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Synthesis and Properties of the Tridecafulvene Derivatives. The Substituent Effect at the 14-Position on the Tropicity of Thirteen-Membered Fulvene System

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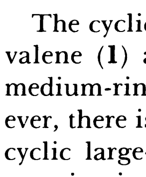
Dimethylbisdehydrotridecafulvene derivatives bearing various substituents at the exocyclic bond have been synthesized and the inductive effect of substituents upon the tropicity of the thirteen-membered ring is discussed on the basis of the spectral data.

The cyclic cross-conjugated π-electron systems, fulvalene (**1**) and fulvene (**2**), containing small- and medium-rings have been extensively studied.[1] However, there is little study on those containing a monocyclic large-membered ring. It is expected that an examination of the ring current effect of the large-membered ring system can be made more readily than those of the small- and medium-ring ones, since the former has both the olefinic inner and outer protons, as compared with that the latter has only the olefinic outer protons.[2]



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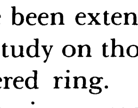

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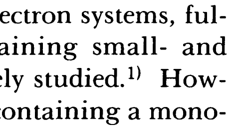

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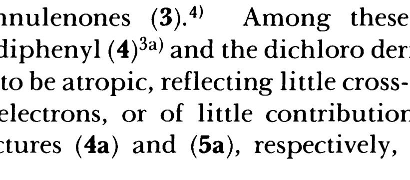
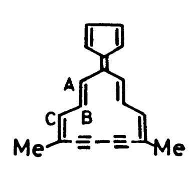
Recently, we have investigated the cross-conjugated π-electron systems **4**—**9** as well as their 15-, 17-, and 19-membered counterparts,[3] which were derived from the bisdehydroannulenones (**3**).[4] Among these compounds, the diphenyl (**4**)[3a] and the dichloro derivative (**5**)[3b] proved to be atropic, reflecting little cross-conjugation of π-electrons, or of little contribution from dipolar structures (**4a**) and (**5a**), respectively, in the ground state. In contrast, the dinitrile derivative (**6**)[3c] exhibited the ring current effect (paratropicity), owing to polarization of an exocyclic bond. These results and relatively easy preparation of **6** directed us to prepare the various derivatives of tridecafulvene in order to study the inductive effect of substituents upon the tropicity of the thirteen-membered ring.



4: R=Ph　4a: R=Ph
5: R=Cl　5a: R=Cl
6: R=CN　6a: R=CN



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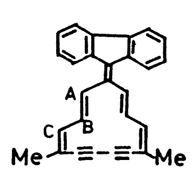

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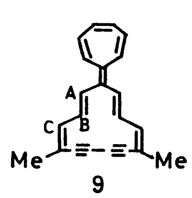

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Results and Discussion

Synthesis. Reduction of **6** with a little excess of diisobutylaluminum hydride (DIBAH)[5] gave only the nitrile aldehyde derivative **11** in 53% yield, along with recovery of a small amount of **6**. A further reduction of **11** with the same reagent resulted in formation of the hydroxy aldehyde derivative **12** (9%) and the hydroxy nitrile derivative **13** (12%), but the diformyl derivative was not obtained in these reductions. Compound **13** was also obtained from **11** by reduction with $NaBH_4$ (75%). Treatment of **13** with phosphorus tribromide gave the bromomethyl nitrile derivative **14** (84%), which was led to the methyl ether derivative **15** (15%) by reaction with NaOMe. The reaction of **11** with MnO_2-NaCN-MeOH, according to the procedure of Corey et al.,[6] afforded the methyl ester derivative (**16**) (42%). Similarly, the reaction of **11** with MnO_2-NaCN-NH_3[7] afforded the amide derivative (**17**) (17%). Oxidation of **11** with Jone's reagent[8] resulted in formation of the annulenone (**10**), arising from the attack of the pinch bond of **11**.

^{1}H NMR and Electronic Spectra. The chemical shifts of the olefinic protons, labeled in the formulas, of the compounds **11**—**17** as well as the closely related compounds **4**—**10**[3a—e,4a] are listed in Table 1. The chemical shift differences between the inner (H^B, $H^{B'}$) and the outer (H^A, $H^{A'}$, H^C, $H^{C'}$) protons, $\Delta\delta$=H^i—H^o (H^i=inner protons; H^o=outer protons), which would be an experimental measure of the magnitude of ring current of these compounds, are also given in Table 1.

Considering the chemical shift differences ($\Delta\delta$), the following decreasing order of the tropicity of the 13-membered ring of these compounds may be established: **6** (CN, CN)>**10** (annulenone)>**16** (CN,

Table 1. ^{1}H NMR Data of Compounds **4**—**17** (δ Values, CDCl$_3$, 90 or 200 MHz)

Compd	A	A′	B	B′	C	C′	$\Delta\delta$(H^i—H^0)
4	6.27		7.05		6.68		0.57
5	6.51		7.45		6.65		0.87
6	6.34		9.78		6.29		3.46
7	6.81		8.19		6.62		1.47
8	6.93		7.97		6.73		1.14
9	6.49		6.63		6.79		−0.01
10	6.10		9.39		6.29		3.19
11	6.59	6.88	9.38	8.48	6.49	6.32	2.36
12	6.66		7.90	6.72	6.65	6.44	0.71
13	6.49	6.31	8.27	8.09	6.51	6.44	1.75
14	6.46	6.29	8.54	8.35	6.46	6.44	2.03
15	6.61	6.32	8.31	8.13	6.54	6.43	1.74
16	6.45	7.11	9.41		6.35[a)]	6.32[a)]	2.85
17	6.42	7.16	9.23	9.19	6.38[b)]	6.34[b)]	2.63

a, b) Assignments may be reversed in each group.

Table 2. Electronic Absorption Maxima of Fulvenes **11**—**17**[a)]

11	a	254 (13500), 266 (12800), 306 (20500), 376 (17300)
	b	251 (0.640), 262 (0.591), 304 (1.000), 375 (0.828)
12	a	257 (11900), 302 (19000), 362 (11100)
	b	255 (0.582), 300 (1.000), 358 (0.539)
13	a	254sh (15200), 268sh (19900), 291 (28400), 351 (15400)
	b	250sh (0.490), 265sh (0.675), 289 (1.000), 347 (0.510)
14	a	254 (14900), 268 (16900), 297 (25000), 362 (17900)
	b	252 (0.554), 266 (0.646), 294 (1.000), 356 (0.667)
15	a	252sh (14700), 266sh (19800), 292 (29100), 349 (15500)
	b	250sh (0.473), 264sh (0.659), 289 (1.000), 345 (0.518)
16	a	247 (14400), 262 (14000), 295 (21800), 366 (19400)
	b	247 (0.645), 262 (0.601), 296 (1.000), 366 (0.873)
17	a	253sh (12600), 266sh (15000), 294 (20300), 361 (14900)
	b	251 (0.581), 265sh (0.678), 293 (1.000), 357 (0.725)

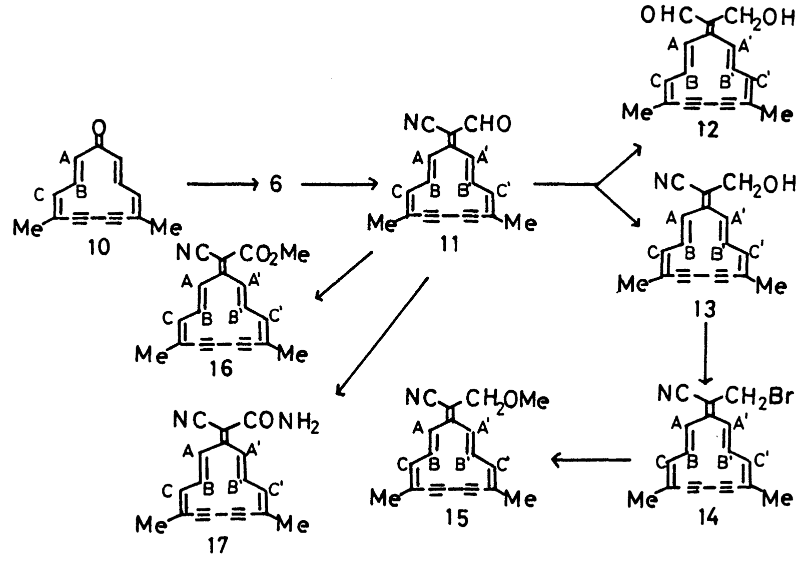
a) a. in THF: λ_{max} (nm) (ε_{max}/l mol^{-1} cm^{-1}); b. in acetonitrile: λ_{max} (nm) (relative extinction coefficients)

CO$_2$Me)>**17** (CN, CONH$_2$)>**11** (CN, CHO)>**14** (CN, CH$_2$Br)>**13** (CN, CH$_2$OH)>**15** (CN, CH$_2$OMe)>**7** (pentafulvalene)>**8** (dibenzopentafulvalene) >**5** (Cl, Cl)≃**12** (CHO, CH$_2$OH)≃**4** (Ph, Ph)>**9** (heptafulvalene). Since both the inner H^B and H$^{B'}$ protons suffer a rather large local anisotropy of the diacetylene bond in these compounds,[9)] the tropicity of **12** as well as **4** and **5** is quite small, i.e., **4**, **5** (as mentioned above), and **12** are atropic. This result also supports the interpretation that the heptafulvalene (**9**) ($\Delta\delta$: −0.01) is diatropic, as reported previously.[3e)] All other tridecafulvene derivatives including the fulvalenes **7** and **8** are paratropic and show the contribution of the dipolar structure such as **6a**.

Among the compounds in which one substituent is nitrile group, the paratropicity decreases in the following order of another substituent: CN (**6**)>COOMe (**16**)>CONH$_2$ (**17**)>CHO (**11**)>CH$_2$Br (**14**)>CH$_2$OH (**13**)>CH$_2$OMe (**15**). This is roughly in accord with a decreasing order of the inductive, electron-withdrawing effect of their substituents, except that of the CHO group.

Since the chemical shifts of H^A, H^B, H^C, and H$^{C'}$ protons are similar in compounds **11** , **16**, and **17**, the deviation of **11** from the order of the electron-withdrawing effect is ascribed to the rather large difference of the chemical shifts of H$^{A'}$ and H$^{B'}$ protons between **11** and **16** (and **17**). Although the higher field shift of H$^{B'}$ proton of **11** as compared with those of **16** and **17**, could not be explained, the higher field shift of H$^{A'}$ proton of **11** might be attributed to a local anisotropic effect of the formyl group at 14-position.

The electronic absorption maxima of compounds **11**—**17**, determined in both tetrahydrofuran (THF) and acetonitrile, are listed in Table 2. It is evident from Table 2 that all the maxima of compounds **11**—**17** show a small hypsochromic shift or do not show any shift on changing the solvent from less polar (THF) to polar (acetonitrile). This solvent effect also supports the interpretation that the polarization, depicted in structure (**6a**), from the large rings to the exocyclic moiety occurs in these systems **11** and **13**—**17**,



as revealed by ^{1}H NMR spectral data.

In conclusion, it was found that the paratropicity of the tridecafulvene system decreases with the decreasing electron-withdrawing order of the inductive effect of substituents at 14-position.

Experimental

Melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on a Hitachi 260—50 spectrophotometer as KBr disk; only significant maxima are reported. Electronic spectra were determined on a Hitachi 220A spectrophotometer (sh=shoulder). ^{1}H NMR spectra were measured on a JEOL FX-90Q (90 MHz) and refer to solutions in $CDCl_3$, in δ-values with TMS as an internal standard. The coupling constants (J) are given in Hz. Assignments were assisted by decoupling experiments where necessary. Mass spectra were determined with a JMS D-200 spectrometer at 75 eV using a direct inlet system. Silica gel (Merck) and alumina (Merck, activity II—III) were used for column chromatography and preparative thin-layer chromatography was carried out on 20×20 cm plate (Merck, 0.5 mm thick). Dichloromethane was distilled over calcium hydride before use. Reactions were followed by TLC aluminum sheets precoated with Merck silica gel F_{254}. Organic extracts were dried over anhydrous sodium sulfate prior to solvent removal.

14,14-Dicyano-5,10-dimethyl-6,8-bisdehydrotridecafulvene (6). This compound was prepared with a slight modification of the reported method.[3c] To a stirred solution of dimethylbisdehydro[13]annulenone (**10**)[4a] (500 mg, 2.40 mmol) and malononitrile (286 mg, 4.33 mmol) in dry dichloromethane (27 ml) was added dropwise a solution of titanium tetrachloride (1.1 ml, 10 mmol) in dry dichloromethane (17 ml) during 50 min under ice-bath. Then a solution of pyridine (2.3 ml) in dry dichloromethane (17 ml) was added dropwise during 40 min to the ice-cooled mixture. After stirring for 1 h at room temperature, a solution of titanium tetrachloride (1.1 ml) in dry dichloromethane (17 ml) was added to the ice-cooled mixture. Then a solution of malononitrile (286 mg) in dry dichloromethane (27 ml) was added dropwise during 90 min, and a solution of pyridine (2.3 ml) in dry dichloromethane (17 ml) was added dropwise during 30 min. The mixture was stirred for 1 h at room temperature. Then 7% hydrochloric acid (17 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 layer was washed with aqueous sodium hydrogencarbonate solution and brine, successively, and dried. The residue after solvent removal was chromatographed on silica gel (4.1×10.5 cm). The fractions eluted with 35% benzene in hexane afforded fulvene **6** (356 mg, 58%).

14-Cyano-14-formyl-5,10-dimethyl-6,8-bisdehydrotridecafulvene (11). To a stirred solution of fulvene **6** (150 mg, 0.59 mmol) in dry toluene (105 ml) was added a solution of diisobutylaluminum hydride (1.8 ml, 1.77 mmol) in toluene by a syringe under argon during 10 min at −7 °C, and the solution was stirred for 50 min at the same temperature. Then 5% sulfuric acid (30 ml) was added and the mixture was extracted with benzene. The combined extracts were washed with aqueous sodium hydrogencarbonate solution and brine, successively, and dried. The residual red liquid was chromatographed on silica gel (3.8×10.0 cm). The early fractions eluted with 30—50% benzene in hexane gave the recovered **6** (18 mg). The later fractions eluted with 80% benzene in hexane afforded fulvene **11** (83 mg, 53%). It formed dark brown needles, mp 195—197 °C (decomp), from hexane-benzene; MS m/z 259 (M^+, 50%) and 214 (100); mol wt 259.2; IR 2225, 2160 (C≡N), 2100 (C≡C), 1665 (CHO), 1610 (C=C), and 980 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR δ=9.89 (s, 1H, CHO), 9.38 (dd, J=16, 10 Hz, 1H, H^B), 8.48 (dd, J=16, 8 Hz, 1H, $H^{B'}$), 6.88 (d, J=16 Hz, 1H, $H^{A'}$), 6.59 (d, J=16 Hz, 1H, H^A), 6.49 (d, J=10 Hz, 1H, H^C), 6.32 (d, J=8 Hz, 1H, $H^{C'}$), 1.82 (s, 3H, Me), and 1.81 (s, 3H, Me).

Found: C, 83.60; H, 5.15; N, 5.41%. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40%.

14-Formyl-14-hydroxymethyl-5,10-dimethyl-6,8-bisdehydrotridecafulvene (12) and 14-Cyano-14-hydroxymethyl-5,10-dimethyl-6,8-bisdehydrotridecafulvene (13). To a stirred solution of fulvene **11** (112 mg, 0.43 mmol) in dry toluene (130 ml) was added a solution of diisobutylaluminum hydride (1.0 ml, 0.99 mmol) in toluene by a syringe at −7 °C. After stirring for 1 h at −7 °C, the mixture was poured into 5% sulfuric acid and extracted with benzene. The combined extracts were worked up as for the isolation of **11**. The residue after solvent removal was chromatographed on silica gel (3.4×8.5 cm). The early fractions eluted with 40% benzene in hexane gave recovered **11** (5 mg). The later fractions eluted with 40—70% benzene in dichloromethane gave a mixture of **12** and **13** as a liquid. The liquid was purified by preparative plate chromatography (dichloromethane-acetone (7 : 3) as eluent). The fast moving, first band gave fulvene **13** (14 mg, 12%). It formed red needles, mp 151—152 °C, from hexane-benzene: MS m/z 261 (M^+, 58%) and 189 (100); mol wt 261.7; IR 3400 (OH), 2200, 2160 (C≡N), 2100 (C≡C), and 970 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR δ=8.27 (dd, J=16.5, 10 Hz, 1H, H^B), 8.09 (dd, J=16.5, 9 Hz, 1H, $H^{B'}$), 6.51 (d, J=10 Hz, 1H, H^C), 6.49 (d, J=16.5 Hz, 1H, H^A), 6.44 (d, J=9 Hz, 1H, $H^{C'}$), 6.31 (d, J=16 Hz, 1H, $H^{A'}$), 4.46 (d, J=5 Hz, 2H, $-CH_2-$), 1.95 (broad t, J=5 Hz, 1H, -OH, exchangeable with D_2O), 1.83 (s, 3H, Me), and 1.84 (s, 3H, Me).

Found: C, 82.40; H, 5.85; N, 5.29%. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36%.

The fast moving, second band gave fulvene **12** (10 mg, 9.0%). It formed red needles, mp 138—139 °C, from hexane-benzene: IR 3400 (OH), 2170 (C≡N), 2100 (C≡C), 1660 (CHO), and 975 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR δ=10.12 (s, 1H, CHO), 7.90 (dd, J=16, 10 Hz, 1H, H^B), 6.72 (dd, J=16, 7 Hz, 1H, $H^{B'}$), 6.66 (d, J=16 Hz, 2H, H^A and $H^{A'}$), 6.65 (d, J=10 Hz, 1H, H^C), 6.44 (d, J=7 Hz, 1H, $H^{C'}$), 4.52 (s, 2H, $-CH_2-$), 2.45 (broad s, 1H, -OH, exchangeable with D_2O), 1.87 (s, 3H, Me), and 1.89 (s, 3H, Me).

HRMS: Found: m/z 264.1088. Calcd for $C_{18}H_{16}O_2$: M, 264.1148.

Preparation of 13 from 11 by Reduction with $NaBH_4$. To a stirred solution of fulvene **11** (158 mg, 0.61 mmol) in dry ethanol (170 ml) was added sodium borohydride (26.5 mg, 0.72 mmol) in one portion, and the mixture was stirred for 3 h at room temperature. After cooling under ice-bath, water (30 ml), and then 2 M hydrochloric acid (27 ml) were added, and the mixture was extracted with benzene. After usual work up, the residual liquid was chromatographed on silica gel (3.2×8.3 cm). The fractions eluted with dichloromethane gave fulvene **13** (120 mg, 75%).

14-Bromomethyl-14-cyano-5,10-dimethyl-6,8-bisdehydrotridecafulvene (14). To a stirred solution of fulvene **13** (142 mg, 0.54 mmol) in dry dichloromethane (21 ml) was added dropwise a solution of phosphorus tribromide (214 mg, 0.79 mmol) in dry dichloromethane (11 ml) during 40 min at −6 °C under argon, and the mixture was stirred overnight at room temperature. After refluxing for a further 3 h, the mixture was poured into water and extracted with dichloromethane. The extracts were washed with aqueous sodium hydrogencarbonate solution and brine, successively, and dried. The residual red liquid after solvent removal was passed through a short column of silica gel (3.2×4.6 cm). The fractions eluted with benzene gave fulvene **14** (148 mg, 84%). It formed dark red needles, mp 159—161 °C, from hexane-benzene: MS *m/z* 325 (M$^+$, 10%), 323 (M+, 10%), and 228 (100); mol wt 323.2; IR 2210, 2175 (C≡N), 2100 (C≡C), 1620, 1600 (C=C), and 980 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR δ=8.54 (dd, *J*=16, 9.5 Hz, 1H, H^B), 8.35 (dd, *J*=16, 9 Hz, 1H, H$^{B'}$), 6.46 (d, *J*=16 Hz, 1H, H^A), 6.46 (d, *J*=9.5 Hz, 1H, H^C), 6.44 (d, *J*=9 Hz, 1H. H$^{C'}$), 6.29 (d, *J*=16 Hz, 1H, H$^{A'}$), 4.23 (s, 2H, -CH$_2$-), and 1.81 (s, 6H, Me).

Found: C, 66.43; H, 4.32; N, 4.20%. Calcd for $C_{18}H_{14}BrN$: C, 66.68, H, 4.35; N, 4.32%.

14-Cyano-14-methoxymethyl-5,10-dimethyl-6,8-bisdehydrotridecafulvene (15). A solution of sodium methoxide, prepared from sodium (45 mg, 1.96 mg atm) and dry methanol (200 ml), was added dropwise during 12 h to a stirred solution of fulvene **14** (148 mg, 0.456 mmol) in dry benzene (60 ml) at room temperature and the solution was stirred for 2 h at the same temperature. The precipitates formed were filtered and washed with hexane. The filtrate was poured into water, and the aqueous layer was extracted with benzene. The combined organic layer was washed with brine, and dried. The residue after solvent removal was chromatographed on alumina (3.2×9.4 cm). The fractions eluted with 10—25% benzene in hexane afforded fulvene **15** (19 mg, 15%). It formed orange cubes, mp 95—96 °C, from hexane: MS *m/z* 275 (M$^+$, 38%) and 228 (100); mol wt 275.3; IR 2200, 2170 (C≡N), 2100 (C≡C), and 970 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR δ=8.31 (dd, *J*=15, 10 Hz, 1H, H^B), 8.13 (dd, *J*=15, 10 Hz, 1H, H$^{B'}$), 6.61 (d, *J*=15 Hz, 1H, H^A), 6.54 (d, *J*=10 Hz, 1H, H^C), 6.43 (d, *J*=10 Hz, 1H, H$^{C'}$), 6.32 (d, *J*=15 Hz, 1H, H$^{A'}$), 4.22 (s, 2H, -OCH$_2$-), 3.40 (s, 3H, OMe), 1.83 (s, 3H, Me), and 1.82 (s, 3H, Me).

Found: C, 82.64; H, 6.29; N, 5.06%. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09%.

14-Cyano-14-methoxycarbonyl-5,10-dimethyl-6,8-bisdehydrotridecafulvene (16). Manganese dioxide (350 mg), sodium cyanide (75 mg), and acetic acid (27 ml) were added in one portion, respectively, to a stirred solution of fulvene **11** (70 mg, 0.27 mmol) in dry methanol (160 ml), and the mixture was refluxed for 3 h. Then a further quantity of manganese dioxide (210 mg) was added and stirring was continued overnight at room temperature. Then a further quantity of manganese dioxide (350 mg), sodium cyanide (37 mg), acetic acid (10 ml) were added and the mixture was refluxed for further 5 h. After cooling, inorganic materials were filtered and washed with dichloromethane. Then the filtrate was poured into water, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with aqueous sodium hydrogencarbonate solution and brine, successively, and dried. The residue after solvent removal was chromatographed on silica gel (3.6×6.0 cm). The fractions eluted with 30—40% benzene in hexane afforded fulvene **16** (33 mg, 42%). It formed dark red needles, mp 147—148 °C, from ether-methanol: MS *m/z* 289 (M$^+$, 63%) and 214 (100); mol wt 289.3; IR 2200, 2150 (C≡N), 2100 (C≡C), 1710 (CO$_2$-), and 960 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR δ=9.41 (dd, *J*=16, 10 Hz, 2 H, H^B and H$^{B'}$), 7.11 (d, *J*=16 Hz, 1H, H$^{A'}$), 6.45 (d, *J*=16 Hz, H^A), 6.35 (d, *J*=10 Hz, 1H, H^C or H$^{C'}$), 6.32 (d, *J*=9 Hz, 1H, H^C or H$^{C'}$), 3.82 (s, 3H, -CO$_2$Me). and 1.74 (s, 6H, Me).

Found: C, 78.58; H, 5.27; N, 4.75%. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84%.

14-Carbamoyl-14-cyano-5,10-dimethyl-6,8-bisdehydrotridecafulvene (17). To isopropyl alcohol (30 ml) saturated with ammonia at −3 °C, was added powdered sodium cyanide (180 mg, 3.65 mmol) in one portion. After 10 min, fulvene **11** (120 mg, 0.463 mmol) was added in one portion, then manganese dioxide (1.10 g) was added in two equal portions 10 min apart. After stirring for 5 h at −3 °C, the mixture was diluted with dichloromethane (30 ml) and was filtered to remove inorganic materials. The filtrate was poured into water, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with aqueous sodium hydrogencarbonate solution and brine, successively, and dried. The residue after solvent removal was chromatographed on alumina (3.2×6.8 cm). The fractions eluted with hexane-dichloromethane (1 : 9) afforded fulvene **17** (22 mg, 17%). It formed brown needles, mp 198 °C (dec), from hexane-benzene: MS *m/z* 274 (M$^+$, 54%) and 214 (100); mol wt 274.3; IR 3350, 3170 (-NH$_2$), 2200, 2100 (C≡N), 2100 (C≡C), 1660 (C=O), 1600 (C=C), and 980 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR δ=9.23 (dd, *J*=16, 10 Hz, 1H, H^B), 9.19 (dd, *J*=15.5, 9 Hz, 1H, H$^{B'}$), 7.16 (d, *J*=16.5 Hz, 1H, H$^{A'}$), 6.42 (d, *J*=16 Hz, 1H, H^A), 6.38 (d, *J*=9 Hz, 1H, H^C or H$^{C'}$), 6.34 (d, *J*=10.5 Hz, 1H, H^C or H$^{C'}$), 6.11 (broad s, 1H, -NH$_2$), 5.61 (broad s, 1H, NH$_2$), 1.76 (s, 3H, Me), and 1.74 (s, 3H, Me).

Found: C, 78.92; H, 5.48; N, 9.54%. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21%.

Oxidation of Fulvene 11. A chromium trioxide solution (0.4 ml), prepared from chromium trioxide (13.3 g), sulfuric acid (11.5 ml), and water (50 ml), was added to a stirred solution of fulvene **11** (70 mg, 0.27 mmol) in acetone (50 ml) at room temperature. After stirring for 1 h at the same temperature, a further quantity of the chromium trioxide solution (0.5 ml) was added, and stirring was continued for a further 4 h. Then the mixture was poured into water and extracted with dichloromethane. The extracts were washed with brine, and dried. The residue after solvent removal was chromatographed on silica gel (3.8×3.5 cm). The fractions eluted with 10% dichloromethane in benzene gave annulenone **10** (12 mg, 16%).

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