2,4-Hexadiynylene Bis(furoate)

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Abstract. $C_{16}H_{10}O_6$, $M_r = 298 \cdot 23$, monoclinic, $C2/c$, $a = 15 \cdot 2161$ (4), $b = 12 \cdot 0269$ (2), $c = 8 \cdot 2297$ (2) Å, $\beta = 108 \cdot 9548$ (2)°, $V = 1424 \cdot 39$ Å³, $D_x = 1 \cdot 3896$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 67$ cm⁻¹, $Z = 4$, $F(000) = 616$, $T = 295$ K, $R = 0 \cdot 0469$ for 1247 unique reflections. The furan rings at each end of the diacetylene moiety are coparallel so that it could be assumed that this diacetylene monomer is suitable for 1,4 addition polymerization between adjacent molecules. However, calculation shows that the distance between the reactive sites in adjacent molecules is $4 \cdot 149$ (3) Å, thus excluding any possibility of 1,4 addition polymerization, since a distance of < 4 Å is required [Ando, Bloor, Hubble & Williams (1980). *Makromol. Chem.* **181**, 453–467]. The bond angles and bond distances are in good agreement with those of comparable molecules.

Experimental. The title compound was prepared from 2,4-hexadiyne-1,6-diol (Stansbury & Proops, 1962) and 2-furoyl chloride. Recrystallization from ethanol gave pale-yellow crystals. (Calc. C = 64·43, H = 3·38, O = 32·19%; found C = 64·42, H = 3·38, O = 32·21%; m.p. 407–408 K.)
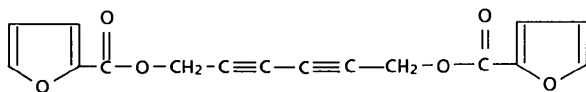
(I)

Single crystals of (I) were grown by slow evaporation of an ethanolic solution. A crystal of approximate dimensions 0·5 × 0·35 × 0·2 mm was used for data collection. D_m was not measured. The X-ray data were collected on an Enraf–Nonius CAD-4 diffractometer. The positions of 25 automatically centred reflections, θ range 15–16°, were used to calculate a least-squares orientation matrix, from which accurate cell parameters were determined. Intensity data for 1247 unique reflections were obtained using graphite-monochromated Mo $K\alpha$ radiation, ω-scan rate 1·0–6·6° min⁻¹,

Table 1. *Atomic parameters with standard deviations in parentheses*

$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
C(1)	0·03900 (14)	0·42199 (14)	−0·17901 (25)	0·0706 (12)
C(2)	0·10687 (14)	0·41752 (13)	−0·05450 (25)	0·0726 (12)
C(3)	0·18830 (14)	0·41108 (15)	0·0990 (26)	0·0757 (12)
C(4)	0·16092 (10)	0·24721 (13)	0·23316 (19)	0·06011 (10)
C(5)	0·13278 (10)	0·20581 (12)	0·37499 (18)	0·0548 (10)
C(6)	0·10460 (12)	0·25492 (14)	0·49589 (22)	0·0701 (11)
C(7)	0·08956 (14)	0·16898 (17)	0·60053 (29)	0·0861 (14)
C(8)	0·10790 (15)	0·07387 (16)	0·53510 (25)	0·0801 (13)
O(1)	0·16520 (8)	0·35841 (10)	0·23816 (14)	0·0695 (8)
O(2)	0·13517 (8)	0·09301 (10)	0·39611 (16)	0·0734 (10)
O(3)	0·17727 (11)	0·19090 (11)	0·12665 (18)	0·0903 (10)

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

C(1)–C(1*)	1·369 (3)	O(2)–C(5)	1·3667 (19)
C(1)–C(2)	1·196 (3)	O(2)–C(8)	1·3569 (25)
C(2)–C(3)	1·456 (3)	O(3)–C(4)	1·1961 (22)
C(4)–C(5)	1·456 (2)	C(3)–C(3A)	1·080 (3)
C(5)–C(6)	1·34 (3)	C(6)–C(7)	1·411 (3)
C(7)–C(8)	1·332 (3)	O(1)–C(3)	1·448 (3)
O(1)–C(4)	1·339 (2)		
O(4)–O(1)–C(3)	115·75 (13)	O(1)–C(4)–C(5)	109·94 (13)
C(5)–O(2)–C(8)	105·83 (14)	O(1)–C(4)–O(3)	124·64 (15)
O(2)–C(5)–C(4)	116·04 (13)	C(5)–C(4)–O(3)	125·41 (15)
O(2)–C(5)–C(6)	110·15 (13)	O(1)–C(3)–C(2)	110·65 (16)
O(4)–C(5)–C(6)	133·81 (14)	O(2)–C(8)–C(7)	110·90 (19)
C(2)–C(1)–C(1*)	177·41 (22)	C(5)–C(6)–C(7)	106·51 (16)
C(1)–C(2)–C(3)	178·79 (21)	C(8)–C(7)–C(6)	106·60 (18)

ω-scan width $(0 \cdot 8 + 0 \cdot 34 \tan\theta)°$, θ range $1 \cdot 5$–$20°$, *hkl* range: ±14, 10, 7. Two standard reflections measured every 2 h showed no decay. No absorption corrections were applied. The structure solution was by direct methods using *SHELX*86 (Sheldrick, 1986). The ring hydrogens and the hydrogens of the CH₂ group were set in idealized positions, and allowed to ride on their respective carbon atoms. Weighted least-squares anisotropic refinement [using *SHELX*76 (Sheldrick, 1976) with inlaid atomic scattering factors] of the non-hydrogen atoms and free isotropic refinement of all hydrogen atoms gave a final $R = 0 \cdot 0469$ and $wR = 0 \cdot 0540$ for 1037 data, $w^{-1} = [\sigma^2(F_o) + 0 \cdot 002(F_o)^2]$,
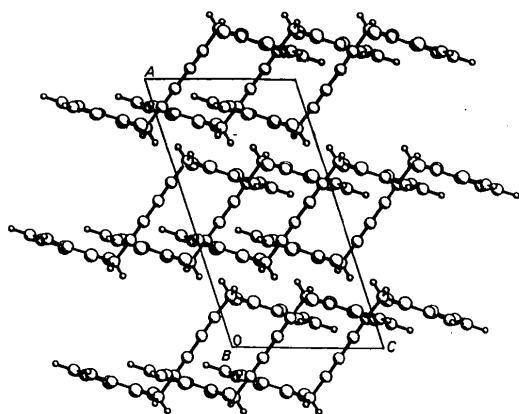
Fig. 1. The packing arrangement in the crystal viewed perpendicular to the *ac* plane.

Fig. 2. The molecular geometry and atomic labelling of a single molecule.

$F \leq 2 \cdot 00\sigma(F_o)$. The final ΔF map showed no peaks or troughs greater than $+0 \cdot 03 \, e \, Å^{-3}$. $(\Delta/\sigma)_{max} = 0 \cdot 01$.

Final atomic parameters are listed in Table 1, while the bond angles and bond lengths appear in Table 2.* The crystal packing is shown in Fig. 1. The atom-numbering scheme is shown in Fig. 2. Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Related literature. We recently reported the structures of 1,4-bis(4-pyridyl)butadiyne (Allan, Beaumont,

Macindoe, Milburn, Werninck & Barrow, 1988) and 1,6-diamino-1,1,1,6-tetramethyl-2,4-hexadiyne (Allan, Beaumont, Macindoe, Milburn, Welch & Werninck, 1988) as part of a study to investigate the possibility of 1,4 addition polymerization between adjacent diacetylene monomers.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51174 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
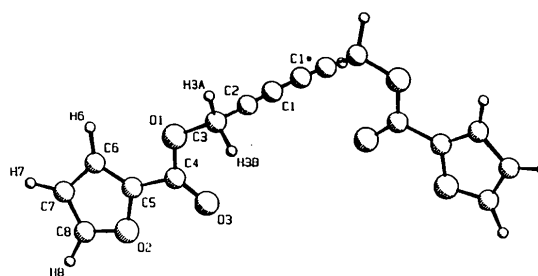
References

ALLAN, J. R., BEAUMONT, P. C., MACINDOE, L. A., MILBURN, G. H. W., WELCH, A. J. & WERNINCK, A. (1988). *J. Coord. Chem.* In the press.
ALLAN, J. R., BEAUMONT, P. C., MACINDOE, L. A., MILBURN, G. H. W., WERNINCK, A. & BARROW, M. J. (1988). *J. Inorg. Chim. Acta.* In the press.
ANDO, D. J., BLOOR, D., HUBBLE, C. L. & WILLIAMS, R. L. (1980). *Makromol. Chem.* **181**, 453–467.
GOULD, R. O. & TAYLOR, P. (1985). *CALC*. Program for molecular geometry calculations, Fortran 77 version. Univ. of Edinburgh, Scotland.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELX86*. Program for crystal structure determination. Univ. of Cambridge, England.
STANSBURY, H. A. JR & PROOPS, W. R. (1962). *J. Org. Chem.* **27**, 320.

Structure of a Dithiolane

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Abstract. Tetrahydropyran-3-spiro-(1',3'-dithiolane)-2-spirocyclohexane, $C_{12}H_{20}OS_2$, $M_r = 244 \cdot 4$, monoclinic, $P2_1/n$, $a = 9 \cdot 0929$ (4), $b = 9 \cdot 9160$ (8), $c = 14 \cdot 015$ (1) Å, $\beta = 100 \cdot 422$ (5)°, $V = 1242 \cdot 8$ (2) Å^3, $Z = 4$, $D_m = 1 \cdot 32$, $D_x = 1 \cdot 306 \, g \, cm^{-3}$, $\lambda(Cu \, K\bar{\alpha}) = 1 \cdot 54178$ Å, $\mu = 35 \cdot 02 \, cm^{-1}$, $F(000) = 528$, $R = 0 \cdot 0387$ for 1799 observed reflections with $F_o \geq 4 \cdot 0\sigma(F_o)$, $T = 296$ (2) K. The five-membered-ring atoms exhibit significant thermal motion possibly due to disorder. The structure displays no other unusual features.

Experimental. The compound was provided by Dr Tsekouras (Tsekouras, 1986). Density measured by

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