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Hexa-2,4-diyne-1,6-diyl Bis(4-hexyloxybenzoate), White Form at 185 K

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Abstract. $C_{32}H_{38}O_6$, $M_r = 518{\cdot}65$, monoclinic, $P2_1/c$, $a = 18{\cdot}971\,(7)$, $b = 7{\cdot}800\,(4)$, $c = 19{\cdot}615\,(4)$ Å, $\beta = 99{\cdot}63\,(2)°$, $U = 2861{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}20$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}076$ mm^{-1}, $F(000) = 1112$, $T = 185$ K, $R = 0{\cdot}039$ and $wR = 0{\cdot}0415$ for 3176 reflections. The structure at 185 K shows little change from that found in an earlier room-temperature study [Shklover, Struchkov, Bagirov, Konstantinov & Amerik (1985). *Z. Kristallogr.* **173**, 25–31]. The crystals do not undergo noticeable solid-state polymerization despite relatively short separations (3·83 and 4·29 Å) between reactive acetylenic C atoms in neighbouring molecules. These 1···4 diyne contacts occur between adjacent molecules related by centres of symmetry in contrast to the unit translation stacking arrangement that is commonly found in diacetylene compounds that do undergo crystal-phase polymerization. The banana-shaped hexadiyne unit ($\langle \text{C—C≡C} \rangle = 176{\cdot}9°$) may result from competition between alternative packing requirements.

Introduction. Part of our studies towards polymeric liquid crystals have been concerned with the syntheses and properties of diacetylenes bearing mesogenic side groups bonded through carboxylate ester linkages and related compounds (Hardy, Milburn, Nyitrai, Horvath, Balazs, Varga & Shand, 1988).

This determination was undertaken to provide information about molecular conformation and packing in a model system where the ester groups are decoupled from the diacetylene unit by only a single methylene group. The restricted mobility of this arrangement

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 are the diagonal elements of the diagonalized orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
O1	0·11908 (9)	0·15062 (21)	0·14362 (8)	0·0388 (8)
O3	0·18633 (9)	0·13716 (22)	0·24868 (8)	0·0429 (9)
O5	0·27691 (9)	0·84370 (21)	0·12470 (7)	0·0393 (8)
C1	0·08551 (17)	−0·00804 (36)	0·15740 (12)	0·0411 (14)
C2	0·06441 (12)	−0·09715 (30)	0·09227 (11)	0·0350 (11)
C3	0·04958 (11)	−0·17417 (28)	0·03950 (11)	0·0322 (11)
C7	0·16857 (11)	0·21098 (29)	0·19440 (10)	0·0310 (11)
C8	0·19721 (11)	0·37681 (29)	0·17578 (10)	0·0292 (10)
C9	0·17802 (11)	0·44926 (31)	0·10984 (11)	0·0319 (11)
C10	0·20592 (12)	0·60405 (31)	0·09490 (11)	0·0336 (11)
C11	0·25299 (11)	0·69034 (29)	0·14481 (11)	0·0322 (11)
C12	0·27246 (12)	0·62170 (32)	0·21047 (11)	0·0353 (12)
C13	0·24474 (12)	0·46450 (32)	0·22461 (11)	0·0336 (11)
C14	0·32542 (13)	0·94320 (32)	0·17302 (12)	0·0376 (12)
C15	0·34519 (14)	1·09567 (33)	0·13352 (12)	0·0381 (12)
C16	0·39617 (14)	1·21804 (33)	0·17638 (12)	0·0398 (12)
C17	0·41121 (13)	1·37436 (33)	0·13535 (12)	0·0397 (12)
C18	0·46106 (16)	1·50316 (39)	0·17530 (15)	0·0514 (16)
C19	0·47634 (24)	1·65370 (49)	0·13167 (22)	0·0672 (23)
O2	0·06929 (8)	−0·60921 (19)	−0·11400 (7)	0·0322 (7)
O4	0·02135 (8)	−0·73718 (20)	−0·21343 (7)	0·0352 (8)
O6	0·24280 (8)	−1·29018 (20)	−0·06234 (7)	0·0342 (8)
C4	0·03612 (12)	−0·27057 (29)	−0·02029 (11)	0·0324 (10)
C5	0·02736 (12)	−0·35818 (29)	−0·07086 (11)	0·0332 (11)
C6	0·01837 (13)	−0·47128 (31)	−0·13045 (11)	0·0339 (11)
C20	0·06233 (11)	−0·74117 (28)	−0·15905 (10)	0·0285 (10)
C21	0·10955 (11)	−0·88501 (27)	−0·13372 (10)	0·0273 (10)
C22	0·11465 (11)	−1·02430 (30)	−0·17674 (10)	0·0313 (11)
C23	0·15811 (12)	−1·16170 (30)	−0·15543 (11)	0·0312 (11)
C24	0·19759 (11)	−1·16297 (28)	−0·08877 (10)	0·0281 (10)
C25	0·19214 (12)	−1·02583 (30)	−0·04453 (11)	0·0312 (11)
C26	0·14881 (12)	−0·88974 (30)	−0·06636 (11)	0·0306 (11)
C27	0·25188 (13)	−1·43462 (32)	−0·10539 (11)	0·0348 (12)
C28	0·30267 (13)	−1·55787 (31)	−0·06397 (12)	0·0355 (12)
C29	0·31744 (13)	−1·71120 (31)	−0·10715 (11)	0·0337 (11)
C30	0·36491 (13)	−1·84651 (32)	−0·06764 (11)	0·0353 (12)
C31	0·37750 (13)	−2·00090 (32)	−0·11137 (13)	0·0384 (12)
C32	0·42681 (20)	−2·13380 (46)	−0·07268 (20)	0·0594 (19)

Table 2. *Molecular geometry*

(*a*) Selected intramolecular distances (Å)

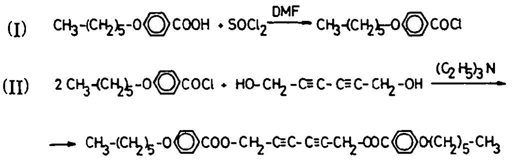
C4—C3	1·381 (3)	C4—C5	1·193 (3)
C5—C6	1·452 (3)	C3—C2	1·189 (3)
C2—C1	1·451 (3)		

(*b*) Selected intramolecular angles (°)

C6—C5—C4	177·32 (24)	C5—C4—C3	176·90 (25)
C4—C3—C2	176·24 (24)	C3—C2—C1	177·31 (26)

might be expected to lead to competition between mutual alignment of side groups among molecules on the one hand, and, on the other hand, the well established tendency for the central diacetylene units to assume an inclined vertical stack appropriate for topochemical 1···4 *trans*-polymerization [as for example in bis(*p*-toluenesulfonate)-hexa-2,4-diyne (Enkelmann, Leyrer & Wegner, 1979)]. Regular searches of the CSSR (1980) database did not indicate any other X-ray structures in this particular area until after this determination was complete when we were alerted to a previous independent room-temperature study of the same compound (Shklover, Struchkov, Bagirov, Konstantinov & Amerik, 1985).

The title compound was prepared by us according to the reaction scheme below (DMF = dimethylformamide).



Experimental. Colourless rectangular crystals grown from methanol/diethyl ether. Crystals did not undergo noticeable polymerization upon heating or X-irradiation. Crystal used for X-ray measurements had dimensions 0·4 × 0·3 × 0·2 mm. Approximate cell parameters from oscillation and Weissenberg photographs (Cu $K\alpha$ radiation). Intensity data and accurate cell parameters measured using an Enraf–Nonius CAD-4 diffractometer equipped with ULT1 attachment and graphite monochromator.

Cell parameters refined from setting angles of 25 automatically centred reflections with $28 \leq 2\theta \leq 30°$. Intensity data for $2 \leq 2\theta \leq 50°$, 5613 reflections measured, $0 \leq h \leq 22$, $0 \leq k \leq 8$, $-23 \leq l \leq 22$, $\omega/2\theta$ scan mode with scan angle $(0{\cdot}8 + 0{\cdot}34\tan\theta)°$. Two check reflections ($\bar{1},3,\overline{11}$ and $11,1,5$) were measured periodically and showed no significant intensity change. Corrections for Lorentz and polarization effects but not absorption. 5026 unique reflections, 3176 with $F_o > 6\sigma(F_o)$ used for all calculations.

Structure solved by direct methods (*SHELXS*86; Sheldrick, 1986); H atoms located from difference Fourier syntheses. Least-squares refinement (*SHELX*76; Sheldrick, 1976) to minimize $\sum w(|F_o| - |F_c|)^2$ with isotropic thermal parameters for H atoms and anisotropic parameters for all others. Final cycle of least-squares refinement had max. $\Delta/\sigma = 0{\cdot}04$. Final

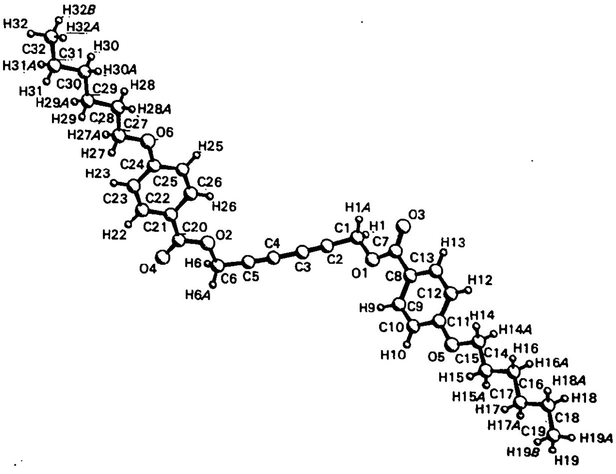


Fig. 1. View of molecule showing atom labels.

weighting scheme was $w^{-1} = 1 + 0{\cdot}0025(F_o - 18{\cdot}5)^2$ for $F_o > 18{\cdot}5$ and $w^{-1} = 1 + 0{\cdot}004(18{\cdot}5 - F_o)^2$ for $F_o < 18{\cdot}5$. Final value of isotropic extinction parameter was $g = 5{\cdot}6\,(16) \times 10^{-8}$ where $F_c' = F_c(1 - gF_c^2/\sin\theta)$. Maximum range on $\Delta\rho$ map $\pm 0{\cdot}19$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed using an Acorn ACW443 workstation.

Final atomic parameters (excluding H atoms) are listed in Table 1 and selected bond lengths and angles are listed in Table 2.* Fig. 1 shows the atomic labelling scheme.

Discussion. The obvious and expected difference between this determination (at low temperature) and the earlier room-temperature study is a sharp reduction in the magnitude of the atomic thermal parameters, which is especially pronounced for the aliphatic end chains. Associated with this is an improvement in the e.s.d.'s of the atomic coordinates. Our coordinates and atom labels have been transformed to correspond to those of the earlier study.

Lowering the temperature makes little difference to the molecular geometry. Torsion angles, bond angles and bond lengths are essentially unchanged, with the exception of a slight enhancement in regularity of bond lengths within the benzene units. The low-temperature structure retains the asymmetry of bond angles at the substituent-bearing carbons of the benzene rings and confirms the banana shape of the central hexadiyne system. The average C≡C—C angle in the hexadiyne unit is 176·9°, and the distortions from linearity are all in the same sense. These are distortions that we would tentatively associate with the type of competition between alternative molecular packing requirements that were described in the *Introduction*. The molecular packing at low temperature is the same as that at room temperature except for rather small changes to intermolecular distances.

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* Lists of structure factors, anisotropic thermal parameters for C and O atoms, and fractional coordinates and isotropic temperature factors for H atoms have been deposited with British Library Document Supply Centre as Supplementary Publication No. SUP 51499 (22 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 1-Methyl-3,3′-dioxo-2′-phenylspiro[indole-2,1′-isoindole], a Novel Rearrangement Product from Reaction of Aniline with a Dioxodibenz[*b,f*]azocine

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Abstract. $C_{22}H_{16}N_2O_2$, $M_r = 340{\cdot}39$, monoclinic, $P2_1/c$, $a = 14{\cdot}096\,(2)$, $b = 13{\cdot}891\,(2)$, $c = 9{\cdot}022\,(2)$ Å, $\beta = 103{\cdot}03\,(1)°$, $V = 1721\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}313$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7170 Å, $\mu = 0{\cdot}796$ cm^{-1}, $F(000) = 712$, $T = 294$ K, $R = 0{\cdot}034$ for 1253 unique reflections with $|F_o| > 3\sigma(|F_o|)$. The present study established the structure of the title compound obtained from a temperature-dependent rearrangement reactions have been found to occur (Letcher & occurs with the two planes at right angles (90·1°) to each other and with no unusual intramolecular distances or angles.

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