AROMATIC AND NON-AROMATIC
14π-ELECTRON SYSTEMS

EMANUEL VOGEL

Institut für Organische Chemie der Universität Köln, Germany

ABSTRACT

The synthesis and aromaticity of 1,6-methano[10]annulene and its analogues with a heteroatom bridge suggested the possibility that the homologous series of bridged [4n + 2]annulenes 1, 2, 3 etc., formally derived from the acene series, could be obtained. In the pursuit of this concept several bridged [14]annulenes with an anthracene perimeter differing in the conformation of the perimeter have been synthesized. The physical and chemical properties of these [14]annulenes dramatically demonstrate the importance of a planar or near-planar π-electron system as a geometrical pre-requisite for aromaticity.

As the lectures presented at this conference have amply demonstrated, the application of quantum-mechanical theories, in particular molecular orbital theory, to organic molecules and processes has become a major factor in promoting progress in organic chemistry. While, in these days, we witness with fascination the stimulus of Woodward and Hoffmann's concept of orbital symmetry conservation1 on the study of mechanistic pathways of organic reactions, the impact which the molecular orbital theory of benzene2, as expressed by Hückel's famous (4n + 2)-rule, has had on the development of aromatic chemistry is almost taken for granted. The fruitful symbiosis between theory and experiment in the latter domain manifests itself impressively in the discovery of an entire realm of novel aromatic structures. Many of these structures, brought to light in the last two decades, have already found their way into textbooks of organic chemistry. It may suffice to mention the tropylium ion3, whose isolation first made the organic chemist aware of the potential of molecular orbital theory, the homologous cyclopropenyl cation4, the cyclononatetraenyl anions5,6 and finally the great variety of annulenes7-10. The class of new aromatic and non-aromatic [14]annulenes that will be the subject of the present lecture is to be regarded as yet another outgrowth of research having derived its inspiration from Hückel's pioneering work.

The efforts at the Cologne laboratory in the field of Hückel-type aromatic compounds had as their initial goal the synthesis of [10]annulene11 in its various configurations. If planar and not unduly strained, this type of species could be expected to be closer to benzene in its physical and chemical properties than any other member of the [4n + 2]annulene series, and would thus promise interesting chemistry. Unfortunately, the stereoisomeric [10]annulenes, regardless of their configuration, possess geometrical features presumed to be detrimental to aromaticity. In view of this handicap it is
hardly surprising that even the seemingly most compelling synthetic routes to [10]annulenes, for example the thermal or photochemical valence isomerization of the 9,10-dihydronaphthalenes, have so far failed to produce benzene-like fully conjugated systems\textsuperscript{12}.

\( I(X = \text{CH}_2, \text{O}, \text{NH}) \)

Some years ago, however, we recognized that 1,6-methano[10]annulene \([1(X = \text{CH}_2)]\)\textsuperscript{13}, a bridged [10]annulene formally derived from the apparently non-planar di-trans-[10]annulene by replacement of its two inner hydrogens by a CH\textsubscript{2}-group—or, alternatively, from naphthalene by inserting a CH\textsubscript{2}-group into the 9,10-bond—would have an approximately planar C\textsubscript{10}-carbon perimeter and could therefore be expected to qualify as an aromatic molecule. Indeed, 1,6-methano[10]annulene, in striking contrast to the olefinic cyclooctatetraene, closely parallels benzene and naphthalene in its physical and chemical behaviour. Thus it can be converted, like these classical aromatic hydrocarbons, into a host of substitution products on treatment with electrophilic reagents. In line with theoretical calculations\textsuperscript{14} substitution preferentially occurs at the 2- or \( \alpha \)-position. While the aliphatic bridge moiety of 1,6-methano[10]annulene may be looked upon as a Schönheitsfehler it has the benefit of adding to the chemical versatility of the hydrocarbon.

The synthesis and aromaticity of 1,6-methano[10]annulene and of its analogues with a heteroatom bridge \([1(X = \text{O} \text{ or NH})]\)\textsuperscript{15,16} suggested the existence of the homologous series of bridged annulenes 1, 2, 3 etc., whose members are formally derived from naphthalene, anthracene, benzantracene, and so on, by insertion of the bridge functions X into the bonds common to two rings and which, like the parent aromatic hydrocarbons, contain \((4n + 2)\) \( \pi \)-electrons. The ‘device of bridging’ thus allows the well-known acene series to be converted into a series of \([4n + 2]\)annulenes\textsuperscript{13b–d,17}. 

\( \text{syn} \)

\( \text{anti} \)
The presence of more than one bridge implies that there will be a syn- and an anti-configuration (4 and 5) for the [14]annulenes (2) and three configurations (syn-syn, syn-anti and anti-anti) for the [18]annulenes (3). Since the Hückel-rule can be considered valid up to the 22π-electron system, the question of whether the aromaticity established for 1 also extends to the higher homologues should depend mainly on the geometry of the carbon perimeter.

From an inspection of Dreiding and space-filling models of the bridged [14]- and [18]annulenes the following conclusions can be drawn:

1. The conformational mobility of these molecules is greatly reduced as compared with that of the corresponding non-bridged annulenes.

2. In the syn-configuration of the [14]annulenes (4) the perimeter can assume an approximately planar conformation provided that no steric interaction between the bridges occurs. By contrast, in the anti-configuration (5) the perimeter appears to be considerably puckered.

3. The efficiency of the 2p-2 orbital overlap in the syn- and anti-configurations of the [14]annulenes is largely determined by the steric conditions in the perimeter segments consisting of neighbouring bridgehead carbon atoms and the carbon atom between them. As illustrated by the drawings 6 and 7, in the syn-configuration the 2p-2 orbitals of such a three-carbon moiety can align themselves in virtually parallel fashion, whereas in the anti-configuration the respective 2p-2 orbitals are noticeably skewed with respect to each other. Accordingly, only the bridged [14]annulenes with the syn-configuration are likely to be distinguished by aromatic character.

4. In the syn-syn-configuration of the [18]annulenes (and in the all-syn-configuration of the higher homologues) analogous steric conditions obtain as in the syn-configuration of the [14]annulenes.

5. Extension of the perimeter from 10 to 14 and 18 carbon atoms eases the restraint on the bridge angle and allows the perimeter for the syn-configuration of the [14]annulenes and the syn-syn-configuration of the [18]annulenes to approach planarity more closely than that for the [10]-annulenes.

That these steric considerations do come quite close to reality is impressively demonstrated by our recent efforts to synthesize bridged [14]annulenes with both syn- and anti-configurations.
Naturally, the most interesting representatives of the bridged [14]annulenes are the hydrocarbons, i.e. syn- and anti-1,6:8,13-bismethano[14]annulene (8 and 9). These molecules, similar to 1,6-methano[10]annulene, have the special virtue of possessing bridge hydrogens whose n.m.r absorptions can be directly related to the degree of π-electron delocalization in the perimeter. However, syn-1,6:8,13-bismethano[14]annulene fails to be an ideal molecule to test our concept, since, as space-filling models indicate, there is appreciable steric interference between the two internal bridge hydrogens, which almost certainly leads to a twisting of the perimeter.

As a survey of the van der Waals radii of the various functionalities that may serve as bridges reveals, oxygen atoms would make ideal syn-bridges in that these atoms permit the syn-configuration to attain an optimally flattened perimeter. The chances for a bridged [14]annulene with an acene perimeter
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to be aromatic should thus be greatest in the case of syn-1,6:8,13-bisoxido-[14]annulene (10). We therefore chose syn-1,6:8,13-bisoxido[14]annulene and, for the sake of testing our concept rigorously, also anti-1,6:8,13-bisoxido[14]annulene (11) as the prime targets of our synthetic efforts.

As reported recently, syn-1,6:8,13-bisoxido[14]annulene could be prepared in a reaction sequence involving only three steps starting from 1,4,5,8,9,10-hexahydroanthracene. This first representative of the bridged [14]annulenes with an acene perimeter was obtained as a brilliantly red compound, showing remarkable stability.

For an aromatic syn-1,6:8,13-bisoxido[14]annulene one would expect an n.m.r. spectrum which, with regard to the absorptions of the eight outer perimeter protons, should be entirely analogous to that of 1,6-oxido[10]-annulene. These protons should accordingly give rise to a single AA'BB'-system at low field. In the spectrum of syn-1,6:8,13-bisoxido[14]annulene one should in addition find a singlet, due to the two central perimeter protons, also at low field. As Figure 1 shows, the red compound possesses the spectrum anticipated. One observes one AA'BB'-system, centred at $\tau$ 2.33, and further downfield a singlet at $\tau$ 2.06. The analogy in the n.m.r. spectra of syn-1,6:8,13-bisoxido[14]annulene and 1,6-oxido[10]annulene furthermore extends to the coupling parameters of the protons associated with the respective AA'BB'-systems. These couplings are virtually identical for the two compounds (Table 1). 1,6-Oxido[10]annulene and syn-1,6:8,13-bisoxido[14]annulene are thus, indeed, members of a homologous series of aromatic [4n + 2]-annulenes.

Additional proof that we are dealing with an aromatic syn-1,6:8,13-bisoxido[14]annulene is provided by an x-ray analysis of the compound that was carried out by Ganis and Dunitz. This analysis shows that the real structure of the compound comes surprisingly close to the geometry previously inferred from the molecular models (Figure 2). Thus, the C—O—C-bridge angle, found to be a normal 108°, is noticeably larger than the C—O—C-bridge angle of 1,6-oxido[10]annulene (102°), and accordingly

<table>
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<tr>
<th>Compound</th>
<th>$\tau_A$</th>
<th>$\tau_B$</th>
<th>$J_{AB}$</th>
<th>$J_{BB}$</th>
<th>$J_{AB'}$</th>
<th>$J_{AA'}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (X = O)</td>
<td>2.54</td>
<td>2.74</td>
<td>8.77</td>
<td>9.28</td>
<td>0.28</td>
<td>1.13</td>
<td>21</td>
</tr>
<tr>
<td>(10)</td>
<td>2.25</td>
<td>2.40</td>
<td>9.01</td>
<td>9.22</td>
<td>0.31</td>
<td>1.14</td>
<td>19</td>
</tr>
<tr>
<td>(19)</td>
<td>2.26</td>
<td>2.45</td>
<td>9.15</td>
<td>9.50</td>
<td>0.41</td>
<td>1.37</td>
<td>31</td>
</tr>
<tr>
<td>(40)</td>
<td>2.43</td>
<td>2.88</td>
<td>9.24</td>
<td>9.31</td>
<td>0.21</td>
<td>1.53</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 1. Chemical shifts ($\tau$-values in p.p.m.) and H,H-coupling constants of some bridged [10]- and [14]annulenes
the C14-perimeter is even flatter than the C10-perimeter in the 10π-electron analogue. Furthermore, the oxygen bridges, as judged by their distance of 2.550 Å, do not interfere sterically to any appreciable extent. In fact, the observed O—O-distance is, to our knowledge, the shortest ever encountered between two non-bonded oxygen atoms in an organic molecule. Probably, the most salient structural finding for syn-1,6:8,13-bisoxido[14]annulene relates to the C—C-bonds in the C14-perimeter: these bonds are almost equal in length, measuring 1.39 ± 0.01 Å, and are thus typical benzenoid aromatic bonds.

Figure 2. Molecular geometry of syn-1,6:8,13-bisoxido[14]annulene (10).
The aromatic character of syn-1,6:8,13-bisoxido[14]annulene deduced from the n.m.r. spectrum and from the x-ray analysis is mirrored chemically in the noteworthy thermal stability of the compound and its relative insensitivity toward oxygen. Recent experiments have further shown that syn-1,6:8,13-bisoxido[14]annulene affords products of substitution on treatment with electrophilic reagents

Reactions in which substituted syn-1,6:8,13-bisoxido[14]annulenes are produced in good yields involve bromination with elementary bromine at 0° in methylene chloride, Friedel–Crafts acylation with acetic anhydride, and nitration with copper(ii) nitrate in acetic anhydride. In each case one of the three possible mono-substitution products was formed in large excess over the others.

An ideal chemical method to locate the substituents in these mono-substituted syn-1,6:8,13-bisoxido[14]annulenes would be deoxygenation with formation of the corresponding anthracene derivatives which are either known or can be readily characterized. In connection with studies originally aimed at the preparation of transition metal complexes of 10 it was found that the oxygen atoms of the bisoxido-compound are smoothly removed by means of chromium hexacarbonyl whereby anthracene is formed in essentially quantitative yield. This deoxygenation method, when applied to the substituted syn-1,6:8,13-bisoxido[14]annulenes, showed that the substituents had entered into the 2-position in each case (with formation of 12, 13 and 14, respectively), and not into the 7-position as one might have inferred from the substitution pattern of anthracene.

After syn-1,6:8,13-bisoxido[14]annulene had been demonstrated to be an aromatic molecule, the question of whether anti-1,6:8,13-bisoxido[14]-annulene (11) would be olefinic, as anticipated from the models, became of utmost interest. The attempted synthesis of 11 involved, as the key intermediate, the anti-bis-(arene oxide) 15 which can be assumed to be in equilibrium with a low concentration of its bis-oxepin valence tautomer 16. When 15 was treated in the temperature range of 80° to 120° with dehydrogenating agents such as 3,4-dichloro-5,6-dicyano-p-benzoquinone or oxygen...
in basic medium the previously described syn-1,6:8,13-bisoxido[14]annulene was invariably obtained. Evidently, at one stage of these reactions an inversion of an oxygen atom through the C_{14}-perimeter had taken place. It was clearly beyond the capability of the molecular models to predict that such an inversion would proceed so readily.

From the subsequent finding that at 80° to 100° it is deduced that inversion occurs at the stage of the non-isolable anti-bisoxepin.

In view of the feasibility of the conversion of 16 into 17 it is almost certain that the hypothetical anti-1,6:8,13-bisoxido[14]annulene (11)—if it is olefinic as we assume—will also be subject to a ready oxygen inversion and thus be converted to the aromatic syn-isomer. That 11 must be an olefinic compound can be concluded with great confidence from the properties of anti-1,6:8,13-bismethano[14]annulene (9), to be discussed subsequently, in which the relatively bulky CH_{2}-groups no longer permit bridge inversion. The occurrence of an anti-syn-configurational (or conformational) change in the 1,6:8,13-bisoxido[14]annulene series (11 → 10) is thus not mere speculation.

The preparation of syn-1,6:8,13-bisoxido[14]annulene and the verification of its aromaticity substantiated the far-reaching potential inherent in our concept of bridged annulenes and encouraged us to tackle next the more demanding synthesis of carbon bridged [14]annulenes with an acene perimeter. Actually, one can think of quite an array of carbon bridged [14]annulenes, each member of which exhibits special features that invite study.
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What comes to one's mind immediately is a stepwise replacement of the oxygen atoms in syn-1,6:8,13-bisoxido[14]annulene (10) by CH₂-groups that would lead via syn-1,6-methano-8,13-oxido[14]annulene (18) to the already mentioned syn-1,6:8,13-bismethano[14]annulene (8). A comparison of these three species promises to be very instructive in that it should reveal the steric demand of CH₂-bridges which can only vaguely be gathered from molecular models.

If syn-1,6:8,13-bismethano[14]annulene (8) should suffer from a severe steric inhibition of resonance due to the interference of the two internal bridge hydrogens, the obvious cure for this steric handicap would be the replacement of these hydrogens in the already familiar fashion by a CH₂-group. By this transformation we arrive at 1,6:8,13-Propanediylidene[14]annulene (19) (previously termed propano[14]annulene\(^1\) which not only possesses as syn-1,6:8,13-bisoxido[14]annulene an approximately planar C\(_{14}\)-perimeter, but has the added advantage of having a totally rigid skeleton. 1,6:8,13-Propanediylidene[14]annulene is thus to be regarded as the actual syn-analogue of anti-1,6:8,13-bismethano[14]annulene (9).

In the following I would like to outline some of the progress that has recently been accomplished in this area of carbon-bridged [14]annulenes.

It turned out that the scheme underlying the synthesis of syn-1,6:8,13-bisoxido[14]annulene (10) could also be adapted, with proper modifications, to the preparation of syn-1,6-methano-8,13-oxido[14]annulene (18), in which one of the oxygens of 10 has been replaced by a CH₂-group. This new bridged [14]annulene is found to be a stable orange-red compound that, similar to syn-1,6:8,13-bisoxido[14]annulene, displays aromatic character.

![Figure 3. The n.m.r. spectrum of syn-1,6-methano-8,13-oxido[14]annulene (18) (in CDCl₃; 60 MHz; internal standard: tetramethylsilane).](image-url)
The aromaticity of syn-1,6-methano-8,13-oxido[14]annulene (18) is clearly evident from its n.m.r. spectrum (Figure 3). Taking the reduced symmetry of 18—C₃ against C₂ᵥ of 10—into account, the n.m.r. spectrum of the compound fully corresponds to that of 10 and also to that of the hydrocarbon 19, to be described later. The two central perimeter protons give rise to a singlet, located at δ 2.25, while the eight outer perimeter protons appear as a multiplet at δ 2.2–2.7, which can be analysed in terms of two partly superimposed AA'BB'-systems. Complementary to the low-field absorption of the perimeter protons one observes at relatively high field, at δ 9.08 and 11.40, an AB-system of the CH₂-bridge protons with J = 10.6 Hz. By analogy with the spectra of other compounds, in which a similar steric relationship between a CH₂-group and an oxygen function obtains as in 18, the doublet at lower field can be assigned to the proton adjacent to the oxygen atom. The remarkably big difference in the chemical shift of these two CH₂-protons, amounting to 2.3 p.p.m., not only proves the syn-configuration of 18, but also, because of its magnitude, reveals appreciable steric interaction between the two bridges. From the n.m.r. data of both the perimeter and the bridge protons it must be concluded that the molecule more easily tolerates a compression at the bridges than a bending of the perimeter.

The same conclusions regarding the geometry of 18 also follow from other spectral data, in particular from the similarities in the u.v. spectra of 18 and 10.

Our efforts to prepare, also, the third member in the series 10, 18 and 8, i.e. syn-1,6:8,13-bismethano[14]annulene, employing the pattern of synthesis used for 10, have so far not met with success. Nevertheless, we are hopeful we shall obtain 8 before too long, since the difficulties encountered appear to lie solely in methodology and not in an inherent instability of the hydrocarbon.

In the meantime, however, we have been able to synthesize the anti-isomer of 8, the anti-1,6:8,13-bismethano[14]annulene (9). At this point we should recall that according to the molecular models anti-1,6:8,13-bismethano[14]-annulene suffers from a more or less severe inhibition of resonance due to puckering of the perimeter and should thus be an olefinic rather than an aromatic molecule. True enough, anti-1,6:8,13-bismethano[14]annulene, in striking contrast to the stable and aromatic syn-1,6:8,13-bisoxido[14]-annulene, turned out to be a highly reactive yellow polyolefin, reminiscent in its chemical behaviour of the carotenoids and related substances. As will be shown in another context, the olefinic nature of anti-1,6:8,13-bismethano[14]annulene, indicated by its chemical reactivity, is just as convincingly borne out by its spectra, especially by its n.m.r. spectrum (see Figures 4 and 5).

While syn-1,6:8,13-bismethano[14]annulene (8) has so far defied synthesis, its more challenging derivative, namely the already mentioned 1,6:8,13-propanediylidene[14]annulene (19), has recently been added to the increasing list of bridged [14]annulenes with an acene perimeter. Although the molecular architecture of 19 looks rather formidable, the preparation of this hydrocarbon was less of a problem than might have appeared. In view of the central position that 19 commands in our studies on bridged [14]-annulenes, the approach to this intriguing molecule will be discussed here in some detail.
As the starting material for the 1,6:8,13-propanediylidene[14]annulene synthesis we chose, as was usual in the synthesis of all of the previously described [14]annulenes, 1,4,5,8,9,10-hexahydroanthracene (24), easily available from anthracene or 9,10-dihydroanthracene by Birch reduction. Quite obviously the crucial problem of this synthesis was the construction of the three-carbon bridge extending above the C_{14}-skeleton.

A clue as to how the bridge could be introduced is provided by Musso's recent preparation of triasteranone (23) from cyclohexa-1,4-diene (20) which involved endo-Δ^{2}-norcarene carboxylic acid (21), its acid chloride and the corresponding diazoketone (22) as intermediates.
As translated to our problem this meant that 24 had to be converted into the acid 27 having the carboxyl group in the endo-position with respect to the central six-membered ring. This transformation was effected by the following processes: (1) Selective addition of dibromocarbene to one of the central double bonds of 24 to give the corresponding dibromocyclopropane 25. (2) Reductive elimination of one of the bromine atoms of 25 by means of tri-n-butyl-tin hydride affording a mixture of about equal amounts of the endo-bromide 26 and its exo-isomer. (3) Treatment of the stereoisomeric bromides with butyl-lithium and subsequent carboxylation of the resulting organo-lithium compounds to yield a 1:1-mixture of endo- and exo-acids. (4) Isolation of the required endo-acid 27 by either crystallization or chromatography.

There are obviously various conceivable routes along which one can proceed from the acid 27. In the latest version of our synthesis (see scheme above), we have introduced into 27 as much unsaturation as possible before completing the three-carbon bridge. Thus 27 was dehydrogenated with palladium to give the aromatic acid 28, and when this acid was submitted to bromination, followed by dehydrobromination of the resulting dibromide with potassium hydroxide in ethanol, the acid 29 containing the norcaradiene unit was obtained. That 29 actually possesses the norcaradiene and not the alternative cycloheptatriene structure follows beyond doubt from its n.m.r. spectrum. In order to complete the bridge, the acid 29 was then converted via its acid chloride into the diazoketone 30 and the latter subjected to a copper-catalysed decomposition. We had anticipated that the intermediate ketocarbene would readily undergo a sterically favoured intramolecular addition with formation of the bis-norcaradiene 31 and that this compound would experience a spontaneous double norcaradiene-cycloheptatriene valence isomerization to give the dihydro[14]annulene ketone 32. Indeed, the thermolysis of 30, carried out in boiling hexane in the presence of copper, afforded 32 in yields of up to 60 per cent. The dihydro[14]annulene ketone could be readily dehydrogenated with 3,4-dichloro-5,6-dicyano-p-benzoquinone to the [14]annulene ketone 33 and this on Wolff–Kishner reduction smoothly produced the desired 1,6:8,13-propanediylidene[14]annulene (19) as a beautifully crystalline orange compound, perfectly stable toward air, even after prolonged exposure.

The aromatic character of 19 expresses itself above all in its n.m.r. spectrum (Figure 4). The absorptions of the perimeter protons are found to be virtually the same as those of the corresponding protons in syn-1,6:8,13-bisoxido[14]annulene, in that we have a singlet at $\tau$ 2.12 for the central perimeter protons and an AA'BB'-system, centred at $\tau$ 2.36, for the eight outer perimeter protons. In addition, the coupling constants of the perimeter protons are essentially equal to those of the bisoxido compound (Table 1). The four bridge protons, consisting of two equivalent external and two equivalent internal protons give rise, as expected according to their environment, to two triplets. In line with the low field signals of the perimeter protons these triplets are located at very high field, at $\tau$ 10.61 and 11.16 ($J = 2.8$ Hz). From deuterium labelling experiments it follows that the triplet at highest field is due to the two external bridge protons.

In order to demonstrate the aromaticity of 1,6:8,13-propanediylidene-
The n.m.r. spectrum of anti-1,6:8,13-bismethano[14]annulene (9) consists only of two broadened singlets at \( \tau \) 3.67 and 3.80, due to the two central and eight outer perimeter protons, and of an AB-system at \( \tau \) 7.52 and 8.12 with \( J = 11.0 \) Hz arising from the protons of the two CH$_2$-bridges. The location of the absorptions of both the perimeter and the bridge protons clearly indicates the presence of an olefinic molecule.

As compared with the respective absorptions in the spectrum of anti-1,6:8,13-bismethano[14]annulene, the resonances of the perimeter protons of 1,6:8,13-propanediylidene[14]annulene have experienced a downfield shift by about 1.5 p.p.m., while, correspondingly, those of its bridge protons have migrated dramatically in the opposite direction. Evidently, 1,6:8,13-propanediylidene[14]annulene is capable of sustaining a diamagnetic ring current whereas its anti-counterpart is not. The syn-anti-configurational change in these bridged [14]annulenes is thus tantamount to the transformation of an aromatic \( \pi \)-electron system into an olefinic one.
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The striking simplicity of the n.m.r. spectrum of anti-1,6:8,13-bismethano-[14]annulene suggests that it is a time-averaged spectrum, indicative of a dynamic exchange process taking place within the molecule. In accordance with this assumption the shape of the spectrum is found to be strongly dependent on temperature (Figure 5).

Figure 5. The n.m.r. spectrum of anti-1,6:8,13-bismethano[14]annulene (9) at +25° (in CDCl₃) and at −135° (in COS/CS₂); (100 MHz).

Between −70° and −120° all the signals except the singlet at τ 3.67 show considerable exchange broadening. The changes in the line shape of the signals cease at about −130°, at which temperature a spectrum is observed corresponding to a polyenic anti-1,6:8,13-bismethano[14]annulene structure, i.e. a structure with seven localized double bonds. The spectrum at −130° shows for the perimeter protons a complex multiplet at τ 3.0–4.6 and for the bridge protons two partly superimposed AB-systems at τ 7.33 and 7.71, and at τ 7.61 and 8.53, each with a coupling constant of 11.0 Hz. As revealed by analysis the multiplet of the perimeter protons consists of two AA'BB'-systems at τ 3.43 (H-10, H-11) and 3.93 (H-9, H-12) as well as 3.66 (H-2, H-5) and 4.26 (H-3, H-4), and of the unchanged singlet at 3.67 (H-7, H-14). From these findings it follows that the simplicity of the n.m.r. spectrum at room temperature is actually due to two factors. First, it is due to the anticipated dynamic process, which on the n.m.r. time-scale
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confers $C_{2v}$-symmetry on the molecule above $-60^\circ$ (as compared to the actual $C_{4v}$-symmetry) and, secondly to an accidental equivalence of the mean values $(\tau_{2,5} + \tau_{9,12})/2$ and $(\tau_{3,4} + \tau_{10,11})/2$.

The nature of the temperature-dependent changes in the line shape of the n.m.r. spectrum of anti-$1,6:8,13$-bismethano$[14]$annulene leads to the conclusion that the dynamic process is a double bond migration, i.e. a valence tautomerism between two identical anti-$1,6:8,13$-bismethano$[14]$annulene structures.

![Diagram](image)

Figure 6. Absorption of the bridge protons of anti-$1,6:8,13$-bismethano$[14]$annulene (9) as a function of temperature [in COS/CS$_2$ (80:20); 100 MHz]; on the left the experimental, on the right the calculated spectra together with the respective rate constants.

In order to determine the kinetic parameters of the double-bond migration the line shape of the bridge-proton resonances between $-65^\circ$ and $-138^\circ$ was simulated using standard techniques$^{33}$. The excellent agreement obtained between the calculated and the experimental spectra is shown in Figure 6. Insertion of the rate constants measured between $-84^\circ$ and $-131^\circ$
into the Arrhenius equation gave an activation energy of 7.1 kcal/mol and a frequency factor of $10^{12.2}$.

\[ E_a = 7.1 \text{ kcal/mol} \]

Figure 7. Presumed reaction path of the double bond migration in anti-1,6:8,13-bismethano-[14]annulene (9).

Mechanistically, the double bond migration is most plausibly explained by assuming that it occurs via the resonance hybrid 34 as a transition state (Figure 7). Regardless of whether this interpretation is correct or not—an alternative mechanism, namely a sequence of electrocyclic reactions with the hitherto unobserved norcaradiene valence isomer 35 of 9 as an intermediate, is conceivable—it remains a fact that in the case of anti-1,6:8,13-bismethano[14]annulene the deviation of the ring skeleton from planarity is such as to render the resonance hybrid (34) higher in energy than the structure with localized double bonds.

The difference in the character of the 14 π-electron systems of 1,6:8,13-propanediylidene[14]annulene and anti-1,6:8,13-bismethano[14]annulene, as borne out by the n.m.r.-spectra as well as by other spectral data, manifests itself just as impressively in the chemistry of the two compounds. Chemically, the two bridged [14]annulenes differ most markedly in their behaviour toward electrophilic reagents, in particular bromine and protons or deuterons.
When 1,6:8,13-propanediylidene[14]annulene is treated with one mole of bromine in methylene chloride at 0°, substitution occurs to give as the main product 2-bromo-1,6:8,13-propanediylidene[14]annulene (36). The same substitution pattern has been observed before in the bromination of syn-1,6:8,13-bisoxido[14]annulene\(^{13b}\). By contrast, anti-1,6:8,13-bis-methano[14]annulene (9), under the same reaction conditions, takes up one mole of bromine at the 7,14-positions, affording the dibromo adduct 37 which shows no tendency to form a substitution product by elimination of hydrogen bromide.

Treatment of 1,6:8,13-propanediylidene[14]annulene with deuteriotri-fluoro-acetic acid in methylene chloride in the presence of a catalytic amount of dideuterio sulphuric acid results in hydrogen deuterium exchange whereby the preferred site of substitution again is found to be the 2-position. An entirely different behaviour toward acids, in particular toward strong mineral acids, is exhibited by anti-1,6:8,13-bismethano[14]annulene. This hydrocarbon, in concentrated sulphuric acid, undergoes irreversible protonation at one of the central positions to give the carbonium ion 38 as a relatively stable entity. When the dark-red sulphuric acid solution of 38 is diluted with water at 0°, nucleophilic attack at the other central position

\[ \text{Figure 8. Molecular geometry of 1,6:8,13-propanediylidene[14]annulene (19).} \]
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takes place with formation of the alcohol 39. The sulphuric acid–water treatment of anti-1,6:8,13-bismethano[14]annulene is thus characterized by hydration in parallel with the behaviour of ordinary olefinic hydrocarbons.

The striking difference that 1,6:8,13-propanediylidene[14]annulene and its anti-counterpart, anti-1,6:8,13-bismethano[14]annulene, exhibit in their spectral and chemical properties amounts to a textbook demonstration of the importance of a planar or near-planar π-electron system as a geometrical pre-requisite for aromaticity.

In order to be able to relate the properties of these two bridged [14]-annulenes more precisely with molecular geometry, x-ray structure determinations would be urgently required. While anti-1,6:8,13-bismethano[14]-annulene still awaits analysis, a structure determination of 1,6:8,13-propanediylidene[14]annulene has recently been performed by Simonetta and co-workers. These authors found that the C14-perimeter of 1,6:8,13-propanediylidene[14]annulene has essentially the same conformation as that of syn-1,6:8,13-bisoxido[14]annulene and that the C—C-bonds of the perimeter again are benzenoid aromatic bonds (Figure 8).

With the synthesis of 1,6:8,13-propanediylidene[14]annulene we have reached a stage which permits our concept of bridged annulenes with an acene perimeter to be extended into various new directions. In the last section of this lecture I would like to focus your attention on some of our more challenging future goals.

1,6:8,13-Propanediylidene[14]annulene may be regarded as a key member of two new homologous series of bridged annulenes, study of which might lead to further development and refinement of current theories on aromaticity.

The first new series is derived from 1,6:8,13-propanediylidene[14]annulene by increasing the number of CH2-groups between the two terminal bridge carbon atoms from one to three or more. From an inspection of models it
appears that on going from 1,6:8,13-propanediylidene[14]annulene (19) to 1,6:8,13-butanediylidene[14]annulene (40) and 1,6:8,13-pentanediylidene-[14]annulene (41) the C_{14}-perimeter will experience progressive bending and/or zig-zagging. This series of bridged [14]annulenes should therefore offer us the unique opportunity of investigating the properties of a cyclic conjugated system in relation to the geometry of the ring skeleton.

Some progress along these lines has been achieved in the last few months by the synthesis of 1,6:8,13-butanediylidene[14]annulene (40). In the approach to 40 we could take advantage of the availability of the dihydro-[14]annulene ketone 32, an intermediate in the preparation of 19. When the ketone 32 was allowed to react in methanol–methylene dichloride with ethereal diazomethane, the homologous ketone 42 was obtained in moderate yield. Dehydrogenation of the expanded ketone to the [14]annulene ketone 43 could be effected by means of 3,4-dichloro-5,6-dicyano-p-benzoquinone, but—in contrast to the dehydrogenation of 32—required heating the reactants in boiling anisole for several hours. The subsequent Wolff–Kishner reduction of 43 proceeded smoothly and afforded the desired 1,6:8,13-butanediylidene-[14]annulene (40) as a stable yellow orange compound displaying aromatic character despite the anticipated bending of the C_{14}-perimeter.

![Figure 9. The n.m.r. spectra of 1,6:8,13-butanediylidene[14]annulene (40) (in CCl₄; 60 MHz; internal standard: tetramethylsilane) and 1,6:8,13-propanediylidene[14]annulene (19) (in CDCl₃; 60 MHz; internal standard: tetramethylsilane).](image-url)
The n.m.r. spectrum of this most recent bridged [14]annulene (Figure 9), showing the familiar absorption pattern, is fully consistent with the assigned structure. At lowest field, at \( \tau \) 2.14, one finds a singlet, due to the two central perimeter protons, and at somewhat higher field, centred at \( \tau \) 2.66, an AA'BB'-system arising from the eight outer perimeter protons. Above the tetramethylsilane signal, at \( \tau \) 10.96, a two-proton multiplet, to be attributed to the tertiary bridge protons, is observed. The remaining multiplet, at \( \tau \) 9.48, accordingly must stem from the four CH\(_2\)-bridge protons.

How does this n.m.r. spectrum compare with that of 1,6:8,13-propanediylidene[14]annulene (Figure 9)? We notice with some surprise that 1,6:8,13-butanediylidene- and 1,6:8,13-propanediylidene[14]annulene possess very similar chemical shifts for the perimeter protons as well as for the tertiary bridge protons. In addition the two compounds have nearly identical coupling constants for the perimeter protons (Table 1). However, they show a noteworthy difference with regard to the chemical shift of the CH\(_2\)-bridge protons, since for 1,6:8,13-butanediylidene[14]annulene the absorptions of these protons appear at considerably lower field than for 1,6:8,13-propanediylidene[14]annulene, namely by about 1.1 p.p.m.

From this comparison it clearly follows that the C\(_{14}\)-perimeter of 1,6:8,13-butanediylidene[14]annulene has almost the same, approximately planar, conformation as that of 1,6:8,13-propanediylidene[14]annulene, and that, contrary to the predictions based on the models, it is rather the bridge moiety than the C\(_{14}\)-perimeter that experiences deformation. As the absorptions of the CH\(_2\)-protons of 1,6:8,13-butanediylidene[14]annulene at relatively low field indicate, the CH\(_2\)–CH\(_2\)-bridge segment must be largely forced out of the space between the two terminal bridge carbon atoms.

*Figure 10. The u.v. and visible spectra of 1,6:8,13-butanediylidene[14]annulene (40) (1) and 1,6:8,13-propanediylidene[14]annulene (19) (2) (in cyclohexane).*
The conclusion, based on the n.m.r. spectra, that the C\textsubscript{14}-perimeters of 1,6:8,13-butanediylidene- and 1,6:8,13-propanediylidene[14]annulene have very similar conformations is corroborated by other spectral investigations. Particularly pertinent is the finding that the electronic spectra of the two hydrocarbons are almost superimposable (Figure 10).

In summary, our study on 1,6:8,13-butanediylidene[14]annulene has demonstrated that the geometry of this molecule is determined by the tendency of its 14\pi-electron system to achieve maximum p-overlap to a much greater extent than was assumed from the consideration of models. Thus, bridge segments appreciably more rigid and space-filling than the CH\textsubscript{2}—CH\textsubscript{2}-grouping will be required to enforce the intended bending of the C\textsubscript{14}-perimeter of bridged [14]annulenes of the present type\textsuperscript{37}.

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=1in]{1}
\includegraphics[width=1in]{19}
\includegraphics[width=1in]{44}
\end{tabular}
\end{center}

Finally, let me comment briefly on the second series of bridged [14]annulenes of which 1,6:8,13-propanediylidene[14]annulene is a member. This series is a homologous series of [4\textit{n} + 2]annulenes that starts out from 1,6-methano[10]annulene and extends via 1,6:8,13-propanediylidene[14]-annulene to the as yet hypothetical 1,6:8,17:10,15-pentane-1',3',5'-triylidene-[18]annulene (44), a molecule whose preparation confronts us with a real challenge. Why do we consider the series 1(X = CH\textsubscript{2}), 19 and 44 so important as to justify the efforts directed at the synthesis of 44?

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=1in]{45}
\includegraphics[width=1in]{46}
\includegraphics[width=1in]{47}
\end{tabular}
\end{center}

The answer to this question is that in the series of the simple annulenes with (4\textit{n} + 2)\pi-electrons, i.e. [10]-, [14]- and [18]annulene (45, 46\textsuperscript{38} and 47\textsuperscript{39}), it is unfortunately not feasible to correlate the physical and chemical properties of the members meaningfully, since these annulenes differ too widely in geometry. [10]Annulene, [14]- and [18]annulene not only differ in the degree of planarity, due to decreasing steric interference of the inner hydrogen atoms as one proceeds from [10]- to [18]annulene, but also vary considerably in their conformational mobility. By contrast, the members of the series 1(X = CH\textsubscript{2}), 19 and 44 of bridged [4\textit{n} + 2]annulenes exhibit a
maximum of common steric features. Thus the latter molecules have $C_{4n+2}$ perimeters showing approximately the same degree of planarity, they possess the same symmetry and, in addition, they are totally rigid due to the bridges functioning as backbones so to speak. Therefore, this series of bridged $[4n+2]$ annulenes seems to be ideally suited for an investigation into the relationships in the physical and chemical properties of cyclic conjugated systems containing $(4n+2)$ $\pi$-electrons. We are confident that from such studies new insights into the nature of aromaticity will ultimately be gained.

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(singlet, methyl protons), 11.65 (singlet, bridge proton)] suggest that 1.6:8,13-ethane-
diylidene[14]annulene, the lower homologue of 19, possesses the most efficiently delocalized
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