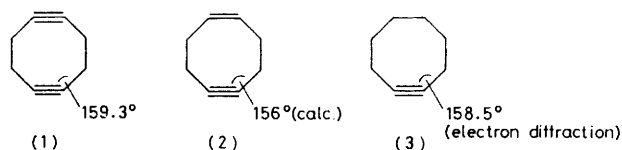


Crystal Structure of 5,6-Didehydrodibenzo[*a,e*]cyclo-octene

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The structure of 5,6-didehydrodibenzo[*a,e*]cyclo-octene $C_{16}H_{10}$ has been determined from single-crystal X-ray analysis by direct methods. The crystals are monoclinic, space group $P2_1/c$, $Z = 8$, $a = 10.130(7)$, $b = 12.434(2)$, $c = 17.031(5)$ Å, $\beta = 99.05(4)^\circ$. Full-matrix least-squares refinement based on 1517 reflexions with intensities $I > 2\sigma(I)$ and 527 non-significant ones in the range $2\sigma(I) > I > \sigma(I)$ converged to $R(R_w) = 0.053$ (0.064) without and to $R(R_w) = 0.086$ (0.066) including non-significant reflexions. The geometry of the two independent molecules A and B is slightly different, A being planar within 0.031 Å, B within 0.174 Å. The benzene rings in B are tilted by 9.9° . The mean angular deformation of the acetylenic bonds is 26.0° .

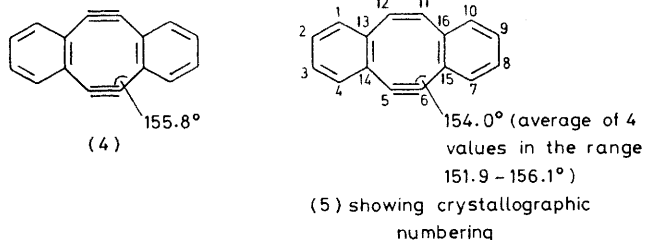
THE synthesis of cyclo-octa-1,5-diyne (1)¹ and cyclo-oct-1-en-5-yne (2)² have been reported by Wirz *et al.* An X-ray crystallographic analysis³ of the strained diacetylene (1) at 103 K showed, *inter alia*, that the deviation of the acetylenic bond angle from the normal value (180°) is 20.7° . This deviation is similar to that found in cyclo-octyne (3)⁴ (21.5°) by an electron diffrac-



tion study of the molecule in the gas phase, whereas the deviation in the cyclic enyne (2) by a strain minimization force field calculation was found to be somewhat greater (24°).²

5,6,11,12-Tetra- (4) and 5,6-didehydrobenzo[*a,e*]cyclo-octene (5) are dibenzannulated conjugated eight-membered ring compounds, formally related to (1) and (2), respectively, which have been synthesized by the University College group.⁵ An X-ray crystallographic analysis⁶ of the diacetylene (4) revealed, *inter alia*, that the angular deformation of the acetylenic bond is 24.2 (1) $^\circ$.

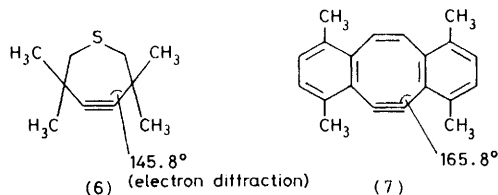
In this paper, we describe the results of an X-ray crystallographic analysis of the cyclic monoacetylene (5).



This had to be carried out at relatively low temperature, since crystalline (5) [unlike (4)] is very unstable at room temperature. By analogy with (1) and (2), the deviation of the acetylenic bond angle from the normal value in (5) was expected to be even greater than in the previously investigated (4), and this proved to be the case

(average deviation, 26.0°). The only cyclic acetylene in which the angular deformation of the acetylene bond appears to be greater than in (5) is 3,3,6,6-tetramethyl-1-thiacycloheptyne (6), in which the deformation was found to be 34.2° by an electron diffraction study of the molecule in the gas phase.⁷

It is useful to mention that the synthesis and X-ray crystallographic analysis of 1,4,7,10-tetramethyl-5,6-didehydrodibenzo[*a,e*]cyclo-octene (7), a compound which is surprisingly more stable than the closely related substance (5), have recently been reported.⁸ The angular deformation of the acetylenic bond in (7) was



found to be only 14.2° , but this value must be taken with some reserve, since the crystal structure was stated to be disordered.⁸

EXPERIMENTAL

(a) *Synthesis of 5,6-Didehydrodibenzo[*a,e*]cyclo-octene (5).*—A solution of 5,6-dibromo-5,6-dihydrodibenzo[*a,e*]cyclo-octene (204 mg, 0.56 mmol)⁹ in dry tetrahydrofuran (2.5 ml) was added dropwise during 1 min to a stirred solution of potassium *t*-butoxide (200 mg, 1.78 mmol, purified by sublimation) in dry tetrahydrofuran (20 ml) at room temperature under nitrogen, and the solution was stirred for 1 min. Aqueous hydrochloric acid (2N, 10 ml) was added, followed by ether (20 ml). The ether extract was washed with water (3×20 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Chromatography of the residue on a column of alumina (20 g; Woelm neutral; grade III) and elution with pentane yielded compound (5) (38.5 mg, 34%) as golden yellow crystals, which melted at *ca.* $85^\circ C$ on attempted m.p. determination. The crystals decomposed after being allowed to stand for a few min at room temperature.

(b) *X-Ray Analysis.*—Compound (5) was crystallized from chloroform as monoclinic needles elongated along [100].

Crystal data. C₁₆H₁₀, $M = 202.2$, $a = 10.130(7)$, $b = 12.434(2)$, $c = 17.031(5)$ Å, $\beta = 99.05(4)^\circ$, $D_c = 1.585$ g, cm⁻³ at 183 K, $Z = 8$, $F(000) = 1248$, $\mu(\text{Mo-K}\alpha) = 0.9$ cm⁻¹. Space group $P2_1/c$ from systematic absences.

The diffraction data were collected at 183 K on a CAD-4 four-circle diffractometer employing graphite-monochromatized Mo-K α -radiation ($\lambda = 0.71069$ Å) using a crystal of dimensions $0.4 \times 0.1 \times 0.1$ mm³. The reflexions

TABLE 1

Fractional co-ordinates ($\times 10^4$) of the carbon atoms of 5,6-didehydridibenzo[*a,e*]cyclo-octene. E.s.d.s referring to the last digit are given in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Molecule A			
C(1)	8 005(5)	2 255(5)	1 104(3)
C(2)	8 501(6)	1 238(5)	1 263(4)
C(3)	8 639(6)	546(5)	647(4)
C(4)	8 221(5)	877(4)	-134(3)
C(5)	7 254(5)	2 319(4)	-1 069(3)
C(6)	6 785(5)	2 975(4)	-1 541(3)
C(7)	5 854(5)	4 322(4)	-2 569(3)
C(8)	5 366(6)	5 336(5)	-2 743(3)
C(9)	5 237(6)	6 054(4)	-2 142(3)
C(10)	5 645(5)	5 738(4)	-1 354(3)
C(11)	6 515(5)	4 480(4)	-290(3)
C(12)	7 039(5)	3 742(4)	244(3)
C(13)	7 567(4)	2 621(4)	337(3)
C(14)	7 716(5)	1 892(4)	-293(3)
C(15)	6 231(5)	3 997(4)	-1 783(3)
C(16)	6 137(5)	4 707(4)	-1 148(3)
Molecule B			
C(1)	-759(6)	-616(5)	3 215(3)
C(2)	-744(6)	-1 298(5)	2 577(3)
C(3)	307(6)	-1 262(4)	2 146(3)
C(4)	1 321(6)	-503(5)	2 353(3)
C(5)	2 301(5)	968(4)	3 231(3)
C(6)	2 853(5)	1 658(4)	3 686(3)
C(7)	4 061(6)	2 955(4)	4 667(3)
C(8)	4 160(6)	3 511(5)	5 363(4)
C(9)	3 137(7)	3 443(5)	5 815(4)
C(10)	2 018(6)	2 822(5)	5 555(3)
C(11)	712(5)	1 581(5)	4 619(3)
C(12)	123(5)	841(4)	4 124(3)
C(13)	226(5)	154(4)	3 435(3)
C(14)	1 294(5)	202(4)	2 991(3)
C(15)	2 958(5)	2 301(4)	4 400(3)
C(16)	1 915(5)	2 228(4)	4 843(3)

were scanned in the ω mode ($2.0 < \theta < 24.7$). The standard reflexions $3\bar{5}4$, $2\ 0\ 6$, and $4\ 2\ 0$ were used for the calculation of a polynomial function of the exposure time in order to correct for loss of scattering (4.3%) during the exposure (120 h). A total number of 3 317 independent reflexions were measured of which 1 517 had intensities with $I > 2\sigma(I)$, 527 non-significant ones had intensities in the range $2\sigma(I) > I > \sigma(I)$, and 1 273 non-observed ones had intensities with $I < \sigma(I)$. Only the first two groups were used during the refinement.

Structure determination and refinement. The structure was readily solved using the multiple solution program package MULTAN.¹⁰ No chemical information was added to the program part NORMAL. The solution with the best combined figure of merit produced all heavy atoms from the positions of peaks in the *E*-map. The least-squares refinement was straightforward. The hydrogen positions were derived from difference Fourier maps. The scattering factors of carbon and hydrogen were taken from ref. 11. During the final cycles the full matrix of normal equations was employed using 2 044 reflexions with $I > \sigma(I)$. The

hydrogen atoms were refined isotropically, the carbon atoms anisotropically. The weight used during the refinement were $\sigma^2[F(hkl)]$, where $\sigma^2 = \sigma^2$ (counting statistics) + ρF^2 obs. The factor $\rho (= 0.02)$ is based upon an estimation for neglected absorption effects and errors in the polynomial correction.

The final reliability indices $R(R_w)$ are 0.053 (0.064 3) for observed reflexions only and 0.086 5 (0.066 5) for reflexions including the group $2\sigma(I) > I > \sigma(I)$. A list of structure factors as well as thermal parameters of carbon atoms and co-ordinates and Debye-parameters of the hydrogen atoms is deposited in Supplementary Publication No. SUP 22994 (8 pp.).* The positional parameters and the standard deviations (e.s.d.s) of the heavy atoms are listed in Table 1. The mean e.s.d.s in C-C bond lengths, C-C-C valency angles, and C-C-C-C dihedral angles are 0.007 5 Å, 0.5, and 0.8°, respectively.

DISCUSSION

The bond lengths and valency angles of the two molecules A and B observed are depicted in Figure 1. It can be seen that local double and triple bonds occur in the eight membered rings whose endocyclic torsion angles are listed in Table 2.

Disregarding small differences in planarity, the most striking features of the heavily strained molecules are the

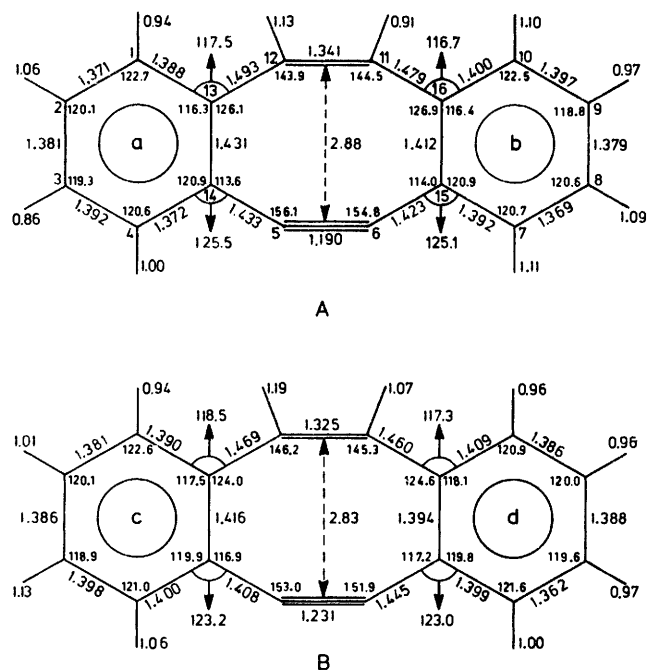


FIGURE 1 Bond lengths in Å and valency angles of 5,6-didehydridibenzo[*a,e*]cyclo-octene (molecules A and B). E.s.d.s in parentheses

serious angular distortion at the double and the triple bonds. The average deviations from their sp^2 and sp values (120 and 180°) are +25.4 (3) and -26.0 (3)°, respectively. The exocyclic benzene valency angles at C(13) and C(16) on the one side and at C(14) and C(15)

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1979, Index issue.

on the other side are distorted to a lesser degree. The former are distorted by an average of $+5.4$ (3) $^\circ$, and the latter by an average of -5.2 (3) $^\circ$ (see Figure 2, which is self-explanatory for the signs of the deviations). In the diacetylene (4), the corresponding distortion in the exocyclic benzene valence angles from 120° had been observed⁶ to be -5.8 (1) $^\circ$.

The benzene rings in compound (5) display significant angular deviations from their ideal value at C(13) and C(16) (average value -2.9°). This distortion is more pronounced in molecule A than in molecule B. We also observe elongated bonds for C(13)–C(14) and C(15)–C(16) in molecule A and for C(13)–C(14) in molecule B. This elongation was also observed by Destro *et al.*⁶ for the diacetylene (4). A similar effect was found by Römning³ in cyclo-octa-1,5-diyne (1) in which the single C–C bonds attain lengths of 1.570 Å.

A number of least-squares planes of all heavy atoms of

TABLE 2

Endocyclic torsion angles ($^\circ$) of the cyclo-oct-1-en-5-yne ring of 5,6-didehydrodibenzo[*a,b*]cyclo-octene

Bond	A	B
C(13)–C(14)	$-2.1(7)$	$-0.5(7)$
C(14)–C(5)	$0.5(15)$	$7.1(13)$
C(5)–C(6)	$1.1(22)$	$0.9(20)$
C(6)–C(15)	$0.1(14)$	$-6.8(13)$
C(15)–C(16)	$-1.7(7)$	$-2.3(8)$
C(16)–C(11)	$2.5(10)$	$9.4(12)$
C(11)–C(12)	$-2.6(14)$	$-2.1(15)$
C(12)–C(13)	$2.9(10)$	$-5.3(11)$

the benzene rings in compound (5) is given in Table 3. It can be seen that the benzene rings a–d are planar within 0.011 Å. Molecule A is planar within 0.031 Å; rings a and b are nearly coplanar, their tilt being 1.4° .

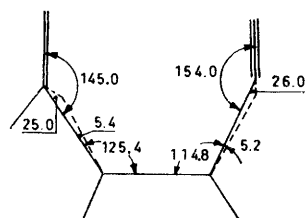


FIGURE 2 Distortion of the exocyclic benzene valency angles of 5,6-didehydrodibenzo[*a,e*]cyclo-octene (average of molecules A and B)

On the other hand, molecule B deviates from planarity by much as 0.174 Å; its lack of planarity is reflected in the tilt between rings c and d (9.9°) and in the not to be neglected torsion angles in the inner ring (see Table 2). A similar, but smaller, deviation from planarity occurs in the diacetylene (4), in which the benzene rings are tilted by 3.6° at 218 K.⁶

The difference in shape between molecules A and B is reflected in the different packing of these molecules.

Within 4.2 Å, molecule A has contacts with 13 neighbours ($5 \times A$ and $8 \times B$), while molecule B has 14 neighbours ($8 \times A$ and $6 \times B$). All molecules are tightly stacked in layers parallel to $(20\bar{2})$. A scanning

TABLE 3

Least-squares planes $PX + QY + RZ + S = 0$ through the carbon atoms of molecules A and B, and through the carbon atoms of the benzene rings a–d, of 5,6-didehydrodibenzo[*a,e*]cyclo-octene. The reference systems are orthogonal axes *a,b,c* *

plane	P	Q	R	S
A	-0.9380	-0.3449	0.0357	8.2208
B	-0.3968	0.7221	-0.5667	2.2902
a	-0.9359	-0.3507	0.0329	8.2233
b	-0.9444	-0.3274	0.0311	8.1390
c	-0.4193	0.6649	-0.6181	3.1578
d	-0.3784	0.7804	-0.4977	2.1322

Deviations (10^3 Å) from the least-squares planes

	A	B	A	B
C(1)	-8	-50	C(14)	-13
C(2)	6	-128	C(5)	1
C(3)	-20	-153	C(6)	18
C(4)	-8	-55	C(15)	31
C(7)	5	-11	C(16)	14
C(8)	-19	-141	C(11)	19
C(9)	-18	-174	C(12)	5
C(10)	-24	-61	C(13)	12
	a	c		c
C(1)	-11	-10	C(4)	6
C(2)	10	11	C(14)	-7
C(3)	-7	-5	C(13)	9
C(15)	7	-6	C(9)	11
C(7)	-5	9	C(10)	-10
C(8)	-3	-2	C(16)	1

procedure¹² for holes in the structure reveals that the largest 'gap' has a diameter of 2.3 Å, all other 'gaps' being much smaller. We may conclude that the tight packing is the cause of the exceptionally high density (1.59 g cm $^{-3}$).

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