Nonbenzenoid Aromatic π-Electron Systems[1]

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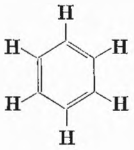
Summary

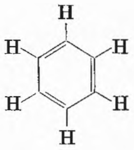
The field of nonbenzenoid aromatic π-electron systems is reviewed. The groups of compounds selected for discussion are annulenes, dehydroannulenes, bridged annulenes, ionic systems and heteroaromatic systems. Some conclusions about the concept of aromaticity are made.

I. Introduction

The field of nonbenzenoid aromatic compounds is now a very large one, and it is impossible to cover the whole field in a review of this nature.[2] It has therefore been necessary for me to be rather selective, and I will concentrate on the high-lights and on the more recent advances. Furthermore, since I am essentially an experimentalist, I will stress the experimental rather than the theoretical side of the subject.

Before discussing *nonbenzenoid* aromatic systems, I would like to say a few words about benzene itself. Benzene may, of course, be represented by the Kekulé structures (**1a**) and (**1b**), or more accurately by formula (**1c**), which indicates the equivalence of all of the ring atoms and bonds. Benzene is the classical aromatic molecule, it is π-electron delocalized, and its aromaticity is shown in a number of ways.


1a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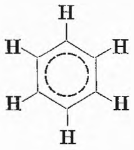
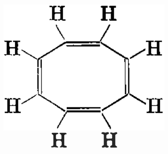

1c

Thus, benzene is unusually stable, it is inert, the type is retained in its reactions, and it undergoes electrophilic substitution rather than addition reactions. These might be called the classical "19th century" aromatic properties of benzene. It was this type of behaviour, so different from that of ordinary olefinic compounds, which puzzled chemists in the last century, and which caused the term "aromatic" to be applied to benzenoid compounds in the first place.

Among other, more recently determined aromatic properties of benzene may be mentioned: (a) all the carbon and hydrogen atoms are equivalent, all the carbon-carbon and carbon-hydrogen bonds are equivalent, it is planar, and it shows diamagnetic anisotropy. Moreover, (b) benzene has a high resonance energy, it shows a diamagnetic ring current as evidenced by the proton nuclear magnetic resonance (NMR) spectrum (such compounds we call "diatropic"), and it shows exaltation of the diamagnetic susceptibility. I have divided these properties into two, since those in group (a) may be observed directly, while those in group (b) depend on the difference in properties of benzene with those of a hypothetical nonaromatic model.

Ever since the structure of benzene was determined by Kekulé over one hundred years ago,[3] chemists have speculated whether it was unique in having these aromatic properties, or whether related substances would show similar behaviour. It was in this connection that Willstätter early in this century[4] prepared cyclooctatetraene (**2**), the next higher vinylogue. He found that this substance was not at all like benzene, but behaved like an ordinary olefin.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At this stage, for the sake of clarity, I would like to anticipate a conclusion of this review. If we consider a compound to be aromatic only if it shows *all* of the

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[1] Based on a lecture given on September 24th 1973 at the 5th International Colour Symposium organized in Basel by the Association of Swiss Chemists.

[2] For recent more extensive reviews, see G.M. Badger, *Aromatic Character and Aromaticity*, Cambridge University Press, Cambridge 1969; *Nonbenzenoid Aromatics* (Ed. J.P. Snyder), Academic Press, New York, Vol. I, 1969; Vol. II, 1971; *International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds*, Sendai (Japan) 1970, *Pure Appl. Chem. 28* (1971); *The Jerusalem Symposia on Quantum Chemistry and Biochemistry*, Vol. III: *Aromaticity, Pseudo-aromaticity, Antiaromaticity* (Ed. E.D. Bergmann and B. Pullman), Jerusalem Academic Press, Jerusalem 1971; P.J. Garratt, *Aromaticity*, McGraw-Hill Book Co. (U.K.) Ltd., Maidenhead 1971; MTP *International Review of Science*, Vol. 3: *Aromatic Compounds* (Ed. H. Zollinger), Butterworths, London 1973.

[3] A. Kekulé, *Bull. Soc. Chim. France* [2] 3 (1865) 98; *Liebigs Ann. Chem. 137* (1866) 129.

[4] R. Willstätter and E. Waser, *Ber. dtsch. chem. Ges. 44* (1911) 3423; R. Willstätter and M. Heidelberger, *ibid. 46* (1913) 517; A.C. Cope and C.G. Overberger, *J. Amer. Chem. Soc. 70* (1948) 1433.

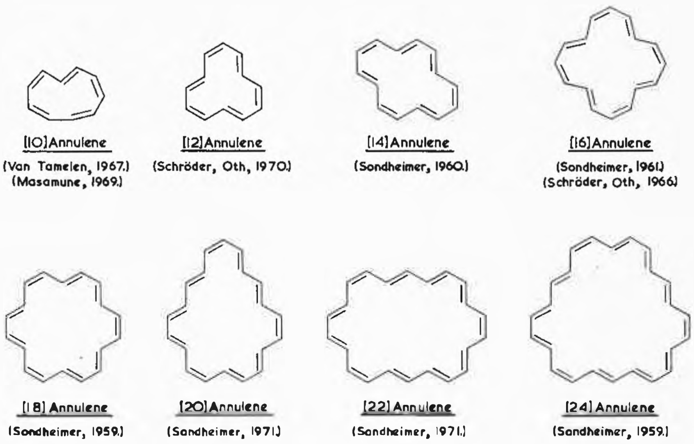
properties of benzene just mentioned, then undoubtedly benzene is the only truly aromatic compound, since it is the only substance to show all of these properties. However, we will see that other substances show some, though not all, of the aromatic properties of benzene.

After the synthesis of cyclooctatetraene by WILLSTÄTTER in 1911[4] the next major advance in this field was a theoretical one, made by HÜCKEL in 1931.[5] He classified planar fully unsaturated carbocyclic systems into two types: (a) those with $(4n+2)$ π-electrons have filled electronic shells with all the electrons in bonding orbitals, and are *aromatic:* (b) those with $4n$ π-electrons have partially filled electronic shells with electrons in non-bonding orbitals, and are *nonaromatic* (and, it is now realized, they may even be antiaromatic; *i.e.*, destabilized by cyclic delocalization).[6] This is the now well-known "HÜCKEL's rule", which, I belive, has been one of the most successful theoretical predictions made in organic chemistry. It explains, of course, why benzene, a $(4n+2)$ π-electron system $(n = 1)$, is aromatic, whereas cyclooctatetraene, a $4n$ system $(n = 2)$, is not. Unfortunately, at the time these were the only two monocyclic conjugated polyenes known, and the validity of the rule could not be tested more widely.

II. Annulenes

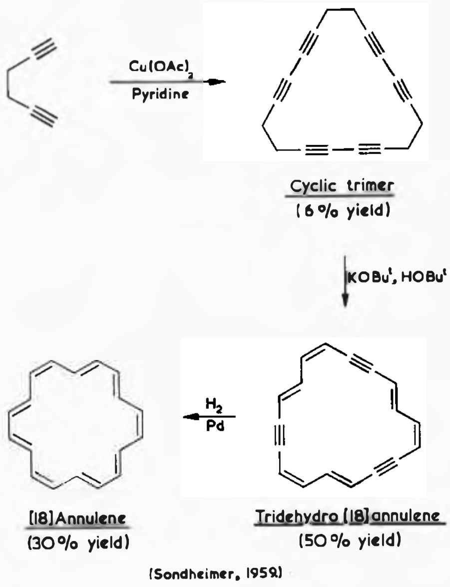
More recently, a wide range of monocyclic conjugated polyenes, which we have named "annulenes"[7] have been synthesized, as shown in Scheme I. A possible configuration is indicated for each annulene in the formulae, and the names of the discoverers and the dates of publication are also given. It may be mentioned that all of the larger annulenes are highly coloured compounds, and this is therefore a suitable subject to be discussed at a Colour Symposium!

Scheme I



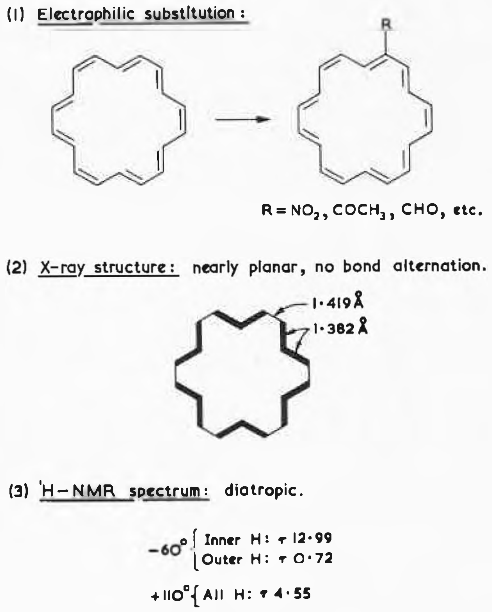
Essentially two basic synthetic methods were used for the synthesis of these annulenes. The first, developed by us, involves oxidative coupling of a terminal diacetylene as the key step. Its application to the synthesis of [18]annulene, the first higher annulene to be prepared, is indicated in Scheme II. Oxidation of hexa-1,5-diyne with cupric acetate in pyridine yielded the corresponding cyclic trimer in *ca.* 6% yield, besides other products.[7] Rearrangement of the trimer with potassium *t*-butoxide in *t*-butyl alcohol led to the symmetrical 1,7,13-tridehydro[18]annulene, which was finally converted to the brown-red [18]annulene by catalytic partial hydrogenation over a palladium catalyst.[7]

Scheme II. Synthesis of [18]Annulene by Acetylene Coupling



[18]Annulene was presumably reasonably planar, and it contains $(4n+2)$ π-electrons $(n = 4)$. The question

Scheme III. "Aromatic" Properties of [18]Annulene



was: is it aromatic, in the same way as benzene? The answer to this question it that [18]annulene resembles benzene in some ways, but not in others. Thus, some "aromatic" properties of [18]annulene are indicated in Scheme III. Under suitable conditions it undergoes electrophilic substitution reactions,[8] the substituent, of course, being introduced on an external position. An X-ray crystallographic analysis[9] shows it to be nearly planar, and there to be no bond alternation in the classical sense. On the other hand, all the carbon-carbon bonds are not exactly equal in lengths, the "cisoid" bonds indicated by thin lines in Scheme III having a little more single bond character (1.419 Å) and the "transoid" bonds indicated by thick lines having a little more double bond character (1.382 Å). The proton NMR spectrum taken at low temperatures shows [18]annulene to be strongly diatropic, the inner protons resonating at very high field and the outer protons at low field.[10] At higher temperatures an average value is seen, due to the relatively rapid interchange of the protons.[10] It may be mentioned that, from an experimental point of view, the determination of the proton NMR spectrum to observe whether a substance is diatropic or not, is usually the simplest way to establish its possible aromaticity.

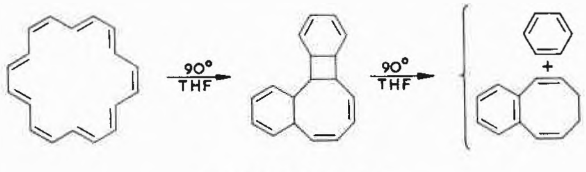
By contrast, some "nonaromatic" properties of [18]-annulene are shown in Scheme IV (the structure indicated for the tetracyclic isomer obtained by heating [18]annulene at 90° is one of several possibilities).[11] It can be seen that [18]annulene in its properties and reactions is certainly not as inert as bezene, and would not have puzzled the 19th century chemists the way benzene did.

Scheme IV. "Non-Aromatic" Properties of [18]Annulene

(1) Not particularly stable, solid decomposes on standing.

(2) Rapidly reacts with bromine, potassium permanganate, maleic anhydride, etc.

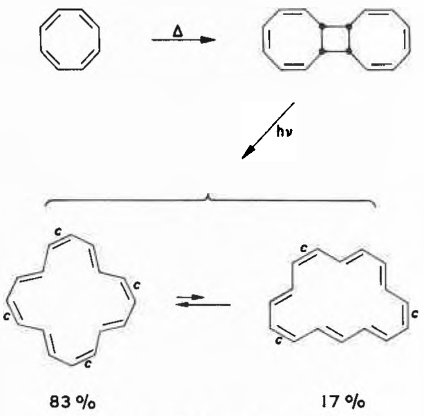
(3) Valence isomerization:



(Sondheimer, Oth, 1972.)

The second type of annulene synthesis involves photolysis of a bicyclic or polycyclic valence isomer. Its application to the synthesis of [16]annulene, by Schröder ant Oth, is shown in Scheme V. Heating cyclooctatetraene yielded the dimer indicated, as well as another dimer.[12] Photolysis of this dimer at 0° then gave the purple coloured [16]annulene in 60% yield,[13,14] which in solution was shown to be an equilibrium mixture of the tetra-*cis* and tri-*cis* isomers (83 : 17 at − 140°).[15,16]

Scheme V. Synthesis of [16]Annulene by Photolysis



[16] Annulene
(60 % yield)
(Schröder, Oth, 1966.)

[16]Annulene, of course, is a $4n$ π-electron system ($n=4$), which should be nonaromatic or even antiaromatic. It may be argued that this annulene should therefore not be mentioned in a review of nonbenzenoid *aromatic* compounds. However, it is appropriate briefly to discuss this substance since its clearly nonaromatic properties (Scheme VI) make some of the aromatic properties of [18]annulene more significant. Thus, the X-ray crystallographic analysis of [16]annulene shows

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[5] E. Hückel, *Z. Physik 70* (1931) 204; *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*, Verlag Chemie, Berlin 1938.

[6] R. Breslow, *Accounts Chem. Res. 6* (1973) 393.

[7] F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc. 84* (1962) 260; F. Sondheimer, R. Wolovsky and Y. Amiel, *ibid. 84* (1962) 274.

[8] I. C. Calder, P. J. Garratt, H. C. Longuet-Higgins, F. Sondheimer and R. Wolovsky, *J. Chem. Soc. (C) 1967*, 1041; E. P. Woo and F. Sondheimer, *Tetrahedron 26* (1970) 3939.

[9] J. Bregman, F. L. Hirschfeld, D. Rabinovich and G. M. J. Schmidt, *Acta Crystallogr. 19* (1965) 227; F. L. Hirschfeld and D. Rabinovich, *ibid. 19* (1965) 235.

[10] Y. Gaoni, A. Melera, F. Sondheimer and R. Wolovsky, *Proc. Chem. Soc. 1964*, 397; F. Sondheimer, *Proc. Roy. Soc. A 297* (1967) 173; F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent and R. Wolovsky, *Aromaticity*, The Chemical Society, Special Publication *21* (1967) 75; J. M. Gilles, J. F. M. Oth, F. Sondheimer and E. P. Woo, *J. Chem. Soc. (B) 1971*, 2177.

[11] K. Stöckel, P. J. Garratt, F. Sondheimer, Y. de Julien de Zélicourt and J. F. M. Oth, *J. Amer. Chem. Soc. 94* (1972) 8644.

[12] W. O. Jones, *Chem. & Ind.* (London) *1955*, 16; G. Schröder and W. Martin, *Angew. Chem. 78* (1966) 117.

[13] G. Schröder and J. F. M. Oth, *Tetrahedron Letters 1966*, 4083.

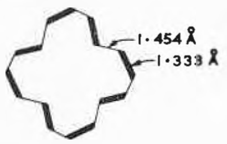
[14] G. Schröder, W. Martin and J. F. M. Oth, *Angew. Chem. 79* (1967) 861.

[15] J. F. M. Oth and J. M. Gilles, *Tetrahedron Letters 1968*, 6259.

[16] J. F. M. Oth, G. Anthoine and J. M. Gilles, *Tetrahedron Letters 1968*, 6265; J. F. M. Oth, H. Baumann, J. M. Gilles and G. Schröder, *J. Amer. Chem. Soc. 94* (1972) 3498.

Scheme VI. [16]Annulene

(1) X-ray structure: nonplanar, bond alternation.



(2) ^{1}H-NMR spectrum: paratropic.

$-120°\left\{\begin{array}{l}\text{Inner H: } \tau\ -0{\cdot}53\\ \text{Outer H: } \tau\ 4{\cdot}60,\ 4{\cdot}89\end{array}\right.$

$+30°\{\ \text{All H: } \tau\ 3{\cdot}27$

(3) Diamagnetic susceptibility exaltation:

$\Lambda\ -4{\cdot}6$

classical bond alternation, single carbon-carbon bonds of length 1.454 Å alternating with double bonds of length 1.333 Å.[17] The proton NMR spectrum at low temperature shows the molecule to be paratropic, the inner protons now resonating at low field and the outer protons at high field.[13, 15] This, of course, is a reversal of the behaviour of [18]annulene and has been explained theoretically for $4n$ π-electron systems[18] (at higher temperatures, an average is observed again). The diamagnetic susceptibility exaltation of [16]annulene has been determined,[19] and its negative value shows the substance also to be nonaromatic. Finally, [16]annulene is also nonaromatic in the more classical sense, since (unlike [18]annulene) it undergoes valence isomerization already at room temperature,[14] and no electrophilic substitution reactions have been reported.

Scheme VII summarizes all of the annulenes, from [10]- to [24]annulene, which have been prepared during the last fifteen years or so, using either of the two general routes described.[20] The Scheme indicates whether the annulene is a $4n$ or a $(4n+2)$ π-electron system, and its proton NMR spectral behaviour, which, as already mentioned, is probably the most convenient way to establish aromaticity. The only exceptional compounds are the two isomers of [10]annulene prepared by MASAMUNE.[21] Although they are $(4n+2)$ π-electron systems, they show no ring current (= atropic), and they are also very unstable. Presumably these medium size ring compounds are nonplanar, due to steric and/or ring angle strain in the hypothetical planar structures. It can be seen for the other annulenes that all the $(4n+2)$ π-electron systems proved to be diatropic, and all the $4n$ systems paratropic. This provides striking experimental confirmation of the validity of HÜCKEL's rule.

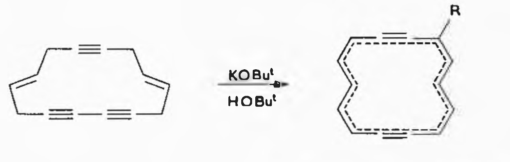
Scheme VII

Annulene	π – Electrons	^{1}H-NMR Spectrum
[10] Annulene, all-*cis*	$4n+2$	Atropic
mono-*trans*	$4n+2$	Atropic
[12] Annulene	$4n$	Paratropic
[14] Annulene, tri-*cis*	$4n+2$	Diatropic
tetra-*cis*	$4n+2$	Diatropic
[16] Annulene, tri-*cis*	$4n$	Paratropic
tetra-*cis*	$4n$	Paratropic
[18] Annulene	$4n+2$	Diatropic
[20] Annulene	$4n$	Paratropic
[22] Annulene	$4n+2$	Diatropic
[24] Annulene	$4n$	Paratropic

III. Dehydroannulenes

I now turn to the dehydroannulenes; *i.e.*, annulenes in which one or more of the double bonds have been replaced by acetylenes. The particular compounds I would like to mention are the symmetrical didehydroannulenes. The first known member was the dark red 1,8-didehydro[14]annulene (Scheme VIII), which was obtained by us in poor yield through base treatment of the unconjugated 14-membered ring precursor shown.[22, 23] No centrosymmetrical classical structure can be written for this dehydroannulene, and the most convenient structural representation is the one shown in Scheme VIII.

Scheme VIII



1,8-Didehydro[14]annulene
(R=H)

(1) Electrophilic substitution: R = NO_2, $COCH_3$, SO_3CH_3.

(2) X-ray structure: planar, centre of symmetry.

(3) ^{1}H-NMR spectrum: diatropic.

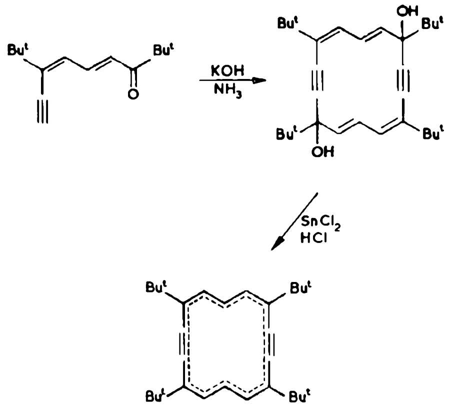
Inner H: τ 15·48
Outer H: τ 0·36, 1·46

(Sondheimer, 1962.)

The same criteria for aromaticity discussed for the annulenes apply, of course, also to the dehydroannulenes as far as the out-of-plane π-electrons are concerned. 1,8-Didehydro[14]annulene was expected to be a relatively rigid planar 14 π-electron system, and should therefore be aromatic. In fact, it proved to be one of the most aromatic monocyclic nonbenzenoid systems known. It was relatively stable, underwent electrophilic substitution reactions at the positions indicated in Scheme VIII,[24] and an X-ray crystallographic analysis showed it to be planar and centrosymmetrical.[25] Most conveniently, the proton NMR spectrum indicated it to be strongly diatropic, the inner protons resonating at very high field and the outer protons at low field.[23]

Quite recently, Nakagawa[26] has reported an efficient synthesis of such 1,8-didehydro[14]annulenes, as shown in Scheme IX. Treatment of the indicated acetylenic ketone with potassium hydroxide in liquid ammonia gave rise to the two possible stereoisomers of the cyclic dimeric diol. Reduction with stannous chloride then produced the tetra-*t*-butyl-1,8-didehydro[14]annulene in an over-all yield of 67%.[26]

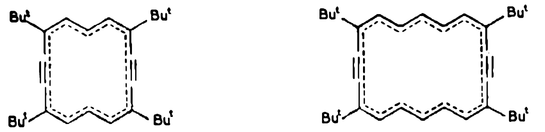
Scheme IX



Tetra-*t*-butyl-1,8-didehydro[14]annulene
67% over-all yield
(Nakagawa, 1972.)

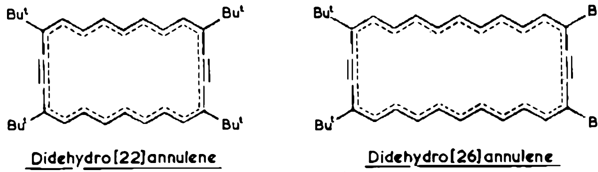
This method has been applied by Nakagawa to the synthesis of the corresponding symmetrical tetra-*t*-butyldidehydro [18] annulene,[27] -didehydro [22] annulene,[28] and -didehydro [26] annulene,[29] as indicated in Scheme X. Unlike the various annulenes, all these didehydroannulenes have essentially the same geometry. This makes it possible to study the effect of increasing the value of n in aromatic $(4n+2)$ π-electron systems, keeping the geometry largely unchanged. It can be seen from the proton NMR spectra (Scheme X) that the diamagnetic ring current becomes progressively less as the value of n is increased, although the ring current is still evident in the 26-membered ring compound. Unfortunately, the NMR spectrum of the 22-membered ring compound cannot be compared with the others, since this substance was reported in *Chemical Communications*,[28] and the authors were only permitted to state that its NMR spectrum indicated it to be aromatic. It should also be mentioned that the didehydroannulenes shown in Scheme X become progressively more coloured, the 26-membered ring compound being black-violet.[29]

Scheme X



Didehydro[14]annulene
^{1}H-NMR spectrum: diatropic
Inner H: τ 14·39
Outer H: τ 0·58

Didehydro[18]annulene
^{1}H-NMR spectrum: diatropic
Inner H: τ 13·42
Outer H: τ 0·62, 0·13



Didehydro[22]annulene
^{1}H-NMR spectrum: diatropic
(Chem. Comm.)

Didehydro[26]annulene
^{1}H-NMR spectrum: diatropic
Inner H: τ 8·4
Outer H: τ 2·05, 1·75

(Nakagawa, 1972.)

IV. Bridged Annulenes

All the nonbenzenoid aromatic compounds discussed so far have been monocyclic. I would now like to pass on to bicyclic and polycyclic systems, which may be considered as bridged annulenes. Probably the best known examples are the 1,6-bridged [10]annulenes prepared by Vogel. His synthesis of 1,6-methano[10]annulene[30] is shown in Scheme XI. The starting material was naphthalene, which was reduced with sodium in liquid ammonia to tetrahydronaphthalene.[31] Addition of dichlorocarbene to the central double bond led to a dichlorocyclopropane derivative, which was reduced to the corresponding hydrocarbon with sodium in liquid ammonia. Finally, a bromination-dehydrobromination sequence yielded 1,6-methano[10]annulene, presumably by valence isomerization of the initially formed tricyclic

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[17] S.M.Johnson and I.C.Paul, *J. Amer. Chem. Soc. 90* (1968) 6555; S.M.Johnson, I.C.Paul and G.S.D.King, *J. Chem. Soc.* (*B*) *1970*, 643.

[18] J.A.Pople and K.G.Untch, *J. Amer. Chem. Soc. 88* (1966) 4811; F.Baer, H.Kuhn and W.Regel, *Z. Naturforsch. A 22* (1967) 103; H.C.Longuet-Higgins, *Aromaticity*, The Chemical Society, Special Publication *21* (1967) 109.

[19] H.J.Dauben, J.D.Wilson and J.L.Laity, *J. Amer. Chem. Soc. 90* (1968) 811, *91* (1969) 1991.

[20] For references, see F.Sondheimer, *Accounts Chem. Res. 5* (1972) 81.

[21] S.Masamune and R.T.Seidner, *Chem. Commun. 1969*, 542; S.Masamune, K.Hojo, K.Hojo, G.Bigam and D.L.Rabenstein, *J. Amer. Chem. Soc. 93* (1971) 4966.

[22] F.Sondheimer and Y.Gaoni, *J. Amer. Chem. Soc. 82* (1960) 5765.

[23] F.Sondheimer, Y.Gaoni, L.M.Jackman, N.A.Bailey and R.Mason, *J. Amer. Chem. Soc. 84* (1962) 4595.

[24] Y.Gaoni and F.Sondheimer, *J. Amer. Chem. Soc. 86* (1964) 521.

[25] N.A.Bailey and R.Mason, *Proc. Chem. Soc. 1963*, 180; *Proc. Roy. Soc. A 290* (1966) 94.

[26] K.Fukui, T.Nomoto, S.Nakatsuji and M.Nakagawa, *Tetrahedron Letters 1972*, 3157.

[27] M.Iyoda and M.Nakagawa, *Tetrahedron Letters 1972*, 3161.

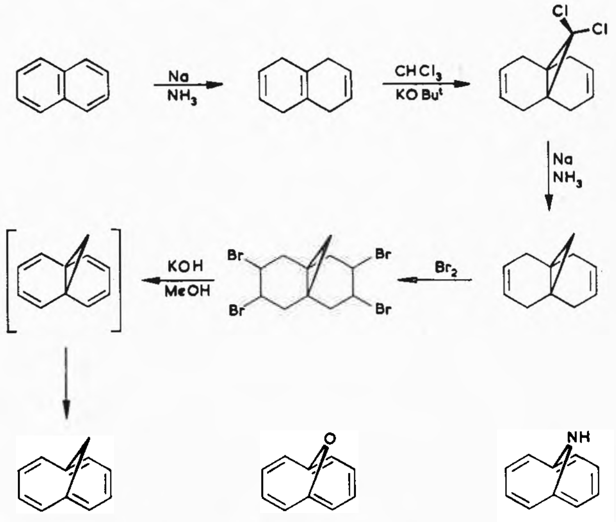
[28] M.Iyoda and M.Nakagawa, *Chem. Commun. 1972*, 1003.

[29] M.Iyoda and M.Nakagawa, *Tetrahedron Letters 1972*, 4253.

[30] E.Vogel and H.D.Roth, *Angew. Chem. 76* (1964) 145.

[31] W.Hückel and H.Schlee, *Chem. Ber. 88* (1955) 346; C.A.Grob and P.W.Schiess, *Helv. Chim. Acta 43* (1960) 1546.

Scheme XI. Bridged Annulenes



1,6-Methano-[10]annulene

1,6-Oxido-[10]annulene

1,6-Imino-[10]annulene

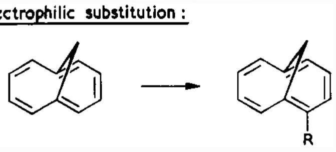
(Vogel, 1964.)

tetraene.[30] Other 1,6-bridged [10]annulenes, such as the 1,6-oxido[32] and the 1,6-imino[33] compounds, shown in Scheme XI, were prepared by essentially analogous methods.

The steric strain present in the hypothetical di-*trans* [10]annulene should be absent in the corresponding 1,6-bridged [10]annulenes, and these were therefore expected to be aromatic 10 π-electron systems. Indeed, this proved to be the case, as indicated in Scheme XII for 1,6-methano[10]annulene. This was a stable colourless substance, which readily underwent electrophilic substitution reactions at the 2-position.[34] An X-ray crystallographic analysis of the corresponding 2-carboxylic acid showed there to be no appreciable bond alternation (all perimeter carbon-carbon bonds are of lengths 1.38 to 1.42 Å).[35] The proton NMR spectrum clearly showed 1,6-methano[10]annulene to be diatropic, the olefinic protons resonating at low field and the methylene protons at high field.[30,36] Many other properties of the substance point to its aromatic nature, such as the diamagnetic susceptibility exaltation,[19] the electronic spectrum,[37] the photoelectron spectrum,[38] the formation enthalpy,[39] the dipole moment,[40] *etc.* In fact, 1,6-methano[10]annulene is probably the most intensively studied of all nonbenzenoid aromatic compounds.

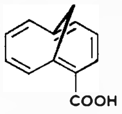
Scheme XII
"Aromatic" Properties of 1,6-Methano[10]annulene

(1) Electrophilic substitution:



R = Br, NO_2, $COCH_3$, etc.

(2) X-ray structure: all bonds 1·38–1·42 Å.



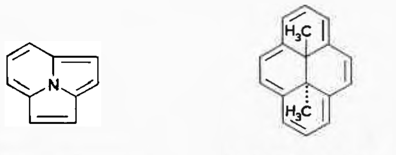
(3) ¹H-NMR spectrum: diatropic.

Olefinic H: τ 2·73, 3·05.
Methylene H: τ 10·52.

(4) Other properties: diamagnetic susceptibility exaltation, electronic spectrum, photoelectron spectrum, formation enthalpy, dipole moment, etc.

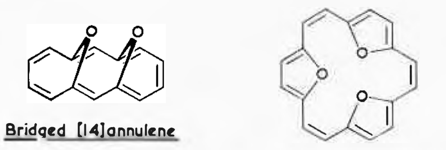
A variety of other aromatic bridged annulenes have been prepared, some of which are shown in Scheme XIII. Thus, cycl[3.2.2]azine, another bridged [10]annulene, was reported, by **Boekelheide**[41] almost 15 years ago. The same investigator synthesized a variety of 15,16-dihydropyrene derivatives, such as the *trans* 15,16-dimethyl derivative shown,[42] which are bridged [14]annulenes. Bridged [14]annulenes with the anthracene perimeter, such as the syn dioxide[43] indicated in Scheme XIII, were prepared by **Vogel**. Finally, some bridged [18]annulenes, like the trioxide shown, were synthesized by **Badger**,[44] and another type has recently been reported by **Boekelheide**.[45] All of these bridged $(4n+2)$ π-electron systems proved to be aromatic in a number of ways, such as in their stability, presence of a diamagnetic ring current as evidenced by proton NMR spectroscopy, and by their ability to undergo electrophilic substitution reactions.

Scheme XIII. Other Aromatic Bridged Annulenes



Bridged [10]annulene
(Boekelheide, 1959.)

Bridged [14]annulene
(Boekelheide, 1964.)



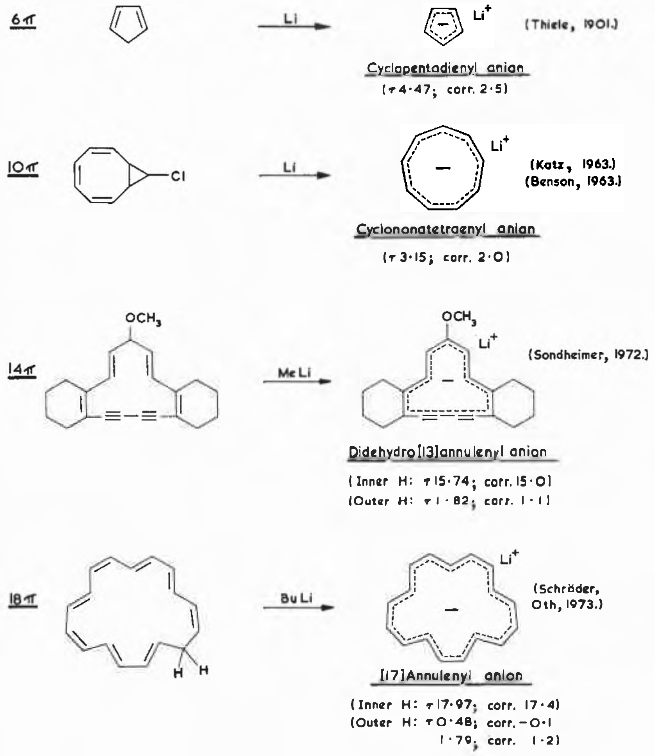
Bridged [14]annulene
(Vogel, 1966.)

Bridged [18]annulene
(Badger, 1965.)

V. Ionic Systems

All the above described compounds have been neutral ones. I would now like to turn to charged nonbenzenoid aromatic systems, some of which were the first such systems to be prepared after benzene. If we consider a conjugated odd-membered ring containing $(4n+1)$ carbon atoms, then the anion will possess $(4n+2)$ π-electrons and should be aromatic. The best known member of this type of aromatic anion is the cyclopentadienyl anion (Scheme XIV), which was prepared (as the potassium salt) by THIELE already over 70 years ago.[46] This 6π-electron system is indeed aromatic, as shown by its ease of formation and by its stability (in the absence of air or moisture). As usual, the most convenient measurement is the proton NMR spectrum,[47, 48] which shows the ion to be diatropic if a correction for the negative charge is made (see Scheme XIV). Similarly, the cyclononatetraenyl anion, containing 10 π-electrons, prepared by the method shown,[49] was found to be diatropic. The fact that this is an aromatic planar system is in marked contrast to the nonaromatic properties of the isoelectronic nonplanar [10]annulenes.[21] The next higher homologue, the [13]annulenyl anion is still unknown. The closest analogue is the substituted didehydro[13]-annulenyl anion shown.[50] This deep red 14 π-electron system is strongly diatropic and this effect can be especially well seen since the ion now contains inner as well as outer protons. Finally, the deep green [17]annulenyl anion, containing 18 π-electrons, was reported very recently by SCHRÖDER and OTH.[51] As expected, this ion proved to be strongly diatropic, and was quite stable in the absence of air or moisture (*e.g.*, it could be heated to 100° for 1 hour without change).

Scheme XIV. Aromatic Anions



I now come to the subject of aromatic cations. Conversely to the anions just mentioned, if we consider a conjugated odd-membered ring containing $(4n+3)$ carbon atoms, it is the cation which will contain $(4n+2)$ π-electrons and should be aromatic. The smallest such cation known is the 2π-electron cyclopropenium cation shown in Scheme XV, prepared by BRESLOW[52] by the method indicated. The next higher homologue, the 6π-electron tropylium cation, was made as shown in Scheme XV over 80 years ago by MERLING,[53] although the nature of this species was recognized only in 1954 by DOERING.[54, 55] The unmodified higher cations are still un-

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[33] E. VOGEL, W. PRETZER and W. A. BÖLL, *Tetrahedron Letters 1965*, 3613.

[34] See E. VOGEL and W. A. BÖLL, *Angew. Chem. 76* (1964) 784; E. VOGEL, W. A. BÖLL and M. BISKUP, *Tetrahedron Letters 1966*, 1569.

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[41] R. J. WINDGASSEN, W. H. SAUNDERS and V. BOEKELHEIDE, *J. Amer. Chem. Soc. 81* (1959) 1459.

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[43] E. VOGEL, M. BISKUP, A. VOGEL and H. GÜNTHER, *Angew. Chem. 78* (1966) 755; E. VOGEL, *Chimia 22* (1968) 21.

[44] G. M. BADGER, J. A. ELIX, G. E. LEWIS, U. P. SINGH and T. M. SPOTSWOOD, *Chem. Commun. 1965*, 269; G. M. BADGER, J. A. ELIX and G. E. LEWIS, *Austral. J. Chem. 19* (1966) 1221.

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[46] J. THIELE, *Ber. dtsch. chem. Ges. 34* (1901) 68.

[47] G. FRAENKEL, R. E. CARTER, A. MCLACHLAN and J. H. RICHARDS, *J. Amer. Chem. Soc. 82* (1960) 5846.

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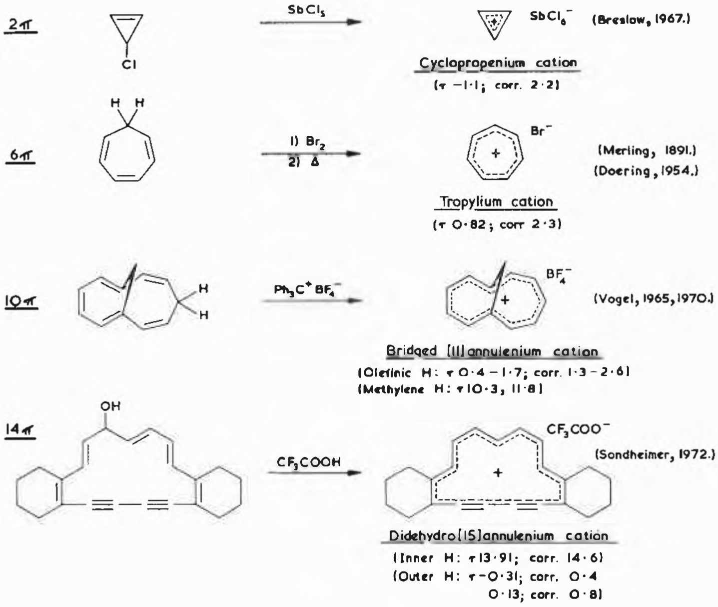
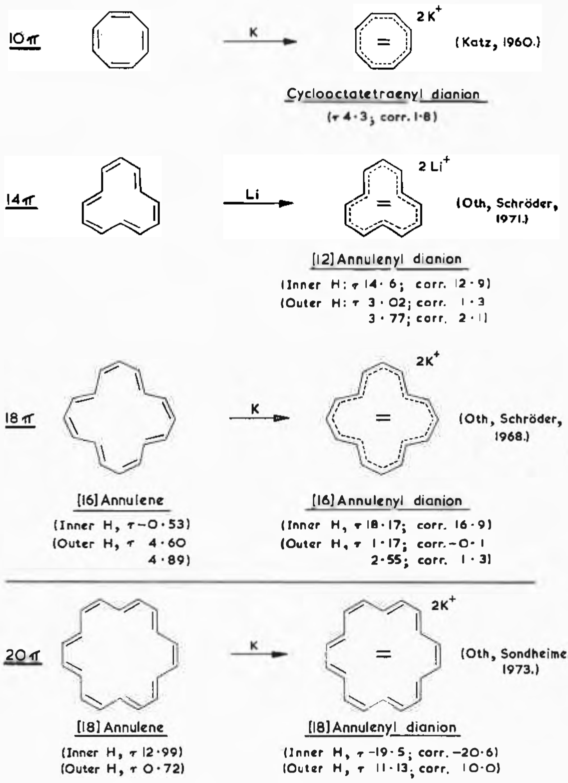
known. However, the 10 π-electron briged [11]annulenium cation and the 14 π-electron didehydro[15]annulenium cation, both shown in Scheme XV, have been synthesized as indicated by VOGEL[56] and by us,[57] respectively. All of the $(4n+2)$ π-electron cations shown in Scheme XV proved to be aromatic in a number of ways. This is most easily seen from the proton NMR spectra, given in the Scheme, which proved all the cations to be diatropic (again, a correction for the charge has been made).

In addition to the aromatic *monoionic* annulenes just described, it is possible to prepare aromatic *diionic* annulenes, the most widely studied being the dianions. Thus, it was found by KATZ[58] that treatment of cyclooctatetraene with potassium leads to the diatropic 10π-electron cyclooctatetraenyl dianion (Scheme XVI). Similarly, OTH and SCHRÖDER[59] showed that reaction of the very unstable [12]annulene with lithium gives rise to the relatively stable diatropic 14π-electron dianion (Scheme XVI). In a similar way, these workers converted [16]annulene to the 18π-electron dianion,[16] which could be heated at 100° for 2 days without change, and proved once again to be strongly diatropic (Scheme XVI). It is instructive to compare the NMR resonances of the inner protons of the *diatropic* [16]annulenyl dianion with those of the inner protons of the *paratropic* [18]annulenyl dianion, a $4n$ π-electron system recently prepared from [18]annulene with potassium.[60] These resonances are at $\tau + 18.2$ in the $(4n+2)$ π-dianion, but at $\tau - 19.5$ in the $4n\,\pi$-dianion, which is a really dramatic difference!

Scheme XV. Aromatic Cations

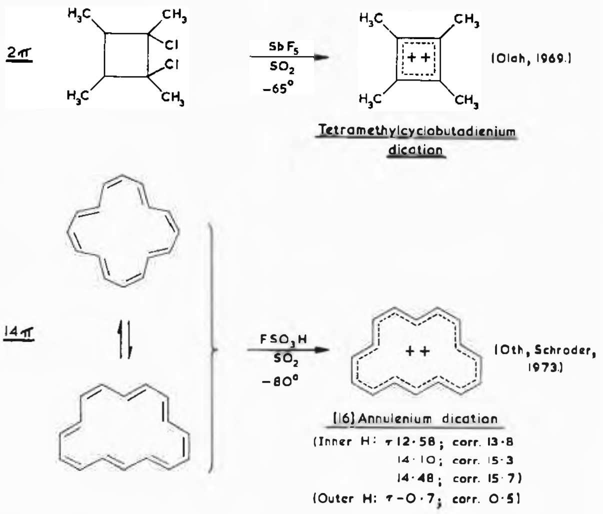


Scheme XVI. Aromatic Dianions



Some success has also been achieved in the synthesis of aromatic dications. In 1969, OLAH[61] obtained some evidence (mainly from ^{13}C NMR spectroscopy) that the tetramethylcyclobutadienium dication, prepared as shown in Scheme XVII, is an aromatic 2π-electron system. However, the corresponding unsubstituted dication has not been obtained. Similarly, the cyclooctatetraenium dication (which should contain 6π-electrons) has not been made, since treatment of cyclooctatetraene with strong acids instead leads to the homotropylium cation.[62] In view of these results, it was rather surprising when OTH and SCHRÖDER[63] reported very recently that treatment of [16]annulene with fluorosulphonic acid at

Scheme XVII. Aromatic Dications



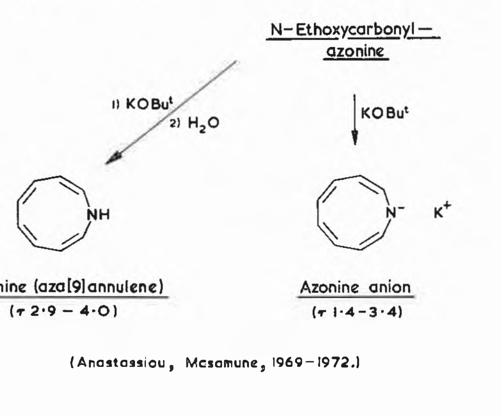
− 80° smoothly leads to the corresponding dication, which possesses the configuration shown in Scheme XVII. This is the first unsubstituted annulenium dication to be observed, and, as expected of a 14π-electron system, its proton NMR spectrum showed it to be strongly diatropic.

VI. Heteroaromatic Systems

All the nonbenzenoid aromatic systems discussed so far have been carbocyclic. I would now like to describe some recent advances that have been made in the field of heteroaromatic chemistry. There are essentially two types of such heterocyclic systems that may be considered. The first type is formally derived from an annulene by replacement of a carbon-carbon double bond by the heteroatom, which contributes two electrons to the π-system. Well known examples are thiophene, pyrrole and furan, which are 5-membered 6π-electron systems. The second type is formally derived from an annulene by replacement of a CH group by the heteroatom, which contributes one electron to the π-system. A representative of this type is pyridine, which, like benzene, is a 6-membered 6π-electron system. I will not mention these common heteroaromatic compounds further, since their aromatic properties are quite well known and a discussion of them is hardly appropriate in a review of this nature.

However, there has been considerable interest in recent years in the synthesis and study of potentially aromatic higher homologues of heterocyclic systems of the thiophene-pyrrole-furan type. Thus, it was found by ANASTASSIOU[64, 65] and by MASAMUNE[66] that irradiation of N-ethoxycarbonyl-9-azabicyclo[6.1.0]nona-2,4,6-triene (Scheme XVIII) gives rise to N-ethoxycarbonylazonine, the monocyclic valence isomer. Treatment of this urethane with potassium *t*-butoxide followed by addition of water yielded 1H-azonine,[65, 67] which, for clarity, we may call aza[9]annulene. This is a potential 10π-electron system, and it was found to be aromatic in certain ways. For instance, the proton NMR spectrum indicated it to be diatropic and it was relatively stable to valence isomerization to a bicyclic isomer.[65, 67, 68] As expected, the corresponding anion (Scheme XVIII) was even more aromatic in these respects.[65, 68, 69, 70] The aromatic properties of these compounds is in contrast to the nonaromatic behaviour of the N-ethoxycarbonylazonine precursor[64, 65, 66, 68] or the corresponding oxa-[9]annulene (oxonin),[65, 68, 71, 72] presumably because of the electron withdrawing properties of the heteroatoms in these substances.

Scheme XVIII. Heteronins (Hetero[9]annulenes)



(Anastassiou, Masamune, 1969–1972.)

Quite recently SCHRÖDER and OTH have succeeded in the synthesis of an N-ethoxycarbonylaza[13]annulene,[73] as well as three isomers each of N-ethoxycarbonylaza-[17]annulene[74] and oxa[17]annulene,[75] through photolysis of corresponding tetracyclic valence isomers (Scheme XIX). These are all coloured compounds, the 13-membered one being yellow, and the 17-membered ones being red. Although these are potentially 14 and 18π-electron systems, they did not appear to be aromatic and the proton NMR spectra revealed little, if any, diamagnetic ring current. This may be due to the fact that in these heteroannulenes, containing relatively strongly electron withdrawing groups, the difference in energy between the localized and delocalized form will not be great. In view of the steric interaction of the internal

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[73] G. SCHRÖDER, G. FRANK and J. F. M. OTH, *Angew. Chem. 85* (1973) 353.

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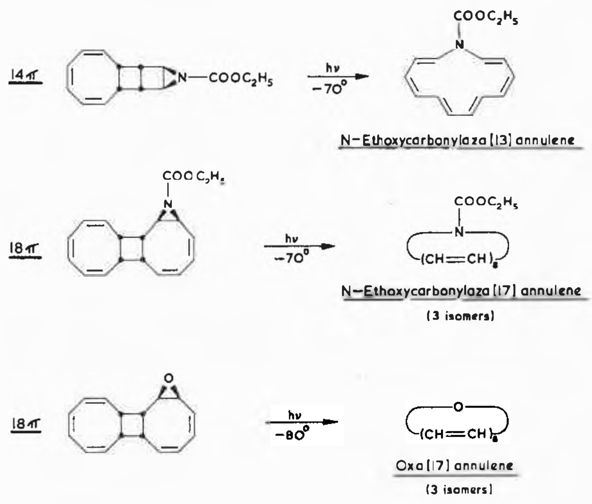
[75] G. SCHRÖDER, G. PLINKE and J. F. M. OTH, *Angew. Chem. 84* (1972) 472.

Scheme XIX
Hetero[13]annulenes and Hetero[17]annulenes



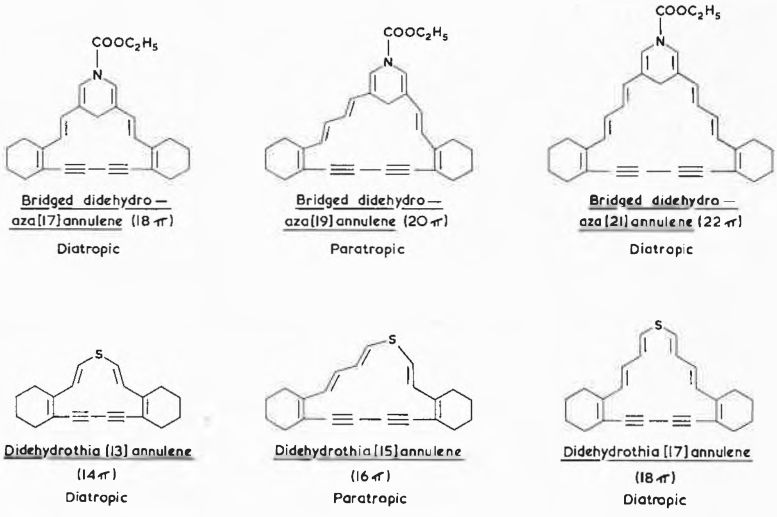
Little, if any, diamagnetic ring current.
(Schröder, Oth, 1972-1973.)

protons in a relatively planar structure, the heteroannulenes may well exist as nonaromatic nonplanar molecules.

In view of these results, it was of interest to synthesize related heteroannulenes in which the macrocyclic rings are more rigid, through incorporation of a bridge and/or acetylenic bonds. Towards this end, we have recently prepared the methylene bridged didehydroaza[17]annulene[76] shown in Scheme XX, as well as the corresponding didehydroaza[19]annulene[77] and didehydroaza-[21]annulene[78] (Scheme XX). These are potentially 18π-, 20π- and 22π-electron systems, respectively, and they should therefore be aromatic, nonaromatic, and aromatic, respectively. In the event, the theoretically aromatic aza[17]- and aza[21]annulenes were found to be diatropic,[76, 78] whereas the theoretically nonaromatic aza[19]annulene was found to be paratropic.[77] This shows that the same alternation of electromagnetic properties between $(4n+2)$ and $4n$ π-electron systems takes places in these heteroannulenes, as has already been found in the carbocyclic series.

Methylene bridging is actually unnecessary for ring current effects to be observed in macrocyclic heteroannulenes. Thus, we have quite recently prepared the unbridged didehydrothia[13]annulene[79] shown in the lower part of Scheme XX, as well as the corresponding didehydrothia[15]annulene[79] and didehydrothia[17]-annulene[80] (Scheme XX). Again, the potentially aromatic $(4n+2)\pi$-systems proved to be diatropic, and the potentially nonaromatic $4n$ system was paratropic, in agreement with theory.

Scheme XX. Dehydroaza-annulenes and Dehydrothia-annulenes



(Sondheimer, 1972-1973.)

VII. Conclusion

There are, of course, a variety of nonbenzenoid aromatic π-electron systems I have not had time to mention. For instance, it has not been possible to deal with cyclic conjugated ketones such as cyclopropenone, with bicyclic and polycyclic hydrocarbons containing "zero" bridges such as azulene, with polycyclic ions such as the pentalenyl dianion, with metallo-organic compounds such as ferrocene, with bicycloaromatic systems, with aromatic transition states, *etc.*[2] As already mentioned at the beginning of this review, I have had to be quite selective in the choice of topics to be covered, and I hope I will be forgiven if the reader does not agree with the exact selection I have decided to make.

In conclusion, I would like to make a few remarks about aromaticity. There is no doubt in my mind that there is only one completely aromatic molecule, and that is benzene. Had most of the other systems I have discussed been investigated by the 19th century chemists, instead of benzene, the term "aromatic" would probably never have been coined. Nevertheless, the concept of aromaticity has been a very useful one. It has stimulated much theoretical work and even more experimental work, and it has greatly advanced the field of organic chemistry. In my opinion, that is what really matters, even if there is still no general agreement about what exactly is meant by aromaticity.

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[78] P. J. Beeby and F. Sondheimer, *Angew. Chem. 85* (1973) 404.

[79] P. J. Beeby and F. Sondheimer, unpublished experiments.

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