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"HEPTAHENDECAFULVALENE"

SYNTHESIS - X-RAY STRUCTURE ANALYSIS - CYCLOADDITION REACTIONS ([18+2]) ? [1]

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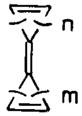
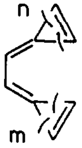
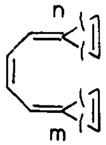
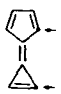
SUMMARY: An efficient synthesis for an 18π-heptahendecafulvalene (**6**), its X-ray structure analysis and its cycloaddition reaction with TCNE - yielding i.a. a potential [$\pi 18a+\pi 2s$]-adduct - are reported.

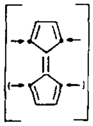
The realization of pericyclic processes involving unusually large numbers of electrons is dictated by the steric orientation of the interacting centers. In this respect, the fulvalenes **A** [2] and the fulvadienes (fulvatrienes) **B**(**C**) [3] were sought as polyelectron components in α,ω-cycloaddition and α,ω-electrocyclization reactions. In the series **A**, examples with up to [16+2] [4], in **B**(**C**) with up to 20 [1] (14 [5])-electron transition states have been observed. In this paper we report on efforts to extend the cycloadditions in the series **A** (**1**-**5**) by [18+2]/[22+2]-cycloadditions to the (newly prepared) heptahendecafulvalene **6** and the (known) hendecafulvadiene **7** [6].

A 

B 

C 


[8+2]
1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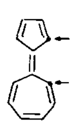
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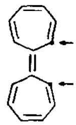
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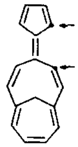
4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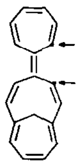
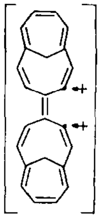
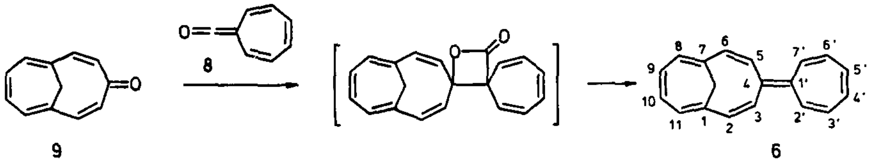
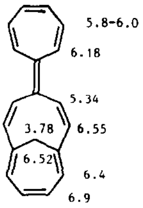
5

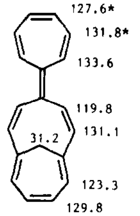

[18+2]
6


[22+2]
7

The synthesis of **6** (4-(2,4,6-cycloheptatrien-1-ylidene)-bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene) was carried out in analogy to the recently described heptahendecafulvadiene **B** (n=3, m=5) [5] by the addition of the cycloheptatrienylidene-ketene **8** [7] (prepared in situ) to the 4,9-methano[11]annulenone **9** [8]. This reaction proceeded with surprising ease (as compared to the nucleophilic additions to **9** [9]), and in good yield (5°C, benzene, 80-85% **6**, red-brown needles, m.p. 104°C). The UV-spectrum (λ_{max}(ethanol) = 390 nm (ε = 23000), 336(28200), 264(23700), λ_{max}(isooctane) = 390 nm, long tail into the visible, ϵ_{500}= 520) exhibits a relatively short longest-wavelength absorption and is relatively solvent independent. This is indicative of a non-planar structure and of a relatively low polarizability of this fulvalene. ^{1}H- and ^{13}C-NMR data are typically fulvalenoid [10,11].

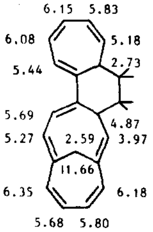


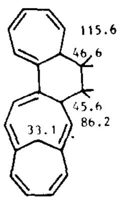




$J_{2,3}$= $J_{5,6}$= 12.0 Hz
$J_{2',3'}$= $J_{6',7'}$= 10.5

q: 136.0, 127.3, 122.0





$J_{2,3}$= 9.0, $J_{6,7}$= $J_{10,11}$= 6.0
$J_{7,8}$= $J_{14,15}$= 9.5; $J_{8,9}$=
$J_{18,19}$=7.5; $J_{9,10}$=11.5
$J_{14,21E}$= 2.0; $J_{17,18}$= 10.5
$J_{19,20}$= 11.5; $J_{21E,21Z}$= 11.2

C≡N: 109.6, 110.0, 111.1, 111.2
d: 122.8, 124.2, 127.2, 128.5
129.3, 129.6, 131.6, 132.9
134.5, 134.9
q: 43.0, 44.2, 116.8, 126.8
134.3, 140.4

In connection with the stereochemical features in cycloaddition and electrocyclization reactions of the fulvalenes **A/B** containing the methano-bridged hendecafulvene unit, the geometrical details of **6** were of interest. The X-ray analysis [12] reveals a structure (Fig. 1) which, when viewed from the side, makes an S-shaped appearance - reminding of the situation in the ketone **9** [13] and in heptafulvalene [14] and of the ways, in which these two molecules accommodate ring strain and steric repulsions (deviation from coplanarity between the planes C3C4C5/C1'C2'C7' = 6.8°). In fact, CCC angles, C-C-bond lengths and the interplanary angles in the heptafulvene unit of **6** are very similar to those found in heptafulvalene. Similar S-type conformations were assumed for the electrocyclization of vinylogous hendecafulvenes [9], penta-/hepta-hendecafulvadienes [15] and hendecafulvadiene [9].

To better contrast **6** as component in cycloaddition reactions the behaviour of the "mixed" 16π-fidecene towards polyenophiles should be recalled. With dimethylacetylenedicarboxylate (benzene, reflux) syn-/anti-[4+2]-adducts (6:4) to the cyclopentadiene-unit, with tetracyanoethylene (benzene, 20°C) the [π16s+π2s]-adduct were formed. The latter could not directly be identified since it underwent a very fast suprafacial (1,9)-H-migration. Such (1,9)-H-migrations are for steric reasons feasible only anti to the methylene bridge [4].

6 reacts rapidly with TCNE (1-3 equiv., -30 to 20°C). ^{1}H-NMR monitoring (C_6D_6, 0°C) reveals the parallel (?) formation of three adducts (10:9:1). By chromatography the red-crystalline 1:1-adduct **10** (40%; m.p. 155-157°C; λ_{max}(ethanol) = 390 nm (ϵ = 9700), 324 (14800), 265 (17100)) and two yellow crystalline 1:1-adducts **12** (36%; m.p. 178-180°C; λ_{max}(ethanol) = 372 nm (ϵ = 10100), 318 (25900), 231 (27200)) and **13** (5%; m.p. 207-210°C; λ_{max}(ethanol) = 378 nm (ϵ = 11200), 320 (27900), 231 (27400)) were separated. When

CH_2Cl_2-solutions of the original 10:9:1-mixture were kept at room temp., the product ratio gradually altered until, after five days, **10** had virtually disappeared (<3%), **12**/**13** having increased to ca. 40% each. Dissolution of each individual adduct restored the 10:9:1 - ratio of **10**, **12** and **13**.

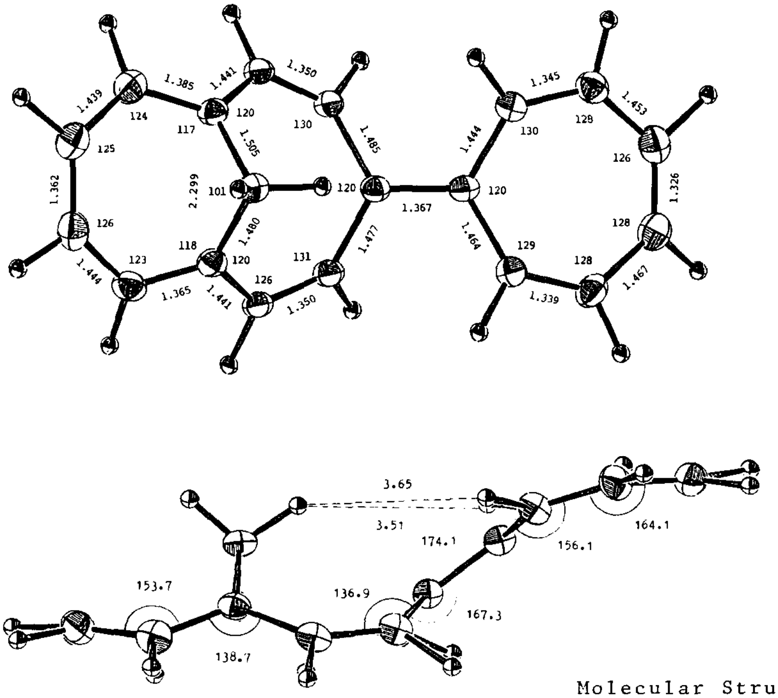
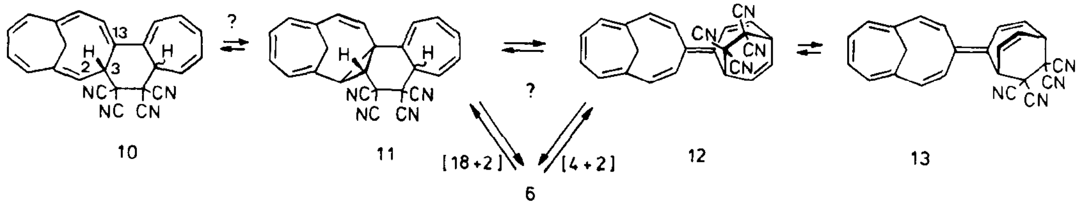


Fig. 1 Molecular Structure of **6**

In assigning the structures **10**, **12** and **13** as derived from the spectral data (MS, ^{1}H-, ^{13}C-NMR, IR, UV), two questions remained open: (i) the distinction between **12**/**13** was based



upon the assumption, that the formation of syn-**12** is kinetically preferred; (ii) the syn-position for 3-H in **10** was deduced indirectly by its failure to undergo [1,9]-H-migration and from its strong NO-effect with 21Z-H. The strong diamagnetic displacement of the 2-H-(δ = 3.97) and 2-C-signal (δ = 86.2) is ascribed to an anisotropic influence of 5endo-CN (half-chair-like conformation of the central six-membered ring) rather than to a significant contribution by the valence tautomer **11** - none of the four quarternary C-signals, one belonging to C-13, shows a similar high-field shift. The [π18a+π2s]-structure **10**, where 6-H seems sterically to be better accommodated in anti- than in syn-position, corresponds to the [π14a+π2s] TCNE-adduct of heptafulvalene [16]. As in comparable cases [3,4,17], such a mechanistic classification is rather speculative - what is equally true for any interpretation of the regio- and stereochemical aspects in the TCNE-additions to **6**.

In contrast to 6 and all other fulvalenes as shown in Scheme 1, the 22π-hendecafulvadiene 7, which most probably has an anti-configuration 6), did not react with TCNE (benzene, 20-80°C) - not even a c.t.-complex being manifested. On the other hand, 7 reacted with N-methyltriazolinedione (0°C, CH_2Cl_2) but yielded only polymeric material.

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12) Crystals are monoclinic, space group $P2_1/n$; $a = 8.958$, $b = 6.672$, $c = 22.520$ Å; $\beta = 91.31°$, $Z = 4$. Number of reflections used in least squares refinement = 1764. Final R-factor: 0.059. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Any request should be accompanied by the full literature citation for this communication.

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