Syntheses and Properties of Dicyanodimethyltetradehydro-trideca-, -pentadeca-, -heptadeca-, and -nonadeca-annulenes, and Benzannelated Tridecafulvene Derivatives

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Syntheses of (5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidene)- (5), (7,12-dimethyl-cyclopentadeca-2,4,6,12,14-pentaene-8,10-diynylidene)- (6), (7,12-dimethylcycloheptadeca-2,4,6, 12,14,16-hexaene-8,10-diynylidene)- (7), and (9,14-dimethylcyclononadeca-2,4,6,8,14,16,18-heptaene-10,12-diynylidene)-malononitrile (8) are described. Examination of the ^{1}H n.m.r. spectra indicates that both compounds (5) and (7) are paratropic, while both (6) and (8) are diatropic. Syntheses of benzannelated derivatives of compound (5), *i.e.* (11-methyl-12,13,14,15-tetrahydro-7*H*-benzocyclotridecen-7-ylidene) (9), and (14,15,16,17-tetradehydrodibenzo[*a,g*]-cyclotridecen-7-ylidene)-malononitrile (10) are also described. The influence of the dicyano substitution at the exocyclic bond of these annulenes, and of benzannelation upon the tropicity of the dicyanotetradehydro[13]annulene, is discussed on the basis of the ^{1}H n.m.r. and u.v. spectra of these compounds.

Recently, we have investigated the cyclic cross-conjugated system of ring-expanded fulvalenes[1] and fulvenes derived from the tetradehydroannulenones of type (1).[2] Of these, the diphenyl- (2)[3] and the dichloro-methylenetetradehydro-annulene derivative (3)[4] were synthesized through the reaction of diphenylketene and dichloroketene, respectively, with the

tetradehydroannulenones (1) and/or the corresponding acyclic ketone precursors. However, both compounds (2) and (3) proved to be atropic, reflecting an absence of any cross-conjugation of π-electrons, or of any contribution from a dipolar structure in the ground state of the annulenes (2) and (3). This prompted us to study the dicyano derivative (4)

(1)
(2) R = Ph
(3) R = Cl
(4)
(4a)

(5)
(6)
(7)
(8)

(9)
(10)
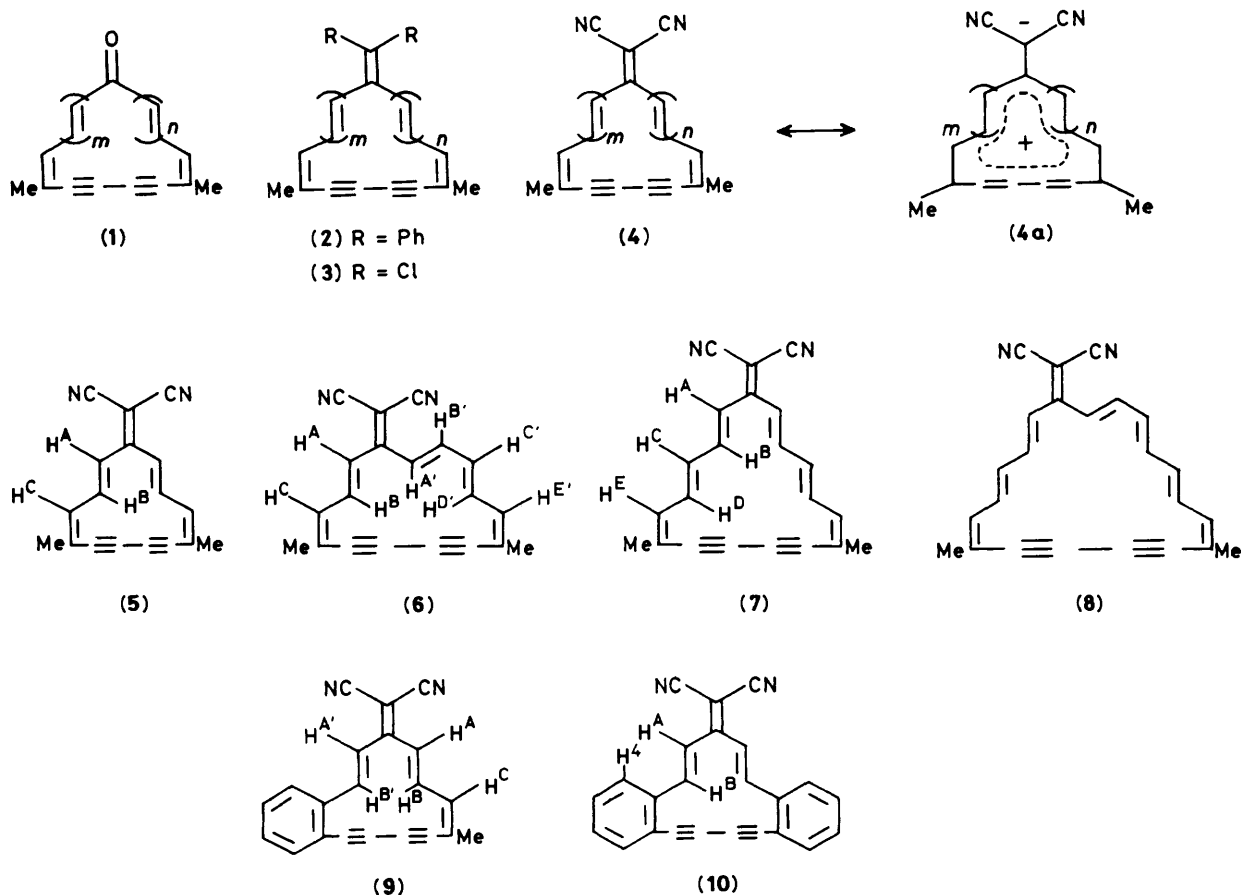
in which the cyano substituent is expected to polarize the fulvene system to a greater extent than do the phenyl and the chloro groups in compounds (2) and (3), respectively. If such polarization of an exocyclic bond occurs, forming a polar structure (4a), the dicyanomethylene[13]annulene (5) and the dicyanomethylene[17]annulene (7) would be potentially paratropic, and the corresponding dicyano[15]annulene (6) and [19]annulene (8) would be potentially diatropic, since the rings of the former contain $4n$ π-electrons and the rings of the latter

$4n + 2$ π-electrons. We have now realized this expectation in practice. Also, the lowering effect of benzannelation for the tropicity of the macrocyclic fulvene system was confirmed by preparing the monobenz- (9) and the dibenz-annelated derivative (10) of the [13]annulene (5). This paper deals with syntheses and properties of the title compounds (5)—(10),[5] of which the dicyanomethyleneannulenes (5)—(8) are the first examples of the fulvene-type system containing large monocyclic rings to show ring current.[6]
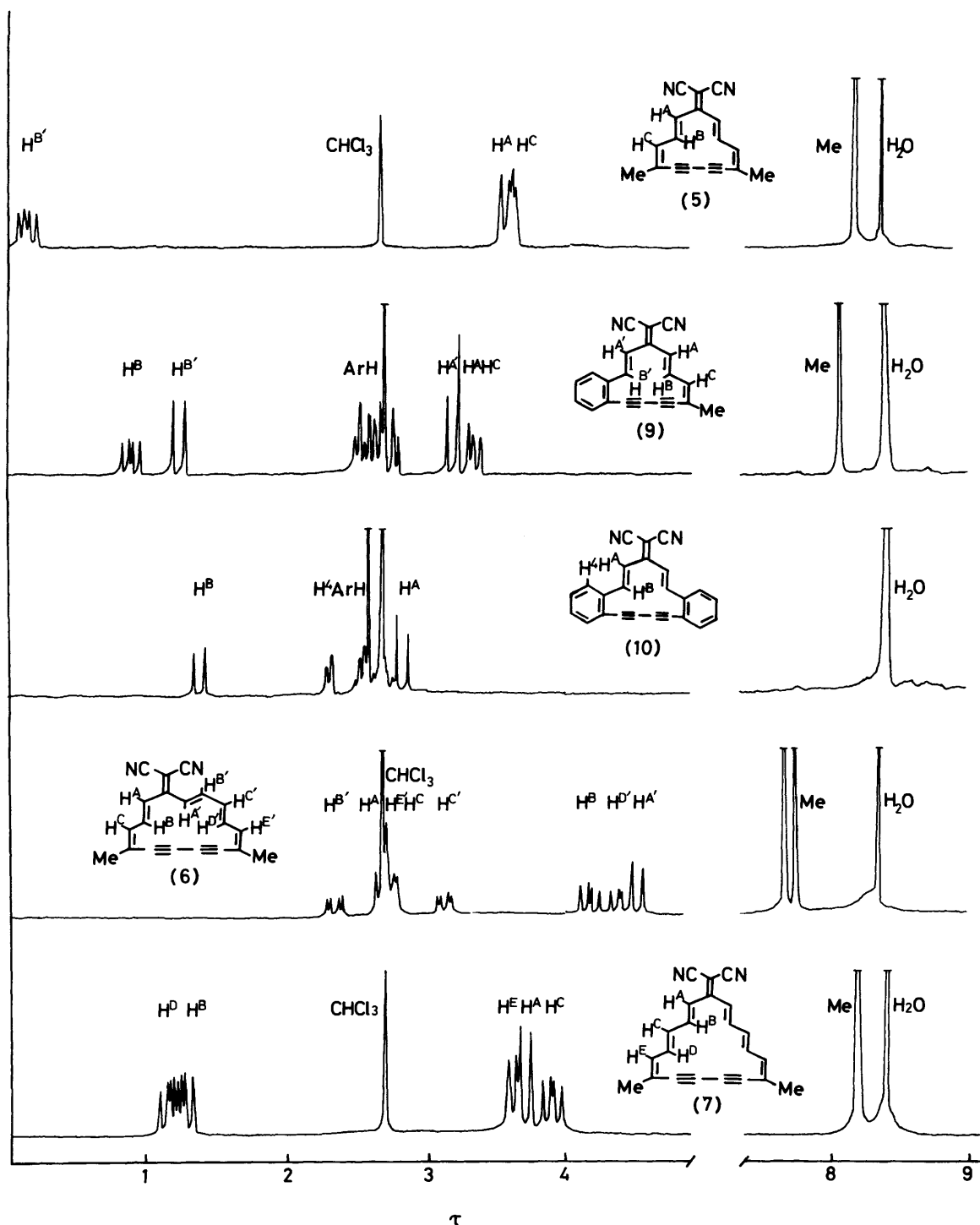

Figure. ¹H N.m.r. spectra of dicyanoannulenes (5)—(7), (9), and (10) in CDCl₃ at 200 MHz, determined at 21 °C (τ values)

Results and Discussion

Synthesis.—Attempts to obtain compounds (4) from the annulenones (1) by the use of β-alanine [7] or acetic anhydride [8] in condensation with malononitrile, or by reaction of dicyanoketene,[9] were fruitless. After a considerable number of unsuccessful experiments, a successful result was obtained on employing the procedure of Ong and Keoshkerian.[10] Reaction of 5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynone,[2a] 11-methyl-12,13,14,15-tetradehydro-7H-benzocyclotridecen-7-one,[11] 14,15,16,17-tetradehydro-7H-dibenzo[a,g]cyclotridecen-7-one,[11] 7,12-dimethylcyclopentadeca-2,4,6,12,14-pentaene-8,10-diynone,[2b] 7,12-dimethylcyclolheptadeca-2,4,6,12,14,16-hexaene-8,10-diynone,[2b] and 9,14-dimethylcyclononadeca-2,4,6,8,14,16,18-heptaene-10,12-diynone[2b] with an excess of malononitrile in the presence of titanium tetrachloride and pyridine in dichloromethane at −10 to 0 °C gave (5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidene)malononitrile (5) (17%), (11-methyl-12,13,14,15-tetradehydro-7H-benzocyclotridecen-7-ylidene)malononitrile (9) (14%), (14,15,16,17-tetradehydro-7H-dibenzo[a,g]cyclotridecen-7-ylidene)malononitrile (10) (23%), (7,12-dimethylcyclopentadeca-2,4,6,12,14-pentaene-8,10-diynylidene)malonontrile (6) (2.3%), (7,12-dimethylcycloheptadeca-2,4,6,12,14,16-hexaene-8,10-diynylidene)malononitrile (7) (4.3%), and (9,14-dimethyl-cyclononadeca-2,4,6,8,14,16,18-heptaene-10,12-diynylidene)-malononitrile (8) (1.7%), respectively. The benzannelated systems (9) and (10) were stable, but the non-annelated ones (5)—(8) were unstable. In particular, the instability of the [19]annulene (8) prevented us from obtaining a satisfactory [1]H n.m.r. spectrum or elemental analysis. Measurement of the [1]H n.m.r. spectrum of a freshly prepared sample of compound (8) in deuteriochloroform solution was performed several times; however, extensive decomposition occurs, leading to unidentified materials, and large, unexpected resonances always appeared at τ 2.3—4.6. Thus a full assignment of the resonances of the olefinic protons of compound (8) was not possible, and only the resonances of the methyl protons could be detected (see below).

[1]H N.m.r. Spectra.—The [1]H n.m.r. spectra of the systems (5)—(7), (9), and (10) are illustrated in the Figure. The assignments of the protons are based on the multiplicities and coupling constants, and were further clarified by decoupling experiments where necessary. The analysis of the spectra is fully in accord with considerations of ring current.

The Figure shows that the olefinic outer protons of the trideca- (5) and the heptadeca-system (7) resonate at high field, while the inner protons' signals appear at low field. Thus, compounds (5) and (7) are paratropic, as expected for 12π- and 16π-electron systems, respectively, owing to polarization of an exocyclic bond. Conversely, the outer protons of compound (6) resonate at low field, while the inner protons appear at high field, indicating that the pentadeca-system (6) is diatropic, as expected for a 14π-electron system. Also, the chemical shifts of the olefinic protons of compounds (9) and (10) suggest the monobenzannelated system (9) to be weakly paratropic and the dibenzannelated system (10) to be atropic, indicating that the tropicity falls off in the sequence (5) > (9) > (10), *i.e.* with increasing number of fused benzene rings on the tetrahydro-[13]annulene system, as revealed by the electronic spectra of these compounds (see below), and as has already been demonstrated for annulene[12] and dehydroannulenone systems.[13] Thus, the fact that the low-field shifts of the inner-proton resonances in the trideca series decrease by benzannelation shows that the shifts observed in compounds (5) and (9) are in part attributed to paramagnetic ring current,[3b] *i.e.* (5) and (9) are really paratropic as described above, since the local anisotropy of a 1,3-diacetylenic linkage in compounds (5) and

Large rings	(1)[a]	(3)[b]	(4)
[13]-	8.26	8.13	8.23
[15]-	7.76, 7.82	8.08	7.75, 7.83
[17]-	8.23	8.06	8.21
[19]-	7.79, 7.83	8.06, 8.09	7.79, 7.83

[a] See ref. 2. [b] See ref. 4.

(9) also shifts the inner-proton resonances considerably downfield.[14]

The simplest test for the nature of ring current in compounds (5)—(8) is provided by the chemical shifts of the methyl protons, since these must always be outside the ring and can readily be recognized. The chemical shifts of the methyl resonances of the dicyano compounds (5)—(8) are listed in Table 1, together with those of the corresponding annulenones (1) and the closely related dichloro compounds (3). Table 1 shows the alternation of the methyl resonances between the [4n + 1]annulenones ([13]-, [17]-annulenone) (relatively high field) and the [4n + 3]-annulenones ([15]-, [19]-annulenone) (relatively low field), confirming the paratropicity of the former and the diatropicity of the latter, as has been discussed previously.[2] An alternation of the methyl resonances between the dicyano-[13]-(5), -[17]- (7) and -[15]- (6), -[19]-annulene (8) shows the same trend and to almost the same degree as that of the annulenones (1), in contrast to the case of the atropic dichloro series (3). This confirms that the annulenes (5) and (7) are paratropic, while their homologues (6) and (8) are diatropic.

Electronic Spectra.—The electronic absorption maxima of compounds (5)—(10), determined in both tetrahydrofuran (THF) and acetonitrile, are listed in Table 2. It is evident from Table 2 that all the bands of compounds (5)—(10) show a small hypsochromic shift on changing the solvent from non-polar (THF) to polar (acetonitrile). This solvent effect strongly supports the interpretation that a π-electron polarization from the large rings to the exocyclic moiety, as depicted in structure (4a), occurs in these systems (5)—(10).

In the spectra of the [13]annulene series, the main maxima shift to longer wavelengths in the order non-benzannelated-(5) < monobenzannelated-(9) < dibenzannelated (10), indicating that fusion of benzene rings results in an appreciable bathochromic shift, as has been recognised for carbocyclic benzannulene series.[15] In contrast, the bands of the longest wavelength exhibit a considerable hypsochromic shift in the order (10) < (9) < (5) as the degree of annelation by benzene rings increases, suggesting that skeletons of the benzannelated compounds contain a less delocalized π-electron system than that of the non-annelated compound, as has been confirmed by [1]H n.m.r. spectroscopy and as has been observed in the corresponding tetradehydro[13]annulenone series.[11]

Table 2 shows that the main maxima of the [4n + 3]-annulenes (6) and (8) are at rather longer wavelength than those of the [4n + 1] homologues (5) and (7). Although the absorption curves are not illustrated, the spectra of compounds (5) and (7), and those of (6) and (8) are similar, the spectra of compounds (5) and (7), and those of (6) and (8) are similar, and differ only in the bathochromic shift of each band. Thus, it is evident that in these dicyano annulenes the same alternation in the wavelengths of the main electronic absorption maxima between [4n + 2] and [4n] systems occurs, as has already been

Table 2. Electronic absorption maxima of annulenes (5)—(10) [a, in THF $\lambda_{max.}$ (nm) ($\varepsilon_{max.}$/l mol^{-1} cm^{-1}); b, in acetonitrile $\lambda_{max.}$ (relative extinction coefficients)]. Strongest absorption indicated in bold type

(5)	a	249 (12 600), 268sh (14 200), **302 (22 200)**, 376 (19 600)
	b	248 (0.56), 265sh (0.60), 299 (1.00), 372 (0.88)
(9)	a	268 (11 900), 282 (11 700), **310 (15 400)**, 370 (9 530)
	b	267 (0.72), 280 (0.70), 307 (1.00), 366 (0.60)
(10)	a	274sh (13 000), 288sh (14 600), **320 (25 300)**, 361 (12 100)
	b	271sh (0.50), 285sh (0.56), 317 (1.00), 258 (0.48)
(6)	a	278 (13 300), **336 (15 600)**, 346sh (15 300), 464 (7 120), 484sh (6 520)
	b	277 (0.82), 335 (1.00), 345sh (0.98), 463 (0.45), 483 (0.42)
(7)	a	248 (10 200), 274sh (14 300), 284 (17 700), 301 17 000), **326 (17 900)**, 345 (17 800), 411 (12 600)
	b	246 (0.52), 272sh (0.78), 282 (1.00), 299 (0.92), 323 (1.00), 343 (0.98), 409 (0.70)
(8)	a	274sh (12 100), 281sh (13 000), 298sh (15 100), 307 (15 800), **371 (18 200)**, 474sh (7 900)
	b	270sh (0.61), 279sh (0.70), 297sh (0.84), 304 (0.86), 369 (1.00), 472sh (0.44)

demonstrated for monocyclic annulenes, dehydroannulenes,[16] and tetradehydroannulenones of type (1).[17]

In addition, both the main and the longest wavelength bands of the dicyano annulenes (5)—(8) appear at longer wavelength than those of the corresponding diphenyl- (2)[3] and dichloro-substituted systems (3)[4] of the same ring size, reflecting the fact that the degree of extended conjugation is larger in the dicyano than in the diphenyl and the dichloro systems.

Experimental

M.p.s. were determined with a hot-stage apparatus and are uncorrected. I.r. spectra were taken with a Hitachi 260-50 spectrophotometer as KBr discs; only significant maxima are described. U.v. spectra were measured in THF or acetonitrile solution and run with a Hitachi 220 A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 200 spectrometer operating at 75 eV using a direct-inlet system. [1]H N.m.r. spectra were recorded as $CDCl_3$ solutions with a Varian XL-200 (200 MHz) or a JEOL GX-270 (270 MHz) spectrometer, tetramethylsilane being used as internal standard. Assignments were clarified by the use of decoupling experiments where necessary. Merck silica gel or alumina (activity II—III) was used for column chromatography, and preparative t.l.c. (p.l.c.) was carried out on 20 × 20 cm silica-gel plates (Merck; 0.5 or 2 mm thick). Progress of most reactions was followed by t.l.c. using Merck precoated silica gel. All preparations were carried out in dry dichloromethane, and dichloromethane was distilled over calcium hydride before use. THF was refluxed over potassium hydroxide pellets and distilled before use. Organic extracts with dichloromethane were washed with saturated aqueous sodium chloride and dried over sodium sulphate prior to removal of solvent. Solvents were evaporated off under water-pump pressure.

(5,10-*Dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidene*)*malononitrile* (5).—To a stirred solution of 5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynone (1; $m = n = 1$)[2a] (367 mg, 1.80 mmol) and malononitrile (210 mg, 3.20 mmol) in dichloromethane (20 ml) in an ice-bath was added dropwise, during 40 min, a solution of titanium tetrachloride (0.8 ml, 7.28 mmol) in dichloromethane (10 ml). Then a solution of pyridine (1.7 ml) in dichloromethane (10 ml) was added dropwise during 30 min to the ice-cooled mixture. After the mixture had been stirred for 1 h at room temperature, 7% hydrochloric acid (10 ml) was added and the mixture was stirred for a further 10 min. Then the mixture was separated and the aqueous layer was extracted with dichloromethane. The combined organic phase was washed with aqueous sodium hydrogen carbonate and dried. The residual red liquid obtained after removal of solvent was chromatographed on silica gel (1.7 × 17 cm). The

fractions of the second band, which were eluted with benzene, were collected and on evaporation afforded the *methylenetetradehydro*[13]*annulene* (5) (79 mg, 17%) as a solid, which formed reddish brown needles, m.p. 118—119 °C (decomp) (from hexane–dichloromethane) (Found: M^+, 256.0911. $C_{18}H_{12}N_2$ requires M, 256.0998); for u.v. data see Table 2; $v_{max.}$ 2 220 (C≡N), 2 160 (C≡C), and 975 cm^{-1} (*trans* C=C); τ (200 MHz) 0.21 (2 H, dd, J 16 and 9 Hz, H^B), 3.65 (2 H, d, J 16 Hz, H^A), 3.69 (2 H, d, J 9 Hz, H^C), and 8.23 (6 H, s, Me); see also Figure (Found: C, 84.2; H, 4.8; N, 11.3. $C_{18}H_{12}N_2$ requires C, 84.35; H, 4.7; N, 10.9%).

(7,12-*Dimethylcyclopentadeca*-2,4,6,12,14-*pentaene*-8,10-*diynylidene*)*malononitrile* (6).—A solution of titanium tetrachloride (0.8 ml, 7.28 mmol) in dichloromethane (10 ml) was added dropwise during 35 min to a stirred solution of 7,12-dimethylcyclopentadeca-2,4,6,12,14-pentaene-8,10-diynone (1; $m = 1$, $n = 2$)[2b] (547 mg, 2.33 mmol) and malononitrile (527 mg, 7.98 mmol) in dichloromethane (50 ml) at 1 °C, and then a solution of pyridine (2.2 ml) in dichloromethane (10 ml) was added dropwise during 35 min at the same temperature. After being stirred for 1 h at 1 °C, the mixture was worked up as for the isolation of compound (5). The product was passed through a short column of alumina (3.7 × 4.0 cm). The fractions eluted with benzene–chloroform (1 : 3) were collected and evaporated to give a dark red liquid, which was further purified by p.l.c. (benzene–chloroform, 4 : 1). The fast moving, second coloured band afforded, on evaporation, the *tetradehydro*[15]*annulene* (6) (12 mg, 2.3%) as a solid, which formed dark red cubes, m.p. 146—147 °C (decomp.) (from hexane–benzene) (Found: M^+, 282.1070. $C_{20}H_{14}N_2$ requires M, 282.1155); for u.v. data see Table 2; $v_{max.}$ 2 230 (C≡N), 2.180 (C≡C), and 980 cm^{-1} (*trans* C=C); τ (270 MHz) 2.39 (1 H, dd, J 15.5 and 5.5 Hz, H^B), 2.73 (1 H, d, J 15.5, H^A), 2.79 (1 H, d, J 11.5 Hz, H^E), 2.81 (1 H, d, J 11 Hz, H^C), 3.18 (1 H, dd, J 15.5 and 5.5 Hz, $H^{C'}$), 4.23 (1 H, dd, J 15.5 and 11. Hz, H^B), 4.45 (1 H, dd, J 15.5 and 11.5 Hz, $H^{D'}$), 4.57 (1 H, d, J 15.5 Hz, $H^{A'}$), 7.75 (3 H, s, Me), and 7.83 (3 H, s, Me); see also Figure (Found: C, 84.3; H, 5.6; N, 9.8. $C_{20}H_{14}N_2$ requires C, 85.1; H, 5.0; N, 9.9%). Attempts to improve the elemental analysis failed.

(7,12-*Dimethylcycloheptadeca*-2,4,6,12,14,16-*hexaene*-8,10-*diynylidene*)*malononitrile* (7).—A solution of titanium tetrachloride (0.6 ml, 3.64 mmol) in dichloromethane (20 ml) was added dropwise during 10 min to an ice-cooled, stirred solution of 7,12-dimethylcycloheptadeca-2,4,6,12,14,16-hexaene-8,10-diynone (1; $m = n = 2$)[2b] (486 mg, 1.90 mmol) and malononitrile (250 mg, 3.80 mmol) in dichloromethane (50 ml). Then a solution of pyridine (2.7 ml) in dichloromethane (20 ml) was added dropwise during 15 min to the ice-cooled mixture. After being stirred for 40 min in the ice-bath, the mixture was worked

up as for the isolation of compound (**5**). The product was passed through a short column of alumina (3.7×4.0 cm). The fractions eluted with benzene–chloroform (1:3) were collected, and on evaporation gave a brown liquid, which was further purified by p.l.c. (benzene). The fast moving orange band afforded, on evaporation, the *tetradehydro*[*17*]*annulene* (**7**) (25 mg, 4.3%) as a solid, which formed purple needles, m.p. 151—152 °C (decomp.) (from hexane–benzene); m/z 308 (M^+, 53%) and 293 (100); for u.v. data see Table 2; $\nu_{max.}$ 2 230 (C≡N), 2 180 (C≡C), and 995 cm^{-1} (*trans* C=C); τ (200 MHz) 1.19 (2 H, dd, J 15 and 11 Hz, H^D), 1.30 (2 H, dd, J 15.5 and 11 Hz, H^B), 3.66 (2 H, d, J 11 Hz, H^E), 3.75 (2 H, d, J 15.5 Hz, H^A), 3.94 (2 H, dd, J 15 and 11 Hz, H^C), and 8.21 (6 H, s, Me); see also Figure (Found: C, 85.9; H, 5.5; N, 8.8. $C_{22}H_{16}N_2$ requires C, 85.7; H, 5.2; N, 9.1%).

(*9,14-Dimethylcyclononadeca-2,4,6,8,14,16,18-heptaene-10,12-diynylidene*)*malononitrile* (**8**).—A solution of titanium tetrachloride (0.6 ml, 3.56 mmol) in dichloromethane (40 ml) was added dropwise during 15 min to a stirred solution of 9,14-dimethylcyclononadeca-2,4,6,8,14,16,18-heptaene-10,12-diynone (**1**; $m = 2, n = 3$)^{2b} (510 mg, 1.78 mmol) and malononitrile (235 mg, 3.56 mmol) in dichloromethane (50 ml) at -15 °C, and then a solution of pyridine (3.0 ml) in dichloromethane (20 ml) was added dropwise during 10 min at -15 °C. After being stirred for 1 h at -15 °C, the mixture was worked up as for the isolation of compound (**5**).The product was passed through a short column of alumina (3.7×4.0 cm). The fractions eluted with chloroform were collected and, on evaporation, gave a dark red liquid, which was further purified by p.l.c. (benzene–chloroform, 1:1). The fast moving purple band gave, on evaporation, the *dicyanotetradehydro*[*19*]*annulene* (**8**) (10 mg, 1.7%) as a solid, which formed dark purple cubes, m.p. 127—128 °C (decomp.) (from hexane–benzene) (Found: M^+, 334.1455. $C_{24}H_{18}N_2$ requires M, 334.1467); for u.v. data see Table 2; $\nu_{max.}$ 2 225 (C≡N), 2 180 (C≡C), and 995 cm^{-1} (*trans*-C=C); τ (270 MHz) 7.79 (s, Me) and 7.83 (s, Me); the resonances of the olefinic protons were submerged by those of unidentified material.

(*11-Methyl-12,13,14,15-tetradehydro-7H-benzocyclotridecen-7-ylidene*)*malononitrile* (**9**).—A solution of titanium tetrachloride (0.65 ml, 5.80 mmol) in dichloromethane (10 ml) was added dropwise during 10 min to a stirred solution of 11-methyl-12,13,14,15-tetradehydro-7*H*-benzocyclotridecen-7-one^{11} (465 mg, 1.56 mmol) and malononitrile (448 mg, 6.79 mmol) in dichloromethane (50 ml) at 3 °C. Then a solution of pyridine (1.8 ml) in dichloromethane (13 ml was added dropwise during 15 min to the mixture at 3 °C. After being stirred for 1 h at 3 °C, the mixture was worked up as for the isolation of compound (**5**). The product was subjected to p.l.c. (benzene–chloroform, 9:1). The fast moving red band afforded, on evaporation, the *monobenzannelated annulene* (**9**) (64.5 mg, 14%) as a solid, which formed red needles, m.p. 215—216 °C (decomp.) (from hexane–benzene); m/z 292 (M^+, 64%) and 264 (100); for u.v. data see Table 2; $\nu_{max.}$ 2 220 (C≡N), 2 180 (C≡C), and 985 cm^{-1} (*trans* C=C); τ (200 MHz) 0.93 (1 H, dd, J 16 and 10 Hz, H^B), 1.27 (1 H, d, J 16 Hz, H$^{B'}$), 2.50—2.85 (4 H, m, ArH), 3.24 (1 H, d, J 16 Hz, H$^{A'}$), 3.31 (1 H, d, J 16 Hz, H^A), 3.40 (1 H, d, J 10 Hz, H^C), and 8.11 (3 H, s, Me); see also Figure (Found: C, 86.0; H, 4.1; N, 10.0. $C_{21}H_{12}N_2$ requires C, 86.3; H, 4.1; N, 9.6%).

(*14,15,16,17-tetradehydro-7H-dibenzo*[*a,g*]*cyclotridecen-7-ylidene*)*malononitrile* (**10**).—A solution of titanium tetrachloride (0.6 ml, 5.46 mmol) in dichloromethane (10 ml) was added dropwise during 10 min to a stirred solution of 14,15,16,17-tetradehydro-7*H*-dibenzo[*a,g*]cyclotridecen-7-

one^{11} (485 mg, 1.47 mmol) and malononitrile (334 mg, 5.06 mmol) in dichloromethane (50 ml) at 1 °C, and then a solution of pyridine (1.4 ml) in dichloromethane (10 ml) was added dropwise during 10 min to the mixture at 1 °C. After being stirred for 1 h at 1 °C, the mixture was worked up as for the isolation of compound (**5**). The residual liquid was chromatographed on alumina (3.7×7.0 cm). The fractions eluted with benzene–chloroform (4:1) afforded the *dibenzannelated annulene* (**10**) (149 mg, 23.4%) as a solid, which formed orange needles, m.p. 258—259 °C (decomp.) (from benzene); m/z 328 (M^+, 100%); for u.v. data see Table 2; $\nu_{max.}$ 2 280 (C≡N), 2 180 (C≡C), and 965 cm^{-1} (*trans* C=C); τ (200 MHz) 1.42 (2 H, d, J 16 Hz, H^B), 2.35 (2 H, d, J 7.5 Hz, H^4), 2.55—2.77 (6 H, m, ArH), and 2.88 (2 H, d, J 16 Hz, H^A); see also Figure (Found: C, 87.6; H, 3.7; N, 9.0. $C_{24}H_{12}N_2$ requires C, 87.8; H, 3.7; N, 8.6%).

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