Synthesis and Properties of Tetramethyloctadehydrotridecapentadecafulvalene

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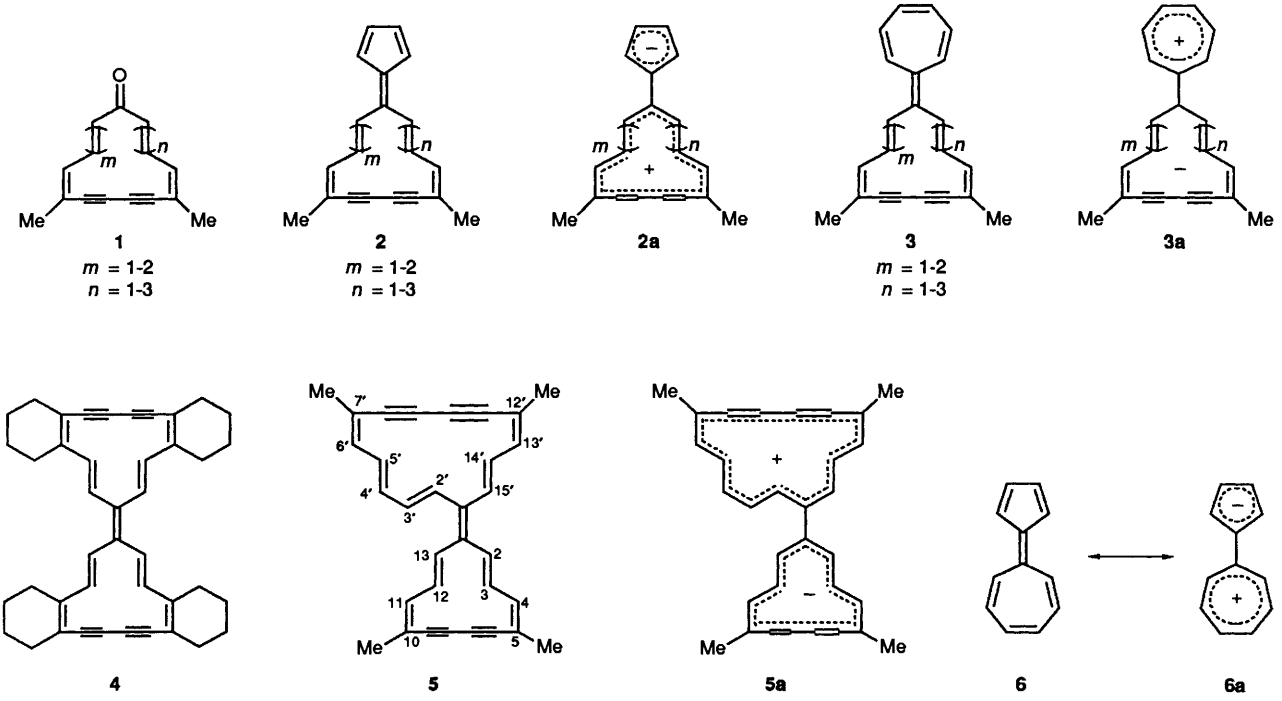
Synthesis of the title compound, 15-(5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidene)-6,11-dimethylcyclopentadeca-1,3,5,11,13-pentaene-7,9-diyne, is described. Examination of ^{1}H and ^{13}C NMR spectra indicated that the tridecapentadecafulvalene derivative shows no ring-current effect but did have polyolefinic character.

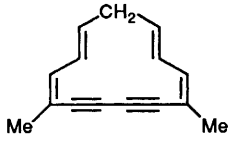
Recently we have investigated cyclic cross-conjugated systems of ring-expanded fulvenes[1] and fulvalenes derived from the tetradehydroannulenones **1**.[2] Of these, the penta- **2** and the hepta-fulvalene derivatives **3** showed a slight π-electron polarization in the ground state from the large ring to the 5-membered ring in compounds **2** and from the 7-membered ring to the large ring in compounds **3**, as depicted in zwitterions **2a** and **3a**, respectively, and both compounds **2** and **3** were isolated as relatively unstable, coloured crystals.[3] An obvious extension of our interest in these compounds directed our efforts to the preparation of fulvalene derivatives composed of two large-membered rings. The only known macrocyclic compound of this type is the tetra(cyclohexene)-annelated tridecatridecafulvalene derivative **4**, which was prepared by Howes and Sondheimer.[4] However, compound **4** was characterized only in solution, and was shown to be very unstable and to have highly polyolefinic character by ^{1}H NMR spectroscopy. The atropic nature of compound **4** reflects the absence of any cross-conjugation of π-electrons or any contribution from a dipolar structure in the ground state. This is reasonable since polarization of the central double bond (pinch bond) could render one ring 14π-aromatic but the other 12π-antiaromatic. This prompted us to study the tridecapentadecafulvalene **5**, the higher analogue of sesquifulvalene **6**, which exhibits slight aromatic stabilization arising from contribution of a dipolar structure **6a**. We considered that compound **5**, in which one ring is 13-membered and the other is 15-membered, is potentially aromatic as is sesquifulvalene **6**,[5] since polarization of the pinch bond would make both rings 14π-electron aromatic systems. The related [13]- (**1**; $m = n = 1$)[2a] and [15]-annulenones (**1**; $m = 1, n = 2$),[2b] from which compound **5** is formally formed by replacement of the oxygen atom of either annulenone with the other ring, show an alternation of ring-current effect.[2] This paper deals with the synthesis and properties of the title compound **5**,[6] which is the first example of a fulvalene-type system containing two large monocyclic rings to be obtained.[7]

Results and Discussion

Synthesis.—Syntheses of a series of dimethyltetradehydroannulenones **1**[2] as well as their α-methyl[8] and α-ethyl substituted[9] derivatives have been described previously. In view of the convenient and relatively easy preparation of compounds **1** they appeared to be desirable starting materials for the synthesis of cross-conjugated fulvalene derivatives. Of the many methods available for the synthesis of the fulvalene system, most



involve addition of one cyclic compound to another cyclic compound followed by elimination, or a condensation reaction between two cyclic compounds, thus producing a central double bond (pinch bond).[10] The syntheses of compounds **2** and **3** have been achieved by these addition or condensation reactions.[3] Therefore, we initially attempted to prepare the corresponding methylene compounds **7** or **8** for the [13]annulenone (**1**: m =



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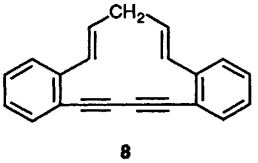

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n = 1) or its dibenzannelated derivative[11] to condense with the [15]annulenone (**1**; m = 1, n = 2). However, several attempts to prepare either compound **7** or compound **8** by reduction of the respective annulenone derivatives with $AlCl_3$–$LiAlH_4$, or by a reaction sequence involving double Wittig condensation with 1,3-bis(triphenylphosphonio)propane dibromide,[12] met without success. Also, we attempted a mixed reductive coupling of the [13]annulenone (**1**; m = n = 1) with the [15]annulenone (**1**; m = 1, n = 2) by employing $TiCl_3$–$LiAlH_4$ in 1,2-dimethoxyethane (DME) according to McMurry's method.[13] However, all attempts were unsuccessful, which led us to search for another approach.

A recent successful preparation of the cyano(formyl)fulvene derivative **9**,[14] which was prepared from the [13]annulenone (**1**; m = n = 1) by condensation with malononitrile, followed by reduction with diisobutylaluminium hydride (DIBAH), intrigued us and stimulated us to elaborate an acyclic exocyclic moiety leading to a 15-membered conjugated system upon the 13-membered ring of monocyclic compound **9**.

Treatment of 3-methylpent-2-en-4-ynyltriphenylphosphonium bromide **10**[15] in tetrahydrofuran (THF) with butyllithium led to the corresponding ylide, which was allowed to react with the cyano(formyl)fulvene **9** to afford a mixture of the *Z*-isomer **11a** (38%) and the *E*-isomer **11b** (23%) of the newly formed double-bond compound. The two isomers were separated and were isolated by chromatography on alumina.

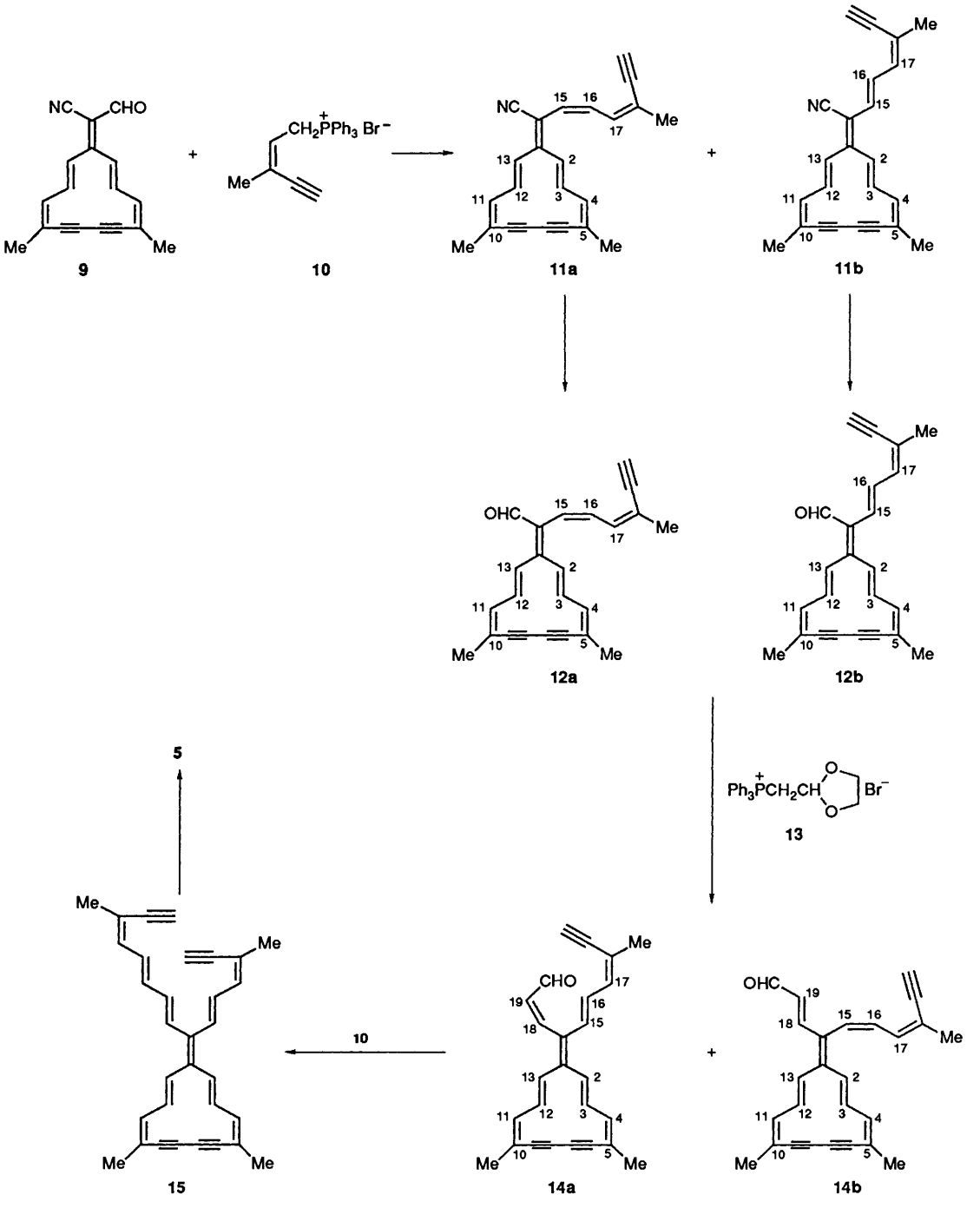
Individual reduction of compounds **11a** and **11b** with DIBAH in toluene at −10 °C afforded the *Z*-isomer **12a** (30%) and the *E*-isomer **12b** (32%) of the ethynyl(formyl)fulvene, respectively, while keeping the *E*- and *Z*-stereochemistry of the substrates **11**. Reduction of a mixture of isomers **11a** and **11b** with DIBAH afforded almost identical yields of aldehydes **12a** and **12b** as those obtained by the respective reduction of substrates **11a** and **11b** (see Experimental section), suggesting that the stereochemistry was also kept in this reduction. Reaction of a mixture of aldehydes **12a** and **12b** with 10 molar equivalents of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide **13**[16] and lithium methoxide in *N*,*N*-dimethylformamide (DMF) at room temperature, followed by hydrolysis with dilute hydrochloric acid in THF–ethanol gave the homologated vinylogue **14** in 30% yield. Among the four possible stereoisomeric products the isomers **14a** and **14b** could be characterized from analysis of their ^{1}H NMR spectra. Wittig reaction of this mixture of compound **14** with the salt **10** as before afforded a stereoisomeric mixture of the acyclic diethynylfulvene **15** as very unstable semi-solid. The instability of compound **15** discouraged us from attempting to separate the stereoisomers. Therefore, although the individual stereoisomers were not followed up, the characterization of the product was confirmed by examination of the IR, ^{1}H NMR, and electronic spectra of this mixture (see Experimental section). An intramolecular oxidative coupling of the fulvene derivative **15** and its stereoisomers containing two terminal acetylene groups with anhydrous copper(II) acetate in pyridine–methanol at 60 °C under high-dilution conditions with diethyl ether as an entraining solvent afforded the desired title compound, 15-(5,10-dimethylcyclotrideca-2,4,10,12-tetraene-6,8-diynylidene)-6,11-dimethylcyclopentadeca-1,3,5,11,13-pentaene-7,9-diyne **5**, in 22% yield as relatively unstable, black-purple needles.

^{1}H *NMR Spectra of Compound* **5**.—The ^{1}H NMR spectrum of compound **5** (Fig. 1) was thoroughly analysed on the basis of homonuclear double resonance and nuclear Overhauser effect (NOE) experiments. Decoupling experiments revealed three d–dd–d sequences of three vicinal protons and one d–dd–dd–dd–d sequence of five vicinal protons. The five-proton sequence was evidently ascribed to $H^{2'}$–$H^{6'}$ protons. The broader one at δ 6.63, of the two doublets was assigned to $H^{6'}$; irradiation of this signal caused sharpening of the signal at δ 1.90, which was then assigned to 7′-Me. Among the three d–dd–d sequences, two showed similar chemical shifts (δ 6.45–6.97–6.70 and δ 6.50–7.02–6.77), while the remaining one behaved differently (δ 7.01–7.34–6.67). Therefore the latter one should be due to $H^{13'}$–$H^{15'}$, while the first two should derive from the 13-membered ring. In any of the three sequences, the broader doublet was assigned to the proton α to a methyl group and irradiation of this signal caused sharpening of the nearby methyl group. Irradiation of $H^{3'}$ at δ 6.23 enhanced the intensity of the doublet at δ 6.50 but not that at δ 6.45, and thus the former was assigned to H^{13} and the latter to H^2. In this way all of the protons were unambiguously assigned (see Experimental section and Table 1).

The smaller degree of polarization of the pinch bond of compound **5** as compared with the heptatridecafulvalene **16** (≡**3**; m = n = 1) and the pentapentadecafulvalene **17** (≡**2**; m = 1, n = 2), both of which are cross-conjugated systems as is sesquifulvalene **6**, is suggested from comparison of the chemical shifts of the olefinic protons of compound **5** with those of analogues **16** and **17**.

The ^{1}H NMR chemical-shift data of compound **5** are listed in Table 1, together with those of analogues **16** and **17**, in which both the 13-membered ring of compound **16** and the 15-membered ring of compound **17** would be expected to be 14π-electron aromatic systems by polarization of the pinch bond. Comparison of the chemical shifts of the olefinic outer and inner protons of the 13-membered ring of compound **5** with those of compound **16** (for example, between 2-H of **16** and 2-H and 13-H of **5**, and between 3-H of **16** and 3-H and 12-H of **5**) indicates that the outer protons of compound **5** resonate at higher field (reduced low-field shift) and the inner protons do so at lower field (reduced high-field shift), respectively, than those of compound **16**. Such a reduced low-field shift for the outer protons and a reduced high-field shift for the inner protons of compound **5** can be seen from comparison of the 15-membered-ring olefinic outer and inner protons of compound **5** with those of the 15-membered ring of compound **17**. Thus, the olefinic protons of both of the large-membered rings of compound **5** show reduced low-field and high-field shifts for the outer and inner protons, respectively, compared with those of analogues **16** and **17**, indicating that the contribution of the dipolar structure **5a** in **5** is smaller than in the cases of analogues **16** and **17**. The methyl protons resonate at almost the same field in these compounds and useful information could not be obtained from comparison of the methyl-proton signals.

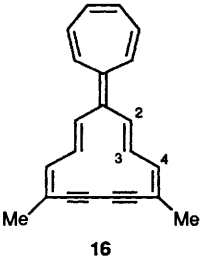
^{1}H NMR spectra of compound **5** in [$^2H_8$]toluene were obtained in the temperature range of −65 to 110 °C. The chemical shifts of the olefinic protons showed only a small movement (~0.15 ppm at most in the 90 °C interval from 25 to −65 °C). The methyl signals also showed no significant change in their chemical shifts. However, at 110 °C the signals due to the 5- and 10-methyl groups showed slight broadening as compared with those due to the 7′- and 12′-methyl groups,



suggesting the occurrence of internal rotation about the pinch bond. The energy barrier to rotation was estimated to be far higher than 19 kcal mol^{-1}.*

^{13}C NMR Spectrum of Compound **5**.—The ^{13}C NMR spectrum of compound **5** showed four peaks due to methyl carbons, eight peaks for the acetylenic carbons, and twenty peaks for the olefinic carbons, fourteen tertiary and six quaternary carbons, completely consistent with the structure **5**. The pinch-bond carbons resonate at δ 136.6 and 141.6. The difference of 5.0 ppm is rather small, even smaller than that of 7.9 ppm in sesquifulvalene **6**.[17] This also suggests quite a small contribution of the dipolar structure **5a**.

The Electronic Spectrum of Compound **5**.—The electronic absorption spectrum of compound **5** is illustrated in Fig. 2, together with those of the related fulvalenes **16** and **17**. The



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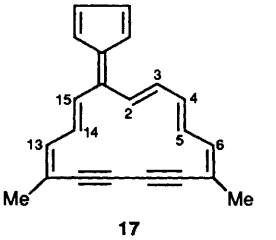
(≡ **3**; $m = n = 1$)



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(≡ **2**; $m = 1, n = 2$)

* 1 cal = 4.185 J.

Table 1 Chemical shifts of olefinic and methyl protons of large-membered rings of heptatridecafulvalene **16**, pentapentadecafulvalene **17** and tridecapentadecafulvalene **5** in $CDCl_3$ (δ-values; $SiMe_4$ internal standard)

Compound	Outer protons	Me	Inner protons
13-membered ring of **16**	6.49 (2-H), 6.79 (4-H)	1.92	6.63 (3-H)
15-membered[a] ring of **17**	6.65 (3-H), 6.51 (4-H), 6.88 (6-H), 7.00 (13-H), 7.13 (15-H)	1.93, 1.97	6.83 (2-H), 6.96 (5-H), 6.82 (14-H)
13-membered ring of **5**	6.45 (2-H), 6.70 (4-H), 6.77 (11-H), 6.50 (13-H)	1.93, 1.91	6.97 (3-H), 7.02 (12-H)
15-membered ring of **5**	6.23 (3'-H), 6.43 (4'-H), 6.63 (6'-H), 6.67 (13'-H), 7.01 (15'-H)	1.92, 1.90	7.22 (2'-H), 7.36 (5'-H), 7.34 (14'-H)

[a] To fit the conformation of the 15-membered ring of compound **17** with that of bicycle **5**, the ^1H NMR data at −60 °C are given.[3f]

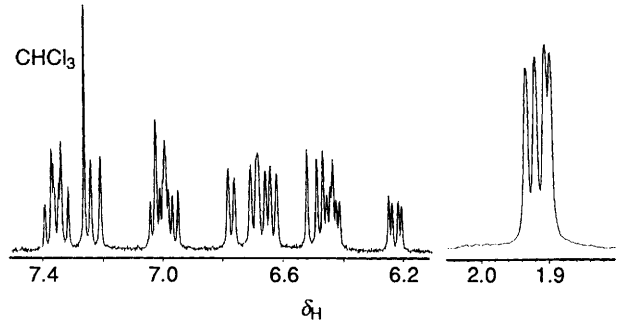

Fig. 1 500 MHz ^1H NMR spectrum of compound **5** (in $CDCl_3$) at room temperature

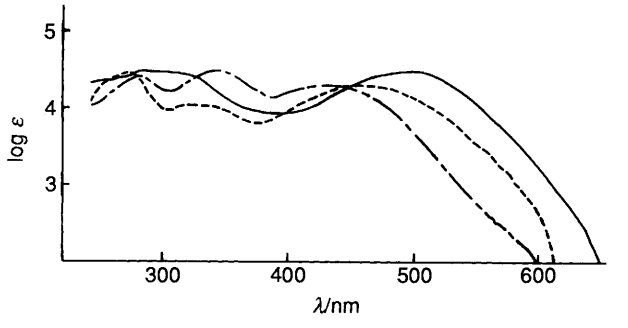

Fig. 2 Electronic absorption spectra of heptatridecafulvalene **16** (- - - -) in EtOH, pentapentadecafulvalene **17** in THF (—·—·—) and tridecapentadecafulvalene **5** (——) in THF

shapes of these absorption curves are quite similar. In the electronic spectrum of compound **5**, the main maximum occurred at 498 nm, the expansion of the 7-membered ring in compound **16**[3d] to a 15-membered ring in compound **5** and that of the 5-membered ring in compound **17**[3f] to a 13-membered ring in compound **5** resulting in a bathochromic shift of 66 nm and 46 nm, respectively, reflecting the degree of extended conjugation of the π-electron system in compound **5**.

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a Hitachi 260–50 or JASCO FT/IR-8000 spectrophotometer as KBr discs unless otherwise stated and were calibrated against polystyrene; only significant maxima are described. Electronic spectra were measured in THF solutions and run with a Hitachi 220A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. ^1H NMR spectra at ambient temperature were recorded as $CDCl_3$ solutions with a JEOL GX-270 or a Bruker AM-500 spectrometer at 270.16 or 500.14 MHz, respectively, $SiMe_4$ being used as an internal standard. *J*-Values are given in Hz. Variable-temperature ^1H NMR measurements were made on the AM-500 in [$^2H_8$]toluene and the temperatures were calibrated with an ethylene glycol sample. ^{13}C NMR spectra were recorded for $CDCl_3$ solutions with a Bruker AM-500 spectrometer at 125.76 MHz, $SiMe_4$ being used as an internal standard (p, primary; t, tertiary; q, quaternary).

Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether. Merck alumina (activity II–III) and Merck silica gel 60 were used for column chromatogaphy. Compounds were pre-adsorbed from hexane, ether, or benzene solution onto the adsorbent before column chromatography. Progress of all reactions was followed by TLC on Merck precoated silica gel. Preparative TLC (PLC) was carried out on 20 × 20 cm, silica gel plates (Merck, 0.5 or 2 mm thick).

The Isomeric 2-(5,10-*Dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidene*)-6-*methylocta*-3,5-*dien*-7-*ynenitrile* **11a** *and* **11b**.—To a stirred suspension of the salt **10**[15] (830 mg, 1.97 mmol) in dry THF (25 cm^3) at −10 °C was added dropwise a solution of butyllithium (1.6 mol dm^{-3}; 1.25 cm^3, 1.96 mmol) in hexane by a syringe during 20 min under argon. After the mixture had been stirred for 15 min at −10 °C, a solution of the cyano(formyl)fulvene **9**[14] (300 mg, 1.16 mmol) in THF (45 cm^3) was added dropwise during 30 min below −10 °C and the solution was stirred for a further 1 h at the same temperature. After addition of ethyl acetate (5 cm^3), the mixture was poured into water (300 cm^3)–benzene (150 cm^3), and the aqueous layer was extracted with benzene. The combined organic layers were washed with brine, filtered through Celite, and dried. The product obtained after removal of solvent was chromatographed on alumina (3.5 × 10.0 cm). The initial fractions eluted with hexane–benzene (2:1) afforded the *Z-isomer* **11a** (141 mg, 38%) as red needles, m.p. 77–78 °C (decomp.) (from hexane–benzene); *m/z* 321 (M^+, 78%) and 290 (100) (Found: M, 321.4); λ_{max}/nm 220 (ε/dm^3 mol^{-1} cm^{-1} 20 700), 263sh (19 500), 273 (20 500), 325 (17 400), 427 (29 800) and 448sh (27 200); ν_{max}/cm^{-1} 3300 (C≡CH), 2220 (C≡N), 2150 (C≡C), 980 (*E*-HC=CH) and 690 (*Z*-HC=CH); δ_H(270 MHz) 8.46 (1 H, dd, *J* 16 and 10, 12-H), 8.14 (1 H, dd, *J* 16 and 9, 3-H), 7.24 (1 H, d, *J* 12, 15-H), 6.75 (1 H, t, *J* 12, 16-H), 6.63 (1 H, d, *J* 16, 13-H), 6.56 (1 H, d, *J* 10, 11-H), 6.41 (1 H, d, *J* 9, 4-H), 6.29 (1 H, d, *J* 16, 2-H), 6.20 (1 H, d, *J* 12, 17-H), 3.43 (1 H, s, C≡CH), 2.03 (3 H, s, Me) and 1.82 (6 H, br s, Me) (Found: C, 89.55; H, 6.1; N, 4.4. $C_{24}H_{19}N$ requires C, 89.7; H, 6.0; N, 4.4%).

The following fractions eluted with hexane–benzene (2:1) afforded the E-*isomer* **11b** (86 mg, 23%) as dark red needles, m.p. 75–76 °C (decomp.) (from hexane–benzene); *m/z* 321 (M^+, 14%) and 295 (100) (Found: M, 321.4); λ_{max}/nm 221 (ε/dm^3 mol^{-1} cm^{-1} 26 300), 272 (23 300), 327 (24 100), 431 (43 600) and 449sh (42 300); ν_{max}/cm^{-1} 3300 (C≡CH), 2220 (C≡N), 2150 (C≡C) and 970 (*E*-HC=CH); δ_H(270 MHz) 8.33 (1 H, dd, *J* 16 and 10, 12-H), 8.06 (1 H, dd, *J* 16 and 10, 3-H), 7.22 (1 H, d, *J* 16, 15-H), 6.67 (1 H, d, *J* 16, 13-H), 6.67 (1 H, dd, *J* 16 and 8, 16-H), 6.59 (1 H, d, *J* 10, 11-H), 6.48 (1 H, d, *J* 10, 4-H), 6.44 (1 H, d, *J* 8, 17-H), 6.38 (1 H, d, *J* 16, 2-H), 3.47 (1 H, s, C≡CH), 2.01 (3 H, s, Me) and 1.84 (6 H, br s, Me) (Found: C, 89.5; H, 5.7; N, 4.7%).

(Z,Z)-2-(5,10-*Dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidene*)-6-*methylocta*-3,5-*dien*-7-*ynal* **12a**.—To a stirred solution of the *Z*-isomer **11a** (83 mg, 0.26 mmol) in dry toluene (45 cm^3) at −10 °C was added a solution of DIBAH (1.02 mol dm^{-3}; 1.4 cm^3, 1.43 mmol) in toluene by a syringe under argon during 20 min, and the solution was stirred for 40 min at the same temperature. Then 5% sulfuric acid (15 cm^3) was added dropwise to the mixture below 0 °C and the mixture was extracted with benzene. The combined extracts were washed with aq. sodium hydrogen carbonate and dried. The residual brown liquid obtained after removal of the solvent was chromatographed on silica gel (3.5 × 10.0 cm). The fractions eluted with benzene afforded the *Z-isomer* **12a** (25 mg, 30%) as red needles, m.p. 89–90 °C (decomp.) (from hexane–benzene); *m/z* 324 (M^+, 5%) and 57 (100) (Found: M, 324.4); λ_{max}/nm 275 (ε/dm^3 mol^{-1} cm^{-1} 30 400) and 416 (13 900); ν_{max}/cm^{-1} 3237 (C≡CH), 2917, 2867 (CHO), 2161 (C≡C), 1649 (C=O), 976 (*E*-HC=CH) and 677 (*Z*-HC=CH); δ_H(270 MHz) 10.10 (1 H, s, CHO), 8.09 (1 H, dd, *J* 16 and 10, 12-H), 7.21 (1 H, dd, *J* 16 and 7, 3-H), 6.88 (1 H, t, *J* 12, 16-H), 6.77 (1 H, d, *J* 16, 13-H), 6.58 (1 H, d, *J* 10, 11-H), 6.45 (1 H, d, *J* 7, 4-H), 6.24 (1 H, d, *J* 16, 2-H), 6.22 (1 H, d, *J* 12, 15-H), 6.04 (1 H, d, *J* 12, 17-H), 3.37 (1 H, s, C≡H), 1.90 (6 H, br s, Me) and 1.84 (3 H, s, Me) (Found: C, 88.65; H, 6.3. $C_{24}H_{20}O$ requires C, 88.85; H, 6.2%).

(3E,5Z)-2-(5,10-*Dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidene*)-6-*methylocta*-3,5-*dien*-7-*ynal* **12b**.—To a stirred solution of the *E*-isomer **11b** (25 mg, 0.078 mmol) in dry toluene (40 cm^3) at −7 °C was added a solution of DIBAH (1.50 mol dm^{-3}; 0.2 cm^3, 0.30 mmol) in toluene by a syringe under argon during 15 min, and the solution was stirred for 1 h at the same temperature. Then 5% sulfuric acid (5 cm^3) was added to the mixture below 0 °C and the mixture was worked up as for the isolation of compound **12a**. The product was chromatographed on silica gel (3.5 × 7 cm). The fractions eluted with benzene afforded the E-*isomer* **12b** (8.0 mg, 32%) as a semi-solid. It formed brown needles, m.p. 115–117 °C (decomp.) (from hexane–benzene); *m/z* 324 (M^+, 2%) and 149 (100) (Found: M, 324.4); λ_{max}/nm 279 (ε/dm^3 mol^{-1} cm^{-1} 22 300), 321sh (15 700) and 446 (13 500); ν_{max}/cm^{-1} 3297 (C≡CH), 2922, 2854 (CHO), 2162 (C≡C), 1662 (C=O) and 967 (*E*-HC=CH); δ_H(270 MHz) 10.14 (1 H, s, CHO), 7.88 (1 H, dd, *J* 16 and 10, 12-H), 7.10 (1 H, dd, *J* 16 and 10, 3-H), 7.07 (1 H, dd, *J* 16 and 8, 16-H), 6.68 (1 H, d, *J* 16, 13-H), 6.66 (1 H, d, *J* 10, 11-H), 6.59 (1 H, d, *J* 16, 2-H), 6.52 (1 H, d, *J* 16, 15-H), 6.46 (1 H, d, *J* 10, 4-H), 6.45 (1 H, d, *J* 8, 17-H), 3.34 (1 H, s, C≡CH), 2.00 (3 H, s, Me), 1.90 (3 H, s, Me) and 1.87 (3 H, s, Me) (Found: C, 88.85; H, 6.25%).

The reaction of a 3:1 mixture of the isomers (*Z*)-**11a** and (*E*)-**11b** with DIBAH afforded a mixture of aldehydes (*Z*)-**12a** and (*E*)-**12b** with the same 3:1 ratio under the same conditions as for the preparation of compounds **12a** and **12b** from substrates **11a** and **11b**, respectively.

Isomeric 4-(5,10-*Dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidene*)-8-*methyldeca*-2,5,7-*trien*-9-*ynals* **14a** *and* **14b**.—Lithium methoxide solution prepared from lithium (85 mg, 12.0 mmol) in dry methanol (50 cm^3) was added dropwise during 4 h under argon to a stirred solution of a mixture of ethynyl(formyl)fulvenes **12a** and **12b** (55:45) (150 mg, 0.47 mmol) and the salt **13**[16] (2.00 g, 4.64 mmol) in DMF (27 cm^3) at room temperature. After being stirred for a further 1 h at room temperature, the solution was poured into water and extracted with benzene (80 cm^3 × 3). The extracts were washed with brine and dried. After removal of solvent, the residue was dissolved in ethanol (10 cm^3)–THF (8 cm^3), and admixed with 0.5 mol dm^{-3} hydrochloric acid (20 cm^3), and the mixture was stirred for 1 h at room temperature. Then the mixture was separated and the aqueous layer was extracted with dichloromethane (50 cm^3 × 3). The combined organic layers were washed with aq. sodium hydrogen carbonate and dried. The residue obtained after removal of solvent was chromatographed on silica gel (3.5 × 10.0 cm). The fractions eluted with hexane–benzene (1:1) afforded a stereoisomeric mixture of the *homologated aldehyde* **14** (48 mg, 30%) as a semi-solid. Recrystallization of the solid from hexane–benzene gave brown needles; *m/z* 350 (M^+, 8%) and 110 (100) (Found: M, 350.1) (Found: C, 88.9; H, 6.55. $C_{26}H_{22}O$ requires C, 89.1; H, 6.3%). The solid was purified by PLC (benzene as developer, 3 times).

The fast moving, second band gave the isomer **14a** as red-brown needles, m.p. 80–82 °C (decomp.) (from hexane–benzene); λ_{max}/nm 260 (ε/dm^3 mol^{-1} cm^{-1} 26 600), 327 (24 600), 432 (26 500) and 458sh (24 700); ν_{max}(CH_2Cl_2)/cm^{-1} 3300 (C≡CH), 2925, 2858 (CHO), 2155 (C≡C), 1681 (C=O) and 1607 (C=C); δ_H(270 MHz) 9.44 (1 H, d, *J* 8, CHO), 7.46–7.16 (3 H, m, 3-, 12- and 18-H), 6.99 (1 H, d, *J* 15, 13-H), 6.74 (1 H, dd, *J* 16 and 11, 16-H), 6.63 (1 H, d, *J* 9, 11-H), 6.57 (1 H, d, *J* 9, 4-H), 6.55 (1 H, d, *J* 16, 2-H), 6.46 (1 H, d, *J* 11, 17-H), 6.33 (1 H, dd, *J* 12 and 8, 19-H), 6.29 (1 H, d, *J* 16, 15-H), 3.38 (1 H, s, C≡CH), 2.00 (3 H, s, Me), 1.91 (3 H, s, Me) and 1.85 (3 H, s, Me).

The fast moving, third band gave the isomer **14b** as dark brown needles, m.p. 120 °C (decomp.) (from hexane–benzene); λ_{max}/nm 270 (ε/dm^3 mol^{-1} cm^{-1} 26 100), 318 (21 400), 418 (18 800) and 430sh (18 500); ν_{max}/cm^{-1} 3274 (C≡CH), 2917, 2853 (CHO), 2156 (C≡C), 1669 (C=O), 972 (*E*-HC=CH) and 705 (*Z*-HC=CH); δ_H(270 MHz) 9.67 (1 H, d, *J* 8, CHO), 7.87 (1 H, dd, *J* 16 and 10, 12-H), 7.78 (1 H, d, *J* 15, 18-H), 7.48 (1 H, dd, *J* 16 and 9, 3-H), 6.88 (1 H, t, *J* 12, 16-H), 6.58 (1 H, d, *J* 16, 13-H), 6.57 (1 H, d, *J* 9, 11-H), 6.56 (1 H, d, *J* 9, 4-H), 6.31 (1 H, d, *J* 16, 2-H), 6.23 (1 H, dd, *J* 15 and 8, 19-H), 6.10 (1 H, d, *J* 12, 15-H), 6.04 (1 H, d, *J* 12, 17-H), 3.36 (1 H, s, C≡CH), 1.90 (3 H, s, Me), 1.88 (3 H, s, Me) and 1.84 (3 H, s, Me).

Isomeric 9-(5,10-*Dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidene*)-3,13-*dimethylpentadeca*-3,5,7,10,12-*pentaene*-1,14-*diynes* **15**.—To a stirred suspension of the salt **10**[15] (1.00 g, 2.38 mmol) in dry THF (40 cm^3) at room temperature was added dropwise a solution of BuLi (1.6 mol dm^{-3}; 1.5 cm^3, 2.40 mmol) in hexane by a syringe during 20 min under argon. After the mixture had been stirred for 15 min at the same temperature, a solution of a stereoisomeric mixture of the fulvene **14** (30 mg, 0.086 mmol) in dry THF (20 cm^3) was added dropwise during 1 h at room temperature, and the solution was stirred for a further 1 h at the same temperature. After addition of ethyl acetate (10 cm^3), the mixture was worked up as for the isolation of nitriles **11**. The residue obtained after removal of the solvent was chromatographed on silica gel (3.5 × 6.0 cm). The fractions eluted with hexane–benzene (3:2) afforded the desired acyclic diacetylene **15** and its stereoisomers (13 mg, 37%) each as brown semi-solid; no satisfactory mass spectra could be obtained by either direct-inlet or chemical ionization methods; λ_{max}(nm) (qualitative) 264 (relative extinction coefficients, 1.00), 272 (0.95), 349 (0.66), 456 (0.70) and 477sh (0.66); ν_{max}/cm^{-1} 3305 (C≡CH), 2150 (C≡C), 996 (*E*-HC=CH) and 698 (*Z*-HC=CH); δ_H(270 MHz) 7.71–6.20 (14 H, m, olefinic H), 3.36–3.30 (2 H, m, C≡CH) and 2.01–1.86 (12 H, m, Me).

15-(5,10-*Dimethylcyclotrideca*-2,4,10,12-*tetraene*-6,8-*diynylidene*)-6,11-*dimethylcyclopentadeca*-1,3,5,11,13-*pentaene*-7,9-*diyne* **5**.—A solution of a stereoisomeric mixture of acyclic diacetylene **15** (50 mg, 0.12 mmol) in a mixture of pyridine (30 cm^3), ether (10 cm^3) and methanol (5 cm^3) was added dropwise during 5 h to a stirred solution of anhydrous copper(II) acetate (2.0 g) in a mixture of pyridine (125 cm^3), ether (65 cm^3) and methanol (35 cm^3) at 60 °C, and the mixture was stirred for a further 1 h before being poured into water and extracted with benzene. The extracts were washed successively with 5% HCl

until they turned acidic (to litmus) and then with aq. sodium hydrogen carbonate, then dried and concentrated. The residue was chromatographed on silica gel (3.2 × 10.0 cm). The fractions eluted with hexane–benzene (4:1) afforded the *tridecapentadecafulvalene* **5** (11 mg, 22%) as a solid. It formed black-purple needles, m.p. 160 °C (decomp.) (from hexane–benzene); *m/z* 410 (M^+, 18%) and 57 (100) (Found: M, 410.5); λ_{max}/nm 269sh (ε/dm^3 mol^{-1} cm^{-1} 24 800), 283 (29 300), 295 (29 100), 322sh (27 600), 473sh (28 000) and 498 (31 300); ν_{max}/cm^{-1} 2149 (C≡C), 972 and 959 (*E*-HC=CH); δ_H(500 MHz) 7.36 (1 H, dd, *J* 15.4 and 10.6, 5′-H), 7.34 (1 H, dd, *J* 15.4 and 11.3, 14′-H), 7.22 (1 H, d, *J* 16.2, 2′-H), 7.02 (1 H, dd, *J* 16.2 and 10.4, 12-H), 7.01 (1 H, d, *J* 15.4, 15′-H), 6.97 (1 H, dd, *J* 16.3 and 9.5, 3-H), 6.77 (1 H, d, *J* 10.4, 11-H), 6.70 (1 H, d, *J* 9.5, 4-H), 6.67 (1 H, d, *J* 11.3, 13′-H), 6.63 (1 H, d, *J* 10.6, 6′-H), 6.50 (1 H, d, *J* 16.2, 13-H), 6.45 (1 H, d, *J* 16.3, 2-H), 6.43 (1 H, dd, *J* 15.4 and 5.8, 4′-H), 6.23 (1 H, dd, *J* 16.2 and 5.8, 3′-H), 1.93 (3 H, s, 5-Me), 1.92 (3 H, s, 12′-Me), 1.91 (3 H, s, 10-Me) and 1.90 (3 H, s, 7′-Me); δ_C(125 MHz) 19.7 (p), 20.3 (p), 20.5 (p), 20.9 (p), 83.0 (q), 83.3 (q), 84.6 (q), 86.3 (q), 90.1 (q), 91.3 (q), 100.4 (q), 101.1 (q), 119.8 (q), 120.4 (q), 121.7 (q), 121.7 (q), 124.6 (t), 127.7 (t), 131.8 (t), 131.8 (t), 132.1 (t), 132.5 (t), 132.7 (t), 133.4 (t), 133.5 (t), 136.6 (q, C-1 or -1′), 138.9 (t), 141.0 (t), 141.6 (t), 141.6 (q, C-1′ or -1), 142.2 (t) and 142.8 (t) (Found: C, 93.4; H, 6.2. $C_{32}H_{26}$ requires C, 93.6; H, 6.4%).

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