Structural and Chemical Properties of Tribenzo-4,7-dihydroacepentalene Derivatives and their Central Pyramidalised Double Bonds

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Dipotassium tribenzodihydroacepentalenediide **4**$^{2-}$ reacts with electrophiles to give 4,7-disubstituted tribenzodihydroacepentalene derivatives **3** with a highly pyramidalised double bond, as evidenced by X-ray structural determinations; protonation of the dianion **4**$^{2-}$ yields an interesting polycyclic [2 + 2] dimer **5**.

Alkenes with C=C double bonds that are strongly out-of-plane distorted have unusual properties.[1] Especially double bonds between extremely pyramidalised carbon atoms such as in tricyclo[3.3.2.$0^{3,7}$]-dec-3(7)-ene **1** are highly reactive towards electrophiles and nucleophiles or [2 + 2] dimerisation. Thus, alkene **1** could only be characterised spectroscopically in an argon matrix and dimerises above 40 K.[2] On the other hand, dodecahedradiene **2** can be handled as a crystalline compound at room temperature.[3] In **2** the four allylic hydrogens provide sufficient steric protection for the pyramidalised double bonds against dimerisation. Tribenzodihydroacepentalene derivatives **3** are related to dodecahedradiene **2**, yet in **3** the bridgehead–bridgehead double bond is not protected by allylic hydrogens at one end. We here report on the degree of pyramidalisation of the doubly bonded carbons C(1) and C(10) in compounds **3** and some chemical consequences.

As reported earlier,[4] dipotassium tribenzodihydroacepentalenediide **4**$^{2-}$ can easily be generated upon reacting tribenzotriquinacene[5] with *n*-butyllithium/potassium-*tert*-pentoxide;[6] weaker bases such as Bu^{n}Li and Bu^{n}Li–*N,N,N′,N′*-tetramethylethylenediamine did not give **4**$^{2-}$. As we have now found, the dianion **4**$^{2-}$ is formed by deprotonation of all three benzylic positions in tribenzotriquinacene, followed by hydride elimination from the central carbon.[7] Dianion **4**$^{2-}$ can be trapped with various electrophiles to yield 4,7-disubstituted tribenzodihydroacepentalenes **3**, *e.g.* with chlorotrimethylsilane or methyl chloroformate the 4,7-bis(trimethylsilyl)derivative **3a**[4] (66%) and dimethyl tribenzo-

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† Crystal structure analysis.

4,7-dihydroacepentalene-4,7-dicarboxylate **3b** (58%), respectively, were obtained.‡

The structural differences in compounds **3**, apparently incurred by the different substitutents, as revealed by X-ray crystal structure analyses of three different derivatives (see Table 1).§ In all three cases, the central C(1)–C(10) double bond is slightly longer than a normal C=C double bond (132 pm), while the C–C single bonds adjacent to C(1) show a trend to be slightly shorter than usual single bonds between two sp^2-hybridised carbon atoms (148 pm). The out-of-plane bending of the four substituents at the central C(1)–C(10) double bond as expressed, for example, by the angle between the C(1)–C(10) bond axis and the line bisecting the plane C(4)–C(7)–C(10), is particularly large in the bismorpholinyl derivative **3c**, in which it is even larger than that calculated for dodecahedradiene **2** (42.9°).[3] This is attributed to the rigid tricyclic system and the two bulky morpholinyl groups in allylic position of **3c**. While in dodecahedradiene **2** the out-of-plane bending of all four substituents on the double bond has to be symmetrically distributed, in **3** the aromatic rings with C(2) and C(9) attached to C(1) are less far out of plane than the allylic carbon atoms C(4) and C(7) (see Table 1).

Table 1 Influence of substituents on the central bond lengths and interplanar angles in 4,7-tribenzodihydroacepentalene derivatives **3**§

	Compounds (R)		
	3a[4] (SiMe$_3$)	**3b**[a] (CO$_2$Me)	**3c**[b] (NR'$_2$)
Bond length/pm			
C(1)–C(10)	134.5(6)	135.6(5)	134.5(4)
C(1)–C(2)	146.0(6)	147.0(6)	146.9(4)
Angles between			
Planes **A**/**B** (°)[c]	36.2(3)	33.8(3)	36.5(2)
Plane **C**/axis C(1)–C(10) (°)[d]	40.4(3)	45.8(5)	47.2(3)
Plane **D**/axis C(1)–C(10) (°)[e]	37.0(3)	27.6(4)	30.2(2)

[a] This structure contains four solvent molecules in the elementary cell. [b] NR'$_2$ = morpholinyl; this compound was prepared by reaction of 1,4,7-tribromotriquinacene with morpholine.[9] [c] Angle between plane **A** [C(2)–C(1)–C(10)–C(4)] and plane **B** [C(9)–C(1)–C(10)–C(7)]. [d] Plane **C** [C(4)–C(7)–C(10)]. [e] Plane **D** [C(1)–C(2)–C(9)].

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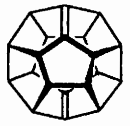

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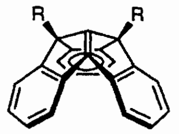

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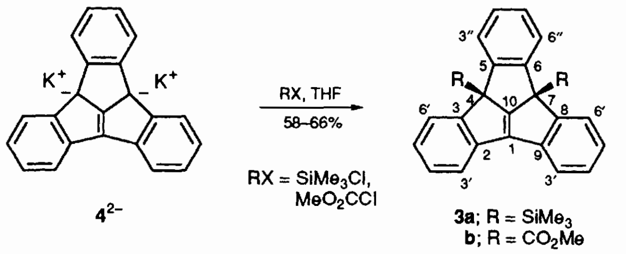

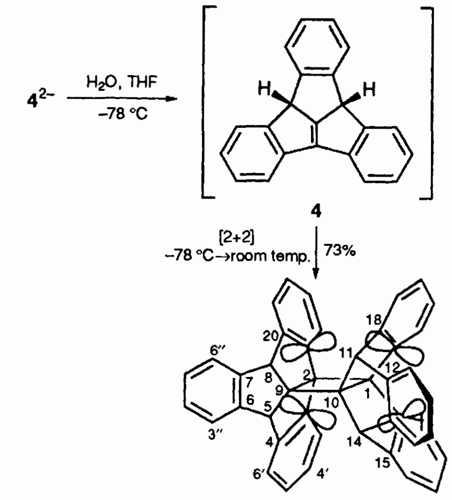

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Upon addition of tetrahydrofuran (THF) (aq) [or dimethoxyethane (aq)] to a solution of the dianion 4^{2-} at −78 °C, the red reaction mixture turned yellow, and became colourless when warmed to room temperature. After workup a white solid (m.p. 338 °C decomp.) was isolated. The mass spectrum of the product shows a molecular ion peak at m/z = 556 corresponds to the mass of a tribenzodihydroacepentalene dimer.‡

The constitution of this dimer could not be fully assigned by NMR spectroscopy. In particular, a distinction between head-to-head (C_s-symmetry) or head-to-tail [2 + 2] connectivity (C_2-symmetry) of two monomer units of **4** was not possible.

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‡ All new compounds were fully characterised by spectroscopic techniques (^{1}H NMR, ^{13}C NMR, IR, MS) and their molecular formulae established by high resolution mass spectrometry; m$_c$ = centrosymmetric multiplet. **3b**: ^{1}H NMR (250 MHz, CDCl$_3$): δ 3.76 (s, 6 H, CO$_2$CH_3), 7.26 (m$_c$, 2 H, 4'-H), 7.39 [m$_c$, 4 H, 5'(4'',5'')-H], 7.57 [AA'BB', 2 H, 3''(6'')-H], 7.67 (m$_c$, 2 H, 3'-H), 7.98 (m$_c$, 2 H, 6'-H). ^{13}C NMR (62.9 MHz, CDCl$_3$, broad-band decoupling and DEPT): δ 52.8 (+, CO$_2$CH$_3$), 64.2 [Φ, C-4(7)], 122.6 (+, C-3'), 125.1 (+, C-4'), 126.1 (+, C-6'), 127.6 [+, C-3''(6'')], 128.6 [+, C-4''(5'')], 128.8 (+, C-5'), 139.2 (Φ, C-3(8)), 143.2 [Φ, C-5(6)], 151.1 (Φ, C-1), 156.5 [Φ, C-2(9)], 158.3 (Φ, CO$_2$Me), 171.1 (Φ, C-10). **5**: ^{1}H NMR (500 MHz, CDCl$_3$, ^{1}H-^{1}H COSY): δ 5.23 [s, 4 H, 5(8,11,14)-H], 6.99 [m$_c$, 8 H, 4'(5')-H], 7.10 [AA'BB', 4 H, 4''(5'')-H], 7.31–7.36 [m, 8 H, 6'(3'',6'')-H], 7.38 (m$_c$, 4 H, 3'-H). ^{13}C NMR (62.9 MHz, CDCl$_3$, broad-band decoupling, DEPT and C-H correlation): δ 57.0 [+, C-5(8,11,14)], 66.0 [Φ, C-1(2)], 74.8 [Φ, C-9(10)], 124.3 (+, C-6'), 124.4 [+, C-3''(6'')], 125.6 (+, C-3'), 127.3 (+, C-4'), 127.4 (+, C-5'), 127.5 [+, C-4''(5'')], 144.3 [Φ, C-4(15,18,20)], 145.4 [Φ, C-3(16,17,19)], 148.8 [Φ, C-6(7,12,13)].

§ *Crystal data* for **3a**: C$_{28}$H$_{30}$Si$_2$, M = 422.70, space group $P2_12_12_1$, a = 8.934(4), b = 11.932(4), c = 23.593(10) Å, V = 2515(2) Å^3, Z = 4, D_c = 1.116 g cm^{-3}. Of the 12703 unique reflections 3241 were considered observed having $I > 2\sigma(I)$ which gave final values of R = 0.0498 and w$R2$ = 0.1326.

For **3b**: C$_{26}$H$_{13}$O$_4$·L$_4$, M = 394.14, space group $Pbca$, a = 8.031(2), b = 19.870(4), c = 28.559(4) Å, V = 4557.3(16) Å^3, Z = 8, D_c = 1.290 g cm^{-3}. Of the 5980 unique reflections 2990 were considered observed having $I > 2\sigma(I)$ which gave final values of R = 0.0846 and w$R2$ = 0.2335.

For **3c**: C$_{30}$H$_{28}$N$_2$O$_2$, M = 448.54, space group $P\bar{1}$, a = 10.561(3), b = 10.630(4), c = 12.025(4) Å, α = 90.60(3), β = 109.71(2), γ = 108.530(10)°; V = 1194.5(7) Å^3, Z = 2, D_c = 1.247 g cm^{-3}. Of the 6273 unique reflections 3131 were considered observed having $I > 2\sigma(I)$ which gave final values of R = 0.0535 and w$R2$ = 0.1333.

For **5**: C$_{44}$H$_{28}$·2THF, M = 556.22, space group $P2_1/n$, a = 15.623(3), b = 16.229(3), c = 16.051(3) Å, β = 112.790(10)°, V = 3751.9(12), Z = 4, D_c = 1.241 g cm^{-3}. Of the 9784 unique reflections 4881 were considered observed having $I > 2\sigma(I)$ which gave final values of R = 0.0844 and w$R2$ = 0.2234.

The diffraction data were recorded on a Stoe-Siemens four circle diffractometer with monochromatic Mo-Kα radiation (λ = 71.069 pm) and solved by direct methods.[8] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 7.

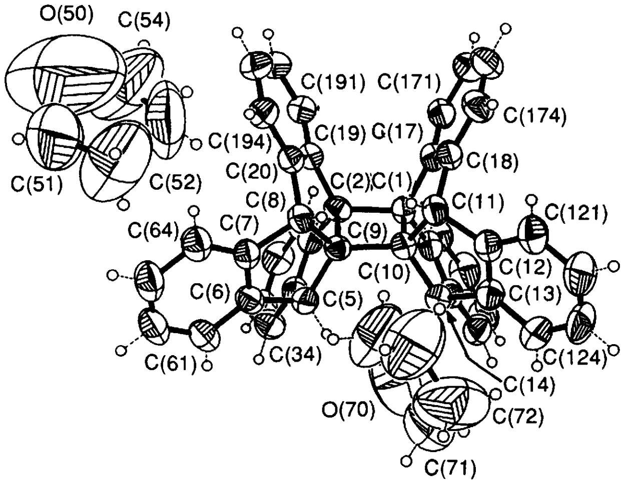

Fig. 1 ORTEP plot of **5** with two THF molecules in the elementary cell (space group: $P2_1/n$)

The X-ray structure analysis of a single crystal, which was obtained by crystallisation of the dimer from THF–hexane under an argon atmosphere, however, reveals the structure as **5**, the head-to-head [2 + 2] dimer (see Fig. 1). The crystal also contains two slightly disordered THF molecules in the elementary cell. The central four-membered ring is almost planar [puckering angle 4.9(4)°].

The bond length C(1)–C(2) [160.2(6) pm] is significantly longer than usual C_{sp^3}–C_{sp^3} single bonds in cyclobutanes (156.0 pm).[10] It is astonishing that the C(1)–C(2) bond is even longer than C(9)–C(10) [156.6(6) pm] which in view of the four bridgehead hydrogen atoms with a distance of approximately 210 ppm [H(8)–H(11) and H(5)–H(14)] pushing each other apart, would have been expected to be longer. An analogous bond lengthening for the central C_{sp^3}–C_{sp^3} single bond (161.8 pm) in a 1,2-diarylindano[1,2-*a*]indan[11] has been attributed to a through-bond-coupling effect.[12]

The ^{1}H NMR spectrum of the yellow solution obtained upon protonation of $\mathbf{4}^{2-}$ in [$^2H_{10}$]dimethoxyethane, when recorded at −60 °C, revealed a diagnostic singlet at δ 4.58, 0.65 ppm up-field from the singlet of the benzylic bridgehead protons in the dimer **5**.‡ The singlet at δ 4.58 was obviously due to the benzylic-allylic 4(7)-protons in the monomer **4**, as it disappeared while the singlet of **5** grew at δ 5.23‡ upon warming the solution to ambient temperature. Apparently, tribenzo-4,7-dihydroacepentalene **4** is sufficiently stable at −60 °C and can be trapped also with other reagents at low temperature.[13]

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