The Synthesis of 1,6-Methano-[12]-, -[18]-, -[20]-, -[22]-, and -[24]-annulenes

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The title annulenes have been synthesized by reductive coupling; their ^{1}H n.m.r. spectra show that they sustain a ring current.

A number of multi-bridged annulenes have been prepared and an extensive examination of their properties has been reviewed by Vogel.[1] However, little is known about annulene series carrying one methano-bridge.[2] We report here a simple, and apparently general, new synthesis of 1,6-methanoannulenes (**7**)—(**10**)[3] which formally have a 1,6-methano-bridge on their perimeter.

Recently, we reported a successful synthesis of a doubly bridged, 1,6:13,18-bismethano[24]annulene, by reductive dimerization of 1,6-(2-formylvinyl)cycloheptatriene (**1**), albeit in low yield.[4] During our attempts to improve the yield of the dimerization, we found that high-dilution addition (10—15 h) of (**1**) to a low-valent titanium reagent resulted unexpectedly in the formation of a monomeric product, the paratropic 1,6-methano[12]annulene (**6**), which had been prepared in a multi-step and low-yield route by Vogel *et al.*[5] This promoted us to attempt the intramolecular coupling of the homologous dialdehydes of (**1**), which should provide an easy access to 1,6-methanoannulenes.

Slow addition of the dialdehydes (**2**)—(**5**)[3][†] to titanium trichloride and $LiAlH_4$ in 1,2-dimethoxyethane or tetrahydrofuran[6] afforded 1,6-methano-[18]- (**7**) (m.p. 138 °C),[‡] -[20]- (**8**) (m.p. 108 °C), -[22]- (**9**) (m.p. 144 °C), and -[24]-annulene (**10**) (m.p. 152 °C), respectively, in 4—12% yield; the dialdehydes (**1**), $m = 2$, $n = 1$ or $m = n = 2$ did not afford the desired annulenes. The ^{1}H n.m.r. spectra[§] of these annulenes show both the [18]- (**7**) and -[22]-annulene (**9**) to be diatropic, since the inner protons, including the methylene protons,[¶] resonate at high field, whereas the outer protons resonate at low field. Conversely, both the [20]- (**8**) and the -[24]-annulene (**10**) are paratropic, since the inner protons, including the methylene protons, resonate at low field, whereas the outer protons resonate at high field. However, in contrast to the spectra of the closely related tetradehydroannulenes (**11**) of similar size,[3] the spectra of the annulenes (**7**)—(**10**), as expected, usually show poorly resolved resonances and a large temperature dependence, despite the presence of a 1,6-methano-bridge, reflecting the fact that molecules (**7**)—(**10**) are conformationally mobile.

In their electronic spectra, taken in tetrahydrofuran, the main maximum of the [18]annulene (**7**) (336 nm) is at longer wavelength than that of the [20]annulene (**8**) (321 nm), and the same applies to the [22]annulene (**9**) (363 nm) and the [24]annulene (**10**) (352 nm). Clearly, this is due to the occurrence of the same sort of alternation between the

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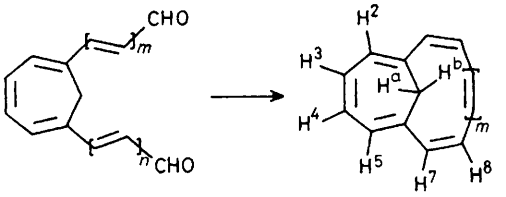
[†] The dialdehydes (**2**) (m.p. 136 °C), (**3**) (m.p. 194 °C), (**4**) (m.p. 144 °C), and (**5**) (m.p. 199 °C) were prepared by repetition of the bis-homologation using Wittig condensation from lower dialdehydes, according to the reported procedure (see ref. 3).

[‡] Elemental analyses, and i.r. and mass spectra of the annulenes were consistent with the assigned structures.

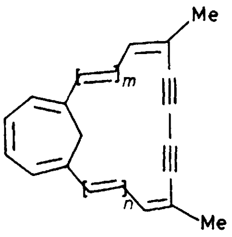
[§] (**7**): $\tau(CDCl_3)$ 2.71—2.84 (H^7, H^{17}, H^{18}), 3.00—3.20 (H^9, H^{14}, H^{13}, H^{11}, H^3, H^4, H^{15}), 3.36 (H^{10}), 3.61—3.65 (H^2, H^5), 5.22 (H^8), 5.84 (H^{16}), 6.02 (H^{12}), 8.43 (H^b), and 10.02 (H^a); (**8**): $\tau(CDCl_3$, −30 °C) 0.65 (H^8, H^{19}), 1.96 (H^{12}, H^{15}), 2.85 (H^{10}, H^{17}), 3.92—4.00 (H^3, H^4), 4.25 (H^7, H^{20}), 4.25—4.27 (H^2, H^5), 4.42 (H^9, H^{18}), 4.50 (H^{13}, H^{14}), 4.65 (H^{11}, H^{16}), and 5.48 (H^a, H^b); (**9**): $\tau(CDCl_3)$ 2.29—3.50 (15 H, outer H), 5.40—6.32 (5 H, inner H), and 9.50 (H^a, H^b); (**10**): $\tau(CDCl_3)$ 1.38—1.64 (5 H, inner H), 3.81—4.30 (17 H, outer H), and 5.96 (H^a, H^b).

[¶] The methylene protons of the dialdehydes (**2**)—(**5**) as a model resonate at τ 7.24—7.27.



(**1**) $m = n = 1$
(**2**) $m = 3, n = 2$
(**3**) $m = n = 3$
(**4**) $m = 4, n = 3$
(**5**) $m = n = 4$

(**6**) $m = 1$
(**7**) $m = 4$
(**8**) $m = 5$
(**9**) $m = 6$
(**10**) $m = 7$



(**11**) $m = 1\text{-}3,\ n = 1\text{-}2$

maxima of [$4n-2$] and [$4n$] systems, as has been observed for monocyclic annulenes and dehydroannulenes [$(4n-2)\pi$ systems absorb at longer wavelengths than $(4n)\pi$ systems].[7]

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