Molecular Structures of Cyclotetradeca-1,3,8,10-tetrayne and Cyclohexadeca-1,3,9,11-tetrayne

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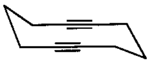
Cyclotetradeca-1,3,8,10-tetrayne (**3**) and cyclohexadeca-1,3,9,11-tetrayne (**4**) have been prepared according to Sondheimer et al. The X-ray crystal structures of **3** and **4** reveal them to be in the chair conformation (**3**) and the twisted chair-chair-conformation (**4**). The tetrayne units in both molecules deviate considerably from linearity, giving rise to transannular distances of the terminal sp centers of 3.098(2) Å (**3**) and 4.147(2), 4.196(2) Å (**4**), and 3.390(2) Å (**3**) and 4.251(2), 4.252(2) Å (**4**) for the central sp atoms, respectively.

The lowest energy conformations of cyclohexane are the chair and the twist forms.[1] Among the ten symmetrical conformations possible for cyclooctane the most stable ones are the boat-chair and the twist-boat-chair conformations.[1] These conformations are the result of minimizing torsion- and angle strain as well as transannular interactions in the corresponding ring systems. The replacement of two opposite C−C bonds in cyclohexane or cyclooctane by one alkyne group each leads to 1,6-cyclodecadiyne (**1**) or 1,7-cyclododecadiyne (**2**). In the cases of **1** and **2** the chair and chair-chair conformations, respectively, were found in the solid state.[2] The higher flexibility of the ten-membered ring with two triple bonds was shown by studying 1,6-diazacyclodeca-3,8-diyne and several of its 1,6-disubstituted derivatives in solution and in the solid state.[3] To extend our studies to species with two butadiyne units we investigated the structures of cyclotetradeca-1,3,8,10-tetrayne (**3**) and cyclohexadeca-1,3,9,11-tetrayne (**4**). The synthesis of **3** and **4** has been reported by Sondheimer et al.[4] Earlier X-ray studies on single crystals of **3** revealed the presence of a center of symmetry (space group $P2_1/c$) which implies a chair conformation for **3** in the solid state.[4] To learn more about the structures of **3** and **4** in the solid state we reinvestigated single crystals of **3** and **4**. The most relevant structural parameters of **3** and **4** obtained from our X-ray studies are displayed in Figure 1. The average bond lengths were found to be 1.19 Å for the triple bonds and 1.39 Å for the sp-sp single bonds. All the 1,3-butadiyne units deviate considerably from linearity. The bond angles at the central sp centers of **3** amount to 173°, while those at the terminal sp centers vary between 176° and 178°. In the case of **4** the bond angles at the terminal sp centers are smaller (173° to 175°) than those at the central sp centers (176° to 178°). Due to the greater bending at the central sp centers the transannular distance between the triple bonds is longer at these centers [**3**: 3.390 (2) Å, **4**: 4.251(2), 4.252(2) Å] than at the terminal centers [**3**: 3.098 (2) Å, **4**: 4.147(2), 4.196(2) Å]. The latter distances are close to the transannular distances in **1** (2.99 Å) and **2** (4.06 Å).



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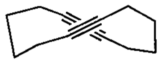

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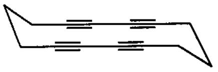

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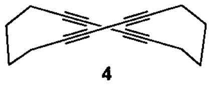

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The CCC bond angles at the sp^3 centers in **3** vary between 114° and 116°, while in the less-strained 16-membered ring the CCC-bond angles lie between 110° and 114°. As anticipated from the work of Sondheimer et al. the 14-membered ring in **3** adopts the chair conformation, while **4** adopts a twisted chair-chair conformation as does **2**.[2] In **4** the torsion angle between the triple bonds amounts to 16.5°; for **2** the angle between the opposite triple bonds was found to be 24°.[2]

So far only four other X-ray studies of cyclic tetraynes have been reported. The compounds studied were 5,5,6,6,11,11,12,12-octamethylcyclododeca-1,3,7,9-tetrayne (**5**),[5] 5,5,6,6-bis(1,2-cyclohexylene)-11,11,12,12-tetramethylcyclododeca-1,3,7,9-tetrayne (**6**),[6] 2′,3′,10′,11′-tetra-*n*-butyldibenzo(*e,k*)-cyclododeca-1,3,7,9-tetrayne-5,11-diene (**7**)[7] and 1,2,7,8-tetrakis(triisopropylsilylethynyl)cyclododeca-1,7-diene-3,5,9,11-tetrayne (**8**).[8]

In **5−8** the two tetrayne units are incorporated into a planar or almost planar 12-membered ring system which imposes a higher strain on the system than in **3** or **4**. As a result the two tetrayne units in all four systems deviate considerably from linearity. The CCC angles at the sp atoms of the tetrayne unit vary from 165° to 167° and are smaller than those found in **3** or **4**.

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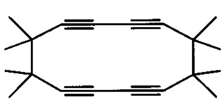

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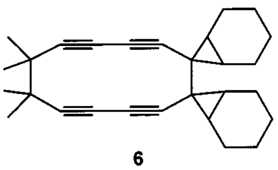

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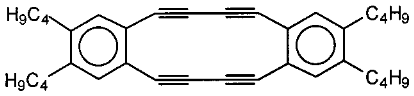

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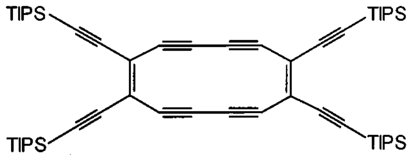

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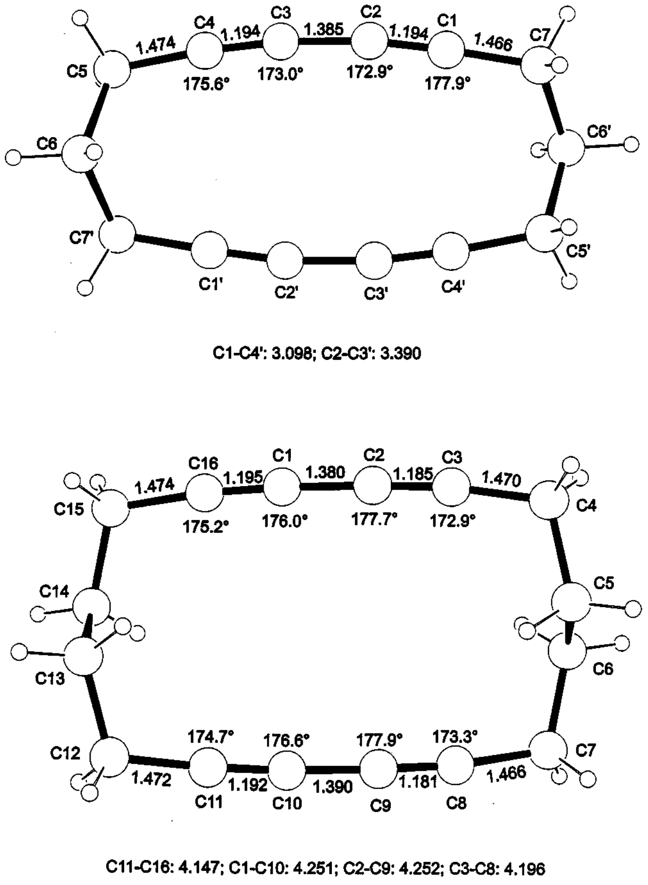
The cyclic tetraynes **3** and **4**, whose structures we have discussed above, are the first members of a series of tetraynes with alkyl chains between the tetrayne units in which the ring size is larger than C_{12}. Despite the longer chains between the butadiyne units, the latter still deviate from linearity.



C1-C4': 3.098; C2-C3': 3.390

C11-C16: 4.147; C1-C10: 4.251; C2-C9: 4.252; C3-C8: 4.196

Figure 1. Molecular structures of **3** and **4** with relevant bond lengths (Å) and angles (°); the standard deviations of the bond lengths are in the range between 0.002 Å (**3**) and 0.004 Å (**4**); the deviations of the bond angles are in the range between 0.1−0.2° (**3**) and 0.3−0.4° (**4**)

Experimental Section

Preparation of Cyclotetradeca-1,3,8,10-tetrayne (3) and Cyclohexadeca-1,3,9,11-tetrayne (4): Compounds **3** and **4** were prepared according to the procedure described by Sondheimer et al.[4] to yield 12% of **3** and 6% of **4**.

3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35−2.4 (m, 8 H), 1.7−1.8 (m, 4 H). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 78.8 (s), 68.3 (s), 24.3 (t), 20.3 (t).

4: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (m, 8 H), 1.74 (m, 8 H). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 78.78 (s), 66.24 (s), 26.99 (t), 19.49 (t).

X-ray Structure Analyses of 3 and 4: The crystallographic data were collected with a Nonius-CAD4 diffractometer (**3**) or with a Syntex R3 diffractometer (**4**). The structures were solved by direct methods (**3**: MULTAN;[9] **4**: SHELX 86[11]).The stuctural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least squares method based on *F* (**3**) or F^2 (**4**) (**3**: MolEN;[10] **4**: SHELXL-97[11]). The hydrogen atoms were refined isotropically. The crystallographic data are listed in Table 1.

Table 1. X-ray crystallographic data of **3** and **4**

Compound	**3**	**4**
Empirical formula	$C_{14}H_{12}$	$C_{16}H_{16}$
Molecular mass [g/mol]	180.24	208.29
Crystal size [mm]	0.5 × 0.45 × 0.4	0.4 × 0.3 × 0.15
Crystal color	slight yellow	yellow
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*P*bca
a [Å]	8.207 (2)	8.937 (2)
b [Å]	7.969 (1)	9.016 (3)
c [Å]	8.806 (2)	31.901 (7)
β [°]	113.32 (1)	90.0
V [Å^3]	528.9 (2)	2570.5 (12)
$D_{calcd.}$ [Mg/m^3]	1.13	1.076
Z	2	8
F(000)	192	896
Temperature [K]	293	298
θ range [°]	2−28	2−25
μ [mm $^{-1}$]	0.06	0.06
Refl. collected	1447	2262
Refl. unique	1265	2262
Refl. observed [$I > 2.5\ \sigma\ (I)$]	935	931
Variables	88	147
$(\Delta/\sigma)_{max}$	<0.01	<0.001
R	0.049	0.062
R_w[a]	0.069	0.151
S (Gof)	3.14	0.917
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.26	0.12
$(\Delta\rho)_{min}$ [e Å^{-3}]	-0.18	-0.14

[a] *F* for **3**; F^2 for **4**.

Crystallographic data for **3** and **4** have been deposited with the Cambridge Cristallographic Data Centre as supplementary publication no. CCDC-119113 (**3**), and CCDC-122734 (**4**). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21E2, UK; [fax: (internat.) + 44-(1223)/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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