

Synthesis and Properties of Methano-[12]-, -[18]-, -[20]-, -[22]-, -[24]-annulene and Dimethano-[20]- and -[24]-annulene

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Reductive couplings of the vinylogues of cyclohepta-1,3,5-triene-1,6-dicarbaldehyde with a low-valent titanium reagent afforded the corresponding monomeric or dimeric products, *i.e.* singly bridged or doubly bridged annulenes in most cases. These annulenes showed diatropicity or paratropicity, depending on the number of peripheral conjugated π -electrons. The ^1H n.m.r. spectra of the methanoannulenes showed a larger temperature-dependency than those of the closely related tetra-dehydromethanoannulenes, reflecting the lower planarity and the larger conformational mobility of the molecular skeleton in the former compounds.

The reductive coupling of carbonyl compounds with a low-valent titanium reagent, developed by McMurry¹ and modified by several workers,² provides a new synthetic tool for formation of carbon-carbon double bonds, and has enabled chemists to synthesize a vast variety of crowded or twisted olefins inaccessible by the usual methods.³ This encouraged us to try to prepare annulenes and dehydroannulenes which had previously been synthesized only *via* lengthy reaction sequences. Although several of our attempts to prepare dehydroannulenes and dehydroannulenoannulenes from conjugated polyenyne ketones or carbaldehydes did not meet with success, mostly owing to incompatibility of the carbonyl compounds or their products with the reaction conditions,⁴ Tanner *et al.* reported a synthesis of 1,6:9,14-dimethano[16]annulene (**10**) by reductive coupling of cycloheptatriene-1,6-dicarbaldehyde (**1**), and showed compound (**10**) to be paratropic.⁵ This, and an availability of a series of vinylogous dicarbaldehydes derived from (**1**), prepared in connection with our study of tetrahydromethanoannulenes,⁶ allowed us to attempt the coupling of these dicarbaldehydes (**2**)—(**9**).⁷

Results and Discussion

Synthesis.—As modelled in the preparation of the dimethano[16]annulene (**10**),⁵ reductive coupling of 1,6-bis(2-formylvinyl)cyclohepta-1,3,5-triene (**3**) with titanium trichloride and lithium aluminium hydride in refluxing 1,2-dimethoxyethane (DME)² afforded a dimeric product, 1,6:13,18-dimethano[24]annulene (**12**), in 4.8% yield. Similarly, coupling of the lower vinylogue, 1-formyl-6-(2-formylvinyl)cyclohepta-1,3,5-triene (**2**), afforded a dimer, 1,6:11,16-dimethano[20]annulene (**11**), in 1.7% yield. Thus, since the couplings gave poor yields of dimeric products, we attempted to improve the yield by changing the reaction conditions.

A relatively slow addition of the diluted dicarbaldehyde (**3**) to a low-valent titanium reagent resulted unexpectedly in formation of a monomeric product, 1,6-methano[12]annulene (**13**), which had been prepared in a multi-step and low-yield route by Vogel *et al.*⁸ This result prompted us to attempt intramolecular couplings of the homologous dicarbaldehydes (**4**)—(**9**) which should provide an easy access to 1,6-methanoannulenes. However, unexpectedly, the dicarbaldehydes (**4**) and (**5**) did not afford monomeric products. The reason for this failure is not clear at present, but the result is in agreement with the prediction from an inspection of Dreiding

Table 1. ^1H N.m.r. parameters of dimethanoannulenes (**10**)—(**12**) in CDCl_3 at 100 or 270 MHz (τ -values)

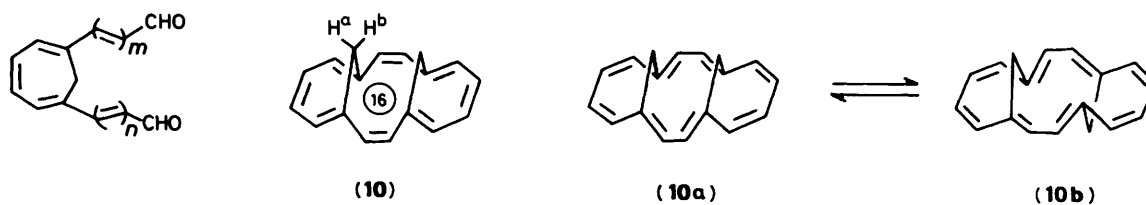
Compd.	H ^A	H ^B	H ^D	H ¹	H ²	H ^C	H ^b	H ^a
[16]- (10) ^a	5.50			5.03—5.15			1.80	4.42
[20]- (11)	3.78			4.24	0.72	5.04	7.19	
[24]- (12)	4.07	1.01		4.05	3.73	4.25	5.89	

^a See ref. 5.

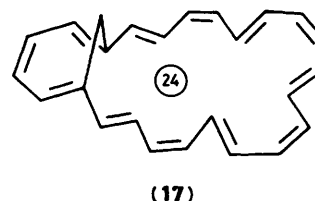
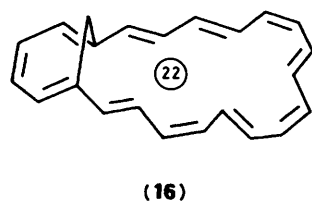
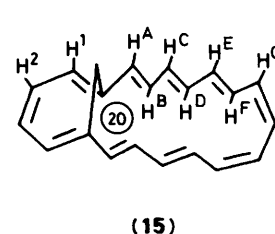
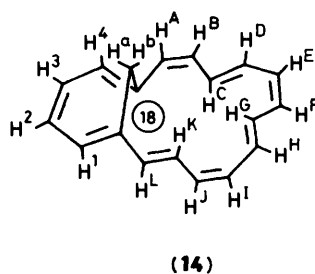
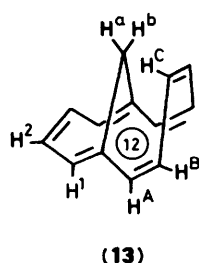
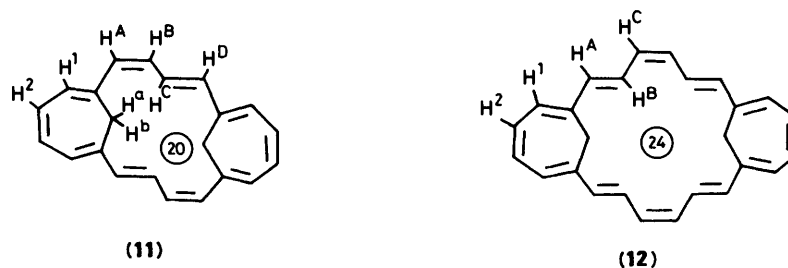
molecular models to the effect that the molecular skeletons of the desired products, 1,6-methano-[14]- and -[16]-annulene, would be difficult to construct. By contrast, couplings of the dialdehydes (**6**)—(**9**) afforded the monomeric products, 1,6-methano-[18]annulene (**14**), -[20]annulene (**15**), -[22]annulene (**16**), and -[24]annulene (**17**), respectively, in 5—15% yield. These methanoannulenes (**14**)—(**17**) as well as the dimethanoannulenes (**11**) and (**12**) were obtained as deeply coloured crystals, and the annulenes (**14**) and (**16**), as compared with (**11**), (**12**), (**15**), and (**17**), were relatively stable on exposure to diffused light and air, in agreement with the fact that they are $[4n + 2]\pi$ -systems.

^1H N.m.r. Spectra.—The ^1H n.m.r. spectra of the annulenes (**11**)—(**17**) were taken using the Fourier transform technique at 200, 270, or 360 MHz. Individual assignments were made on the basis of multiplicities and coupling constants given in the Experimental section and were further clarified by decoupling experiments or from examination of the two-dimensional spectra taken on a Bruker WM-360 spectrometer.

The ^1H n.m.r. chemical shifts of the dimethano-[20]- (**11**) and [24]-annulene (**12**) are listed in Table 1, together with those of the dimethano[16]annulene (**10**).⁵ Table 1 shows that both the annulenes (**11**) and (**12**) are paratropic, since the annulene inner protons resonate at low field, and the annulene outer protons at high field, while the bridged methylene protons resonate at lower field than those of the model dicarbaldehydes (**1**)—(**9**), which resonate at τ 7.2—7.3. Also, comparison of the chemical shifts of the annulene outer and inner protons (including methylene protons) shows that the paratropicity decreases in the sequence [16]- (**10**) > [20]- (**11**) > [24]-annulene (**12**), suggesting that the molecular planarity decreases in that order. Thus, although conjugation of the π -electrons is hindered to



- (1) $m = n = 0$
 (2) $m = 1, n = 0$
 (3) $m = n = 1$
 (4) $m = 2, n = 1$
 (5) $m = n = 2$
 (6) $m = 3, n = 2$
 (7) $m = n = 3$
 (8) $m = 4, n = 3$
 (9) $m = n = 4$



some extent, the annulene rings of compounds (11) and (12) are essentially planar. As regards the position of the bridge protons with respect to the annulene ring of compound (11), the low-field half of the AX-pattern may be assigned to the inner proton residing above the ring, with the high-field half assigned to the outer proton pointing away from the ring. The two bridging protons of the [24]annulene (12) might reside above the ring, resulting in their signal appearing as a singlet.

Thus, the appearance of the paratropicity in compounds (11) and (12) suggests that the relative geometry of the two bridging methylene groups in (11) and (12) might be *syn*, since the *anti*-species of dimethano[14]annulene is known to be atropic due to less efficient π -electron conjugation than in the *syn*-isomer.⁹ It was for this reason that the dimethano[16]annulene (10) was initially thought to exist in *syn*-form as indicated.⁵ However, subsequent detailed analysis of a more elaborate ¹H n.m.r. spectrum and of X-ray data as well as force-field calculations

established that the molecule (10) exists in rapid equilibrium between stereoisomers (10a) and (10b).¹⁰ Therefore, as a result, owing to insufficient spectral data we cannot indicate more detailed structures for compounds (11) and (12).

We now turn our attention to the spectra of the methanoannulenes (13)—(17). Variable-temperature ¹H n.m.r. spectra were taken at 90 or 100 MHz; the chemical shifts at 60 and -60°C are listed in Table 2, and the spectra of the [18]annulene (14) are illustrated in Figure 1. Table 2 shows that the [18]- (14) and the [22]-annulene (16) are diatropic, since the annulene outer protons resonate at low field, whilst the annulene inner protons, including the methylene protons (see above), do so at high field. On the other hand, the [20]- (15) and the [24]-annulene (17) are paratropic, since the outer protons resonate at high field, whereas the inner protons, and the CH₂ protons (see above), do so at low field. Also, with decreasing temperature the resonances of the inner (and CH₂) protons and

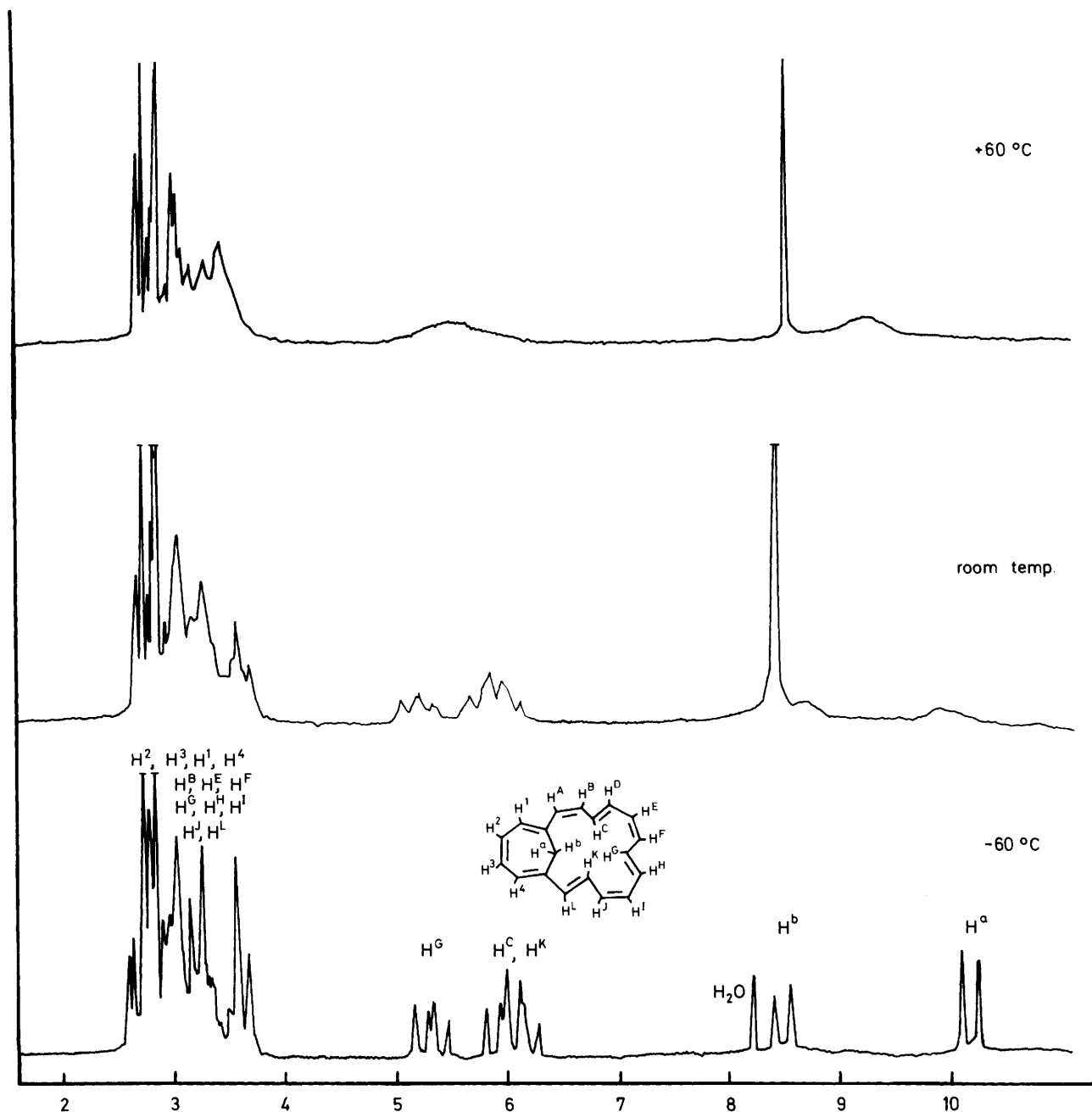


Figure 1. ¹H N.m.r. spectra of 1,6-methano[18]annulene (14) in CDCl₃ at 90 MHz (τ-values)

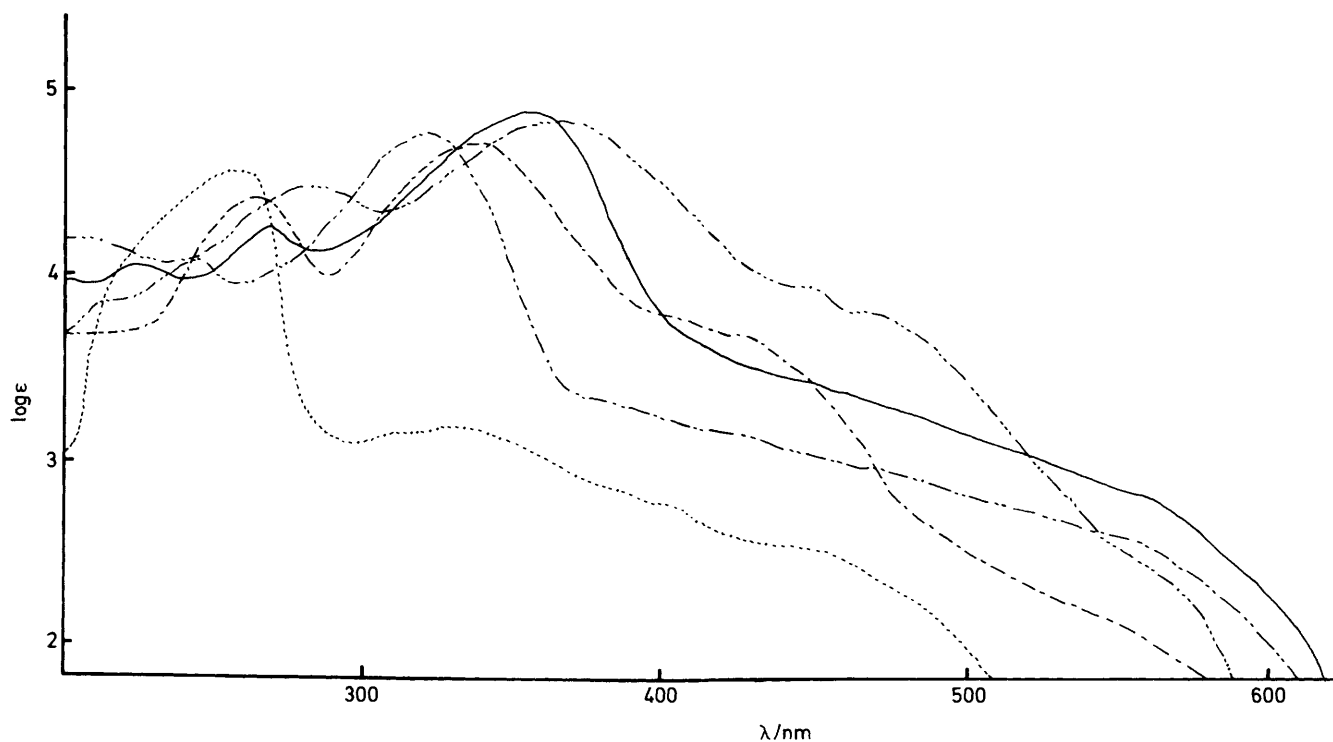
the outer protons of the $[4n + 2]$ annulenes (14) and (16) move to slightly higher and lower field, respectively, whereas the resonances of the inner (and CH₂) protons and the outer protons of the $[4n]$ annulenes (15) and (17) move to slightly lower and higher field, respectively, indicating that these annulenes have higher planarity at lower temperatures. Except for the case of the [12]annulene (13),⁸ all the spectra were poorly resolved at room temperature, the broad lines showing no fine structure; however, these features were explained after it was realized that the spectra are temperature-dependent. As is seen from Figure 1, the spectra of the [18]annulene (14) show that the mobility of the molecular skeleton is sufficiently slow for discrete inner and outer proton signals to be observed at room temperature and below, whereas the molecule is mobile at

60 °C and the methylene proton resonances coalesce at the weighted average (τ ca. 9.3) of the two methylene proton chemical shifts (τ 8.50 and 10.18) observed at -60 °C. As compared with the spectra of the [22]- (16) and the [24]-annulene (17) (Table 2), the spectrum of the [20]annulene (15) shows well defined resonances over the range -60 to 60 °C, suggesting that the molecular perimeter of (15) is more rigid than those of (16) and (17), which do not show the 'non-mobile' spectrum even at -60 °C. Thus, the [22]annulene (16) and the [24]annulene (17) are conformationally mobile over the range -60 to 60 °C, and no particular conformation is implied in the formulae (16) and (17).

Thus, it was found that the spectra of these annulenes (14)—(17) show a larger temperature-dependency than those of the

Table 2. ¹H N.m.r. parameters of the methanoannulenes (13)–(17) in CDCl₃ at 90 or 100 MHz (τ-values)

Compd.	<i>T</i> (°C)	outer H				inner H			CH ₂	
		H ¹		H ²		H ^A	H ^B	H ^C	H ^b	H ^a
[12]- (13)	+60	4.14–4.23		3.72–3.78		4.41	4.48		2.90	7.65
	–60	4.08–4.11		3.66–3.73		4.34	4.44		2.91	7.68
[18]- (14)	+60	2.70—3.70				H ^K H ^C H ^G			9.3	
	–60	2.60—3.68				5.32	5.97	6.15	8.50	10.18
[20]- (15)	+23	H ^A	H ^C	H ^E	H ^G	H ¹	H ²	H ^B	H ^F	H ^D
	–60	4.13	4.60		3.90–3.98		0.76	2.08	2.92	5.53
[22]- (16)	+60	2.64—3.80				4.84—5.60			8.72	
	–60	2.25—3.37				5.41—6.32			8.73	
[24]- (17)	+23	3.82—4.29				1.38—1.80			5.96	
	–60	3.80—4.78				0.60—1.77			4.98	7.22


Figure 2. Electronic absorption spectra of 1,6-methano-[12]-(13) (.....), -[18]-annulene (14) (- · - · - · - · -), -[20]-annulene (15) (---), -[22]-annulene (16) (- · · - · · -), and -[24]-annulene (17) (—) in THF

closely related tetrahydroannulenes,⁶ reflecting the lower planarity and the conformational mobility of the molecular skeleton of the former compounds.

Electronic Spectra.—The electronic absorption maxima of the annulenes (10)–(17) are listed in Table 3, and the absorption spectra of the methanoannulenes (13)–(17) are illustrated in Figure 2. As expected, the spectra of the dimethano[4*n*]annulenes (10)–(12) are similar, and each band (Table 3) exhibits an almost regular bathochromic shift as the ring size increases. As is seen from Figure 2, it is noteworthy that

the spectra of the methano[4*n*]annulenes such as (13), (15), and (17) exhibit broadening of the absorption curves, as compared with the spectra of the methano[4*n* + 2]annulenes (14) and (16), as has been observed in the monocyclic annulene series.¹¹ Table 3 shows that the main maxima of the [4*n* + 2]annulenes (14) and (16) are at rather longer wavelengths than those of the [4*n*]annulenes (15) and (17). Thus, it is evident that in these methanoannulenes the same alternation in the wavelengths of the main electronic absorption maxima between (4*n* + 2) and (4*n*) systems occurs, as has already been demonstrated for monocyclic annulenes and dehydroannulenes.¹²

Table 3. Electronic absorption maxima of the dimethanoannulenes (10)–(12) (in cyclohexane) and methanoannulenes (13)–(17) (in THF) [λ_{\max} (nm) (ϵ_{\max})]. The strongest absorptions are indicated in bold type

[16]- (10) ^a	286 (29 100), 296sh (25 000), 310 (14 400), 326 (13 700)
[20]- (11)	243 (17 000), 319sh (61 000), 328 (64 000), 397sh (2 560)
[24]- (12)	228 (4 200), 257 (2 040), 310sh (11 500), 326 (25 200), 351 (31 200), 435sh (840)
[12]- (13)	254 (36 400), 262 (36 200), 332 (1 520)
[18]- (14)	262 (26 700), 336 (55 000) , 413sh (6 300)
[20]- (15)	243 (12 000), 310sh (52 400), 321 (61 800)
[22]- (16)	258sh (19 600), 283 (30 700), 363 (72 500) , 466sh (6 750)
[24]- (17)	265 (18 900), 339sh (69 900), 352 (81 500)

^a See ref. 5.

Experimental

The 100 MHz ¹H n.m.r. spectra were taken using a JEOL FX-100 spectrometer. Tetrahydrofuran (THF) and DME were distilled from sodium benzophenone ketyl under nitrogen before use. For other general points see ref. 6.

1,6:11,16-Dimethano[20]annulene (11).—Lithium aluminium hydride (LiAlH₄) (0.26 g, 7 mmol) was added in one portion to a solution of titanium trichloride (TiCl₃) (1.77 g, 0.012 mol) in dry DME (50 ml) under argon. The resultant black mixture was heated under reflux for 30 min, and was stirred and treated dropwise, under reflux, with a solution of the dialdehyde (2)⁶ (0.50 g, 2.87 mmol) in DME (50 ml) during 6 h. Then the mixture was chilled and was passed through Hyflo Super-Cel to remove inorganic materials. The filtrate and washings (benzene) were combined and the organic layer was concentrated. The residue was chromatographed on silica gel (20 g) and was eluted with hexane. The brownish fractions were collected and evaporated to afford the *dimethano[20]annulene (11)* (7 mg, 1.7%). It formed black-brown needles, m.p. 205–207 °C (from hexane–benzene); *m/z* 284 (*M*⁺, 100%); *M*, 284.3; for u.v. data see Table 3; ν_{\max} 975, 965 (*E C=C*), and 740 cm⁻¹ (*Z C=C*); τ (100 MHz) 0.72 (2 H, dd, *J* 15 and 10 Hz, H^C), 3.78–4.24 (14 H, m, H^A, H^B, H^D, H^E, and H^F), 5.04 (2 H, d, *J* 13 Hz, H^B), and 7.19 (2 H, d, *J* 13 Hz, H^A) (Found: C, 92.7; H, 7.1. C₂₂H₂₀ requires C, 92.9; H, 7.1%).

1,6:13,18-Dimethano[24]annulene (12).—To a refluxing mixture of LiAlH₄ (0.11 g, 3.0 mmol) and TiCl₃ (0.77 g, 5.0 mmol) in dry DME (25 ml), prepared as described above, was added dropwise a solution of the dialdehyde (3)⁶ (0.25 g, 1.25 mmol) in dry DME (25 ml) during 6 h under argon and the mixture was stirred under reflux for a further 6 h. After work-up as for the isolation of (11), the residue was chromatographed on silica gel (20 g). The fractions eluted with hexane–benzene (4:1) afforded the [24]annulene (12) (10 mg, 4.8%). It formed black-brown needles, m.p. 200 °C (decomp.) (from hexane–benzene); *m/z* 336 (*M*⁺, 100%); *M*, 336.4; for u.v. data see Table 3; ν_{\max} 995 (*E C=C*) and 720 cm⁻¹ (*Z C=C*); τ (270 MHz) 1.01 (4 H, dd, *J* 15 and 9 Hz, H^B), 3.72–3.74 (4 H, m, H²), 4.04–4.06 (4 H, m, H¹), 4.07 (4 H, d, *J* 15 Hz, H^A), 4.25 (4 H, d, *J* 9 Hz, H^C), and 5.89 (4 H, s, CH₂) (Found: C, 92.9; H, 7.2. C₂₆H₂₄ requires C, 92.8; H, 7.2%).

1,6-Methano[12]annulene (13).—To a refluxing mixture of LiAlH₄ (87 mg, 2.3 mmol) and TiCl₃ (0.62 g, 4 mmol) in dry DME (30 ml) was added dropwise a solution of the dialdehyde

(3)⁶ (200 mg, 1.0 mmol) in dry DME (30 ml) during 15 h under argon and the mixture was stirred under reflux for a further 4 h. After the usual work-up, the residue was chromatographed on silica gel (20 g). The fractions eluted with hexane afforded the [12]annulene (13) (20 mg, 12%) as a pale yellow liquid; *m/z* 168 (*M*⁺, 72%) and 167 (100); *M*, 168.2; for u.v. data see Table 3 and Figure 2; ν_{\max} 720 and 650 cm⁻¹ (*Z C=C*); τ (90 MHz) 2.91 (1 H, d, *J* 11.5 Hz, H^B), 3.72–3.78 (2 H, m, H²), 4.14–4.21 (2 H, m, H¹), 4.41–4.50 (6 H, m, H^A, H^B, and H^C), and 7.67 (1 H, d, *J* 11.5 Hz, H^A)⁸ (Found: C, 92.6; H, 7.4. C₁₃H₁₂ requires C, 92.8; H, 7.2%).

The later fractions eluted with hexane–benzene (4:1) afforded the dimethano[24]annulene (12) (5 mg, 3%).

1,6-Methano[18]annulene (14).—To a refluxing mixture of LiAlH₄ (70 mg, 1.0 mmol) and TiCl₃ (0.51 g, 3.32 mmol) in dry DME (30 ml) was added dropwise a solution of the dialdehyde (6)⁶ (0.23 g, 0.83 mmol) in dry DME (30 ml) during 12 h under argon and the mixture was stirred under reflux for a further 3 h. After the usual work-up, the residue was chromatographed on silica gel (20 g). The fractions eluted with hexane afforded the [18]annulene (14) (25 mg, 12%). It formed black needles, m.p. 138–139 °C (from hexane); *m/z* 246 (*M*⁺, 100%); *M*, 246.3; for u.v. data see Table 3 and Figure 2; ν_{\max} 990, 980 (*E C=C*), and 700 cm⁻¹ (*Z C=C*); τ (360 MHz) 2.71–2.84 (3 H, m, H^E, H^F, and H^A), 3.00–3.24 (7 H, m, H¹, H^E, H^F, H^H, H^I, H^J, and H^D), 3.61–3.65 (2 H, m, H¹ and H⁴), 3.36 (1 H, dd, *J* 11 and 5 Hz, H¹), 5.22 (1 H, t, *J* 13 Hz, H^K), 5.84 (1 H, t, *J* 13.5 Hz, H^C), 6.02 (1 H, t, *J* 13.5 Hz, H^G), 8.43 (1 H, d, *J* 12.5 Hz, H^B), and 10.02 (1 H, d, *J* 12.5 Hz, H^A) (Found: C, 92.5; H, 7.4. C₁₉H₁₈ requires C, 92.6; H, 7.4%).

1,6-Methano[20]annulene (15).—To a refluxing mixture of LiAlH₄ (87 mg, 2.3 mmol) and TiCl₃ (0.62 g, 4.0 mmol) in dry DME (30 ml) was added dropwise a solution of the dialdehyde (7)⁶ (0.30 g, 1.0 mmol) in dry THF (40 ml) during 14 h under argon and the mixture was stirred under reflux for a further 4 h. After the usual work-up the residue was chromatographed on silica gel (20 g). The reddish fractions eluted with hexane afforded the [20]annulene (15) (12 mg, 4.5%). It formed black needles, m.p. 108–109 °C (from hexane); *m/z* 272.1543 (C₂₁H₂₀ requires *M*, 272.1563); for u.v. data see Table 3 and Figure 2; ν_{\max} 990, 960, 950 (*E C=C*), and 750 cm⁻¹ (*Z C=C*); τ (100 MHz, –30 °C) 0.65 (2 H, dd, *J* 15 and 10 Hz, H^B), 1.96 (2 H, dd, *J* 15 and 8 Hz, H^F), 2.85 (2 H, dd, *J* 15 and 8 Hz, H^D), 3.92–4.00 (2 H, m, H²), 4.25 (2 H, d, *J* 15 Hz, H^A), 4.25–4.27 (2 H, m, H¹), 4.42 (2 H, dd, *J* 15 and 10 Hz, H^C), 4.50 (2 H, d, *J* 8 Hz, H^G), 4.65 (2 H, dd, *J* 15 and 8 Hz, H^E), and 5.48 (2 H, s, CH₂) (Found: C, 92.2; H, 7.4. C₂₁H₂₀ requires C, 92.6; H, 7.4%).

1,6-Methano[22]annulene (16).—To a refluxing mixture of LiAlH₄ (0.11 g, 3.0 mmol) and TiCl₃ (0.80 g, 5.2 mmol) in dry DME (40 ml) was added dropwise a solution of the dialdehyde (8)⁶ (0.43 g, 1.3 mmol) in dry DME (50 ml) during 12 h under argon and the mixture was stirred under reflux for a further 3 h. After the usual work-up, the residue was chromatographed on silica gel (20 g). The fractions eluted with hexane–benzene (5:1) afforded the [22]annulene (16) (29 mg, 7.5%). It formed black needles, m.p. 144–145 °C (from hexane); *m/z* 298 (*M*⁺, 75%) and 165 (100); *M*, 298.4; for u.v. data see Table 3 and Figure 2; ν_{\max} 950 (*E C=C*) and 700 cm⁻¹ (*Z C=C*); τ (90 MHz, –30 °C) 2.29–3.50 (15 H, m, outer H), 5.40–6.32 (5 H, m, inner H), and 8.73 (2 H, s, CH₂) (Found: C, 92.3; H, 7.4. C₂₃H₂₂ requires C, 92.6; H, 7.4%).

1,6-Methano[24]annulene (17).—To a refluxing mixture of LiAlH₄ (70 mg, 1.9 mmol) and TiCl₃ (0.51 g, 3.32 mmol) in dry THF (30 ml) was added dropwise a solution of the dialdehyde

(9)⁶ (0.30 g, 0.84 mmol) in dry THF (50 ml) during 12 h under argon and the mixture was stirred under reflux for a further 4 h. After the usual work-up, the residue was chromatographed on silica gel (20 g). The fractions eluted with hexane afforded the [24]annulene (17) (20 mg, 7.3%). It formed black needles, m.p. 152–153 °C (from hexane); *m/z* 324.1842 (C₂₅H₂₄ requires *M*, 324.1876); for u.v. data see Table 3 and Figure 2; ν_{\max} 1 000 (*E* C=C) and 740 cm⁻¹ (*Z* C=C); τ (100 MHz) 1.38–1.80 (5 H, m, inner H), 3.82–4.29 (17 H, m, outer H), and 5.96 (2 H, s, CH₂) (Found: C, 92.1; H, 7.55. C₂₅H₂₄ requires C, 92.5; H, 7.5%).

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