controlled by localization of excitation energy. Rather it appears that this reaction is being guided by a reluctance of the β position of the naphthalene moiety to involve itself in the bridging process. This can be ascribed to residual aromaticity still present in the triplet, with the result that an excessive electron localization energy is demanded in the excited state paralleling the ground-state situation.

The results and deductions regarding the excited-state reactivity preferences are summarized in Chart I.

Chart I. Summary of and Deductions from the Photochemistry

Reactant and conditions	Bonding[a]
1,2-NB,[b] sensitized	α-Naphtho-vinyl
1,2-NB, direct	α-Naphtho-vinyl (17%), vinyl-vinyl (13%) Naphtho-vinyl cycloaddition (70%)
2,3-NB, sensitized	Vinyl-vinyl
2,3-NB, direct	Vinyl-vinyl
Order of Preference of Processes	
For the triplet	α-Naphtho-vinyl bridging > Vinyl-vinyl bridging > β-Naphtho-vinyl bridging
For the singlet	α-Naphtho-vinyl bridging $\simeq$ Vinyl-vinyl bridging > β-Naphtho-vinyl bridging

[a] All are two-center bridging processes except for the four-center cycloaddition indicated. [b] Naphthobarrelene (NB).

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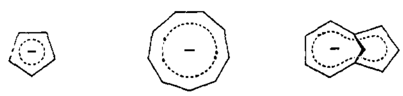
The Synthesis of the 1-Methoxy-2,8,10-tridehydro[17]annulenyl Anion, an Aromatic 17-Membered Ring Cyclic System[1]

Sir:

The cyclopentadienyl anion (**1**) is a well-known member ($n = 1$) of a series of aromatic monoanions containing $(4n + 2)$ out-of-plane π electrons in a single $(4n + 1)$-membered carbocyclic ring.[2] The only higher members known are the cyclononatetraenyl ([9]annulenyl) anion (**2**, $n = 2$)[3] and the 1,5-methano-



1 **2** **3**

cyclononatetraenyl anion (**3**, $n = 2$),[4] both of which also proved to be aromatic. It was of interest to investigate the synthesis of macrocyclic members of this series in order to determine whether they would also show aromatic character.[5] We now report the synthesis of the 1-methoxy-2,8,10-tridehydro[17]annulenyl anion (**8**), the first known macrocyclic member ($n = 4$). The anion **8** is isoelectronic with [18]annulene[6] and was found to possess marked aromaticity.

It has been reported by our group that treatment of **4** in freshly distilled tetrahydrofuran with potassium *t*-butoxide in *t*-butyl alcohol gives rise to two unstable red substances.[7] These substances are best obtained by a modified process,[8] whereby each is formed in *ca.* 10–15% yield. The compound more strongly adsorbed on alumina proved to be the 2,8,10-tridehydro[17]-annulenone **5**. It formed unstable dark red crystals which decomposed on attempted melting point determination; mass spectrum (all at 70 eV), *m/e* 230 (M) and 202 (M − CO, base peak); $\lambda_{max}^{Et_2O}$ 293 nm (ϵ 61,000), 304 (74,000), 463 (1000), *ca.* 500 sh (820), and *ca.* 540 sh (360); $\nu_{max}^{CHCl_3}$ (cm^{-1}) 2190 (C≡C) and 1625 (C=O). The nmr spectrum ($CDCl_3$, 100 MHz) of **5** consisted of three superimposed quartets (total 3 H) at τ −0.50, −0.26, and −0.10 (H_5, H_{14}, and H_{16}; $J_{5,6} = J_{14,13} = J_{16,15} = 12$ Hz, $J_{5,4} = J_{14,15} = J_{16,17} = 16$ Hz), a multiplet (2 H) at 3.53–3.88 (H_6 and H_{13}), a quartet (1 H) at 4.00 (H_{15}; $J_{15,16} = 12$ Hz, $J_{15,14} = 16$ Hz), a doublet (1 H) at 4.28 (H_{17}; $J_{17,16} = 16$ Hz), a doublet (1 H) at 4.70 (H_4; $J_{4,5} = 16$ Hz), and a doublet (2 H) at 4.84 (H_7 and H_{12}; $J_{7,6} = J_{12,13} = 10$ Hz). Catalytic hydrogenation of **5** in ethanol over 10% palladium–charcoal led to cycloheptadecanone. The data show **5** to be a dehydro[17]annulenone made up of three acetylenic, three *trans*, and two *cis* ethylenic bonds, as well as a carbonyl group. The sequence of these groups, as in **5**,[9] follows from its nmr spectrum and the nmr spectra of the derived substances described below. The low-field position of the inner protons and the high-field position of the outer protons indicate the existence of a paramagnetic ring current, as already found for 2,8,-10,16-tetradehydro[17]annulenone.[7]

Reduction of **5** in ether–methanol with an excess of sodium borohydride at room temperature for 25 min gave the alcohol **6** in essentially quantitative yield as unstable yellow crystals, which decomposed on attempted melting point determination; mass spectrum, *m/e* 232 (M) and 202 (M − OH − CH); $\lambda_{max}^{Et_2O}$ 253 nm (ϵ 15,000), 282 (48,000), 291 (60,000), 408 (4100), and 433 (2900); $\nu_{max}^{CH_2Cl_2}$ (cm^{-1}) 3680, 3580 (OH), 2200 (C≡C), and 1605 (C=C); nmr spectrum ($CDCl_3$, 100 MHz), broad band (1 H) at τ 8.24 (removed by addition of D_2O) assigned to the hydroxyl group. Oxidation of **6** in ether–cyclohexane with manganese dioxide regenerated **5**, showing that the polyenyne system had been unaffected in the reduction.

Methylation of **6** in ether by shaking with methyl iodide and silver oxide for 5 hr, followed by tlc on

(1) Unsaturated Macrocyclic Compounds. LXVII. For part LXVI, see D. A. Ben-Efraim and F. Sondheimer, *Tetrahedron*, **25**, 2837 (1969).

(2) See A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 10.

(3) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964); E. A. La Lancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).

(4) W. Grimme, M. Kaufhold, U. Dettmeier, and E. Vogel, *Angew. Chem.*, **78**, 643 (1966).

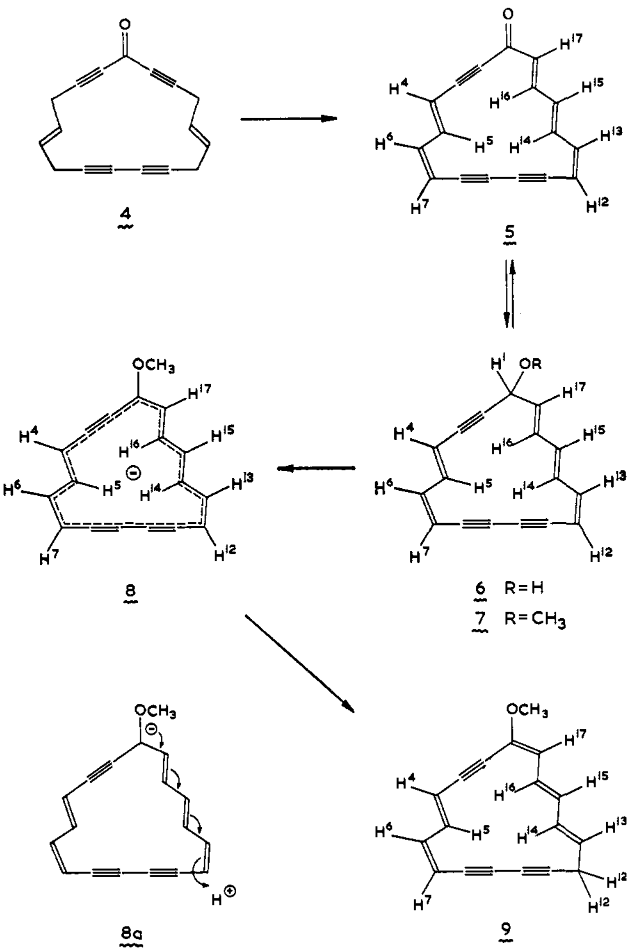
(5) In the parallel series of dianions made up of a 4*n*-membered carbocyclic ring, it has been shown recently that the macrocyclic [16]-annulenyl dianion ($n = 4$) is aromatic (J. F. M. Oth, G. Anthoine, and J. M. Gilles, *Tetrahedron Letters*, 6265 (1968)).

(6) See F. Sondheimer, *Proc. Roy. Soc.* (London), **A297**, 173 (1967), and references cited there.

(7) G. W. Brown and F. Sondheimer, *J. Am. Chem. Soc.*, **91**, 760 (1969).

(8) The process involves addition of **4** in tetrahydrofuran to a solution of freshly sublimed potassium *t*-butoxide in tetrahydrofuran at −70° under strictly anhydrous conditions, warming to −40° after 15 min, and then pouring into water. The conditions were found to be critical, small changes leading to inferior results.

(9) A molecular model of **5** indicates that it can exist in a relatively strainless planar conformation.



kieselgel, yielded 78% of the methyl ether **7** as unstable yellow crystals, mp ~120° dec (rapid heating); mass spectrum, *m/e* 246 (M), 215 (M − OCH_3), and 202 (M − OCH_3 − CH, base peak); $\lambda_{max}^{Et_2O}$ 253 nm (ϵ 14,300), 281 (47,000), 290 (59,000), 407 (4100), and 433 (2900); $\nu_{max}^{CCl_4}$ (cm^{-1}) 2190 (C≡C) and 1605 (C=C). The nmr spectrum ($CDCl_3$, 100 MHz) of **7** consisted of a multiplet (3 H) at τ 1.93–2.77 (H_5, H_{14}, and H_{16}), another multiplet (3 H) at 3.15–3.68 (H_6, H_{13}, and H_{15}), a double doublet (1 H) at 4.22 (H_{17}; $J_{17,1}$ = 4 Hz, $J_{17,16}$ = 16 Hz), a broadened doublet (1 H) at 4.32 (H_4; $J_{4,5}$ = 16 Hz), two doublets (1 H each) at 4.58 and 4.67 (H_7 and H_{12}; $J_{7,6}$ = $J_{12,13}$ = 10 Hz), a broadened doublet (1 H) at 5.48 (H_1; $J_{1,17}$ = 4 Hz), and a singlet (3 H) at 6.70 (OCH_3). The fact that H_5, H_{14}, and H_{16} still occur at significantly lower field than the other olefinic protons suggests that a paramagnetic ring current due to "homo-antiaromaticity"[10] may be present, although this effect could be due to deshielding by the acetylenes.

Treatment of **7** with a saturated solution of methyllithium in tetrahydrofuran-d_8 at −77° immediately gave a dark blue solution of the lithium salt of the 1-methoxy-2,8,10-tridehydro[17]annulenyl anion (**8**),[11] methane being evolved. The mixture was warmed to −30°, centrifuged, and sealed under N_2 in an nmr tube. The nmr spectrum at −35° (Figure 1) consisted of a triplet (1 H) at τ −0.47 (H_{15}; $J_{15,14}$ = $J_{15,16}$ = 13 Hz), two superimposed quartets at 0.09 and 0.18 (H_6 and H_{13}; $J_{6,7}$ = $J_{13,12}$ = 9 Hz, $J_{6,5}$ = $J_{13,14}$ = 13 Hz), a doublet at 0.34 (H_4 and H_{17}; $J_{4,5}$ = $J_{17,16}$ = 13 Hz),[12] two broadened doublets (1 H each) at 1.60 and 2.16 (H_7 and H_{12}; $J_{7,6}$ = $J_{12,13}$ = 9 Hz), a singlet (3 H) at 5.38 (OCH_3), and three superimposed triplets (total 3 H) at 18.54, 18.85, and 19.09 (H_5, H_{14}, and H_{16}; $J_{5,4}$ = $J_{5,6}$, = $J_{14,13}$ = $J_{14,15}$ = $J_{16,15}$ = $J_{16,17}$ = 13 Hz). The low-field position of the outer protons and the very high-field position of the inner protons[13] is a reversal of the behavior of **5** and clearly demonstrates the existence of a pronounced diamagnetic ring current in **8**. The relatively low-field position (τ 5.38) of the methoxyl proton resonance in **8** (*cf.* anisole, τ 6.22) is also indicative of a marked diamagnetic ring current. The anion **8** is therefore aromatic, as expected of a system containing 18 out-of-plane π electrons. It is of interest that H_7 and H_{12} resonate at unusually higher field than the other outer protons, a phenomenon which suggests that the charge densities at C_7 and C_{12} are greater than at the other carbon atoms.

Treatment of **7** in tetrahydrofuran-d_8 with potassium at −77° gave the potassium salt of the anion **8**, since the nmr spectrum at −35° was essentially identical with that described. Evidently, potassium removes H_1 rather than the methoxyl group.

Quenching of **8** with water did not regenerate **7**, but gave 50% of the isomeric ether **9** (isolated by tlc on kieselgel) as unstable yellow crystals, mp ~113° dec (rapid heating); mass spectrum, *m/e* 246 (M), 215 (M

(10) See S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, p 5.

(11) The anion **8**, prepared by treatment of **7** with methyllithium in ether at room temperature, showed λ_{max} (>350 nm) 404 (30,000) and 657 nm (ϵ >8000).

(12) The total area of the two quartets at τ 0.09 and 0.18 and the doublet at 0.34 corresponded to 4 H.

(13) The value of τ ~19 for the inner protons appears to be the highest yet recorded for a proton bound to carbon.

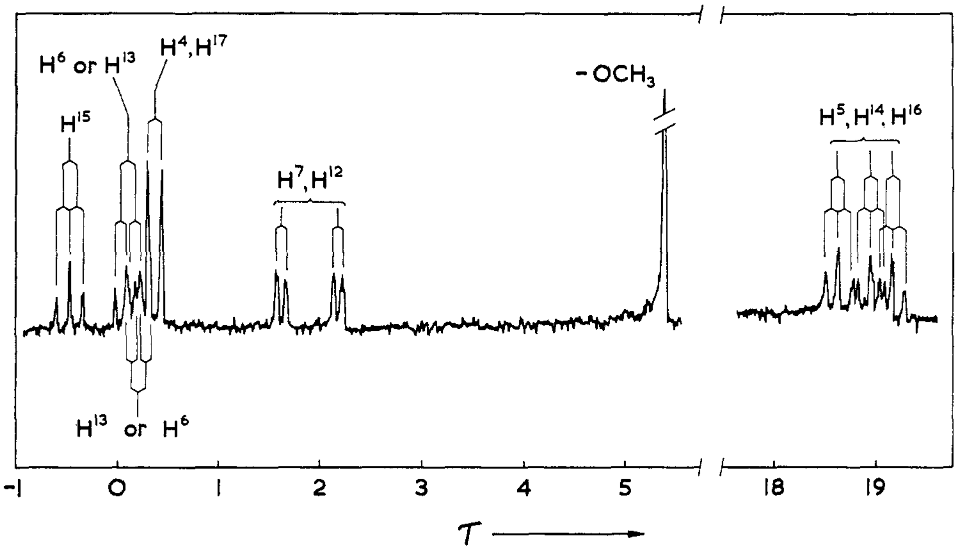


Figure 1. Nmr spectrum at −35° of the 1-methoxy-2,8,10-tridehydro[17]annulenyl anion (**8**), measured in tetrahydrofuran-d_8 at 100 MHz.

− OCH_3), and 202 (M − OCH_3 − CH, base peak); $\lambda_{max}^{Et_2O}$ 254 nm (ε 38,000), 289 (50,000), 298 (56,000), 402 (5300), *ca.* 455 sh (2800), *ca.* 485 sh (1800), and *ca.* 525 sh (520); $\nu_{max}^{CCl_4}$ (cm^{-1}) 2210, 2180 (C≡C), and 1600 (C=C); nmr spectrum ($CDCl_3$, 100 MHz), complex series of bands (9 H) at τ 2.84–4.50 (olefinic protons), singlet (3 H) at 6.30 (OCH_3), and doublet (2 H) at 7.08 (H_{12}; $J_{12,13}$ = 4 Hz). Structures isomeric with **9** can be eliminated, since the position (τ 7.08) of the methylene proton resonance in the nmr spectrum (*cf. trans*-4-octene-1,7-diyne, τ 7.08)[14] and its multiplicity show that the methylene group is situated between an acetylenic and an ethylenic bond. The presence of an enol ether grouping in **9** was confirmed by the fact that the methoxyl proton resonance has been shifted downfield by τ 0.4 as compared with **7**, and by the result of catalytic hydrogenation. This reaction (5% palladium–calcium carbonate, ethyl acetate) smoothly led to 1-methoxy-1-cycloheptadecene [mass spectrum, *m/e* 266 (M, base peak); $\nu_{max}^{CCl_4}$ 1662 cm^{-1} (enol ether)], hydrolyzed with dilute hydrochloric acid to cycloheptadecanone. By comparison, catalytic hydrogenation of **7** under these conditions gave methoxycycloheptadecane [mass spectrum, *m/e* 268 (M, base peak)].

Quenching of **8** with D_2O gave monodeuterio-**9** [mass spectrum, *m/e* 247, 216, and 203 (base peak)]. The formation of **9** from **8** is unexceptional, a possible mechanism being indicated in structure **8a** (arrows).

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(14) Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *J. Am. Chem. Soc.*, **90**, 4940 (1968).
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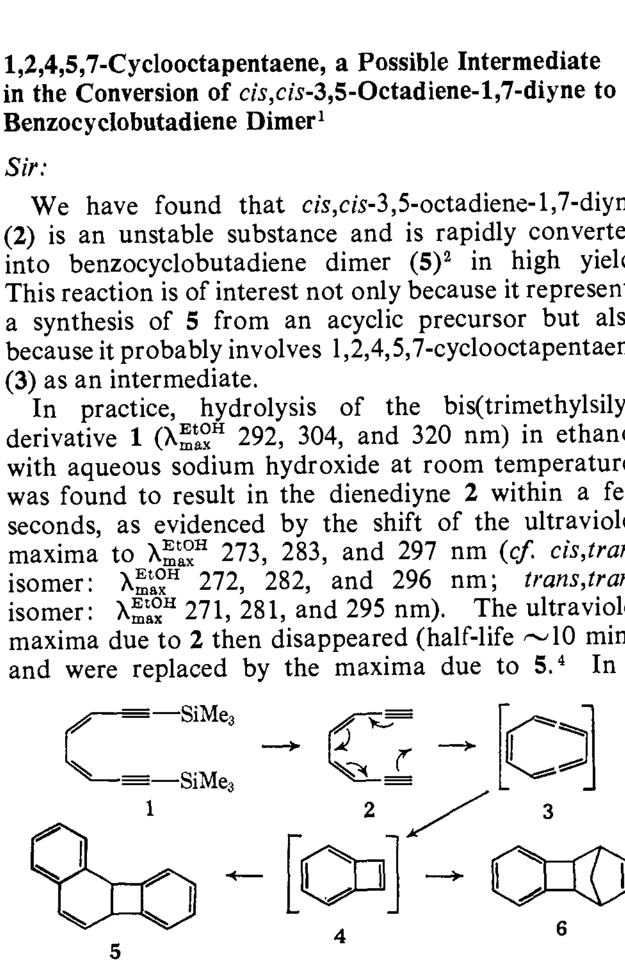
1,2,4,5,7-Cyclooctapentaene, a Possible Intermediate in the Conversion of *cis,cis*-3,5-Octadiene-1,7-diyne to Benzocyclobutadiene Dimer[1]

Sir:

We have found that *cis,cis*-3,5-octadiene-1,7-diyne (**2**) is an unstable substance and is rapidly converted into benzocyclobutadiene dimer (**5**)[2] in high yield. This reaction is of interest not only because it represents a synthesis of **5** from an acyclic precursor but also because it probably involves 1,2,4,5,7-cyclooctapentaene (**3**) as an intermediate.

In practice, hydrolysis of the bis(trimethylsilyl) derivative **1** (λ_{max}^{EtOH} 292, 304, and 320 nm) in ethanol with aqueous sodium hydroxide at room temperature[3] was found to result in the dienediyne **2** within a few seconds, as evidenced by the shift of the ultraviolet maxima to λ_{max}^{EtOH} 273, 283, and 297 nm (*cf. cis,trans* isomer: λ_{max}^{EtOH} 272, 282, and 296 nm; *trans,trans* isomer: λ_{max}^{EtOH} 271, 281, and 295 nm). The ultraviolet maxima due to **2** then disappeared (half-life ~10 min), and were replaced by the maxima due to **5**.[4] In a



(1) Unsaturated Eight-Membered Ring Compounds. X. For Part IX, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, in press.
(2) M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957); **80**, 2255 (1958).
(3) See C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, 4, 217 (1965).
(4) The conversion of **2** into **5** is not base catalyzed, since the rate of reaction was unaffected when the mixture was acidified after **2** had been generated from **1** with base. Moreover, **5** was also obtained when the trimethylsilyl groups in **1** were removed by the silver nitrate–potassium cyanide method (H. M. Schmidt and J. F. Arens, *Rec. Trav. Chim.*, **86**, 1138 (1967)).