Synthesis, structure and tropicity of an [11][13]fulvalene derivative

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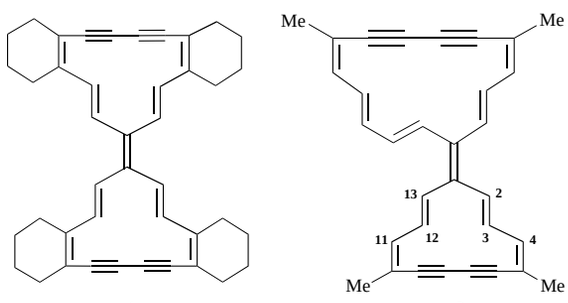
An [11][13]fulvalene derivative, 13-(4,9-methanocycloundeca-2,4,6,8,10-pentaenylidene)-4,9-dimethylcyclotrideca-1,3,9,11-tetraene-5,7-diyne, has been synthesized. Examination of ^{1}H and ^{13}C NMR spectra indicates that the compound shows no detectable ring-current effect in nonpolar solvents arising from 10π- and 14π-electron systems, which is verified by X-ray crystallographic structural analysis. In a polar solvent, [$^2H_6$]dimethyl sulfoxide, a small contribution of the dipolar resonance structure is suggested.

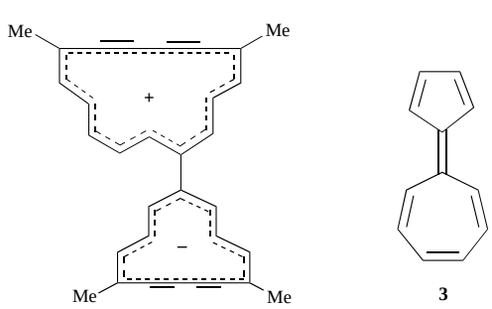
Introduction

An extension of our interests in ring-expanded fulvalenes led us to the preparation of fulvalene derivatives composed of two large-membered rings.[1] The only known macrocyclic compound of this type was a tetra(cyclohexane)-annulated [13][13]-fulvalene derivative **1**,[2] which was prepared by Howes and Sondheimer in 1978 and was found to be thermally unstable and completely atropic. The fact that compound **1** carries two rings of the same size can be associated with the absence of any cross-conjugation of π-electrons or any contribution from a dipolar resonance structure. Then we considered that the [13][15]fulvalene **2**,[3] in which one ring is 13-membered and the other is 15-membered, is potentially aromatic as is sesquifulvalene **3**,[4] since polarization of the pinch bond would make both rings 14π-electron aromatic systems, as shown in a dipolar structure **2a**. However, although compound **2** was isolated as thermally, relatively stable crystals, unlike compound **1**, the compound shows no ring-current effect, but instead a polyolefinic character, indicating the absence of any contribution from a dipolar structure.

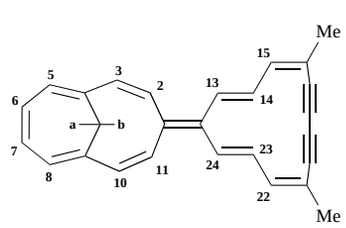
It is recognized[5] that tropicity of annulenes usually increases with a decrease in the ring size. We considered that the replacement of one ring in compound **2** by a smaller ring with larger tropicity would facilitate polarization of the pinch bond. Thus we chose a fulvalene derivative **4** with 11- and 13-membered rings. Polarization of the pinch bond of compound **4** would afford a 10π/14π aromatic system. Another expectation was that the compound would give thermally stable crystals that would be suitable for X-ray crystallographic study.



1 **2**



2a **3**



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Results and discussion

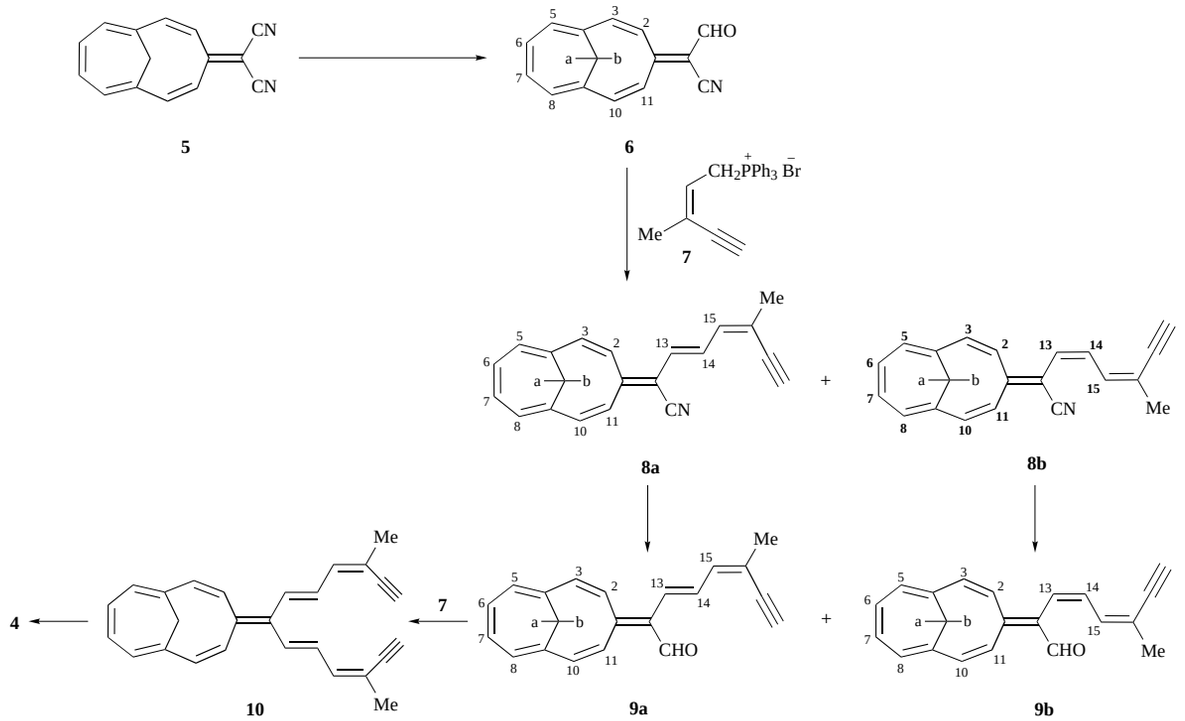
Synthesis

A successful preparation of compound **2** stimulated us to elaborate an acyclic exocyclic moiety leading to a 13-membered conjugated system upon the methano-bridged 11-membered ring of compound **5**. Thus the synthesis of compound **4** was planned and performed according to the reaction sequence outlined in Scheme 1.

Reduction of the dicyanofulvene **5**[6] with diisobutylaluminium hydride (DIBAH) in toluene at −10 °C afforded the cyano(formyl)fulvene **6** in 40% yield. Treatment of 3-methylpent-2-en-4-ynyltriphenylphosphonium bromide **7**[7] in tetrahydrofuran (THF) with butyllithium led to the corresponding ylide, which was allowed to react with the cyano(formyl)fulvene **6** to afford a mixture of the *E*-isomer **8a** and the *Z*-isomer **8b** of the newly formed double bond in a ratio of 5:3, which were separately isolated by chromatography on silica gel.

Individual reduction of compounds **8a** and **8b** with DIBAH in toluene at −10 °C afforded the *E*-isomer **9a** (40%) and *Z*-isomer **9b** (30%) of the ethynyl(formyl)fulvene, respectively, retaining the stereochemistry of the substrates **8**. However, the *Z*-isomer **9b** proved to be less stable than the *E*-isomer **9a** and gradually isomerized to the *E*-isomer during chromatography.

The ylide derived from the salt **7** was treated with an isomeric mixture of compounds **9** to afford a stereoisomeric mixture of the acyclic diethynylfulvene **10** as a semi-solid in 37% yield, which was too unstable to give satisfactory spectral and analytical data. The structure of a desirable isomer of com-



Scheme 1

Table 1 ^{1}H NMR data of compound **4**[a]

Proton	in $CDCl_3$	in [$^2H_6$]DMSO	$\Delta\delta$[b]/ppm
CH_3	1.915s	1.907s	−0.01
CH_2 a	0.161d (11.1)	0.041d (10.8)	−0.12
b	3.266d (11.1)	3.082d (10.8)	−0.18
2	6.674d (11.8)	6.774d (11.8)	0.10
3	6.058d (11.8)	6.168d (11.8)	0.11
5	6.604m	6.730m	0.13
6	7.031m	7.072m	0.04
13	6.777d (15.9)	6.889d (16.3)	0.11
14	7.071dd (15.9, 10.4)	6.788dd (16.3, 9.7)	−0.28
15	6.757d (10.4)	6.998d (9.7)	0.24

[a] Chemical shifts are given in δ-values. Coupling constants (J/Hz) are given in parentheses. [b] Negative values mean upfield shifts upon going from $CDCl_3$ to [$^2H_6$]DMSO.

Table 2 ^{13}C NMR data of compound **4**[a]

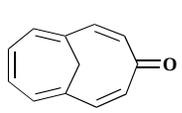
Carbon	in $CDCl_3$	in [$^2H_6$]DMSO	$\Delta\delta$[b]/ppm
CH_3	19.84	19.16	−0.7
CH_2	31.11	30.83	−0.3
1	142.23	143.52	1.3
2	130.84	131.04	0.2
3	118.51	118.21	−0.3
4	121.10	119.93	−1.2
5	124.53	124.56	0.0
6	130.04	130.10	0.1
12	134.15	132.93	−1.2
13	125.71	125.94	0.2
14	131.56	130.44	−1.1
15	142.19	142.86	0.7
16	120.35	119.25	−1.1
17	100.72	100.96	0.2
18	85.30	84.55	−0.8

[a] Chemical shifts are given in δ-values. [b] Negative values mean upfield shifts upon going from $CDCl_3$ to [$^2H_6$]DMSO.

pound **10** is shown in Scheme 1. An intramolecular oxidative coupling of compound **10** as a mixture with its stereoisomers using anhydrous copper(II) acetate in pyridine–diethyl ether at 50 °C under relatively dilute conditions afforded the desired [11][13]fulvalene, 13-(4,9-methanocycloundeca-2,4,6,8,-10-pentaenylidene)-4,9-dimethylcyclotrideca-1,3,9,11-tetraene-5,7-diyne **4**, in 25% yield as relatively stable black–purple needles.

NMR spectral studies

The ^{1}H NMR spectrum of compound **4** obtained in $CDCl_3$ was analysed with the aid of homonuclear double resonance and nuclear Overhauser effect (NOE) experiments, and the data are given in Table 1. The chemical shift data in $CDCl_3$ indicate that no appreciable ring-current effect is detected, judging from a comparison with the data for the precursors **8** and **9** and with those for the [13][15]fulvalene **2**[3] and 1,6-methano[11]annulen-9-one **11**,[8] both of which have been concluded to be atropic. Thus it should be concluded that compound **4** is atropic and the



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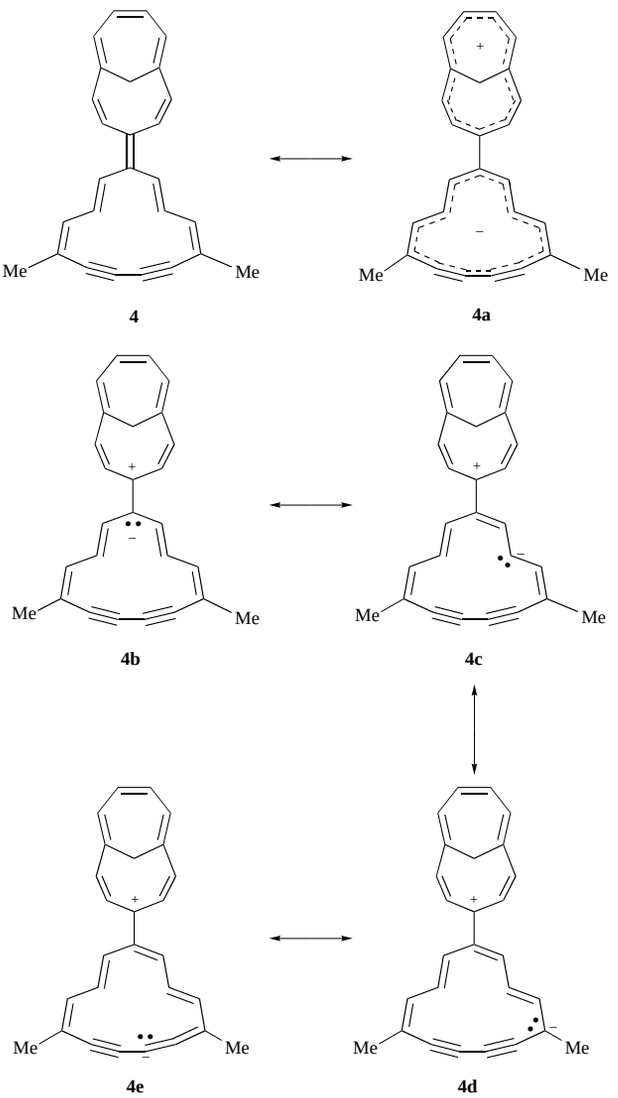
contribution of the dipolar resonance structure **4a** is negligibly small, if any.

The ^{13}C chemical shifts of compound **4** were also thoroughly assigned on the basis of the CH-chemical shift correlation spectroscopy (CH-COSY), ^{1}H-coupled and selectively ^{1}H-decoupled spectra and are compiled in Table 2. The chemical shift difference between the pinch bond carbons is 8.1 ppm in $CDCl_3$, a similar value to that in sesquifulvalene **3**[4] (7.9 ppm), but it would be dangerous to consider that the large chemical shift difference is an indication of the contribution of the dipolar structure.

The contribution of the dipolar structure **4a** was naturally expected to increase in more polar media, and thus the ^{1}H and ^{13}C NMR spectra were examined in [$^2H_6$]dimethyl sulfoxide ([$^2H_6$]DMSO), and the data are included in Tables 1 and 2. In the ^{1}H spectrum, the signals of the methylene protons shift upfield by ~0.15 ppm and those of the olefinic protons of the 11-membered ring shift downfield by ~0.1 ppm upon going from $CDCl_3$ to [$^2H_6$]DMSO. Similarly, the signal of the inner olefinic protons of the 13-membered ring moves upfield, and those of the outer olefinic protons downfield, though the methyl proton signal shows no significant shift. These shifts

clearly indicate the increase in diatropicity in a more polar solvent, although the extent is very small.

The solvent effect on the ^{13}C chemical shifts seems compatible with the increased contribution of the dipolar structure **4a** in [$^2H_6$]DMSO. The arithmetic average of the shifts upon the solvent change is −0.38 ppm for the 13-membered ring carbons and −0.10 ppm for the 11-membered ring carbons. The larger upfield shifts for the 13-membered ring carbons presumably reflect the increase in the negative charge in this ring due to the increased contribution of the dipolar structure. The C-4 signal moves upfield by 1.2 ppm, and we have no explanation for this. If it is assumed that the solvent shift reflects the change in the π-electron density at that carbon, the data suggest that the increase in the positive charge is almost localized at C-1 while the increase in the negative charge is delocalized at one-carbon intervals, *i.e.* at C-12, C-14, C-16 and C-18, as shown by the resonance structures **4b**–**4e**.



X-Ray crystallographic study

Single crystals of compound **4** suitable for X-ray crystallography were obtained by recrystallization from hexane–dichloromethane and one of them was submitted for the analysis. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are compiled in Table 3.

The geometry around the pinch bond (C-1–C-12) is almost planar, though C-1 is slightly pyramidalized, the angle sum being 358.5°. The 13-membered ring is slightly twisted from planarity while retaining the local C_2 symmetry. The 11-membered ring part is significantly folded. The interplanar

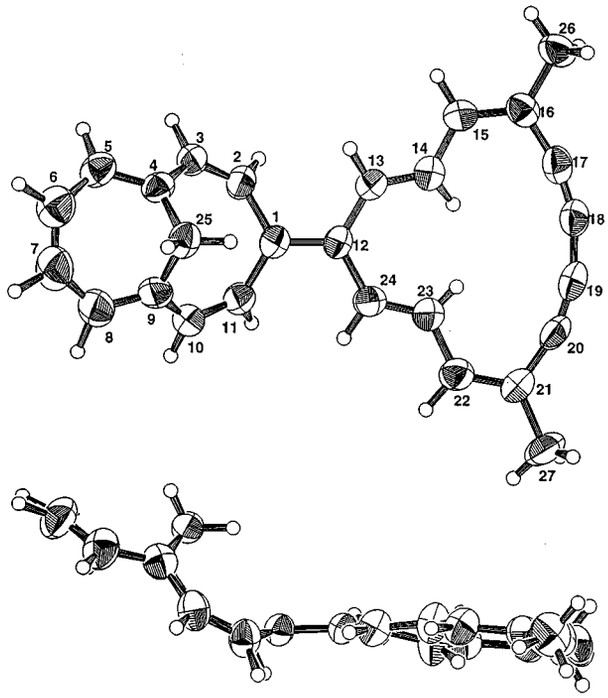


Fig. 1 Top and side views of the molecular structure of compound **4**, with crystallographic numbering scheme

angle between the C-1–C-2–C-11 and C-2–C-3–C-10–C11 planes is 41.5°. This large folding might be responsible for the localization of the positive charge in the resonance structures **4b**–**4e**.

The length of the pinch bond is 1.384 Å and thus is significantly longer than the usual C=C double bonds. The lengths of the formal double bonds other than the pinch bond range from 1.308 to 1.383 Å, while those of the sp^2–sp^2 single bonds range from 1.414 to 1.496 Å.

These structural features seem to be consistent with the polyolefinic nature of compound **4** as suggested by NMR spectroscopy mentioned above.

In conclusion, the [11][13]fulvalene **4** shows no detectable tropicity in a medium with low polarity such as $CDCl_3$ and behaves as a polyolefin, and the molecular structure obtained by X-ray crystallography is compatible with this feature. Meanwhile, in a polar medium, such as DMSO, the dipolar resonance structure **4a** is stabilized and contributes to some very small extent.

Experimental

Mps were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO-7300 spectrophotometer as KBr discs, unless otherwise specified; only significant maxima are described. Electronic (UV/visible) spectra were measured in THF solution with a Shimadzu 2200A 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 in $CDCl_3$, unless otherwise indicated, on a Bruker ARX-300 spectrometer at 300.13 MHz with internal $SiMe_4$ (TMS) as the reference. *J* Values are given in Hz. ^{13}C NMR spectra were recorded in $CDCl_3$ on the ARX-300 at 75.48 MHz with $CDCl_3$ at δ_C 77.0 as the reference. The letters p, s, t and q given with the ^{13}C NMR chemical shifts, refer to primary, secondary, tertiary and quaternary, respectively.

Progress of all reactions was followed by TLC on Merck precoated silica gel plates. Alumina (Merck, activity II–III) and silica gel (Daiso gel 1001 W or Daiso gel 1002 W) were used for column chromatography. Compounds were pre-adsorbed from

Table 3 Selected bond lengths (Å), bond angles (°) and torsional angles (°)

1–2	1.496(6)	2–1–11	117.9(4)	11–1–2–3	55.9
1–11	1.468(7)	2–1–12	119.4(4)	12–1–2–3	−137.9
1–12	1.384(6)	11–1–12	121.2(4)	2–1–11–10	−56.8
2–3	1.318(6)	1–2–3	132.1(5)	12–1–11–10	137.2
3–4	1.454(6)	2–3–4	127.1(5)	2–1–12–13	5.9
4–5	1.383(6)	3–4–5	122.0(5)	2–1–12–24	−173.6
4–25	1.482(6)	3–4–25	119.8(4)	11–1–12–13	171.7
5–6	1.412(8)	5–4–25	117.8(5)	11–1–12–24	−7.8
6–7	1.344(9)	4–5–6	123.7(6)	1–2–3–4	4.4
7–8	1.435(9)	5–6–7	126.4(6)	2–3–4–5	−160.6
8–9	1.363(7)	6–7–8	126.3(6)	2–3–4–25	11.8
9–10	1.436(8)	7–8–9	123.2(7)	3–4–5–6	156.7
9–25	1.505(8)	8–9–10	122.5(6)	25–4–5–6	−15.9
10–11	1.351(7)	8–9–25	118.3(6)	3–4–25–9	−93.7
12–13	1.464(7)	10–9–25	118.9(5)	5–4–25–9	79.0
12–24	1.454(7)	9–10–11	127.5(6)	4–5–6–7	−29.7
13–14	1.316(7)	1–11–10	132.2(6)	5–6–7–8	0.9
14–15	1.431(8)	1–12–13	119.7(5)	6–7–8–9	27.6
15–16	1.358(6)	1–12–24	118.6(5)	7–8–9–10	−156.2
16–17	1.419(7)	13–12–24	121.8(5)	7–8–9–25	17.5
16–26	1.510(7)	12–13–14	129.4(5)	8–9–10–11	160.9
17–18	1.210(7)	13–14–15	127.7(6)	25–9–10–11	−12.7
18–19	1.377(8)	14–15–16	123.4(6)	8–9–25–4	−80.2
19–20	1.197(8)	15–16–17	117.2(5)	10–9–25–4	93.7
20–21	1.423(8)	16–17–18	165.0(6)	9–10–11–1	−2.6
21–22	1.356(7)	17–18–19	160.7(5)	1–12–13–14	−161.1
21–27	1.498(7)	18–19–20	162.1(6)	24–12–13–14	18.4
22–23	1.445(7)	19–20–21	163.8(5)	1–12–24–23	−175.4
23–24	1.308(7)	20–21–22	115.3(5)	13–12–24–23	5.1
		21–22–23	125.6(5)	12–13–14–15	179.9
		22–23–24	127.5(6)	13–14–15–16	167.2
		12–24–23	130.8(6)	14–15–16–17	−1.8
				20–21–22–23	−2.0
				21–22–23–24	167.6
				22–23–24–12	−176.2

benzene solution onto the adsorbent before column chromatography. Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to the removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

12,12-Dicyano-4,9-methanoundecafulvene 5[6]

A stirred mixture of 1,6-methano[11]annulen-9-one **11**[8] (150 mg, 0.89 mmol) and malononitrile (117 mg, 1.78 mmol) in acetic anhydride (4 cm^3) was refluxed for 2.5 h. The solution was cooled to room temperature, poured onto water and extracted with dichloromethane. The combined extracts were washed with aq. $NaHCO_3$ and dried. The residue obtained after removal of solvent was chromatographed on silica gel (3.5 × 10 cm). The fractions eluted with benzene afforded the undecafulvene **5** (101 mg, 52%) as red needles, mp 248–250 °C (from hexane–dichloromethane) (lit.,[6] mp 250–252 °C).

12-Cyano-12-formyl-4,9-methanoundecafulvene 6

To a stirred solution of the dicyanofulvene **5** (100 mg, 0.453 mmol) in toluene (70 cm^3) at −8 °C was added dropwise a solution of DIBAH (1.5 mol dm^{-3}; 0.9 cm^3, 1.4 mmol) in toluene by a syringe under argon during 10 min, and the solution was then stirred for 1 h at the same temperature. Then 5% sulfuric acid (20 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. $NaHCO_3$ and dried. The residue obtained after removal of solvent was chromatographed on silica gel (3.2 × 10 cm). The initial fractions eluted with benzene–dichloromethane (1:1) afforded the unchanged dicyanofulvene **5** (3 mg recovery). The following fractions eluted with benzene–dichloromethane (1:4) afforded the *cyano(formyl)fulvene* **6** (40 mg, 40%) as dark red needles, mp 213–214 °C (from hexane–dichloromethane); *m/z* 221 (M^+, 100%) ($C_{15}H_{11}NO$ requires *M*, 221.2); ν_{max}/cm^{-1} 2923, 2884 (CHO), 2209 (C≡N), 1655 (C=O) and 1582 (C=C); λ_{max}/nm 239 (ε/dm^3 mol^{-1} cm^{-1} 18 900), 330 (17 000) and 451 (12 600); δ_H 9.977 (1 H, s, CHO), 7.390 (2 H, m, 6- and 7-H), 7.276 (1 H, d, *J* 12, 10-H), 7.234 (1 H, d, *J* 12, 3-H), 7.001 (2 H, m, 5- and 8-H), 6.873 (1 H, d, *J* 12, 2-H), 6.582 (1 H, d, *J* 12, 11-H), 2.167 (1 H, dt, *J* 11.3 and 1.5, H^b) and 0.173 (1 H, d, *J* 11.3, H^a); δ_C 185.46 (CHO), 161.95 (q), 139.29 (t), 139.27 (t), 132.67 (t), 132.62 (t), 127.76 (t), 127.62 (t), 122.95 (q), 122.45 (q), 116.70 (t), 115.86 (q), 114.98 (t), 111.99 (q) and 33.87 (s) (Found: C, 81.3; H, 5.2; N, 6.3. $C_{15}H_{11}NO$ requires C, 81.4; H, 5.0; N, 6.3%).

Isomeric 2-(4,9-methanocycloundeca-2,4,6,8,10-pentaenylidene)-6-methylocta-3,5-dien-7-ynenitriles 8a and 8b

To a stirred suspension of 3-methylpent-2-en-4-ynyltriphenylphosphonium bromide **7**[7] (1.58 g, 3.75 mmol) in dry THF (45 cm^3) at −40 °C was added dropwise a solution of butyllithium (1.6 mol dm^{-3}; 2.34 cm^3, 3.75 mmol) in hexane by a syringe during 20 min under argon. After the mixture had been stirred for 1 h at −40 °C, a solution of the cyano(formyl)fulvene **6** (166 mg, 0.750 mmol) in THF (30 cm^3) was added dropwise during 1.5 h below −30 °C and the solution was stirred for further 2 h at −15 °C. After addition of ethyl acetate (14 cm^3), the mixture was poured into ice–water and extracted with benzene. The combined organic layers were washed with brine and dried. The product obtained after removal of solvent was chromatographed on silica gel (3.2 × 12 cm). The initial fractions eluted with hexane–ether (9:1) afforded the *Z-isomer* **8b** (53 mg, 25%) as dark red needles, mp 137–140 °C (decomp.) (from hexane–dichloromethane); *m/z* 283 (M^+, 100%) ($C_{21}H_{17}N$ requires *M*, 283.3); ν_{max}/cm^{-1} 3290 (C≡CH), 2203 (C≡N), 2083 (C≡C), 1600 (C=C) and 768 [(*Z*)-HC=CH]; λ_{max}/nm 239 (ε 32 100), 285 (13 300), 343 (31 600) and 427 (29 000); δ_H 7.416 (1 H, d, *J* 12.2, 15-H), 7.17–7.07 (2 H, m, 6- and 7-H), 6.879 (1 H, d, *J* 11.9, 3-H), 6.809 (1 H, d, *J* 11.8, 10-H), 6.751 (1 H, t, *J* 12, 14-H), 6.70–6.62 (2 H, m, 5- and 8-H), 6.242 (1 H, d, *J* 12, 2-H), 6.164 (1 H, d, *J* 11.8, 13-H), 5.817 (1 H, d, *J* 11.9, 11-H), 3.422 (1 H, s, C≡CH), 2.923 (1 H, dt, *J* 11.3 and 1.3, H^b), 2.046 (3 H, s, Me)

and 0.371 (1 H, d, *J* 11.3, H^a); δ_C 134.71 (t), 134.62 (t), 132.42 (t), 131.38 (t), 131.01 (t), 129.76 (t), 125.64 (t), 125.32 (t), 123.38 (q), 121.67 (q), 121.55 (q), 120.11 (t), 118.58 (q), 118.54 (t), 116.46 (t), 110.67 (q, C≡N), 85.17 (t, C≡CH), 82.59 (q, –C≡), 32.54 (s) and 23.68 (p) (Found: C, 88.9; H, 6.2; N, 5.0. $C_{21}H_{17}N$ requires C, 89.0; H, 6.05; N, 4.9%).

The following fractions eluted with hexane–ether (9:1) afforded the E-*isomer* **8a** (32 mg, 15%) as dark red needles, mp 163–164 °C (decomp.) (from hexane–dichloromethane); *m*/*z* 283 (M^+, 100%); ν_{max}/cm^{-1} 3287 (C≡CH), 2214 (C≡N), 2080 (C≡C), 1603 (C=C) and 960 [(*E*)-HC=CH]; λ_{max}/nm 234 (ε 32 900), 283 (12 300), 345 (36 100) and 429 (38 200); δ_H 7.209 (1 H, dd, *J* 15.2 and 11.2, 14-H), 7.13–7.04 (2 H, m, 6- and 7-H), 6.823 (1 H, d, *J* 11.7, 3-H), 6.783 (1 H, d, *J* 11.7, 10-H), 6.676 (1 H, d, *J* 15.2, 13-H), 6.65–6.63 (2 H, m, 5- and 8-H), 6.443 (1 H, d, *J* 11.2, 15-H), 6.231 (1 H, d, *J* 11.9, 2-H), 5.881 (1 H, d, *J* 11.9, 11-H), 3.436 (1 H, s, C≡CH), 3.054 (1 H, dt, *J* 11.3 and 1.3, H^b), 2.006 (3 H, s, Me) and 0.441 (1 H, d, *J* 11.3, H^a); δ_C 136.73 (t), 134.71 (t), 134.29 (t), 131.40 (t), 131.29 (t), 131.0 (t), 125.50 (t), 125.19 (t), 124.84 (t), 121.88 (q), 121.74 (q), 121.59 (q), 119.14 (t), 116.35 (q), 116.14 (t), 114.66 (q, C≡N), 84.98 (t, C≡CH), 82.55 (q, −C≡), 32.56 (s) and 23.48 (p) (Found: C, 89.3; H, 6.05; N, 4.8%).

(3*Z*,5*Z*)-2-(4,9-Methanocycloundeca-2,4,6,8,10-pentaenylidene)-6-methylocta-3,5-dien-7-ynal 9b

To a stirred solution of the *Z*-isomer **8b** of the cyanofulvene (104 mg, 0.367 mmol) in dry toluene (56 cm^3) at −10 °C was added dropwise a solution of DIBAH (1.5 mol dm^{-3}; 1.2 cm^3, 1.84 mmol) in toluene during 15 min by a syringe under argon, and the solution was then stirred for 30 min at the same temperature. Then 5% sulfuric acid (13 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. $NaHCO_3$ and dried. The product obtained after removal of solvent was chromatographed on silica gel (3.5 × 10 cm). The fractions eluted with benzene afforded the *Z*-*isomer* **9b** of the formylfulvene (32 mg, 30%) as orange needles, mp 94–96 °C (from hexane–benzene); *m*/*z* 286 (M^+, 100%) ($C_{21}H_{18}O$ requires *M*, 286.3); ν_{max}/cm^{-1} 3295 (C≡CH), 2923, 2852 (CHO), 2092 (C≡C), 1659 (C=O), 1596 (C=C) and 741 [(*Z*)-HC=CH]; λ_{max}/nm 246 (ε 11 500), 332 (7200) and 421 (4900); δ_H 10.231 (1 H, s, CHO), 7.18–7.10 (2 H, m, 6- and 7-H), 6.877 (1 H, d, *J* 12, 10-H), 6.842 (1 H, t, *J* 11.4, 14-H), 6.761 (1 H, d, *J* 11.9, 3-H), 6.732 (1 H, m, 8-H), 6.694 (1 H, m, 5-H), 6.455 (1 H, dd, *J* 11.9 and 1.7, 11-H), 6.225 (1 H, d, *J* 11.3, 15-H), 6.067 (1 H, d, *J* 11.4, 13-H), 5.822 (1 H, dd, *J* 11.8 and 1.4, 2-H), 3.353 (1 H, s, C≡CH), 3.004 (1 H, dt, *J* 11.2 and 1.3, H^b), 1.895 (3 H, s, Me) and 0.265 (1 H, d, *J* 11.1, H^a); δ_C 191.84 (t, CHO), 151.18 (q), 134.81 (t), 134.17 (q), 133.84 (t), 132.54 (t), 131.35 (t), 130.86 (t), 130.86 (t), 125.45 (t), 125.42 (t), 123.99 (t), 121.05 (q), 120.98 (q), 120.77 (q), 117.52 (t), 115.26 (t), 83.93 (t, C≡CH), 82.71 (q, −C≡), 32.15 (s) and 23.39 (p) (Found: C, 88.0; H, 6.5. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%).

(3*E*,5*Z*)-2-(4,9-Methanocycloundeca-2,4,6,8,10-pentaenylidene)-6-methylocta-3,5-dien-7-ynal 9a

The conversion of the cyanofulvene **8a** into the formylfulvene **9a** was carried out in the exactly same manner as that of **8b** into **9b**, using substrate **8a** (47 mg, 0.17 mmol) in dry toluene (65 cm^3) with DIBAH (0.91 mmol) in toluene. The product obtained after removal of solvent was chromatographed on silica gel (3.5 × 10 cm). The fractions eluted with benzene afforded the E-*isomer* **9a** of the formylfulvene (20 mg, 41%) as dark red needles, mp 136–140 °C (decomp.) (from hexane–benzene); *m*/*z* 286 (M^+, 96%) and 115 (100) ($C_{21}H_{18}O$ requires *M*, 286.3); ν_{max}/cm^{-1} 3285 (C≡CH), 2931, 2851 (CHO), 2081 (C≡C), 1664 (C=O), 1598 (C=C) and 983 [(*E*)-HC=CH]; λ_{max}/nm 239 (ε 13 100), 293 (8900), 338 (9300) and 431 (8200); δ_H 10.402 (1 H, d, *J* 1.3, CHO), 7.554 (1 H, dd, *J* 15.8 and 11.1, 14-H), 7.18–7.00 (2 H, m, 6- and 7-H), 6.841 (1 H, d, *J* 11.8, 10-H), 6.816 (1 H, d, *J* 11.8, 3-H), 6.75–6.68 (2 H, m, 5- and 8-H), 6.577 (1 H, d, *J* 15.8, 13-H), 6.430 (1 H, d, *J* 11.0, 15-H), 6.288 (1 H, d, *J* 11.9, 11-H), 5.979 (1 H, d, *J* 11.8, 2-H), 3.385 (1 H, s, C≡CH), 2.990 (1 H, dt, *J* 11.2 and 1.3, H^b), 1.993 (3 H, s, Me) and 0.161 (1 H, d, *J* 11.5, H^a); δ_C 192.65 (t, CHO), 149.74 (q), 138.98 (t), 133.27 (t), 132.46 (t), 132.46 (t), 131.19 (q), 130.68 (t), 130.64 (t), 125.52 (t), 125.33 (t), 125.33 (t), 121.03 (q), 120.91 (q), 120.16 (q), 115.97 (t), 114.59 (t), 83.67 (t, C≡CH), 83.06 (q, −C≡), 31.74 (s) and 23.25 (p) (Found: C, 88.0; H, 6.3%).

Isomeric 7-(4,9-methanocycloundeca-2,4,6,8,10-pentaenylidene)-3,11-dimethyltrideca-3,5,8,10-tetraene-1,12-diyne 10

To a stirred suspension of the salt **7**[7] (2.37 g, 5.60 mmol) in dry THF (70 cm^3) at −50 °C was added dropwise a solution of butyllithium (1.6 mol dm^{-3}; 3.6 cm^3, 5.60 mmol) in hexane by a syringe during 20 min under argon. After the mixture had been stirred for 1 h at −50 °C, a solution of a stereoisomeric mixture of the formylfulvene **9** (161 mg, 0.560 mmol) in dry THF (110 cm^3) was added dropwise during 1.5 h at −30 °C, and the solution was stirred for further 2 h at the same temperature. After addition of ethyl acetate (15 cm^3), the mixture was worked up as for the isolation of the nitrile **6**. The product obtained after removal of solvent was passed through a short column of alumina (3.2 × 5 cm). The fractions eluted with hexane–ether (4:1) afforded the acyclic diacetylene **10** (72 mg, 37%) as a dark brown semi-solid. Since compound **10** proved to be extremely unstable towards diffused light and air, it was used for the following reaction without further purification.

13-(4,9-Methanocycloundeca-2,4,6,8,10-pentaenylidene)-4,9-dimethylcyclotrideca-1,3,9,11-tetraene-5,7-diyne 4

A solution of a stereoisomeric mixture of the acyclic diacetylene **10** (72 mg, 0.21 mmol) in a mixture of pyridine (20 cm^3) and ether (7 cm^3) was added dropwise during 2.5 h to a stirred solution of anhydrous copper(II) acetate (262 mg, 1.45 mmol) in a mixture of pyridine (43 cm^3) and ether (14 cm^3) at 50 °C, and the mixture was stirred for further 1 h before being poured into water and extracted with benzene. The extracts were washed with 5% HCl until they turned acidic (to litmus) and then with aq. $NaHCO_3$, and dried. The product obtained after removal of solvent was chromatographed on silica gel (3.8 × 12 cm). The fractions eluted with 5% benzene in hexane afforded the [11][13]*fulvalene* **4** (18 mg, 25%) as black-purple needles, mp 182–185 °C (decomp.) (from hexane–dichloromethane); *m*/*z* 346 (M^+, 36%) and 28 (100) ($C_{27}H_{22}$ requires *M*, 346.4); ν_{max}/cm^{-1} 2148 (C≡C), 970 [(*E*)-HC=CH] and 756 [(*Z*)-HC=CH]; λ_{max}/nm 237 (ε 28 300), 267 (26 200), 308 (26 800) and 452 (24 300) (Found: C, 93.8; H, 6.5. $C_{27}H_{22}$ requires C, 93.6; H, 6.4%).

X-Ray crystallographic analysis of compound 4

Crystals of compound **4** were grown from hexane–dichloromethane. Intensity data were collected on a Rigaku AFC-7R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) with ω scan mode. Accurate unit-cell dimensions and crystal-orientated matrix were obtained from least-squares refinement of 25 strong reflections in the range $21° < 2\theta < 25°$. The structure was solved by direct methods using SHELXS-86[9] and subsequent calculations were carried out by the SHELXL-93[10] program. The positions of all hydrogen atoms were located by difference Fourier synthesis. The refinement was accomplished on F_o^2 by means of full-matrix least-squares methods anisotropically for all carbons and isotropically for all hydrogens. Final difference map peaks were in the range from 0.150 to −0.16 Å^{-3} and the maximal Δ/σ being 0.001. The crystal data and parameters for data collection,

Table 4 Crystal data for compound **4** and parameters for data collection, structure determination and refinement

Empirical formula	$C_{27}H_{22}$
Relative molecular mass	346.45
Crystal dimension (mm)	0.6 × 0.3 × 0.1
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a (Å)	11.745(2)
b (Å)	26.259(4)
c (Å)	6.334(2)
V (Å^3)	1953.6(6)
Z	4
D_c (g cm^{-3})	1.178
F(000)	736
μ(Mo-Kα) (cm^{-1})	0.066
Temp. (°C)	20.0
Scan width (°)	0.997 ± 0.30 tan θ
$2\theta_{max}$ (°)	55
No. of reflections measured	
Total	2598
With $I > 2\sigma(I)$	1062
No. of refinement variables	332
Final R; R_w [a]	0.050; 0.097

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = [\sigma^2(F_o^2) + (0.0422P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

structure determination and refinement are summarized in Table 4.†

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† Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/139.

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