

account for the observed displacement (Δ) of C8 from the plane defined by the atoms to which it is bonded (Table 7). For compounds (I), (II) and (III), the observed out-of-plane displacements (Δ) are 0.139, 0.122 and 0.289 Å respectively. The more extensively O8 is hydrogen bonded, the more electron deficient C8 becomes and, thus, the more susceptible to interaction with the N lone pair. Therefore, the extent of hydrogen bonding to O8 can be correlated with the displacement (Δ) and in turn correlated with the C8–N bond length. This is consistent with the previous survey by Dunitz (1979) involving a number of compounds with interacting carbonyl and amino groups, where the C–N distances were correlated with the observed out-of-plane displacements.

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Structure of Dibenzo[*a,g*]cyclotrideca-4a,8a-diene-5,7-diyne-15-one

BY R. MORRIN ACHESON

Department of Biochemistry, University of Oxford, South Parks Road, Oxford OX1 3QU, England

ZBIGNIEW DAUTER

Department of Biochemistry, Technical University of Gdansk, Gdansk, Poland

ALEXANDER KARAULOV

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, England

GARY C. M. LEE

Department of Biochemistry, University of Oxford, South Parks Road, Oxford OX1 3QU, England

AND COLIN D. REYNOLDS

Biophysics Laboratory, Department of Physics, Liverpool Polytechnic, Liverpool L3 3AF, England

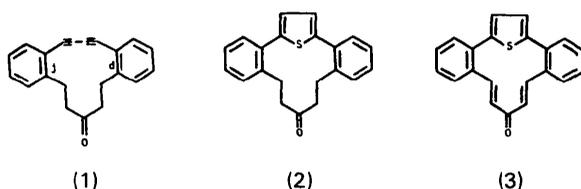
(Received 22 June 1987; accepted 9 May 1988)

Abstract. C₂₁H₁₆O, $M_r = 284.36$, monoclinic, $P2_1/c$, $a = 14.442$ (3), $b = 17.917$ (3), $c = 6.085$ (1) Å, $\beta = 94.17$ (1)°, $V = 1570.4$ Å³, $Z = 4$, $D_x = 1.204$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu(\text{Cu } K\alpha) = 0.487$ mm⁻¹, $F(000) = 600$, $T = 290$ (1) K, $R = 0.078$ for 1039 observed reflections. In the structure reported here, the 13-membered ring contains seven synperi-

planar, two antiperiplanar and four anticlinal conformational units. The diyne system is slightly non-linear. The phenyl rings are not coplanar but are twisted with respect to each other by 27°.

Introduction. The title compound (1) was prepared (Acheson & Lee, 1987) by a synthetic route expected to

give a compound of this constitution. With hydrogen sulfide dissolved in methanolic sodium methoxide (1) yielded the corresponding thiophene (2). Oxidation of (2) by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and by 3,4,5,6-tetrachloro-1,2-benzoquinone, instead of removing H atoms to give double bonds conjugated with the carbonyl group and structure (3), removed H₂S from the molecule in a reversal of the original thiophene synthesis to give back the original diyne (1) (Acheson & Lee, 1987). Since the destruction of the aromatic thiophene system in this way was so novel and unexpected, an X-ray crystal structure determination for the diyne (1) was carried out; suitable crystals of the thiophene (2) for a similar study have not yet been obtained.



Experimental. Colourless crystals were grown from ether. Unit-cell and space-group data from Weissenberg photographs, lattice parameters from least-squares refinement of 26 reflections with $20 < \theta < 30^\circ$. Systematic absences $h0l$, l odd and $0k0$, k odd confirmed space group $P2_1/c$.

Hilger & Watts Y290 four-circle diffractometer controlled by an LSI-11 microcomputer, ω scanning technique, crystal $\sim 0.40 \times 0.35 \times 0.25$ mm, count time per step 1 s, range of scan 0.6° , $\theta_{\max} = 51^\circ$ ($-14 \leq h \leq 13$, $0 \leq k \leq 15$, $0 \leq l \leq 6$), $R_{\text{int}} = 0.022$; 1449 independent reflections, 410 of which, with $I < 2.5\sigma(I)$, classified as unobserved; standard reflections 372, 192, 343; no intensity variation over period of data collection; Lorentz and polarization corrections but no absorption correction made [$\mu(\text{Cu K}\alpha) = 0.487 \text{ mm}^{-1}$].

The structure was solved by direct methods using the program *RANTAN* (Yao Jia-Xing, 1981). Structure refined by full-matrix least squares on F with *SHELX76* (Sheldrick, 1976). Atomic scattering factors and f' and f'' from *International Tables for X-ray Crystallography* (1974). All non-H atoms refined anisotropically. All the hydrogens were located from a difference Fourier map but calculated positions for the hydrogens were used in the refinement. Six reflections affected by extinction omitted. Refinement converged at $R = 0.078$, $wR = 0.102$ for 1039 observed reflections; weighting scheme $w = 1.0/[\sigma^2(F) + 0.003F^2]$. Final calculated shifts $\leq 0.02\sigma$; residual electron density in final difference map: $-0.17 \leq \Delta\rho \leq 0.18 \text{ e \AA}^{-3}$. Figure drawn with *ARTIST* (Valley, 1982).

Discussion. A perspective view of (1) showing the atomic nomenclature used in the analysis, is given in Fig. 1. The atomic coordinates for the non-hydrogen atoms are listed in Table 1 and selected bond distances and angles in Table 2.* The endocyclic torsion angles for the 13-membered carbocyclic system are also given in Table 2. The 13-membered ring contains seven synperiplanar, two antiperiplanar and four anticlinal conformational units.

An interesting feature of the structure is the slight bowing of the diyne system (Fig. 1) with $\text{C}(5)\text{—C}(6)\text{—C}(7)$, $\text{C}(6)\text{—C}(7)\text{—C}(8)$, $\text{C}(7)\text{—C}(8)\text{—C}(9)$ and $\text{C}(8)\text{—C}(9)\text{—C}(10)$ angles of $168.9(5)$, $167.0(5)$, $168.8(5)$ and $168.7(5)^\circ$ respectively. The phenyl rings are essentially planar with maximum deviations from the mean least-squares plane of $0.015(12)$ and $0.006(4) \text{ \AA}$ for rings *A* and *B* respectively. The phenyl rings are not coplanar but are twisted with a dihedral angle of $27.0(5)^\circ$. Apart from one hydrogen-bonded intermolecular contact in the crystal, $\text{C}(16)\text{—H}(16)\cdots\text{O}(1)$ ($1-x, -y, -z$) $3.34(1) \text{ \AA}$ (discussed below), the crystal structure is stabilized by van der Waals contacts.

The unusual stability of the diyne (1) with respect to the thiophene (2) could be related to some additional resonance stabilization of (4) leading to the formation of the hydrogen bond† in the solid phase. The

* 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 51015 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† We thank the referee for drawing our attention to this possibility and to some of the data discussed.

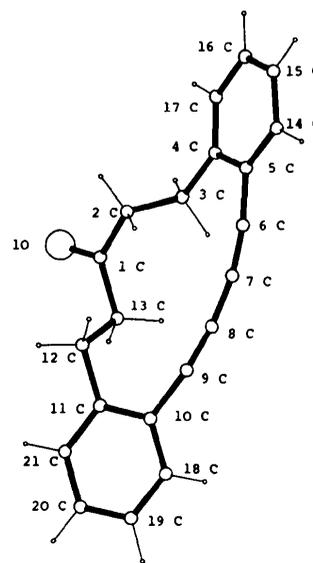


Fig. 1. Perspective view of the molecule with atomic nomenclature.

additional resonance structure (5) is unlikely to be a significant contributor for steric reasons; the cumulene form should be linear. The resonance stabilization in

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^4$) with e.s.d.'s in parentheses

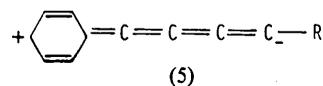
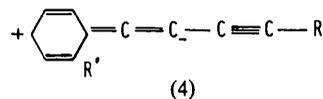
$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	2223 (3)	340 (3)	-1771 (9)	1028
O(1)	2369 (2)	-62 (2)	-3282 (6)	1274
C(2)	2997 (3)	804 (3)	-636 (7)	1046
C(3)	3339 (3)	444 (3)	1589 (8)	1138
C(4)	4099 (3)	899 (3)	2825 (9)	1103
C(5)	3891 (3)	1545 (3)	4021 (8)	1046
C(6)	2940 (4)	1772 (3)	3921 (8)	1043
C(7)	2122 (4)	1887 (3)	3528 (8)	1008
C(8)	1228 (4)	1914 (3)	2688 (8)	964
C(9)	466 (4)	1833 (3)	1721 (9)	1007
C(10)	-335 (3)	1632 (2)	338 (7)	950
C(11)	-190 (4)	1264 (3)	-1658 (8)	989
C(12)	772 (3)	1081 (3)	-2329 (8)	1015
C(13)	1248 (3)	436 (3)	-1043 (8)	995
C(14)	4588 (4)	1940 (3)	5223 (9)	1165
C(15)	5512 (4)	1703 (4)	5150 (11)	1355
C(16)	5712 (5)	1097 (4)	3968 (11)	1429
C(17)	5016 (4)	682 (4)	2844 (9)	1272
C(18)	-1217 (3)	1803 (3)	945 (9)	1073
C(19)	-1999 (4)	1594 (3)	-415 (11)	1147
C(20)	-1868 (4)	1227 (3)	-2398 (12)	1180
C(21)	-983 (4)	1062 (3)	-2992 (9)	1086

Table 2. Bond distances (\AA), angles ($^\circ$) and endocyclic torsion angles ($^\circ$) of compound (1) with e.s.d.'s in parentheses

1	2	3	4	1-2	1-2-3	1-2-3-4
O(1)	C(1)	C(2)	C(3)	1.198 (7)	121.0 (4)	
C(2)	C(1)	C(13)	C(12)	1.517 (7)	118.3 (4)	
C(13)	C(1)	O(1)		1.517 (7)	120.6 (4)	
C(13)	C(1)	C(2)	C(3)			81.1
C(1)	C(2)	C(3)	C(4)		110.3 (4)	-178.5
C(2)	C(3)	C(4)	C(5)	1.549 (7)	112.4 (4)	78.6
C(3)	C(4)	C(5)	C(6)	1.522 (7)	121.5 (4)	-3.2
C(3)	C(4)	C(17)			120.7 (5)	
C(4)	C(5)	C(6)	C(7)	1.411 (8)	116.8 (4)	-17.7
C(5)	C(4)	C(17)			117.9 (5)	
C(4)	C(5)	C(14)			121.0 (5)	
C(6)	C(5)	C(14)			122.2 (5)	
C(5)	C(6)	C(7)	C(8)	1.430 (8)	168.9 (5)	-2.2
C(6)	C(7)	C(8)	C(9)	1.205 (9)	167.0 (5)	15.0
C(7)	C(8)	C(9)	C(10)	1.355 (8)	168.8 (5)	-8.3
C(8)	C(9)	C(10)	C(11)	1.219 (7)	168.7 (5)	-17.9
C(9)	C(10)	C(11)	C(12)	1.426 (7)	117.4 (4)	0.0
C(9)	C(10)	C(18)			120.6 (4)	
C(11)	C(10)	C(18)		1.411 (7)	122.0 (4)	
C(10)	C(11)	C(12)	C(13)		122.1 (4)	73.7
C(10)	C(11)	C(21)			116.9 (5)	
C(12)	C(11)	C(21)		1.511 (7)	121.0 (4)	
C(11)	C(12)	C(13)	C(1)		114.4 (4)	-176.6
C(12)	C(13)	C(1)	C(2)	1.530 (7)	109.2 (4)	-86.7
C(5)	C(14)	C(15)		1.394 (7)	118.8 (5)	
C(14)	C(15)	C(16)		1.403 (8)	120.2 (6)	
C(15)	C(16)	C(17)		1.346 (10)	121.2 (6)	
C(4)	C(17)	C(16)		1.378 (7)	120.9 (6)	
C(16)	C(17)			1.390 (9)		
C(10)	C(18)	C(19)		1.386 (6)	120.0 (5)	
C(18)	C(19)	C(20)		1.402 (7)	118.8 (5)	
C(19)	C(20)	C(21)		1.399 (9)	120.7 (5)	
C(11)	C(21)	C(20)		1.402 (7)	121.7 (7)	
C(20)	C(21)			1.386 (9)		

thiophene itself, per ring atom, is almost the same as that of benzene (Acheson, 1976), but the destabilizing effects of possible steric crowding and planarity distortions in the thiophene (2) cannot be estimated, as



suitable crystals for X-ray diffraction studies have not been obtained. The postulate of a hydrogen bond is consistent with the bond length criteria of Taylor & Kennard (1982) since in our case their '*d*' parameter [van der Waals radii of (H) + (O) = (H...O distance)] is 0.32 \AA and greater than their cut-off distance of 0.30 \AA , and the C-H...O angle of 147 $^\circ$ is consistent with this hypothesis. The idea of a benzene proton being involved in a hydrogen bond is not new, but the acetylene (1) appears to be the first compound without Cl atoms which possesses a bond of this type. Allerhand & Schleyer (1963), on the basis of infrared studies of substituted benzenes, concluded that at least three Cl atoms were necessary before the proton acidity was sufficiently increased to permit hydrogen bond formation. However, acetylenes are electron acceptors and the bond lengths for bis(3-chlorophenyl)acetylene (Espiritu & White, 1977), where the Cl atoms are cross conjugated and cannot interact with the acetylenic bond, indicate that resonance of the type shown in (4) must be present and the triple bond is longer than that of acetylene itself (van Nes & van Bolhuis, 1979). One may conclude that hydrogen bonds involving benzene protons may be formed more easily than hitherto suspected, and that the discovery of more examples may be expected.

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