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Synthesis and Properties of Extended Tridecafulvenes. The Substituent Effect on the Paratropicity of This Fulvene System as a Measure of Polarizability

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The vinylogues of 14,14-dicyano-5,10-dimethyl-6,8-bisdehydrotridecafulvene have been synthesized and the effect of increasing exocyclic double bonds upon the paratropicity of the thirteen-membered ring is discussed by comparing the polarizability of 2,2-dicyanovinyl, 4,4-dicyano-1,3-butadienyl, and 6,6-dicyano-1,3,5-hexatrienyl groups.

Organic active media which show optical nonlinear behavior will play an important role in the next generation of computing systems and image processing. Conjugated π-electron systems are well-known to possess exceptionally large nonlinear optical susceptibilities and show ultrafast nonresonant nonlinear optical responses.[1,2] Two-dimensional conjugated systems are considered to show the more extensive electronic conjugation for the third nonlinear optical property than one-dimensional conjugated systems, since the latter has main component tensor only along the conjugation chain backbone.[3]

We have measured the nonresonant third harmonic susceptibilities $\chi^{(3)}_{ijkl}(-3\omega:\omega,\omega,\omega)$ for a series of macrocyclic conjugated compounds of bisdehydromethanoannulenes.[4] In this paper, novel push-pull conjugated cyclic system is designed and its synthesis have now been accomplished for measurement of third order nonlinear optical property.

Recently, we have investigated the cross-conjugated π-electron system 1 as well as their 15-, 17-, and 19-membered counterparts.[5] The dinitrile derivative 1 exhibited the ring current effect (paratropicity), reflecting contribution from dipolar structure (**1a**) in the ground state.

Bearing these results in mind, we undertook to prepare a series of push-pull compounds **6**—**8** as possible candidates for nonlinear optical materials. We were also expected to estimate the polarizability of 2,2-dicyanovinyl, 4,4-dicyano-1,3-butadienyl, and 6,6-dicyano-1,3,5-hexatrienyl groups by measuring contribution of the dipolar structures of **6**—**8**.

The dinitrile derivative **1** was converted to nitrile aldehyde derivative **2** by reduction with diisobutylaluminum hydride (DIBAH), as reported.[6] Successive homologation of the fulvene **2** to vinylogous aldehyde derivatives **4** and **5** was carried out by Witting condensations with a large excess of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide **3**, followed by immediate hydrolysis.[7] However, only the *Z*-isomer, as depicted in **5**, was characterized from the product by the second homologation. Reactions of these formyl derivatives **2**, **4**, and **5** thus obtained, with an excess of malononitrile in the presence of titanium

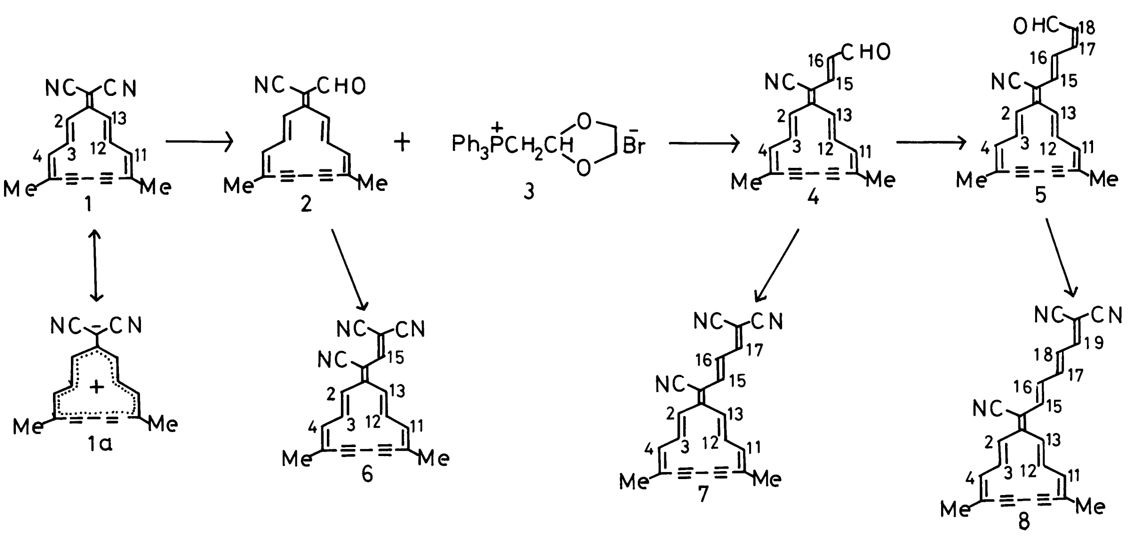
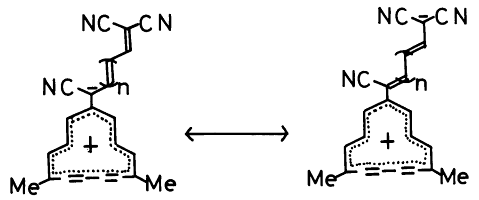


Table 1. ^{1}H NMR Data of Compounds **1**, **6—8** (δ values, $CDCl_3$, 90, 270, or 500 MHz)

Compd	H^2	H^{13}	H^3	H^{12}	H^4	H^{11}	Δδ(H^i—H^o)
1	6.34		9.78		6.29		3.46
6	6.61	6.57	9.72	8.39	6.46	6.28	2.58
7	6.60	6.37	9.24	8.63	6.48	6.32	2.49
8	6.62	6.38	8.90	8.48	6.52	6.40	2.20



6a: n=0 6b: n=0
7a: n=1 7b: n=1
8a: n=2 8b: n=2

tetrachloride and pyridine in dichloromethane at −10 to 0 °C afforded the desired trinitrile tridecafulvenes **6—8**.

The chemical shifts of the olefinic protons, labeled in the formulas, of the compounds **1** and **6—8** are listed in Table 1. The chemical shift differences between the inner (H^3, H^{12}) and the outer (H^2, H^4, H^{11}, H^{13}) protons, Δδ=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 (Δδ), the following decreasing order of the paratropicity of the 13-membered ring of these compounds may be established: **1**>**6**≈**7**>**8**. Although dicyanovinyl group is known to have a large dipole moment,[1] **6** shows the smaller paratropicity, or the smaller contribution of the dipolar structure than **1**. The compounds **6—8** can be represented by two dipolar structures **6a—8a** and **6b—8b**. However, the chemical shifts and the values of the coupling constants of the exocyclic olefinic protons (see Experimental) reveal that the contribution of the structures **6b—8b** is rather small. Thus, Table 1 shows that 2,2-dicyanovinyl, 4,4-dicyano-1,3-butadienyl, and 6,6-dicyano-1,3,5-hexatrienyl groups are the equally good, electron-withdrawing groups, and an increase of double bonds may affect a little decrease of the inductuve effect of dicyano substituents.

The electronic absorption maxima of compounds **6—8**, determined in both tetrahydrofuran (THF) and acetonitrile, are listed in Table 2. The longest absorption maxima of **6**, **7**, and **8** show a regular bathochromic shift (20—30 nm) in accord with an increasing double bond at 14 position. It is evident from Table 2 that all the maxima of compounds **6—8** (and also of the compounds **4** and **5**, see Experimental) show a small hypsochromic shift on changing the solvent from less polar (THF) to polar (acetonitrile), as observed in the case of **1**.[5,6] The solvent effect also supports the interpretation that the polarization, depicted in structures **6a—8a**, from the large rings to the exocyclic moiety occurs in the systems **6—8**, as revealed by ^{1}H NMR spectral data.

Table 2. Electronic Absorption Maxima of Fulvenes **6—8**
a. in THF: λ_{max} (nm) (ε_{max}/l mol^{-1} cm^{-1});
b. in Acetonitrile: λ_{max} (nm) (Relative Extinction Coefficients)

6a	221 (13100), 267 (12900), 304 (10300), 427 (16300)
6b	219 (0.33), 263 (0.35), 312 (0.25), 423 (0.55)
7a	254 sh (12100), 274 (14400), 332 (8260), 446 (33100)
7b	253 (0.29), 271 (0.32), 331 (0.19), 442 (0.73)
8a	256 (19200), 275 sh (13800), 293 sh (11600), 353 (8480), 457 sh (50200), 477 (52800)
8b	254 (0.36), 272 sh (0.26), 287 sh (0.23), 349 (0.18), 450 sh (0.91), 468 (0.95)

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), a JEOL GX-270 (270 MHz), or a JEOL GX-500 (500 MHz) spectrometer 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 sspectrometer at 75 eV using a direct inlet system. Silica gel (Merck) and alumina (Merck, activityt II-III) were used for column chromatography. 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-Cyano-14-(2-formylvinyl)-5,10-dimethyl-6,8-bisdehydrotridecafulvene (4). Methanolic lithium methoxide solution (10 ml), prepared from lithium (32 mg, 4.64 mmol) in dry methanol (24 ml), was added dropwise during 4 h at room temperature to a stirred solution of the fulvene **2**[6] (150 mg, 0.58 mmol) and the salt **3**[7] (2.00 g, 4.64 mmol) in dry *N*,*N*-dimethylformamide (DMF) (87 ml). Then the mixture was poured onto water and extracted with benzene. The combined extracts were washed with brine, dried and evaporated. The residue after solvent removal was chromatographed on alumina (3.8×4.2 cm). The fractions eluted with 10% ether in hexane afforded the acetal of **4**[7] as dark drown solid (91 mg, 48%). The solid was dissolved in tetrahydrofuran (8 ml) and ethanol (37 ml) and was admixed with 0.5 M (M=mol dm^{-3}) hydrochloric acid (57 ml), and the mixture was stirred for 1 h at room temperature. Then the mixture was poured onto water and extracted with dichloromethane. The combined extracts were washed with aqueous sodium hydrogencarbonate solution and brine, successively, and dried. The residue after removal of solvent was chromatographed on silica gel (3.3×6.5 cm). The fractions eluted with 60% hexane in benzene afforded the fulvene **4** (48 mg, 29% from **2**). It formed brown needles, mp 164—166 °C (decomp), from hexane–benzene: MS m/z 285 (M^+, 30%) and 240 (100); mol wt 285.3; IR 2810, 2720 (CHO), 2200, 2150 (C≡N), 2100 (C≡C), 1690 (CHO), and 970 cm^{-1} (trans C=C); UV λ_{max} (THF) 318 (12100) and 402 nm (21900); λ_{max} (acetonitrile: relative extinction coefficient) 318 (0.53) and 398 nm (0.96); ^1H NMR (90 MHz) δ=9.70 (d, J=7 Hz, 1H, CHO), 8.99 (dd, J=16, 11 Hz, 1H, H^3), 8.49 (dd, J=15, 10 Hz, 1H, H^{12}), 7.51 (d, J=15 Hz, 1H, H^{15}), 6.62 (dd, J=15, 7 Hz, 1H, H^{16}), 6.62 (d, J=16 Hz, 1H, H^2), 6.51 (d, J=11 Hz, 1H, H^4), 6.45 (d, J=15 Hz, 1H, H^{13}), 6.43 (d, J=10 Hz, 1H, H^{11}), and 1.83 (s, 6H, Me).

Found: C, 83.90; H, 5.35; N, 5.20%. Calcd for $C_{20}H_{15}NO$: C, 84.18; H, 5.30; N, 4.91%.

14-Cyano-14-(4-formyl-1,3-butadienyl)-5,10-dimethyl-6,8-bisdehydrotridecafulvene (5). Methanolic lithium methoxide solution (2.0 ml), prepared from lithium (7.4 mg, 1.05 mmol) in dry methanol (5.6 ml) was added dropwise during 1 h at room temperature under argon to a stirred solution of the fulvene **4** (95 mg, 0.35 mmol) and the salt **3**[7] (460 mg, 1.05 mmol) in dry N,N-dimethylformamide (53 ml). Then the mixture was worked up as for the isolation of acetal of **4**. The residue was chromatographed on alumina (3.6×3.2 cm). The fractions eluted with 5—10% ether in hexane afforded the acetal of **5** as dark brown solid. The solid was dissolved in tetrahydrofuran (3.4 ml) and ethanol (26 ml), and was admixed with 0.5 M hydrochloric acid (40 ml), and the mixture was stirred for 1 h at room temperature. Then the mixture was worked up as for the isolation of **4**. The residue after solvent removal was chromatographed on silica gel (6.5×3.2 cm). The fractions eluted with 10—20% dichloromethane in benzene afforded a mixture of E- and Z-isomers of the homologated fulvene (36 mg, 35% from **4**). Recrystallization from hexane–benzene afforded brown needles, mp 262—264 °C (decomp), which proved to be Z-isomer, as depicted in **5**, from an analysis of ^1H NMR spectrum; MS m/z 311 (M^+, 54%) and 227 (100); mol wt 311.3; IR 2200, 2150 (C≡N), 2100 (C≡C), 1680 (CHO), 980 (trans C=C), and 760 cm^{-1} (cis C=C); UV λ_{max} (THF) 265sh (16200), 275 (17700), 324 (16100), 420 (40400), and 448 nm sh (32000); λ_{max} (acetonitrile: relative extinction coefficient) 262sh (0.38), 272 (0.41), 323 (0.39), and 417 nm (0.93); ^1H NMR (270 MHz) δ=10.30 (d, J=8 Hz, 1H, CHO), 8.74 (dd, J=15, 10 Hz, 1H, H^3), 8.37 (dd, J=16, 9 Hz, H^{12}), 7.66 (dd, J=15, 12 Hz, 1H, H^{16}), 7.04 (t, J=12 Hz, 1H, H^{17}), 6.96 (d, J=15 Hz, 1H, H^{15}), 6.63 (d, J=16 Hz, 1H, H^2), 6.54 (d, J=10 Hz, 1H, H^4), 6.44 (d, J=9 Hz, 1H, H^{11}), 6.40 (d, J=16 Hz, 1H, H^{13}), 5.99 (dd, J=11, 8 Hz, 1H, H^{18}), and 1.83 (s, 6H, Me).

Found: C, 85.14; H, 5.61; N, 4.58%. Calcd for $C_{22}H_{19}NO$: C, 84.86; H, 5.50; N, 4.50%.

14-Cyano-14-(2,2-dicyanovinyl)-5,10-dimethyl-6,8-bisdehydrotridecafulvene (6). To a stirred solution of the fulvene 2 (200 mg, 0.77 mmol) and malononitrile (150 mg, 2.27 mmol) in dry dichloromethane (43 ml) was added dropwise during 1 h under ice-bath a solution of titanium tetrachloride (0.34 ml) in dry dichloromethane (11 ml). Then a solution of pyridine (0.74 ml) in dry dichloromethane (11 ml) was added dropwise to the ice-cooled mixture during 1 h. After stirring for 1 h at room temperature, 7% hydrochloric acid (15 ml) was added to the solution and the mixture was stirred for a further 10 min. Then the mixture was worked up as for the isolation of **4**. The residue after solvent removal was chromatographed on silica gel (3.8×9.5 cm). The fractions eluted with 20% dichloromethane in benzene afforded the fulvene **6** (77 mg, 33%). It formed dark purple needles, mp 118—120 °C (decomp), from hexane–benzene; MS m/z 307 (M^+, 30%) and 242 (100); mol wt 307.3; IR 2250, 2170 (C≡N), 2100 (C≡C), and 980 cm^{-1} (trans C=C); UV Table 2; ^1H NMR (90 MHz) δ=9.72 (dd, J=16, 11 Hz, 1H, H^3), 8.39 (dd, J=16, 8 Hz, 1H, H^{12}), 7.56 (s, 1H, H^{15}), 6.61 (d, J=16 Hz, 1H, H^2), 6.57 (d, J=16 Hz, 1H, H^{13}), 6.46 (d, J=10 Hz, 1H, H^4), 6.28 (d, J=8 Hz, 1H, H^{11}), and 1.81 (s, 6H, Me).

Found: C, 82.30; H, 4.40; N, 13.42%. Calcd for $C_{21}H_{13}N_3$: C, 82.06; 4.26; N, 13.67%.

14-Cyano-14-(4,4-dicyano-1,3-butadienyl)-5,10-dimethyl-6,8-bisdehydrotridecafulvene (7). To a stirred solution of the fulvene **4** (153 mg, 0.54 mmol) and malononitrile (89 mg, 1.35 mmol) in dry dichloromethane (100 ml) was added dropwise during 2 h a solution of titanium tetrachloride (0.24 ml) in dry dichloromethane (8.0 ml) under ice-bath. Then a solution of pyridine (0.52 ml) in dry dichloromethane (8.0 ml) was added dropwise during 2 h to the ice-cooled solution. After stirring for 1.5 h at room temperature, a solution of malononitrile (89 mg, 1.35 mmol) in dry dichloromethane (5.0 ml) was added to the ice-cooled mixture. Then a solution of titanium tetrachloride (0.2 ml) in dry dichloromethane (6.0 ml) was added dropwise during 1 h and then a solution of pyridine (0.39 ml) in dry dichloromethane (6.0 ml) was added dropwise during 1 h under ice-bath. After stirring for 30 min at room temperature, 7% hydrochloric acid (15 ml) was added to the mixture, and the mixture was stirred for a further 10 min. Then the mixture was worked up as for the isolation of **4**. The residue after solvent removal was chromatographed on silica gel (3.3×8.0 cm). The fractions eluted with 5% dichloromethane in benzene afforded the fulvene **7** (63 mg, 35%). It formed dark purple needles, mp 188—190 °C (decomp), from hexane–tetrahydrofuran; MS m/z 333 (M^+, 2%) and 57 (100); mol wt 333.3; IR 2200, 2150 (C≡N), 2100 (C≡C), and 960 cm^{-1} (trans C=C); UV Table 2; ^1H NMR (270 MHz) δ=9.24 (dd, J=16, 11 Hz, 1H, H^3), 8.63 (dd, J=16, 10 Hz, 1H, H^{12}), 7.48 (d, J=11 Hz, 1H, H^{17}), 7.20 (d, J=14 Hz, 1H, H^{15}), 7.10 (dd, J=14, 11 Hz, 1H, H^{16}), 6.60 (d, J=16 Hz, 1H, H^2), 6.48 (d, J=11 Hz, 1H, H^4), 6.37 (d, J=16 Hz, 1H, H^{13}), 6.32 (d, J=10 Hz, 1H, H^{11}), and 1.80 (s, 6H, Me).

Found: C, 82.72; H, 4.75; N, 12.35%. Calcd for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54; N, 12.61%.

14-Cyano-14-(6,6-dicyano-1,3,5-hexatrienyl)-5,10-dimethyl-6,8-bisdehydrotridecafulvene (8). To a stirred solution of a mixture of E- and Z-isomers of the fulvene **5** (39 mg, 0.12 mmol) and malononitrile (21 mg, 0.32 mmol) in dry dichloromethane (24 ml) was added dropwise during 30 min a solution of titanium tetrachloride (0.06 ml) in dry dichloromethane (3 ml) under ice-bath. Then a solution of pyridine (0.13 ml) in dry dichloromethane (3 ml) was added dropwise during 30 min to the ice-cooled solution. After stirring for 1 h at room temperature, a solution of titanium tetrachloride (0.06 ml) in dry dichloromethane (2 ml) was added dropwise during 20 min and then a solution of pyridine (0.13 ml) in dry dichloromethane (2 ml) was added dropwise during 30 min under ice-bath. After stirring for a further 20 min at room temperature, 7% hydrochloric acid (10 ml) was added to the mixture, and the mixture was stirred for a further 10 min. Then the mixture was worked up as for the isolation of **4**. The residue after solvent removal was chromatographed on silica gel (8.5×3.2 cm). The fractions eluted with 10—30% dichloromethane in benzene afforded the fulvene **8** (14 mg, 30%). It formed dark purple needles, mp 190—192 °C(decomp), from hexane–tetrahydrofuran; MS *m/z* 359 (M^+, 27%) and 193 (100); mol wt 359.4; IR 2200, 2150 (C≡N), 2100 (C≡C), 1000, and 980 cm^{-1} (trans C=C); UV Table 2; ^{1}H NMR (500 MHz) δ=8.90 (dd, *J*=16, 10 Hz, 1H, H^3), 8.48 (dd, *J*=16, 9 Hz, 1H, H^{12}), 7.44 (d, *J*=12 Hz, 1H, H^{19}), 7.06 (d, *J*=15 Hz, 1H, H^{15}), 6.97 (m, 2H, H^{16} and H^{17}), 6.89 (dd, *J*=14, 12 Hz, 1H, H^{18}), 6.62 (d, *J*=16 Hz, 1H, H^2), 6.52 (d, *J*=10, 1H, H^4), 6.40 (d, *J*=9 Hz, 1H, H^{11}), 6.38 (d, *J*=16 Hz, 1H, H^{13}), 1.83 (s, 3H, Me), and 1.82 (s, 3H, Me).

Found: C, 83.46; H, 4.83; N, 11.72%. Calcd for $C_{25}H_{17}N_3$: C, 83.54; H, 4.77; N, 11.67%.

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