The Fulvalenes

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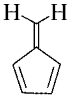
The fulvalenes are the class of hydrocarbons obtained by formally cross-conjugating two rings through a common exocyclic double bond. Although the first report of such a compound dates to 1915, study of the series began in earnest only in the 1950s, and even today many of the unsubstituted parent hydrocarbons remain unknown. The following report, the first to specifically address this class of molecules, summarises the information available from research published to the end of 2004 and offers some suggestions for future study. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

The term *fulvene* was coined by Thiele for (methylidene)cyclopentadiene (**1**), in his 1900 paper[1] *Ketone Reactions Related to Cyclopentadiene* in which he describes the first derivatives of the ring system. Because these derivatives were yellow coloured the term "fulvus" (dull yellow, tawny) was applied to them. When derivatives of the three-membered analogue **2** appeared in the 1960s Bergman and Agranat suggested that the name for this class of compounds be *triafulvene* thereby indicating the three-membered ring.[2] However, some 15 years earlier in 1949, when describing the thermodynamic properties of a range of hydrocarbons calculated by Hückel Molecular Orbital methods, R. D. Brown[3] advanced the notion that the molecule formed by cross conjugating two cyclopentadiene rings through a common exocyclic double bond, namely **5**, be termed *fulvalene.* This clearly linked **5** to its monocyclic congener **1**.



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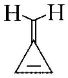

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The term fulvalene was applied subsequently to the entire family of compounds **3**–**13**, etc., in which the ring sizes are described by prefixes in analogy to the use of triafulvene for **2**. The nomenclature has been retained, at least trivially, such that **3** becomes triafulvalene, **5**, pentafulvalene, and **8**, heptanonafulvalene. In this last case with dissimilar ring sizes a prefix is applied for each ring with that of the smaller ring placed first; numbering commences at the first double bond of the larger ring. Systematically IUPAC have the molecules as cycloalkene-1-ylidene derivatives of the larger cross-conjugated ring; **4** is thus 5-(cyclopropene-1-ylidene)-5*H*-cyclopenta-1,3-diene – triapentafulvalene, but it adopts another trivial name, namely calicene! The larger **8** becomes 9-(cyclohepta-2,4,6-triene-1-ylidene)-9*H*-cyclonona-1,3,5,7-tetraene.

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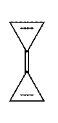
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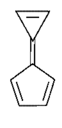
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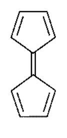
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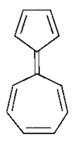
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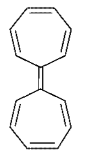
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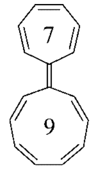
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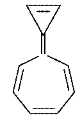
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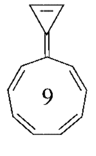
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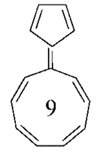
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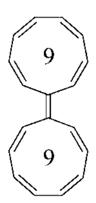
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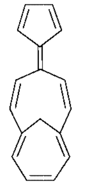
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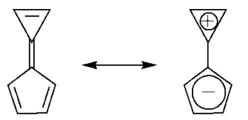
The field of fulvalene hydrocarbon chemistry has not been the subject of an independent review previously, rather it has be included within reviews[4,5] and book sections[6,7] on the fulvenes. Our own reviews on cycloproparene chemistry have included the (alkylidene)cycloproparenes that also are regarded as benz-annulated fulvalenes.[8] More recent compilations encompassing fulvalenes have provided for specific sub-classification with works on azafulvalenes,[9] azathiafulvalenes,[10] fulvalene ylides,[11] organometallic derivatives[12] and (especially) on the use of tetrathiafulvalenes in material science endeavours,[13] with the publication of a thematic issue of *Chemical Reviews* on *Molecular Conductors*.[14] These are not discussed further here.

From a historical perspective, parent **5** was not formally characterised until the 1960s although (fluorenylidene)cyclopentadiene, a dibenzo derivative, was prepared by Courtot as early as 1915 from his description of the dark red colour[15] that was subsequently shown to be due to **18** by Prinzbach (Scheme 2).[16] Parent **5** has been ascribed to von Doering in two reports (1958[17] and 1960[18]) that do not appear to carry experimental detail, although his lecture to the 1958 Kekulé symposium[19] provides some details. However, the 1956 PhD Thesis of W. W. Spooncer (University of Washington, Seattle, USA) lays claim to fulvalene in the title *Synthesis and properties of trimethylammoniocyclopentadienylide - synthesis of fulvalene* though generally this has not been cited.[20] Despite these works, fulvalene studies became common only from the early 1950s even though there were earlier claims.[5,21]

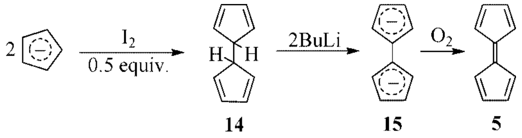
The appearance of derivatives of pentaheptafulvalene[22] (**6**) and triapentafulvalene[23] (**4**) date from 1952 and 1965, respectively. Heptafulvalene **7** appeared between these dates as an almost black crystalline compound of limited stability,[17,18,24] with triahepta-**9**,[25] trianona-**10**[26] pentanona-**11**,[27] and nona-**12** fulvalenes,[28] emerging over a 16 year period from the early 1970s; attempts to prepare heptanonafulvalene[29] (**8**) give valence bond isomers, while the triafulvalenes, cf. **3**, remained unknown until our very recent evidence for a reactive benzannulated derivative.[30] Novel fiddle-shaped molecules with the bridged pentaundecapenta-1,3,5,7,9-ene structure **13** appeared from the Prinzbach group[31] in 1968, and now fulvalenes comprised of even larger rings are known[32,33] and discussed below.

Many of the early studies of the fulvalenes encompassed calculations on molecules unknown at the time. These provided rudimentary information on molecular geometry, the nature of cross-conjugated π systems, and the presence or absence or aromaticity. While there are far too many studies to cite here it is appropriate to recall the initial studies of R. D. Brown,[3,34] the 1951 diamagnetic anisotropies that included fulvalene,[35] its localisation energy and reactivity from Fukui,[36] the ground and excited state electronic structure and torsional potentials from Hoffmann,[37] and the SCF MO studies of Dewar;[38–40] ground state electronic properties were studied by SCF-CI LCAO-πMO method as early as 1968,[41] and resonance energies and stabilities came from Hess and Schaad[42] in 1971. These provided much valuable information but it will be realised that recent ab initio computations provide the most reliable information.[43–45] What can be said here is that the early results predicted nonpolar, bond alternating structures for the symmetrical non-alternant $(4n + 2)$ π electron hydrocarbons such as **5**, and **7**. The unsymmetrical homologues **4**, **6** and **8**, however, were expected to show some polarisation from the generation of two separate $(4n + 2)$ non-benzenoid aromatic moieties as shown by the polar cyclopropenyl-cyclopentadienyl structure **4b** of triapentafulvalene (calicene). The most favourable molecular symmetries and geometries received attention from the early 1970s from which the magnetic susceptibilities and electronic spectra were computed[46] and the magnitude of the dipole moments calculated.[47] The ion-radicals of fulvalene systems were predicted to undergo a molecular symmetry reduction from D_{2h} to C_{2v} on the basis of the 2nd-order Jahn–Teller theorem.[48] Predictions on the sites of reactivity followed,[49] as did the inclusion of fulvalenes in graph theoretical treatments[50] that continue to be assessed,[51,52] and in particular in the use of relative hardness as a good index for identifying aromatic, nonaromatic and antiaromatic character.[53] Nonempirical calculations for the vertical ionisation potentials of **3**–**6** using the outer valence Green function (OVGF) approach that incorporates the main portion of electron correlation and reorganisation effects, have provided an overall interpretation of the salient features in the photoelectron spectra.[54]

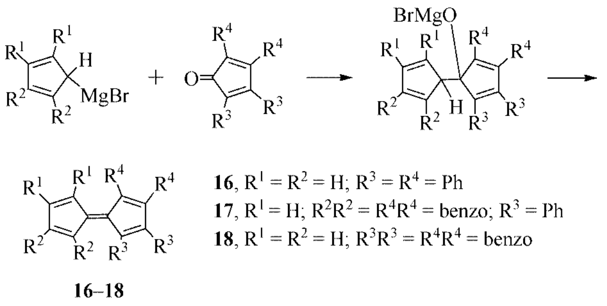

4a **4b**

Pentafulvalenes (Fulvalenes)

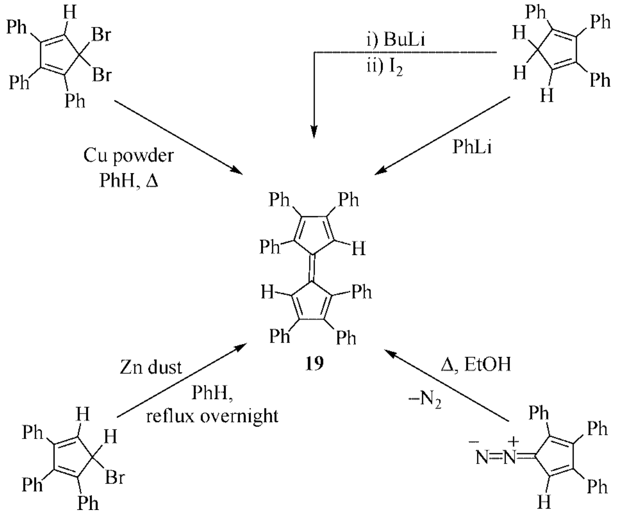
As noted earlier, **5** is ascribed to von Doering[17,19] with the reaction sequence (Scheme 1) abstracted from his 1958 lecture.[19] Coupling of the cyclopentadienyl anion gives dihydrofulvalene (**14**) that is double deprotonated (BuLi) to dianion **15**, and subsequently oxidised (O_2). The principles embodied in this sequence are precisely those that gave the first pentafulvalenes[55–57] and, upon refinement,[58,59] have provided for the less common ring systems, **8** and **12** (see below). The early work, so nicely summarised by Bergmann,[5] is not repeated here save to note that deprotonation of cyclopentadiene by sodium ethoxide in the presence of a stabilised cyclopentadienone does not always work,[60] but that exposure to air of solutions of cyclopentadienyl anion show the characteristic UV absorptions of **5**.[61] Grignard reaction of a cyclopentadienyl bromide with a cyclopentadienone was often used for synthesis (Scheme 2)[55] and upon modification provided the fluorenylidene **18** as brilliant red crystals (λ_{max} 370 nm) stable at –20 °C for a considerable time;[16] Courtot's failure to isolate **18** stems from its facile [4 + 2] Diels–Alder dimerisation of the cyclopentadienyl moiety. The coupling of a *gem*-dibromocyclopentadiene with Cu,[21] shown for **19**, was also used. This last compound, prepared by Pauson and Williams in five different ways (Scheme 3)[57] also demonstrates that steric crowding about the formally planar interconnecting double bond demands that the *E* isomer be formed.



Scheme 1.

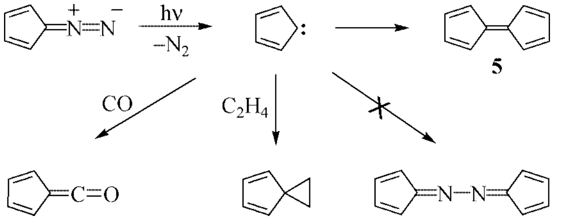


Scheme 2.



Scheme 3.

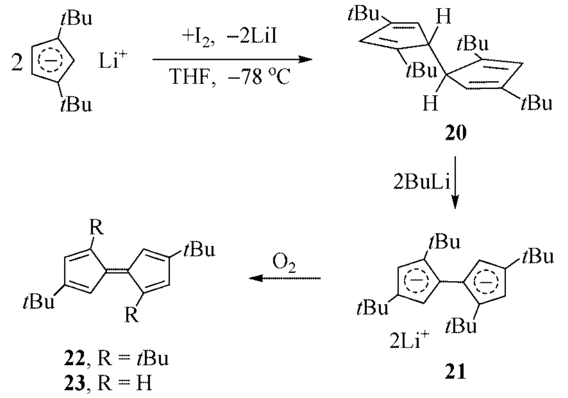
Pauson and Williams also demonstrated thermal nitrogen loss from a diazoalkane as a preparative method for **5**.[57] The photolysis of diazocyclopentadiene in low temperature matrices (20 and 77 K) was one of a series of diazo compounds examined by DeMoore and co-workers in 1959[62] who confirmed the formation of **5** from UV studies of the product. Their matrix sample was compared to one of authentic **5** supplied by Doering and showed absorption maxima near 295 and 310 nm in the matrix; more recent studies give the maxima at 287, 299, 313 and 416 nm.[58] Subsequently, Baird et al. demonstrated that photolysis of diazocyclopentadiene proceeds via cyclopentadienylidene that can be diverted to ketene in the presence of CO (Scheme 4).[63,64] The loss of nitrogen is irreversible and the detailed study confirmed that **5** does not arise from carbene addition to unchanged diazo compound; a UV band was recorded at 296 nm.[63] Subsequently, cyclopentadienylidene was held in an Ar/N$_2$O matrix without the carbene dimerizing[65] and its reaction with ethene studied.[66] Gas phase studies of the cyclopentadienyl anion radical formed from diazocyclopentadiene have shown that it too provides **5**, this time by coupling with unchanged starting material and subsequent loss of nitrogen.[67] Bulk oxidation of cyclopentadiene in liquid ammonia[68] also leads to **5**.



Scheme 4.

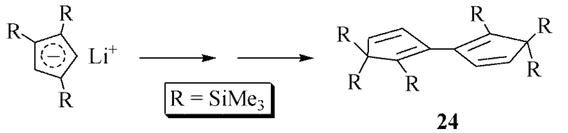
The first stable alkyl-substituted pentafulvalenes were provided by Hafner and his group in 1982 using the bulk of the *tert*-butyl group to provide steric protection to the fulvalene core.[69] Thus, reaction of the 1,3-di-*tert*-butylcyclopentadienyl anion with iodine provides a tautomeric mixture of coupled products (illustrated by **20**), which with BuLi afford dianion **21** that is oxidised to **22** in 65% yield upon treatment with oxygen (Scheme 5); an *E*/*Z* mixture of the 1,1′-di-*tert*-butyl compounds is similarly obtained from which the *E* isomer **23** can be crystallised in 22% yield. Both **22** and **23** are air stable, the latter reacting with oxygen only after several days; they are deep red crystalline solids, **22** being stable in boiling xylene.

The coupling of cyclopentadienyl anions is not always as straightforward as might be expected. In the case of the 1,2,4-tris(trimethylsilyl) anion[70] stoichiometric FeCl$_3$ gives rise to an iron(III) complex that on treatment with FeCl$_2$ yields the non-symmetrically coupled product **24**; the compound appears not to have been desilylated to give a dianion for pentafulvalene synthesis. It is the effective oxidative coupling of appropriate anions that has allowed fulvalene chemistry to develop and many of the advances are due to the elegant studies of Neuenschwander and his former group in Bern. In the course of experiments directed



Scheme 5.

towards nonafulvenes these workers discovered that oxidative coupling of the cyclononatetraenyl anion with $AgBF_4$ provided 9,9′-dihydrononafulvalene almost quantitatively.[59] The reaction proves to be quite general and Cu^{II} is often an alternative to Ag^{I}. Thus the pathway of Scheme 1 can be markedly improved by using $CuCl_2$ in THF at –30 °C for the cyclopentadienide coupling (dihydrofulvalene **14** is formed in 84% yield)[58,71] and, after essentially quantitative deprotonation to **15** (BuLi), a second treatment with $CuCl_2$ and concentration provides a red solution (ca. 0.3 M) of spectroscopically pure **5**.



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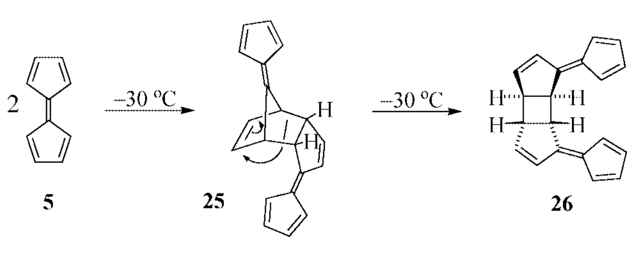
Pentafulvalene (**5**) is a very reactive compound – markedly more so than pentafulvene – dimerizing in concentrated solution to Diels–Alder adduct **25** that is itself unstable and rearranges to the formal [2 + 2] product **26** at the same temperature (Scheme 6).[58] The ability of the cyclopentadiene moieties of a pentafulvalene to participate in Diels–Alder additions with dienophiles is common as the NMR spectra of **5** show it to be more "ene"-like than fulvene.[59,72]



Scheme 6.

The coupling of two five-membered rings, as in **5**, demands coplanarity and a nonpolar molecule. The most recent calculations[43,44] on **5** at the HF/6-311G(3d,2p) and BLYP/6-311++G(3d,2p) levels of theory[45] have such planarity and bond alternation as expected (Figure 1). Furthermore, the recent all electron mapping of ring currents by Fowler and Jenneskens and their groups[73] shows **5** and its 2,3-benzo derivative with the expected pattern of paratropic ring currents for the σ electrons. Both show π currents relatively localised on the formal double bonds and following the fulvalene-diene Kekulé structure. In derivatives that could impart steric strain the *E* isomer is favoured over the *Z* isomer. This was demonstrated through the synthesis of **17** and is further illustrated by **27**–**29**.[74] Coplanarity has to be sacrificed in cases where spatial conflict cannot be avoided, as in the dark blue octabromopentafulvalene[75] and its octachloro analogue. This latter molecule distorts by lengthening the double bond to 136.5 pm and twisting to a dihedral angle of 37° between the planes containing the rings; the chlorine atoms displaced from the planes of the five-membered rings.[76] Such distortions, first addressed on a theoretical basis in 1972,[77] result in a degree of twisting dependent upon the level of congestion as one might expect. In the tetrabenzopentafulvenes, **30** has a twist of 33° from the *o*/*o*' H interactions, whereas in the "bent back" homologue **31** this is reduced to 26°.[78] This last compound resists oxidative cyclodehydrogenation with tetrachloro-1,2-benzoquinone to the C_{30} bowl-shaped aromatic by adding the quinone across the linking C5–C5′ double bond in a hetero-Diels–Alder manner.[78]

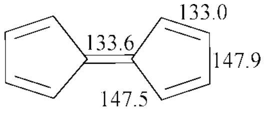


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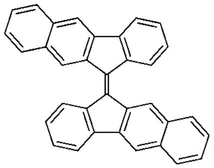
Figure 1. Calculated bond lengths (Ångstrom units) of pentafulvalene; see ref.[45].



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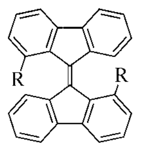
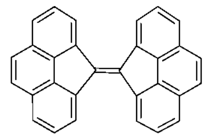


28, R = Cl
29, R = Me
30, R = H



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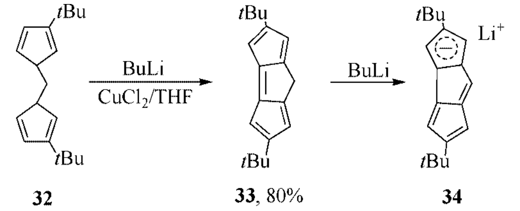
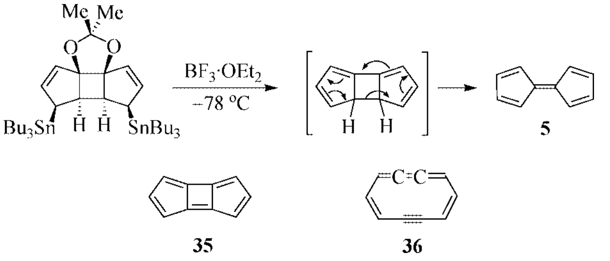
Constraints within the fulvalene moiety that retain an essentially planar molecule arise in tricycle **33**, synthesised by Hafner and Thiele[79] from **32** (Scheme 7). The molecule is bent, but not twisted, and deprotonation yields the novel 12π conjugated anion **34**. Recent attempts to synthesise the lower homologue **35**, expected to be planar with D_{2h} symmetry and some 20 kJ·mol^{-1} higher in energy than its ring-opened 1,5-didehydro[10]annulene isomer **36**, have yet to succeed;[80] attempted formation (Scheme 8) provides pentafulvalene **5** likely via the dihydro derivative. Alternative routes employing (cyclobutadiene)cobalt complexes also failed.

Other pentafulavalenes that have been addressed are "exploded" derivatives in which the two five-membered rings of **5** are separated by two or more conjugated double bonds,[69,81] through cumulene linkages as discussed by Bergmann,[5] or by interposing a spacer group such as a paraquinodimethane. In this last case it is interesting to

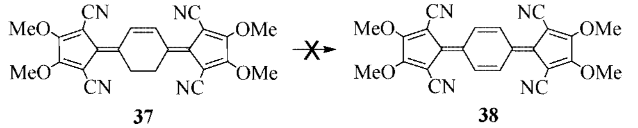


Scheme 7.

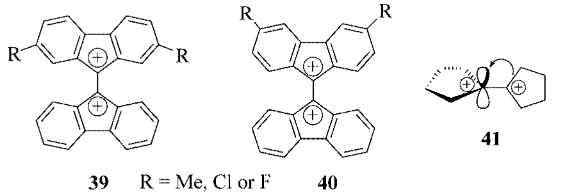


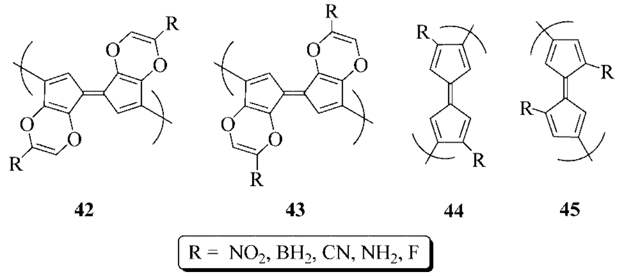
Scheme 8.

note that "spaced" cross-conjugated **38** does not arise from oxidation of the cyclohexendiylidene **37** despite use of a variety of conditions.[82] Such compounds are beyond the scope of the present discussion.



The electronic structures and excited states of fulvalenes in general and pentafulvalenes in particular, have been the subject of numerous theoretical investigations.[83,84] Predictions[85] that the first excited singlet states of penta- and nonafulvalene belong to the same point group as the ground states of the corresponding cations created interest in the generation of the antiaromatic pentafulvalene cation and dication. Recent studies have been concerned primarily with establishing adequate criteria for aromaticity and the more difficult antiaromaticity. The cation is expected to have a distorted C_{2v} symmetry with interelectronic repulsive and nuclear-electron attractive terms due to electrons contributing to its stability.[86,87] Characteristic electronic properties inherent in the radical, and the charge and unpaired spin density distributions in the distorted structure have been predicted. The triplet state of the dication should be markedly more stable than a bispyramidal D_{4h} structure that lies some 90 kJ·mol^{-1} above the singlet D_{2h} structure.[88] Quite recently SbF_5 oxidation of 2,7- and 3,6-disubstituted tetrabenzopentafulvalenes was shown to give dications **39** and **40** that behave like independent antiaromatic fluorenyl cations connected by a single bond. In both systems the fluorenyl cations exhibit paratropic shifts and nucleus independent chemical shifts (NICS) characteristic of antiaromatic species. Comparison between **39** and **40** reveals that the antiaromaticity of the ring system varies substantially with substituent location, possibly due to changes in the delocalisation of charge in the system. Substituents in the 3,6-position decrease the antiaromaticity because of the increase in the benzylic resonance compared to 2,7-substituents.[89] The two fluorenyl rings are held perpendicular and can interact either through the charge on one ring system influencing the degree to which charge is delocalised in the other, or through σ to p donation as depicted by **41** (benzenoid rings omitted for clarity), or both. The most recent studies[90] conclude that the dication from **30** is *more* antiaromatic than the fluorenyl cation itself. In addition, the singlet excited state has been shown to be lower in energy than the triplet for these species. The trication radical of pentafulvalene has also received attention[91] as have double layered mono- and trications in a fulvalenophane structure.[92]



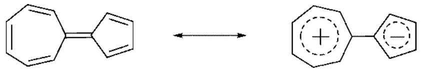


By comparison to the cations, generation of the pentafulvalene anion radical is uncomplicated by photochemical oxidation of cyclopentadienyllithium or from dilithium fulvalenediide with O_2, or by reduction of **5** either electrolytically or with sodium. The ESR spectrum shows *a*(H1/H1′, H4/H4′) 1.55, *a*(H2/H2′, H3/H3′) 3.70, *a*(^{13}C5/^{13}C5′) 2.90 *a*(^{13}C1/^{13}C1′, ^{13}C4/^{13}C4′) 1.40, and *a*(^{13}C2/^{13}C2′,^{13}C3/^{13}C3′) 2.15 G with the assignments for *a*(H) based on the HMO and those for *a*(^{13}C) on the Yonezawa-Kawamura-Kato relationship.[93]

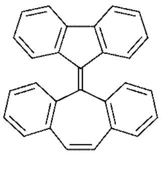
The possible use of pentafulvalenes and polypentafulvalenes as environmentally stable semiconductive or conductive polymers has been examined[94] via theoretical studies of substituent effects on the stabilisation energies and nucleus independent chemical shifts of **42**–**45**. The polypentafulvalene **44** (R = H) is predicted to be semiconductive with a HOMO–LUMO gap of 1.13 eV and electron donating or withdrawing groups further decrease the gap depending upon the substitution site. Finally, it should be noted that pentafulvalenes, including **22**,[95] are used as ligands in the formation of organometallic complexes.[96]

Pentaheptafulvalenes (Sesquifulvalenes)

Pentaheptafulvalenes were expected to derive considerable stabilisation from charge separation that gives a 6π cycloheptatrienyl cation and a 6π cyclopentadienyl anion as depicted by **6b**. However, early calculations[97–99] showed that the polar form makes little contribution to the ground state as bond length alternation was comparable to that in open chain polyenes – bond alternation parameter values close to 0.55 were assigned. The same conclusion was reached by others as computational chemistry became more common and the excited state was recognised as being more polar but with the direction reversed.[100,101] For **6** (at least) the energy needed for the seven-membered ring to attain the planarity of a cation exceeds that gained by charge separation and formation of independent aromatic rings.[102] The contribution from the polar forms to the ground state is now calculated as about 23%.[44,103]



6a **6b**



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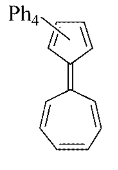

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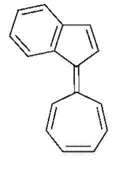
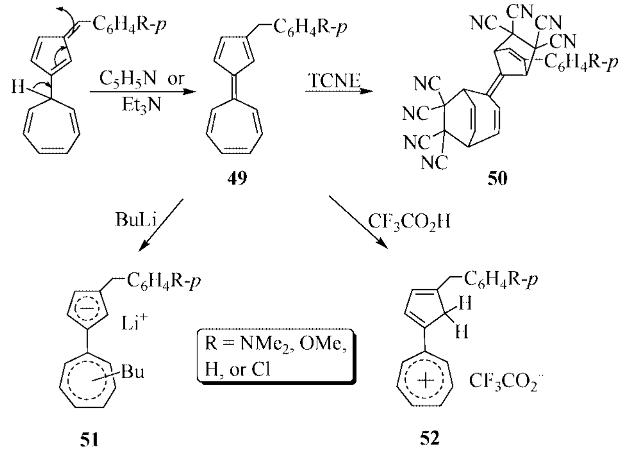
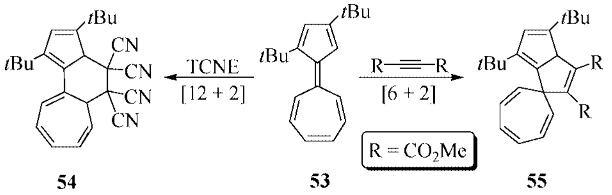


48

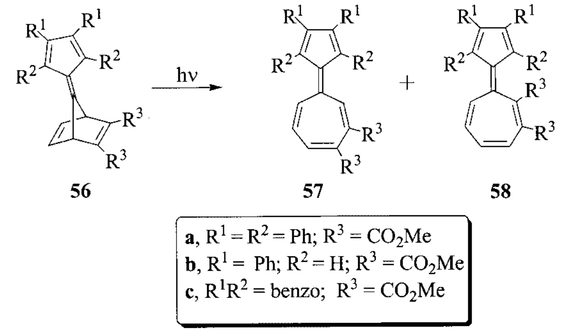
As early as 1951 the then *hypothetical* sesquifulvalenes were expected to be relatively stable[104] and the tetrabenzo derivative **46** appeared a year later from condensation of lithium 9-fluorenide with suberone; it has a dipole moment of 0.83 D.[22] This was followed by the tetraphenyl derivative **47** (a green solid that is red in solution)[105] and the benzo derivative **48** (from reactions of bromocycloheptatriene with the corresponding cyclopentadienyl anion and subsequent oxidation with DDQ).[106] Shortly afterwards a range of benzyl[107,108] derivatives **49** was obtained from base-induced (C_6H_5N or Et_3N) prototropic shift in 6-arylfulvenes as shown in Scheme 9. These crystalline, but thermally labile and air-sensitive, coloured compounds readily add bromine, rapidly hydrogenate under very mild conditions, and react instantaneously with TCNE to give bis adducts **50** from addition across diene components of *both* the five- and seven-membered rings. The polar character of **49** is demonstrated by formation of a cyclopentadienyl salt **51** with BuLi and a cycloheptatrienyl salt **52** from addition of CF_3CO_2H in such a way that conjugation is maximised. In light of this, one can expect electron withdrawing substituents in the five-membered ring and electron donating substituents in the seven-membered ring to enhance the polar nature of the compounds. Reaction of tropylium bromide with lithium 1,3-di-*tert*-butylcyclopentadienide and subsequent reactions with trityl tetrafluoroborate and then triethylamine provides sesquifulvalene **53** that is stable in the dark at 0 °C for a period of days;[109] it adds TCNE in a [12 + 2] fashion to yield **54**, while DMAD provides the [6 + 2] product **55** (Scheme 10). A less common synthesis involves photoisomerisation of the 7-(cyclopentadienylidene)-norbornadienes **56**, themselves formed from Diels–Alder addition to the requisite pentafulvalene. Suprafacial [1,3] shifts from C1 to C3 and C5 and norcaradiene ring opening account for the isomeric products that are formed in solvent dependent ratios (Scheme 11).[110] In acetone the **57c**:**58c** ratio is 90:10, whereas in ether the regioselectivity is almost completely reversed at 15:85. While furan-fused derivatives **59** and **60** are also known,[111] it was ease of preparation that had a range of isoelectronic heterocyclic analogues such as **61** described in the 1960s,[112] but mesoionic analogues, e. g. **62**, did not appear until much later.[113]



Scheme 9.

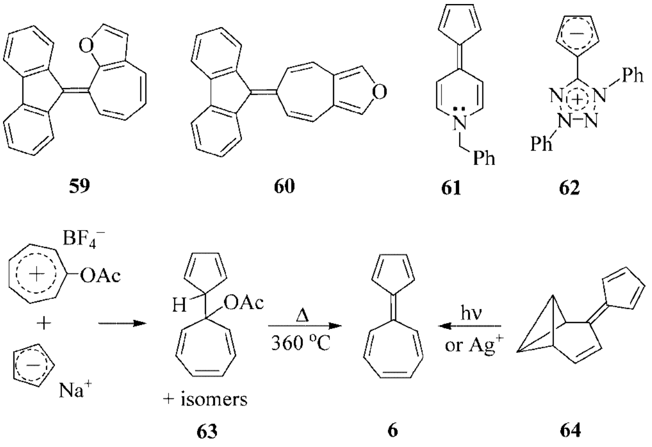


Scheme 10.

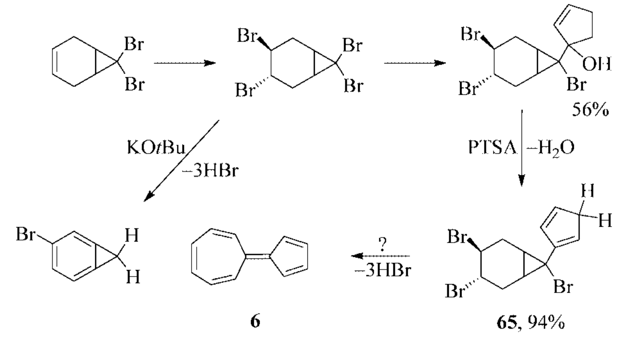


Scheme 11.

Attempted synthesis of parent **6** in 1961 from coupling tropylium bromide with sodium cyclopentadienide and subsequent oxidation gave a red solution of **6** that was too unstable to be isolated at the time (Scheme 12).[105] A change to thallium cyclopentadienide and tropylium tetrafluoroborate provided a solution of **6** that could be held at –40 °C and trapped by TCNE as the [12 + 2] adduct (cf. **54)** that was then hydrolysed and cyclised to lactam.[114] At about the same time Neuenschwander and his students[115,116] obtained **6** in 75–85% yield from gas phase pyrolysis of **63** at 360 °C and provided an analysis of the NMR spectroscopic data.[102] Shortly thereafter Prinzbach reported almost quantitative isomerisation of tricyclic fulvene **64** into **6** by Ag^I catalysis (90%) and upon photolysis (97%),[117] while Hoffmann et al. demonstrated that the norbornadiene **56d** ($R^1 = R^2 = R^3 = H$) also gave **6** among a range of products from thermolysis at 500 °C.[118] Much more recently, Li and Neuenschwander[119] have provided a potentially new general pathway to **6** (and heptafulvene and heptafulvalene **7**) that currently terminates at **65** (Scheme 13). A detailed experimental examination of the dehydrobromination of **65** is still needed to complete the sequence for which it must be noted that trisdehydrobromination of the precursor yields 3-bromocyclopropabenzene (Scheme 13).[120]



Scheme 12.



Scheme 13.

As with pentafulvalene, the NMR spectra of **6** show that the molecule is essentially olefinic in nature.[102,116] However, the chemical shifts do reflect the predicted small contribution from the polar form.[44,103] The longest wavelength UV maximum is at 393 nm and the EI mass spectrum displays the molecular ion as base peak.[116]

The molecular structure, determined by high-level calculation, shows a very slightly nonplanar C_s arrangement of the five- and seven-membered rings,[44] and a substantially reduced resonance energy compatible with the olefinic nature is reflected in kinetic instability in the sense of bond resonance energies.[121,122] The salient features of the PE spectrum of **6** are rationalised by nonempirical calculations using the outer valence Green function approach,[54] with the small aromatic character of the ground state transformed into antiaromaticity in the lowest excited singlet as indicated by quantum chemical methods.[123] However, it is the attention given to the singlet biradical and twisted states of the pentaheptafulvalenes and their potential non-linear properties that have attracted much recent attention. The first hyperpolarizibility of conjugated organic molecules is markedly increased by the presence of donor and acceptor groups at opposite end of the conjugation path. Such molecules find increased application in non-linear optics as second harmonic generators and electro-optic modulators. In this context, organometallic complexes of the sesquifulvalenes exhibit unusually large nonlinear optical properties and their β values are among the largest ever measured for organometallic NLO chromophores;[124] this is possibly caused by *sudden polarisation* where there is a large dipole moment difference between the ground and excited states. To assess these features twisting about the C7–C8 interconnecting double bond has been addressed for **6** as part of a general study of the fulvalenes,[125] specifically for **6**,[126] and on π extended derivatives[127] that have been known for many years.[128] The β of the twisted form originates from a single low lying excited state that is characterised by transfer of one electron from the five- to the seven-membered ring – a twisted internal charge transfer state. The enhancement due to twisting supports the sudden polarisation phenomenon and results in β values that approach those of push-pull polyenes of similar size. The incorporation of heteroatoms into the molecular framework and their position influence the NLO properties.[129]

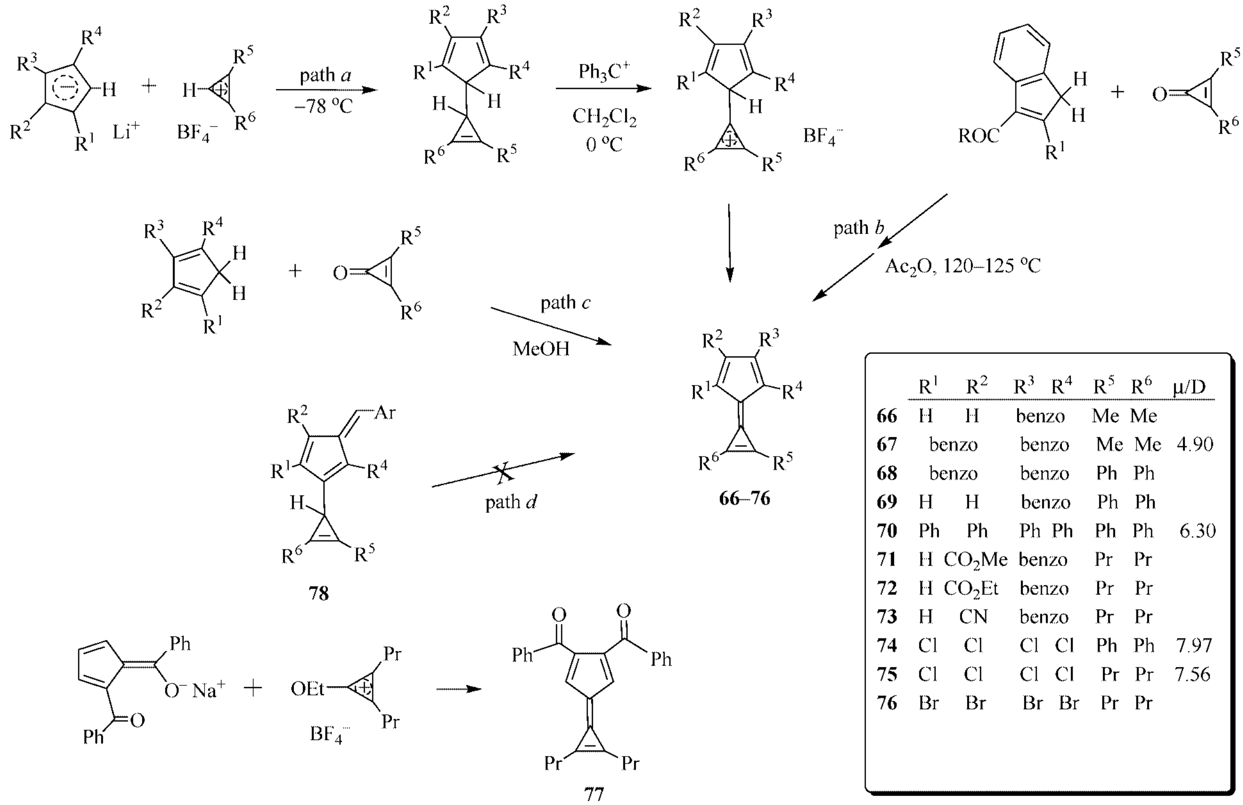
Finally, compound **6** has been described as a chemical chameleon. Ottosson and his group[103] have provided a sound theoretical basis for fulvenes in their T_1 state to be polarised in the opposite direction to S_0. For the [*m*,*n*]fulvalenes, and specifically **6**, this occurs in the lowest quintet state (Q_1). A 28% contribution to the π population of Q_1 and 24% to that of S_0 for **6** was obtained thus showing comparable, but opposing influences to the dipolar resonance structures. There must exist, therefore, the possibility for the design of appropriately functionalised sesquifulvalenes as novel compounds for molecular magnets.

A simple criterion for establishing the extent of π delocalisation in five-membered ring of the various pentafulvalenes has been described by Neuenschwander.[130] Thus, correlations of NMR spectroscopic data for the range of [*5.n*]-fulvalenes **4**, **5**, **6**, **11**, and bicalicene **116** provide a simple criterion for estimating the extent of π delocalisation (aromaticity) in the planar five-membered ring. A plot of the ^3J(H,H) vicinal coupling constants of the five-membered ring against the Hammett $\sigma_p{}^+$ constant of the substituent present provides a linear correlation of $\sigma_p{}^+$. The absence of known Hammett values for the various bridges in not insurmountable and **6** is shown to be about 14% aromatic. Pentafulvalene **5** (and presumably **7** and **12** also) have essentially zero aromaticity as expected. Moreover, as the electron donating ability of the substituents in the *"n"* ring increases, the contribution from the polar aromatic form increases; complete delocalisation in bicalicene **116** emerges (see below). Comparable correlations of $\delta = {}^{13}C$ (ppm)/σ_p^+ have been made despite not being as easy; the same substituent-induced high-field shifts occur in the pentafulvalenes as in the pentafulvenes. These are in the order C5 > C2/C3 > C1/C4 and for non-polar pentafulvalenes C5 is at highest ppm value followed by C2/C3 and C1/C4, but this changes as polarity increases.

Triapentafulvalenes (Calicenes)

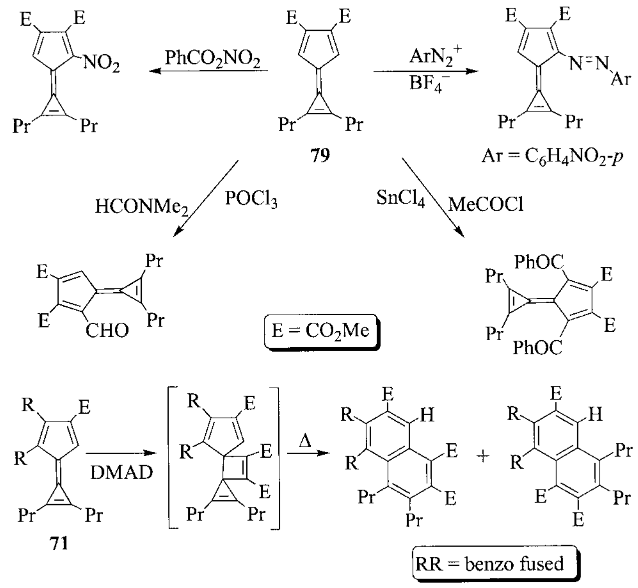
Like the sesquifulvalenes, the triapentafulvalenes are expected to derive stabilisation from charge separation in the ground state with formation of partial cyclopropenyl cation and cyclopentadienyl anion character as depicted by **4b**. A theoretical consideration of the ring system by Dewar[39] appeared at the time of the first reports on the compounds. A flurry of activity in 1965 saw seven publications describing the synthesis of calicene (*calix*) derivatives [named as such by Prinzbach[108] in 1964 from their goblet (or wine glass-like) structure]. The groups of Prinzbach,[131,132] Jones,[133] Kende,[134,135] Kitihara,[23] and Bergmann[136] provided derivatives **66**–**77** by the routes shown in Scheme 14. In one way or another all of these involve reaction of a cyclopentadienyl moiety with a cyclopropenyl cation whether this be a specific anion-cation coupling by path *a* (as for **66**–**70**), formation of a cyclopropenium acetate followed by proton abstraction from a more acidic cyclopentadiene and then loss of acetic acid (path *b*; as for **71**–**73**), or direct proton abstraction from the acidic diene by the ketone (path *c*, as for **74**–**76**); dibenzoyl **77** results from the pentafulvene enolate.[134,137] Attempted prototropic shift in **78** in analogy to the synthesis of pentaheptafulvalenes (see above) does not give rise to calicenes.[131]

The syntheses of **66**–**69** proceed by way of isolable dihydro intermediates (Scheme 14) that lose hydride (removal by Ph_3C^+) and then proton (by Me_3N); for **66** and **67** the intermediate cyclopropenium tetrafluoroborates are isolable.[131,132] Synthesis of **70** from lithium 1,2,3,4-tetraphenylcyclopentadienide and 1,2-diphenyl-3,3-dichlorocyclopropene proceeds directly to product in a one pot operation.[136] Kende's work[134,135] used the enhanced acidity of the cyclopentadiene ester (and amide) moiety to provide **71**–**73** and, subsequently,[138] other derivatives that all undergo electrophilic substitution. Scheme 15 illustrates the range of reactions from diester **79** and the cycloaddition of DMAD across the central bond of **71** to give isomeric phenanthrenes. Importantly, the aldehyde **80** was prepared[137] and rotation about the central double bond monitored by NMR study; $\Delta E^{\ddagger}$ is about 80 kJ·mol^{-1}. This clearly shows that an electron withdrawing group(s) in the five-membered ring increases dipolar contributions and weakens the central linkage as illustrated by the selected dipole mo-



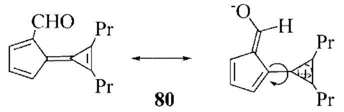
	R^1	R^2	R^3	R^4	R^5	R^6	μ/D
66	H	H	benzo		Me	Me	
67	benzo		benzo		Me	Me	4.90
68	benzo		benzo		Ph	Ph	
69	H	H	benzo		Ph	Ph	
70	Ph	Ph	Ph	Ph	Ph	Ph	6.30
71	H	CO_2Me	benzo		Pr	Pr	
72	H	CO_2Et	benzo		Pr	Pr	
73	H	CN	benzo		Pr	Pr	
74	Cl	Cl	Cl	Cl	Ph	Ph	7.97
75	Cl	Cl	Cl	Cl	Pr	Pr	7.56
76	Br	Br	Br	Br	Pr	Pr	

Scheme 14.

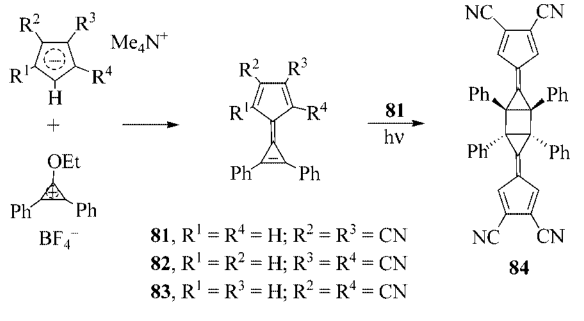


Scheme 15.

ments shown in Scheme 14. The crystal structure of the tetrachlorodipropyl derivative **75** shows bond alternation with C1–C2: 136; C3–C4: 146; C5–C6: 137; C6–C7: 139; and C7–C8: 131 pm, respectively; interbond angles are normal.[139]

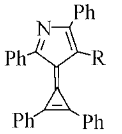

80

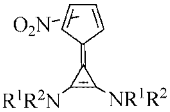
Coupling of dicyanocyclopentadienides with 1-ethoxy-2,3-diphenylcyclopropenyl tetrafluoroborate yield the calicenes **81**–**83** (Scheme 16) that have appreciable charge separation in their ground states; the dipole moments of **81** and **83** in dioxane are 14.3 and 11.1 D, respectively.[140] Dimerisation to a tricyclohexane, e. g. **84**, occurs on photolysis as illustrated for **81**. A comparable reaction gives tetrachloro-7,8-di-*tert*-butylcalicene but only in low (12%) yield.[141]

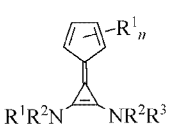


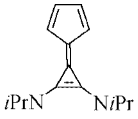
Scheme 16.

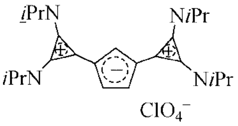
Heterocalicenes can be prepared by just the same approach as that outlined above using a thio substituted cation. Thus, when di- and triphenylpyrroles are heated with (methylthio)diphenylcyclopropenylium perchlorate in AcOH or with dichlorodiphenylcyclopropene in MeCN, azacalicenes, e. g. **85** and **86**, are obtained in good yield via the azatriafulvalenium salts.[142] The provision of 7,8-dithia substituted calicenes that would benefit from enhanced charge separation through electron donation from the three-membered ring sulfur substituents is not always successful as reaction of tris(*tert*-butylthio)cyclopropenium tetrafluoroborate with sodium cyclopentadienide gives only 10% of the desired product.[143] The most studied calicenes that contain electron-donating substituents in the three-membered ring are amino substituted. Yoshida has provided a number of patents[144,145] that describe the preparation of these compounds from diaminohalocyclopropenyl cations and a cyclopentadienide salt as illustrated by **87**–**89**. Of these diamines, **89** is surprisingly stable to oxygen (air) in the crystalline state but it is rapidly oxidised in solution. The NMR resonances indicate a considerable contribution from the polar charge-separated form.[26]

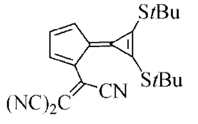

85, R = H (50%)
86, R = Ph (59%)


87


88, R^1 = CN, CO_2R'
n = 1–4

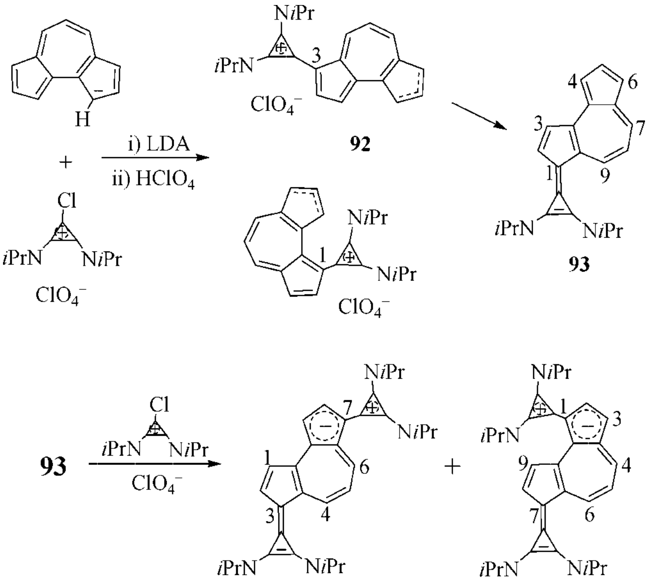

89


90


91

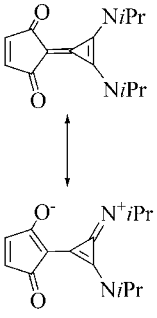
The reaction sequence has been extended[146] to the cyclopropenium-containing calicenes **90** that have a definite contribution to the total structure from the tripolar (+ – +) form depicted, while the vinyldithiacalicene **91** is formed directly by reaction of di(*tert*-butylthio)dichlorocyclopropene with cyclopentadiene and TCNE in the presence of sodium hydride;[147] some of this work has appeared in published plenary lecture format.[26] The incorporation of markedly more complex cyclopentadienylidene units into a calicene is demonstrated by the azulenocalicene **93** Thus, reaction of lithium cyclopent[*e*]azulenide with chlorobis(diisopropylamino)cyclopropenium perchlorate, treatment with an equimolar quantity of lithium diisopropylamide, and then aqueous perchloric acid provides a 71:29 mixture of 3-substituted **92** and its 1-isomer (Scheme 17) from which only **93** (32%) is isolated chromatographically as reddish purple crystals (mp, 171–174 °C); subsequent reaction with additional cyclopropenium salt gives the 3,7- and 1,7-salts shown in Scheme 17 rather than the overcrowded 1,9-product.[148] Reaction of the same cyclopropenyl cation with cyclopent-4-ene-1,3-dione affords the calicenequinone **94** that is formally stabilised by charge separation but has antiaromatic character from the 4π electron zwitterion.[149]

Calicene derivatives with the cyclopropene ring fused into an aromatic are also known. The synthesis of these compounds employs Peterson olefination of a ketone using a silyl-substituted cycloproparenyl anion and derivatives

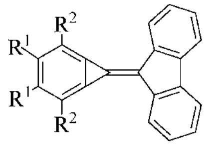


Scheme 17.

95–**97** are stabilised by the arene fusion.[150,151] The molecules are polar and the crystal structures of **95** and **96** have been determined.[152]

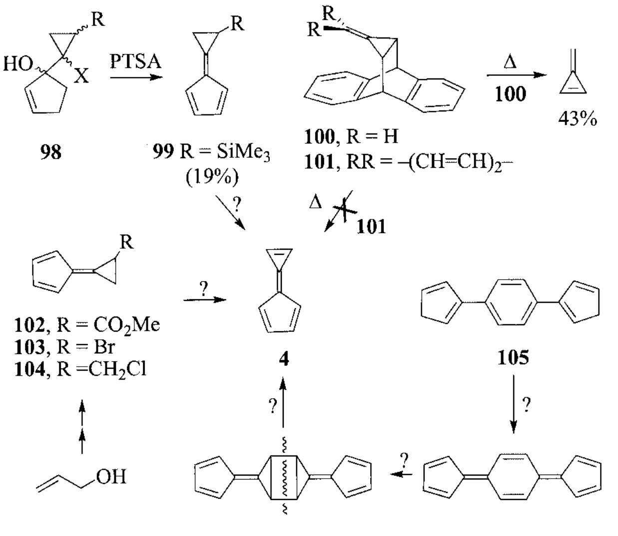


94



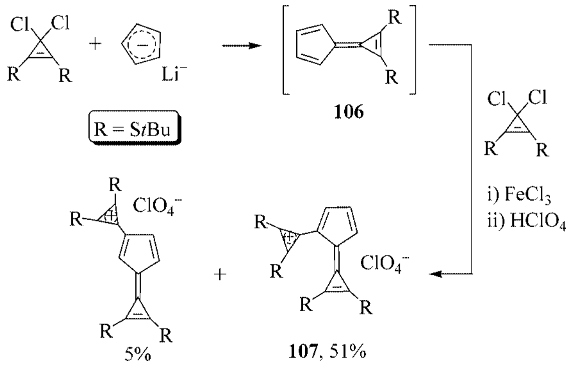
95, $R^1 = R^2 = H$; μ 2.6 D
96, R^1R^1 = benzo; $R^2 = H$; μ 3.3 D
97, R^1R^1 = benzo; $R^2 = OMe$; μ 3.7 D

Despite these various studies parent **4** has not yet been prepared. Again, it is Neuenschwander that has directed most attention to its synthesis (Scheme 18). He noted that use of cyclopropenium salts and *gem*-dihalocyclopropenes, as described above for the substituted derivatives, fail for the parent compound, as do sequences involving sequential hydride and proton removals. The cyclopropylcyclopentenols **98** either fail to lose water and halide upon acid treatment or, when successful, as for silylated **99**,[153] the yield is poor and the dihydro derivative does not subsequently give rise to **4**. Moreover, while retro-Diels–Alder cleavage of **100** yields 43% of triafulvene, the analogous reaction of **101** gives anthracene as the sole isolable product of reaction.[154] In similar vein, the same group has provided the precursors **102**–**105** (of which bromide **103** appears the most promising)[155,156] and, while the yield of this last compound is currently only 10% an alternative path to it has been proposed.[156] The development of this chemistry remains open for investigation.



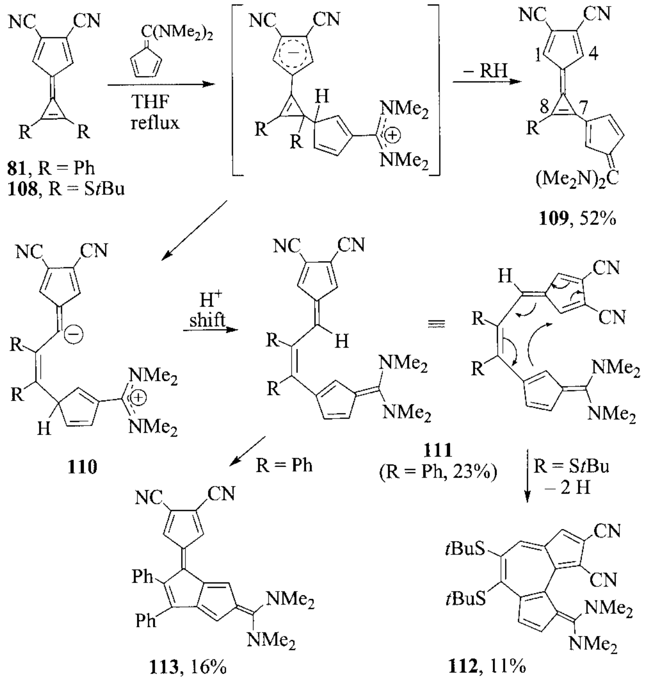
Scheme 18.

It was noted above that the structure of azulenocalicene **93** was deduced from subsequent electrophilic substitution by additional cyclopropenium salt. The incorporation of a cyclopropenyl electrophile into a calicene molecule is further demonstrated by 7,8-bis(*tert*-butylthio)calicene (**106**) (Scheme 19). Reaction of lithium cyclopentadienide with bis(*tert*-butylthio)dichlorocyclopropene (as for **91)** provides the calicene **106** in situ as a reactive compound especially sensitive to air.[26] It is transformed into the 1-substituted doubly cross-conjugated 3-5-3 ring system **107** in 51% yield with only traces (5%) of the 2-substituted derivative (Scheme 19).[157] Unlike the tetramine **90**, there is only a small contribution from the tripolar (+ – +) form and the major contributing structure is that shown. In contrast, the more polar dicyanodithio analogue **108** reacts with *nucleophilic* 6,6-bis(dimethylamino)pentafulvene in refluxing THF to give products with both retention and loss of the three-membered ring (Scheme 20).[158] Capture of the nucleophile at the three-membered ring followed by loss of *t*BuSH gives the C7 substitution product **109** (52%), while ring opening prior to elimination leads via zwitterion **110** to **111** (R = SBu^t). Subsequent 10π electrocyclic ring closure and oxidative dehydrogenation gives the 5-7-5 ring fused **112** that is isolated as dark blue crystals in 11% yield. While the di-



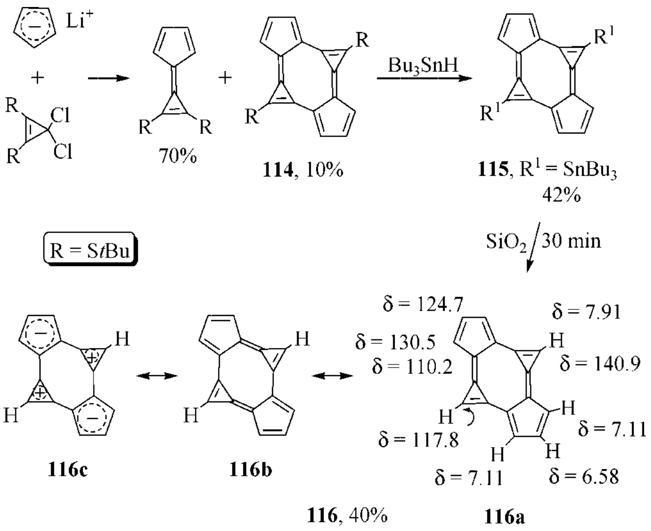
Scheme 19.

phenyl analogue **81** also ring-opens to **110** (R = Ph), final closure from **111** (R = Ph) is to the 5-5 fused product **113** (16%); at room temperature reaction of **81** proceeds to **111** (23%) only.[159] Compound **113** is noted for possible optical recording usage.[160]

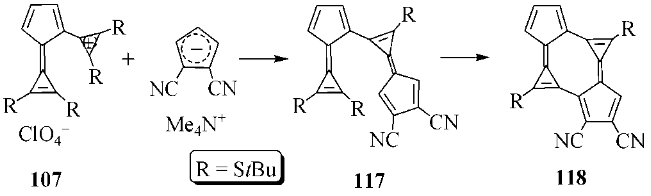


Scheme 20.

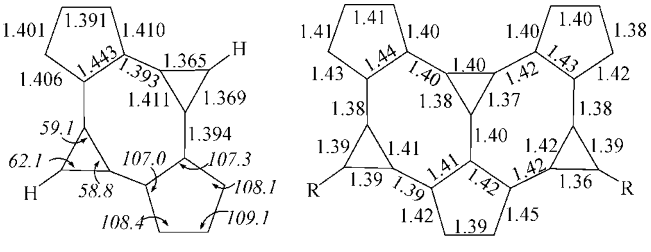
The preparation of 7,8-bis(di-*tert*-butylthio)calicene (**106**) noted above[145] provides a side product that has proved more than interesting,[161] namely the cyclic bicalicene **114**.[26] Refinement of the synthesis and use of lithium cyclopentadienide gives **114** in 10% yield, and it and its chemistry have been examined in some detail.[162,163] Bis(thioether) **114** reacts with tributyltin hydride to give bisstannane **115** (42%) and treatment of this with silica gel (routine acids and bases were without success) affords the parent bicalicene **116** in 40% yield (Scheme 21). Unlike the simple calicenes, **114** and **116** are air stable solids, the latter forming orange plates with a melting range of 125–30 °C.[163] Furthermore, the cyclopropenium calicene **107** reacts with tetramethylammonium dicyanocyclopentadienide to give the dicalicene **117** (Scheme 22) but in low (5%) yield. However, on standing in dichloromethane at room temperature **117** cyclizes to the dicyanobicalicene **118** in 73% yield thereby demonstrating sequential formation of the bicalicene framework.[163] The crystal structures of **114**[163] and **116**[162] have been determined and the ring system is held almost completely planar; bond lengths/angles for **116** are shown in Figure 2. The ring system encasing the bicalicenes contains a 16π electron periphery but the NMR spectroscopic data (appended to **116** in Scheme 21) are consistent only with contributions to the structure from **116a**–**c**, in which there is polarisation in both calicene units as opposed to a peripheral [16]annulene. The Neuenschwander $^3J_{H,H}/\sigma_p^+$ correlation provides for 100% aromaticity.[130] The bicalicene ring system is characterised by weak long wavelength absorption at ca. 500 nm.



Scheme 21.



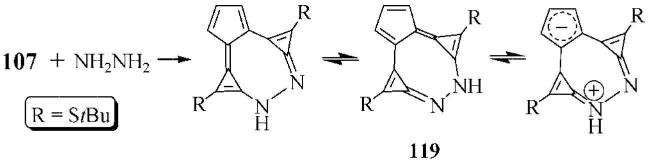
Scheme 22.



116 **121**, R = StBu

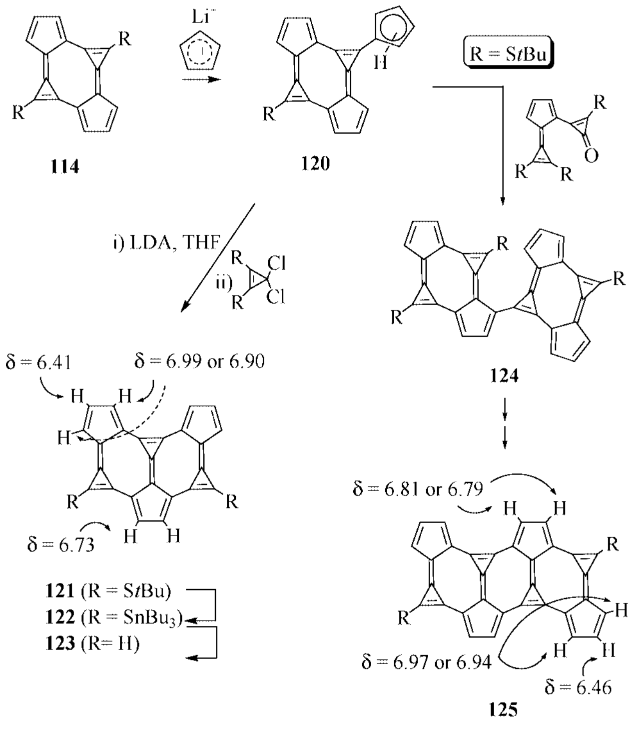
Figure 2. Structural data for **116** and **121** (bond lengths in Angstrom units, angles in deg.); data taken from ref.[162,165]).

Cyclopropenium salt **107** reacts with nucleophiles other than the cyclopentadienyl anion such that **114**–**116** are not the only cyclised products known. Thus, reaction of **107** with hydrazine also captures the nucleophile at the three-membered ring and leads to cyclisation, this time to the cyclic diaza-containing **119** (43%) (Scheme 23).[164] Again, the NMR spectroscopic data point to a significant contribution from the polarised cyclopentadienide structure with the proton in tautomeric equilibrium between the two nitrogen sites.



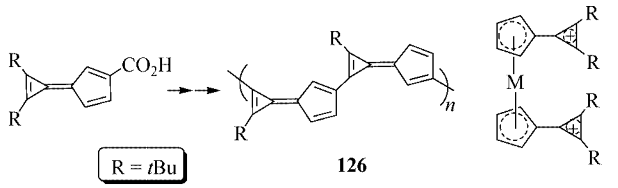
Scheme 23.

The bicalicene ring system is not inert. Reaction of dithienyl **114** with lithium cyclopentadienide results in nucleophilic substitution of one thioether moiety and formation of **120** in 83% yield (Scheme 24).[165] Subsequent successive reaction with LDA (2 equiv.) and bis(di-*tert*-butyl)dichlorocyclopropene gives dark green crystals of tercalicene **121**, which is transformed into hydrocarbon **123** via the stannyl derivative **122** as for **116**.[165,166] Furthermore, and in similar vein, **120** is converted into the quatercalicene **125** via the di(bicalicene) **124** as shown in Scheme 24, but the attempts to provide the parent hydrocarbon stalled at the bis-stannyl derivative **125** (R = $SnBu_3$).[165] The X-ray crystal structure of **121** has been determined and the bond lengths reported are shown in Figure 2.[165] Like **114** and **116**, the ring systems of **121** are essentially planar. The "outer" calicene rings are very similar to those of **114** while the inner one is different. The ^1H NMR spectroscopic data for the thioethers **121** and **125** (R = SBu^t) are shown in Scheme 24 and the chemical shifts of hydrocarbon **123** are similar complimenting the structure analysis. The external peripheries of **123** and **125** carry 22π and 28π electrons respectively. As with cyclic bicalicene there is no evidence for the presence of a paramagnetic ring current in **125**, nor is there a diamagnetic one in **123**. Furthermore, the chemical shift and structural data imply that about 50% of the total structure comes from polar contributions and this is supported by calculation.[167] The redox behaviour of the ring systems has been examined and stable anion radicals are produced. The bicalicene **114** exhibits large reduction potentials indicating that the 16π electron ring system is comprised of two polar calicene units with the anion radicals having partial localisation of the unpaired electron on the five-membered ring. Importantly, the EPR results[168] show the polycalicenes to be quite different from simple calicenes.[169]



Scheme 24.

Potential for calicenes to serve as functional materials is illustrated by the fact that 7,8-di-*tert*-butylcalicene-2-carboxylic acid has been converted into a polyanhydride from which CO and CO_2 have been eliminated photolytically in an electric field; head-to-tail coupling gives poly(7-*tert*-butylcalicene) (**126**), prepared for electrical conductivity studies.[170] The transformation of various calicenes into organometallic complexes of group 6 (Cr, Mo, W), group 8 (Fe), and group 9 (Co, Rh), e. g. **127**, have been the subject of several industrial patents granted in 1978.[171] Moreover, the possibility of nonlinear optical phenomena being associated with the calicene chromophore has formed part of a theoretical study.[172]

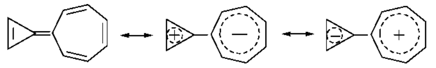


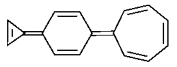
127, M = Fe or Co;
R = N*i*Pr_2

The structural dependence of the rotational barrier in calicenes received theoretical consideration as early as 1973.[173] Comparisons of singlet biradical and zwitterionic states in the planar and 90° twisted forms allows for predictions on the relative stabilities of the two states from the degree of polarisation in the planar structure.[125] The excitation of calicene is associated with considerable molecular charge transfer[174] and the electro-optical absorption spectrum of tetrachlorodiphenyl **74** (see Scheme 14) has been examined.[175] There is now little doubt that the molecules display partial aromatic behaviour in the ground state and antiaromatic character in the excited singlet states[123] with clear similarities to the sesquifulvalenes. The prospect of Bergman-like cyclisation of a 3-cyclopropenylpenta-1,4-diyne into a calicene 1,4-diradical shows that the development of partial aromatic character in the transition state has little stabilizing influence on the intermediate and the activation barrier is high, such that reaction is not likely to be observed.[176]

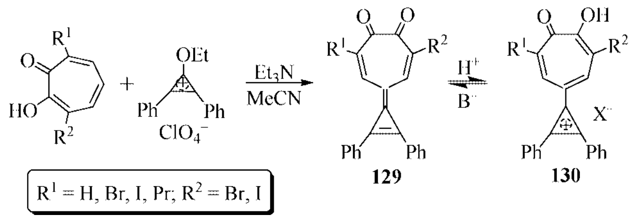
Triaheptafulvalenes

Studies of triaheptafulvalene (**9**) and its derivatives are few with the parent hydrocarbon unknown. Cross conjugation of the [3,7] type provides two rings each of which is electron-releasing and the question that arises is which of the 2π3C or 6π7C aromatic cations dominates. High level computed structures for **9** (among a series of fulvalenes examined)[44,45] predict a planar structure with the three- and seven-membered rings quite similar to those in tria- and heptafulvene, respectively. The molecule is expected to have a small contribution (ca. 15%) from the polar form **9b** in which the seven-membered ring assumes 8π antiaromatic character with electron donation *from* the cyclopropene moiety, while polarisation in the opposite sense, viz. to the cycloheptatrienyl cation/cyclopropenyl anion **9c**, is expected to make no contribution.[44] Recent experimental findings confirm the donation of electrons from the three-membered ring.[177] The electronic state properties have been assessed,[83] and a variety of derivatives including the exploded quinonoid derivative **128** were studied as early as 1975.[178]


9a **9b** **9c**

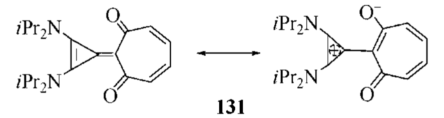

128

The first derivatives obtained were ones in which the larger ring was able to provide an appropriate electron sink with charge separation favouring the cyclopropenyl cation.[25,179] Thus cyclopropenylation of appropriate halotropolones results in capture of the three-membered ring at C5 with formation of the triaheptafulvalenediones **129**. Protonation gives rise to the cyclopropenium tropolones **130** (Scheme 25). Use of tropolone itself with the ethoxycyclopropenyl cation does provide **129** ($R^1 = R^2 = H$) with an unsubstituted seven-membered ring but the yield is a mere 6%; the cyclopropenium salt has been produced also.[179]



Scheme 25.

More recently, use of the chlorobis(diisopropylamino)cyclopropenyl bromide with β-tropolone had provided 1,6-dione derivative **131** by analogy to the synthesis of the calicenequinone **94**. However, unlike the latter, the polar form dominates.[149] While the derivatives **132**[180] and **133**[181] have been prepared, no evidence has been provided to suggest contributions to the structures from **132b** or **133b**. In fact, **132** reacts in an inverse electron demand Diels–Alder reaction by way of the 7,8-dihydro-1,6-dione tautomer **132c**.



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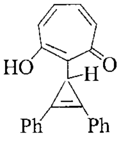
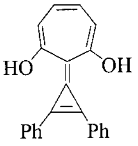
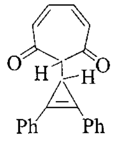


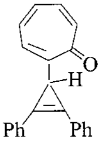
132a



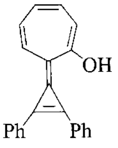
132b



132c

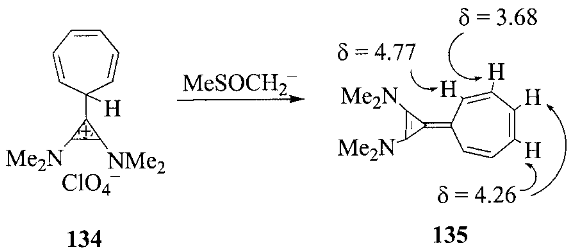


133a

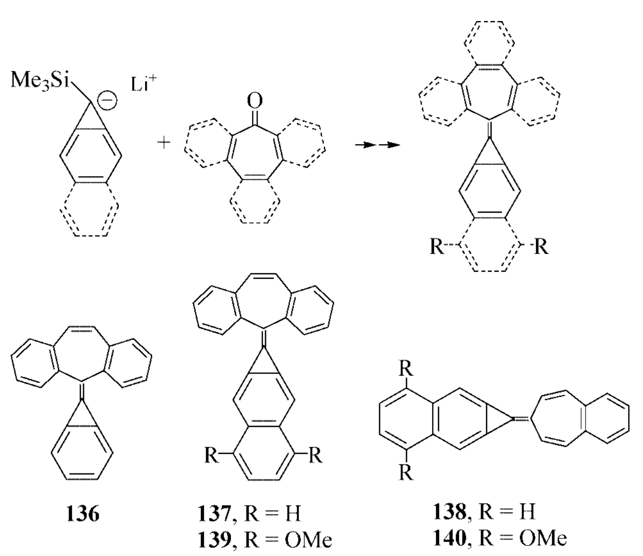


133b

The preparation of 9,10-bis(trimethylamino)triaheptafulvalene was reported in 1982 by Yoshida.[26] Reaction of diaminocyclopropenium perchlorate with phenylmagnesium bromide and then 7-methoxycycloheptatriene gives salt **134** which, with dimsylsodium, gives an immediate dark blue solution of **135** (Scheme 26) whose ^1H NMR spectroscopic data (appended to the structure) and coupling constants infer olefinic character in the seven-membered ring as one might expect for 3:7 ring fusion. The simplest hydrocarbons with this fusion have come from the group of the author.[182] Reaction of the 1-(trimethylsilyl)cycloproparenyl anion with suberone or benzo[*d*]cycloheptatriene leads to the arene-fused triaheptafulvalenes **136**–**138** (Scheme 27) by analogy to the synthesis of **95**–**97**. The molecules are polar but the polarity is small and the range 1.2–1.6 D.[150,151]



Scheme 26.



Scheme 27.

More recently, the diethers **139** and **140** have become available[151] and they confirm that electron donation in these compounds is *from* the cycloproparene moiety *to* the cycloheptatriene in agreement with calculation.[152] Furthermore, crystal structure determinations on **136** and **139** show that the ring system is not planar but has the seven-membered ring bent from the plane containing the cycloproparene. The extent of this depends upon electron donation – the stronger electron donating ether **139** is bent more than hydrocarbon **136** (Figure 3) indicating a resistance to the development of 8π antiaromaticity in the cycloheptatrienylidene moiety.[177]

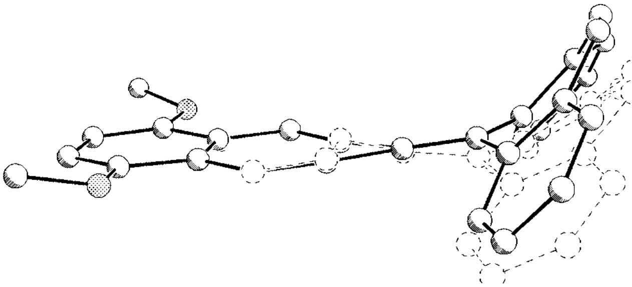
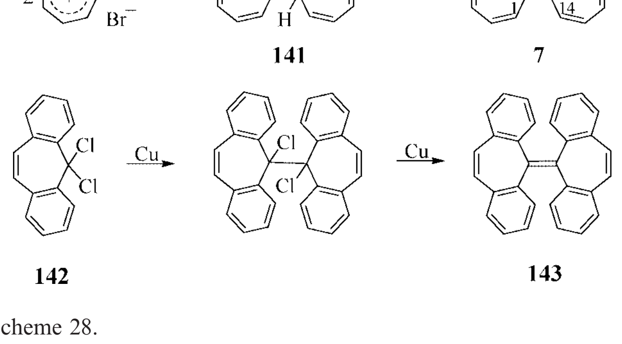


Figure 3. Superimposed side perspectives of the triaheptafulvalenes **136** (broken lines) and **139** (solid lines) (reprinted from ref.[177] with permission, copyright 2004, Elsevier).

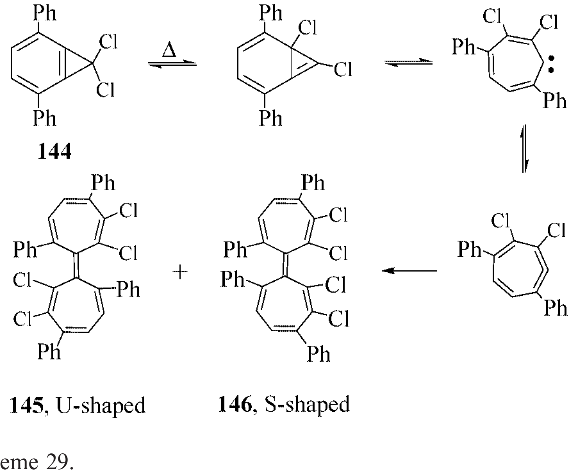
Heptafulvalenes

The [7,7] coupling in heptafulvalene (**7**) provides a molecule with an element of strain and a degree of interaction between the pairs of hydrogen atoms H-1···H-14 and H-6···H-9 adjacent to the fusion bond. This class of molecules has been the topic of early book chapters.[7,183] On reporting the heat of formation $\Delta_f H°$ of **7** as 130.77 ±0.13 kcal·mol^{-1} (547.14 ±0.54 kJ·mol^{-1}) in 1957, Doering et al.[24] accredited the first preparation of **7** to J. R. Mayer, the details of which subsequently appeared in Doering's discourses.[17,18] The synthesis was achieved from reductive dimerisation of tropylium bromide with zinc to give the dihydro derivative **141**, which upon bromination and dehydrobromination yields **7** (Scheme 28). By comparison, use of the dichlorocycloheptatriene **142** gave the first stable heptafulvene[184] **143** from Cu-catalysed dimerisation and subsequent dechlorination, in analogy to the early syntheses of symmetrical (penta)fulvalenes.[5] Parent **7** was the subject of early calculations that included the resonance (stabilisation) energy,[40,101] electronic spectra,[97,185] bond order/reactivity,[98] and diamagnetic susceptibility exaltation.[186] Recent studies employing the exact many electron treatment have addressed hyperpolarizibility for which conventional MO treatments can lead to the incorrect sign of the average π polarizability.[187]



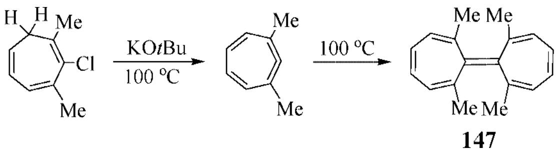
Scheme 28.

The steric and strain effects in heptafulvalenes lead to non-planarity in each ring with the deformation providing for both *syn* and *anti* conformers. The latter is the more common and the S-shaped *anti*-folded C_{2h} arrangement of **7** became evident from crystal structure analysis and subsequent discussions that date to the early 1970s from which the H-1···H-9 (and H-6···H-14) separations are 213 pm.[188] Subsequent theoretical consideration of the stabilisation energy and Kekulé contribution (derived from the experimental bond lengths) were made,[189] but it is the recent high level calculations that replicate the structural data and confirm that the H···H interactions dictate the bend from planarity; the loss of overlap is partially compensated by pyramidalisation of the carbon centres of the seven-membered rings.[44,45,190] A unique though serendipitous synthesis of distinct *syn*- and *anti*-heptafulalvenes is provided by our own work on the thermal dimerisation of *gem*-dichlorocyclopropabenzene **144**.[191] Heating **144** gives pale and deep yellow dimers that are isomeric heptafulvalenes as shown by crystallographic analysis. The pale yellow (*E*) isomer **145** has a *syn* (or "U"-shaped) orientation of the bent seven-membered rings,[192] while the more highly conjugated **146** has *Z* orientation of the substituents about the linking π bond with an S-shaped *anti* bending of the two seven-membered rings.[193] The dimerisation that gives these products rather than styrenes or cyclobutanes implies[192] that the mild thermolysis proceeds by way of the cycloheptatrienylidene/cycloheptatetraene of Scheme 29.



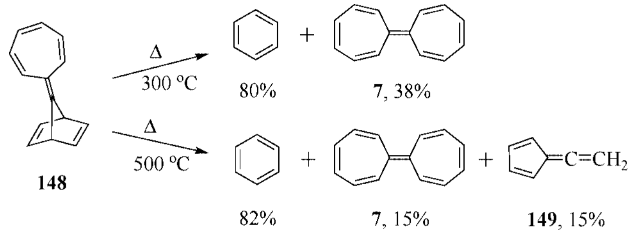
Scheme 29.

The dimerisation of cycloheptatrienylidenes (tropylidenes) to heptafulvalene has been recognised for many years with Jones and Ennis isolating up to 50% of **7** from photolysis of the sodium salt of tropone tosylhydrazone.[194] Subsequent studies,[195] the inclusion of phenylcarbene within the C_7H_6 manifold,[196] and recognition that cycloheptate-



147

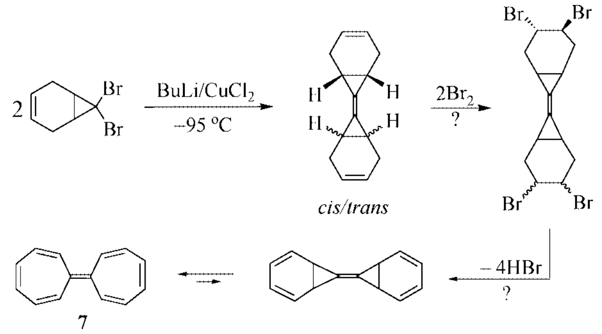
traene is an energetically viable valence bond isomer[197] served to delineate the reactivity of C_7H_6 and demonstrate the involvement of substituents at the 1- and 1,6-positions. Thus, dehydrochlorination of 2-chloro-1,3-dimethylcycloheptatriene at 100 °C gives **147** in 92% yield.[197] It was McMahon and his students, however, who showed that the key intermediate in C_7H_6 rearrangements is 1,2,4,6-cycloheptatetraene.[198] Entry into the C_7H_6 manifold has also been provided by (trimethylsilyl)cycloheptatriene,[199] but the gas phase thermolysis of 7-acetoxybicyclo[2.2.1]hepta-2,5-diene deserves mention since loss of acetic acid and rearrangement provides **7** in 58% yield.[200] Use of spirocyclic analogue **148** demonstrates a temperature effect in the decomposition (Scheme 30).[201] At 300 °C, entry to the C_7H_6 manifold provides a 38% yield of **7** whereas at 500 °C equal amounts of it and the allene **149** (15%) are produced; the yield of benzene remains essentially constant at ca. 80%. Entry to C_7H_6 has also been achieved by atom-molecule chemistry. Thus the reaction of arc-generated carbon atoms with benzene give a plethora of products with heptafulvalene **7** comprising almost 17%.[202] Traces of **7** also come from the reaction of tropone with oxoheptafulvene [(cycloheptatrienylidene)methanone] but carbenes seem not to be involved.[203] However, reaction of tricarbonyl(tropone)iron with this same ketene gives tricarbonyl(heptafulvalenyl)-iron.[204] Not surprisingly, synthetic efforts directed towards isoelectronic hetero analogues of **7** have succeeded with a range of derivatives characterised.[205]



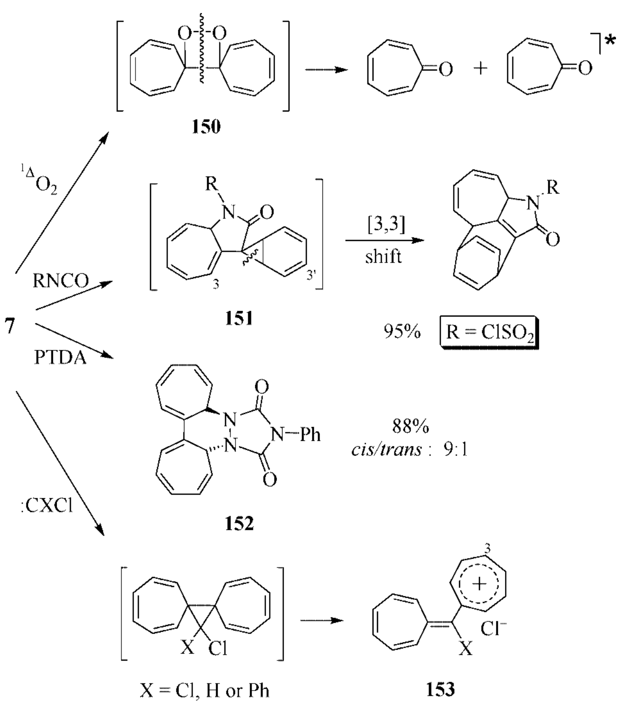
Scheme 30.

For recent approaches to **7** the work of Neuenschwander and Li again deserves mention.[119] While carbenoid formation from 1,1-dibromobicyclo[4.1.0]hept-3-ene and coupling of it to a *cis*/*trans* mixture of bicyclopropanylidenes proceeds in 65% yield (Scheme 31), the bromination and subsequent tetradehydrobromination to give **7** via norcaradiene-cycloheptatriene ring opening remains an area for exploration.

The reactivity of heptafulvalene stems from the electron-rich nature of the linking double bond as illustrated in Scheme 32.[206] Singlet oxygen gives the dioxetane **150** that fragments to tropone, one molecule generated in the excited state as expected. Chlorosulfonylisocyanate undergoes [8 + 2] addition to give **151** as an unstable product that Cope rearranges, while *N*-phenyltriazolinedione encompasses the entire molecule with a [14 + 2] addition to a *cis*/*trans* product mixture of **152** with the *trans* isomer dominating.[206] With carbenes (:CCl_2, :CHCl, :CPhCl) the initially formed chlorocyclopropanes open to provide cycloheptatrienylheptafulvenyl cations **153** that capture nucleophile at C3 to give a cycloheptatriene-substituted heptafulvene.[207] On reaction with $Cr(CO)_3(MeCN)_3$, compound **7** complexes chromium to each ring to form a biscomplex that subsequently reacts photochemically with 1,3-butadiene to give successive [6 + 4] reactions.[208]



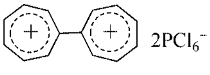
Scheme 31.



Scheme 32.

Mixing **7** with TCNQ in MeCN gives rise to a solution whose UV spectrum is a superimposition of those of its components; the hoped for charge transfer complex with an expected absorption maximum at 1050 nm is not formed.[209] In contrast, reaction of **7** with an excess of PCl_5 gives rise to the heptafulvalene dication **154** as an extremely unstable red solid characterised as the bis(hexachlorophosphate); the aromatic protons appear at δ =

9.55 ppm.[210] Ag^{I}-catalysed one-electron reduction of **7** provides radical cation **155** that dimerises (Scheme 33). Thermal cleavage of the dimer in the range 30–60 °C regenerates **155** whose hyperfine spectrum is fully consistent with three sets of four protons each as required;[211] the species is predicted to have D_{2h} symmetry.[87] At –80 °C, **7** reacts with potassium to give the anion radical **156** that dimerizes at higher temperatures in analogy to **155**; the purple dimer is then in equilibrium thermal cleavage with **156**. The EPR spectrum of **156** is particularly temperature dependent but associated with only one of the rings. Rapid exchange between the rings occurs to an extent dependent upon the conditions with the K^+ cation "jumping" from one ring to the other.[211] Anion radical **156** is expected to have C_{2v} symmetry.[86] Reaction of **156** with excess potassium gives a dianion and then a trianion radical[212] with predicted C_{2v} symmetry in the ground state. Geometry optimisations of the lowest (2nd) excited singlet state of **7** have been addressed.[213]



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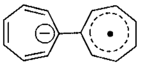

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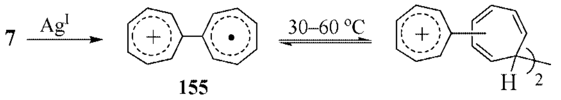

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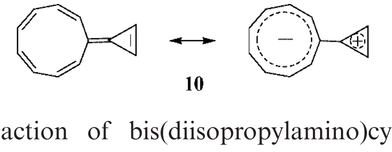
Scheme 33.

The Nonafulvalenes

The larger and more flexible ring system of cyclononatetraene has been transformed into notably fewer fulvalenes than for the smaller rings and consequently these are discussed together under the one heading. Moreover, it is largely the work of Neuenschwander and his students who have provided the advances recorded.

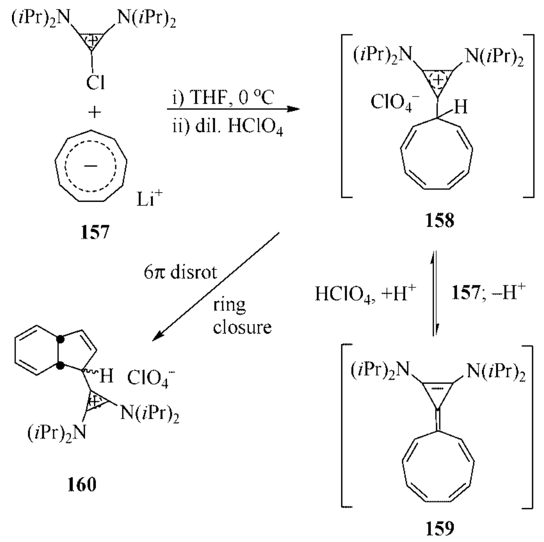
Trianonafulvalenes

The energy characteristics of the 12π trianonafulvalene (**10**) were addressed in 1966,[214] but it was not until 1982 that the first potential syntheses were published. In the account of his 1979 ISNA-9 plenary lecture,[26] Yoshida records that attempts to prepare derivatives carrying the diaminocyclopropene moiety had been unsuccessful largely because, upon formation, the nine-membered ring undergoes facile electrocyclic closure to an 8,9-dihydroindene.



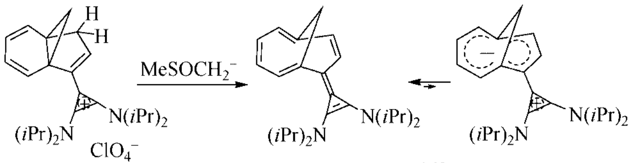
10

Thus, reaction of bis(diisopropylamino)cyclopropenyl perchlorate with two equivalents of lithium cyclononatetraenide **157** gives **158** that is deprotonated by excess **157** to the sought **159** (Scheme 34); diamine **159** is very sensitive to air and is protonated with dilute perchloric acid. Salt **158** is especially reactive and undergoes electrocyclic ring closure to the *cis*-dihydroindene **160** thereby negating its isolation.



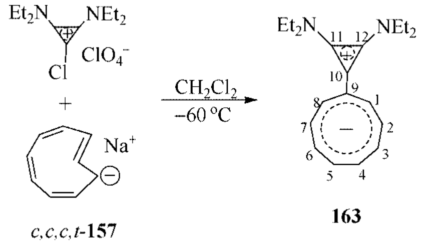
Scheme 34.

Use of the analogous 1,6-bridged ion provides added stability and perchlorate **161** is obtained as a stable salt that is easily deprotonated to give the bridged trianonafulvalene **162** as an orange solid. The ^{1}H NMR spectroscopic data indicate very little contribution to the structure from polar forms. Thus the bridged molecule is essentially olefinic,[26] likely a result of non-planarity that is further facilitated by the presence of the bridge and an insufficient stabilisation from π electron delocalisation (see below).



161 **162**

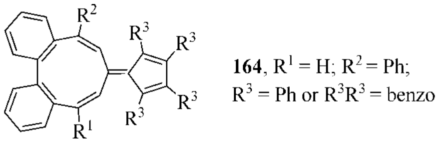
More than a decade later Chai and Neuenschwander[215,216] were able to isolate bis(diethylamino)trianonafulvalene (**163**) as pale yellow cubic crystals. The successful route, almost the same as that described above, employed sodium (*c,c,c,t*)-cyclononatetraenide (**157**) with the bis(diethylamino)chlorocyclopropenyl perchlorate as shown in Scheme 35. A detailed analysis of the NMR spectra show **163** to be characterised by proton resonances around δ = 6 ppm, strongly alternating $^3J_{H,H}$ couplings, and ^{13}C absorptions in the δ = 110 ppm region consistent only with **163** existing as a dipole with the nine-membered ring held planar.[217] Subsequent calculations at the HF/6-31G//CID/STO-3G level confirm that the molecule is indeed aromatic and that solvent does not alter the aromaticity.[218] This molecule is the sole example of a trianonafulvalene at the time of writing. It is stable for days in both the solid state and solution under argon.



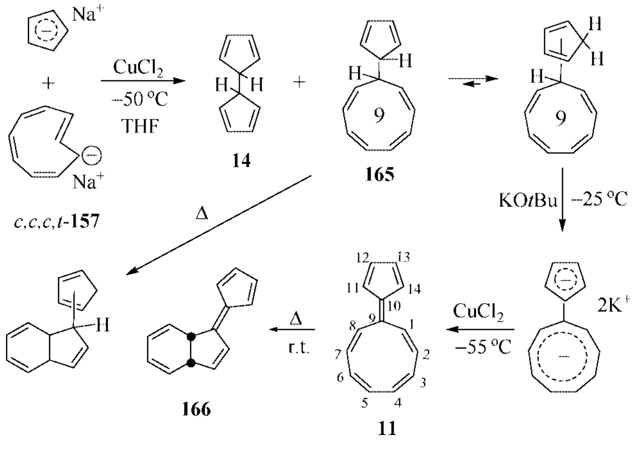
Scheme 35.

Pentanonafulvalenes

The energy characteristics of **11** were also addressed[214] in 1966 and the first derivatives characterised by Rabinowitz and Gazit some six years later.[219] The coupling of dibenzocyclononatetraenyl anions with fluorenone and tetracyclone gives alcohols that dehydrate to fulvalenes **164** with *p*-toluenesulfonic acid (PTSA), cf. Scheme 2.

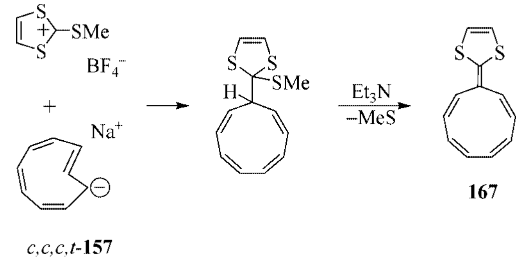


However, the existence of parent **11** was not confirmed until 1984.[27] Because each of the rings contain 4*n* electrons the oxidative coupling approach to the parent, as demonstrated for the pentafulvalenes (Scheme 1), is applicable here. Escher and Neuenschwander showed that such coupling can be brought about, but use of five molar equivalents of sodium cyclopentadienide with one of **157** in the presence of 6.6 mol. equivalents of $CuCl_2$ in THF at –50 °C results in the dihydro derivatives **165** and **14** (Scheme 36) with only traces of the [9.9] coupled molecule.[27,220]



Scheme 36.

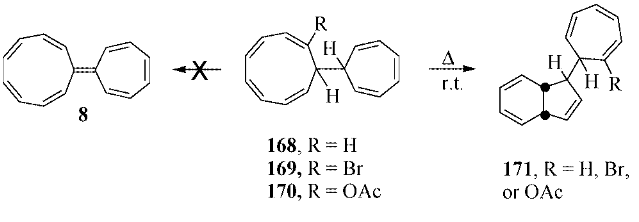
Compound **165** is the minor component of its H-shift isomers, all of which can be separated from **14** chromatographically at –20 °C. Subsequent double deprotonation of the isomeric mixture with *tert*-butoxide at –25 °C precipitates the dipotassium salt and this is oxidised with Cu^{II} at –55 °C to **11** in about 35% yield. Like **165**, **11** is thermally unstable undergoing facile electrocyclic ring closure to **166** at room temperature (Scheme 36).[220] The NMR spectroscopic data confirm **11** as olefinic with strongly alternating bond lengths and a nine-membered ring that is bent markedly from planarity. Furthermore, comparison with data from various pentafulvenes and nonafulvenes demonstrates that the large ring of **11** acts as a weak electron donor to the five-membered ring, viz. there is a slight tendency towards cyclopentadienide character. Chai and Neuenschwander[215] have also provided the olefinic **167**, the TTF analogue of **11**, in 30% yield. The synthesis (Scheme 37) involves coupling of sodium (*c,c,c,t*)-**157** with (thiomethyl)dithiolium tetrafluoroborate followed by removal of methanethiol with triethylamine.



Scheme 37.

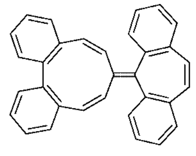
Heptanonafulvalenes

To date parent **8** has not been prepared. However, the availability of dihydro **168**, an entirely plausible precursor (see path *a*, Scheme 14), was reported in 1972 from the coupling of tropylium tetrafluoroborate with the potassium salt of **157**.[221] Despite this, and the 1-bromo derivative **169** and 1-acetoxy derivative **170** that followed in 1977,[222] the needed elimination has not been brought about as each compound is thermally labile and undergoes 6π electrocyclisation in the nine-membered ring at about 20 °C to give the cycloheptatrienyl-substituted dihydroindenes **171** (Scheme 38). Thus the only known heptanonafulvalenes are those prepared in the early 1970s by Garratt and Knapp[223] and Rabinovitz and Gazit.[219]



Scheme 38.

The condensation of the dibenzo[*a.c*]cyclononatetraenyl anion with suberone followed by PTSA dehydration provided **172** and **173** in 29 and 59% yield, respectively,[223] while the cyclononatetraenyl anion used to prepare **164** gives the cycloheptatrienylidenes **174** and **175** with the relevant tropone.[219]



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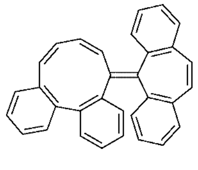

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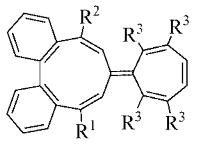
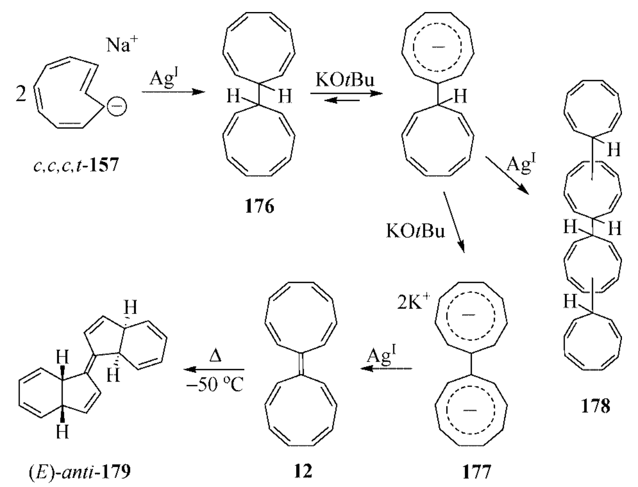


174, $R^1 = R^3 = H$, $R^2 = Ph$,
175, $R^1 = H$, $R^2 = Ph$, R^3R^3 = benzo

Nonafulvalenes

The 18π electron compound **12**, whose Hückel characteristics were calculated in 1966,[214] was reassessed in 1982 as polyolefinic with strong bond length alternation, while its derived dianion **177** is predicted to have independent 10π electron aromatic rings.[224] As with other fulvalenyl anion radicals, symmetry reduction from D_{2h} to C_{2v} is expected for that from **12** on the basis of the second order Jahn–Teller theorem.[48]

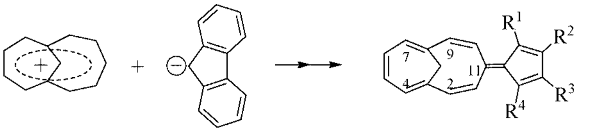
The synthesis of hydrocarbon **12** is due to Escher and Neuenschwander[225] and involves coupling two cyclononatetraenyl anions to give bicyclononatetraenyl (**176**) employing Ag^I rather than Cu^{II} (Scheme 39). The key step is dideprotonation of this to dianion **177** with *tert*-butoxide. This is possible only after equilibration of **176** with its monoanion, otherwise monodeprotonation occurs and is followed by $AgBF_4$ oxidative coupling to quater(cyclononatetraenyl) (**178**) as a mixture of isomers (Scheme 39).[28] Not surprisingly, **12** is thermally very reactive and undergoes 6π electrocyclic closure in *both* rings at –50 °C to an isomeric mixture of (tetrahydrodibenzo)pentafulvalenes **179** from which the (*E*)-*anti*-isomer shown was characterised by X-ray crystallography.



Scheme 39.

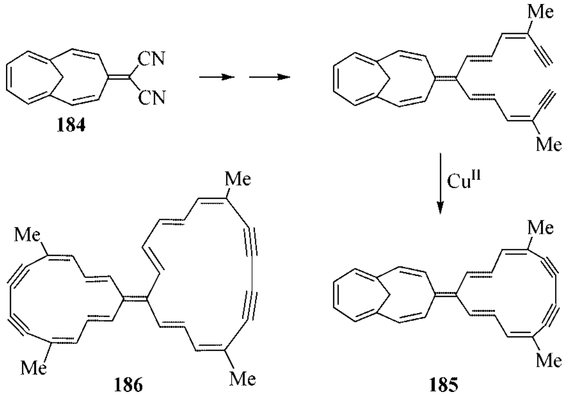
Large Ring Fulvalenes

The ability to construct fulvalenes of ever increasing ring sizes became evident as early as 1967 when Prinzbach and Knothe[226] reported the synthesis of the bridged 16π pentaundecafulvalene **180** and named the parent ring system **13** *fidecene* (L: *fides*) from its likeness to a stringed instrument; more than likely Prinzbach's love of music played a role in this choice. The synthesis became possible from the availability of the bridged 10π cycloundecapentaenyl cation[123] which couples with the 6π fluorenyl anion to give the dihydro precursor that is dehydrogenated with chloroanil; the tetracyclone derivative [31] **181** and the di-*tert*-butyl[227] derivative **182** followed shortly thereafter. The notable feature of the cation-anion pairing is that, of the 168 dihydro isomers which Prinzbach points out as possible,[16] that from (linear) C11 coupling predominates with the C2 (angular) interaction next most prevalent. By carefully controlling the reaction conditions for dehydrogenation Prinzbach and his students were able to isolate the bridged, but otherwise unsubstituted parent **183** from reaction with cyclopentadienyl anion.[16,228] The ^1H NMR spectroscopic data[16] show the contribution to the structure from the polar forms is minimal as confirmed by calculation.[101]



180, $R^1R^2 = R^3R^4$ = benzo
181, $R^1 = R^2 = R^3 = R^4 = Ph$
182, $R^1 = R^3 = tBu$, $R^2 = R^4 = H$
183, $R^1 = R^2 = R^3 = R^4 = H$

Much more recently the methanoundecapentaenyl moiety has been attached to a 13-membered ring.[32] The synthesis involves the construction of the tridecahexaene ring of **185** from the (acyclic) dicyanoundecafulvene **184**, stability being gained from incorporation of the conjugated diyne moiety (Scheme 40). Fulvalene **185** is a relatively stable black-purple crystalline solid whose NMR characteristics imply no appreciable ring current, and thus it is atropic. Yamamoto and his students had shown ear-



Scheme 40.

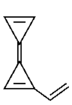
lier[33,229] that the [13.15]fulvalene **186** is a polyolefin and relatively thermally stable. Derivatives of pentapentadeca[5.15]-, heptapentadeca[7.15]-, and heptaheptadeca[7.17]fulvalenes were reported in 1979 but they do not justify discussion here.[230]

Triafulvalenes

Consideration of the simplest but most highly strained fulvalene, triafulvalene (**3**), has been deferred until last as it remains unknown with comparatively few reports directed towards the synthesis of it or its derivatives. Nonetheless, the inclusion of **3**, a C_6H_4 valence bond isomer, in the extensive literature of computational fulvalene chemistry dates to the earliest reports[41,231] with resonance energy and stabilities included in the landmark studies by Hess and Schaad.[42] The orthonormality-constrained procedure for SCF calculations[232] generating localised HF orbitals was successful for **3** and extended further by Moyano and Paniagua.[233] The 1977 Jahn–Teller-based prediction of symmetry reduction[48,87] from D_{2h} to C_{2v} for the anion radical of **5** applies also to **3**, and D_{2h} symmetry is predicted for the for cation radical. The studies have been improved upon quite recently returning more reliable geometrical parameters.[86,213] Large electron correlation and structure dependence on the second order hyperpolarizibility of **3** (up to the Moller–Plesset fourth order) have been predicted[234] and the static third-order hyperpolarizibility[235] computed. In addition, **3** (among a range of fulvalenes) has been included in an examination of π bond contributions to the topological resonance energy; high reactivity is predicted.[122] The electronic properties of the triafulvalenes have been assessed with a view to possible use of the compounds in the synthesis of organic semiconductors.[236]

The more recent theoretical studies have provided a more reliable molecular geometry[45] and the prediction that planar **3** is highly destabilised with localised bonding consistent with Hückel [4*n* + 2] considerations.[44] Reactivity at the central double bond is expected by analogy with the heptafulvalenes and from the computational results. A graph-theoretical study (with PM3 support) of non-alternant hydrocarbons has shown that it is essential to differentiate between even non-alternant bicycles, which have occupied antibonding MOs, and those which have vacant bonding MOs.[52] Triafulvalene (**3**) fits the class of contiguous, nonfused bicycles in which the rings have (4*J*+3) carbon atoms. It should therefore have one occupied antibonding MO, the HOMO, making it a powerful π electron donor. The studies, which includes fulvalene, encompasses a range derivatives of **3**, e. g. 1-vinyl derivative **187**, 1-(1′-buta-1′,3′-dienyl) derivative **188**, and 1-(1′-triafulvalenyl)-triafulvalene derivative **189** (n = 0); derivative **188** is included as it is an isoconjugate nonalternant isomer of fulvalene (**5**). The study has been extended[237] to encompass a range of polymeric (triafulvalenyl)triafulvalenes **189** ($n >$ 0)[238] and PM3 procedures were used to test the kinetic stability predictions for a wide range of (hypothetical) triafulvalene (and other) derivatives such as **190** and **191**.


3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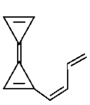
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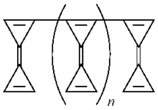
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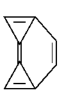
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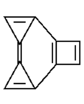
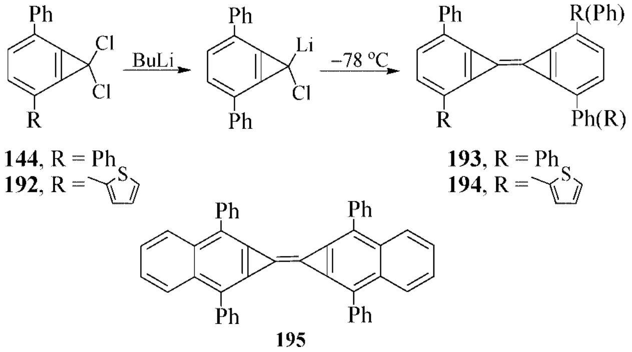
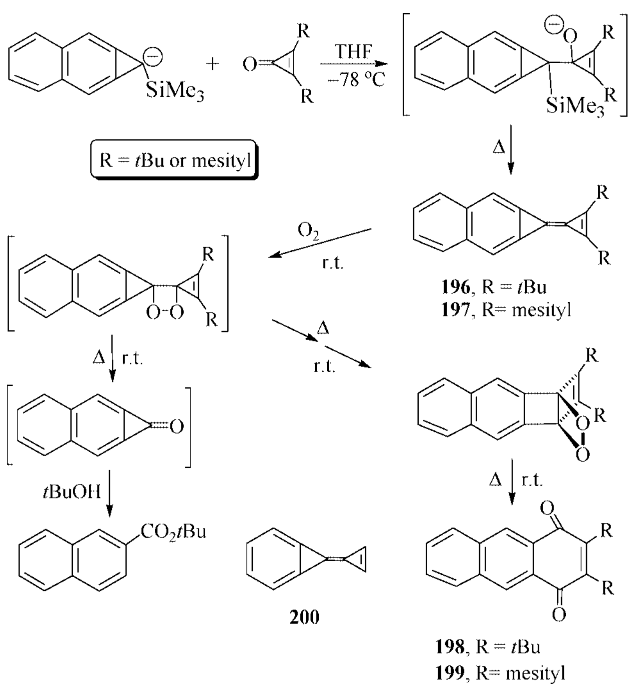

191

The experimental demonstration of triafulvalenes is restricted to three accounts of ring-fused derivatives. The earliest date to 1986 when Neidlein and his students showed[239] that the carbenoid derived from low temperature reaction of the cyclopropabenzene **144** with butyllithium dimerises to the cyclopropabenzenylidene **193** in 23% yield (Scheme 41); the 2-phenyl-5-(2′-thienyl) analogue **192** behaves similarly and gives an *E*/*Z* mixture of isomers **194** (19%). In our laboratories, reaction of the benzo analogue of **144** (the analogous cyclopropa[*b*]naphthalene) provided a deep red material that is both air and light sensitive and, while not characterised, it is presumed to be **195**.[240] In our view, the instability of **195** stems from reduced steric protection of the linking bond by the bulky flanking substituents. In **193** and **194** the substituents should rotate from the plane of the triafulvalene to a lesser extent than occurs for the pendant phenyl groups of **195** because there are no *peri* interactions.



Scheme 41.

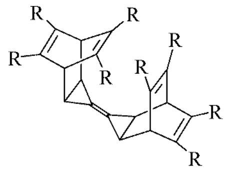
Much more recently, our efforts to provide simpler triafulvalene derivatives have led to the characterisation of **197** (Scheme 42) from Peterson olefination of the (trimethylsilyl)cycloproparenyl anion with 2,3-dimesitylcyclopropenone (cf. Scheme 27). As we have reported,[30] reactions of the anion with di-*tert*-butyl- and (dimesityl)cyclopropenone provide anthracene-1,4-diones **198** and **199** in low yield (Scheme 42), the latter characterised from crystallographic analysis. The formation of these quinones involves the annulated triafulvalenes **196** and **197** since the unstable yellow solid isolated from the (dimesityl)cyclopropenone reaction (that subsequently transformed into **199**) was characterised from its molecular ion at *m*/*z* 412 in the electron impact mass spectrum.[30] Reaction of the electron rich central π bond **196** and **197** with molecular oxygen has analogy to the instability of cyclobutadienes in air[241] and pathways to **198** and **199** have been proposed; *tert*-butyl 2-naphthoate is formed from metathesis of the dioxetane intermediate (Scheme 42). Unknown parent (cyclopropenylidene)cyclopropabenzene (**200**) has been the subject of detailed theoret-



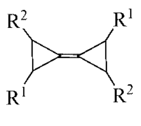
Scheme 42.

ical examination that predicts electron donation *from* the three-membered cyclopropene moiety *to* the cycloproparene core; the stability is expected to be lower than that of (methylidene)cyclopropabenzene, the triafulvene homologue.[152] The naphtho-fused triafulvenes **196** and **197** are the simplest derivatives of **3** known. It seems to us that kinetic stabilisation requires appropriately large groups to block access to the central π bond before a simpler derivative can be isolated.[30]

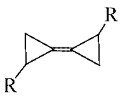
It is not surprising that Neuenschwander has also addressed **3**. In a series of four papers[242–244] a range of potential building blocks for ultimate triafulvalene formation were described. Not one of these compounds has provided **3**, but then the potential of most has not been examined fully. Thus the series of bicyclopropenylidenes **201**–**203** were prepared by carbenoid dimerisation (from the appropriate *gem*-dibromocyclopropane and BuLi in the presence of $CuCl_2$).[244] The bis(bicyclooctadienyl)-fused bicyclopropenylidenes **201** appear to be ideal substrates for retro-Diels–Alder cleavage but, as yet, neither has been successfully thermolyzed.[243] It seems FVT with matrix isolation of the products is more than worthwhile investigating. The bis(disilyl) substituted **202** carrying phenylsulfonyl groups failed to give **3** on treatment with fluoride ion even though it was regarded as potentially more useful than the dibenzyl ether analogue. The range of simple disubstituted derivatives includes the bicyclopropenylidenes **203**, of which the diacetate and dibromide were regarded as the most promising;[242,244] detailed examination of these compounds targeting low temperature isolation and/or trapping of **3** appears justified.



201, R =H or
RR = benzo fused



202, R^1 = $SiMe_3$, R^2 = $PhSO_2$
or R^1R^2 = $–CH_2OCMe_2OCH_2–$



203, R = OBn, CO_2H, CO_2Me, CO_2iPr, CO_2tBu,
CO_2Bn, CH_2OCMe_2OMe, AcO, $–H=CH_2$, or Br

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