

Annulenes, 1980–2000

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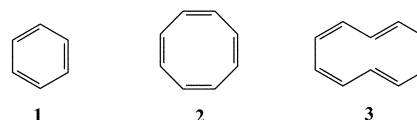
Covering: 1980–2000

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1 Introduction

The first fully conjugated carbocyclic compound to be recognised and described, early in the nineteenth century, was benzene **1**. The differences between the properties of this compound and those of other unsaturated compounds, alkenes and alkynes puzzled early organic chemists. Consequently they associated this unusual character with the complete cyclic conjugation in the carbon ring. Further confusion arose when cyclooctatetraene **2** was prepared and it showed no chemical resemblance to benzene. A major contribution to the understanding of the nature of cyclic conjugated compounds came from Hückel¹ whose famous rule predicted that only those compounds whose conjugated systems involved $(4n+2)$ π -electrons ($n =$ an integer) would have special properties resem-

bling those of benzene and could be classified as benzene-like. They could be described as *aromatic*, the term used to describe benzene since the early nineteenth century. It was later suggested² that analogous compounds having $4n$ π -electrons might be termed *antiaromatic* and could have contrasting properties to those of benzene. Confusion reigned however, over the precise meaning of these terms.



The name *annulenes* was suggested for all conjugated cyclic polyenes, irrespective of their properties. All annulenes have complete cyclic conjugated systems of double bonds. The ring sizes are indicated by prefixing to the annulene a number, enclosed in square brackets, indicating the number of atoms in the ring. Thus cyclodeca-1,3,5,7,9-pentaene **3** becomes [10]annulene. This system of nomenclature is now in general use although the name *benzene* is still always used rather than [6]annulene. There are also other cyclic analogues wherein one or more double bonds have been replaced by triple bonds; these compounds are described as *dehydroannulenes*.

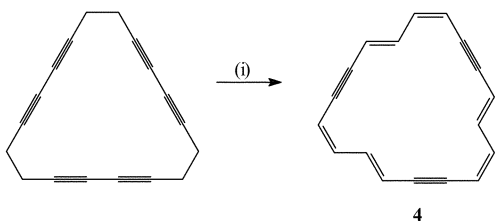
Hückel's rule has some theoretical shortcomings, but in general terms it works. It has had an enormous influence on organic chemistry and has inspired much work on organic compounds and was largely responsible for the work that has been undertaken on the synthesis and properties of annulenes.

Until 1911 the only known annulene was benzene; it was joined in that year by cyclooctatetraene, [8]annulene **2**. Any real development in the study of annulenes did not arise until the late 1950s and 1960s when Sondheimer and coworkers synthesised a series of larger ringed annulenes.

Since studies of the chemistry of annulenes have been greatly concerned with the extent to which annulenes can be regarded as aromatic, *i.e.* resembling benzene, or alternatively as antiaromatic or as non-aromatic, it seems appropriate, before delving into their story for the period 1980–2000, to emphasise the fact that the latter terms are remarkable in that, although they are used continually by all chemists, all of whom know in general terms what is meant, they have no universally agreed upon precise definition.³ The meaning and the features it embraces have gradually changed over decades and have been modified over the very many years that the term *aromatic* has been in use. Properties considered include chemical properties (stability, reactivity, *etc.*), delocalisation of π -electrons, spectroscopy, especially NMR and magnetic anisotropies. Investigations of all these properties have been key factors in the whole history of annulene chemistry.

2 A brief history of the annulenes

In 1959, Sondheimer, very much the pioneer of annulene chemistry, synthesised⁴ the first higher annulene, 1,2,7,8,13,14-hexadehydro[18]annulene **4** (Scheme 1) which was subsequently



Scheme 1 Reagents and conditions: (i) KOBu^t, Bu^tOH, 90 °C, 25 min.

hydrogenated to [18]annulene itself. This initial synthesis opened the gates to a vast area of chemistry which resulted in intense activity over the next 20 years. The next decade witnessed the first syntheses of [18]-, [20]-, [24]- and [30]annulenes (1962), [14]annulene (1964) and [16]annulene (1966).⁵ There was also evidence for the formation of [10]annulene (1967).⁶ By 1972 all the parent annulenes up to [30]annulene, with the exception of [26]- and [28]annulenes had been synthesised.⁵ Corresponding dehydroannulenes, often obtained as annulene precursors, and a small number of bridged and hetero-derivatives had also been investigated.⁵ Anions and cations derived from the annulene systems have also proved to be of interest.

Work on monocyclic annulenes waned in the 1970s, giving way to studies of bridged and heteroatom derivatives. Increasingly, annulenes were being used to explore the concept of aromaticity, and bridging the rings provided an effective method of holding the annulene ring rigidly in the planar geometry most conducive for delocalisation. By 1980, research into the unfunctionalised (CH)_n annulenes had also spread from laboratories into the realm of the theoretical chemist. As more powerful computers and increasingly sophisticated models became available, various questions about annulenes and aromaticity could be asked with very real chances of obtaining meaningful answers. Initially, the models were often inadequate and the results obtained were in consequence inaccurate, but by the early 1980s they had become more reliable, often supporting or explaining the original experimental observations.

This review has focused on the last two decades of the chemistry, preparation and computer modelling of carbocyclic annulenes and their utility in the ongoing study of aromaticity from the perspective of an organic chemist. Earlier work has been comprehensively reviewed, including two books by one of the present authors.⁷ Some other areas of annulene chemistry are mentioned briefly at the end of the review. The continued interest in the general concept of 'aromaticity' is highlighted by recent thematic issues of *Chemical Reviews*⁸ and *Tetrahedron*.⁹

3 Specific annulenes

Work in this area has been dominated by theoretical, structural and spectroscopic studies. With few exceptions the synthetic routes remain those which were pioneered in the 1960s and 1970s. Similarly, few new reactions of these systems have been reported.

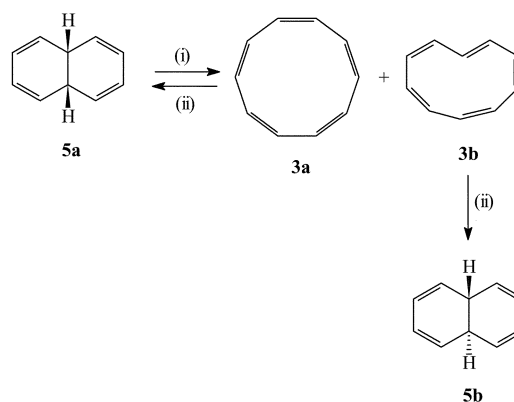
3.1 [10]Annulene

As a [4n+2] annulene, [10]annulene **3** is potentially aromatic. However, the molecule must adopt a near planar geometry for the π -electrons to be fully delocalised, while angle strain and unfavourable steric interactions of internal protons tend to force the molecule into non-planar configurations. Many different conformations have been proposed for the structure of

[10]annulene but it has yet to be characterised unambiguously by X-ray analysis and spectroscopic methods. Problems arise because of low energy interconversions between different structures and rapid bond shifts leading to an averaging of bond lengths and indefinite bond angles.

The determination of which of the structures is lowest in energy has been a topic of much debate amongst theoretical chemists. Over the past 20 years computational methods have become more sophisticated but at the same time it has been recognised that these methods need to be used with caution when applied to these complex conjugated systems. Some methods have, in particular, led to extreme over-estimation or under-estimation of the various factors contributing to the molecular structure. Continuous refinement of the computer models has constituted a major part of [10]annulene research over the past 20 years.

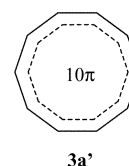
Preparations of [10]annulene **3** were first reported in 1967.⁶ In 1969, Masamune and Seidner observed NMR signals from two different configurations assigned as **3a** and **3b**,¹⁰ which were separated by chromatography at -80 °C from products obtained by irradiation of *cis*-4a,8a-dihydronaphthalene **5a** (Scheme 2).¹¹ Both crystalline isomers underwent thermal



Scheme 2 Conditions: (i) *hν*; (ii) heat.

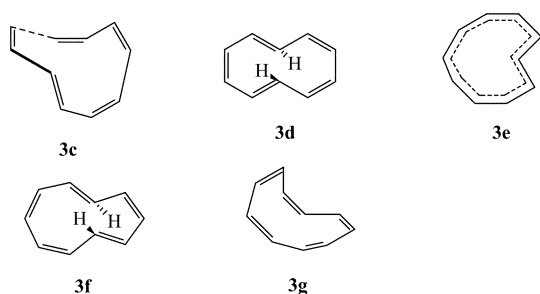
cyclisation to produce *cis* and *trans*-4a,8a-dihydronaphthalenes **5a** and **5b** respectively. At low temperatures (-100 °C) photochemical interconversions between the all-*cis* and mono-*trans* forms proceed rapidly, the mono-*trans* being the favoured form. Catalytic hydrogenation at -70 °C of a solution containing the [10]annulenes provides cyclodecane in good yield, thus giving chemical evidence in support of the presence of the annulenes.

An all-*cis*-configuration **3a** was attributed to the isomer which reverted to *cis*-dihydronaphthalene. This isomer gave only one peak (at δ_{H} 5.66 ppm) in its NMR spectrum over the range -40 to -160 °C, but the planar delocalised configuration, **3a'**, was discounted because of the severe angle strain (144°) involved in the ring system. A corresponding planar structure but with localised double bonds, **3a** was similarly rejected. An alternative non-planar all-*cis* structure with alternate single and double bonds seemed more reasonable. It was suggested that it exists as a mixture of conformations. The energy barrier to interchange between these non-planar conformations is only small and on the NMR time scale (even at -160 °C) an averaged structure, with the CH groups all equivalent to one another, is recorded.¹¹ The other isomer is assigned a non-planar mono-*trans* structure **3b**.

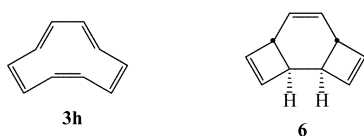


There has been a difference of opinion as to which is the lowest energy structure.^{12–18} The problem is that the potential energy surface for [10]annulene is very flat, resulting in very small differences between the possible structures. Low temperature NMR spectra are in accord with this and favour non-delocalised structures, although it is suggested that the double and single bond lengths should be less different than the difference between ethane and ethene.

In the most recent paper, which provides a summary and critical evaluation of earlier work, the five conformations **3c–g** are considered.¹⁷ These are described as the ‘twist’ **3c** (corresponding to Masamune’s mono-*trans* structure), the ‘naphthalene-like’ **3d**, the ‘heart’ **3e** (in which all the C–C bond lengths are almost equal), the ‘azulene-like’ **3f** (which may or may not have delocalised bonds) and the ‘boat’ **3g** (corresponding to Masamune’s all-*cis*-isomer). The calculations agree with the experimental conclusion that the ‘twist’ structure **3c** is low in energy, but on the other hand the ‘naphthalene-like’ structure **3d** was found to be lower in energy than the ‘boat’ **3f**. Given the recent history of this problem, it is perhaps unlikely that these results will be definitive and it is clear that fresh experimental data are required to complement the calculations. It is noteworthy that the only samples of [10]annulenes ever isolated were those prepared in Masamune’s laboratory over 30 years ago.

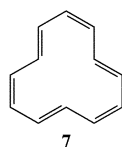


It has also been suggested that the tricyclic compound **6** may be formed, by pericyclic bond formation from an alternative di-*trans* form **3h**. Calculations suggest that this would involve synchronous rather than two-step cyclisations.¹⁹



3.2 [12]Annulene

[12]Annulene **7** was first prepared in 1970,²⁰ but there has been very little recent work. It has been shown to form a very stable dianion which contains a 14π electron system.²¹ A radical anion has been characterised by EPR spectroscopy; this species is severely distorted from a planar geometry.²¹



3.3 [14]Annulene

Solutions of [14]annulene were shown to contain two isomers **8a** and **8b** which are in dynamic equilibrium. At $-10\text{ }^\circ\text{C}$ **8a** was the major constituent (92%).²²

Calculations^{23,24} suggest that the most stable conformation has delocalised π -bonds and C_{2h} symmetry, as shown in Fig. 1,

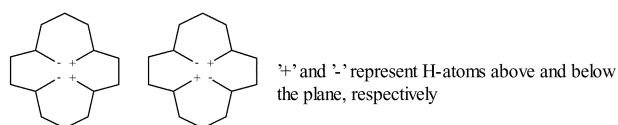
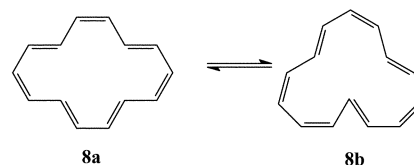


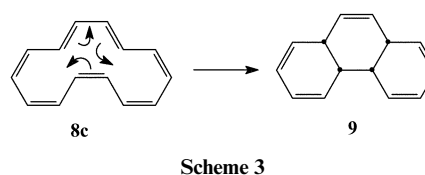
Fig. 1 Configurations of [14]annulene.



with two intra-annular hydrogen atoms above the plane of the periphery and two below the plane.

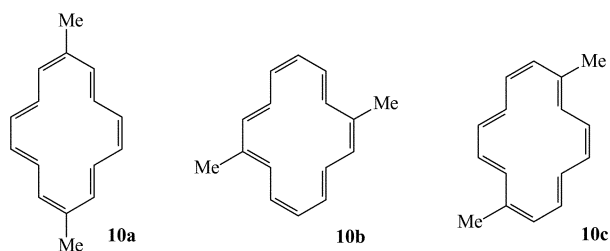
An X-ray structure determination agrees with this structure.²⁵ The ring is significantly non-planar, due to non-bonding interactions between the inner hydrogen atoms, and there is apparent delocalisation of the double bonds. That the delocalisation is real and not the consequence of averaged localised bonds is also in accord with variable temperature NMR spectra,²² low temperature UV-vis spectra²⁶ and a combination of photoelectron spectrum determination and calculations.²³

Calculations suggest that the [14]annulene **8** might be converted into a tetrahydrophenanthrene **9** by synchronous cycloaddition or independent electrocyclic reactions of yet another possible structural form **8c** (Scheme 3).¹⁹



Scheme 3

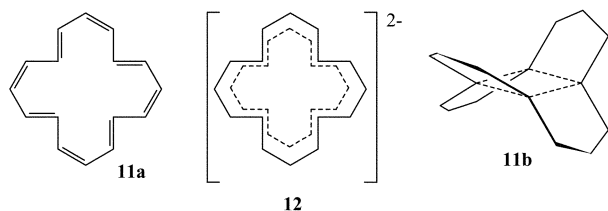
An X-ray structure of 1,8-dimethyl[14]annulene **10** prepared by reaction of dimethyl sulfate with the dilithium salt of octalene, provided similar information. It indicated structure **10a** in the solid state while NMR spectra showed that in solution there is equilibration between forms **10a**, **10b** and **10c**.²⁷ Torsional angles in the carbon skeleton are up to 20° indicating that a $(4n+2)\pi$ cyclic system can tolerate quite large deviations from planarity without substantial loss of delocalisation; these deviations are of the form shown in Fig. 1. EPR studies on the radical ion of **10** show that the molecule has a flexible framework allowing configurational and conformational mobility.²⁸



3.4 [16]Annulene

[16]Annulene^{29–31} **11** and substituted derivatives³¹ were initially prepared by photolysis of a dimer of cyclooctatetraene (or its substituted derivatives) but yields were very low. It is very sensitive to oxygen and in solution is rapidly lost, but, just for this reason, crystals can be kept for several months because a protective layer is formed on their surface.²⁹ As a consequence of the low yields and its sensitivity to air, [16]annulene **11** was little studied until more recent years, when a modified version of its preparation, involving the dimerisation of cyclooctatetraene radical anions in HMPA was developed.^{32–34} This preparation provides the relatively stable [16]annulene dianion

12 which can be stored, and it has made [16]annulene more readily available, generated from the dianion as required. Although the yield is still low (*ca.* 10%) this has provided a much more satisfactory source.³⁴



X-Ray crystallographic studies³⁵ suggested that the crystalline [16]annulene **11** is weakly antiaromatic and has a well-defined 'saddle' geometry (*cf.* **11b**) with four almost equatorial internal hydrogen atoms. The non-planarity serves to minimise any steric interaction between the four inner hydrogen atoms.³⁶ This isomer is in equilibrium with another structure **11c** (12% of the equilibrium at 163 K²²) which has five internal hydrogen atoms. The low temperature configurations of these isomers is shown in Fig. 2 (*cf.* ref. 39). In yet another conformation

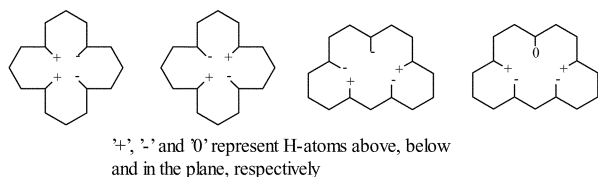
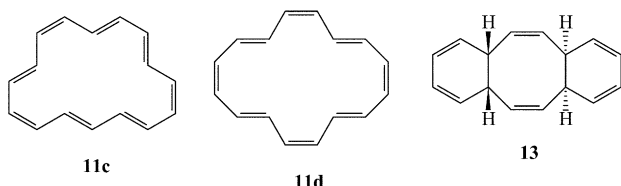


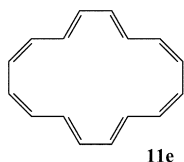
Fig. 2 The low temperature configurations and conformations of [16]annulene.

11d, the ring is set up for intramolecular cyclisation to give a tricyclic compound **13**,¹⁹ whose formation has been previously reported.³⁰



Proton NMR studies have indicated that there is a rapid exchange mechanism between the inner and outer protons.^{22,36,37} Below $-100\text{ }^{\circ}\text{C}$ another exchange mechanism exists leading to further structures.²² As the temperature is lowered [16]annulene **11** becomes more planar, the bond angles approach 180° and paratropicity increases.

Calculations¹⁹ have located a further valence bond isomer **11e** of slightly higher energy than **11a**, the lowest energy form of [16]annulene. This isomer has a notable structure in that it appears to involve a Möbius twist distributed through the whole ring. Heilbronner had suggested that $4n$ -annulenes could reverse their aromaticity by a so-called Möbius twist of the ring.³⁸ Calculations suggest that the Möbius twist has indeed reversed the aromaticity of this species, although the effect is a small one.

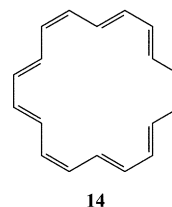


[16]Annulene is readily reduced to its dianion **12** by reaction with alkali metals.^{36,39,40} The resultant nearly planar $(4n+2)$ π -system is more stable than the parent annulene and supports a strong diatropic ring current, stronger than that of [18]annulene. Calorimetric experiments and calculations involving the [16]annulene dianion have suggested that this dianion is more stable than the [8]annulene dianion, probably because there is less electron repulsion in the larger anion.⁴¹

Much information has been obtained from studies of structural perturbations deriving from deuteration and formation of perdeuterio[16]annulene *cf.* **11** and its anions.^{36,39,40} The dianion has 18 π -electrons and thus could be expected to be diatropic. The perdeuterio[16]annulene obtained was 95% deuterated and this permits comparison by ^1H NMR analysis of the systems. Since C–D bonds are shorter than C–H bonds deuteration leads to decreased crowding within the rings and apparently allows flattening of the ring; associated with this the paratropicity of the annulene and the diatropicity of its dianion are increased compared with the tropicities of the undeuterated molecules. Paratropicity in [16]annulene **11** and diatropicity in [18]annulene **14**³⁹ are quite sensitive to steric interactions involving their internal hydrogen atoms. Alterations to these steric interactions, either by isotopic substitution or by changes in the stacking of the internal hydrogen atoms in the planes above and below the plane of the ring, perturbs the aromaticity and antiaromaticity, as measured in terms of ^1H NMR chemical shifts, in the annulene.

3.5 [18]Annulene

[18]Annulene **14** belongs to a subgroup of the $[4n+2]$ annulenes containing $6(2p + 1)$ π -electrons ($p = \text{integer}$).⁴² These annulenes have the correct number of atoms for optimum D_{6h} symmetry with C–C–C bond angles of 120° , and are without severe non-bonded interactions. Before 1980 [18]annulene **14** was the most thoroughly investigated annulene, as it is the most stable higher annulene although its decomposition is accelerated by light. Like many of the other annulenes, it undergoes reactions typical of localised π -bonding, many of which were performed in the 1960s and 70s. Thus its chemistry differs markedly from that of benzene. Under special conditions it undergoes reactions which provide products typical of electrophilic substitution, but these reactions may not proceed by straightforward electrophilic substitution mechanisms. However, more recent computational studies have indicated that [18]annulene **14** has delocalised π -electrons, a proposal which is in agreement with infra-red, UV-vis, NMR and fluorescence spectroscopic data,⁴³ as well as X-ray crystallographic data.⁴⁴ Photoelectron spectroscopic studies of [18]annulene **14** at $150\text{ }^{\circ}\text{C}$ in the early 1980s⁴³ also indicated delocalised character; the experimental spectrum was consistent with D_{6h} symmetry. Initial calculations in the 1960s, 70s and early 80s using basic molecular orbital theory predicted definite localised structures,¹² but these calculations lacked the sophistication to handle such a complex problem and only more recently have calculations predicted a delocalised system.^{45,46}



Although [18]annulene **14** has a strong diamagnetic ring current, its large size and flexibility leads to the averaging of ^1H NMR signals at higher temperatures due to bond rotation. In a similar fashion to [16]annulene **11**, three nearly degenerate structures have been proposed which explain the low temper-

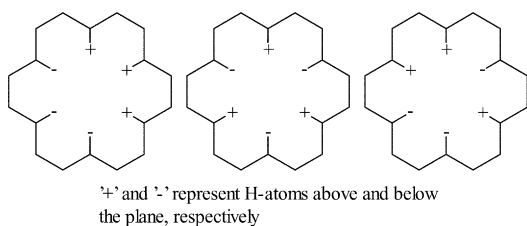


Fig. 3 The low temperature conformations of [18]annulene.

ature ^1H NMR spectra³⁹ (Fig. 3). Steric interactions between internal protons still prevent [18]annulene **14** from adopting a fully planar geometry. Deuteriation of the molecule reduces this steric crowding and, consequentially, the ring current increases due to more effective p-orbital overlap and π -electron delocalisation. This is clearly observed in the ^1H NMR spectrum of [18]annulene- d_{17} .³⁹

[18]Annulene **14** forms long red-brown needles suitable for X-ray analysis. The crystal structure of [18]annulene **14** was re-investigated in 1995 and this has revealed unexpected deviations in the structure as well as confirming the original observations.⁴⁴ [18]Annulene **14** has D_{6h} symmetry and is centrosymmetric indicating bond delocalisation **14b**. An alternating bond structure would have D_{3h} symmetry and be non-centrosymmetric. The crystal is disordered with the minor form (13.7%) being rotated at $\sim 30^\circ$ to the mean plane, probably as a result of close packing restrictions (Fig. 4). In the major

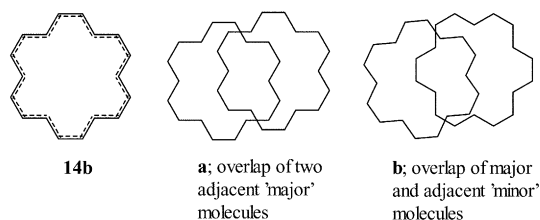


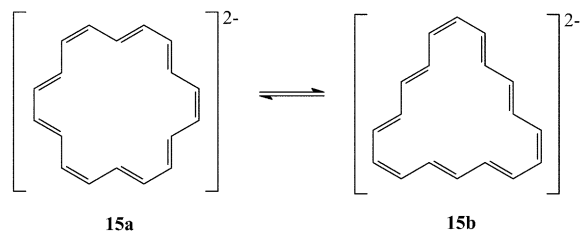
Fig. 4 The crystal structure of [18]annulene.

form, the C–C bond lengths are unequal; the ‘inner’ bond and ‘outer’ bond lengths are 1.385(2) Å and 1.405(3) Å respectively, and the external and internal C–C–C bond angles are 127.9(4)° and 124.0(2)° respectively. Each molecule in this major orientation has 14 near neighbours, two of which display staggered stacking. Arranged in this fashion, the molecules pack together efficiently, with the bulky rim of one ring nestling in the centre of the other (Fig. 4a). The minor orientation has slightly different molecular dimensions [(C–C)_{inner} = 1.382 Å; (C–C)_{outer} = 1.392 Å; (C–C–C)_{external} = 128.9°; (C–C–C)_{internal} = 124.3°] and packs in a staggered conformation with molecules of the major isomer (Fig. 4b). Although [18]annulene **14** is essentially planar with D_{6h} symmetry, small deviations are present, with carbon atoms removed from the mean plane of the molecule by 0.08 and 0.14 Å.

Reduction of [18]annulene with alkali metals forms antiaromatic [18]annulene dianions, perturbing the structure of the molecule into two non-planar conformations **15a** and **15b** in a 2.3 : 1 ratio, with double bond localisation. The dianion is paratropic and less stable than the neutral annulene.⁴⁷ The radical anion displays Jahn–Teller distortion as a result of the single electron occupying only one of two degenerate molecular orbitals. This effect is also seen in the $(\text{CH})_{18}^{3-}$ anion, and *pseudo* Jahn–Teller distortion may be seen in the neutral molecule due to the small HOMO–LUMO gap. This, in addition to vibrational–electronic (vibronic) coupling, presents the possibility that high temperature superconductors may be based on [18]annulenes.^{48–50}

3.6 Higher annulenes

All the annulenes up to and including [30]annulene, except



[26]annulene and [28]annulene, have been synthesised. As the size of the ring increases, conformational flexibility leads to a loss of π -electron delocalisation and the ring current decreases. The aromatic stabilisation energy decreases, and as the ring size increases, the energy gap between the HOMO and LUMO is reduced. In the larger annulenes this causes nearly degenerate energy levels resulting in pseudo Jahn–Teller distortion.⁵¹ Where the transition point between a delocalised system and a localised system would occur in the $[4n+2]$ annulenes has provoked considerable interest.

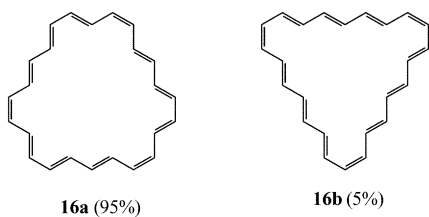
Originally, this transition had been incorrectly placed at [14]annulene, but [18]annulene has now been shown to have delocalised bonds. In 1965 Dewar and Gleicher predicted that the limit lay at [22]annulene, based on calculated resonance energies becoming negative and destabilising above this point.⁵² Later, in 1969, Dewar amended this to [20]annulene, deciding that resonance energies thereafter would converge to ~ 2.8 kcal mol⁻¹, favouring bond alternation. More recent computational investigations⁴⁵ have placed this transition at [30]annulene, but have also shown that [30]annulene has localised bonds and yet its ^1H NMR spectrum suggests that it should be classified as aromatic. It has been suggested that bond delocalisation is not required to provide NMR spectra characteristic of aromatic character.⁴⁵

Various indicators of aromaticity have been calculated as a function of ring size for the $[4n+2]$ series up to [66]annulene. Peierls’ theorem,⁵³ when applied to polyacetylene, states that as $n \rightarrow \infty$, bond localisation becomes more prevalent: in polyacetylene, the difference in bond length between double and single bonds is believed to be ~ 0.06 Å. It has been calculated that as the size of the $[4n+2]$ annulene increases, bond length alternation also increases and the aromatic stabilisation energy, which peaks at [18]annulene **14**, levels out at about 23 kcal mol⁻¹.⁴⁵ This contradicts Dewar’s original prediction that bond localisation occurs due to loss of resonance energy. Calculated nucleus independent chemical shifts, indicative of ring current and delocalised π -electrons, are at a maximum at [26]annulene and then fall gradually to zero for larger annulenes. Therefore, it has been suggested that bond localisation in the higher annulenes does not occur due to a dramatic decrease in aromatic stabilisation energy as the ring size increases, but as a result of pseudo Jahn–Teller effects as the HOMO–LUMO gap decreases and converges to 2eV.

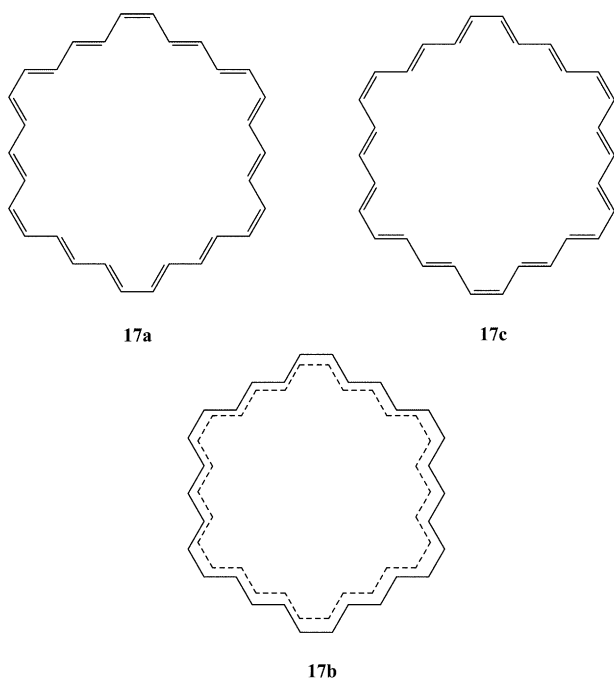
Calculations first performed in the 1980s predicted another curious result: large $[4n]$ annulenes should become weakly aromatic (where $4n \geq 16$) but still possess a *paramagnetic* ring current. However, this is not observed experimentally owing to the strong bond alternation usually present in these compounds. Charged $[4n]$ annulenes were predicted to remain antiaromatic regardless of their size.

[24]Annulene **16** has been the subject of a recent detailed report,⁵⁴ investigating conformational mobility and migration of π -bonds, using temperature dependent ^1H NMR spectroscopy. [24]Annulene **16** is a blue-black crystalline substance which forms a violet solution. In solution, [24]annulene exists as two equilibrating conformers, **16a** and **16b**, with C_{3h} and C_3 symmetry respectively. The two conformers have the same configuration of localised double and single bonds with *CTTCTTTCTTT* (*C* = *cis* and *T* = *trans*) connectivity. Structures **16a** and **16b** interconvert extremely rapidly. The signal of the 9 internal protons is at a higher frequency than the

signal of the 15 external protons (by 7.72 ppm) indicating a paramagnetic ring current.

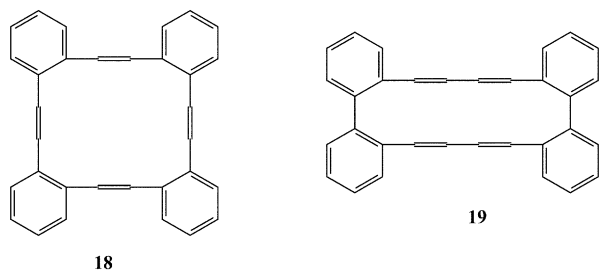


Despite being of obvious interest as it may potentially possess D_{6h} symmetry, [30]annulene **17** has not been investigated experimentally since the first syntheses in the 1960s. It was never accurately characterised and awaits new research. It has been suggested that D_{3h} symmetry represents a global minimum in [30]annulene as in **17a,c**, and that the structure with D_{6h} symmetry **17b** does not represent a stable state but rather the transition state between the two equivalent D_{3h} conformations.⁴² In this respect [30]annulene is thought to differ from the smaller [6] and [18] $6(2p + 1)$ annulenes.

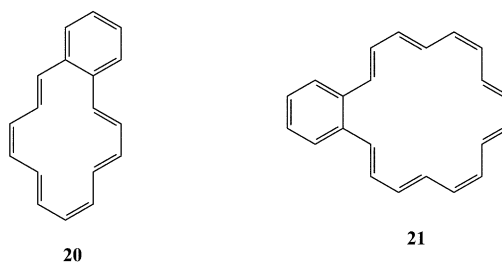


3.7 Benzoannulenes

A number of benzoannulenes have been prepared. The first examples to be made, the tetrabenzoannulenes **18** and **19**, were prepared purely as annulene derivatives; it had been hoped that the benzene rings would serve to stabilise the annulene rings and make them easier to handle. In fact both had buckled rings, which reduces angle strain and inhibits the destabilising interactions of the $4n\pi$ perimeters.^{55,56} Both compounds are best regarded as benzene rings linked by alkene chains.



Benzo[14]annulenes **20** and benzo[18]annulenes **21** have been prepared.⁵⁷⁻⁶⁰ In each case the annulene ring is diatropic, but markedly less so than in the corresponding non-annulated annulenes.



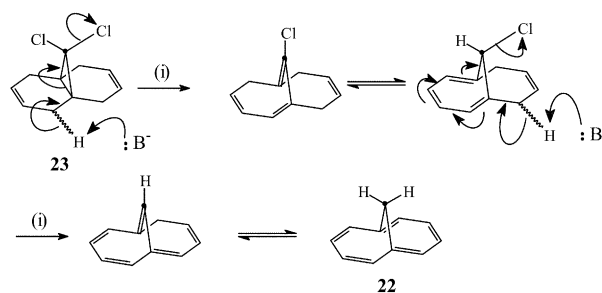
4 Hydrocarbon bridged annulenes

Unlike benzene, which has the ideal geometry and σ -framework for π -delocalisation, the smaller [n]annulenes ($6 < n \leq 16$), due to steric interactions between internal protons, have problems adopting sufficient planarity and the larger annulenes have too much conformational mobility to remain sufficiently planar for this π -delocalisation to occur. However, the internal crowding of hydrogen atoms in—for example—*di-trans*-[10]annulene **3d** can be eliminated if the 1- and 6-hydrogen atoms are replaced by one atom (or group) attached to both the 1- and 6-positions. Any annulene might be bridged in this way. The next section considers such bridged molecules. There has been much more activity in this area in recent years than for the annulenes themselves and this is reflected in new synthetic work as well as studies of the chemistry, spectroscopic and structural properties of the systems.

4.1 1,6-Methano[10]annulene

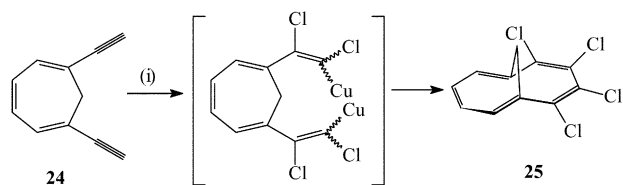
The most investigated of the simple bridged annulenes is 1,6-methano[10]annulene **22**, first synthesised by Vogel and Roth in 1964,⁶¹ with an improved modified method being described later.⁶² The chemistry of 1,6-methano[10]annulene was extensively studied in the 1980s. Functionalisation of the annulene ring at specific sites and at the bridging methylene group constituted the majority of the research, often using detailed NMR spectroscopy to unravel the mechanisms.

The mechanism of the low-yielding conversion of the dichloropropellane **23** to the bridged annulene **22** (and other products) has been studied by ¹³C-labelling and is consistent with the sequence of eliminations and tautomerisms shown in Scheme 4.⁶³



Scheme 4 Reagent: (i) KOBu^t.

En route to methano-bridged dehydro[20]- and [30]annulenes (see below), the first chloro-substituted 1,6-methano[10]annulene derivative **25** was accidentally synthesised (3.5% yield) (Scheme 5).⁶⁴ The Cu(I)Cl used in the Glaser coupling of the terminal alkyne groups of the monomer units **24** contained small amounts of Cu(II)Cl₂ as an impurity. This formed an intermediate copper complex which underwent cyclisation to **25** *via* radical coupling. Compound **25**, as may be expected from the presence of such bulky electronegative substituents, is less diatropic than 1,6-methano[10]annulene itself.

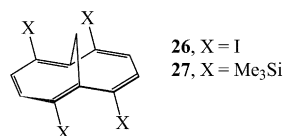


Scheme 5 Reagents: (i) CuCl–CuCl₂.

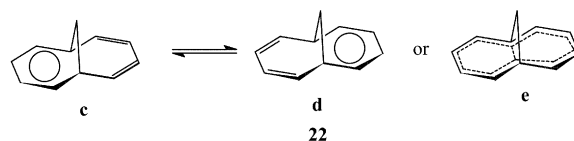
The detailed structure of 1,6-methano[10]annulene **22** has been extensively studied. An alternative form, the norcaradiene structure **22b**, could be possible and indeed in equilibrium with the annulene structure. In the case of **22** itself, NMR,⁶¹ infra-red and Raman spectra⁶⁵ indicate that any contribution from the norcaradiene form is very small (see below) and that **22a** represents the most stable form of the molecule. An X-ray study showed that the periphery is not planar, however, but that the 1- and 6-carbon atoms lie above the plane of the remainder of the ring and, together with the bridging atom C(11), provide a pyramidal structure.⁶⁶ There is, none the less, significant delocalisation of the π -electrons in the periphery as indicated by the NMR spectrum. Calculations suggest that overlap of the π -orbitals, with consequent improvement of delocalisation and stabilisation of the system, is enhanced by some modest rehybridisation of the orbitals.⁶⁷ The distance apart of the C(1) and the C(6) atoms [2.235(3) Å] implies that there is effectively no bonding between these two atoms.



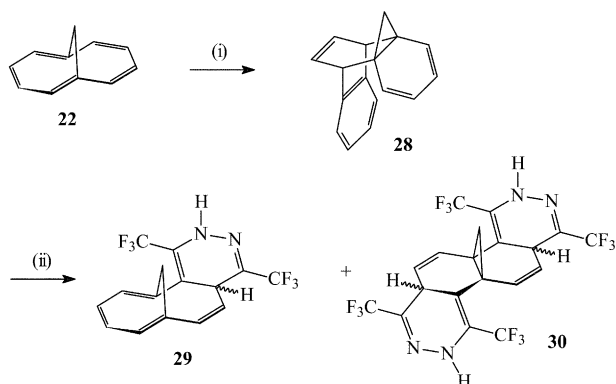
Certain substituent groups on the bridging carbon atom, notably methyl or cyano groups, result in differences in the carbon–carbon distances. There is a marked alternation of bond lengths in the periphery and the distances between the C(1) and the C(6) atoms are much shorter (*ca.* 1.6–1.8 Å).⁶⁸ It is thought that these compounds exist preferentially in a norcaradiene form, although still in equilibrium with the annulene form. It was calculated that for the parent compound **22** the annulene form **22a** is more stable than **22b** by 4.5 kcal mol⁻¹ (corresponding to an equilibrium concentration of **22b** of 0.05% at room temperature) and that the activation energies for the forward and reverse reaction are 7.3 and 2.3 kcal mol⁻¹ respectively.⁶⁹ Both electron-withdrawing groups and sterically hindered substituents should help to favour the norcaradiene form.^{70,71} The presence of large groups on atoms next to the bridge can also affect the structure of the annulene rings. Thus, X-ray and NMR spectra indicate that the most stable forms of 2,5,7,10-tetraiodo-⁷² and 2,5,7,10-tetra(trimethylsilyl)⁷³ derivatives **26** and **27** respectively have annulene-type structures but with fixation of the single and double bonds in the periphery. NMR spectroscopy indicates that there is valence isomerism between the two Kekulé forms in the latter case.



There is another possible complication, namely the possibility of homoconjugation across the 1,6-positions of the ring, as shown in **22c–e**. There is good evidence from absorption and polarised fluorescence spectra and from magnetic circular dichroism in support of some contribution from this type of structure.⁷⁴ Such a homonaphthalene structure could also help to account for the observed alternation in peripheral bond lengths.



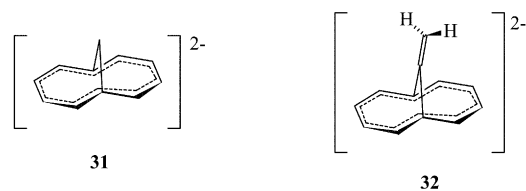
In keeping with the complexity of the structure of **22**, its chemistry is not entirely straightforward, showing resemblances to alkene and to benzene chemistry. For example, it does not undergo Diels–Alder reactions with simple dienophiles such as maleic anhydride but does react with more reactive dienophiles such as benzyne⁷⁵ to give adduct **28** (18%) and with 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine⁷⁶ to give products **29** (5%) and **30** (20%) after loss of N₂ (Scheme 6). Some 11-substituted



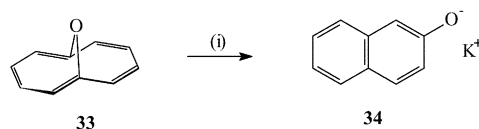
Scheme 6 Reagents: (i) benzyne; (ii) 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine.

derivatives, which have more localised peripheries, react with alkynes.

When a solution of 1,6-methano[10]annulene was shaken vigorously with lithium at –80 °C, it provided a solution of a dianion **31**.⁷⁷ This was remarkably stable at room temperature and its NMR signals only disappeared after *ca.* 20 h. It could be re-oxidised to the parent annulene. The interesting 1,6-bridged [10]annulene dianion **32** also displays extraordinary thermal stability; there is no change in its ¹H NMR spectrum up to +60 °C.⁷⁸ This dianion provides little evidence of paratropicity which is ascribed to non-planarity of the π -system, and results in peripheral bond fixation.



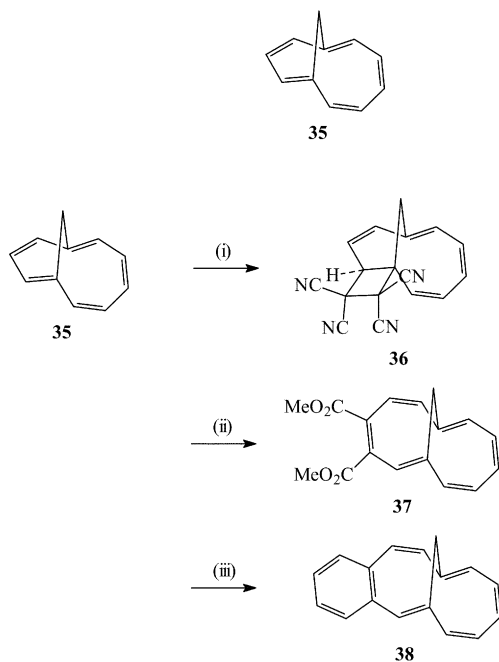
Reaction of 1,6-epoxy[10]annulene **33** with potassium amide in liquid ammonia provides the potassium salt of 2-naphthol **34** (Scheme 7); no comparable reaction occurs with 1,6-methano[10]annulene.⁷⁹



Scheme 7 Reagents: (i) KNH₂–NH₃.

4.2 1,5-Methano[10]annulene

1,5-Methano[10]annulene **35** is a moderately stable compound which undergoes cycloaddition reactions with electron-deficient alkenes and alkynes to give products such as **36–38** (Scheme 8).⁸⁰ The latter two products arise by electrocyclic ring opening of

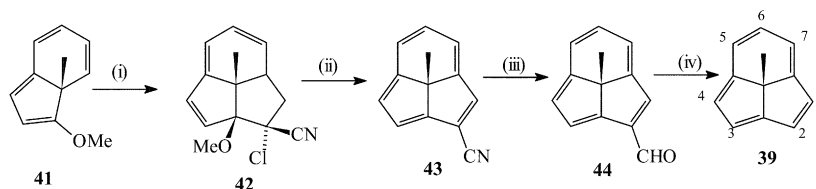


Scheme 8 Reagents: (i) tetracyanoethylene; (ii) dimethyl acetylenedicarboxylate; (iii) benzyne.

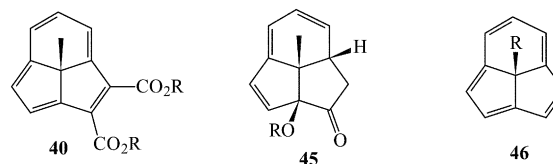
initial [2+2]cycloadducts. Compound **35** is, however, less stable than its 1,6-analogue **22** and polymerises in air.⁸¹ It supports a diamagnetic ring current very like that of its 1,6-analogue **22**.⁸² Its electronic spectrum extends deeply into the visible region and resembles that of azulene rather than that of an alternant hydrocarbon.⁸³ In consequence, the alternative name homoazulene has been suggested for this compound.⁸⁴ It can be regarded as an alternant hydrocarbon with non-alternant character; this is ascribed to homoconjugation across the ring.⁸³ Measurements of heats of hydrogenation and force field calculations suggest that 1,5-methano[10]annulene **35** has a lower resonance energy than its 1,6-analogue **22**, as does azulene compared with naphthalene.⁸¹ *Ab initio* calculations suggest that for the 1,5-isomer there is only a small energy difference between localised and delocalised forms, steric misalignment of the $p\pi$ atomic orbitals probably diminishing the contribution of the delocalised form.¹² As in the case of the 1,6-methano isomer **22**, the misalignment may be somewhat alleviated by modest rehybridisation of the orbitals.

4.3 1,4,7-Metheno[10]annulene (7b-methyl-7bH-cyclopenta[cd]indene)

An example of another type of bridged [10]annulene is 11-methyl-1,4,7-metheno[10]annulene **39** which is a stable yellow oil, first synthesised in 1981⁸⁵ from a bis(methoxycarbonyl) derivative **40** ($R = \text{Me}$) which had been prepared a year earlier.⁸⁶ Other preparative routes were described in succeeding years,^{87,88} exemplified by that shown in Scheme 9. This involves treating the isoindene **41** with 2-chloroacrylonitrile to produce the tricyclic structure **42** which is aromatised to **43** with DBU, followed by reduction to the aldehyde **44**. Decarbonylation using $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ in benzene completes the synthesis of **39**. 1,4,7-Metheno[10]annulenes can also be produced from tricyclic ketones **45** via the Shapiro reaction.



Scheme 9 Reagents: (i) $\text{H}_2\text{C}=\text{C}(\text{Cl})\text{CN}$; (ii) DBU; (iii) DIBAL-H; (iv) $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$.



Dicarboxylic acid derivatives and their esters **40** have also been described,^{86,89} as have analogues **46** in which an ethyl, isopropyl or benzyl group replace the bridging methyl group.⁹⁰

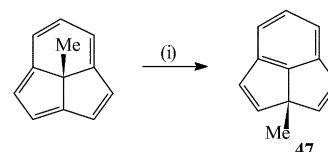
In these compounds, the transannular positions are sufficiently far apart to make homoconjugation unlikely and as a result there is pronounced aromatic character in the periphery. Calculations making allowance for electron correlation predicted delocalised electronic systems in the periphery.^{12,91,92} Photoelectronic spectra of **39** are in accord with this,⁹² as are NMR spectra of **39**, in which the peripheral hydrogen atoms provide signals at δ_{H} 7.53–7.92 ppm and the methyl group a signal at δ_{H} –1.67 ppm,⁸⁵ thus demonstrating the diatropicity of the annulene.

An X-ray study of the dicarboxylic acid derivative **40** ($R = \text{H}$)^{86,89} shows that the molecules are dish-shaped and that the central carbon atom has tetrahedral symmetry. All the peripheral bonds have partial double bond character.

Like benzene, **39** undergoes electrophilic substitution^{87,93} and has been nitrated (copper nitrate, acetic anhydride), acetylated and alkylated. It is interesting that when similar reactions are carried out on the analogue **46** ($R = \text{CH}_2\text{Ph}$), substitution takes place exclusively on the peripheral 10- π -electron system rather than on the benzene ring of the benzyl group.⁹⁰

11-Alkylmetheno[10]annulenes such as **39** do not undergo cycloaddition reactions at room temperature but give a 1 : 2 adduct with 4-phenyltriazoline-3,5-dione when the mixture is heated.⁸⁵

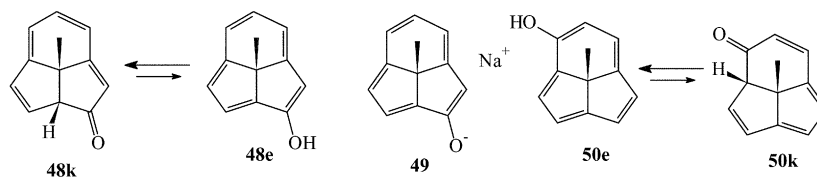
Compound **39** is hydrogenated over palladium/charcoal to give the corresponding tricycloalkane.⁸⁵ When **39** is heated in boiling xylene or subjected to flash vacuum pyrolysis at 400 °C the methyl group migrates to a peripheral bridgehead site to give **47** (Scheme 10).^{86,89} In this process, the [10]annulene



Scheme 10 Conditions: (i) heat.

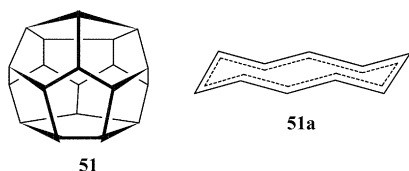
system is replaced by a benzene system, which is energetically favoured.

In the case of 1,4,7-metheno[10]annulene-3-ol **48**, unlike phenol, keto–enol tautomerism lies more to the keto side **48k** than the enol side **48e**.⁹⁴ In fact, there was considerable doubt as to whether tautomerism occurred at all, as no deuterium exchange was observed when the annulenone was shaken with D_2O . However, addition of catalytic amounts of tetrabutylammonium hydroxide caused exchange at the 2a position (**48k**, D replacing the H shown in the structure). The reaction with NaH to form a solution of the sodium annulenoxide **49** indicated formation of an enolate anion. Superiority of the keto form **48k** has been explained by the *keto* tautomer gaining greater



stability from being less planar and less strained. Any stabilisation afforded by the annulene structure in the enol form is insufficient to compensate for the increased steric strain on going from the keto to the enol form. In 1983 1,4,7-methano[10]annulene-8-ol **50** was prepared and shown to exist exclusively in the enol form **50e**.⁹⁵ This compound was therefore the first example of a stable annulenol tautomer with a ring size larger than six-membered to be isolated. There is no spectroscopic evidence for the presence of any keto tautomer **50k**, and it does not undergo H–D exchange in D₂O.

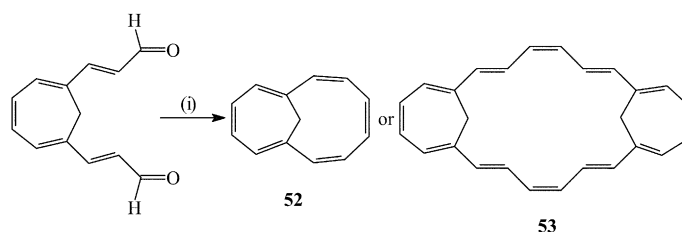
More recently, a very interesting novel bridged [10]annulene carbon skeleton shown in **51**, has been proposed and calculated to be stable. This would permit overlap of adjacent p-orbitals, resulting in “in-plane” cyclic delocalisation. This was described as “in-plane aromaticity” and **51** could be the first member of a new all-*trans* annulene family with in-plane conjugation. Bridging at every carbon atom would provide a polyhedral structure with the p-orbitals of the [10]annulene sub-unit directed inward. An all-*trans* [10]annulene unit **51a** is provided by the ring of 10 carbon atoms which form the central ‘horizontal’ plane of the molecule. These so-called [*n*]trannulenes have been predicted to follow Hückel’s rules exactly and should be aromatic.⁹⁶



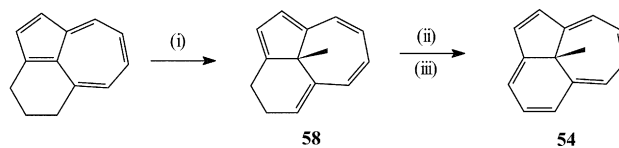
4.4 Bridged [12]annulenes

Bicyclic bridged 1,6- and 1,7-[12]annulenes had been synthesised in the mid 1970s, and appeared to be weakly antiaromatic and paratropic.⁹⁷ An alternative synthesis of 1,6-methano[12]annulene **52** was realised unexpectedly whilst dimerisation–coupling routes to 1,6:13,18-dimethano[24]annulene **53** were being investigated (Scheme 11); addition of TiCl₃ to the reaction mixture in an attempt to improve the yield of the [24]annulene **53** led instead to the formation of 1,6-methano[12]annulene **52** through intramolecular coupling.⁹⁸ 3,4-Bis(methoxycarbonyl)-1,7-metheno[12]annulene **37** was also prepared by addition of dimethyl acetylenedicarboxylate to 1,5-methano[10]annulene **22** (Scheme 8).⁸⁰ Its NMR spectra indicated that the double bonds were localised and that it existed preferentially in one Kekulé form.

In 1986 the first tricyclic [12]annulene was synthesised.⁹⁹ This blue hydrocarbon 1,4,8-metheno[12]annulene (or 9b-methyl-9b*H*-benzo[*c,d*]azulene) **54** was obtained by the three step route shown in Scheme 12 and was described by the authors as “an antiaromatic annulene *par excellence*”. It allowed the first

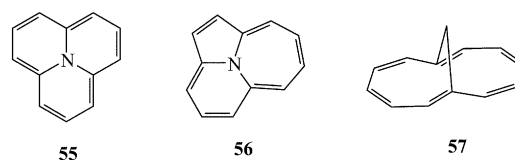


Scheme 11 Reagents and conditions: (i) reductive dimerisation (different methods).

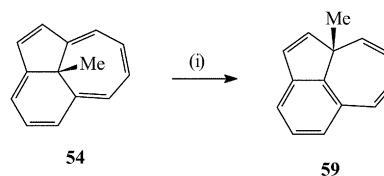


Scheme 12 Reagents: (i) LDA, Me₂SO₄; (ii) NBS; (iii) Hunig’s base.

proper studies of an antiaromatic 12 π -electron system: [12]annulene **7** and 1,6-methano[12]annulene **52** are conformationally mobile and only weakly antiaromatic; in cyclo[3.3.3]azine **55** and cyclo[4.3.2]azine **56** there is an electronic interaction between the nitrogen atom and the peripheral atoms and only limited studies were possible with 1,7-methano[12]annulene⁹⁷ **57** due to transannular interactions.



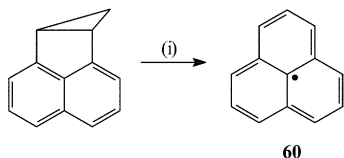
1,4,8-Metheno[12]annulene **54** is very antiaromatic in character and displays marked paratropicity. The ¹H NMR spectrum indicates that only the double bond isomer shown in **54** is present. The methyl protons resonate at a much higher frequency ($\delta_{\text{H}} = 4.75$ ppm) than typical methyl protons, and the ring protons resonate between δ_{H} 3.88 and 4.69 ppm—at much lower frequency than the ring protons in compounds **7**, **52** and **57**. 5,6-Dihydro-1,4,8-metheno[12]annulene **58** is atropic showing no paratropicity: thus its methyl protons resonate at δ_{H} 0.76 ppm—a shift to a lower frequency of *ca.* 4 ppm—the ring C–H protons resonate at δ_{H} 5.86–6.66 ppm (compared with δ_{H} 3.88–4.69 ppm in compound **54**) and the CH₂ protons resonate between δ_{H} 2.42 and 2.93 ppm. These resonances provide further evidence that 1,4,8-metheno[12]annulene **54** does indeed possess a very strong paratropic ring current which probably reflects its enforced planarity. It is stable in solution up to 80 °C but the solid rapidly changes into yellow, high molecular weight products even at –30 °C. At higher temperatures migration of the methyl group occurs to give **59**; in boiling xylene the reaction is rapid and quantitative (Scheme 13).⁹⁹



Scheme 13 Conditions: (i) heat.

This resembles the process which occurs with metheno[10]-annulene **39** (Scheme 10) and similarly can be attributed to the formation of an energetically favoured benzenoid structure.

The phenalenyl radical **60** is also of interest; it has been used as an internal temperature probe in low temperature systems.¹⁰⁰ It is best represented as having a 12 π -electron periphery with the odd electron on the central atom,¹⁰¹ but there must be interaction between the two (Scheme 14). It has temperature



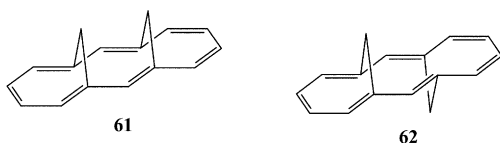
Scheme 14 Conditions: (i) $h\nu$, 254 nm, 40 K.

dependent spectroscopic features and gives accurate temperature measurements in the 10–70 K region.

4.5 Bridged [14]annulenes

The larger ring size of [14]annulene provides the possibility of a number of different bridged annulenes.

4.5.1 1,6:8,13- and 1,6:7,12-Dimethano[14]annulenes and analogues thereof. The period 1980–2000 started with a concise summary of the significance of these compounds by E. Vogel and co-workers who had synthesised most of the simpler examples of bridged annulenes (e.g. **61** and **62**) in the 1970s.

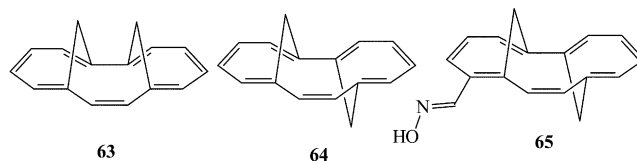


“The influence of ring conformation on the π -electron structure of a bridged [14]annulene manifests itself most impressively in the case of *syn*- and *anti*-1,6:8,13-bismethano derivatives. Whereas the *syn*- is aromatic, although it contains a noticeably bent annulene ring, the *anti*- with its strongly puckered ring, is olefinic, with fluxional π -bonds. That geometric factors do not cause lack of aromaticity in the *syn*- is consistent with information gained from other bridged [14]annulenes, according to which, a $[4n+2]$ annulene tolerates considerable distortion of the ring skeleton without substantial weakening of the π -delocalisation, provided that the torsion angles of the $C(sp^2)$ – $C(sp^2)$ bonds in the ring are not greater than ca. 45–55°.”¹⁰²

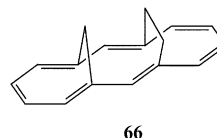
In keeping with this, the NMR and UV spectra of the *syn*-isomer **61** show it to be unequivocally an arene with a delocalised periphery,¹⁰³ whereas the *anti*-isomer **62** is a puckered polyalkene with fluxional π -bonds.¹⁰⁴ The *syn*-isomer forms stable orange crystals but the *anti*-form is sensitive to oxygen. Variable temperature NMR studies on the *anti*-isomer confirm that the two possible Kekulé forms are rapidly interconverting. An X-ray study of *anti*-1,6:8,13-bis(difluoromethano)[14]annulene (cf. **62**) showed the presence of alternate single and double bonds in the periphery and that it was non-planar with misalignments as big as 70° between adjacent p-orbitals.¹⁰⁵

The 1,6:7,12-dimethano[14]annulenes **63** and **64** were prepared in 1986 by multi-step procedures using 1,6-disubstituted cycloheptatrienes as starting materials.^{106,107} The *syn*-isomer **63** is weakly diatropic whilst the *anti*-isomer **64** is atropic; the valence isomer shown in **64** represents the major constituent. The NMR spectrum of **63** indicates that, although the peripheral electronic system is delocalised, the Kekulé form shown in **63** is the major contributor. An X-ray study confirms this and indicates that torsion angles of up to 45° are involved. Bond lengths in the end rings alternate but are within the range

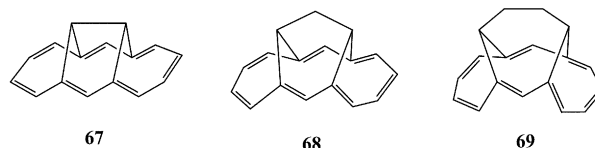
of aromatic bond lengths, but in the central portion of the molecule the bond lengths approximate to those in polyalkenes; this is probably associated with steric forces due to repulsion between the CH_2 atoms. The *syn*-isomer **63** is an orange crystalline compound which is stable in air; **64** is a pale yellow liquid. An X-ray study of the oxime **65** shows that the C–C bonds are mostly twisted. Torsion angles for most bonds are 22–35° but for the C(6)–C(7) bond the torsion angle is 84°; $2p\pi$ overlap in this bond is thus minimal, which accounts for the lack of aromaticity and pronounced alternation of single and double bonds.



1,6-Ethano-8,13-methano[14]annulene **66** has been prepared.^{102,108} The ethano bridge distorts the geometry of the rings sufficiently to give the molecule polyalkene character. NMR spectra show that the molecule exists as a mixture of valence isomeric polyalkenes, the structure shown in **66** being the preferred isomer at low temperatures. It polymerises readily in air but can be stored under an inert gas at low temperatures.



A number of methano-bridged [14]annulenes, in which the bridging carbon atoms are themselves joined together, as in compounds **67**, **68** and **69** have been prepared. This bridging offers the advantage that the π -perimeters are geometrically fixed with a particular ring configuration and conformation.⁷⁸ Larger bridges might be expected to compel more bending and/or zig-zagging of the periphery but NMR spectra suggest that distortion takes place more in the bridge than in the periphery. All are diatropic, but diatropicity decreases with an increase in the length of the alkyl bridge and this can be attributed to geometric factors.¹⁰⁹ EPR studies indicate that there is less hyperconjugative interaction across the peripheral ring in **68** than in **67**.¹¹⁰ Partial rate factors for protodetritiation and protodesilylation of 2-substituted derivatives of **68** have been measured.¹¹¹

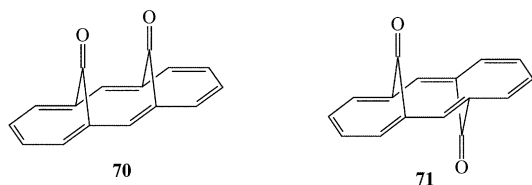


Reduction of bridged [14]annulenes with lithium provides strongly coloured dianions.⁷⁸ The dianions are paratropic; their relative paratropicities reflect the conformational changes in a much more sensitive way than the diatropicities of the neutral annulenes, and further reveal the interdependence of steric and conjugative effects in the molecules.

The cations of dimethano[14]annulenes have also been studied, produced by treating the neutral annulenes with superacid mixtures of SbF_5 and $HfSO_3-CISO_2F$ at $-80^\circ C$.¹¹² In the cases of **68** and **69**, this process results initially in the formation of symmetrical monocations protonated at the central 7-carbon atom. Loss of aromaticity due to the interrupted π -system is readily observed with 1H NMR spectroscopy. As the mono-protonated species warm to room temperature, the unprotonated dicationic species are formed. These antiaromatic 12

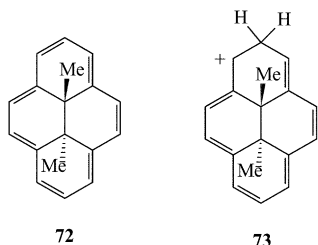
π -electron systems have a marked paratropic ring current visible in the ^1H NMR spectrum (also apparent is the relative deshielding of *all* the protons as electron density is removed from the system in the dication). As is observed with the dianions, variations in the paratropicity of these dications is more sensitive to conformational factors than is the case for the related neutral annulenes. The perimeters increasingly deviate from a coplanar arrangement with increase in chain length revealing again the subtle interdependence of steric and conjugational phenomena.⁷⁸ Compound **67** behaves differently; no similar mono-protonated or dicationic species are observed under the superacidic conditions. This could be a result of the neutral molecule being strongly aromatic. Therefore the dication would be more strongly antiaromatic, highly destabilised and less willing to form. Alternatively, a rearrangement may be possible for the dication of compound **67** *via* pathways unavailable to **68** and **69**.

Other related 1,6:8,13-bridged [14]annulenes include the *syn* and *anti* dicarbonyl bridged compounds **70** and **71**.^{113,114} Either of these compounds might be expected to decompose readily to give the stable products anthracene and carbon monoxide, but the *syn*-isomer **70** is very stable and resists flash vacuum pyrolysis at 500 °C. X-Ray structures show that the periphery of **70** is virtually planar, despite repulsion between the two adjacent carbonyl groups. Spectra indicate that it has a delocalised π -system and is diatropic. On the other hand, crystals of the *anti*-isomer **71** are sensitive to light and it polymerises readily in air. NMR spectra show that **71** is a polyalkene and that there is rapid valence tautomerism between the two Kekulé forms. The great difference between these *syn*- and *anti*-isomers again provides impressive evidence of the effects of molecular geometry on the electronic structure of cyclic conjugated molecules.



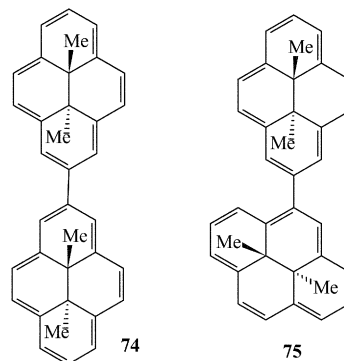
4.5.2 trans-10b,10c-Dimethyl-10b,10c-dihydropyrene (DMDHP). 15,16-Dimethyl-1,5:8,13-ethanediylidene[14]-annulene or *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (DMDHP) **72** has been intensively investigated because of its availability and the properties associated with its π -system. Indeed, in the period 1980–2000, more has been published on the chemistry of this compound than any other annulene and it is only possible here to give a brief summary of the more important discoveries. In particular the papers of R. H. Mitchell and co-workers should be consulted for more detailed discussion.

DMDHP **72** has a delocalised 14 π -electron perimeter and is strongly aromatic. An X-ray structure carried out at 173 K shows that all peripheral bonds are essentially equal in length [1.388(2)–1.398(2) Å] and the peripheral atoms are coplanar [mean deviation 0.028(1) Å].¹¹⁵ The protons of the two internal methyl groups, arranged above and below the plane of the ring respectively, resonate at δ_{H} –4.25 ppm.¹¹⁶

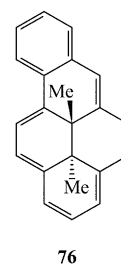


New chemistry of DMDHP includes protonation at the 2-position with super acids to give stable cations **73**,¹¹⁷ sulfonation with SO_3 to give mono-, di-, tri- and tetra-sulfonated derivatives,¹¹⁸ photoisomerisation and photo-oxidation,¹¹⁹ (and a discussion of its photophysical properties¹²⁰) and formation of arylated derivatives by the Gomberg–Bachmann reaction with diazonium salts.¹²¹

A symmetrical biaryl-type derivative **74** consisting of two DMDHP units has been synthesised¹²² and more recently the unsymmetrical isomer **75** has been obtained by nickel-catalysed coupling of 2- and 4-bromo-DMDHP derivatives.¹²³ A cyclophane consisting of two DMDHP units has also been made.¹²⁴



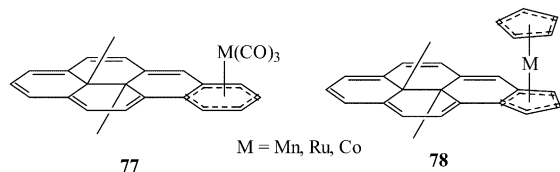
When two diatropic annulene rings of different sizes are fused together the ring which is inherently more diatropic reduces the diatropicity of the other ring; thus in benzo[18]-annulene **21** the inner and outer protons of the 18-ring provide NMR signals at δ_{H} 6.45–8.03 ppm and 4.75–4.95 ppm respectively whereas in [18]annulene **14** itself the corresponding signals are at δ_{H} 9.28 and 2.99 ppm respectively. Bond localisation in the annulene ring is also increased. In the case of DMDHP **72**, fusion with a benzene ring, as in **76**, reduces the ring current to such an extent that the methyl protons provide signals at δ_{H} –1.62 ppm, the peripheral proton resonances are shifted to lower frequency and the peripheral bonds become more localised. It has been shown that, if different arene rings are fused to DMDHP, these rings cause different shifts and it was suggested that the extent of the shifts can be correlated with the diatropicity or aromaticity of the fused ring.¹²⁵ The effects caused by rings fused to DMDHP thus provide an excellent probe for the diatropicity/aromaticity of the relevant fused ring.¹¹⁶



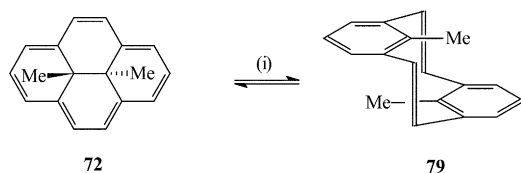
Annulation of the DMDHP unit has proved to be a fertile area of research; as well as benzene fusion.^{125,126} DMDHP derivatives with fused phenanthrene,¹²⁷ acenaphthene,¹²⁸ biphenylene,¹²⁹ cyclopentanone¹³⁰ and cyclopentadienide¹³¹ units have been synthesised and the effects on the diatropicity of the DMDHP system have been investigated (see also Section 5.3).

In the cases where the fused rings are metal complexes of benzene or cyclopentadiene, as in **77** and **78**, there is greater bond localisation in the DMDHP periphery and a greater shift in the NMR signals of the methyl groups than when DMDHP is fused to benzene. By analogy with the above work, it is suggested that a possible explanation is that the metal com-

plexes are more “aromatic” than benzene. Calculations have indicated that the shifts of the methyl resonances are not due to tropic influences from the annelated ring, because of the distance between them, but that there is a real change in the delocalisation of the whole π -system.¹¹⁶ The relative double-bond fixing ability of the organometallic moieties were thus estimated by their effects on the 14-ring and the use of DMDHP provides another method for estimating the aromaticity of arenes.

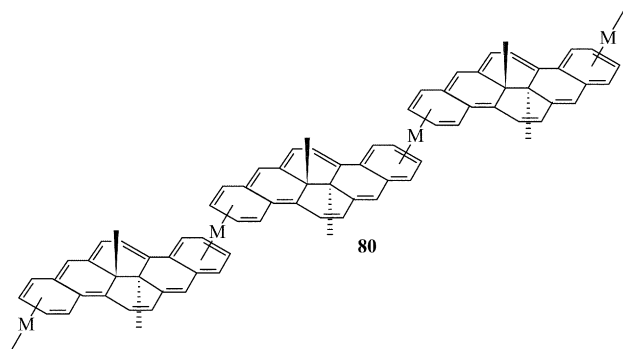


It has also been suggested that DMDHP may have potential as a photo-switch, as it undergoes reversible ring-opening isomerisation to a stepped cyclophane **79** when irradiated (Scheme 15). If many dibenzo-annelated DMDHP units were



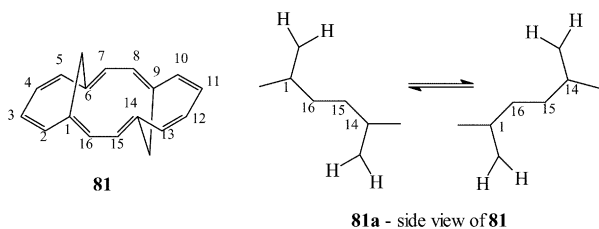
Scheme 15 Conditions: (i) $h\nu$.

linked through co-ordination with metal atoms as in **80**, the resulting polymer could, upon irradiation, switch between conductive polyannulene structures and non-conductive structures related to **79**.¹³² Conversion of DMDHP to **79** is brought about by visible light and can be reversed either by UV light or thermally.¹³²



4.6 Bridged [16]annulenes

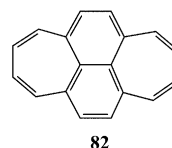
1,6:9,14-Dimethano[16]annulene **81** has been prepared and forms gold-brown needles which are stable in air.^{133,134} NMR spectra and an X-ray study show that it is paratropic and has alternate single and double bonds as shown in **81**.¹³⁴ It is *anti*-bridged and is largely planar but atoms 1,16–14 and 6–9 of the periphery are slightly stepped as shown in the side view **81a**, and the torsion angles in these bonds are as much as 46°



At room temperature the bridging methylene groups provide two distinct ^1H NMR signals but these signals coalesce at higher temperatures; this is explained by the interconversion of the two forms shown in **81a**. There appears to be no migration of the double bonds which remain in the positions shown in **81**.

It can be reduced with lithium to form a dianion.¹³⁵ The lithium salt forms violet crystals and is stable in air in solution in THF. With $\text{SbF}_5\text{-SOCl}_2$ **81** forms a dication.¹³⁵ The dication and dianion have 14 and 18 π -electrons, respectively. Both are strongly diatropic; NMR signals from the methylene group protons show large low frequency shifts compared with their signals in the neutral annulene. ^{13}C NMR spectroscopy indicates that the structure of the parent annulene is preserved in these ions. These ions therefore provided the first opportunity to compare two geometrically identical $(4n+2)$ π -systems, which differ from each other by 4 π -electrons. On making allowance for the charges in each case, the ring currents in the 14π dication and the 18π dianion are of similar magnitude. Whereas studies of neutral $(4n+2)$ π annulenes show that the ring current decreases with increase in ring size, due to the tendency to increase fixation of the single and double bonds, this trend appears to be much less for ionic $(4n+2)$ systems and diatropicity is much greater in the charged species

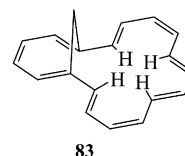
Diplediadiene† **82** is of interest in that it could be regarded either as an etheno-bridged [16]annulene or as a di-*peri*-bridged naphthalene. This air-stable compound forms reddish-black needles. X-Ray analysis shows slight puckering due to non-bonding hydrogen interactions.¹³⁶ From the bond lengths it appears that the naphthalene nucleus essentially retains its integrity, but that there is strong bond alternation in the *peri*-bridges. Coupling constants in the ^1H NMR spectrum confirm this, but there is an overall weak paratropic ring current due to the peripheral paratropic ring current overpowering the diatropic effect of the naphthalene sub-cycle.



4.7 Higher bridged annulenes

For annulenes with larger rings than [18]annulene, simple bridging alone has little tendency to make the molecule rigid enough for any noticeable difference in planarity and aromaticity, especially in the case of anti-aromatic systems which have a drive to deviate from planarity.

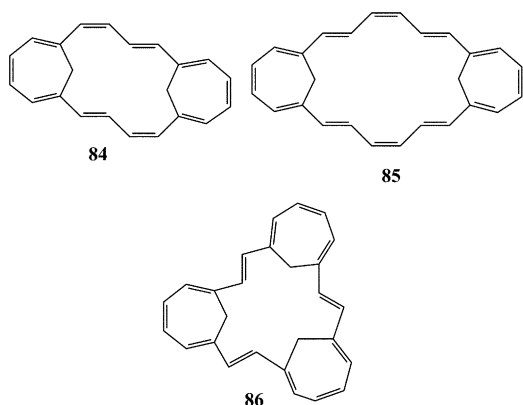
Bridging between the 1 and 6 positions prevents [18]annulene from adopting its optimum $D_{6h}\text{-}D_{3h}$ planar geometry **83**. This results in a reduction in ring current and aromaticity. The larger of the two cycles in **83** is conformationally mobile; this is apparent from the temperature dependent ^1H NMR spectrum which indicates exchange between the internal and external ring protons. As the temperature is lowered, the diatropic ring current increases.¹³⁷



Similarly, 1,6-methano-bridged derivatives of [20]-, [22]- and [24]annulene have been prepared, and they display similar trends.^{98,137} Conformational mobility gives rise to temperature dependent ^1H NMR spectra and, as the temperature is lowered,

† The IUPAC name for diplediadiene is dicyclohepta[*de,i*]naphthalene.

the ring current increases. The temperature dependence is greater than in the dehydro-analogues, which will be discussed later. The antiaromatic $[4n]$ π -electron systems, 1,6:11,16-dimethano[20]annulene **84** and 1,6:13,18-dimethano[24]-annulene **85** have been prepared and are nearly atropic due to the severe deviation from planarity.^{133,137} The triply bridged system, 1,6:9,14:17,22-trimethano[24]annulene **86**, is non-planar and weakly paratropic. However, reduction with lithium metal forms a strongly diatropic 26 π -electron system, apparently with a C_3 symmetry axis.¹³⁵ It appears not to be conformationally mobile, unlike **86** itself and the corresponding neutral annulenes, which are atropic and weakly diatropic respectively.



As the size of the 1,6-methano-bridged annulenes increases, the wavelengths of the main absorption peaks in the electronic spectra alternate between the annulenes with $4n$ or $(4n+2)$ π -electrons, as also occurs with the unbridged annulenes, e.g. for the 1,6-methano-[18]-, [20]-, [22]- and [24]-annulenes, $\lambda_{\max} = 331, 321, 361$ and 352 nm respectively.

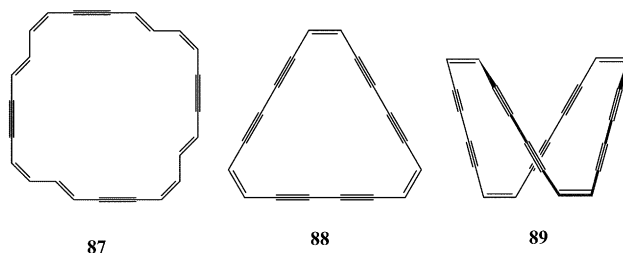
5 Dehydroannulenes

Hydrocarbon bridging is an effective method of reducing the flexibility of the ring in an annulene and of restricting it to a planar conformation ideal for p-orbital overlap and π -delocalisation. Another widely investigated method of achieving this is the introduction of linear triple bonds, which are rigid and free from interacting C–H groups. These structural features are often used in combination with other functional groups, for example fused arene rings and other cyclic structures and functionalisation with bulky groups (*tert*-butyl), to provide a kinetic barrier to bond rotation.

Dehydroannulenes are in fact of considerable interest in themselves; it had been suggested as long ago as 1948¹³⁸ that they should be aromatic compounds provided that they have the correct number of conjugated π -electrons to form a delocalised π -orbital and that the rings were planar. However, the introduction of triple bonds in place of double bonds might have a number of effects on the stability and bond structure of the ring. First, as mentioned above, this increases the rigidity of the ring, which could have a stabilising or destabilising effect, depending on the geometry of the ring. If the triple bond holds the ring in an unstrained configuration the stability is increased but if it results in the introduction of angle strain, stability is decreased. Second, crowding of hydrogen atoms is reduced because there are fewer of them. Third, the presence of the triple bond may induce bond alternation, especially in larger rings.

Many dehydroannulenes were made in the 1960s and 1970s, often as precursors to target annulenes. Sondheimer's route to the first [18]annulene **14** went *via* 1,7,13-tridehydro[18]annulene **4** (*cf.* Scheme 1) which was planar and diatropic.⁴ Tetra-dehydro[24]annulene **87** was similarly a precursor to [24]annulene. As polyynes, dehydroannulenes tend to be unstable, for example both compounds **88** and **89** are highly

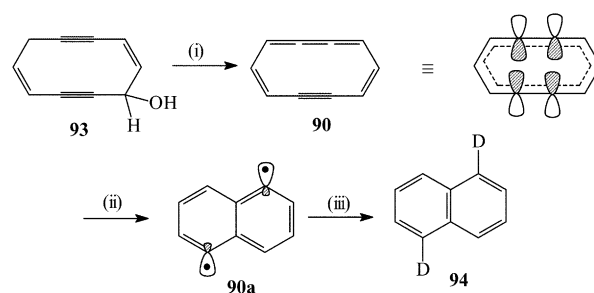
explosive yellow solids which explode when heated or even just when rubbed.¹³⁹ When kept in air at room temperature 99% of **87** is lost.



There is considerable potential for structural diversity within the series of dehydroannulenes, since in principle any one (or more) of the formal double bonds within an annulene system may be oxidised. [60]Fullerene is perhaps the dehydroannulene *par excellence*. We have therefore adopted a more selective approach than in the earlier sections and only highlight some of the major advances in this area.

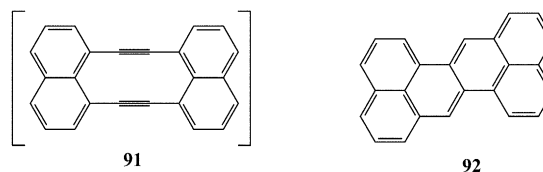
5.1 Dehydro[10]annulenes

1,6-Didehydro[10]annulene **90**, despite its simple structure, had not been synthesised until 1992.¹⁴⁰ In the late 60s and early 70s, Sondheimer and Staab and their coworkers made several attempts to synthesise the benzo-fused analogue **91**, but instead produced the polyaromatic molecule, zethrene ‡ **92**.¹⁴¹ The annulene **90** was obtained by a multi-step route in which the key step was dehydration of the alcohol **93** at -90 °C (Scheme 16).¹⁴⁰ ¹H and ¹³C NMR spectra indicate that, at -90



Scheme 16 Reagents and conditions: (i) $(CF_3SO_2)_2O$, Et_3N , -90 °C; (ii) -50 °C; (iii) deuteriated solvent.

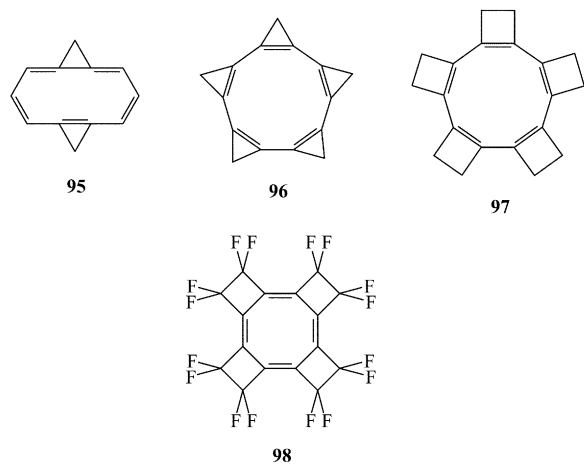
°C, compound **90** has static or time-averaged D_{2h} symmetry and supports a diatropic ring current. It rapidly undergoes valence isomerism above -90 °C to form a 1,5-dehydronaphthalene diradical **90a**. Cyclisation to naphthalene **94** in the presence of deuteriated solvent leads to incorporation of deuterium at the 1 and 5 positions only (Scheme 16). This diradical forming cycloaromatisation is very fast ($t_{1/2}$ 25 min at -51 °C). Calculations have suggested that the angle strain in compound **90** is negligible (C–C≡C bond angle to be 171.6°), but triple bonds do not conjugate well and there are strong transannular interactions.



Recent calculations have shown that, although angle strain in **90** is negligible, the presence of the "triple bonds" provide undesirable factors; they suggest that highly aromatic, planar

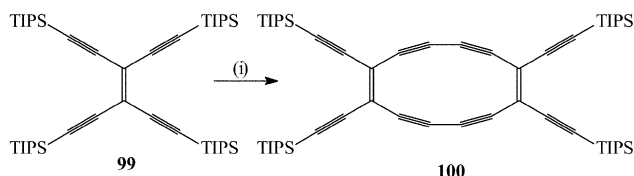
‡ The IUPAC name for zethrene is dibenzo[*de,mm*]naphthacene.

all-*cis*-[10]annulene derivatives **95**, **96** and **97** (which have some affinity with dehydroannulenes but with cycloalkane moieties taking the place of triple bonds) may be stable compounds with little bond alternation–localisation.¹⁴² The C=C–H bond angles in the cyclopropene and cyclobutene “monomer” units are 154° and 134° respectively, very close to the 144° required for D_{10h} symmetry. These compounds await synthesis as the first non-bridged planar aromatic [10]annulenes, and compound **95** has sites available for aromatic substitution chemistry. Recent studies of the related cyclooctatetraene derivative **98** suggest that the synthesis of **95**, **96** and **97** is indeed a possibility.¹⁴³



5.2 Dehydro[12]annulenes

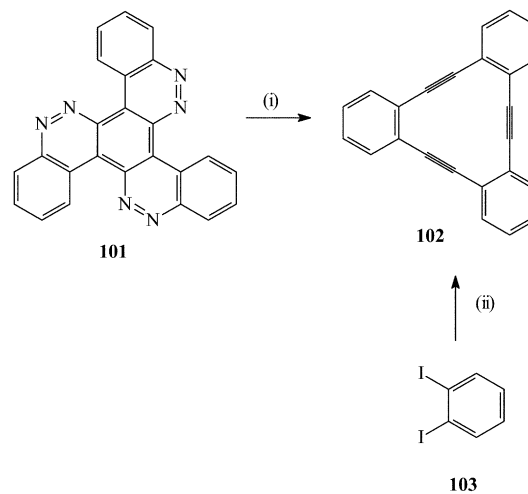
Monodehydro-, didehydro- and tridehydro[12]annulene were all synthesised in the 1960s and 1970s. More recently, there has been growing interest in the production of dehydro[12]-annulenes functionalised with acetylene groups as precursors in the synthesis of theoretical non-graphitic carbon sheets. One such compound **100** and its trimeric analogue (a dehydro-[18]annulene) have been synthesised *via* the Hay coupling of ‘monomer’ unit **99** (Scheme 17).¹⁴⁴ Although compound **100**



Scheme 17 Reagents: (i) CuCl, TMEDA.

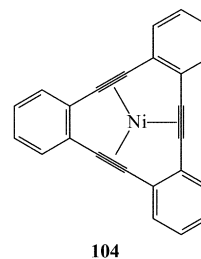
contains highly strained triple bonds, it is air-stable for several days and forms dark red needles which have been studied by X-ray diffraction. The carbon skeleton of **100** is planar [mean deviation 0.089(6) Å] and its optical properties suggest that it is antiaromatic.¹⁴⁴

In recent years, attention has been paid to the benzo-fused derivative, tribenzocyclyne (TBC) **102**. This compound was first synthesised in 1966, but since then there have been new developments in its preparation. A novel cyclisation–ring-opening reaction of **101** under FVP conditions gives **102** in 8% yield,¹⁴⁵ and a palladium catalysed reaction of monomer unit **103** with acetylene in the presence of CuI in morpholine leads to the direct formation of **102** in 36–39% yield (Scheme 18).¹⁴⁶ It has been shown to be paratropic.¹⁴⁷ TBC has been of interest because of its ability to form stable transition metal complexes. Smaller metal atoms, such as nickel¹⁴⁸ form slightly distorted trigonal planar complexes with TBC, where the metal atom is situated in the centre of the cycle **104**. A crystal structure shows that the metal–triple bond distance is *ca.* 1.958(5) Å.¹⁴⁸ Larger metal atoms, such as silver, form 1 : 2 complexes with TBC, with the metal centre sandwiched between the two TBC



Scheme 18 Reagents and conditions: (i) FVP (750 °C, 0.005 Torr); (ii) HC≡CH, PdCl₂(PPh₃)₂, CuI, morpholine.

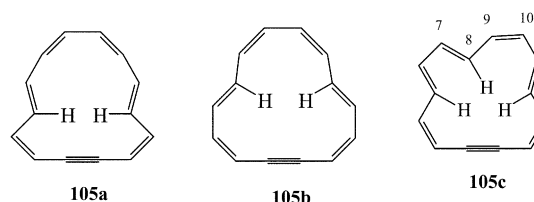
ligands (either eclipsed or staggered).¹⁴⁶ These complexes have novel conducting properties; addition of the metal complex to un-complexed TBC greatly enhances its electrical conductivity.¹⁴⁸



5.3 Dehydro[14]annulenes and relatives

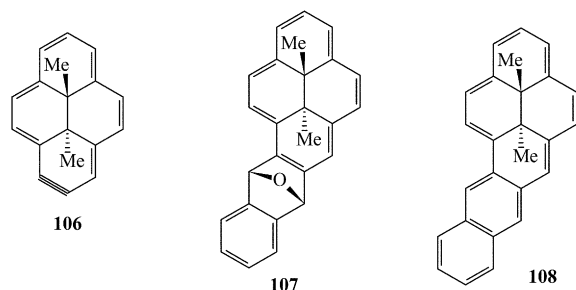
Although monodehydro[14]annulene **105** was first synthesised in the 1960s, its detailed structure was not fully understood. It exists as two isomers: an ‘unstable’ isomer that decomposes at 95–100 °C, which may be converted into a ‘stable’ isomer (mp 153 °C) *via* reflux or irradiation. Both isomers show a diatropic ring current.

Later NMR studies clarified the structures of these isomers.¹⁴⁹ The ¹H NMR spectrum of the ‘unstable’ isomer was temperature independent between –80 and 25 °C, with a well defined double doublet at δ_{H} –1 ppm, and indicated symmetrical structures **105a** or **105b**. The spectrum of the ‘stable’ isomer proved to be dramatically temperature dependent. At –80 °C, the molecule is essentially locked in conformation **105c**, with 3 internal protons. As the temperature is increased, the peaks corresponding to protons 7, 8, 9 and 10 become broad and flat and eventually indistinguishable whereas the other peaks remain sharp and precise. This indicates the reversible conversion to a more symmetrical structure. An initial designation of the wrong structure was due to the original ¹H NMR being recorded at 25 °C: an important signal had been neglected, as it was too broad.

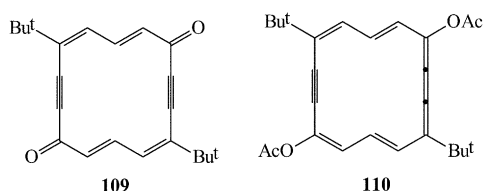


Monodehydro[14]annulene does not appear to have any benzyne-like reactivity. However, a monodehydro ethane-bridged [14]annulene, a dehydrodihydropyrene **106** has been

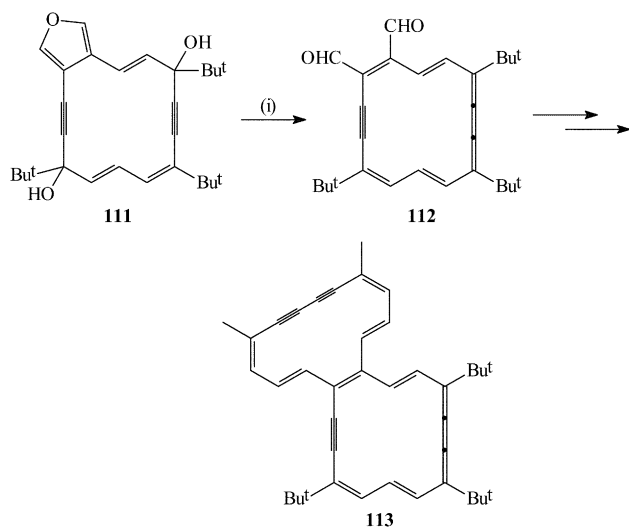
prepared by reaction of a bromodimethyldihydropyrene (bromo-DMDHP, cf. Section 4.5.2) with sodium amide and this compound undergoes cycloaddition reactions to provide annelated DMDHP's.¹⁵⁰ Its reaction with furan provides an adduct that can lose an oxygen atom, so that, for example, benzo[*c*]furan adds to give compound **107**, which on deoxygenation by $\text{Fe}_2(\text{CO})_9$ is converted into the naphtho-DMDHP **108**.¹⁵⁰ Fusion of two annulene rings causes modification of the NMR spectra of each ring, for example fusion of a benzo-ring lowers the diatropicity of the 14-ring in DMDHP **72** (see also Section 4.5.2).¹²⁶ Comparison of the NMR spectrum of **108** with that of DMDHP itself thus provides an indication of the relative aromaticity of the system fused to it.^{150,151} This method can provide a valuable way of comparing the relative aromaticity of different systems.



The chemistry of didehydro[14]annulene and its derivatives continues to be studied. The quinone-like dione **109** has been made and reductively converted into the diacetate **110**



(81%) using zinc and acetic anhydride.¹⁵² A tetrahydro[14]-annuleno[14]annulene **113** has been obtained by elaboration of the dialdehyde **112**, obtained by acid hydrolysis of the fused furan **111** (Scheme 19).¹⁵³ Didehydro[14]annulenes such as **114**,

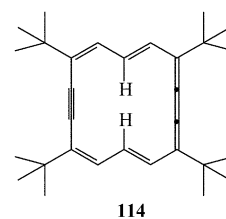


Scheme 19 Reagents: (i) H^+ , THF.

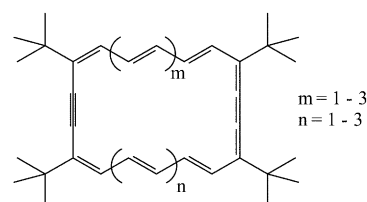
its ions and their homologues **115**, have been used as model systems in exploring the influence of external factors such as ion-pairing, on NMR chemical shifts.¹⁵⁴

5.4 The higher dehydroannulenes

One family of bridged annulenes which has proved to be of

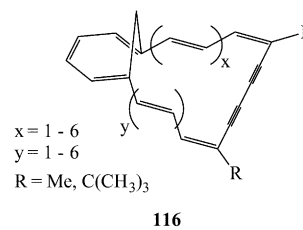


114



115

great value in the study of aromaticity is a series of 1,6-methanotetrahydro[*n*]annulenes ($n = 18, 20, 22, 24, 26, 28, 30, 32, 34, 38$).^{155,156} These highly stable crystalline compounds, which have a metallic lustre, are functionalised with methyl or *tert*-butyl groups to prevent bond rotation **116**, and rigidity is imposed by the triple bonds. This makes them less conformationally mobile than the non-dehydro methano-bridged analogues mentioned earlier. Since research into annulenes began, the experimental limit for aromaticity has been steadily increasing. Until the synthesis of this group of compounds **116** in 1986, the limit for aromaticity or ring current had been placed at around [22]- or [24]annulene. Comparison of the proton resonances in the acyclic precursors with the corresponding resonances in the cyclic structures indicated that diatropicity is present in this series even in the [34]dehydroannulene. Further proof was obtained by comparing the resonances of the methyl and methylene groups of the annulene which lie inside and outside the ring, respectively. The [32]- and [38]dehydroannulenes are atropic: formally the [32]annulene should be anti-aromatic, which could deform its large structure from planarity and, even though the [38]annulene is formally aromatic, the aromatic stabilisation energy (limited at this size) is not enough to overcome the conformational flexibility. The limit for paratropicity for this family of compounds was found to lie at the [28]annulene.

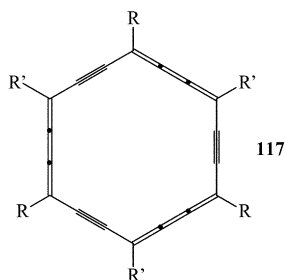


116

A series of dehydro[$4n+2$]annulenes **115** was also synthesised and the properties of their anions studied.¹⁵⁴ Although lacking the stabilisation of the methano-bridge present in the previous group of compounds, these dehydroannulenes have relatively little angle strain, no transannular interactions, contain two rigid triple bonds, and have four stabilising *tert*-butyl groups. The larger dehydroannulenes in the series ($m = 1-3, n = 1-3$) may be reduced to the tetraanions (the dehydro[14]annulene is reduced no further than the dianion).¹⁵⁴ The tetraanions of these dehydroannulenes are more strongly diatropic than the neutral molecules.

The interesting hexadehydro[18]annulenes **117** have been prepared with $\text{R} = \text{R}' = \text{aryl}$ or *tert*-butyl^{157,158} and also with $\text{R} = \text{H}$ and $\text{R}' = p\text{-tert-butylphenyl}$.¹⁵⁸ They are stable at room temperature, both in the crystalline form and in solution in chloroform. An X-ray study of **117** ($\text{R} = \text{R}' = \text{Ph}$) shows that it is planar, with D_{6h} symmetry and internal bond angles at the

corners within the range 116–121°. ¹⁵⁸ Each side consists of one short and two long bonds (average lengths 1.217 and 1.390 Å respectively) and the length of each C₄ side is 4.997 Å, close to that of three benzene bond lengths. These compounds are strongly diatropic and the NMR spectra remain unchanged from –60 to +180 °C.



5.5 Some annelated dehydroannulenes

Hexadehydro[18]annulene **88** and octadehydro[24]annulene **89** are very unstable and potentially explosive compounds, as mentioned in the introduction to Section 5. However, such annulene systems can be stabilised by annelation with functionalised cyclobutene rings. Whereas annelated arene rings reduce the tropicity of the annulene with their own more effective aromaticity (more than increasing it by imposing planarity), cyclobuteno groups are non-aromatic systems and serve only to force the annulene into a planar conformation and also sterically protect it. ¹⁵⁹ Coupling of monomer unit **118** (CuCl, TMEDA, O₂) leads to the formation of dehydroannulenes **119** [*n* = 1 (2.1%), 2 (6.6%) and 3 (1.8%)] as a mixture of diastereomers. ¹⁶⁰

It is interesting to note that these compounds have no hydrogen atoms directly attached to the annulene rings. A prime interest in preparing the compounds **119** and other related compounds, has been to attempt their thermal—or other—decomposition with the loss of the annelated moieties to form cyclo[*n*]carbons such as **122**. Cyclo[*n*]carbons are defined as all-carbon molecules in which *n*-carbon atoms are connected to form monocyclic ring structures. ¹⁶⁰

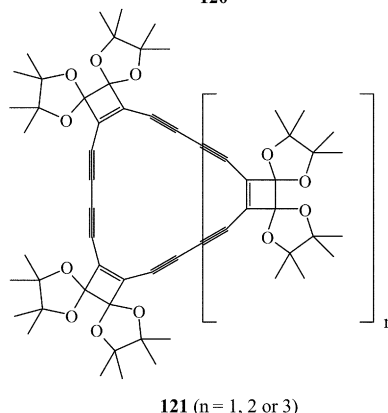
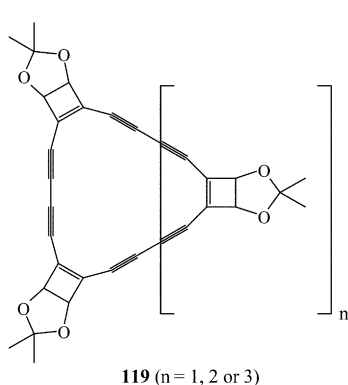
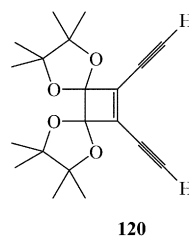
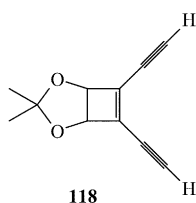
Compound **119** (*n* = 1) is unstable in the solid state and must be kept in solution, but the tetramer **119** (*n* = 2) is very stable and can be stored at room temperature in an ambient

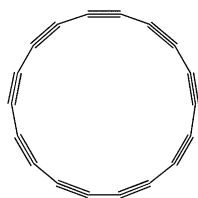
atmosphere for months without significant decomposition. The pentamer **119** (*n* = 3) is less stable and must be kept below 0 °C to avoid decomposition. Similar coupling of **120** leads to a mixture of very stable crystalline dehydroannulenes **121** [*n* = 1 (3.8%), 2 (5.1%) and 3 (0.8%)], all of which can be stored at room temperature. Trimer **121** (*n* = 1) is pale yellow, tetramer **121** (*n* = 2) is orange–red and pentamer **121** (*n* = 3) is bright yellow.

The [18]annulenes **119** (*n* = 1) and **121** (*n* = 1) are planar and provide diatropic ring currents as expected for [4*n*+2] aromatic systems. Although the methyl groups whose NMR chemical shifts are used to indicate the aromaticity of the molecules are at a considerable distance from the annulene ring, the difference between the shifts and those of the related monomer unit are quite apparent. Similarly, a weak paratropic ring current is observed for the [4*n*] π-electron annulenes **119** (*n* = 2) and **121** (*n* = 2). These planar tetramers are amongst the most stable of reported [24]annulenes; ¹⁶¹ there is a great similarity between the C–C=C bond angles in the monomer units and in the tetramer, and angle strain is negligible. In addition, in such large rings, the destabilisation due to transannular interactions is relatively small. The pentamers **119** (*n* = 3) and **121** (*n* = 3) are very weakly diatropic although they are less planar due to conformational flexibility. It has been suggested that the planarity of the pentamers could perhaps be increased by using cyclopropene monomer units in place of cyclobutene.

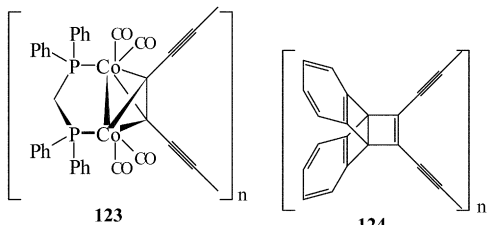
Other dehydroannulenes have been prepared which are stabilised by annelated groups such as cobalt complexes **123**, propellane derivatives obtained from Diels–Alder reactions **124**, **125**, bicyclo[2.2.2]octene frameworks **126**, heterocycles **127**, metallocyclobutadieno derivatives **128** and ferrocene analogues, and bicyclo[2.2.1]heptane frameworks **129**. ^{162–165} The NMR signals from the bridging methylene group in the dehydroannulenes prepared from **129** have provided valuable information about ring currents in the annulene rings; the trimer is diatropic and the tetramer is paratropic. ¹⁶⁵

It is thought possible that these compounds might prove to be precursors to fullerenes and other novel carbon allotropes and might provide interesting metal coordination chemistry. For example, one such compound, nonadehydro[18]annulene or cyclo[18]carbon **122**, whose possible preparation from annelated dehydro[18]annulenes has already been mentioned, has been proposed as a constituent of molecular clouds and to be present in the hearts of dying stars. Compound **122** is expected to provide unique chemistry since it has two con-



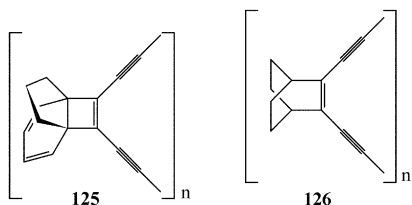


122



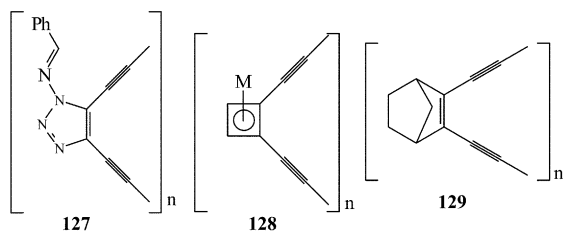
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124



125

126



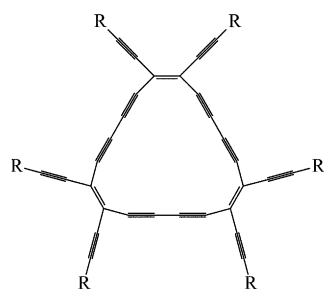
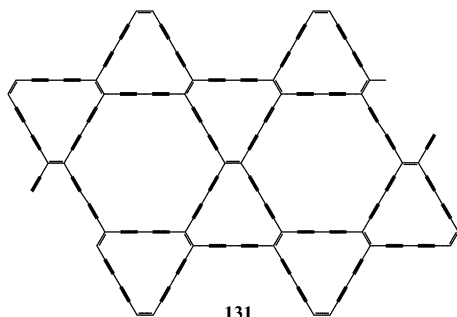
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128

129

jugated π -systems perpendicular to each other but it has so far eluded synthetic isolation.^{166,167} It may also display novel coordination chemistry with larger metal atoms such as lanthanides and actinides.

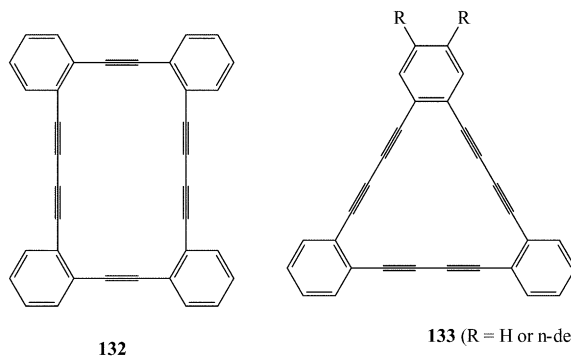
Compounds **130** are of interest since they are potential precursors to a non-graphite all-carbon sheet **131**. They are stable yellow solids which support diatropic ring currents.¹⁴⁴ An analogous dehydro[12]annulene **100** has been prepared and is discussed in Section 5.2.

130 (R = SiPr₃ or SiMe₃)

131

5.6 Benzodehydroannulenes

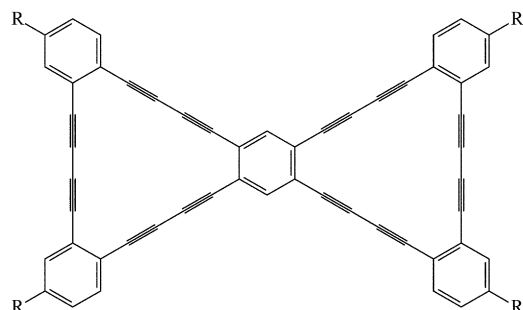
A tribenzodehydro[12]annulene **102** has been mentioned in Section 5.2. Examples of larger ring analogues include **132** and **133**.^{168,169} The tetrabenzohexadehydro[20]annulene **132** decomposes *in vacuo* at 243 °C; it explodes violently, emitting a flash of orange light and forms a mixture of methane, hydrogen and a black powder which is essentially carbon, consisting of amorphous carbon, graphite and ordered layers of tube-and onion-type structures.¹⁶⁸ Other analogues with different length polyene chains linking three or more benzene rings have been prepared. Many are remarkably stable but many undergo exothermic decomposition prior to melting.^{170–173}



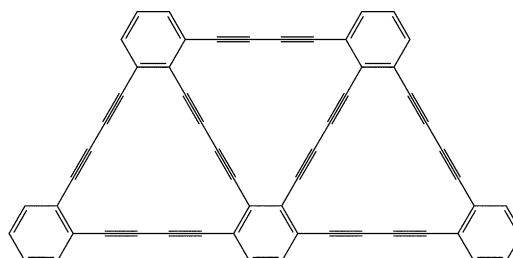
132

133 (R = H or n-decyl)

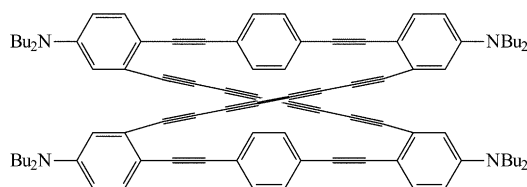
The benzodehydroannuleno compound **134** has been prepared. It has a diameter of nearly 2.2 Å and represented the first example of a subunit of a so-called graphdiyne structure **135**, a diacetylenic carbon allotrope made up from sp and sp^2 hybridised carbon atoms.¹⁶⁹ Spectroscopic evidence suggests that the dehydro[18]annulene cores of **133** and **134** retain their diatropies.



134 (R = t-butyl or n-decyl)



135

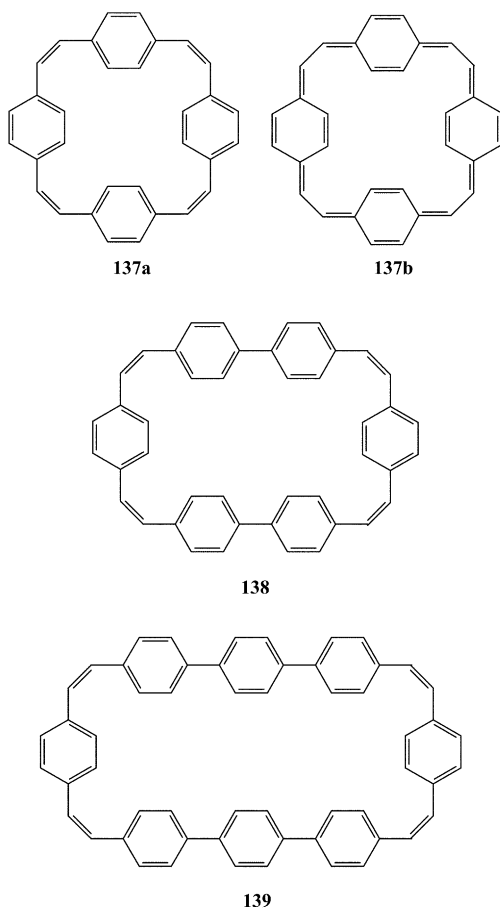


136

Another interesting large dehydroannulene is **136**, which is an example of a twisted macrocycle.¹⁷⁴ As is the case with many of the structures in this section, it was made by *in situ* desilylation and oxidative dimerisation of a TIPS-protected diyne.

6 Annulenes with 1,4-etheno bridges; cyclophanes, ring currents in charged annulenes

The cyclophanes **137**, **138** and **139** might be classified as relatives of benzoannulenes since they are a family of molecules with large conjugated peripheral cyclic systems. They can be regarded either as large annulenes bridged by $-\text{CH}=\text{CH}-$ units or as a series of benzene rings linked *via* their *p*-positions by ethylene bonds. These molecules are rigid, well defined and planar up to very large ring size.



The neutral cyclophanes which formally have 24, 32 and 40 π -electrons, respectively, in their peripheries are best regarded as benzene derivatives with no significant contribution from the large π -conjugated perimeters. Thus structure **137b** makes little contribution to the overall bonding and the molecule is adequately represented by **137a**.¹⁷⁵

As has been mentioned earlier in Sections 3–5, addition of two electrons to an annulene or a dehydroannulene provides a dianion in which the tropicity is reversed; a $[4n+2]$ annulene forms a paratropic anion while a $[4n]$ annulene forms a diatropic anion.^{78,109,135} Furthermore, the tropicity of the anions appear to be greater than that of neutral annulenes having the same number of π -electrons. Similarly annulenes have been oxidised to dications with reversed tropicity. Cyclophane-type annulenes have proved to be ideal substrates for studying the conversion of annulenes into anions.¹⁷⁵

With compounds **137–139** rapid rotation of the benzene rings leads to an averaging of the NMR signals from the inner and outer protons at temperatures above -60°C . Their structure is a balance between stabilisation gained from extended

delocalisation of π -electrons and steric interactions causing deviation from planarity. Thus in compound **137** the ethylene bridges are coplanar and the benzene rings are tilted.

The highest stage of reduction achieved when they are reduced by potassium or lithium is related to the annulene ring size; compound **137** can be reduced by potassium to a tetra-anion, compound **138** to a penta-anion and **139** to a hexa-anion. Each of these cyclophane–annulenes, which could formally be paratropic with 24, 32 and 40 π -electrons, respectively, can be reduced to dianions whose NMR spectra show, from the chemical shifts of the outer protons, that they are diatropic. Compound **139** could be reduced by potassium to give in turn a diatropic dianion, a paratropic tetra-anion and, eventually, a diatropic hexa-anion. This provides the opportunity to observe two different diamagnetic anions derived from the same carbon network. The outer proton chemical shifts of the hexa-anion are similar to those in the dianion, but there is a difference between the chemical shifts of the inner protons from *ca.* $\delta_{\text{H}} -2$ ppm for the dianion to *ca.* $\delta_{\text{H}} -6$ ppm for the hexa-anion. This is associated with the magnetic field induced in the cavity of the annulenes. In each of the three anions the difference in tropicity is very evident from the proton NMR spectra.

It is interesting to note that the anions derived from **138** and **139** sustain noteworthy ring currents whereas in neutral annulenes there appears to be a limiting size at 26 π -electrons beyond which the rings become atropic.

The ring currents in anions formed by reduction with potassium are amplified in comparison to the ring currents observed in the corresponding lithium salts. This has been ascribed to the greater distortion of the π -electron cloud by the smaller and more polarising lithium cation.

The smaller cyclophanes such as **137** and **138** have an average molecular plane formed by the nearly coplanar olefinic portions and the arene rings are to a large extent rotated out of this plane. In some cases the central cavities may be large enough to allow host–guest inclusion complexes with small substrates. Because of the rigidity of the framework such a cavity is small and would not collapse in the absence of the guest molecule. Hence substituted cyclophanes could act as organic matrices for inclusion of a defined guest molecule. The influence of the unique magnetic behaviour of the charged annulenes on a guest molecule could lead to interesting characteristics.¹⁷⁵

7 Coda

As mentioned in Section 2 of this review, the initial flood of interest in annulenes waned somewhat after questions about their more fundamental preparation and properties had been addressed. Nevertheless, there have been few improvements to the original, inefficient synthetic routes in the intervening years and many structural and spectroscopic questions remain unanswered. In more recent years their study has aroused new interest in them and also notably in anions derived from them and their possible applications. There has also been interest in heterocyclic analogues but this has not been dealt with in the present review.

In addition to the possible contributions of annulene chemistry to both practice and theory, they are also attracting attention in other areas of chemistry such as novel all-carbon allotropes with unique properties, organic conductors, high temperature semiconductors, liquid crystals and their ability to form novel metal complexes. This is a situation which may perhaps be best summed up by a quotation from one of the masters of annulene chemistry:

“With his compounds being ‘alive’ in their relevance, the annulene chemist is somewhat like the husband, who, only with the passing years, begins to appreciate the beauty and virtue of his neglected wife.”¹⁰⁹

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