The Highly Stable 1,6-Methanotetradehydro-[26]-, -[28]-, -[30]-, -[32]-, -[34]-, and -[38]-annulenes. Limiting Ring Size for Dia- and Para-tropicity

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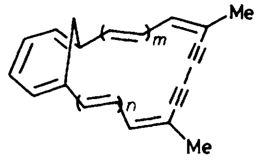
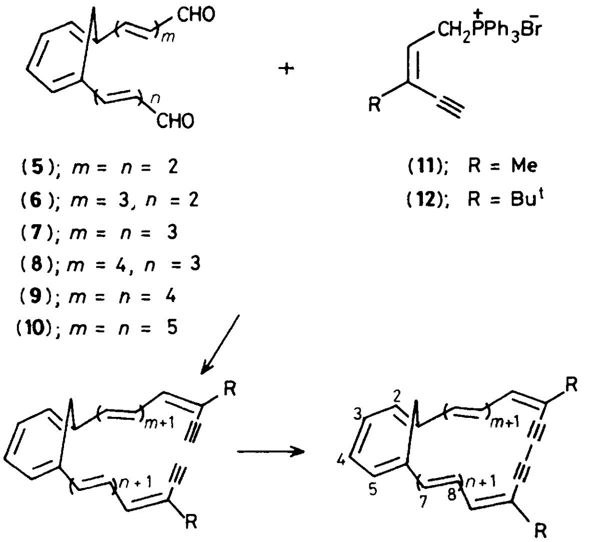
The title annulenes have been synthesized and their ^1H n.m.r. spectra indicate that the [28]- and [34]-annulenes as well as the lower-membered ones can sustain a ring current.

Although theoretical calculations on monocyclic annulenes predicted that the limit of aromaticity of $(4n + 2)$ π-electron systems would lie between 22- and 24-membered rings,[1] didehydro[26]annulene,[2] tetradehydro[26]annulene,[3] and tetrahydro[30]annulene[4] have proved to be diatropic. Also, the hexadehydro[24]annulene[5] is known to have the largest ring among the paratropic [4*n*]annulenes. As has been demonstrated in multi-bridged annulenes[6] and dehydroannulenes,[7] the introduction of a bridging group into a monocyclic annulene ring as well as the incorporation of an acetylenic linkage makes the molecular perimeter more rigid, and therefore enhances the thermal and conformational stability. This led us to expect that the limiting ring size for tropicity should be larger for bridged dehydroannulenes than for monocyclic annulenes. We have now verified this expectation experimentally.



(**1**); $m = n = 1$ [18]
(**2**); $m = 2, n = 1$ [20]
(**3**); $m = n = 2$ [22]
(**4**); $m = 3, n = 2$ [24]



(**5**); $m = n = 2$
(**6**); $m = 3, n = 2$
(**7**); $m = n = 3$
(**8**); $m = 4, n = 3$
(**9**); $m = n = 4$
(**10**); $m = n = 5$

(**11**); R = Me
(**12**); R = Bu^t

(**13**); R = Me, $m = n = 2$
(**14**); R = Me, $m = 3, n = 2$
(**15**); R = Me, $m = n = 3$
(**16**); R = Bu^t, $m = 4, n = 3$
(**17**); R = Bu^t, $m = n = 4$
(**18**); R = Bu^t, $m = n = 5$

(**19**); R = Me, $m = n = 2$ [26]
(**20**); R = Me, $m = 3, n = 2$ [28]
(**21**); R = Me, $m = n = 3$ [30]
(**22**); R = Bu^t, $m = 4, n = 3$ [32]
(**23**); R = Bu^t, $m = n = 4$ [34]
(**24**); R = Bu^t, $m = n = 5$ [38]

Scheme 1

Table 1. ^1H N.m.r. chemical shifts (τ, $CDCl_3$, Me_4Si) of methylene and methyl (or t-butyl) protons of annulenes (**1**)—(**4**) and (**19**)—(**24**) at 200, 270, or 360 MHz.[a]

	-[CH_2]-	Me or Bu^t
(**1**) [18]	10.45	7.47
(**2**) [20]	5.36	8.44
(**3**) [22]	9.19	7.64
(**4**) [24]	5.88	8.36, 8.30
(**19**) [26]	8.50	7.76
(**20**) [28]	6.35	8.27, 8.29
(**21**) [30]	8.07	7.86
(**22**) [32]	7.24	8.80
(**23**) [34]	7.78	8.74
(**24**) [38]	7.60	8.76

[a] The methylene and methyl (or t-butyl) protons of the acyclic compounds of these annulenes resonate at τ 7.15—7.29 and 8.01—8.05 (or 8.80—8.84), respectively (see text and ref. 8).

Recently, we reported that the 1,6-methano-tetradehydroannulenes (**1**)—(**4**) showed dia- and para-tropism, and a high thermal and conformational stability, which may reasonably be ascribed to a fair amount of rigidity of the molecular skeleton imposed by the presence of the bridging methylene group and the 1,3-diacetylenic linkage.[8] We have now synthesized the higher analogues, the title annulenes (**19**)—(**24**), which have an analogous framework to that of (**1**)—(**4**).

As shown in Scheme 1, the synthesis was carried out according to the reported procedure.[8] Reaction of the phosphonium salt (**11**)[8] or (**12**)† with n-butyl-lithium at −70 °C gave the corresponding ylide, which was then treated with the dialdehydes (**5**)—(**10**)† (−65 to 25 °C), to afford the acyclic compounds (**13**)—(**18**),†‡ in 20—50% yields, which were oxidatively coupled with anhydrous copper(II) acetate in pyridine–ether,[9] giving rise to the tetradehydroannulenes (**19**)—(**24**),‡ respectively, in 30—50% yields as highly stable crystals with a metallic lustre.

Comparison of the ^1H n.m.r. chemical shifts§ of the various protons of the annulenes (**19**)—(**24**) with those of the corresponding protons of the respective acyclic model compounds (**13**)—(**18**) indicates that the tetradehydro[26]- (**19**), -[30]- (**21**), and -[34]annulene (**23**) are diatropic, and the tetradehydro[28]annulene (**20**) is paratropic, while the tetradehydro[32]- (**22**) and -[38]annulene (**24**) are atropic. This follows from the fact that essentially all the outer protons in (**19**), (**21**), and (**23**) (including the methyl protons) resonate at lower field than the corresponding protons in (**13**), (**15**), and (**17**), respectively, whereas the inner protons (including the methylene protons) resonate at higher field. Conversely, essentially all the outer protons in (**20**) (including the methyl protons) resonate at higher field than the corresponding protons in (**14**), whereas the inner protons (including the methylene protons) resonate at lower field. On the other hand, the protons in (**22**) and (**24**) resonate in almost the same

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† The salt (**12**) was prepared in a similar manner to (**11**).[8] The dialdehydes (**5**)—(**9**)[10] and (**10**) [m.p. 208 °C (decomp.)] were prepared as reported.[8] The elemental analyses, except for unstable acyclic compounds (**14**), (**15**), (**16**), and (**18**), ^1H n.m.r., and i.r. spectra for all new compounds were consistent with the assigned structures.

‡ The substances decomposed on attempted melting point determination.

§ The protons of the acyclic model compounds (**13**)—(**18**) resonate at τ ($CDCl_3$) 3.10—3.90 (C=C and 7-membered ring H), 6.56—6.64 (–C≡CH), 7.27—7.30 (CH_2), 8.00—8.04 (Me), and 8.80—8.84 (Bu^t); (**19**) [26]: τ ($CDCl_3$) 2.83—2.94 (H-7, H-9, H-11, H-13), 3.00—3.03 (H-3), 3.23—3.26 (H-2), 5.03 (H-12), 5.17 (H-8), 5.36 (H-10), 7.76 (Me), 8.50 (CH_2); (**20**) [28]: 1.54 (H-14), 1.85 (H-23), 1.91 (H-8), 1.95 (H-27), 2.18 (H-12), 2.24 (H-10, H-25), 3.72—3.75 (H-3, H-4), 3.83 (H-15), 3.98—4.16 (H-22, H-7, H-26, H-2, H-5, H-11, H-13, H-28, H-9, H-24), 6.35 (CH_2), 8.27 (Me), 8.29 (Me); (**21**) [30]: 3.06—3.18 (H-3, H-7, H-9, H-11, H-13, H-15), 3.41—3.43 (H-2), 4.36—4.47 (H-14, H-8), 4.71—4.77 (H-10, H-12), 7.86 (Me), 8.07 (CH_2); (**22**)[32]: 2.98—3.93 (C=C and 7-membered ring H), 7.28 (CH_2), 8.80 (Bu^t); (**23**) [34]: 3.17—3.39 (H-3, H-7, H-9, H-11, H-13, H-15, H-17), 3.51—3.55 (H-2), 3.83—3.96 (H-8, H-16), 4.19—4.38 (H-10, H-12, H-14), 7.78 (CH-2), 8.74 (Bu^t); (**24**) [38]: 3.24—3.62 (H-2, H-3, H-7, H-9, H-11, H-13, H-15, H-17, H-19, H-8, H-18), 3.90—4.13 (H-10, H-12, H-14, H-16), 7.60 (CH_2), 8.76 (Bu^t). The methylene proton resonances of the atropic [38]annulene (**24**) do not correlate completely with those of the acyclic model (**18**) (Table 1). This might be explained by a homoconjugative effect exerted by the cycloheptatriene moiety in (**24**).

region as the corresponding protons of (**16**) and (**18**), respectively.

The simplest test of the nature of the ring current in these annulenes is provided by the chemical shifts of the methyl and the methylene protons, since these must be external and internal, respectively. The ^{1}H n.m.r. chemical shifts of these protons of (**19**)—(**24**) as well as the lower analogues (**1**)—(**4**) are summarized in Table 1. The alternation of the methyl and the methylene proton resonances between the [4*n* + 2]-annulenes (**1**), (**3**), (**19**), (**21**), (**23**) (relatively low- and high-field, respectively) and the [4*n*]annulenes (**2**), (**4**), (**20**) (relatively high- and low-field, respectively) confirms the diatropicity of the former and the paratropicity of the latter. Also, comparison of the chemical shifts shows that both the diatropicity and the paratropicity decrease as the ring size increases, and these tropicities disappear in the 38-membered ring in [4*n* + 2]π-systems and in the 32-membered ring in [4*n*]π-systems, since the chemical shifts move towards and correlate with those of the acyclic model compounds.§

To our knowledge, the 1,6-methanotetradehydro[28]- (**20**) and -[34]annulene (**23**) are the first examples of paratropic 28π- and diatropic 34π-electron neutral annulenes, respectively.

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