The Benzannelated Annulenones. Syntheses and Properties of 10-Methylbenzo[*d*]-6,8-bisdehydro[15]annulenone and 12-Methylbenzo[*f*]-8,10-bisdehydro[15]annulenone

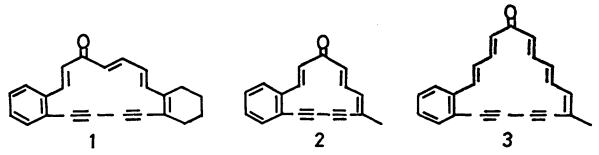
Jūro Ojima* and Yūji Shiroishi

Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930

(Received October 20, 1977)

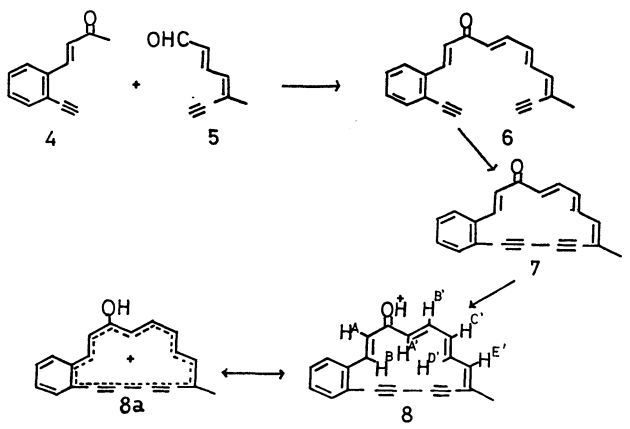
Synthesis of two methylated monobenzannelated bisdehydro[15]annulenones is described. It was found by means of ^{1}H-NMR spectra that the protonated annulenones are diatropic.

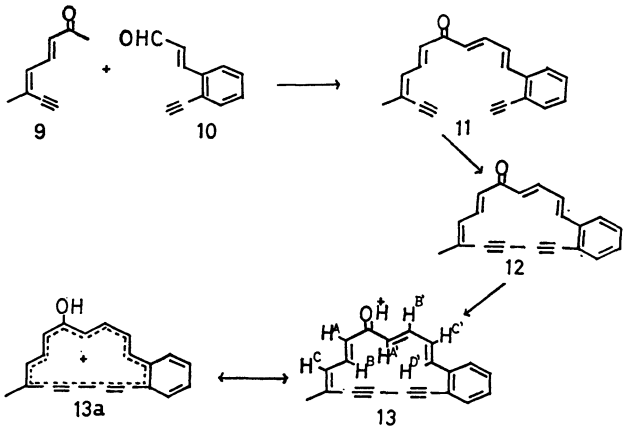
The effect of benzannelation on a conformationally fixed, potentially diatropic bisdehydro[15]annulenone was studied for compounds fused by cyclohexene and benzene rings by Weavers *et al.*[1] It was shown that the monobenzannelated annulenone **1** is atropic, protonated **1** showing diatropic nature. On the other hand, we have shown that the monobenzannelated bisdehydro[13] **2** and [17]annulenone **3** are paratropic themselves.[2] It was therefore decided to prepare the methylated monobenzobisdehydro[15]annulenones **7** and **12**, as well as



the respective protonated species **8** and **13**. As reported by Sondheimer *et al.*, the methyl substituent should be more desirable as compared with cyclohexene moiety for the study of ring current effects.[3] Information on the conjugative effects between the annulenone ring and the benzene nucleus can be obtained from these isomeric compounds, since **7** and **12** have similar geometry and planarity. The present paper deals with the synthesis and properties of two monobenzobisdehydro[15]annulenones, *viz.*, 10-methylbenzo[*d*]-6,8-bisdehydro[15]annulenone **7** and 12-methylbenzo[*f*]-8,10-bisdehydro[15]annulenone **12**.

Synthesis. Aldol condensation of the ketone **4**[4] and the dienyne aldehyde **5**[2c] by means of methanolic potassium hydroxide gave the acyclic ketone **6** in 49% yield. Oxidative coupling of **6**, under Eglinton's conditions using copper(II) acetate monohydrate in pyridine,[5] afforded the desired annulenone **7** as yellow crystals in 31% yield. The condensation of the dienyne ketone **9**[6] and the aldehyde **10**,[7] under the same conditions gave acyclic ketone **11** in 68% yield. Oxidation of **11** with copper(II) acetate monohydrate as before gave the annulenone **12** as yellow crystals in 27% yield. Treatment of **7** or **12** with trifluoroacetic acid gave the corresponding protonated species, **8** (purple; λ_{max} 272 sh, 332 sh, 367, 468 sh, 498, 559 sh, 599 nm) or **13** (red purple; λ_{max} 271, 346, 368 sh, 507 sh, 539 nm), respectively. Quenching of **8** and **13** with aqueous sodium hydrogencarbonate resulted in regeneration of **7** and **12**, respectively.





Properties. Electronic absorption maxima of **7** and **12** are given in Table 1. Little difference in these spectra seems to suggest that a difference in the annelated-position of benzene gives no essential change on the conjugative effects between the benzene nucleus and bisdehydro[15]annulenone skeleton. The NMR spectra indicate that both **7** and **12** are atropic, since not much shifts were observed for the resonances of the olefinic protons of **7** and **12** except for the slightly low field shift of methyl protons, as compared with those of the corresponding acyclic ketone **6** and **11**, respectively(see Experimental). The NMR data of the protonated

Table 1. Electronic absorption maxima of **7** and **12** in ether; λ_{max} (ε, in parentheses)

7	**12**
223 (18700)	228 (25200)
262 sh (13200)	256 (18700)
278 sh (18200)	274 sh (21600)
299 (22100)	302 (28900)
377 (8130)	372 sh (8210)

* Author to whom inquiries should be addressed.

Table 2. ^{1}H-NMR parameters of **8** and **13** in CF_3COOD at 90 MHz
(τ-Values; internal standard, TMS; J values in Hz in parentheses).

Proton	8	13
$H^{A'}$	5.55 d (16)[a]	4.91 d (15.5)[c]
$H^{D'}$	5.43 dd (16, 12)	4.87 d (15.5)[c]
H^{B}	4.75 d (16)[a]	4.80 dd (15.5, 12)
H^{A}	1.92 d (16)	2.60 d (15.5)
$H^{B'}$	1.35 dd (16, 7)[b]	1.90—2.35 (m, 6H)
$H^{C'}$	2.55 dd (16, 7)[b]	
H^{C}	——	
$H^{E'}$	2.17d (12)	
Benzenoid H	1.96—2.08 (m, 3H)	
Benzenoid H	1.32—1.42 (m, 1H)	1.58—1.70 (m, 1H)
$-CH_3$	7.47 s	7.40 s

a), b), c) These are tentative assignments and may be reversed in each group, but most probable values are given in Table 2 referring to the chemical shifts of the related compounds.[1]

monobenzobisdehydro[15]annulenones **8** and **13** (in CF_3COOD) are given in Table 2. Compounds **8** and **13** are diatropic, as indicated by the relative chemical shifts of the inner and outer protons, as well as the low field methyl resonances. We expected that annulenones **7** and **12** would also exhibit the diatropic nature corresponding to the paratropic [13] **2** and [17]annulenone **3**. However, it was found that the protonated species **8** and **13** are diatropic and can be represented by delocalized formulae **8a** and **13a**, respectively. This result is in line with that obtained by Weavers *et al.*[1]

Experimental

Freshly deoxygenated ether and 20% methanolic potassium hydroxide solutions were prepared and used as reported previously.[2b,c] All melting points are uncorrected. Brockmann alumina (Act. II—III) was used for column chromatography. The ^{1}H-NMR, IR, UV, and mass spectra were taken with the instruments Varian EM-930 or Varian XL-100, Hitachi EPI-S2, Hitachi-124, and JEOL-MS-OI-SG-2, respectively. Shoulders in UV spectra are denoted by sh. Wavelength of absorption maximum is recorded in nm and ε-values are given in parentheses. Chemical shifts are given in τ-values with respect to TMS as an internal standard, while the coupling constants (J) are given in Hz.

1-(o-Ethynylphenyl)-9-methyl-1,4,6,8-undecatetraen-10-yn-3-one **6**. To a mixture of the dienyne aldehyde (**5**, 1.00 g, 8.32 mmol) and the ketone (**4**, 1.84 g, 10.8 mmol) in ether (35 ml) was added a 20% methanolic potassium hydroxide solution (3.3 ml) with stirring at −5—0 °C. The mixture was then stirred for 3.5 h at the same temperature under nitrogen atmosphere. Neutralization with acetic acid (4 ml) followed by pouring into water (100 ml) and extraction with benzene gave an organic extract which was worked up as usual. The residue obtained by evaporation of the solvent was chromatographed on alumina (150 g) with light petroleum ether −ethyl ether (20: 80) to give the ketone (**6**, 1.12 g, 49%) as yellow needles from benzene–hexane, mp *ca.* 75 °C (dec), MS: *m/e* 272 (M^+, 100); mol wt, 272.3; IR (KBr disk): 3270, 3240 (−C≡CH), 2100 (−C≡C−), 1670, 1625, 1600 (C=O, C=C), 1005 cm^{-1} (*trans* C=C); UV (ether): λ_{max} 227 (17100), 250 sh (13800), 255 (14400), 277 (10400), 292 (11100), 356 nm (30800); NMR (90 MHz, $CDCl_3$): 1.97 (d, 16, 1H, olefinic H), 2.30—3.80 (m, 10H, olefinic and benzenoid H), 6.53 (s, 2H, −C≡CH), 8.05 (s, 3H, $-CH_3$). Found: C, 88.34; H, 6.00%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

10-Methylbenzo[d]*-6,8-bisdehydro*[*15*]*annulenone* **7**. A solution of **6** (600 mg, 2.20 mmol) in pyridine (46 ml) was added with stirring over a period of 15 min to a solution of copper(II) acetate monohydrate (9.1 g) in pyridine (30 ml) at 50 °C; the mixture was stirred for 3 h at 63 °C. The mixture was then chilled, diluted with benzene (100 ml), and filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene (100 ml×4). The filtrate was washed with dilute hydrochloric acid until it turned slightly acidic. It was then worked up in the usual way. The residual red liquid, after solvent removal, was chromatographed on alumina (150 g) with light petroleum ether–ethyl ether (80: 20—35: 65) to give **7** (185 mg, 31%). Recrystallization from benzene gave yellow needles, mp *ca.* 140 °C (dec); MS: m/*e* 270 (M^+, 45), 269 (100); mol wt, 270.3; IR (KBr disk): 2150 (−C≡C−), 1650, 1620, 1600 (C=O, C=C), 970 cm^{-1} (*trans* C=C); NMR (100 MHz, $CDCl_3$): 1.98—2.05 (m, 1H, benzenoid H), 2.65—3.54 (m, 10H, olefinic and benzenoid H), 7.90 (s, 3H, $-CH_3$); UV: see Table 1. Found: C, 88.59; H, 4.96%. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22%.

1-(o-Ethynylphenyl)-9-methyl-1,3,6,8-undecatetraen-10-yn-5-one **11**. A mixture of ketone (**9**, 0.98 g, 7.30 mmol) and aldehyde (**10**, 1.65 g, 10.6 mmol) in ether (30 ml) was treated with a 20% methanolic potassium hydroxide (3 ml) under nitrogen atmosphere at 0 °C, and stirred at −8——4°C for 4 h. After addition of acetic acid (4 ml), the mixture was worked up as in the preparation of **6**, giving a red liquid. Chromatography of the liquid over alumina (180 g) with light petroleum ether–ethyl ether (75: 25—70: 30) gave the desired ketone (**11**, 1.35 g, 68%) as a partly crystalline, orange liquid, which formed yellow needles from hexane–benzene, mp 97.0—98.6 °C; MS: *m/e* 272 (M^+, 100); mol wt, 272.3; IR (KBr disk): 3300, 3250 (−C≡CH), 2100 (−C≡C−), 1660, 1600 (C=O, C=C), 1000 cm^{-1} (*trans* C=C); UV (ether): λ_{max} 228 sh (17300), 233 (17500), 255 (16300), 263 sh (15400), 295 sh (11200), 352 nm (33000); NMR (100 MHz, $CDCl_3$): 2.14—3.61 (m, 11H, olefinic and benzenoid H), 6.45 (s, 1H, −C≡CH), 6.60 (s, 1H, −C≡CH), 7.95 (s, 3H, $-CH_3$). Found: C, 87.94; H, 5.91%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

12-Methylbenzo[f]*-8,10-bisdehydro*[*15*]*annulenone* **12**. A solution of **11** (1.34 g, 4.92 mmol) in pyridine (50 ml) was added dropwise to a stirred solution of copper(II) acetate monohydrate (20.3 g) in pyridine (68 ml) for 15 min at 50 °C, and the reaction mixture was stirred for 3 h at 63 °C. The mixture was then worked up as in the preparation of **7**, affording a dark red liquid. The liquid was chromatographed on alumina (180 g) and annulenone (**12**, 359 mg, 27%) was eluted with light petroleum ether–ethyl ether (40: 60—30: 70). Recrystallization from benzene–hexane gave yellow needles, mp 176 °C (dec); MS: *m/e* 270 (M^+, 70), 241 (100); mol wt, 270.3; IR (KBr disk): 2150 (−C≡C−), 1645, 1615, 1600 (C=O, C=C), 985 cm^{-1} (*trans* C=C); NMR (100 MHz, $CDCl_3$): 2.12—2.23 (m, 1H, benzenoid H), 2.36—3.64 (m, 10H, olefinic and benzenoid H), 7.87 (s, 3H, $-CH_3$); UV: see Table 1. Found: C, 88.89; H, 5.09%. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22%.

The authors wish to thank Drs. S. Akiyama and F. Ogura, and Prof. M. Nakagawa, Osaka University, for the measurement of the NMR spectra at 100 MHz. One of the authors (J. O.) is grateful to the Ministry

of Education for financial support of this investigation through a Grant-in-Aid (054103, 1975) for Scientific Research.

References

1) R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Lett.*, **1975**, 1043.

2) a) J. Ojima, M. Ishiyama, A. Kimura, and Y. Yokoyama, *Tetrahedron Lett.*, **1975**, 1909; b) J. Ojima, Y. Yokoyama, and M. Enkaku, *Bull. Chem. Soc. Jpn.*, **50**, 1522 (1977); c) J. Ojima, M. Ishiyama, and A. Kimura, *Bull. Chem. Soc. Jpn.*, **50**, 1584 (1977).

3) a) R. L. Wife and F. Sondheimer, *Tetrahedron Lett.*, **1974**, 195; b) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, **42**, 2130 (1977); Although no decision was made on the tropicity of bis(cyclohexene)-annelated bisdehydro[13]annulenone in an early study (P. D. Howes, E. LeGoff, and F. Sondheimer, *Tetrahedron Lett.*, **1972**, 3691), it seems that the compound is paratropic in analogy with the result on the dimethyl analogue (Ref. 3b).

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

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

6) J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **49**, 292 (1976).

7) J. Ojima, A. Kimura, Y. Yokoyama, and T. Yokoyama, *Bull. Chem. Soc. Jpn.*, **48**, 367 (1975).