AROMATIC AND NON-AROMATIC 14π-ELECTRON SYSTEMS

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ABSTRACT

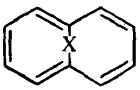
The synthesis and aromaticity of 1,6-methano[10]annulene and its analogues with a heteroatom bridge suggested the possibility that the homologous series of bridged [4*n* + 2]annulenes 1, 2, 3 etc., formally derived from the acene series, could be obtained. In the pursuit of this concept several bridged [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 conservation[1] on the study of mechanistic pathways of organic reactions, the impact which the molecular orbital theory of benzene[2], 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 ion[3], whose isolation first made the organic chemist aware of the potential of molecular orbital theory, the homologous cyclopropenyl cation[4], the cyclononatetraenyl anions[5, 6] and finally the great variety of annulenes[7–10]. 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]annulene[11] 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 [4*n* + 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[12].

1(X = CH_2, O, NH)

Some years ago, however, we recognized that 1,6-methano[10]annulene [**1**(X = CH_2)][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_2-group—or, alternatively, from naphthalene by inserting a CH_2-group into the 9,10-bond—would have an approximately planar C_{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[14] substitution preferentially occurs at the 2- or α-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.



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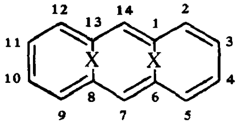

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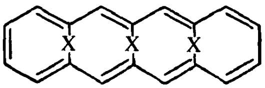

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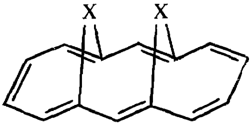
The synthesis and aromaticity of 1,6-methano[10]annulene and of its analogues with a heteroatom bridge [**1**(X = O or NH)][15,16] suggested the existence of the homologous series of bridged annulenes 1, 2, 3 etc., whose members are formally derived from naphthalene, anthracene, benzanthracene, and so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



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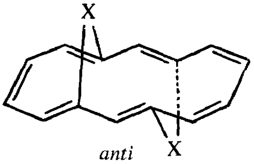

anti
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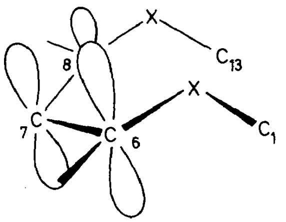
The presence of more than one bridge implies that there will be a *syn*- and an *anti*-configuration (**4** and **5**) for the [14]annulenes (**2**) and three configurations (*syn-syn*, *syn-anti* and *anti-anti*) for the [18]annulenes (**3**). Since the Hückel-rule can be considered valid up to the 22π-electron system[18], 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 $2p_z$-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 $2p_z$-orbitals of such a three-carbon moiety can align themselves in virtually parallel fashion, whereas in the *anti*-configuration the respective $2p_z$-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.



syn

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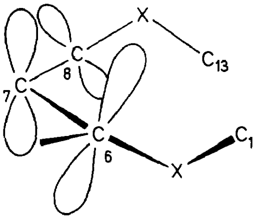

anti

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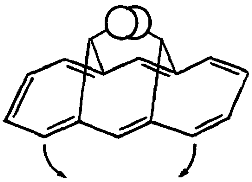
(4) In the *syn-syn*-configuration of the [18]annulenes (and in the all-*syn*-configuration of the higher homologues) analogous steric conditions obtain as in the *syn*-configuration of the [14]annulenes.

(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.



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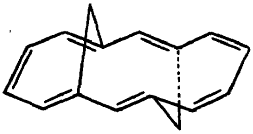

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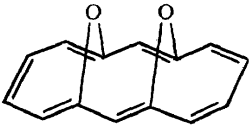
Naturally, the most interesting representatives of the bridged [14]annulenes are the hydrocarbons, i.e. *syn*- and *anti*-1,6:8,13-bismethano[14]annulene (**8** and **9**). These molecules, similar to 1,6-methano[10]annulene, have the special virtue of possessing bridge hydrogens whose n.m.r absorptions 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.



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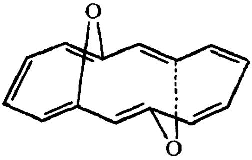

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As a survey of the van der Waals radii of the various functionalities that may serve as bridges reveals, oxygen atoms would make ideal *syn*-bridges in that these atoms permit the *syn*-configuration to attain an optimally flattened perimeter. The chances for a bridged [14]annulene with an acene perimeter

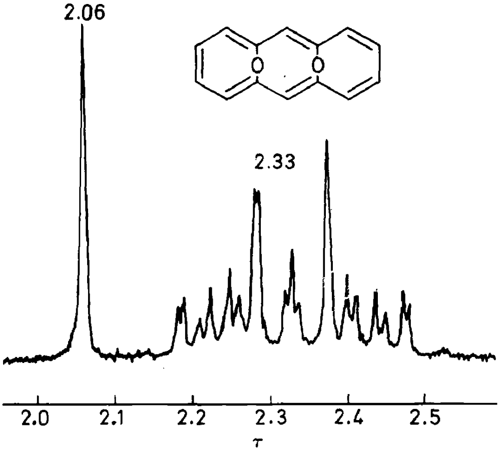


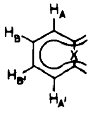
Figure 1. The n.m.r. spectrum of *syn*-1,6:8,13-bisoxido[14]annulene (**10**) (in $CDCl_3$; 100 MHz; internal standard: tetramethylsilane).

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[19], *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[20]. 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[21]. 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 τ 2.33, and further downfield a singlet at τ 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.

Table 1. Chemical shifts (τ-values in p.p.m.) and H,H-coupling constants of some bridged [10]- and [14]annulenes



Compound	τ_A	τ_B	J_{AB}	$J_{BB'}$	$J_{AB'}$	$J_{AA'}$	Ref.
1 (X = O)	2.54	2.74	8.77	9.28	0.28	1.13	21
(**10**)	2.25	2.40	9.01	9.22	0.31	1.14	19
(**19**)	2.26	2.45	9.15	9.50	0.41	1.37	31
(**40**)	2.43	2.88	9.24	9.31	0.21	1.53	36

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[22]. 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°)[23], and accordingly

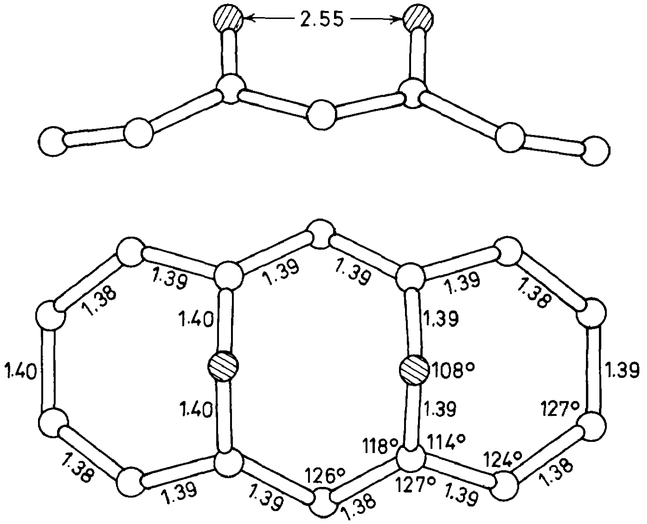
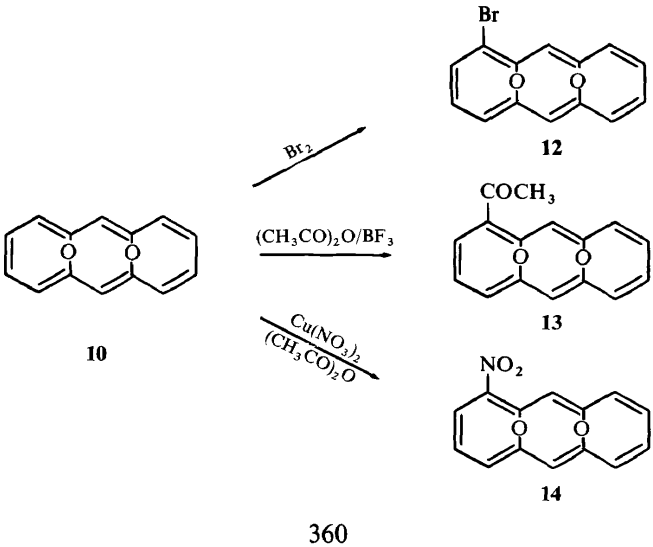


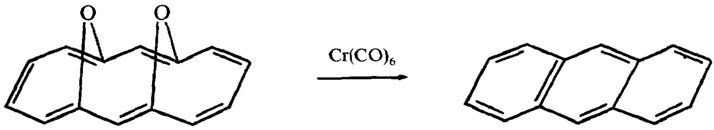
Figure 2. Molecular geometry of *syn*-1,6:8,13-bisoxido[14]annulene (**10**).

the C_{14}-perimeter is even flatter than the C_{10}-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 C_{14}-perimeter: these bonds are almost equal in length, measuring 1.39 ± 0.01 Å, and are thus typical benzenoid aromatic bonds.

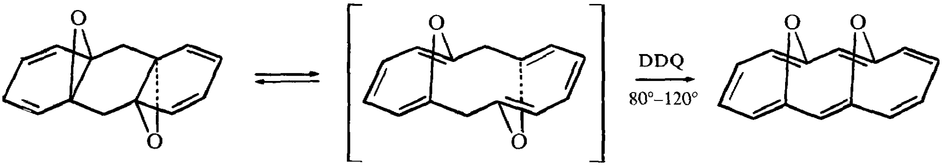


The aromatic character of *syn*-1,6:8,13-bisoxido[14]annulene deduced from the n.m.r. spectrum and from the x-ray analysis is mirrored chemically in the noteworthy thermal stability of the compound and its relative insensitivity toward oxygen. Recent experiments have further shown that *syn*-1,6:8,13-bisoxido[14]annulene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

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 in the presence of boron trifluoride, 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.

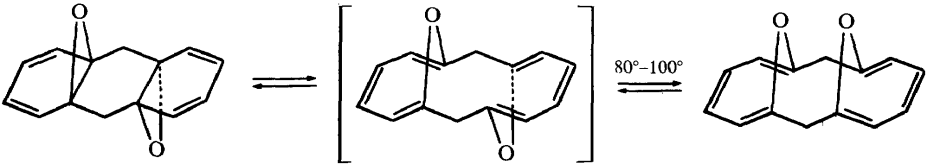


An ideal chemical method to locate the substituents in these mono-substituted *syn*-1,6:8,13-bisoxido[14]annulenes would be deoxygenation with formation of the corresponding anthracene derivatives which are either known or can be readily characterized. In connection with studies originally aimed at the 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.



15 **16** **10**

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**[24]. 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.



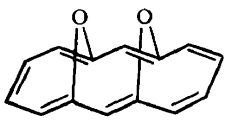
15 **16** **17**

From the subsequent finding that at 80° to 100° **15** is in mobile equilibrium with **17**[24] it is deduced that inversion occurs at the stage of the non-isolable anti-bisoxepin **16**[25].

11 **10**

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**)[17], 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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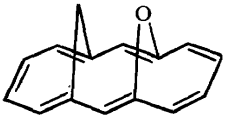

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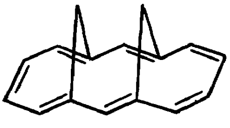

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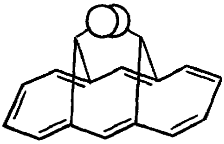
What comes to one's mind immediately is a stepwise replacement of the oxygen atoms in *syn*-1,6:8,13-bisoxido[14]annulene (**10**) by CH_2-groups that would lead via *syn*-1,6-methano-8,13-oxido[14]annulene (**18**) to the already mentioned *syn*-1,6:8,13-bismethano[14]annulene (**8**). A comparison of these three species promises to be very instructive in that it should reveal the steric demand of CH_2-bridges which can only vaguely be gathered from molecular models.



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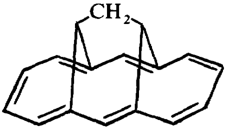

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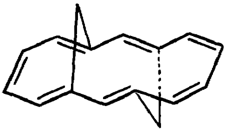

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If *syn*-1,6:8,13-bismethano[14]annulene (**8**) should suffer from a severe steric inhibition of resonance due to the interference of the two internal bridge hydrogens, the obvious cure for this steric handicap would be the replacement of these hydrogens in the already familiar fashion by a CH_2-group. By this transformation we arrive at 1,6:8,13-propanediylidene[14]-annulene (**19**) (previously termed propano[14]annulene[13c–d]) 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**)[24], in which one of the oxygens of **10** has been replaced by a CH_2-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.

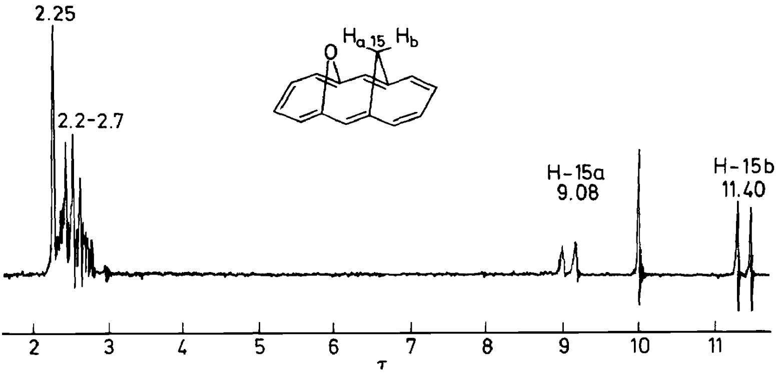


Figure 3. The n.m.r. spectrum of *syn*-1,6-methano-8,13-oxido[14]annulene (**18**) (in $CDCl_3$; 60 MHz; internal standard: tetramethylsilane).

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**—C_s, against C_{2v} 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 τ 2.25, while the eight outer perimeter protons appear as a multiplet at τ 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 τ 9.08 and 11.40, an AB-system of the CH_2-bridge protons with $J = 10.6$ Hz. By analogy with the spectra of other compounds, in which a similar steric relationship between a CH_2-group and an oxygen function obtains as in **18**[26], 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 CH_2-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.

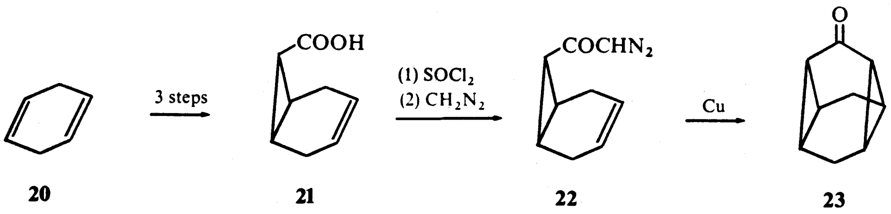
The same conclusions regarding the geometry of **18** also follow from other spectral data, in particular from the similarities in the u.v. spectra of **18** and **10**.

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.

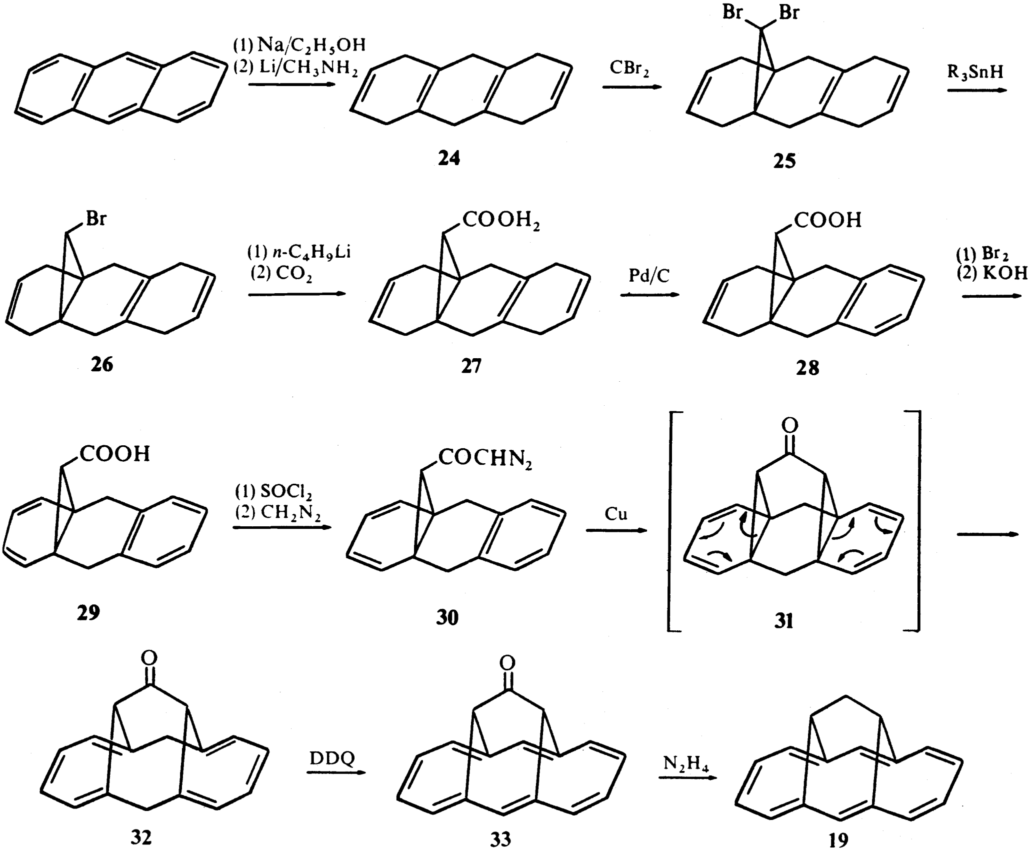
In the meantime, however, we have been able to synthesize the *anti*-isomer of **8**, the *anti*-1,6:8,13-bismethano[14]annulene (**9**)[17]. At this point we should recall that according to the molecular models *anti*-1,6:8,13-bismethano[14]-annulene suffers from a more or less severe inhibition of 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[27] 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**)[20], 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[28] recent preparation of triasteranone (**23**) from cyclohexa-1,4-diene (**20**) which involved *endo*-Δ^3-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**[29] 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[30] 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[31] (*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 τ 2.12 for the central perimeter protons and an AA'BB'-system, centred at τ 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 τ 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-

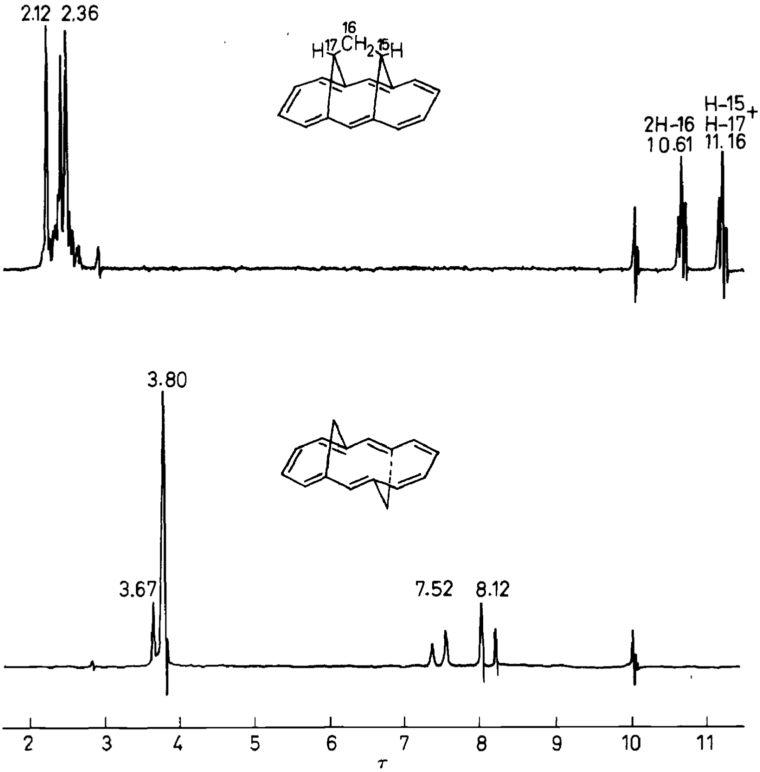


Figure 4. The n.m.r. spectra of 1,6:8,13-propanediylidene[14]annulene (**19**) and *anti*-1,6:8,13-bismethano[14]annulene (**9**) (in $CDCl_3$; 60 MHz; internal standard: tetramethylsilane).

[14]annulene even more convincingly we might contrast its n.m.r. spectrum with that of its *anti*-counterpart, *anti*-1,6:8,13-bismethano[14]annulene (**9**), which has previously been diagnosed chemically as an olefinic compound[17].

The n.m.r. spectrum of *anti*-1,6:8,13-bismethano[14]annulene (*Figure 4*) consists only of two broadened singlets at τ 3.67 and 3.80, due to the two central and eight outer perimeter protons, and of an AB-system at τ 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 π-electron system into an olefinic one.

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*).

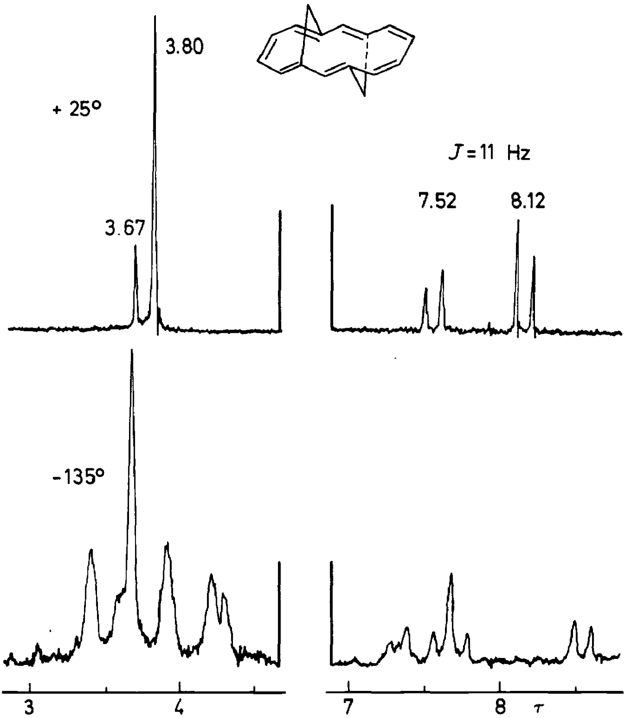
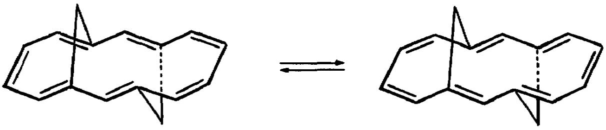


Figure 5. The n.m.r. spectrum of *anti*-1,6:8,13-bismethano[14]annulene (9) at +25° (in $CDCl_3$) and at −135° (in COS/CS_2); (100 MHz).

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[32]. 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 confers C_{2h}-symmetry on the molecule above −60° (as compared to the actual C_s-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.

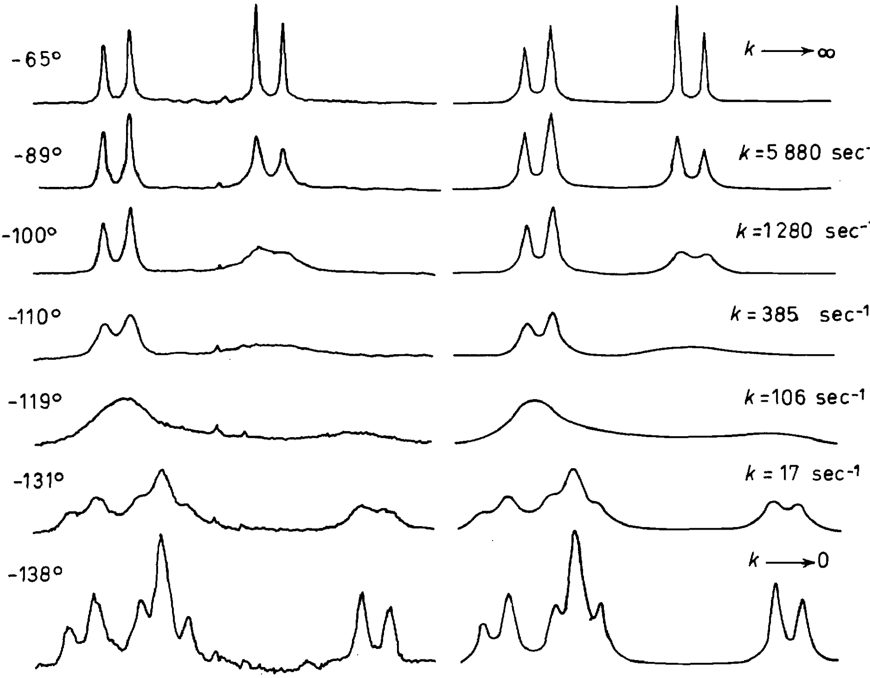


Figure 6. Absorption of the bridge protons of *anti*-1,6:8,13-bismethano[14]annulene (**9**) as a function of temperature [in COS/CS_2 (80:20); 100 MHz]; on the left the experimental, on the right the calculated spectra together with the respective rate constants.

In order to determine the kinetic parameters of the double-bond migration the line shape of the bridge-proton resonances between −65° and −138° 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° and −131°

into the Arrhenius equation gave an activation energy of 7.1 kcal/mol and a frequency factor of $10^{12.2}$.

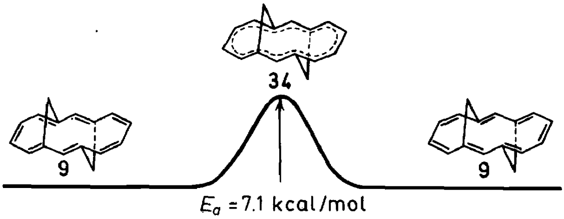
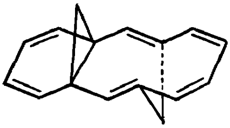


Figure 7. Presumed reaction path of the double bond migration in *anti*-1,6:8,13-bismethano-[14]annulene (**9**).

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.



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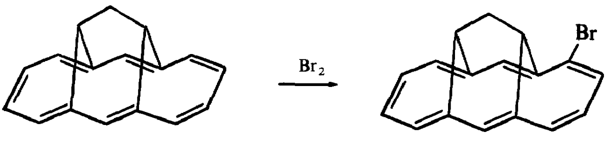
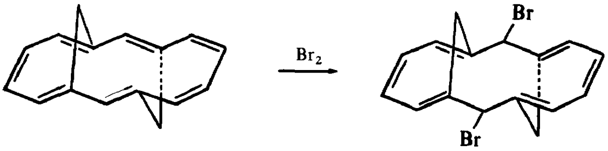
The difference in the character of the 14 π-electron systems of 1,6:8,13-propanediylidene[14]annulene and *anti*-1,6:8,13-bismethano[14]annulene, as borne out by the n.m.r.-spectra as well as by other spectral data, manifests itself just as impressively in the chemistry of the two compounds. Chemically, the two bridged [14]annulenes differ most markedly in their behaviour toward electrophilic reagents, in particular bromine and protons or deuterons.

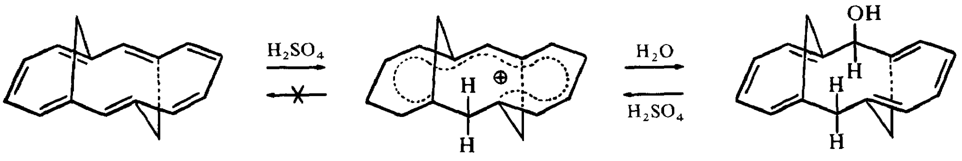


19 **36**



9 **37**

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-bismethano[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.



9 **38** **39**

Treatment of 1,6:8,13-propanediylidene[14]annulene with deuteriotrifluoro-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

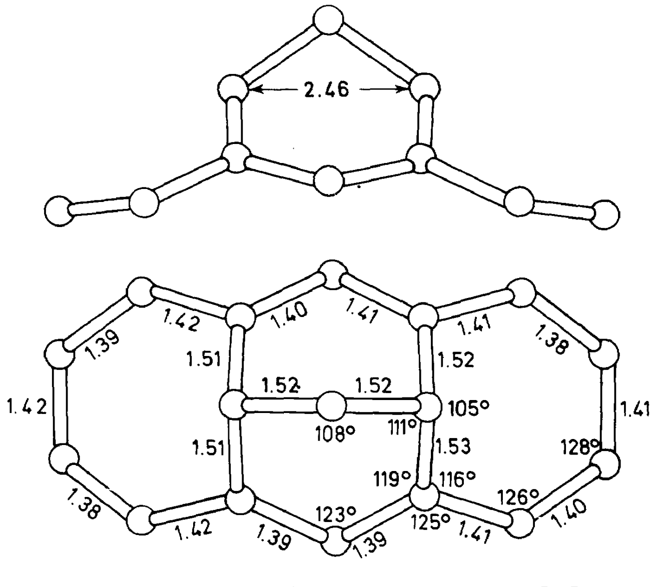


Figure 8. Molecular geometry of 1,6:8,13-propanediylidene[14]annulene (**19**).

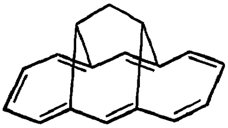
takes place with formation of the alcohol **39**. The sulphuric acid–water treatment of *anti*-1,6:8,13-bismethano[14]annulene is thus characterized by hydration in parallel with the behaviour of ordinary olefinic hydrocarbons.

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[34]. These authors found that the C_{14}-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.



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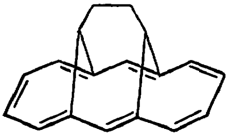

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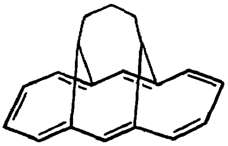

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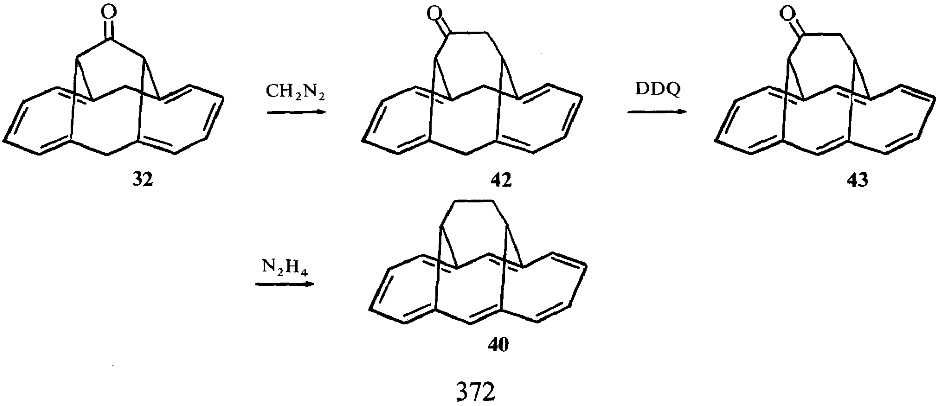
The first new series is derived from 1,6:8,13-propanediylidene[14]annulene by increasing the number of CH_2-groups between the two terminal bridge carbon atoms from one to three or more. From an inspection of models it



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[35].

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**)[36]. 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**[27]. 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.

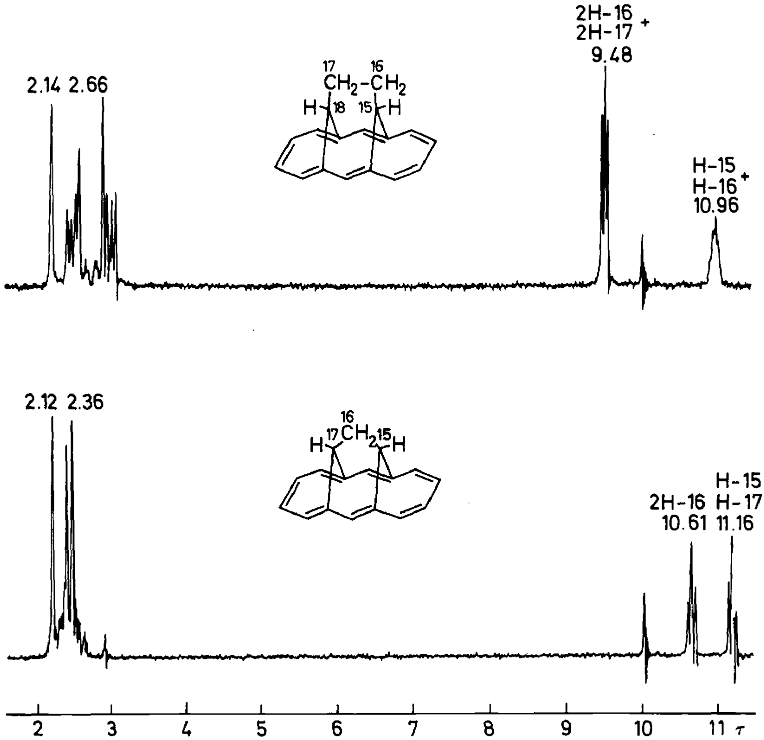


Figure 9. The n.m.r. spectra of 1,6:8,13-butanediylidene[14]annulene (**40**) (in CCl_4; 60 MHz; internal standard: tetramethylsilane) and 1,6:8,13-propanediylidene[14]annulene (**19**) (in $CDCl_3$; 60 MHz; internal standard: tetramethylsilane).

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 τ 2.14, one finds a singlet, due to the two central perimeter protons, and at somewhat higher field, centred at τ 2.66, an AA′BB′-system arising from the eight outer perimeter protons. Above the tetramethylsilane signal, at τ 10.96, a two-proton multiplet, to be attributed to the tertiary bridge protons, is observed. The remaining multiplet, at τ 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.

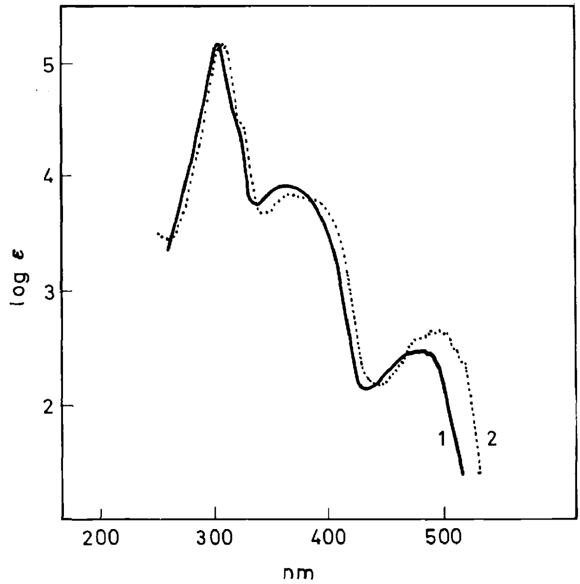
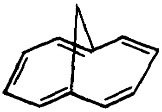


Figure 10. The u.v. and visible spectra of 1,6:8,13-butanediylidene[14]annulene (**40**) (1) and 1,6:8,13-propanediylidene[14]annulene (**19**) (2) (in cyclohexane).

The conclusion, based on the n.m.r. spectra, that the C_{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 14π-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_2—CH_2-grouping will be required to enforce the intended bending of the C_{14}-perimeter of bridged [14]annulenes of the present type[37].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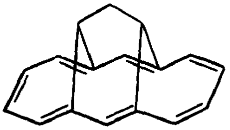
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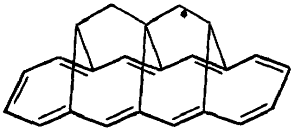
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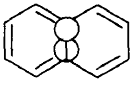
Finally, let me comment briefly on the second series of bridged [14]annulenes of which 1,6:8,13-propanediylidene[14]annulene is a member. This series is a homologous series of [$4n + 2$]annulenes that starts out from 1,6-methano[10]annulene and extends via 1,6:8,13-propanediylidene[14]-annulene to the 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_2), **19** and **44** so important as to justify the efforts directed at the synthesis of **44**?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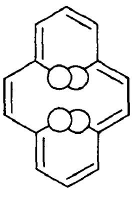
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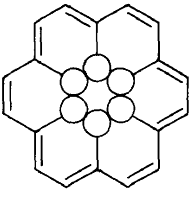
47

The answer to this question is that in the series of the simple annulenes with ($4n + 2$)π-electrons, i.e. [10]-, [14]- and [18]annulene (**45**, **46**[38] and **47**[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_2), **19** and **44** of bridged [$4n + 2$]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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