The Planar Dehydro[8]annulenes

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The first satisfying structural formula for benzene was proposed by Kekulé over 100 years ago.[1] However, Kekulé's formula did not explain the low reactivity of benzene or its preference for substitution rather than addition reactions. Bamberger[2] suggested that these properties were concerned with the hexavalent nature of the benzene nucleus, and he showed how this idea could be extended to pyrrole. This concept was later reformulated in electronic terms by Armit and Robinson.[3]

Why six, rather than four or eight, electrons formed a stable system remained unanswered until Hückel, on the basis of molecular orbital theory, introduced his famous rule,[4] which states that a monocyclic conjugated polyene will be aromatic only if it possesses a closed shell of $[4n + 2]$ π electrons. At the time Hückel introduced this rule there were only two neutral species to which the rule could be applied, benzene ([6]-annulene) and cyclooctatetraene ([8]annulene), and even the existence of the latter was in dispute. Over the last two decades, commencing with the synthesis of [18]annulene in 1959,[5] a large number of neutral molecules have been prepared with which the validity of Hückel's rule could be tested. A clear distinction in properties between the $[4n + 2]$ and $4n$ π-electron systems has been discerned and Hückel's rule completely justified. Of particular significance has been the difference in the ^{1}H NMR spectra of the two series. In the $[4n + 2]$annulenes, the outer protons are at low field (shielded) and the inner protons at high field (deshielded), and these chemical shifts can be accounted for by the circulation of π electrons in the applied field (diamagnetic ring current).[6] In the $[4n]$annulenes, the outer protons are at high field and the inner protons at low field, in complete contrast to the $[4n + 2]$ π systems. The reversal of shifts in the $[4n]$annulene has been attributed to a paramagnetic contribution arising from the mixing of excited states with the ground state, and this paramagnetic contribution outweighs the contribution from the diamagnetic ring current.[7]

Whereas HMO theory originally predicted only that the $4n + 2$ systems would be more stable than the $4n$, later theories have suggested that the $4n$ systems will

be destabilized by delocalization and will, in fact, be antiaromatic.[8] The smallest member of the $[4n]$-annulenes, cyclobutadiene, is extremely elusive, but its isolable derivatives, though unstable, are paratropic.[9] The properties of cyclooctatetraene (1) are completely

different from those of the larger $[4n]$annulenes. Cyclooctatetraene is nonplanar[10] and has the character of a polyene; it bears no resemblance whatsoever to benzene. Cyclooctatetraene is best represented by the "tub" or "boat" conformation which belongs to the D_{2d} symmetry point group. Such a structure is strainless, but the adjacent π bonds will not be able to overlap effectively since they are at right angles to each other. The nonplanarity of cyclooctatetraene arises not only from the geometrical strain in the planar conformation but also, and perhaps more importantly, from the pseudo-Jahn–Teller effect[11] which comes into operation with the unfavorable arrangement of the molecular orbitals in planar symmetrical cyclooctatetraene.[11] Therefore, in order to make cyclooctatetraene planar, it is important both to ease the geometrical strain in the molecule and to eliminate the pseudo-Jahn–Teller effect.

We reasoned that if a triple bond were introduced into cyclooctatetraene, it would cause bond alternation and split the degenerate nonbonding molecular orbitals of the theoretical planar cyclooctatetraene.[7] The planar molecule would not then suffer the bond stretching distortion required by the pseudo-Jahn–Teller effect.[7] Moreover, the presence of one or two acetylenes in the cyclooctatetraene ring system would result in strained

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Franz Sondheimer: The biography of F. S. has appeared in a previous issue; see Acc. Chem. Res. 1972, 5, 81.

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(1) A. Kekulé, *Bull. Soc. Chim. Paris*, [2] 3, 98 (1865); A. Kekulé, *Liebigs Ann. Chem.* 137, 129 (1866).
(2) E. Bamberger, *Liebigs Ann. Chem.*, 257, 1 (1890); 273, 373 (1893); *Chem. Ber.*, 24, 1758 (1891).
(3) J. W. Armit and R. Robinson, *J. Chem. Soc.*, 127, 1604 (1925).
(4) E. Hückel, *Z. Phys.*, 70, 204 (1931); E. Hückel, *Z. Elektrochem.*, 43, 752 (1937); E. Hückel, "Grundzuge der Theorie ungesättigter und aromatischer Verbindungen", Verlag Chemie, Berlin, 1938.
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(6) J. A. Pople, *J. Chem. Phys.*, 24, 1111 (1956).
(7) H. C. Longuet-Higgins, *Chem. Soc. Spec. Publ.*, No. 21, 109 (1967); J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, 88, 4811 (1966); F. Baer, H. Kuhn, and W. Regal, *Z. Naturforsch., A*, 22a, 103 (1967).
(8) R. Breslow, *Acc. Chem. Res.*, 6, 393 (1973); M. J. S. Dewar, *Adv. Chem. Phys.*, 8, 121 (1965).
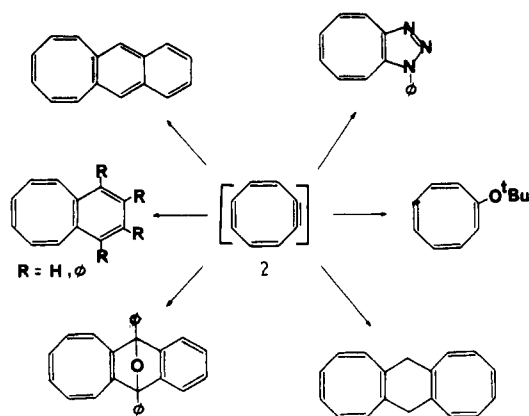(9) See T. Bally and S. Masamune, *Tetrahedron*, 36, 343 (1980).
(10) J. Bordner, R. G. Parker, and R. H. Stanford, *Acta Cryst., Sect B*, B28, 1069 (1972).
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Scheme I

R = H, φ

sp–sp hybrid bonds, which would be expected to contribute to the planarity of a fully conjugated eight-membered carbocycle. Cyclooctatrienyne (2) is therefore expected to be planar. The preparation of 2 was realised by Krebs.[12] However, it is impossible to prove that 2 is planar (e.g., by means of X-ray crystallographic methods) because of its instability, although the ESR spectrum of the anion radical derived from 2 is best accommodated by a planar structure. There are ample examples in the literature of unstable systems being stabilized by fusion to benzene rings, and we considered this to be an attractive method for the stabilization of planar [8]annulenes. The preparation, isolation, and identification of this extremely interesting class of compounds would fill an obvious gap in the family of [4n]annulenes.

Dehydro[8]annulenes

The elegant work of Krebs[12] provided the first example of the dehydro[8]annulene family. By treatment of bromocyclooctatetraene with potassium *tert*-butoxide (KO-*t*-Bu), Krebs showed that cyclooctatrienyne (2) could be trapped with a variety of reagents[12-14] (Scheme I).

Stevenson and co-workers[15] prepared the cyclooctatrienyne radical anion (3) by treatment of a solution of bromocyclooctatetraene in THF–HMPA (98:2) with a potassium mirror at −100 °C under high vacuum. The ESR spectrum of the radical anion showed three triplets due to three sets of equivalent protons. The results of the INDO calculation based on a planar system compared relatively well with the observed values for 3, which can thus be assumed to have a planar structure.
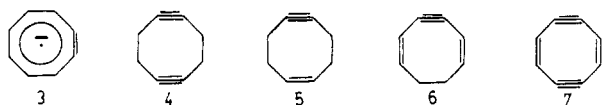
The relatively stable cycloocta-1,5-diyne (4) was isolated in 2% yield[16] from the polymerization of buta-

triene. Cyclooct-1-en-5-yne (5) has also been reported,[17] and it is less stable than 4. Moreover, Meier and his co-workers have recently observed that cycloocta-1,5-dien-3-yne (6)[18] is sufficiently stable for it to be isolated as a crystalline compound. These surprising discoveries suggested that the presumably planar fully conjugated cycloocta-1,5-diene-3,7-diyne (7) might be more stable than the fugitive cyclooctatrienyne (2) and thus might be susceptible to isolation.

Our preliminary experiments[19] to synthesize cycloocta-1,5-diene-3,7-diyne (7) were based on the method of Krebs.[12] It was presumed that 1,4-dibromocyclooctatetraene (8) when treated with base would lead to
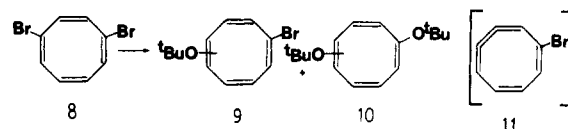
the desired dienediyne 7. In fact, treatment of the dibromide 8 with KO-*t*-Bu did not give 7, but afforded a mixture of the isomeric bromo-*tert*-butoxycyclooctatetraenes (9) or di-*tert*-butoxycyclooctatetraenes (10) (depending on the reaction temperature and the amount of base used). These results did not necessarily implicate the dienediyne 7 as an intermediate, and deuterium labeling experiments suggested that a cumulene type compound 11 was the more probable intermediate in these reactions.[19]

Fritch and Vollhardt have proposed[20] the (cycloocta-1,5-diene-3,7-diyne)cobalt complex as an intermediate of a thermal rearrangement reaction, but the actual presence of this intermediate, which could not be confirmed by theoretical treatments,[21] is open to question.

Dehydro[8]annulenes Fused with One Benzene Ring

Treatment of a solution of 5,10-dibromobenzocyclooctene (12) in THF with KO-*t*-Bu yielded 5,6,9,10-tetradehydrobenzocyclooctene (13),[22] which is the sim-

(12) A. Krebs, *Angew. Chem.*, **77**, 966 (1965); *Angew. Chem. Int. Ed. Engl.*, **4**, 954 (1965); A. Krebs and D. Byrd, *Liebigs Ann. Chem.*, **707**, 66 (1967).
(13) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 962 (1970).
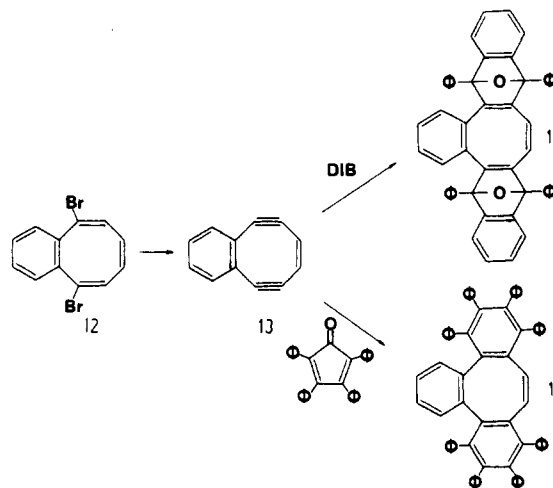(14) A. S. Lankey and M. A. Ogliaruso, *J. Org. Chem.*, **36**, 3339 (1971).
(15) G. R. Stevenson, M. Colón, J. G. Concepción, and A. McB. Block, *J. Am. Chem. Soc.*, **96**, 2283 (1974).
(16) E. Kloster-Jensen and J. Wirz, *Helv. Chim. Acta*, **58**, 162 (1975); E. Kloster-Jensen and J. Wirz, *Angew. Chem.*, **85**, 723 (1973); *Angew. Chem. Int. Ed. Engl.*, **12**, 671 (1973).

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(18) H. Meier, T. Echter, and H. Peterson, *Angew. Chem.*, **90**, 997 (1978); *Angew. Chem., Int. Ed. Engl.*, **17**, 942 (1978).
(19) H. N. C. Wong, Ph.D. Thesis, University College London, 1976.
(20) J. R. Fritch and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **100**, 3643 (1978).
(21) P. Hofmann and T. A. Albright, *Angew. Chem.*, **92**, 747 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 728 (1980).

plest known, isolable planar neutral [8]annulene. The diacetylene 12 is a yellow oil, decomposing rapidly even at 0 °C, and it is not stable in solution. However, its ^{1}H NMR spectrum (–20 °C) exhibited a sharp olefinic singlet at τ 5.07, which disappeared slowly in standing. The location of this signal at relatively high field (the corresponding olefinic protons of 12 gave a signal at τ 4.25) confirms that the diacetylene 13 possesses paratropic character, as expected for a planar $4n\ \pi$ system. It is also of interest to note that the electronic spectrum of a pentane solution of 13 showed evidence for extensive electron delocalization in this compound, probably due to the essentially planar eight-membered carbocycle. The presence of acetylenes in 13 was shown by the IR spectrum (C≡C stretching band at 2100 cm^{-1}), as well as by the reaction of 13 with 1,3-diphenylisobenzofuran (DIB) and 2,3,4,5-tetraphenylcyclopentadienone (TC) to give compounds 14 and 15, respectively.

It was of interest to prepare the related 5,6-didehydrobenzocyclooctene (16), for which 5,6-dibromo-5,6-dihydrobenzocyclooctene (17) seemed to be a suitable precursor. Treatment[23] of the dibromide 17 with
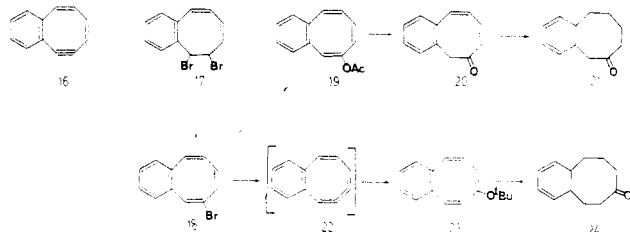
1.3 molar equiv of KO-t-Bu in THF gave 6-bromobenzocyclooctene (18). The structure of 18 was established by its transformation to the corresponding acetate 19, which was subsequently hydrolyzed to the unsaturated ketone 20. Hydrogenation of 20 gave the known 5,6,7,8,9,10-hexahydrobenzocycloocten-6-one (21).[24] Further dehydrobromination of the monobromide 18 with excess KO-t-Bu led to 7-$tert$-butoxybenzocyclooctene (23). The structure of 23 was confirmed by catalytic hydrogenation of the two less hindered double bonds and hydrolysis of the resulting enol ether to the known 5,6,7,8,9,10-hexahydrobenzocycloocten-7-one (24).[25] Undoubtedly, the conversion of the bromide 18 to the $tert$-butoxy compound 23 must involve the cyclic conjugated eight-membered cumulene 22 as a transient intermediate. The cumulene 22 was too unstable for it to be isolated, and therefore no physical data could be obtained in order to indicate its degree of planarity.

It appeared that 5-bromobenzocyclooctene (25a) would be a more appropriate starting material for the preparation of 5,6-didehydrobenzocyclooctene (16). We reasoned[26] that 5-bromo-10-methylbenzocyclooctene (25b) would be an even better precursor to this type of system because of its easy accessibility and the presence of the methyl group which could serve as a much more

(22) H. N. C. Wong and F. Sondheimer, *Angew. Chem.*, **88**, 126 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 117 (1976).
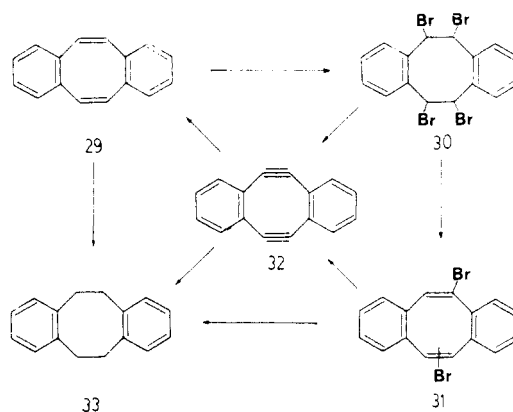(23) H. N. C. Wong, T.-L. Chan, and F. Sondheimer, *Tetrahedron Lett.*, 667 (1978).
(24) R. Huisgen, E. Rauenbusch, and G. Seidl, *Chem. Ber.*, **90**, 1958 (1957).
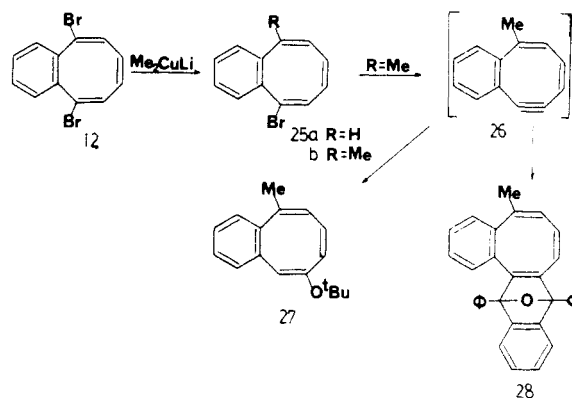(25) E. M. Fry and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 3489 (1940).
(26) H. N. C. Wong and F. Sondheimer, *Tetrahedron Lett.*, **21**, 983 (1980).

Scheme II

convenient probe for the determination of paratropicity. The monobromide 25b was prepared from the dibromide 12. Dehydrobromination[26] of the bromide 25b

with excess KO-t-Bu led to 6-$tert$-butoxy-10-methylbenzocyclooctene (27), presumably via the intermediate 5,6-didehydro-10-methylbenzocyclooctene (26). The existence of the acetylene 26 was supported by the isolation of the adduct 28 when 25 was allowed to react with KO-t-Bu in the presence of DIB, but all efforts to isolate 26 failed. The relative stability of the diacetylene 13 as compared to the instability of the monoacetylene 26 is in keeping with the relative stabilities of cycloocta-1,5-diyne (4)[16] and cyclooct-1-en-5-yne (5).[17]

Dehydro[8]annulenes Fused with Two Benzene Rings

Dehydrobromination[27,28] of 5,6,11,12-tetrabromo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (30) or a mixture of 5(6),11-dibromodibenzo[a,e]cyclooctene (31) with an excess of KO-t-Bu in THF afforded 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (32)[28] (Scheme II). The carbon skeleton of 32 was established by catalytic hydrogenation to give both the known dibenzo[a,e]-cyclooctene (29) and the known 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (33). The diacetylene 32 formed pale yellow plates which decomposed at ca. 110 °C on attempted melting point determination. The ^{1}H NMR spectrum of 32 consisted of an AA'BB' system at τ 2.76–3.64 (centered at τ 3.20). A complete ^{1}H NMR spectral analysis[29] of 32 gave strong support to the view

(27) H. N. C. Wong, P. J. Garratt, and F. Sondheimer, *J. Am. Chem. Soc.*, **96**, 5604 (1974).
(28) H. N. C. Wong and F. Sondheimer, *Tetrahedron, R. B. Woodward Memorial Issue*, **99** (1981).
(29) H. Günther, M.-E. Günther, D. Mondeshka, and H. Schmickler, *Liebigs Ann. Chem.*, 165 (1978).

Scheme III

Scheme IV
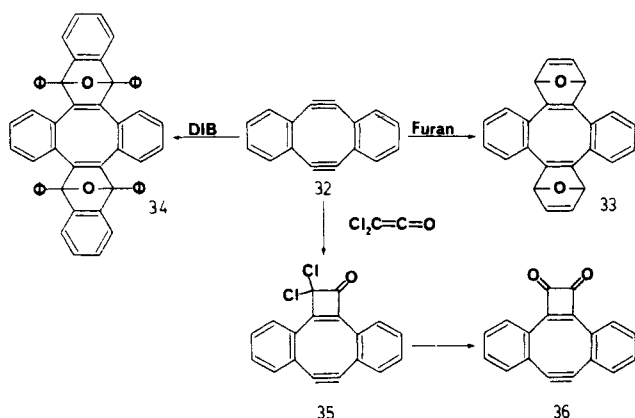
that the eight-membered carbocycle ring was anti-aromatic. Furthermore, the Q value[30] of 32 was found to be 0.961,[29] which convincingly belongs to the family of delocalized $4n$ π systems. The IR spectrum of 32 showed a weak C≡C stretching band at ca. 2180 cm^{-1}. The UV spectrum[28] was very similar to that of 13, showing both an extensive bathochromic shift and a hyperchromic effect as compared to the spectrum of the related nonplanar 29.[28]

A thorough investigation of the electronic structure and photophysical property of the diacetylene 32 was recently reported by Wirz,[31] who discovered that the electronic absorption spectrum of 32 differed radically from the well-known pattern of benzenoid hydrocarbons. The triplet-state absorption spectrum and the free energy of 32 were measured by means of flash photolysis as well as by energy-transfer experiments. The presence of an avoided surface corssing phenomenon was proposed[31] in order to explain the observed trend in fluorescence and triplet yields in 32 and a number of other compounds containing planar $4n$-membered rings.

Wirz also reported the photoelectron spectral analysis of 32.[32] By examination of the results obtained from LCBO, SPINDO, MINDO/2, and PPP SCF calculations, Wirz was able to associate the bonding and antibonding orbitals with the ionization potential bands shown in the photoelectron spectrum of 32. It was observed that the ionization bands of 32 were sharp, and the first ionization potential was measured to be 7.76 eV. In comparison, the nonplanar dibenzo[a,e]-cyclooctene (29) exhibits broad ionization bands, and its first vertical ionization potential is shifted to higher energy (8.24 eV).[32] This readiness of electron excitation in 32 would also appear to be an indication of the electron delocalization in the planar $4n$ system.

X-ray crystallographic analysis[33] shows that the diacetylene 32 is essentially planar and that the acetylenic bonds are highly strained (average angular deformation 24.2°). The strain of the acetylenic bonds is also reflected by the chemical reactivity of 32 which undergoes a number of cycloaddition reactions to give a variety

of adducts (Scheme III). From an examination of the ^{13}C NMR spectra of a number of cycloalkynes it appears that the acetylenic chemical shifts are closely related to ring strain. The value of 109.3 ppm found for 32 is at by far the highest field of all eight-membered cycloalkynes so far investigated.

The dichloro ketone 35 reacted smoothly with silver trifluoroacetate to give, after hydrolysis of the resulting diacetate, the $4n\pi + 4n\pi$ cyclobutadienoquinone 36.[34]
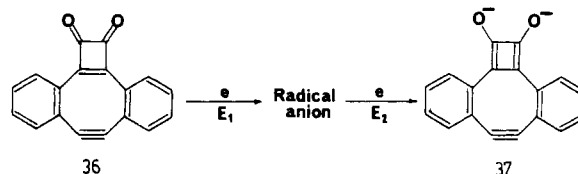
Compound 36 exhibited unique properties upon electroreduction, using the technique of second harmonic ac polarography, being reduced first to the radical anion and then to the dianion 37. The sum of the two potentials $E_1 + E_2$ was found to be -2.44 V, which hinted that the reduction of 36 to 37 was thermodynamically very easy. This finding suggests that the two fused $4n$ π systems are acting as an overall $4n + 2$ system.[34]

It is unfortunate that the diacetylene 32 does not possess protons which can serve as a convenient probe for the determination of paratropicity in the planar eight-membered system. It was desirable to prepare an analogue of 32 which would contain protons in the eight-membered ring. Dehydrobromination[27,28] of 5,6-dibromo-5,6-dihydrodibenzo[a,e]cyclooctene (38) or 5-bromodibenzo[a,e]cyclooctene (39) with KO-t-Bu in THF yielded 5,6-didehydrodibenzo[a,e]cyclooctene (40) (Scheme IV) as golden yellow plates that decomposed upon rapid heating at ca. 85 °C. Compound 40 was relatively unstable, and the crystals decomposed after a few minutes at room temperature. The carbon skeleton of 40 was established by catalytic hydrogenation to 29 and 33. A well-resolved ^{1}H NMR spectrum (400 MHz) of 40[35] shows a 4H multiplet centered at τ 3.33 and a 2H singlet at τ 4.55 (olefinic protons). The relatively high field signal of the olefinic protons of 40, in comparison to the olefinic signals in the ^{1}H NMR spectrum of dibenzo[a,e]cyclooctene (29),[36] clearly indicates the paratropicity which is inherent in its eight-membered ring. The UV spectrum of 40[28] is
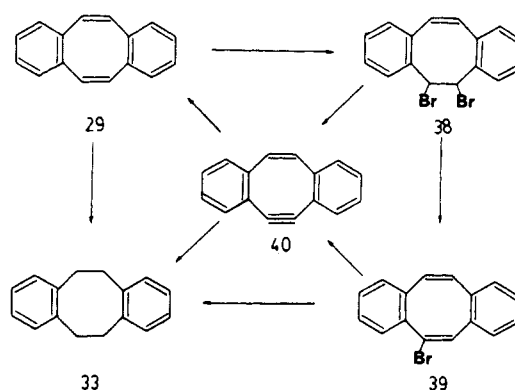
(30) H. Günther, H. Skyoukh, D. Cremer, and K. H. Frisch, *Tetrahedron Lett.*, 781 (1974); D. Cremer and H. Günther, *Liebigs Ann. Chem.*, 763, 87 (1972).

(31) J. Wirz in "Excited States in Organic Chemistry and Biochemistry", B. Pullman and N. Goldblum, Eds., D. Reidel Publishing Co., Dordrecht, Holland, 1977, pp 283–294.

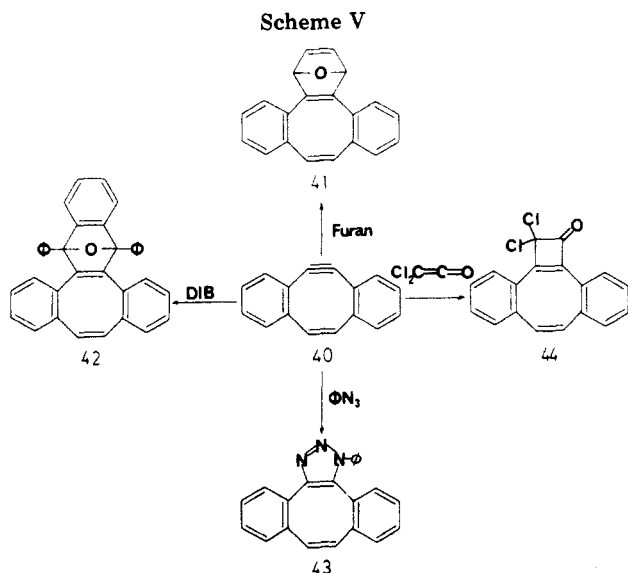(32) J. Wirz, *Helv. Chim. Acta*, 59, 1647 (1976).

(33) R. Destro, T. Pilati, and M. Simonetta, *J. Am. Chem. Soc.*, 97, 658 (1975); *Acta Cryst., Sect. B*, B33, 447 (1977).

(34) H. N. C. Wong, F. Sondheimer, R. Goodin, and R. Breslow, *Tetrahedron Lett.*, 2715 (1976).

(35) H. Günther, private communication.

(36) G. W. Buchanan and A. R. Carville, *Can. J. Chem.*, 51, 177 (1973).

Scheme V

Scheme VI

similar to those of **13** and **32**. The acetylenic carbon ^{13}C NMR chemical shift of the monoacetylene **40** was found to be 108.5.[35] The planarity of **40** was firmly established by low-temperature X-ray crystallography.[37] The eight-membered ring in **40** was found to be essentially planar, and the acetylenic bonds are highly strained, with an average angular deformation of 26°, which is the largest among all known eight-membered cycloalkynes. The strain inherent in compound **40** was shown most convincingly by its willingness to undergo cycloaddition reactions with a variety of reagents[28] (Scheme V).

The monoacetylene **40** could be reduced by treatment with potassium in THF-d_8 to the dianion **45**.[27,28] The
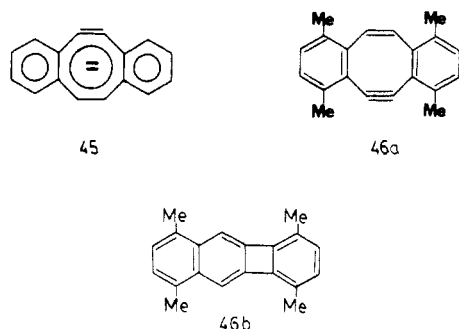
^{1}H NMR (−40 °C) of **45** showed that the olefinic proton resonance has shifted downfield to τ 3.33 (compared with τ 4.55 of **40**), as expected for a 10π-electron diatropic system. This observation is in full accord with the result by Katz et al.[38] on the dibenzo[a,e]cyclooctene dianion.

A synthesis of the tetramethyl derivative of **40**, namely 1,4,7,10-tetramethyl-5,6-didehydrodibenzo[a,-e]cyclooctene (**46a**), has been claimed,[39a] although the ^{1}H NMR spectrum of the system showed no evidence for any paratropic contribution from the eight-membered ring. X-ray crystallographic studies[39b] have now shown that the compound has structure **46b**, and the
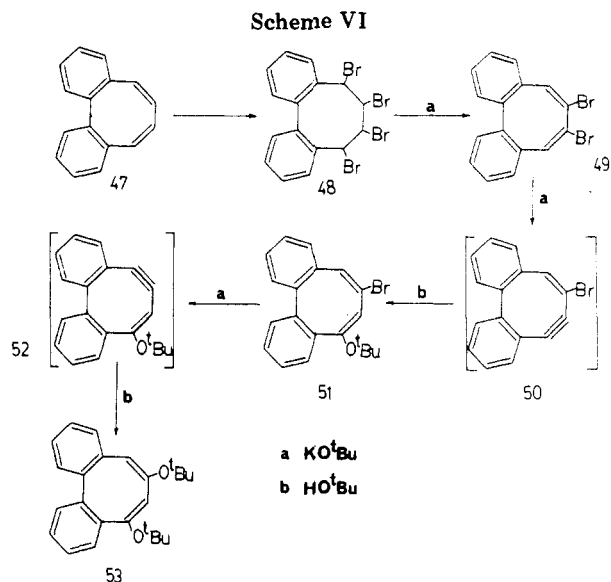
physical properties are fully in accord with this formulation.

The ESR spectra of the radical anions of dibenzo-[a,e]cyclooctene (**29**), 5,6,11,12-tetradehydrodibenzo-[a,e]cyclooctene (**32**), and 5,6-didehydrodibenzo[a,e]-cyclooctene (**40**) have been recorded,[40] and the hyperfine coupling constants were found to be similar in magnitude. This indicates that the radical anion of **29** must also be planar,[40] thus solving a longstanding controversy between Katz[38] and Carrington.[41] The proton coupling constants calculated by means of HMO–McLachlan procedure based on planar models for the radical anions of **29**, **32**, and **40** compared well with those measured empirically. Furthermore, proton coupling constants calculated by INDO procedure for planar **32**, planar **29**, and nonplanar **29** clearly conclude that the radical anion of **29** should be planar.[40]

Studies on the electrochemical reduction of **29**, **32**, and **40** by the cyclic voltammetric method have also been reported.[42] The first reversible half-wave potential for the reduction of **29** to its radical anion was found to be larger than those of **32** and **40**, while the second reversible half-wave potentials for the reduction of all three corresponding radical anions were almost equal. These experimental results show that the nonplanar dibenzo[a,e]cyclooctene (**29**) suffers a geometrical change upon one-electron reduction to its planar radical anion, whereas this does not occur in the already planar **32** and **40**. Moreover, the similar magnitudes of the second reversible half-wave potentials suggest the radical anions and dianions of **29**, **32**, and **40**[42] have similar planar structures. The planarity found for the radical anion of **29** is in complete agreement with the ESR studies.[40]

Dibenzo[a,c]cyclooctene (**47**) has been known[43,44] since 1963. We have reported a modified method for the preparation[45] of **47**, as well as the investigation of

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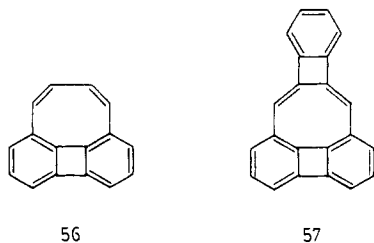(43) J. Wolpers, Ph.D. Thesis, University of Cologne, 1964.

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its dehydro derivatives[45] (Scheme VI). Dehydrobromination of 5,6,7,8-tetrabromo-5,6,7,8-tetrahydrodibenzo[a,c]cyclooctene (48) with 2 molar equiv of KO-t-Bu in THF provided 6,7-dibromodibenzo[a,c]cyclooctene (49). Further dehydrobromination of the dibromide 49 with excess KO-t-Bu yielded 5,7-di-tert-butoxydibenzo[a,c]cyclooctene (53) whereas dehydrobromination of 48 with 5 molar equiv of KO-t-Bu gave 49 and 53 as well as 51. The most likely explanation for these results is that the dehydrobrominations are stepwise, going through intermediates 50 and 52 (Scheme VI), although we are not able to trap these intermediates. Nonetheless, treatment of the dibromide 49 with KO-t-Bu in the presence of DIB resulted in the isolation of the *bis*-DIB-adduct 54. The formation of

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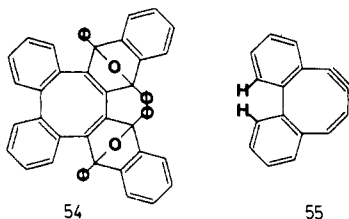
54 could also be explained by our proposed stepwise mechanism.[45] A possible reason for the instability of the 5,6-didehydrodibenzo[a,c]cyclooctene systems 50 and 52 is that there would be severe nonbonded interaction of the 1 and 12 protons as indicated in 55.

Wilcox and his co-workers discovered that when the 1 and 12 positions of dibenzo[a,c]cyclooctene were linked by a C–C single bond, the eight-membered ring became planar.[46,47] They have successfully prepared cycloocta[def]biphenylene (56),[46,47] which showed unmistakably antiaromatic properties. The ¹H NMR spectral data of 56 shows that the eight-membered ring possesses a small paramagnetic ring currents, presumably due to the planar cyclooctatetraene ring. The X-ray crystallographic structural analysis of 56 seems still to be in progress.[48] By contrast, cycloocta-[1,2,3,4-def]benzo[3,4]cyclobuta[6,7]biphenylene (57), also prepared by the same research group,[49] shows diatropic ¹H NMR spectral properties, which is very unusual for the multiple fused 4n-membered rings. Compound 56 has been studied extensively, and interpretations of its electronic spectrum,[50,51] as well as resonance energy[52,53] and ionization potential calcula-


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tions,[54] have been reported.

A closely related compound, cycloocta[def]fluorene (58), which also possesses a planar cyclooctatetraene ring, has recently been synthesized by Willner and Rabinovitz.[55,56] The antiaromatic anion 59 could be prepared from 58 by reaction with n-BuLi in THF-d₈.[55,56] Moreover, oxidation of 58 with oxygen in the

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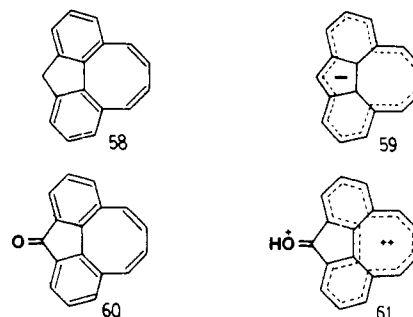
presence of Triton B or with air in the presence of KOH/18-crown-6 afforded the ketone 60,[57] which upon further reaction with magic acid at 31 °C gave the protonated dication 61.[57] Compounds 58–61 were shown to be planar by ¹H NMR spectrometry.

Dehydro[8]annulenes Fused with Three Benzene Rings

Tribenzo[a,c,e]cyclooctene (62) was first prepared in 1944,[58] but no further research work has been reported on this compound since that time. We have recently prepared 62 by three methods,[19,59] and we have also studied the possibility of preparing 9,10-didehydrotribenzo[a,c,e]cyclooctene (64).[19] Dehydrobromination

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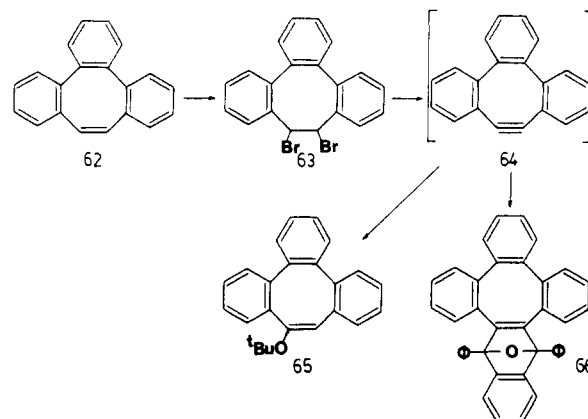
of 9,10-dibromo-9,10-dihydrotribenzo[a,c,e]cyclooctene (63) with KO-t-Bu yielded only 9-tert-butoxytribenzo-[a,c,e]cyclooctene (65), presumably via the intermediacy of the acetylene 64. The existence of 64 was substantiated by trapping experiments; for example, dehydrobromination of 63 in the presence of DIB gave the adduct 66. Gugel and Meier[60] have recently independently reported the trapping of the fugitive acetylene 64,

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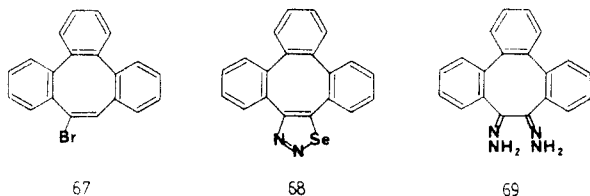(56) I. Willner and M. Rabinovitz, *J. Org. Chem.*, 45, 1628 (1980).

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which was generated from **67, 68,** or **69,** and their results

are fully in accord with ours. The instability of **64** may possibly be attributable to the nonbonded interactions of the 1,14 and 4,5 protons in the planar structure of **64.**

Conclusion

It was pointed out by Rabinovitz[56] that the introduction of acetylenes into cyclooctatetraene has two disadvantages: first, the anisotropy due to the triple bond may also introduce a paratropic shift in the ^{1}H NMR spectrum; second, the acetylene removes protons that would otherwise serve as probes for the determination of paratropicity. Nevertheless, we consider that the presence of triple bonds in fully conjugated eight-membered ring compounds not only causes a dramatic structural change from the originally nonplanar rings but that the resulting systems, which contain bent and highly strained triple bonds, are themselves of interest. Despite a large amount of experimentation, the diacetylene **7** remains unknown. There is still ample challenge, amusement, and hard labor to be found in the study of planar cyclooctatetraenes.