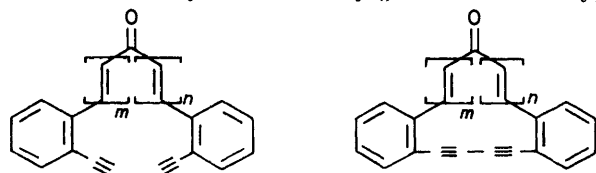


Benzannulenones. Synthesis of 22,23,24,25-Tetrahydrodibenzo[*a,g*]-cycloheicosen-11-one

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The conjugated ω -(*o*-ethynylphenyl)alka-dienal (6) and -trienal (7) were prepared and converted by aldol condensations into acyclic ketones, required as potential precursors of tetrahydrodibenzannulenones. Only the bis(ethynylphenyl)tridecahexaenone (1d) afforded the corresponding annulenone, 22,23,24,25-tetrahydrodibenzo[*a,g*]cycloheicosen-11-one (2d). The ^1H n.m.r. spectrum showed that (2d) is an atropic molecule.

It was expected that an aldol condensation between an aldehyde and a ketone containing terminal acetylene groups, followed by oxidative coupling of the resulting conjugated ketone of type (1), would lead to a tetrahydrodibenzannulenone of type (2). In fact, the [13]- (2a) and the [17]-annulenone (2b) were formed from the corresponding acyclic ketones (1a and b).^{1,2} We describe here the synthesis of conjugated ketones of type



(1) a; $m = n = 1$
 b; $m = n = 2$
 c; $m = 2, n = 3$
 d; $m = n = 3$
 e; $m = 3, n = 4$
 f; $m = n = 4$

(2) a; $m = n = 1$
 b; $m = n = 2$
 c; $m = 2, n = 3$
 d; $m = n = 3$
 e; $m = 3, n = 4$
 f; $m = n = 4$

(1) as potential precursors of dibenzannulenones of ring size larger than seventeen members. In one case a tetrahydrodibenzannulenone (2d) was obtained.

The starting material was the readily available *o*-ethynylcinnamaldehyde (3).³ This was converted into the vinylogue (6) in high yield by Wittig condensation with 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide (4), followed by hydrolysis of the resulting acetal (5), as described for the preparation of (3) from *o*-ethynylbenzaldehyde.^{3,4} The homology was then repeated, giving rise to the higher vinylogue (7) in 60% yield. The

structures of the conjugated aldehydes (6) and (7) were established from spectral data and elemental analyses.

The ketone (8)² was condensed with the aldehyde (6) in the presence of methanolic potassium hydroxide, giving the acyclic ketone (1c) in 63% yield. Oxidative couplings were attempted with the ketone (1c), in the hope of obtaining the dibenz[19]annulenone (2c). First we treated the ketone with copper(II) acetate in pyridine,⁵ by which procedure the dibenz- [13]- and -[17]-annulenones were prepared from the corresponding acyclic

^1H N.m.r. parameters of compounds (1d) and (2d) in CDCl_3 at 100 MHz^a (τ values; internal standard Me_4Si ; J in Hz)

Proton	(1d) ^b	(2d)
H ^A	3.54 (d, J 15)	3.99 (d, J 16)
H ^B	(2.34—2.65) ^c	2.64 (dd, J 16, 11) ^e
H ^C	3.22 (dd, J 15, 11)	3.39 (dd, J 16, 11) ^f
H ^D	(2.34—2.65) ^c	2.52 (dd, J 16, 11) ^e
H ^E	3.06 (dd, J 15, 11) ^d	3.06 (dd, J 16, 11) ^f
H ^F	(2.34—2.65) ^c	2.35 (d, J 16)
Benzenoid	2.67—2.84 (m)	2.7—2.8 (m)
H		

^a Assignments by referring to chemical shifts of related compounds.² ^b In addition, a singlet at 6.62 (C \equiv CH). ^c It is not possible to assign H^B, H^D, and H^F signals of (1d) unequivocally because of the similarity of their chemical shifts. ^{d-f} Assignments may be reversed.

ketones.^{1,2} However, no cyclization product was found. Similarly, treatment with copper(II) acetate in *NN*-dimethylformamide, which was successfully applied in synthesis of a dibenz[15]annulenone,⁶ was also unsuccessful.

Condensation of acetone with 2 mol. equiv. of the aldehyde (6) afforded the acyclic ketone (1d) in high yield. In this case, oxidative coupling with copper(II) acetate in pyridine gave the desired dibenz[21]annulenone (2d) in 16% yield.

¹ J. Ojima, Y. Yokoyama, T. Yokoyama, *Chem. Letters*, 1974, 1261; J. Ojima, Y. Yokoyama, and M. Enkaku, *Bull. Chem. Soc. Japan*, 1977, **50**, 1522.

² J. Ojima, A. Kimura, and T. Yokoyama, *Chem. Letters*, 1975, 207; J. Ojima, M. Ishiyama, and A. Kimura, *Bull. Chem. Soc. Japan*, 1977, **50**, 1584.

³ J. Ojima, A. Kimura, Y. Yokoyama, and T. Yokoyama, *Bull. Chem. Soc. Japan*, 1975, **48**, 367.

⁴ J. Ojima, T. Yokomachi, and A. Kimura, *Bull. Chem. Soc. Japan*, 1976, **49**, 2840.

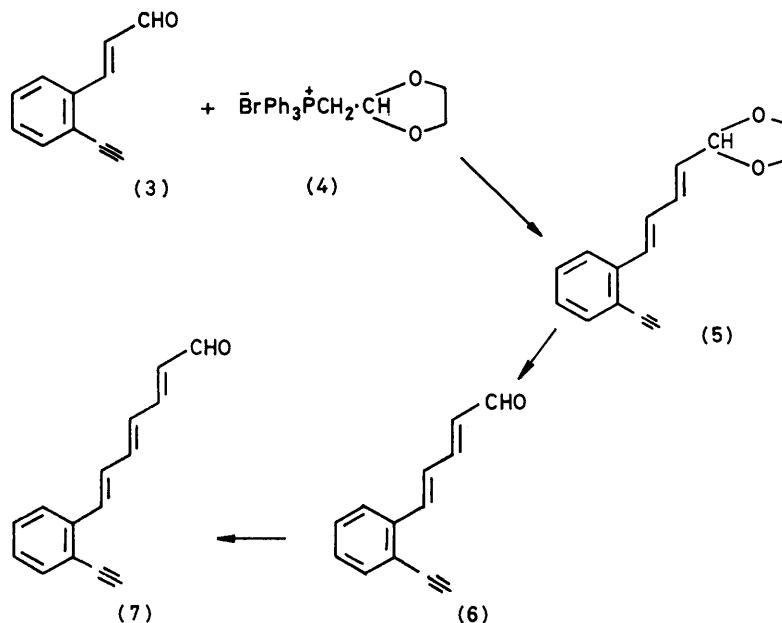
⁵ G. Eglinton and A. R. Galbraith, *Chem. and Ind.*, 1956, 737; *J. Chem. Soc.*, 1959, 889.

⁶ R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Letters*, 1975, 1043.

The aldehyde (6) on treatment with acetone gave the ketone (9) (56%), which was then condensed with the aldehyde (7) to afford the acyclic ketone (1e) in 27%

groups are so remote that intramolecular cyclization cannot be achieved.

As shown in the Table, a comparison of the chemical

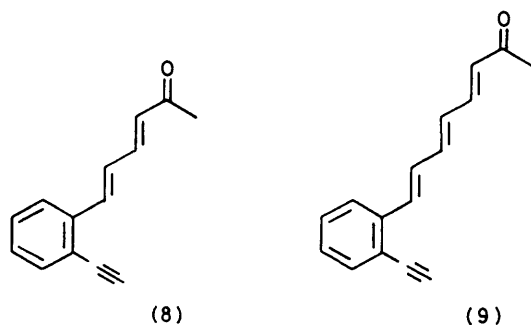


yield. Aldol condensation of the aldehyde (7) with acetone as for that between (6) and (8) gave the ketone (1f) in high yield. However, all attempts to obtain

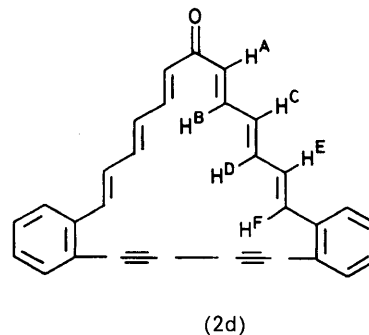
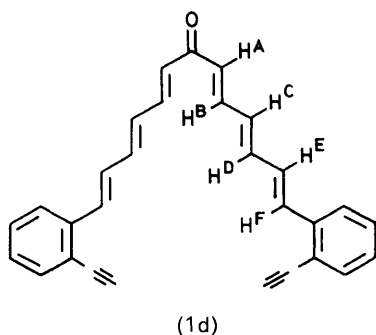
shifts of olefinic protons of compounds (1d) and (2d) demonstrated that the latter is an atropic molecule.

EXPERIMENTAL

Deoxygenated ether, tetrahydrofuran, methanol, and acetone were used to minimize oxidation of the compounds used for aldol condensation, and were prepared immediately before use. The ether and tetrahydrofuran were freed from peroxides by passing through a short column of basic alumina (activity I) followed by flushing with nitrogen. The methanol and acetone were flushed with nitrogen. All methanolic 20% potassium hydroxide solutions were prepared by dissolving potassium hydroxide (10 g) in methanol (50 ml) flushed with nitrogen immediately before use. M.p.s were determined with a hot-stage apparatus. Mass spectra were recorded with a JEOL JMS-OI-SG-2 spectrometer operating at 75 eV, by using the direct inlet system. I.r. and u.v. spectra were taken with a Hitachi EPI-S2 or 124 spectrophotometer, respectively. N.m.r.



dibenzannulenones (2e and f) from the ketones (1e and f), respectively, were unsuccessful [copper(II) acetate in either pyridine or *NN*-dimethylformamide].



As shown by Dreiding models, in the structure for (1d) the acetylene groups are sufficiently close for intramolecular cyclization to (2d), whereas in (1e) the acetylene

spectra were recorded with a Varian XL-100 or a JEOL JNM-MH-60 spectrometer (Me_4Si as internal standard).

5-(*o*-Ethylphenyl)penta-2,4-dienal (6).—Lithium methoxide

[from lithium (409 mg, 0.059 g atom)] in dry methanol (208 ml) was added dropwise with stirring under nitrogen at 80–90 °C over 3 h to *o*-ethynylcinnamaldehyde (3) (6.7 g, 0.0429 mol) and 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide (4) (25.3 g, 0.0589 mol) in dry *NN*-dimethylformamide (208 ml). The mixture was then stirred at 77–78 °C for another 4 h, cooled, poured into water (1500 ml), and extracted with ether. The extracts were washed with saturated aqueous sodium chloride (twice), dried (Na_2SO_4), and concentrated. The product (5) was dissolved in tetrahydrofuran (208 ml) and mixed with 10% hydrochloric acid (208 ml), and the mixture was stirred at room temperature for 3 h. Water (208 ml) was added, the organic layer was separated, and the aqueous layer was extracted with ether. The extracts combined with the organic layer were worked up in the usual way. The residue obtained on concentration was chromatographed on alumina (250 g). Fractions eluted by light petroleum–ether (6 : 4) gave the aldehyde (6) (4.9 g, 63%), obtained as yellow needles from hexane, m.p. 95.5–96.5 °C; *m/e* 182 (M^+ , 80%) and 154 (100); *M* 182.2; ν_{max} (KBr) 3250 ($\text{C}\equiv\text{CH}$), 2100 ($\text{C}\equiv\text{C}$), 1670 (C=O), 1620 (C=C), 1095, and 985 cm^{-1} (*trans*-C=C); λ_{max} (EtOH) 247 (ϵ 13 000), 253 (16 000), 261 (15 400), and 323 nm (18 000); τ (CDCl_3 ; 60 MHz) –0.33 (1 H, d, *J* 8 Hz, CHO), 1.97–2.73 (7 H, m, aromatic and olefinic H), 3.85 (1 H, dd, *J* 16 and 8 Hz, olefinic H), and 6.45 (1 H, s, $\text{C}\equiv\text{CH}$) (Found: C, 85.85; H, 5.3. $\text{C}_{13}\text{H}_{10}\text{O}$ requires C, 85.7; H, 5.55%).

7-(*o*-Ethynylphenyl)hepta-2,4,6-trienal (7).—A solution of lithium methoxide [from lithium (0.406 g, 0.0585 g atom)] in dry methanol (180 ml) was added drop by drop to a stirred solution of the aldehyde (6) (7.1 g, 0.039 mol) and 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide (4) (25.1 g, 0.0585 mol) in *NN*-dimethylformamide (189 ml) at 80–90 °C over 1 h. After an additional 4 h stirring under a slow stream of nitrogen at 77–78 °C, the mixture was poured into water (500 ml), and extracted with ether. The combined extracts were washed with saturated brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was dissolved in tetrahydrofuran (189 ml), mixed with 10% hydrochloric acid (189 ml), and stirred for 3 h at room temperature. The aqueous layer was extracted with ether, and the organic layer combined with the extracts was worked up in the usual fashion. The semisolid obtained was chromatographed on alumina (300 g); elution with light petroleum–ether (55 : 45) afforded the aldehyde (7) (4.8 g, 59%). Recrystallization from hexane–benzene gave orange cubes, m.p. 85.0–86.0 °C, *m/e* 208 (M^+ , 63%) and 179 (100); *M*, 208.2; ν_{max} (KBr) 3250 ($\text{C}\equiv\text{CH}$), 2850 ($\text{C}\equiv\text{O}$), 2200, 2100 ($\text{C}\equiv\text{C}$), 1695 ($\text{C}\equiv\text{O}$), 1630, 1605, 1595 (C=C), 1005, and 905 cm^{-1} (*trans*-C=C); λ_{max} (tetrahydrofuran) 229 (ϵ 20 100), 255 (11 800), 272 (9 880), and 357 nm (55 000); τ (CDCl_3 ; 60 MHz) –0.40 (1 H, d, *J* 8 Hz, CHO), 1.67–2.82 (9 H, m, aromatic and olefinic H), and 3.35 (1 H, dd, *J* 16 and 9 Hz, olefinic H) (Found: C, 86.7; H, 5.9. $\text{C}_{15}\text{H}_{21}\text{O}$ requires C, 86.5; H, 5.8%).

1,11-Bis-(*o*-ethynylphenyl)undeca-1,3,6,8,10-pentaen-5-one (1c). Methanolic 20% potassium hydroxide (3 ml) was added during 18 min to a stirred solution of the ketone (8)² (2.3 g, 0.012 mol) and the aldehyde (6) (2.6 g, 0.014 mol) in deoxygenated ether (113 ml) under nitrogen at 6–7 °C. The solution was stirred at the same temperature for a further 2 h, quenched with acetic acid and then poured into water. The organic layer, combined with benzene extracts from the aqueous layer, was worked up as usual. The

liquid obtained was chromatographed on alumina (150 g); elution with light petroleum–ether (1 : 1) gave the ketone (1c) (2.6 g, 60%). Recrystallization from benzene afforded orange needles, m.p. 157–158.7 °C; *m/e* 360 (M^+ , 85%) and 152 (100); *M*, 360.4; ν_{max} (KBr) 3270, 3200 ($\text{C}\equiv\text{CH}$), 2100 ($\text{C}\equiv\text{C}$), 1640 (C=O), 1620, 1595 (C=C), 1015, and 1000 cm^{-1} (*trans*-C=C); λ_{max} (tetrahydrofuran) 237 (ϵ 31 100), 258sh (23 300), 267 (26 700), 328sh (25 100), and 389 nm (65 900); τ (CDCl_3 ; 100 MHz) 2.31–2.80 (10 H, m, aromatic and olefinic H), 2.89–3.60 (6 H, m, aromatic and olefinic H), 6.62 (1 H, s, $\text{C}\equiv\text{CH}$), and 6.63 (1 H, s, $\text{C}\equiv\text{CH}$) (Found: C, 90.0; H, 5.6. $\text{C}_{27}\text{H}_{20}\text{O}$ requires C, 89.95; H, 5.6%).

1,13-Bis-(*o*-ethynylphenyl)trideca-1,3,5,8,10,12-hexaen-7-one (1d).—A solution of acetone (0.58 g, 0.01 mol) in deoxygenated ether (10 ml) and methanolic 20% potassium hydroxide (1.5 ml) were added simultaneously to a stirred solution of the aldehyde (6) (3.6 g, 0.02 mol) in deoxygenated ether (90 ml) over 15 min at 18 °C. The mixture was stirred for an additional 2 h at the same temperature, acidified with acetic acid (1 ml), and poured into water. The organic layer was combined with benzene extracts from the aqueous layer, and worked up in the usual way to give dark red crystals. Chromatography over alumina (100 g) and elution with ether afforded the product (1d) (3.4 g, 88%). Recrystallization from benzene gave orange needles, m.p. 153.5–154.5 °C; *m/e* 386 (M^+ , 30%) and 149 (100); *M*, 386.4; ν_{max} (KBr) 3250 ($\text{C}\equiv\text{CH}$), 1650, 1620, 1600 (C=O, C=C), and 1000 cm^{-1} (*trans*-C=C); λ_{max} (tetrahydrofuran) 266 (ϵ 21 600), 275 (22 000), 303sh (24 100), 311 (24 500), and 405 nm (72 300); for n.m.r. see Table (Found: C, 89.75; H, 5.7. $\text{C}_{29}\text{H}_{22}\text{O}$ requires C, 90.1; H, 5.75%).

22,23,24,25-Tetrahydrodibenzo[a,g]cycloheptacosen-11-one (2d).—A solution of the ketone (1d) (0.6 g, 0.0016 mol) in pyridine (26 ml) was added to a stirred solution of copper(II) acetate monohydrate (9.0 g) in pyridine (19 ml) at 55 °C over 30 min. The mixture was stirred for another 2 h at 60–75 °C, cooled to room temperature, poured into 6% hydrochloric acid (800 ml), and extracted three times with benzene. The combined extracts were washed successively with aqueous sodium hydrogen carbonate and saturated brine, dried (Na_2SO_4), and concentrated *in vacuo*. The resulting solid was chromatographed on alumina (80 g); elution with light petroleum–ether (1 : 9) gave yellow crystals (0.10 g, 16%) which were recrystallized from benzene to afford yellow needles (2d), m.p. 213 °C (decomp.); *m/e* 384 (M^+ , 60%) and 340 (100); *M*, 384.4; ν_{max} (KBr) 2200 ($\text{C}\equiv\text{C}$), 1620, 1605, 1595 (C=O, C=C), and 1005 cm^{-1} (*trans*-C=C); λ_{max} (tetrahydrofuran) 283sh (ϵ 23 200) and 310 nm (72 800); for n.m.r. see Table. Satisfactory analytical figures were not obtained.

8-(*o*-Ethynylphenyl)octa-3,5,7-trien-2-one (9).—Aqueous 5% sodium hydroxide (103 ml) was added to a stirred solution of the aldehyde (6) (4.0 g, 0.022 mol) in acetone (172 ml) at 16–18 °C over 45 min. After stirring for an additional 2 h at the same temperature, acetic acid was added. The mixture was poured into water, and extracted with ether. The extracts were worked up in the standard way. The resulting oily product was chromatographed on alumina (200 g); elution with light petroleum–ether (6 : 4) yielded partially crystalline ketone (9) (3.8 g, 78%). Recrystallization from benzene gave orange plates, m.p. 139.5–140.5 °C; ν_{max} (KBr) 3300, 3250 ($\text{C}\equiv\text{CH}$), 2100 ($\text{C}\equiv\text{C}$), 1680, 1680 (C=O), 1620, 1600 (C=C), and 1010 cm^{-1} (*trans*-C=C); λ_{max} (tetrahydrofuran) 264 (ϵ 17 100), 281

(13 200), 358sh (53 400), 376 (70 700), and 394 nm (61 000); τ (CDCl₃; 60 MHz) 1.73—2.98 (9 H, m, aromatic and olefinic H), 3.40 (1 H, d, J 16 Hz, olefinic H), 6.40 (1 H, s, C≡CH), and 1.57 (3 H, s, Me) (Found: C, 86.35; H, 6.3. C₁₆H₁₄O requires C, 86.45; H, 6.35%); m/e 248 (60) and 206 (100%) (no M^+).

1,15-Bis-(*o*-ethynylphenyl)pentadeca-1,3,5,8,10,12,14-heptaen-7-one (1e).—Methanolic 20% potassium hydroxide (3.0 ml) was added to a stirred solution of the ketone (9) (3.3 g, 0.014 8 mol) and the aldehyde (7) (3.0 g, 0.014 4 mol) in tetrahydrofuran (128 ml) over 10 min at 10 °C. After a further 3 h stirring at the same temperature under nitrogen, the mixture was poured into water and extracted with benzene. The product, obtained by the usual work-up, was dissolved in benzene and chromatographed on alumina (100 g); elution with benzene-chloroform (1:1) gave a powder (1.58 g, 27%) which was recrystallized from benzene to afford deep red *microcrystals*, m.p. 179.5—180.0 °C; m/e 414 (M^+ , 50%) and 179 (100); M , 412.5; ν_{\max} (KBr) 3 300, 3 250 (—C≡CH), 2 100 (—C≡C—), 1 650 (C=O), 1 620, 1 600, 1 580 (C=C), and 1 005 cm⁻¹ (*trans*-C=C); λ_{\max} (tetrahydrofuran) 265 (ϵ 12 500), 276 (11 900), 282 (11 000), 314sh (16 900), 418 (54 700), and 430sh nm (50 800); τ (CDCl₃; 100 MHz) 2.36—3.64 (22 H, m, aromatic and olefinic H), 6.62 (1 H, s, C≡CH), and 6.63 (s, C≡CH) (Found: C, 89.65; H, 5.85. C₃₁H₂₄O requires C, 90.25; H, 5.85%).

1,17-Bis-(*o*-ethynylphenyl)heptadeca-1,3,5,7,10,12,14,16-

octaen-9-one (1f).—To a stirred solution of the aldehyde (7) (1.58 g, 0.007 6 mol) in deoxygenated ether (32 ml) were added simultaneously a solution of acetone (0.22 g, 0.003 8 mol) in deoxygenated ether (3.6 ml) and methanolic 20% potassium hydroxide (0.36 ml) over 15 min at 15—16 °C under nitrogen. The reaction was continued for a further 2 h at the same temperature under a slow stream of nitrogen, then quenched with acetic acid, and the mixture was poured into water. The organic layer combined with benzene extracts was worked up as usual. The product, dissolved in benzene, was chromatographed on alumina (200 g) and eluted with solvents of increasing polarity. Elution with ether-chloroform (1:9) gave a crude solid which was recrystallized from toluene to give deep red *microcrystals*, m.p. 211 °C (decomp.); m/e 438 (M^+ , 7%) and 149 (100); M , 438.5; ν_{\max} (KBr) 3 300, 3 250 (—C≡CH), 2 100 (—C≡C—), 1 660 (C=O), 1 620, 1 600, 1 580 (C=C), and 1 005 cm⁻¹ (*trans*-C=C); λ_{\max} (tetrahydrofuran) 262 (ϵ 13 300), 272 (12 600), 281sh (11 900), 328 (19 700), 341sh (20 600), and 432 nm (52 000); τ (CDCl₃; 100 MHz) 2.33—3.61 (24 H, m, aromatic and olefinic H) and 6.61 (2 H, s, C≡CH).

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