calculations performed using an Acorn ACW443 Workstation. Final atomic parameters are listed in Table 1 and bond lengths and angles in Table 2.* The atomic labelling scheme is shown in Fig. 1.

Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = (U_1 U_2 U_3)^{1/3}$ where U_i are the diagonal elements of the diagonalized orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(\text{Å}^2)$
O1	−0.3529 (4)	0.1125 (4)	0.5754 (3)	0.055 (3)
O2	−0.2843 (4)	0.2864 (4)	0.5763 (4)	0.068 (4)
C1	−0.1324 (6)	0.0899 (6)	0.4451 (6)	0.059 (5)
C2	−0.1695 (6)	0.0855 (6)	0.5119 (6)	0.054 (5)
C3	−0.2148 (7)	0.0753 (7)	0.5946 (6)	0.056 (5)
C4	−0.3748 (7)	0.2208 (6)	0.5683 (5)	0.053 (5)
C5	−0.5167 (6)	0.2504 (5)	0.5473 (4)	0.042 (4)
C6	−0.6145 (7)	0.1739 (6)	0.5434 (5)	0.052 (5)
C7	−0.7459 (7)	0.2071 (6)	0.5243 (5)	0.055 (5)
C8	−0.7825 (6)	0.3153 (6)	0.5088 (4)	0.050 (4)
C9	−0.6836 (7)	0.3922 (6)	0.5110 (5)	0.058 (5)
C10	−0.5533 (7)	0.3584 (6)	0.5296 (5)	0.057 (5)
C11	−0.9266 (9)	0.3524 (9)	0.4846 (9)	0.068 (7)
O1'	0.1324 (4)	0.1376 (4)	0.2406 (3)	0.057 (3)
O2'	0.0680 (4)	0.3121 (4)	0.2449 (4)	0.068 (4)
C1'	−0.0903 (6)	0.0949 (6)	0.3668 (6)	0.050 (5)
C2'	−0.0507 (6)	0.1018 (6)	0.3019 (5)	0.053 (5)
C3'	−0.0067 (7)	0.1030 (7)	0.2193 (5)	0.060 (5)
C4'	0.1571 (7)	0.2463 (6)	0.2533 (5)	0.057 (5)
C5'	0.2988 (6)	0.2725 (6)	0.2738 (4)	0.047 (4)
C6'	0.3980 (7)	0.1921 (7)	0.2898 (5)	0.059 (5)
C7'	0.5305 (7)	0.2215 (7)	0.3085 (5)	0.063 (6)
C8'	0.5679 (6)	0.3283 (7)	0.3100 (4)	0.054 (5)
C9'	0.4702 (8)	0.4095 (7)	0.2948 (6)	0.065 (6)
C10'	0.3362 (7)	0.3820 (6)	0.2758 (5)	0.058 (5)
C11'	0.7122 (8)	0.3606 (9)	0.3311 (8)	0.070 (7)

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

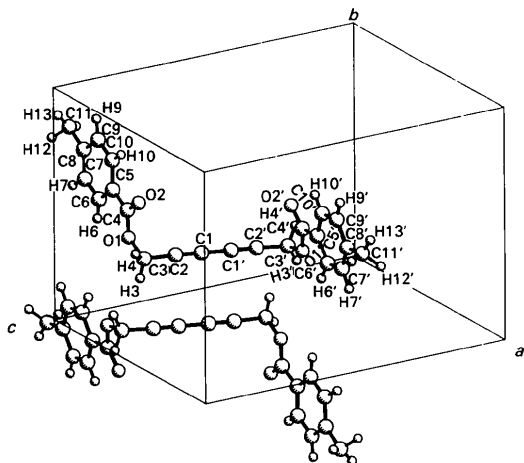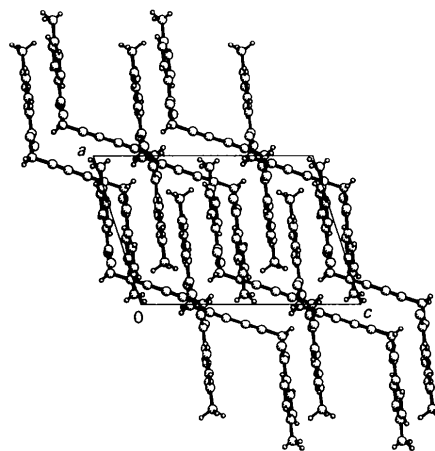|		C1—C1'	1.379 (11)		
O1—C3	1.466 (9)			O1'—C3'	1.464 (9)
O1—C4	1.332 (9)			O1'—C4'	1.347 (9)
O2—C4	1.220 (9)			O2'—C4'	1.210 (9)
C1—C2	1.185 (11)			C1'—C2'	1.175 (11)
C2—C3	1.467 (11)			C2'—C3'	1.453 (11)
C3—H3	0.97 (7)			C3'—H3'	1.06 (5)
C3—H4	1.02 (5)			C3'—H4'	1.02 (5)
C4—C5	1.475 (10)			C4'—C5'	1.466 (10)
C5—C6	1.376 (10)			C5'—C6'	1.395 (10)
C5—C10	1.368 (10)			C5'—C10'	1.384 (10)
C6—C7	1.386 (11)			C6'—C7'	1.386 (11)
C6—H6	0.91 (5)			C6'—H6'	0.95 (5)
C7—C8	1.367 (10)			C7'—C8'	1.353 (12)
C7—H7	0.94 (6)			C7'—H7'	0.98 (8)
C8—C9	1.393 (10)			C8'—C9'	1.393 (11)
C8—C11	1.518 (13)			C8'—C11'	1.508 (12)
C9—C10	1.378 (11)			C9'—C10'	1.393 (12)
C9—H9	0.97 (6)			C9'—H9'	0.91 (6)
C10—H10	0.98 (6)			C10'—H10'	0.94 (5)
C11—H11	0.75 (10)			C11'—H11'	0.98 (9)
C11—H12	1.06 (8)			C11'—H12'	1.06 (7)
C11—H13	0.90 (7)			C11'—H13'	0.89 (9)
C4—O1—C3	117.2 (6)			C4'—O1'—C3'	116.7 (6)
C2—C3—O1	111.9 (6)			C2'—C3'—O1'	112.4 (6)
O2—C4—O1	121.6 (6)			O2'—C4'—O1'	121.4 (7)
C5—C4—O1	113.4 (6)			C5'—C4'—O1'	112.4 (6)
C5—C4—O2	125.0 (6)			C5'—C4'—O2'	126.1 (7)
C1'—C1—C2	179.5 (8)			C2'—C1'—C1	177.5 (8)
C3—C2—C1	177.7 (8)			C3'—C2'—C1'	175.9 (8)
C6—C5—C4	122.9 (6)			C6'—C5'—C4'	123.2 (7)
C10—C5—C4	118.8 (6)			C10'—C5'—C4'	118.5 (6)
C10—C5—C6	118.3 (7)			C10'—C5'—C6'	118.3 (7)
C7—C6—C5	120.2 (7)			C7'—C6'—C5'	120.7 (7)
C9—C10—C5	121.9 (7)			C9'—C10'—C5'	119.9 (7)
C8—C7—C6	121.7 (7)			C8'—C7'—C6'	121.4 (7)
C9—C8—C7	117.9 (7)			C9'—C8'—C7'	118.5 (7)
C11—C8—C7	122.3 (7)			C11'—C8'—C7'	121.5 (8)
C11—C8—C9	119.7 (7)			C11'—C8'—C9'	120.0 (8)
C10—C9—C8	120.0 (7)			C10'—C9'—C8'	121.2 (7)

Fig. 1. View to indicate the atomic labelling scheme and to show the close approach, in anti-parallel alignment, between the diacetylene units of two molecules related by a symmetry centre.

Discussion. The molecules have an approximate two-fold rotation axis perpendicular to the C1—C1' bond. The compound does not undergo solid-state polymerization and its crystal structure does not exhibit the inclined close stack of diacetylene units that is associated with materials that are reactive. The structure here is quite different to either form (active and inactive) of the unmethylated benzoate compound (III). The molecular packing in crystals of the title compound seems to be dominated by a systematic alignment of all the 4-methylbenzoate groups so that

Fig. 2. View of unit-cell contents in projection down the *b* axis.

all benzene rings are normal to the direction of the *c* axis but with opposing orientations of ester group dipoles (see Fig. 2). Within this overall framework there are pairs of molecules (related one to each other by a symmetry centre) such that the diacetylene units are mutually anti-parallel with a *trans*-type

separation between reactive C atoms of 4·25 Å, between C2···C2 (at $-x$, $-y$, $1-z$). Nevertheless this does not afford a mechanism for polymerization since the shortest approach between reactive C atoms in *different* pairings is 5·61 Å, between C2'···C2 (at x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$). This is both too long and chemically incompatible for an infinite reaction which would here require alternating contacts of type C2···C2 and C2'···C2'. The shortest C2'···C2' approach between different pairs of molecules is at 6·43 Å.

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(E)-1-Cyano-2,6-dimethoxy-3-fulvenyl Acetate

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Abstract. (E)-1-Cyano-2,6-dimethoxy-3-fulvenyl acetate, $C_{11}H_{11}NO_4$, $M_r = 221·21$, monoclinic, $P2_1$, $a = 4·079$ (7), $b = 8·096$ (2), $c = 16·518$ (5) Å, $\beta = 95·07$ (6)°, $V = 543$ (1) Å^3, $Z = 2$, $D_x = 1·352$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·112$ mm^{-1}, $F(000) = 232$, room temperature, $R = 0·044$ for 631 observed reflections. In contrast to other fulvenes with electron-donor substituents on the exocyclic C atom (C6), which have intermediate single–double bond lengths, the title compound shows a clear double-bond fixation in the fulvenic system. The dipolar canonical forms do not contribute significantly to the structure description.

Introduction. The fulvenes are an interesting class of compounds with properties that lie between those of polyenes and aromatic compounds such as benzene. Their behaviour depends on the contribution of each canonical form to the real structure. If form (II) is predominant the fulvene has aromatic character because of the presence of 6π electrons delocalized in the ring; conversely, if form (I) is predominant the molecule exhibits polyenic character. The contribution of each canonical form is strongly determined by the substituents. The structures of fulvenes have

been analyzed by means of different physical and chemical methods, but whenever X-ray diffraction is possible it is preferred. Thus it has been shown that alkyl and aryl fulvenes are basically polyenic like fulvene (Norman & Post, 1961; Mano, Takusagawa, Hinamoto & Kushi, 1973), whereas a large number of 6-heterosubstituted fulvenes show aromatic character (Ammon, 1974; Ammon & Wheeler, 1975; Ammon & Erhardt, 1980; Böhme & Burzlaff, 1974). Other fulvenes have been described that have extended non-aromatic delocalization showing special features (Ferguson, Marsh, Restivo & Lloyd, 1975; Ficini, Revial & Jeannin, 1981; Fuess & Lindner, 1975; Bruce, Walton, Williams, Hall, Skelton & White, 1982). Recently our group has designed a synthesis for new highly functionalized fulvenes (Victory, Alvarez-Larena, Barbera, Batllori, Borrell & Córdoba, 1989). We present here the X-ray structure determination of the title compound in the context of a general study of the nature of these fulvenes.

(I)   (II)
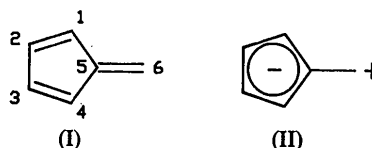
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