Synthesis of Dibenzotrisdehydro[16]annulene-1,4-dione and the Related Compounds

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Synthesis of 7,8:13,14-dibenzo-2,9,11-trisdehydro[16]annulene-1,4-dione is described. Attempts to prepare diaza[18]annulene derivatives by ring expansion of the dibenz[16]annulenedione and its dimethyl analog are also described. Examination of ^{1}H NMR spectra indicates that the dibenz[16]annulenedione shows no ring current effect.

In the previous papers, we reported the synthesis of a series of the monocyclic bisdehydroazaannulenes **2**, the higher analogs of pyridine, starting from a series of the bisdehydroannulenones **1**,[1] and showed the alternation of the tropic nature between $[4n+2]\pi$- and $[4n]\pi$-electron systems in the azaannulenes **2** with 14- to 22-membered rings[2] (Chart 1).

The systematic synthesis of azaannulenes **2** starting from the annulenones **1** involved essentially (i) preparation of the corresponding oximes, (ii) Beckmann rearrangement to lactams, and finally (iii) O-alkylation of the lactams with Meerwein's reagent. This successful sequence of reactions stimulated us to expect that, starting from appropriate annulendiones, diazaannulenes, the higher analogs of pyrimidine or pyrazine, might be prepared by application of this general sequence of reactions. In practice, we achieved this expectation only very recently and could prepare the bisdehydromethanodiaza[22]annulene **4**,[3] starting from the bisdehydromethano[20]annulenedione **3**[4] (Chart 1). However, from our studies on methano-bridged bisdehydroannulenes[5] we had initially considered that the methano-bridge should contribute to keep the diazaannulene perimeter rigid, but the diaza[22]annulene **4** proved to be atropic, presumably because the presence of the ethoxyl groups which should be located outside the macrocycle, enhances the ring strain to prevent **4** to adopt planar conformation.

Bearing these results in mind, we were interested in preparing monocyclic diazaannulenes from monocyclic annulenediones according to the reaction sequence described above, since the theoretical calculations predict that pyrimidine or pyrazine has a similar resonance energy and thus similar degree of aromaticity as pyridine.[6]

Results and discussion

Synthesis. For this purpose, we chose 8,13-dimethyl-2,9,11-trisdehydro[16]annulene-1,4-dione (**5**) as the starting diketone (Chart 2). The compound had been prepared by Lombardo and Sondheimer, but the details of the preparation had not been described.[7] Thus we prepared compound **5** according to their procedure with a slight modification, as illustrated in Scheme 1. Treatment of (2*E*, 4*Z*)-5-methyl-2,4-heptadien-6-ynal (**6**)[8] with ethynylenedimagnesium dibromide[9] in benzene and THF afforded a diastereoisomeric mixture of the diol **7** in 36% yield and the compound **7** was relatively unstable for diffused light and air, as reported.[7] This acyclic diol **7** was oxidatively cyclized with copper (II) acetate monohydrate in a mixture of pyridine, diethyl ether, and methanol under high dilution conditions. Chromatography of the product on silica gel afforded a diastereoisomeric mixture of the cyclic diol **8** in 37% yield. Oxidation of **8** with $Ba(MnO_4)_2$[10] in dichloromethane afforded the desired compound **5** in 45% yield.

Treatment of compound **5** with an excess of hydroxylamine hydrochloride in methanol, tetrahydrofuran (THF), and water gave the dioxime **9** as a sole product in 76% yield. The ^{1}H NMR spectrum of **9** (see Experimental) indicated the unsymmetrical structure for this compound as shown in the formula. Double

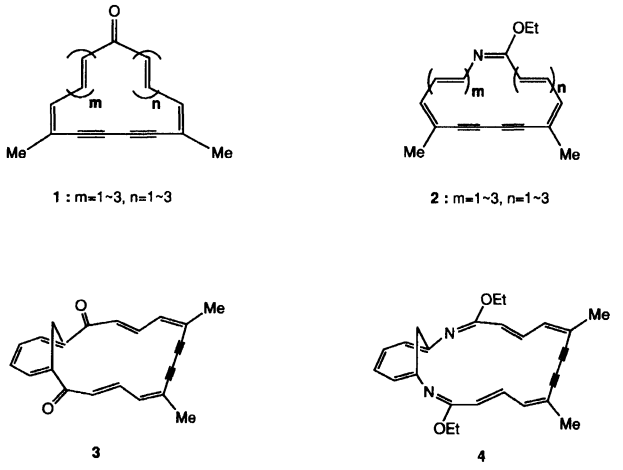


Chart 1.

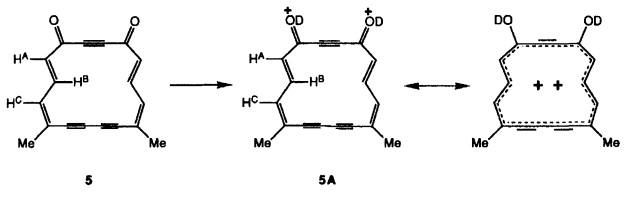
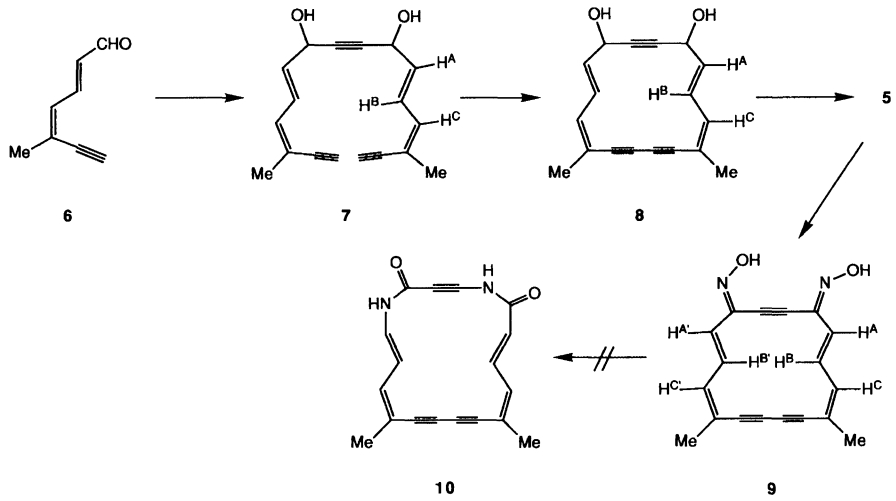


Chart 2.



Scheme 1.

Beckmann rearrangement of the dioxime **9** with phosphorus pentachloride in THF was attempted under several different conditions by changing the reaction temperature and the reaction time, but the desired dilactam **10**[11] was not obtained. An attempt to force the rearrangement using *p*-toluenesulfonyl chloride in pyridine[12] was made, but was also unsuccessful.

We reasoned that the failure to obtain the desired dilactam **10** from **9** is ascribed to the instability of the dilactam **10** under reaction conditions. Then we undertook to prepare the dibenzannelated derivative of the dioxime **9**, since benzannelated dilactams were expected to be more stable than nonannelated ones, as has been observed in the synthesis of monoazaannulenes.[2c,2e]

The dibenz[16]annulene-1,4-dione **14** was prepared by two routes, as illustrated in Scheme 2. The preferred route involved the oxidative cyclization of the acyclic diol **12**. Treatment of *o*-ethynylcinnamaldehyde (**11**)[13] with ethynylenedimagnesium dibromide in benzene and THF afforded a diastereoisomeric mixture of the diol **12** in 49% yield. This acyclic diol **12** was oxidatively cyclized with copper(II) acetate monohydrate in a mixture of pyridine, diethyl ether, and methanol under high dilution conditions. Chromatography of the product on silica gel afforded a diastereoisomeric mixture of the cyclic diol **13** in 65% yield. Oxidation of **13** with $Ba(MnO_4)_2$ in dichloromethane afforded the dibenz[16]annulene-1,4-dione **14** in 74% yield. The second route to compound **14** involved the oxidative cyclization (38%) of the acyclic diketone **15** which was obtained in 55% yield by oxidation of the acyclic diol **12** with $Ba(MnO_4)_2$.

The olefinic protons of compound **14** appear as a pair of doublets at $\delta=8.15$ and 7.10 ($J=16.3$ Hz), the lower-field one being somewhat broader than the higher-field one because of couplings with aromatic protons. This indicates that the compound has a symmetric structure which renders the two CH=CH moieties equivalent and that the double bond has E configuration. The lower-field doublet is assigned to H^B which is β to a carbonyl and α to a benzene ring. Two symmetric conformations **14A** and **14B** are possible that are consistent with the ^1H NMR spectral data. Although the chemical shift data do not afford the answer to the conformation problem, the nuclear Overhauser effect (NOE) experiments give information on this point. Irradiation of H^4 at $\delta=7.71$ enhances the intensity of the H^A signal at $\delta=7.10$ by ca. 8% together with a similar magnitude of NOE on the multiplet signal at $\delta=7.51$—7.45 ascribed to H^3. Interestingly, quite small NOE was detected for the H^B signal upon irradiation of H^4. These NOE results suggest that the major conformation **14** is **14A** but **14B** may have a finite population and be in rapid equilibrium with **14A**.

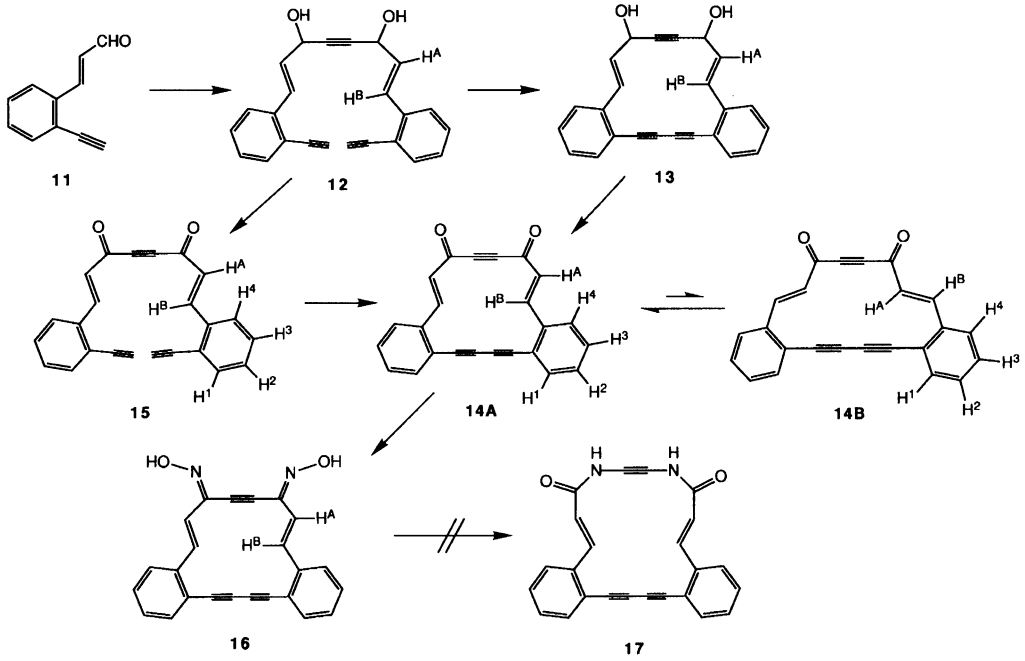
Treatment of the dibenz[16]annulene-1,4-dione **14** with hydroxylamine hydrochloride as before gave the dioxime **16** as a single isomer in 47% yield. The ^1H NMR spectrum suggested a symmetric structure as for the oxime configurations and the structure **16** given in Scheme 2 was tentatively assigned. It is noted that the dioxime **16** gave crystals containing water in a molar ratio of 1:1, as evidenced by the elemental analysis (see Experimental).

Several attempts to convert the dioxime **16** with phosphorus pentachloride into the corresponding dilactam **17** were made, but no trace of the compound **17** was detected.

Thus, in this study all attempts to convert both the dioximes **9** and **16** into the corresponding dilactams **10** and **17**, respectively, were unsuccessful and therefore the objective compounds, diazaanulenes could not be prepared.

The failure of the Beckmann rearrangements might be ascribed partly to the increase of strain upon the ring expansion.

Tropicity of Compound 14. Since the trisde-



Scheme 2.

hydro[16]annulenedione **5** showed diatropicity as 14π-electron system arising from polarization of the two carbonyl groups and even much stronger diatropicity in D_2SO_4, suggesting the formation of the dictation **5A**, the ^1H NMR spectra of the dibenz[16]annulenedione **14** were studied in $CDCl_3$, CF_3CO_2D, and D_2SO_4. The chemical shift data of the compound **14** are listed in Table 1 together with those of the closely related compounds **18**, **5**, and **15**.

Comparison of the proton chemical shifts of the dibenz[16]annulenedione **14** with those of the corresponding acyclic model compound **15** (Table 1) indicates that the compound **14** is atropic, because both the downfield shift of the outer protons H^A and the upfield shift of the inner protons H^B are quite small as compared with those of compound **5** relative to the precursor model **18** (Chart 3). This reflects that annelation of two benzene rings strongly reduces the ring current effect observed for compound **5**, as has been demonstrated for annulene,[14] dehydroannulene,[14] and dehydroannulenone[15] system.

In CF_3CO_2D, the olefinic protons show downfield shifts by 0.17—0.22 ppm from those in $CDCl_3$, while the benzenoid protons show no significant shift. This suggests that deuteration of the carbonyl groups of **14** in this medium is rather insufficient and that compound **14** exists predominantly as a rapidly equilibrating, monodeuterated species (**14C**⇌**14C′**) (Chart 4). Upon changing the medium from CF_3CO_2D to D_2SO_4 , the benzenoid proton signals move further downfield, suggesting that the population of the dideuterated species **14D** increased and the species **14D** is at most weakly diatropic in D_2SO_4. In this medium the signals of the olefinic H^A and H^B protons appear as an extremely broad hump at $\delta=6$—9, suggesting the occurrence of flipping of the CH^A=CH^B moieties (**14D**⇌**14D′**) on the NMR time scale, although variable temperature measurements were not made (Chart 4).

Electronic Spectra. The electronic absorption spectra of the [16]annulene-1,4-diones **5** and **14** are illustrated in Fig. 1. As expected, the spectra are similar

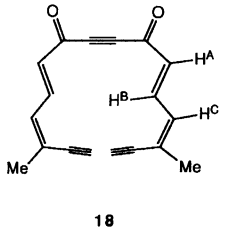


Chart 3.

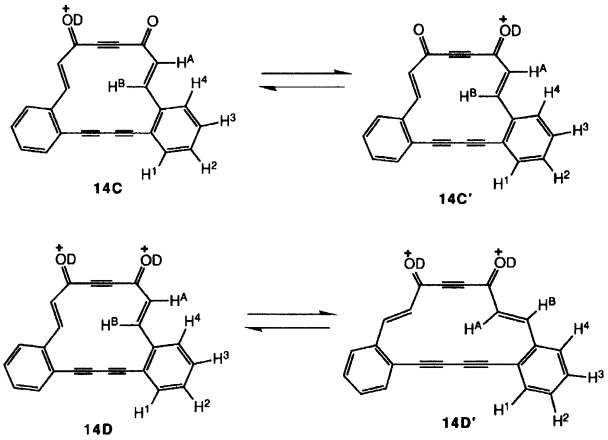


Chart 4.

Table 1. ^{1}H NMR Chemical Shifts of Compounds **5**, **14**, **15**, and **18** (δ-values, TMS as internal standard)

Compound	Solvent	H^A	H^B	H^C	H^1	H^2	H^3	H^4	Me
18[a]	$CDCl_3$	6.30	7.97	6.51					2.08
5[a]	$CDCl_3$	6.59	7.09	6.98					2.16
5[a]	CF_3CO_2D	6.99	6.79	7.32					2.32
5[a]	D_2SO_4	9.07	1.04	9.48					3.35
15	$CDCl_3$	6.96	8.54		7.59	7.43—7.41		7.70	
14	$CDCl_3$	7.10	8.15		7.61	7.51—7.45		7.71	
14	CF_3CO_2D	7.32	8.32		7.64	7.57—7.52		7.79	
14	D_2SO_4	b)	b)		8.17	8.14	7.90	8.45	

a) See Ref. 7. b) Extremely broadened because of conformational interchange on the NMR time scale. See text.

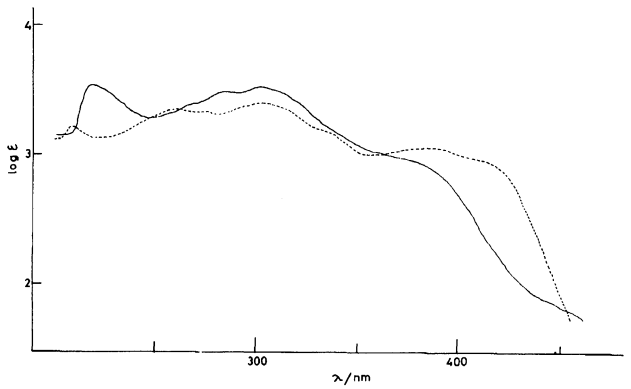


Fig. 1. Electronic spectra of **5** (---) and **14** (—) in THF.

to one another, the shortest and medium wavelength bands of compound **5** appear at shorter wavelength than those of **14**, revealing that the fusion of benzene rings for annulenedione system results in an appreciable bathochromic shift, as has been observed for the benzannelated carbocyclic annulenes.[16] In contrast, the longest wavelength band of **5** appears at longer wavelength than that of **14**, demonstrating that the skeleton of the benzannelated annulenedione **14** contains less delocalized π-electron system than that of the nonannelated one **5**, in accordance with the result from an examination of ^{1}H NMR spectra of these annulenediones described above.

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 disks unless otherwise specified; only significant maxima are reported. Electronic spectra were determined in THF solutions on a Hitachi 220A spectrophotometer (sh=shoulder). Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. ^{1}H NMR spectra were measured on a JEOL FX-90Q or a Bruker AM-500 spectrometer at 89.60 or 500.14 MHz, respectively, 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 assisted by decoupling experiments where necessary. ^{13}C NMR specta were recorded with a Bruker AM-500 spectrometer at 125.76 MHz, TMS being used as an internal standard. The marks p, t, and q denote the primary, tertiary, and quarternary carbons, respectively. Silica gel (Daiso Gel 1001 W or 1002 W) or alumia (Merck, activity II—III) was used for column chromatography. Progress of reactions was followed by TLC using aluminum sheets precoated with Merck silica gel F_{254}. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride before use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen atmosphere before use. Organic extracts were washed with brine and dried over anhydrous Na_2SO_4 prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

3,14-Dimethyl-3,5,11,13-hexadecatetraene-1,8,15-triyne-7,10-diol (7). A solution of ethynylenedimagnesium dibromide,[9] prepared from magnesium (0.42 g, 17.2 mmol), ethyl bromide (1.6 cm^3, 20.4 mmol), and gaseous acetylene, in dry benzene (11 cm^3) and THF (11 cm^3) was added dropwise during 10 min to a stirred solution of (2*E*, 4*Z*)-5-methyl-2,4-heptadien-6-ynal (**6**)[8] (3.57 g, 29.7 mmol) in dry benzene (120 cm^3) at room temperature and the mixture was stirred for 8 h at room temperature under argon.

Then sat. aq NH_4Cl (80 cm^3) was added to the mixture with ice-cooling. Then the mixture was poured onto H_2O and extracted with benzene. The residue obtained after removal of the solvent was chromatographed on Daiso Gel (3.2×7.0 cm). The fractions eluted with benzene–acetone (9:1) afforded the acyclic diol **7** (1.41 g, 36%; lit,[7] quantitative yield) as an unstable brown liquid; No satisfactory mass spectra could be obtained by direct-inlet method; IR (neat) 3350 (OH), 3300 (C≡CH), 2100 (C≡C), and 970 cm^{-1} (*E*-HC=CH); UV 256 (sh, ε 28600), 264 (31700), 275 (25600), 311 (1470), and 327 nm (sh, 1200); ^{1}H NMR (90 MHz) δ=6.83 (2H, dd, J=15 and 11 Hz, H^B), 6.28 (2H, d, J=11 Hz, H^C), 5.82 (2H, dd, J=15 and 6 Hz, H^A), 4.98 (2H, d, J=6 Hz, CHOH), 3.46 (2H, br s, OH), 3.31 (2H, s, C≡CH), and 1.92 (6H, s, Me). Although compound **7** was a ca. 1:1 mixture of the *dl* and meso diastereomers, as clearly indicated for compound **8** (see below), no apparent difference in chemical shifts between the diastereomers was observed at 90 MHz.

Found: C, 78.55; H, 7.39%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%. Attempts to improve the elemental analysis

failed.

8,13-Dimethyl-5,7,13,15-cyclohexadecatetraene-2,9,11-triyne-1,4-diol (8). This reaction was performed using a high-dilution apparatus. A solution of the acyclic diol **7** (845 mg, 3.17 mmol) in pyridine (102 cm^3) and ether (51 cm^3) was added dropwise during 7 h to a stirred and refluxing solution of copper(II) acetate monohydrate (10.4 g) in a mixture of pyridine (118 cm^3), ether (163 cm^3), and MeOH (38 cm^3) at 48 °C. After being stirred for further 1 h, the mixture was poured onto H_2O and extracted with benzene. The extracts were washed with 3 mol dm^{-3} HCl until they turned acidic, and then with aq sodium hydrogencarbonate and dried. The residue after removal of the solvent was chromatographed on Daiso Gel (3.2×7.0 cm). The fractions eluted with benzene–acetone (4:1) afforded the cyclic diol **8** (313 mg, 37%; lit,[7] ca. 50%) as pale yellow needles, mp 104—105 °C (dec), from hexane–benzene; MS *m/z* 264 (M^+, 4%) and 52 (100); mol wt 264.3; IR 3200 (OH), 2200 (C≡C), and 985 cm^{-1} ((*E*)-HC=CH); UV 255 (ε 30000), 262 (35000), 292 (7200), 311 (7100), 329 (7700), 347 (9000), and 372 nm (7200). ^1H and ^{13}C NMR indicated that compound **8** was a ca. 1:1 mixture of the *dl* and meso diastereomers. ^1H NMR (500 MHz) δ=6.96 and 6.90 (2H, dd, *J*=15.5 and 10.1 Hz, H^B), 6.47 and 6.45 (2H, d, *J*=10.1 Hz, H^C), 6.08 (2H, br d, *J*=15.5 Hz, H^A), 5.28 and 5.21 (2H, d, *J*=3.7 Hz, C<u>H</u>OH), 2.96 and 2.58 (2H, br s, OH), 1.902 and 1.896 (6H, s, Me); ^{13}C NMR (125 MHz; $CDCl_3$) δ=139.2 (t, both isomers), 132.0 and 131.9 (t),129.8 and 129.7 (t), 120.24 and 120.18 (q), 86.4 and 85.90 (q, ≡C), 86.1 and 85.94 (q, ≡C), 80.44 and 80.41 (q, ≡C), 63.3 and 63.1 (CHOH), and 21.2 (p, both isomers).

Found: C, 81.49; H, 6.37%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

8,13-Dimethyl-2,9,11-trisdehydro[16]annulene-1,4-dione (5). The cyclic diol **8** (102 mg, 0.39 mmol) in dry CH_2Cl_2 (70 cm^3) was stirred with activated $Ba(MnO_4)_2$[10] (0.5 g) for 40 min at room temperature. The mixture was filtered by suction. The filtrate was concentrated in vacuo. The residue was chromatographed on Daiso Gel (3.2×5.5 cm). The fractions eluted with benzene–CH_2Cl_2 (1:1) afforded the [16]annulenedione **5** (45 mg, 45%) as yellow needles, mp 139—140 °C (dec) (lit,[7] 100 °C (dec)), from hexane–benzene; MS *m/z* 260 (M^+, 13%) and 189 (100); mol wt 260.2; IR 2190 (C≡C), 1630 (C=O), 1605 (C=C), and 980 cm^{-1} ((*E*)-HC=CH); UV 253 (sh, ε 21000), 263 (22400), 274 (sh, 21400), 301 (25000), 338 (sh, 14000), 386 (11200), and 416 nm (sh, 8500) and see Fig. 1; ^1H NMR (500 MHz) δ=7.05 (2H, dd, *J*=15.5 and 11.2 Hz, H^B), 6.96 (2H, dq, *J*=11.2 and 0.4 Hz, H^C), 6.56 (2H, d, *J*=15.5 Hz, H^A), and 2.15 (6H, s, Me); ^{13}C NMR (125 MHz; $CDCl_3$) δ=177.0 (q), 145.2 (t), 139.7 (t), 132.9 (t), 130.4 (q), 87.2 (q, ≡C), 83.9 (q, ≡C), 83.9 (q, ≡C), and 21.9 (p).

Found: C, 82.77; H, 4.67%. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65%.

1,4-Bis(hydroxyimino-8,13-dimethyl-5,7,13,15-cyclohexadecatetraene-2,9,11-triyne (9). A solution of hydroxylamine hydrochloride (828 mg, 12 mmol) in H_2O (4.0 cm^3) was added in one portion to a stirred solution of the diketone **5** (53 mg, 0.20 mmol) in MeOH (10 cm^3) and THF (3 cm^3) and the solution was stirred for 10 h at 35 °C. Then a further quantity of hydroxylamine hydrochloride (828 mg, 12 mmol) in H_2O (4 cm^3) was added and stirring was continued for further 16 h at room temperature. Then the solution was poured onto H_2O and the mixture was extracted with $CHCl_3$. The residue after removal of the solvent was chromatographed on alumina (3.2×5.2 cm). The fractions eluted with 4% EtOH in $CHCl_3$ afforded the dioxime **9** (45 mg, 76%). It formed yellow microcrystals, mp 210—212 °C (dec), from THF; MS *m/z* 290 (M^+, 23%) and 203 (100); mol wt 290.3; IR 3200 (OH), 2175 (C≡C), 1630 (C=N), 1005, and 980 cm^{-1} ((*E*)-HC=CH); UV 250 (ε 21700), 310 (46200), 312 (47400), 372 (sh, 6200), 390 (6700), and 424 nm (4800); ^1H NMR (90 MHz; DMSO-d_6) δ=12.65 (1H, s, OH, disappeared by addition of D_2O), 12.45 (1H, s, OH, disappeared by addition of D_2O), 7.34 (1H, dd, *J*=15 and 10 Hz, H^B or $H^{B'}$), 7.28 (1H, dd, *J*=15 and 10 Hz, H^B or $H^{B'}$), 7.18 (1H, d, *J*=15 Hz, H^A or $H^{A'}$), 6.92 (1H, d, *J*=10 Hz, H^C or $H^{C'}$), 6.90 (1H, d, *J*=10 Hz, H^C or $H^{C'}$), 6.61 (1H, d, *J*=15 Hz, H^A or $H^{A'}$), and 1.90 (6H, br s, Me).

Found: C, 74.61; H, 5.03; N, 9.32%. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65%.

1,8-Bis(*o*-ethynylphenyl)-1,7-octadien-4-yne-3,6-diol (12). To a stirred solution of *o*-ethynylcinnamaldehyde (**11**)[13] (1.91 g, 12.2 mmol) in dry benzene (110 cm^3) was added dropwise during 10 min a solution of ethynylenedimagnesium dibromide[9] in THF and benzene (6.0 cm^3; 3.91 mmol) at room temperature under argon. After being stirred for 1.5 h, a further quantity of ethynylenedimagnesium dibromide in THF and benzene (5.0 cm^3; 3.26 mmol) was added. After being stirred for a total of 5.5 h, the mixture was worked up as for the isolation of compound **7** except for the use of CH_2Cl_2 as the extraction solvent. The dark red liquid obtained after removal of the solvent was chromatographed on Daiso Gel (3.2×8.0 cm). The fractions eluted with benzene–acetone (9:1) afforded a diastereoisomeric mixture of the acyclic diol **12** (1.02 g, 49%). It formed white needles, mp 129—130 °C, from hexane–benzene; MS *m/z* 338 (M^+, 1%) and 128 (100); mol wt 338.3; IR 3300 (OH), 3280 (C≡CH), 2110 (C≡C), and 960 cm^{-1} ((*E*)-HC=CH); UV 230 (ε 41600), 234 (41600), 240 (39300), 252 (26500), 258 (31900), 266 (35800), 277 (sh, 25800), and 300 nm (sh, 1400); ^1H NMR (90 MHz) δ=7.63—7.14 (8H, m, Ar-H), 7.32 (2H, d, *J*=16 Hz, H^B), 6.39 (2H, dd, *J*=16 and 6 Hz, H^A), 5.19 (2H, t, *J*=6 Hz, C<u>H</u>OH), 3.29 (2H, s, C≡CH), and 2.14 (2H, d, *J*=6 Hz, OH, disappeared by addition of D_2O).

Found: C, 84.95; H, 5.43%. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%.

7,8:13,14-Dibenzo-5,7,13,15-cyclohexadecatetraene-2,9,11-triyne-1,4-diol (13). This reaction was performed using a high-dilution apparatus. A solution of the diol **12** (537 mg, 1.59 mmol) in a mixture of pyridine (70 cm^3), ether (18 cm^3), and MeOH (18 cm^3) was added dropwise during 6 h to a stirred and refluxing solution of copper(II) acetate monohydrate (2.16 g) in a mixture of pyridine (400 cm^3), ether (400 cm^3), and MeOH (100 cm^3) at 50 °C. After being stirred for further 1 h, the mixture was worked up as for the isolation of compound **8** except for the use of CH_2Cl_2 as the extraction solvent. The residue after removal of the solvent was chromatographed on Daiso Gel (3.2×8.0 cm). The fractions eluted with 10% acetone in benzene afforded a diastereoisomeric mixture of the cyclic diol **13** (347 mg, 65%). It formed white needles, mp 179—181 °C (dec), from hexane–benzene; MS *m/z* 336 (M^+, 27%) and

276 (100); mol wt 336.3; IR 3300 (OH), 2220 (C≡C), and 970 cm^{-1} ((*E*)-HC=CH); UV 222 (ε 45200), 266 (35400), 312 (14200), 331 (21000), and 358 nm (19600); ^1H NMR (90 MHz) δ=7.54—7.12 (8H, m, Ar-H), 7.22 (2H, d, J=16 Hz, H^B), 6.66 (2H, dd, J=16 and 5 Hz, H^A), 5.23 (2H, m, CHOH), and 2.00 (2H, br s, OH, disappeared by addition of D_2O).

Found: C, 85.44; H, 5.00%. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%.

7,8:13,14-Dibenzo-2,9,11-trisdehydro[16]annulene-1,4-dione (14). The cyclic diol **13** (357 mg, 1.06 mmol) in dry CH_2Cl_2 (130 cm) was stirred with activated $Ba(MnO_4)_2$ (1.50 g) at room temperature for 40 min. The mixture was filtered by suction. The filtrate was concentrated in vacuo and the residue was chromatographed on Daiso Gel (3.2×6.5 cm). The fractions eluted with benzene–CH_2Cl_2 (4:1) afforded the dibenz[16]annulenedione **14** (261 mg, 74%). It formed orange needles, mp 190—192 °C (dec), from hexane–benzene; MS m/z 332 (M^+, 47%) and 275 (100); mol wt 332.3; IR 2200 (C≡C), 1630 (C=O), and 980 cm^{-1} ((*E*)-HC=CH); UV 269 (sh, ε 24900), 283 (30800), 303 (33100), and 382 nm (sh, 8100) and see Fig. 1; ^1H NMR (500 MHz) δ=8.15 (2H, d, J=16.3 Hz, H^B), 7.70 (2H, d, J=7.3 Hz, H^4), 7.61 (2H, dd, J=7.1 and 1.8 Hz, H^1), 7.50 (2H, td, J=7.4 and 1.6 Hz, H^3), 7.47 (2H, td, J=7.3 and 1.7 Hz, H^2), and 7.10 (2H, d, J=16.3 Hz, H^A); (500 MHz; CF_3CO_2D) δ=8.32 (2H, d, J=16.1 Hz, H^B), 7.79 (2H, m, H^4), 7.64 (2H, m, H^1), 7.57—7.52 (4H, m, H^2 and H^3), and 7.32 (2H, d, J=16.1 Hz, H^A); (500 MHz; D_2SO_4) δ=8.8—6.6 (4H, br, H^A and H^B), 8.45 (2H, br s, H^4), 8.17 (2H, d, J=7.4 Hz, H^1), 8.14 (2H, t, J=7.4 Hz, H^2), and 7.90 (2H, t, J=7.4 Hz, H^3); ^{13}C NMR (125 MHz; $CDCl_3$) δ=176.3 (q), 146.3 (t), 137.5 (t), 132.4 (t), 130.9 (t), 130.1 (t), 130.0 (t), 128.3(t) 122.1 (q), 84.1 (q, ≡C), 82.7 (q, ≡C), and 80.4 (q, ≡C); (125 MHz; CF_3CO_2D) δ=182.2 (q), 153.9 (t), 138.5 (q), 134.5 (t), 134.3 (t), 132.1 (t), 130.6 (t), 130.1 (t), 125.3 (q), 87.9 (q, ≡C), 84.3 (q, ≡C), and 82.6 (q, ≡C).

Found: C, 86.57; H, 3.78%. Calcd for $C_{24}H_{12}O_2$: C, 86.73; H, 3.64%.

1,8-Bis(*o*-ethynylphenyl)-1,7-octadien-4-yne-3,6-dione (15). The diol **12** (1.19 g, 3.52 mmol) in dry CH_2Cl_2 (150 cm^3) was stirred with activated $Ba(MnO_4)_2$ (2.10 g) at room temperature for 7.5 h. The mixture was filtered by suction. The filtrate was concentrated in vacuo and the residue was chromatographed on Daiso Gel (3.2×7.0 cm). The fractions eluted with benzene–CH_2Cl_2 (9:1) afforded the diketone **15** (642 mg, 55%). It formed pale yellow needles, mp 139—142 °C (dec), from hexane–$CHCl_3$; MS m/z 334 (M^+, 2%) and 155 (100); mol wt 334.3; IR 3250 (C≡CH), 2100 (C≡C), 1640, 1630 (C=O), and 980 cm^{-1} ((*E*)-HC=CH); UV 233 (ε 37600) and 318 nm (32400); ^1H NMR (500 MHz) δ=8.54 (2H, d, J=16.3 Hz, H^B), 7.70 (2H, m, H^4), 7.59 (2H, m, H^1), 7.43—7.41 (4H, m, H^2 and H^3), 6.96 (2H, d, J=16.3 Hz, H^A), and 3.41 (2H, s, C≡CH); ^{13}C NMR (125 MHz; $CDCl_3$) δ=176.8 (q), 148.1 (t), 135.3 (q), 133.7 (t), 131.1 (t), 129.3 (t), 129.0 (t), 126.5 (t), 124.1 (q), 84.4 (q, ≡C–H), 84.2 (q, ≡C), and 80.6 (q, ≡C).

Found: C, 86.17; H, 4.41%. Calcd for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22%.

The Dibenz[16]annulenedione 14 from the Acyclic Diketone 15. This reaction was performed using a high-dilution apparatus. A solution of the diketone **15** (576 mg, 1.72 mmol) in pyridine (70 cm^3) and ether (35 cm^3) was added dropwise during 4.5 h to a stirred and refluxing solution of copper(II) acetate monohydrate (3.5 g) in a mixture of pyridine (80 cm^3), ether (160 cm^3), and MeOH (26 cm^3) at 50 °C. After being stirred for further 1.5 h at 50 °C, the mixture was worked up as for the isolation of the compound **8**. The product was chromatographed on Daiso Gel (3.2×7.0 cm). The fractions eluted with benzene–CH_2Cl_2 (4:1) afforded the dibenz[16]annulenedione **14** (218 mg, 38%).

1,4-Bis(hydroxyimino)-7,8:13,14-dibenzo-5,7,13,15-cyclohexadecatetraene-2,9,11-triyne (16). A solution of hydroxylamine hydrochloride (1.80 g, 26 mmol) in H_2O (12 cm^3) was added in one portion to a stirred solution of the diketone **14** (218 mg, 0.66 mmol) in MeOH (40 cm^3) and THF (90 cm^3), and the solution was stirred for 9.5 h at 40 °C. Then a further quantity of hydroxylamine hydrochloride (1.80 g) in H_2O (12 cm^3) was added and stirring was continued for further 7 h at 40 °C. The mixture was worked up as for the isolation of compound **9**. The product was chromatographed on Daiso Gel (2.6×8.5 cm). The fractions eluted with benzene–acetone (9:1) afforded the dioxime **16** (113 mg, 47%). It formed white needles, mp 242—244 °C (dec), from THF; MS m/z 362 (M^+, 18%) and 317 (100); mol wt 362.3; IR 3200 (OH), 2200 (C≡C), 1640 (C=N), and 965 cm^{-1} ((*E*)-HC=CH); UV 225 (ε 38000), 284 (54500), 299 (43800), 341 (14100), and 364 nm (sh, 12500); ^1H NMR (90 MHz; DMSO-d_6) δ=ca. 12.8 (2H, br s, OH, disappeared by addition of D_2O), 8.03 (2H, d, J=16.5 Hz, H^B), 7.70—7.43 (8H, m, Ar-H), and 7.28 (2H, d, J=16.5 Hz, H^A).

Found: C, 75.61; H, 3.98; N, 7.01%. Calcd for $C_{24}H_{14}N_2O_2 \cdot H_2O$: C, 75.78; H, 4.24; N, 7.37%.

Attempted Beckmann Rearrangement of the Dioximes 9 and 16. a) Using Phosphorus Pentachloride. A solution of phosphorus pentachloride (100 mg, 0.476 mmol) in THF (5 cm^3) was added dropwise to a stirred solution of the dioxime **9** (71 mg, 0.245 mmol) in THF (30 cm^3) during 10 min at −7 °C and the mixture was stirred overnight at room temperature. Then the mixture was poured onto H_2O and then aq sodium hydrogencarbonate was added to the mixture. The mixture was extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on Daiso Gel (2.6×7.5 cm). The early fractions eluted with 10% ethyl acetate in CH_2Cl_2 afforded a pale yellow solid (2 mg), which showed the ion peak at m/z 290 (mol wt 290.3 for the desired dilactam **10**) in the mass spectrum. However, the ^1H and ^{13}C NMR spectral data were found to be inconsistent with the structure of the dilactam **10**.

The later fractions eluted with ethyl acetate–CH_2Cl_2 afforded the recovered dioxime **9** (32 mg).

The rearrangement reaction for the dioxime **16** was carried out in almost the same conditons as that for the dioxime **9** described above. However, no desired dilactam **17** could be obtained. Also, these reactions were attempted under serveral different conditions by changing the reactin temperature and reaction time, but all attempts were unsuccessful.

b) Using *p*-Toluenesulfonyl Chloride. To a stirred solution of the dioxime **9** (26 mg, 0.09 mmol) in pyridine (1 cm^3) was added in one portion *p*-toluenesulfonyl chloride (17 mg, 0.09 mmol) and the mixture was stirred for 5 h at 40 °C. The mixture was poured onto H_2O and extracted

with $CHCl_3$. The extracts were washed successively with 10% HCl and aq sodium hydrogencarbonate, and dried. The residue after removal of the solvent was chromatographed on alumina (2.2×6.5 cm). The fractions eluted with hexane–CH_2Cl_2 (1:1) afforded a yellow solid (2 mg). However, the structure of the material was not established.

The later fractions eluted with 10% ethanol in CH_2Cl_2 afforded the recovered dioxime **9** (8 mg).

This reaction for the dioxime **9** was also attempted under several different conditions, but all attempts were unsuccessful.

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References

1) a) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, **42**, 2130 (1977); J. Ojima, Y. Shiroishi, K. Wada, and F. Sondheimer, *J. Org. Chem.*, **45**, 3564 (1980); J. Ojima, K. Wada, and M. Terasaki, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 51.

2) a) J. Ojima, T. Nakada, M. Nakamura, and E. Ejiri, *Tetrahedron Lett.*, **26**, 635 (1985); b) J. Ojima, T. Nakada, E. Ejiri, and M. Nakamura, *Tetrahedron Lett.*, **26**, 639 (1985); c) J. Ojima, T. Nakada, E. Ejiri, and M. Nakamura, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 933; d) J. Ojima, Y. Yagi, T. Nakada, S. Manaka, E. Ejiri, S. Ishizaka, and Y. Shiraiwa, *Chem. Lett.*, **1985**, 1767; e) J. Ojima, Y. Yagi, E. Ejiri, S. Ishizaka, and T. Kato, *Bull. Chem. Soc. Jpn.*, **59**, 1791 (1986); f) J. Ojima, Y. Yagi, S. Manaka, T. Nakada, and Y. Shiraiwa, *Bull. Chem. Soc. Jpn.*, **59**, 1801 (1986).

3) H. Higuchi, H. Yamamoto, J. Ojima, and G. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 975.

4) G. Yamamoto, H. Higuchi, Y. Takai, and J. Ojima, *Chem. Lett.*, **1992**, 875; H. Higuchi, K. Asano, K. Nakafuku, Y. Takai, J. Ojima, and G. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 89.

5) J. Ojima, E. Ejiri, T. Kato, S. Kuroda, S. Hirooka, and M. Shibutani, *Tetrahedron Lett.*, **27**, 2467 (1986); J. Ojima, E. Ejiri, T. Kato, M. Nakamura, S. Kuroda, S. Hirooka, and M. Shibutani, *J. Chem. Soc., Perkin Trans. 1*, **1987**, 831; J. Ojima, S. Fujita, M. Masumoto, E. Ejiri, T. Kato, S. Kuroda, Y. Nozawa, and H. Tatemitsu, *J. Chem. Soc., Chem. Commun.*, **1987**, 534; J. Ojima, S. Fujita, M. Masumoto, E. Ejiri, T. Kato, S. Kuroda, Y. Nozawa, S. Hirooka, Y. Yoneyama, and H. Tatemitsu, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 385.

6) A. R. Katritzky, M. Karelson, and N. Malhotra, *Heterocycles*, **32**, 127 (1991).

7) L. Lombardo and F. Sondheimer, *Tetrahedron Lett.*, **1976**, 3841.

8) J. Ojima, M. Kirita, Y. Murosawa, and T. Nakada, *Bull. Chem. Soc. Jpn.*, **56**, 1467 (1983).

9) L. Brandsma, "Preparative Acetylenic Chemistry," 2nd ed, Elsevier, Amsterdam (1988), p. 28.

10) H. Firouzabadi and E. Ghaderi, *Tetrahedron Lett.*, **1978**, 839.

11) The indicated structures for the dilactams **10** and **17** were supposed on the basis of an assumption that Beckmann rearrangement proceeds in *anti*-migration with respect to hydroxyl group; see: L. G. Donaruna and W. L. Heldt, *Org. React.*, **11**, 1 (1960), and see also Ref. 2.

12) L. A. Paquette, H. C. Berk, and S. V. Ley, *J. Org. Chem.*, **40**, 902 (1975); J. Ojima, M. Masumoto, S. Kuroda, S. Hirooka, and Y. Nozawa, *Bull. Chem. Soc. Jpn.*, **60**, 3803 (1987).

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

14) For reviews, see: M. Nakagawa, *Pure Appl. Chem.*, **44**, 885 (1975); R. H. Mitchell, *Isr. J. Chem.*, **20**, 594 (1980).

15) a) J. Ojima and M. Fujiyoshi, *Chem. Lett.*, **1978**, 569; *J. Chem. Soc., Perkin Trans. 1*, **1980**, 466; b) J. Ojima, K. Kanazawa, K. Kusaki, and K. Wada, *Chem. Lett.*, **1978**, 1099; *J. Chem. Soc., Perkin Trans. 1*, **1980**, 473; c) J. Ojima, K. Wada, and K. Kanazawa, *Chem. Lett.*, **1979**, 1035; J. Ojima, K. Wada, K. Kanazawa, and Y. Nakagawa, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 947; d) J. Ojima, K. Wada, Y. Nakagawa, M. Terasaki, and Y. Juni, *Chem. Lett.*, **1980**, 225; *J. Chem. Soc., Perkin Trans. 1*, **1982**, 31; e) J. Ojima, Y. Nakagawa, K. Wada, and M. Terasaki, *Chem. Lett.*, **1980**, 1299; *J. Chem. Soc., Perkin Trans. 1*, **1982**, 43.

16) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, **42**, 1960 (1977).