Synthesis of 1-(2,2-Dicyanovinyl)-, 1-(2,4,4-Tricyano-1,3-butadienyl)-, 1,6-Bis(2,2-dicyanovinyl)-1,3,5-cycloheptatriene and Their Vinylogs

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The 1-(2,2-dicyanovinyl)-, 1-(2,4,4-tricyano-1,3-butadienyl)-, 1,6-bis(dicyanovinyl)-substituted 1,3,5-cycloheptatriene, and their vinylogs have been synthesized by condensation of 1-formyl-, 1-(2-cyano-2-formylvinyl)-, 1,6-diformyl-1,3,5-cycloheptatriene, and their vinylogs, respectively, with malononitrile mediated with $TiCl_4$ as a Lewis acid.

Conjugated π-electron systems are well known to possess exceptionally large nonlinear optical susceptibilities and show ultra fast nonresonant nonlinear optical responses (Chart 1).[1]

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 (**1**) and showed that the third order optical response increases with increased ring size of the macrocyclic conjugated system in a manner analogous to the behavior of conjugated linear chains.[2] Also, it was found that the second-order polarizabilities (β) of 14,14-dicyano-5,10-dimethyl-6,8-bisdehydrotridecafulvene and its vinylogs **2** increase with increasing number of exocyclic double bonds.[3] Thus, it was shown that extension of the conjugation length and introduction of two or three cyano groups at the terminal position(s) of the conjugated chain resulted in the increase of the nonlinear optical properties in these two-dimensional conjugated compounds **1** and **2**. In view of these results, it seemed important to examine the effects of the above-mentioned structural features in one-dimensional conjugated systems. For this purpose, conjugated systems **3**, **4**, and **5** (Chart 1), which have electron-withdrawing cyano groups at the terminal position(s) and would be prepared more easily than **1**[4] and **2**,[5] were designed for measurement of the second and third order nonlinear optical property. In this paper, the synthesis and characterization of these compounds are described.

Results and Discussion

The key compound for the synthesis of compounds **3** was 1-formyl-1,3,5-cycloheptatriene (**6a**), which had been prepared by Asao et al.[6] They obtained compound **6a** by direct introduction of a formyl group into 1,3,5-cycloheptatriene by Vilsmeier reaction, but the yield was low (10—30%). To improve the yield we prepared **6a** as outlined in Scheme 1.

1-Acetyl-1,3,5-cycloheptatriene (**9**), which was the intermediate for the synthesis of 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (**8a**), was prepared by the reaction of 1,3,5-cycloheptatriene with acetyl chloride in the presence of zinc chloride according to the reported method.[7] Compound **9** was converted to 1,3,5-cycloheptatriene-1-carboxylic acid (**10**) by haloform reaction. Reaction of the acid **10** with thionyl chloride gave the acid chloride **11** which without isolation was led to the ethyl ester **12** by treatment with ethanol. Reduction of the ester **12** with $LiAlH_4$ gave the alcohol **13**.[6] Subsequently, it was found that the acid **10** was directly reduced to the alcohol **13** with $LiAlH_4$ in a higher overall yield. The alcohol **13** was then converted to 1,3,5-cycloheptatriene-1-carbaldehyde (**6a**) by oxidation with $BaMnO_4$ (Scheme 1).[8]

The aldehyde **6a** was converted to the higher vinylogs **6b**—**d** by successive Wittig condensation with a large excess of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide (**14**)[9] and lithium ethoxide in *N*,*N*-dimethylformamide at 75°C, followed by chromatographic purification of the acetals of **6b**—**d**,[10] and then by hydrolysis of these acetals with dilute hydrochloric acid in ethanol.[4] The yields of these homologations from the corresponding lower homologs were 50—60% (Chart 2).

Condensations of these aldehydes **6a**—**d** with malononitrile were carried out employing the procedure of Ong and Keoshkerian[11] using $TiCl_4$ as a Lewis acid and pyridine as a base, affording the dinitrile derivatives **3a**—**d** in 70—90% yields (Chart 3).

The dinitrile **3a** was converted to the nitrile aldehyde **7** in 57% yield by reduction with diisobutylaluminium hydride (DIBAH). As similarly to the cases of preparation of a series of compounds **2**,[3] several attempts to obtain the homologous aldehyde of the compound **7** by Wittig condensation using the salt **14** were made, but met without success (Chart 4). The 1,3,5-cycloheptatriene-1,6-dialdehyde (**8a**) and its vinylogs **8b**—**e** were prepared as reported.[4a,10] Condensations of the aldehyde **7** and the dialdehydes **8a**—**e** with malononitrile afforded the trinitrile **4** and the tetranitrile derivatives **5a**—**e**, respectively, in 32—55% yields (Chart 5). Among them satisfactory elemental analyses were not obtained for the compounds **4d** and **4e**, due to the instability of these compounds against air.

We have shown here convenient synthetic methods of a variety of 1-monosubstituted or 1,6-disubstituted 1,3,5-cycloheptatriene derivatives starting from 1-acetyl-1,

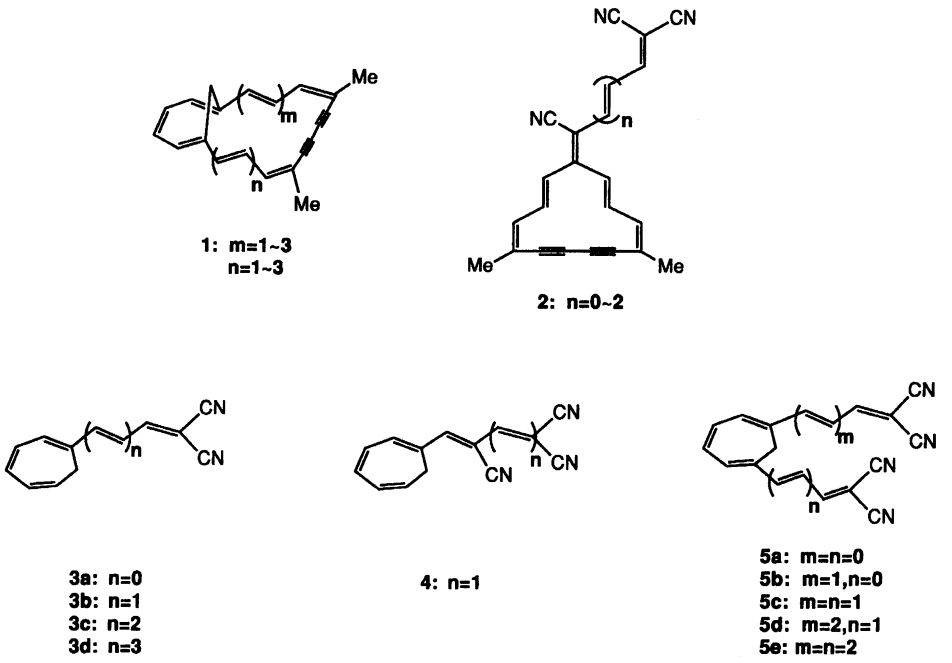
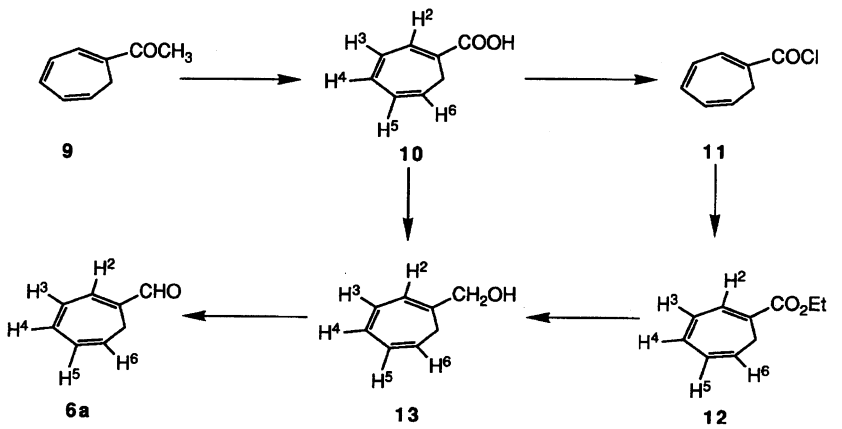


Chart 1.



Scheme 1.

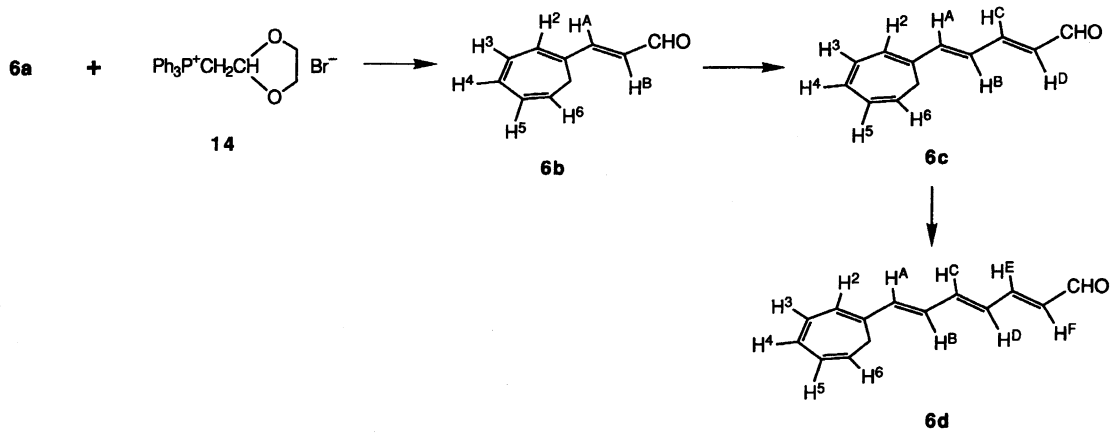


Chart 2.

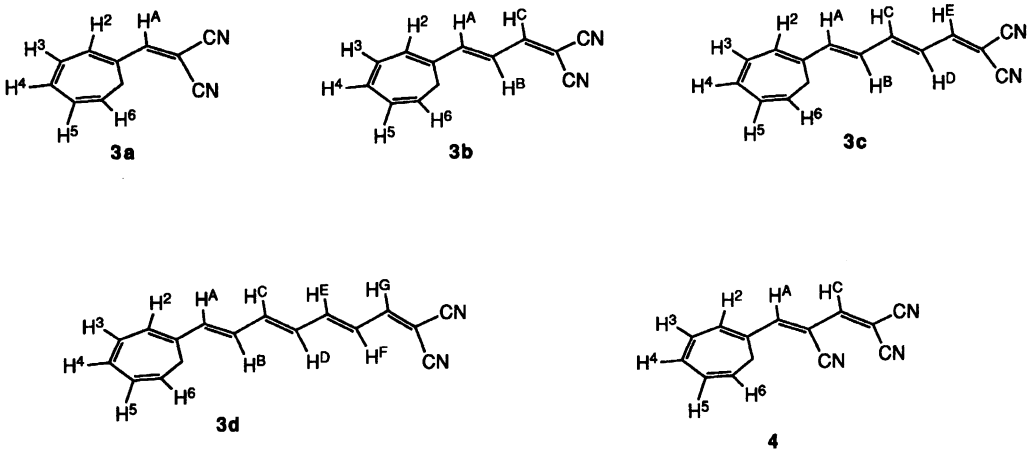


Chart 3.

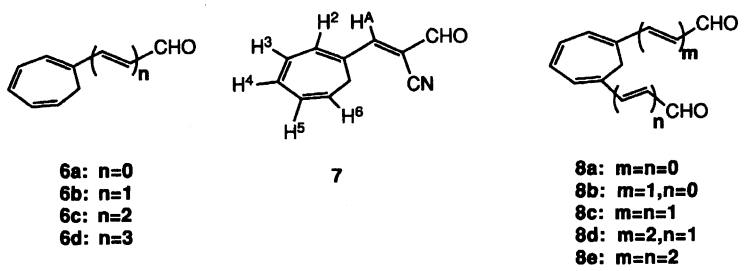


Chart 4.

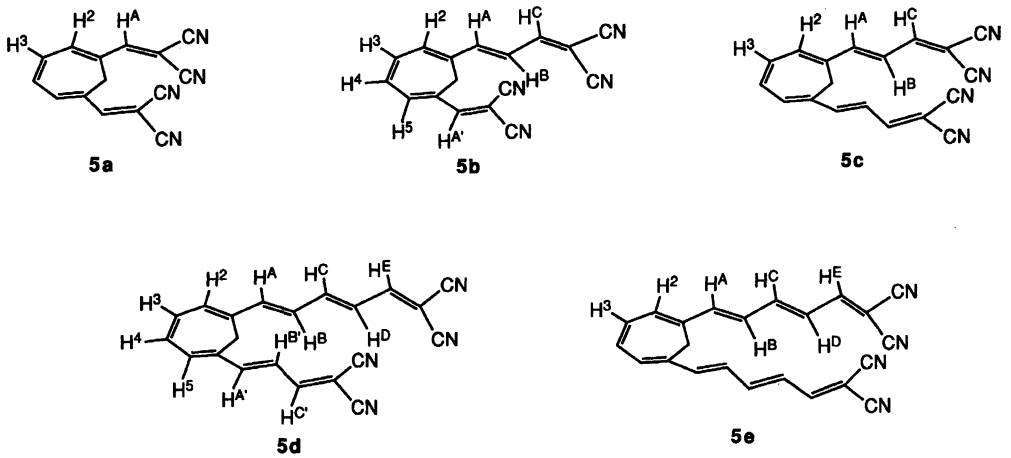


Chart 5.

3,5-cycloheptatriene.

The nonlinear optical properties of compounds **3**, **4**, and **5** are now under investigation.

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) or a JEOL GX-400 (400 MHz) spectrometer and refer to solutions in $CDCl_3$, in δ-values with TMS as an internal standard, unless otherwise stated. The coupling constants (J) are given in Hz. Assignments were made on the basis of the spectra taken in the presence of Eu(fod)$_3$ and were assisted by decoupling experiments where necessary. Mass spectra were recorded with a JMS D-300 spectrometer operating at 75 eV using a direct inlet system. Silica gel (Merck), Daiso gel or alumina (Merck, activity II-III) was used for column chromatography. Reactions were followed by aluminium TLC sheets precoated with Merck silica gel F_{254}. Organic extracts were washed with brine and dried over anhydrous sodium sulfate prior to removal of solvent.

1,3,5-Cycloheptatriene-1-Carboxylic Acid (10). Bromine (215 g, 1.34 mol) was added dropwise to a stirred solution of 8.3 mol dm^{-3} aqueous sodium hydroxide (538 cm^3) during 2 h and then a solution of 1-acetyl-1,3,5-cycloheptatriene (**9**)[7] (60 g, 0.45 mol) in dioxane (40 cm^3) was added to the solution during 20 min at −10°C. After stirring for 2 h at 0—5°C, the mixture was stirred for further 30 min at 20°C. Then the cooled mixture was washed with chloroform. To the aqueous solution was added slowly 20% aqueous sodium hydrogensulfite (25 cm^3) and then concentrated hydrochloric acid was added dropwise under ice-cooling until the solution turned acidic. The precipitates formed were collected by suction filtration and washed with water, giving the acid 10 (34.2 g, 56%). It formed white needles, mp 61—62°C, from hexane; MS m/z 136 (M^+, 20%) and 91 (100); mol wt 136.1; IR 1680 (C=O) and 1610 cm^{-1} (C=C); UV (THF) 215 (ε 16200) and 276 nm (4570); ^{1}H NMR (90 MHz) δ=8.65 (1H, br s, $CO_2\underline{H}$), 7.36 (1H, d, J=5.5 Hz, H^2), 6.77 (2H, m, H^3 and H^4), 6.29 (1H, dd, J=9 and 5.5 Hz, H^5), 5.60 (1H, m, H^6), and 2.65 (2H, d, J=7 Hz, CH_2).

Found: C, 70.35; H, 5.93%. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92%.

Ethyl 1,3,5-Cycloheptatriene-1-carboxylate (12). A mixture of the acid **10** (24.0 g, 0.18 mol), a few drops of pyridine, and thionyl chloride (48 cm^3) was heated under reflux for 1h. After cooling, the mixture was evaporated under reduced pressure to remove the excess thionyl chloride. The residue was dissolved in dry benzene (48 cm^3). To the solution was added dropwise with stirring dry ethanol (72 cm^3) during 10 min at room temperature and the solution was heated under reflux for 30 min. The solution was poured onto water (450 cm^3) and then the aqueous layer was extracted with benzene. The combined organic layers were washed with brine and dried. The residue after removal of the solvent was distilled to afford the ethyl ester **12** (37.0 g, 79%); bp 66—68°C/133 Pa (1 mmHg=133 Pa); MS m/z 164 (M^+, 13%) and 91 (100); mol wt 164.2; IR 1710 cm^{-1} (C=O); UV (THF) 219 (ε 11400), 275 (5000), and 307 nm (sh, 3940); ^{1}H NMR (90 MHz) δ=7.23 (1H, d, J=5 Hz, H^2), 6.90—6.52 (2H, m, H^3 and H^4), 6.24 (1H, dd, J=9 and 5 Hz, H^5), 5.55 (1H, m, H^6), 4.22 (2H, q, J=7 Hz, $-C\underline{H}_2CH_3$), 2.64 (2H, d, J=7 Hz, CH_2), and 1.30 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$).

Found: C, 73.42; H, 7.37%. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%.

1,3,5-Cycloheptatrienemethanol (13). A solution of the ester **12** (16.4 g, 0.11 mol) in dry THF (90 cm^3) was added dropwise to a suspension of lithium aluminium hydride (3.80 g, 0.1 mol) in dry ether (130 cm^3) during 1 h at −10°C. After stirring for a further 1 h at room temperature, the mixture was cooled to −30°C. Then water (3.8 cm^3), 15% aqueous sodium hydroxide (3.2 cm^3), and water (15.2 cm^3) were added dropwise successively at −30°C. Then the mixture was filtered by suction and the inorganic precipitates formed were washed with benzene. The filtrate was concentrated under reduced pressure and the residue was distilled to afford the alcohol 13[6] (10.4 g, 85%) as a colorless liquid; bp 95—96°C/665 Pa; MS m/z 122 (M^+, 13%) and 91 (100); mol wt 122.1; IR 3300 cm^{-1} (–OH); UV (THF) 216 (ε 5040) and 266 nm (2980); ^{1}H NMR (90 MHz) δ=6.57—6.49 (2H, m, H^2 and H^3), 6.23—6.06 (2H, m, H^4 and H^5), 5.37 (1H, dt, J=9 and 7 Hz, H^6), 4.19 (2H, br s, $C\underline{H}_2OH$), 2.57 (1H, br s, OH, disappeared by addition of D_2O), and 2.36 (2H, d, J=7 Hz, CH_2).

Found: C, 78.41; H, 8.45%. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25%.

The Alcohol 13 from the Acid 10. To an ice-cooled, stirred solution of the acid **10** (160 mg, 1.2 mmol) in dry THF (10 cm^3) was added $LiAlH_4$ (30 mg, 0.8 mmol) in small portions under argon atmosphere and the mixture was refluxed for 3 h. After addition of ethyl acetate (1.0 cm^3), water (250 cm^3) was added dropwise to the mixture cautiously and the product was extracted with dichloromethane. After removal of the solvent, the residue was chromatographed on Daiso gel (2.0×6.5 cm). The fractions eluted with benzene afforded the alcohol **13** (128 mg, 89%).

1-Formyl-1 3,5-cycloheptatriene (6a). The alcohol **13** (6.1 g, 0.05 mol) in dry dichloromethane (340 cm^3) was stirred with activated $BaMnO_4$[8] (70 g) at room temperature for 23 h, and the mixture was filtered by suction. The collected solid was further extracted with dichloromethane using a Soxhlet apparatus. The dichloromethane solution was combined with the original filtrate and the combined solution was concentrated in vacuo. The residue was distilled, giving the aldehyde **6a** (3.80 g, 64%) as a yellow liquid; bp 63—69°C/655 Pa (lit, 60—65°C/655 Pa);[6] MS m/z 120 (M^+, 49%) and 91 (100); mol wt 120.1; IR 1680 cm^{-1} (CHO); UV (THF) 223 (ε 7910), 275 (sh, 3960), and 298 nm (4300); ^{1}H NMR (90 MHz) δ=9.51 (1H, s, CHO), 7.00—6.74 (3H, m, H^2, H^3, and H^4), 6.28 (1H, m, H^5), 5.57 (1H, m, H^6), and 2.68 (2H, d, J=7 Hz, CH_2).

Found: C, 79.67; H, 6.83%. Calcd for C_8H_8O: C, 79.97; H, 6.71%.

1-(2-Formylvinyl)-1,3,5-cycloheptatriene (6b). Ethanolic lithium ethoxide, prepared from lithium (853 mg, 123 mmol) in dry ethanol (120 cm^3), was added dropwise to a stirred solution of the salt **14**[9] (52.7 g, 123 mmol) in *N*,*N*-dimethylformamide (DMF) (200 cm^3) during 1 h at 70°C under argon. After stirring for further 1 h, a solution of the aldehyde **6a** (3.00 g, 24.6 mmol) in DMF (20 cm^3) was added dropwise to the solution with stirring during 30 min at 70°C. After stirring for further 3.5 h at 70°C, the reaction mixture was poured onto water and extracted with benzene. Then the extracts were washed with brine and dried. The residue after removal of the solvent was chromatographed on alumina (4.2×5.6 cm). The fractions containing the acetal of **6b**, eluted with 5—10% ether in hexane were collected and evaporated. The residue was dissolved in ethanol (95 cm^3) and the solution was admixed with 0.5 mol dm^{-3} hydrochloric acid (100 cm^3). The solution was stirred for 30 min at room temperature, poured onto water and extracted with benzene. The extracts were washed with aqueous sodium hydrogencarbonate and dried. The residue after removal of the solvent was chromatographed on Daiso gel (4.2×5.5 cm). The fractions eluted with 5—10% ether in hexane afforded the aldehyde **6b** (2.18 g, 61%) as a yellow liquid; MS m/z 146 (M^+, 73%) and 117 (100); mol wt 146.1; IR 1670 (CHO) and 975 cm^{-1} (E–HC=CH); UV (THF) 241 (ε 19400) and 329 nm (14200); ^{1}H NMR (90 MHz) δ=9.58 (1H, d, J=7.5 Hz, CHO), 7.15 (1H, d, J=15.5 Hz, H^A), 6.76—6.53 (3H, m, H^2, H^3, and H^4), 6.41 (1H, dd, J=15.5 and 7.5 Hz, H^B), 6.27 (1H, m, H^5), 5.53 (1H, m, H^6), and 2.57 (2H, d, J=7 Hz, CH_2).

Found: C, 82.28; H, 6.95%. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90%.

1-(4-Formyl-1,3-butadienyl)-1,3,5-cycloheptatriene (6c). Ethanolic lithium ethoxide, prepared from lithium (475 mg, 68.5 mmol) in dry ethanol (69 cm^3), was added dropwise to a stirred solution of the salt **14** (29.3 g, 68.4 mmol) in DMF (112 cm^3) during 45 min at 72°C under argon. After stirring for further 1 h, a solution of the aldehyde **6b** (2.0 g, 13.7 mmol) in DMF (11 cm^3) was added dropwise to the solution with stirring during 1 h at 72°C. After stirring for further 3 h at 72°C, the reaction mixture was worked up as for the isolation of the acetal of **6b**. The residue after removal of the solvent was chromatographed on alumina (4.2×6.0 cm). The fractions containing the acetal of **6c**, eluted with 10—15% ether in hexane were collected and evaporated. The residue was dissolved in ethanol (53 cm^3) and the solution was admixed with 0.5 mol dm^{-3} hydrochloric acid (56 cm^3). The solution was stirred for 30 min at room temperature. Then the solution was worked up as for the isolation of **6b**. The residue after removal of the solvent was chromatographed on Daiso gel (3.8×5.5 cm). The fractions eluted with 10—20% benzene in hexane afforded the aldehyde **6c** (1.25 g, 53%) as a red liquid; MS m/z 172 (M^+, 40%) and 128 (100), mol wt 172.2; IR 1670 (CHO) and 985 cm^{-1} (E-HC=CH); UV (THF) 267 (ε 13300), 329 (24000), and 361 nm (sh, 19500); ^{1}H NMR (400 MHz) δ=9.58 (1H, d, J=8 Hz, CHO), 7.18 (1H, m, H^C), 6.74 (2H, m, H^A and H^B), 6.68—6.60 (2H, m, H^3 and H^D), 6.39 (1H, d, J=5 Hz, H^2), 6.30—6.19 (2H, m, H^4 and H^5), 5.52 (1H, dt, J=9 and 7 Hz, H^6), and 2.65 (2H, d, J=7 Hz, CH_2).

Found: C, 83.35; H, 7.01%. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02%.

1-(6-Fromyl-1,3,5-hexatrienyl)-1,3,5-cycloheptatriene (6d). Ethanolic lithium ethoxide, prepared from lithium (403 mg, 58.1 mmol) in dry ethanol (58 cm^3), was added dropwise to a stirred solution of the salt **14** (24.9 g, 58.1 mmol) in DMF (95 cm^3) during 1 h at 72°C under argon. After stirring for further 1 h, a solution of the aldehyde **6c** (2.0 g, 11.6 mmol) in DMF (9 cm^3) was added dropwise to the solution with stirring during 40 min at 72°C. After stirring for further 1.5 h at 72°C, the mixture was worked up as for the isolation of the acetal of **6b**. The residue after removal of the solvent was chromatographed on alumina (4.2×5.0 cm). The fractions containing the acetal of **6d**, eluted with 20—30% ether in hexane were collected and evaporated. The residue was disssolved in ethanol (45 cm^3) and THF (40 cm^3), and the solution was admixed with 0.5 mol dm^{-3} hydrochloric acid (47 cm^3). The solution was stirred for 1 h at room temperature and was worked up as for the isolation of **6b**. The residue after removal of the solvent was chromatographed on Daiso gel (4.2×6.0 cm). The fractions eluted with 50—70% benzene in hexane afforded the aldehyde **6d** (1.41 g, 61%) as an orange liquid; MS m/z 198 (M^+, 100%), mol wt 198.2; IR 1670 (CHO), 1010, 990, and 975 cm^{-1} (E-HC=CH); UV (THF) 289 (ε 13900) and 364 nm (39800); ^{1}H NMR (400 MHz) δ=9.56 (1H, d, J=8 Hz, CHO), 7.43—6.16 (9H, m, H^2, H^3, H^4, H^5, H^A, H^B, H^C, H^D, and H^E), 6.15 (1H, dd, J=15 and 8 Hz, H^F), 5.47 (1H, dt, J=9 and 7 Hz, H^6), and 2.63 (2H, d, J=7 Hz, CH_2).

Found: C, 84.65; H, 6.90%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

1-(2,2-Dicyanovinyl)-1,3,5-cycloheptatriene (3a). To a stirred solution of the aldehyde **6a** (1.0 g, 8.3 mmol) and malononitrile (1.70 g, 25.7 mmol) in dry dichloromethane (50 cm^3) was added dropwise during 10 min a solution of titanium tetrachloride (3.0 cm^3, 27.3 mmol) in dry dichloromethane (15 cm^3) under ice-cooling. Then a solution of pyridine (6.0 cm^3, 20.2 mmol) in dry dichloromethane (15 cm^3) was added dropwise during 10 min to the ice-cooled solution. After stirring for a further 1 h at room temperature, 7% hydrochloric acid (5 cm^3) was added to the mixture until it turned acidic, and stirring was continued for further 10 min. Then the solution was poured onto water and extracted with dichloromethane. The combined organic layers were washed with aqueous sodium hydrogencarbonate and dried. The residue after removal of the solvent was chromatographed on Daiso gel (3.8×10 cm). The fractions eluted with 30—40% benzene in hexane afforded the dinitrile derivative **3a** (678 mg, 83%). It formed yellow cubes, mp 64—67°C, from hexane–benzene; MS m/z 168 (M^+, 64%) and 141 (100); mol wt 168.1; IR 2220 cm^{-1} (C≡N); UV (THF) 243 (ε 12000), 310 sh (7290), and 365 nm (13000); ^{1}H NMR (90 MHz) δ=7.44 (1H, s, H^A), 7.13—6.65 (3H, m, H^2, H^3, and H^4), 6.46 (1H, dd, J=9 and 5 Hz, H^5), 5.86 (1H, dt, J=7 and 5 Hz, H^6), and 2.81 (2H, d, J=7 Hz, CH_2).

Found: C, 78.66; H, 5.08; N, 16.40%. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66%.

1-(4,4-Dicyano-1,3-butadienyl)-1,3,5-cycloheptatriene (3b). To a stirred solution of the aldehyde **6b** (600 mg, 4.1 mmol) and malononitrile (677 mg, 10.2 mmol) in dry dichloromethane (50 cm^3) was added dropwise a solution of titanium tetrachloride (1.2 cm^3, 10.9 mmol) in dry dichloromethane (15 cm^3) during 15 min and then a solution of pyridine (2.4 cm^3, 8.1mmol) in dry dichloromethane (15 cm^3) was added dropwise during 15 min in an ice bath. After stirring for further 30 min at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on Daiso gel (4.2×7.5 cm). The fractions eluted with 20% benzene in hexane afforded the dinitrile derivative **3b** (554 mg, 70%). It formed orange needles, mp 101—103°C, from hexane–benzene; MS m/z 194 (M^+, 66%) and 193 (100); mol wt 194.2; IR 2220 cm^{-1} (C≡N); UV (THF) 272 (ε 10800), 283 (sh, 9680), and 397 nm (30000); ^{1}H NMR (400 MHz) δ=7.49 (1H, d, J=11 Hz, H^C), 6.99—6.93 (2H, m, H^A and H^B), 6.79 (1H, dd, J=11 and 6 Hz, H^3), 6.67 (1H, dd, 11 and 6 Hz, H^4), 6.58 (1H, d, J=6 Hz, H^2), 6.33 (1H, dd, J=9 and 6 Hz, H^5), 5.60 (1H, dt, J=9 and 7 Hz, H^6), and 2.69 (2H, d, J=7 Hz, CH_2).

Found: C, 80.54; H, 5.27; N, 14.25%. Calcd for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.42%.

1-(6,6-Dicyano-1,3,5-hexatrienyl)-1,3,5-cycloheptatriene (3c). To a stirred solution of the aldehyde **6c** (300 mg, 1.70 mmol) and malononitrile (317 mg, 5.40 mmol) in dry dichloromethane (30 cm^3) was added dropwise during 30 min a solution of titanium tetrachloride (0.7 cm^3, 5.9 mmol) in dry dichloromethane (8 cm^3) and then a solution of pyridine (0.9 cm^3, 3.0 mmol) in dry dichloromethane (8 cm^3) was added dropwise during 30 min under ice-cooling. After stirring for further 1 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on Daiso gel (3.8×3.0 cm). The fractions eluted with 30—40% benzene in hexane afforded the dinitrile derivative **3c** (248 mg, 65%). It formed red needles, mp 130—131°C, from hexane–ben-

zene; MS m/z 220 (M^+, 85%) and 219 (100); mol wt 220.2; IR 2220 (C≡N) and 1005 cm^{-1} (E–HC=CH); UV (THF) 301 (ε 8130) and 429 nm (40800); ^1H NMR (400 MHz) δ=7.46 (1H, d, J=12 Hz, H^E), 7.00 (1H, m, H^C), 6.78 (1H, dd, J=14 and 12 Hz, H^D), 6.73 (2H, m, H^A and H^B), 6.72—6.61 (2H, m, H^3 and H^4), 6.43 (1H, d, J=6 Hz, H^2), 6.29 (1H, dd, J=9 and 6 Hz, H^5), 5.53 (1H, dt, J=9 and 7 Hz, H^2), and 2.66 (2H, d, J=7 Hz, CH_2).

Found; C, 82.09; H, 5.58; N, 12.52%. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72%.

1-(8,8-Dicyano-1,3,5,7-octatetraenyl)-1,3,5-cycloheptatriene (3d). To a stirred solution of the aldehyde **6d** (300 mg, 1.5 mmol) and malononitrile (307 mg, 4.6 mmol) in dry dichloromethane (30 cm^3) was added dropwise during 30 min a solution of titanium tetrachloride (0.54 cm^3, 4.9 mmol) in dry dichloromethane (8 cm^3) and then a solution of pyridine (1.1 cm^3, 3.7 mmol) in dry dichloromethane (8 cm^3) was added dropwise during 30 min under ice-cooling. After stirring for further 1.5 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on Daiso gel (3.8×5.3 cm). The fractions eluted with 5—10% benzene in hexane afforded the dinitrile derivative **3d** (150 mg, 41%). It formed purple microcrystals, mp 139—141°C, from hexane-benzene; MS m/z 246 (M^+, 100%); mol wt 246.3; IR 2220 (C≡N) and 1000 cm^{-1} (E–HC=CH); UV (THF) 320 (ε 8490) and 452 nm (50000); ^1H NMR (400 MHz) δ=7.44 (1H, d, J=12 Hz, H^G), 7.01—6.46 (8H, m, H^3, H^4, H^A, H^B, H^C, H^D, H^E, and H^F), 6.35 (1H, d, J=5 Hz, H^2), 6.26 (1H, dd, J=9 and 6 Hz, H^5), 5.50 (1H, dt, J=9 and 7 Hz, H^6), and 2.65 (2H, d, J=7 Hz, CH_2).

Found: C, 83.16; H, 5.77; N, 11.05%. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37%.

1-(2-Cyano-2-formylvinyl)-1,3,5-cycloheptatriene (7). To a stirred solution of the dinitrile derivative **3a** (350 mg, 2.08 mmol) in dry toluene (200 cm^3) was added a solution of diisobutylaluminium hydride (1.5 mol dm^{-3}; 3.5 cm^3, 5.3 mmol) in toluene by a syringe during 1 h at −15°C under argon, and the solution was stirred for 30 min at the same temperature. The 5% sulfuric acid (150 cm^3) was added dropwise below 0°C and the mixture was extracted with benzene. The combined extracts were washed with aqueous sodium hydrogencarbonate and dried. The residual orange liquid obtained after removal of the solvent was chromatographed on Daiso gel (3.8×4.0 cm). The fractions eluted with 40% benzene in hexane afforded the nitrile aldehyde derivative **7** (408 mg, 57%). It formed yellow needles, mp 76—78°C, from hexane-benzene; MS m/z 171 (M^+, 58%) and 115 (100); mol wt, 171.1; IR 2210 (C≡N) and 1680 cm^{-1} (CHO); UV (THF) 245 (ε 12000), 305 (sh, 7400), and 364 nm (14200); ^1H NMR (400 MHz) δ=9.46 (1H, s, CHO), 7.59 (1H, s, H^A), 7.01 (1H, dd, J=11 and 6 Hz, H^3), 6.89 (1H, d, J=6 Hz, H^2), 6.78 (1H, dd, J=11 and 6 Hz, H^4), 6.46 (1H, dd, J=9 and 6 Hz, H^5), 5.93 (1H, dt, J=9 and 7 Hz, H^6), and 2.91 (2H, d, J=7 Hz, CH_2).

Found: C, 77.23; H, 5.27; N, 7.90%. Calcd for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18%.

1-(2,4,4-Tricyano-1,3-butadienyl)-1,3,5-cycloheptatriene (4). To a stirred solution of the nitrile aldehyde derivative **7** (200 mg, 1.17 mmol) and malononitrile (386 mg, 5.85 mmol) in dry dichloromethane (160 cm^3) was added dropwise a solution of titanium tetrachloride (0.58 cm^3, 5.85 mmol) in dry dichloromethane (16 cm^3) during 1.5 h, and then a solution of pyridine (1.28 cm^3) in dry dichloromethane (16 cm^3) was added dropwise during 1.5 h at −10°C. After stirring for further 1 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on Daiso gel (3.2×7.0 cm). The fractions eluted with hexane–benzene (1:4) afforded the trinitrile derivative **4** (82 mg, 32%). It formed orange plates, mp 188—190°C (decomp), from hexane–benzene; MS m/z 219 (M^+, 70%) and 218 (100); mol wt 219.2; IR 2220 cm^{-1} (C≡N); UV (THF) 271 (ε 7360), 321 (sh, 8250), and 410 nm (23600); ^1H NMR (400 MHz) δ=7.39 (1H, s, H^C), 7.24 (1H, s, H^A), 7.07 (1H, dd, J=11 and 6 Hz, H^3), 6.90 (1H, d, J=6 Hz, H^2), 6.81 (1H, dd, J=11 and 6 Hz, H^4), 6.51 (1H, dd, J=9 and 6 Hz, H^5), 5.99 (1H, dt, J=9 and 7 Hz, H^6), and 2.90 (2H, d, J=7 Hz, CH_2).

Found: C, 76.79; H, 4.19; N, 18.42%. Calcd for $C_{14}H_9N_3$: C, 76.69; H, 4.14; N, 19.17%.

1,6-Bis(2,2-dicyanovinyl)-1,3,5-cycloheptatriene (5a). To a stirred solution of the dialdehyde **8a** (500 mg, 3.35 mmol) and malononitrile (2.20 g, 33.5 mmol) in dry dichloromethane (25 cm^3) was added dropwise during 1 h a solution of titanium tetrachloride (8 cm^3, 72.7 mmol) in dry dichloromethane (11 cm^3) under ice-cooling and then a solution of pyridine (16 cm^3) in dry dichloromethane (11 cm^3) was added dropwise during 1 h under ice-cooling. After stirring for 1 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on silica gel (3.2×8.0 cm). The fractions eluted with 30—80% dichloromethane in benzene afforded the tetranitrile derivative **5a** (430 mg, 52%). It formed orange needles, mp 140—141°C, from hexane–benzene; MS m/z 244 (M^+, 85%) and 217 (100); mol wt 244.2; IR 2220 (C≡N) and 960 cm^{-1} (E–HC=CH); UV (THF) 302 (ε 31900) and 405 nm (10000); ^1H NMR (90 MHz) δ=7.60 (2H, s, H^A), 7.22 (2H, m, H^3), 7.07 (2H, m, H^2), and 3.18 (2H, s, CH_2).

Found: C, 73.98; H, 3.52; N, 22.64%. Calcd for $C_{15}H_8N_4$: C, 73.76; H, 3.30; N, 22.94%.

1-(4,4-Dicyano-1,3-butadienyl)-6-(2,2-dicyanovinyl)-1,3,5-cycloheptatriene (5b). To a stirred solution of the dialdehyde **6b** (300 mg, 1.72 mmol) and malononitrile (1.14 g, 17.3 mmol) in dry dichloromethane (30 cm^3) was added dropwise during 1 h a solution of titanium tetrachloride (4.0 cm^3, 37.1 mmol) in dry dichloromethane (10 cm^3) and then a solution of pyridine (8.0 cm^3, 0.1 mol) in dry dichloromethane (10 cm^3) was added dropwise during 1 h under ice-cooling. After stirring for further 1 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on silica gel (3.2×5.0 cm). The fractions eluted with 10—30% dichloromethane in benzene afforded the tetranitrile derivative **5b** (230 mg, 50%). It formed red needles, mp 207—208°C, from dichloromethane; MS m/z 270 (M^+, 82%) and 269 (100); mol wt 270.2; IR 2220 (C≡N) and 985 cm^{-1} (E–HC=CH); UV (THF) 320 (ε 49300) and 436 nm (14200); ^1H NMR (400 MHz) δ=7.51 (1H, d, J=11 Hz, H^C), 7.31 (1H, s, $H^{A'}$), 7.14 (1H, dd, J=15 and 11 Hz, H^B), 7.05 (1H, d, J=15 Hz, H^A), 7.02—6.98 (2H, m, H^3 and H^5), 6.87 (1H, dd, J=11 and 6.5 Hz, H^4), 6.83 (1H, d, J=7 Hz, H^2), and 3.25 (2H, s, CH_2).

Found: C, 75.19; H, 3.98; N, 19.97%. Calcd for $C_{17}H_{10}N_4$:

C, 75.54; H, 3.73; N, 20.73%. Attempts to improve the elemental analysis failed.

1,6-Bis(4,4-dicyano-1,3-butadienyl)-1,3,5-cycloheptatriene (5c). To a stirred solution of the dialdehyde **8c** (700 mg, 3.50 mmol) and malononitrile (2.30 g, 35.0 mmol) in dry dichloromethane (35 cm^3) was added dropwise during 1 h a solution of titanium tetrachloride (8.5 cm^3, 77.2 mmol) in dry dichloromethane (12 cm^3) and then a solution of pyridine (17 cm^3) in dry dichloromethane (12 cm^3) was added dropwise during 1 h under ice-cooling. After stirring for 1 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on silica gel (3.2×10.0 cm). The fractions eluted with 10—40% dichloromethane in benzene afforded the tetranitrile derivative **5c** (550 mg, 53%). It formed purple needles, mp 217—219°C, from dichloromethane; MS m/z (M^+, 100%); mol wt 269.3; IR 2200 (C≡N) and 980 cm^{-1} (E–HC=CH), UV (THF) 338 (ε 74800) and 439 nm (12700); ^{1}H NMR (400 MHz) δ=7.50 (2H, d, J=10.5 Hz, H^C), 7.03 (2H, dd, J=15 and 10.5 Hz, H^B), 6.96 (2H, d, J=15 Hz, H^A), 6.87 (2H, m, H^3), 6.71 (2H, m, H^2), and 2.91 (2H, s, CH_2).

Found: C, 77.08; H, 4.22; N, 18.45%. Calcd for $C_{19}H_{12}N_4$: C, 77.01; H, 4.08; N, 18.91%.

6-(4,4-Dicyano-1,3-butadienyl)-1-(6,6-dicyano-1,3,5-hexatrienyl)-1,3,5-cycloheptatriene (5d). To a stirred solution of the dialdehyde **8d** (550 mg, 2.43 mmol) and malononitrile (1.60 g, 24.3 mmol) in dry dichloromethane (40 cm^3) was added dropwise during 1 h a solution of titanium tetrachloride (6.0 cm^3, 55.5 mmol) in dry dichloromethane (13 cm^3) and then a solution of pyridine (12 cm^3, 146 mmol) in dry dichloromethane (13 cm^3) was added dropwise during 1 h under ice-cooling. After stirring for further 1 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on silica gel (3.2×8 cm). The fractions eluted with 30—50% dichloromethane in benzene afforded the tetranitrile derivative **5d** (400 mg, 51%). It formed purple needles, mp 199—200°C, from dichloromethane; MS m/z 322 (M^+, 100%); mol wt 322.3; IR 2225 (C≡N) and 1000 cm^{-1} (E–HC=CH); UV (THF) 360 (ε 71600) and 480 nm (12600); ^{1}H NMR (400 MHz) δ=7.52 (1H, d, J=11 Hz, $H^{C'}$), 7.44 (1H, d, J=12 Hz, H^E), 7.13 (1H, dd, J=13 and 12 Hz, H^D), 7.08 (1H, dd, J=15 and 11 Hz, $H^{B'}$), 7.04—6.74 (6H, m, H^A, H^B, H^C, $H^{A'}$, H^3, and H^4), 6.71 (1H, d, J=6.5 Hz, H^2), 6.59 (1H, d, J=6.5 Hz, H^5), and 2.86 (2H, s, CH_2).

Found: C, 79.39; H, 4.95; N, 13.97%. Calcd for $C_{21}H_{14}N_4$: C, 78.24; H, 4.38; N, 17.38%. Attempts to improve the elemental analysis failed.

1,6-Bis(6,6-dicyano-1,3,5-hexatrienyl)-1,3,5-cycloheptatriene (5e). To a stirred solution of the dialdehyde **8e** (700 mg, 2.78 mmol) and malononitrile (1.83 g, 27.8 mmol) in dry dichloromethane (30 cm^3) was added dropwise during 1 h a solution of titanium tetrachloride (7 cm^3, 63.6 mmol) in dichloromethane (9 cm^3) and then a solution of pyridine (13 cm^3) in dry dichloromethane (9 cm^3) was added dropwise during 1 h under ice-cooling. After stirring for 1 h at room temperature, the mixture was worked up as for the isolation of **3a**. The residue after removal of the solvent was chromatographed on silica gel (3.2×10.0 cm). The fractions eluted with 10% dichloromethane in benzene afforded the tetranitrile derivative **5e** (497 mg, 51%). It formed dark purple needles, mp 202—203°C, from dichloromethane; MS m/z 348 (M^+, 100%); mol wt 348.3; IR 2200 (C≡N) and 1000 cm^{-1} (E–HC=CH); UV (THF) 381 (ε 81700) and 494 nm (16000); ^{1}H NMR (400 MHz) δ=7.46 (2H, d, J=12 Hz, H^E), 7.02 (2H, dd, J=15 and 10 Hz, H^C), 6.86 (2H, dd, J=14.5 and 12 Hz, H^D), 6.81—6.70 (6H, m, H^A, H^B, and H^3), 6.59—6.57 (2H, m, H^2), and 2.82 (2H, s, CH_2).

Found: C, 78.25; H, 4.46; N, 15.06%. Calcd for $C_{23}H_{16}N_4$: C, 79.29; H, 4.63; N, 16.08%. Attempts to improve the elemental analysis failed.

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