

## NEW ASPECTS OF THE CHEMISTRY OF NONBENZENOID POLYCYCLIC CONJUGATED $\pi$ -ELECTRON SYSTEMS

Klaus Hafner

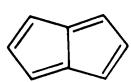
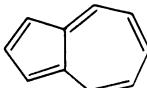
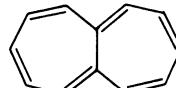
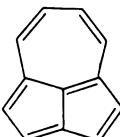
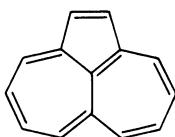
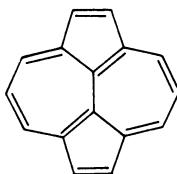
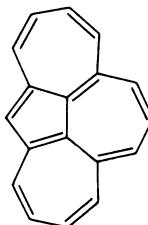
Institut für Organische Chemie der Technischen Hochschule  
Darmstadt, Germany

**Abstract** - Nonbenzenoid polycyclic conjugated  $\pi$ -electron systems proved to be exceptional model compounds for testing theoretical predictions and provide interesting information on the relation between electronic structure and physical as well as chemical properties. The continuing need for additional examples of different nonbenzenoid polycyclic  $\pi$ -electron systems has stimulated the synthesis of new building blocks as well as the development of new synthetic methods. These in turn led to the preparation of highly reactive pentafulvenoid chloroform-amidinium salts and 6-chloropentafulvenes which open an easy access to stabilized s-indacenes, 2-azapentalenes and 5-aza-azulenes besides other ring systems. The first isolable s-indacenes provide an opportunity to study the influence of substituents on the bonding character of the  $12\pi$ -electron system. Different cycloaddition reactions turned out to be a versatile method for annelations and homologizations of nonbenzenoid polycyclic conjugated systems. In the pursuit of this strategy azulenes could be transformed into pentalenes, heptalenes as well as cyclopentacyclononenes.

### INTRODUCTION

The coincidence of the 4th Symposium on the Chemistry of Novel Aromatic Compounds with the 50th anniversary of Hückel's famous molecular orbital theory of benzene (Ref. 1) reflects the strong and still continuing impact of this fundamental theory, expressed by the  $(4n+2)$ -rule, on the development of aromatic chemistry. The most fruitful pioneering work of Hückel confirms the saying of Boltzmann that "nothing else will be more practical than a theory". The tremendous stimulation of organic chemistry by Hückel's theory manifests itself impressively in the discovery of a vast number of novel aromatic and antiaromatic structures, most of them brought to light in the last three decades. Many of these turned out to be valuable model compounds for the experimental elucidation of the principles governing the relation between structure and reactivity of carbo- and heterocyclic conjugated  $\pi$ -electron systems. The same compounds also proved to be useful touchstones for the evaluation of quantum chemical calculations.

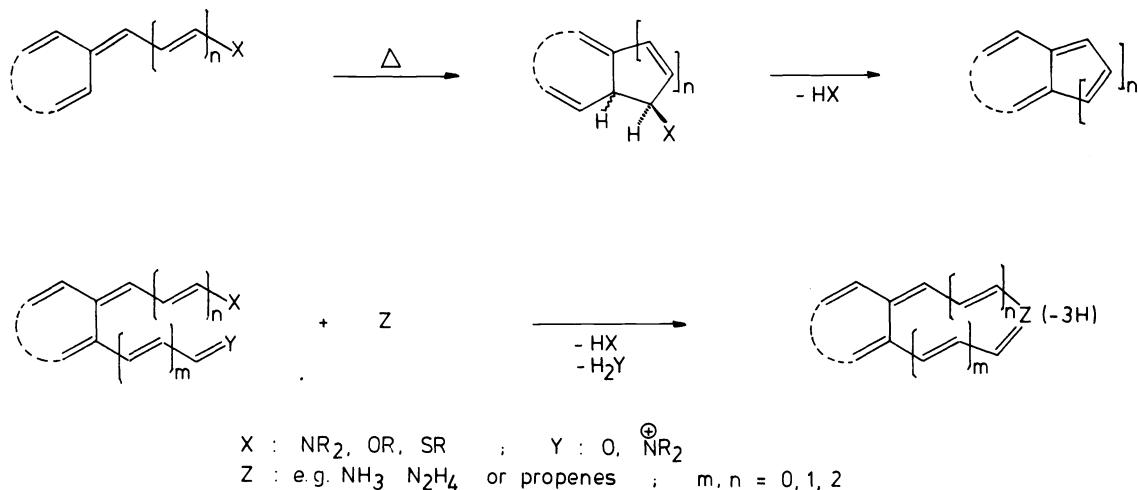
Important aspects of these studies have been the examinations of annulenes (Ref. 2) containing larger and smaller Hückel systems than benzene as well as numerous nonbenzenoid bi- and polycyclic conjugated  $\pi$ -electron systems (Ref. 3). These include the bicycloannulenes pentalene (1) (Ref. 4), azulene (2) (Ref. 5), and heptalene (3) (Ref. 6) as well as several of their tri-

12345678

and tetracyclic derivatives, e.g., the hydrocarbons 4 - 8 (Ref. 7). Some of these ring systems show rather unusual and partly unexpected chemical and physical properties for hydrocarbons, as revealed recently. Pentalene (1) and several of its methylated derivatives e.g. show a surprisingly strong tendency for dimerization even below -100°C (Ref. 4). The activation energy for the isodynamic double-bond shift of the thermally stable 1,3,5-tri-t-butyl-pentale (Ref. 8) of about 4 kcal·mol<sup>-1</sup> characterize this molecule - like cyclobutadiene (Ref. 9) - as a borderline case between an antiaromatic species and a cyclopolyolefine (Ref. 10). Yet as another example the tetracyclic azuleno[8,8a,1,2-def]heptalene (8) exhibits an unusual high basicity unique for a hydrocarbon as indicated by its facile transformation into the conjugated acid even by 0.01 N acetic acid (Ref. 3a). The striking spectroscopic properties of this system led to the postulation of aromatic and antiaromatic portions in this molecule at the same time, which points to the limits of common criteria or definitions for aromaticity (Ref. 11).

Cross-conjugated structural elements are common features to all of these hydrocarbons. This leads - contrary to the monocyclic annulenes - sometimes to a branching of the π-electron systems and complicates efforts to establish general rules for a classification of such compounds into aromatic, nonaromatic or even antiaromatic systems. The PMO method allows an extension of Hückel's rule to certain polycyclic systems, as Dewar (Ref. 12) showed. It seemed, however, advisable for a better understanding of the relation between structure, bond character and reactivity of polycyclic compounds to synthesize a representative group of different polycycles and to study their properties.

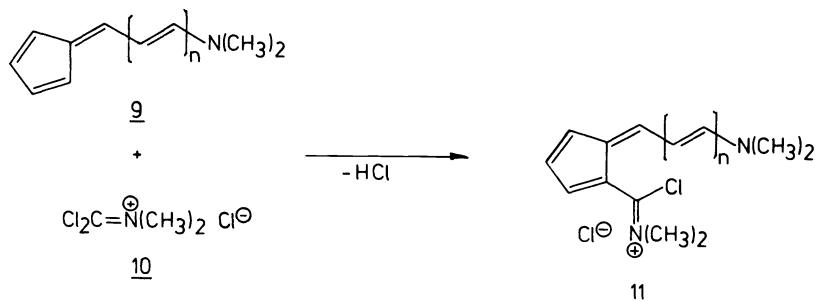
For the synthesis of numerous nonbenzenoid polycyclic conjugated π-electron systems in our laboratory electrocyclic reactions (Ref. 3) as well as



cyclizing condensations (Ref. 3, 13) of mono- or polycyclic pentafulvenoid compounds proved to be general principles. They allow the annelation of 5- or 7-membered rings to an existing polycycle. In spite of the broad applicability of these methods, several nonbenzenoid polycyclic conjugated  $\pi$ -electron systems are inaccessible by these synthetic routes. Either the required starting materials are not available or the intermediates lack stability under the conditions of the mostly thermal induced ring closure reactions. This, in turn, has made necessary the development of better synthetic methods to provide access to several new molecules of theoretical interest. In a search for synthetic alternatives, cyclizing condensation reactions of some new pentafulvene derivatives as well as cycloaddition reactions of several mono- and polycyclic  $\pi$ -electron systems proved to be suitable for the synthesis of so far difficult accessible or even unknown ring systems. It is with some of these aspects that the following discussion is concerned.

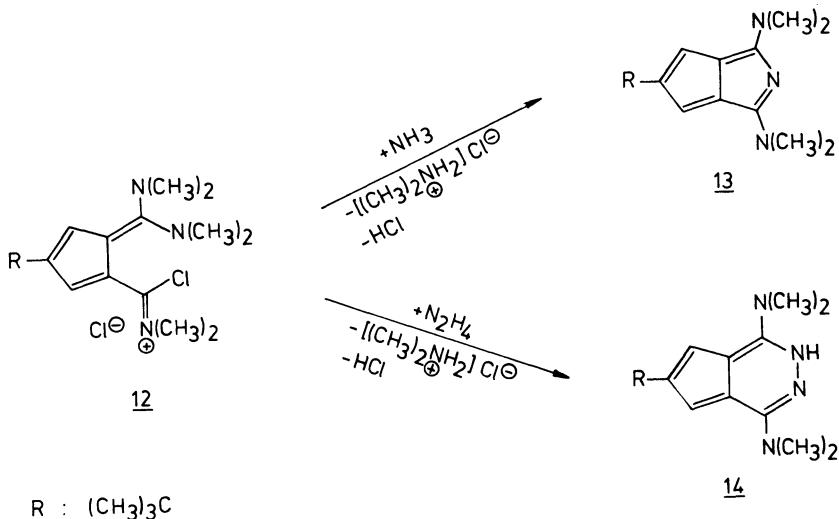
#### CYCLIZING CONDENSATION REACTIONS OF PENTAFULVENES

The approach mentioned at first is based on a surprisingly facile generation of so far unknown highly reactive pentafulvenoid synthons by acylation of 6-dialkylaminopentafulvenes 9 or their vinyllogues with dimethyldichloromethyleniminium chloride (10) (Ref. 14). By this reaction the pentafulvenoid chloroformamidinium chlorides 11 are formed, which display a pronounced reactivity towards a variety of nucleophilic compounds (Ref. 15).

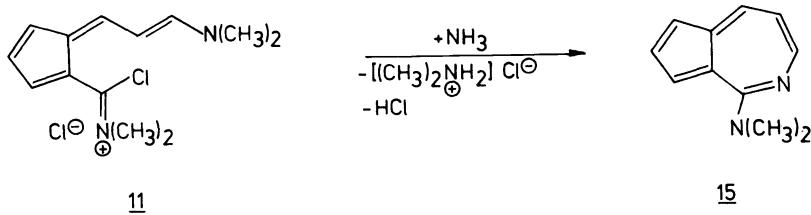


$$n = 0, 1$$

With suitable nucleophiles these 1,4- or 1,6-bifunctional pentafulvenes react via cyclization. This allows the annelation of one or more 5-, 6- or even 7-membered rings to the cross-conjugated systems. Thus 3-t-butyl-6,6-bis-(dimethylamino)pentafulvenyl-1-dimethylchloroformiminium chloride (12) reacts with ammonia already at  $0^\circ C$  to give the blue-violet 5-t-butyl derivative 13 of the parent compound, 1,3-bis(dimethylamino)-2-azapentalene, which has already been synthesized by a different route several years ago (Ref. 16).



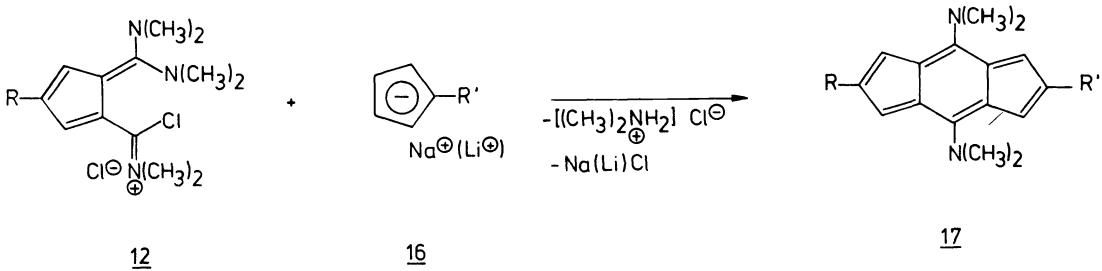
With hydrazine the green 6-t-butyl-1,4-bis(dimethylamino)-2H-cyclopenta[d]-pyridazine (14) is formed from 12, while the vinylogous pentafulvenoid chloroformamidinium chloride 11 ( $n=1$ ) yields, upon treatment with ammonia,



under similar reaction conditions the red 4-dimethylamino-5-azaazulene (15) (Ref. 15).

The synthetic potential of cyclizing condensations of these new pentafulvenes is not limited to the annelation of 5-, 6- or 7-membered heterocycles. They also open an easy access to carbocyclic systems, e.g., s-indacene, a perturbed [12]annulene, which is closely related to pentalene (1).

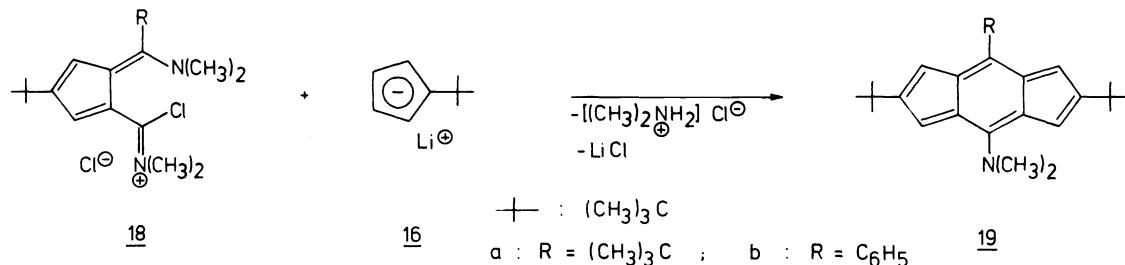
As it turned out, the pentafulvenoid chloroformamidinium chlorides 12 react also with sodium or lithium cyclopentadienides 16 by a twofold condensation, which enabled us for the first time to synthesize the stable derivatives 17 of the elusive s-indacene (Ref. 3b, 17). Surprisingly enough, the 4,8-bis-(dimethylamino)-s-indacenes 17 obtained by this route as beautiful crystalline green or yellow compounds with yields up to 50 %, proved to be perfectly stable towards heat and air, even after prolonged periods of exposure (Ref. 15, 18). Obviously the two dimethylamino groups in positions of lowest electron density (Ref. 19) stabilize considerably the  $12\pi$ -electron system.



a :  $R = R' = H$  ;      b :  $R = (CH_3)_3C$  ;  $R' = H$  ;      c :  $R = R' = (CH_3)_3C$

to an extent which is comparable to the stabilization of the  $8\pi$ -electron systems of pentalene (1) and its 2-aza derivative in the corresponding 1,3-bis(dimethylamino) derivatives 13 ( $R=H$ ,  $t\text{-Bu}$ ) and 2o synthesized several years ago (Ref. 16, 2o).

Contrary to this, the chemical stability of the monoamino-s-indacenes 19 is remarkably reduced compared with that of the 4,8-bis(dimethylamino) derivatives 17. The 8-dimethylamino-s-indacenes 19 are obtained by cyclizing



condensation of 3,6-di-*t*-butyl- or 3-*t*-butyl-6-phenyl-6-dimethylaminopentafulvenyl-1-dimethylchloroformiminium chloride 18 with lithium *t*-butylcyclopentadienide (16) as air-sensitive red needles (Ref. 18).

In accordance with these findings, the results of x-ray analyses of 1,3-bis(dimethylamino)pentalene (2o), the 2-aza derivative 13 ( $R=t\text{-Bu}$ ), the 4,8-bis(dimethylamino)-s-indacene 17c, and the 8-dimethylamino-s-indacene 19a reflect striking differences in the electronic structures of these systems (Ref. 21). While 5-*t*-butyl-1,3-bis(dimethylamino)-2-azapentalene (13) exhibits localized bonds of the bicyclic  $8\pi$ -electron system (Fig. 1),

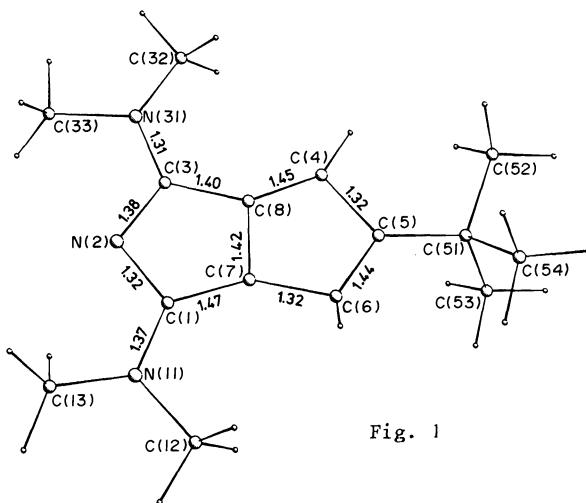


Fig. 1

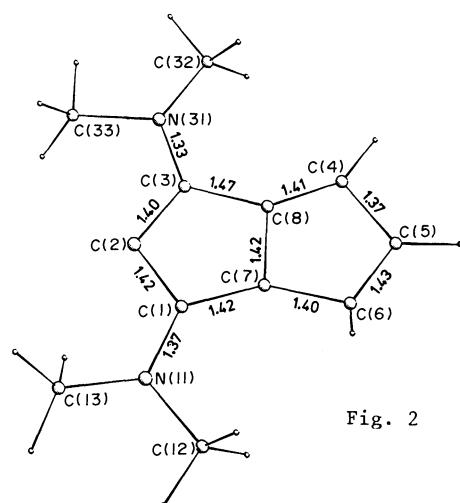
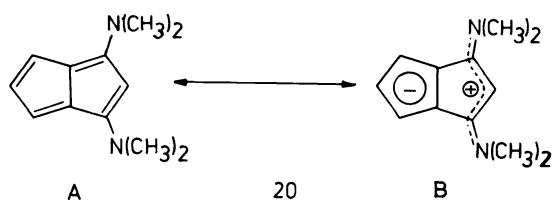


Fig. 2

Figure 1. Molecular geometry of 5-*t*-butyl-1,3-bis(dimethylamino)-2-azapentalene (13).

Figure 2. Molecular geometry of 1,3-bis(dimethylamino)pentalene (2o).

Preliminary data for the bond length of 1,3-bis(dimethylamino)pentalene (2o) (Fig. 2) suggest that this system should be described by the dipolar structure 2oB with an equilibration of bond length. This can be rationalized by the perturbation of the  $\pi$ -system by the nitrogen in 2-position of 13,



which stabilizes the localized pentalene structure and destabilizes a dipolar structure with a cyclopentadienide moiety. A similar influence of dimethylamino groups on the perimeter is observed in the s-indacene system. Two dimethylamino groups in 4- and 8-position effect a delocalization in the perimeter (Fig. 3), whereas only one dimethylamino group in one of these

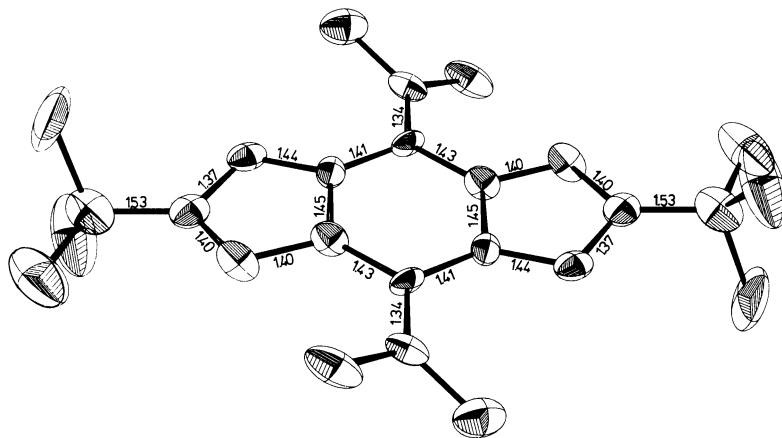


Figure 3. Molecular geometry of 2,6-di-t-butyl-4,8-bis(dimethylamino)-s-indacene (17c).

positions as in 2,4,6-tri-t-butyl-8-dimethylamino-s-indacene (19a) leads to a structure with bond fixation showing fulvenoid moieties (Fig. 4).

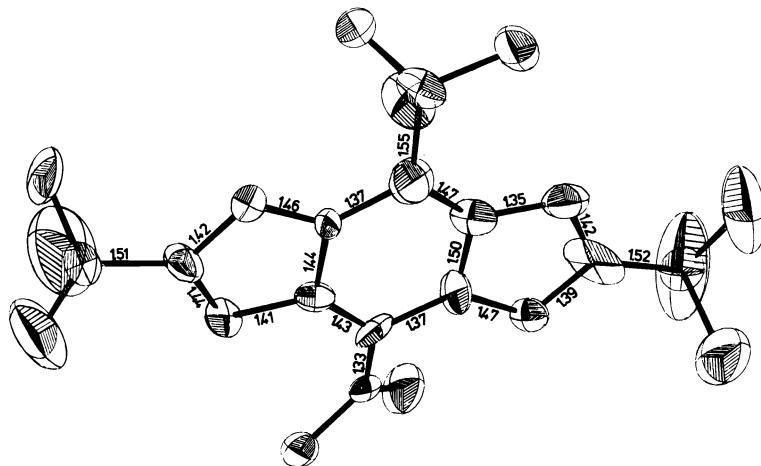
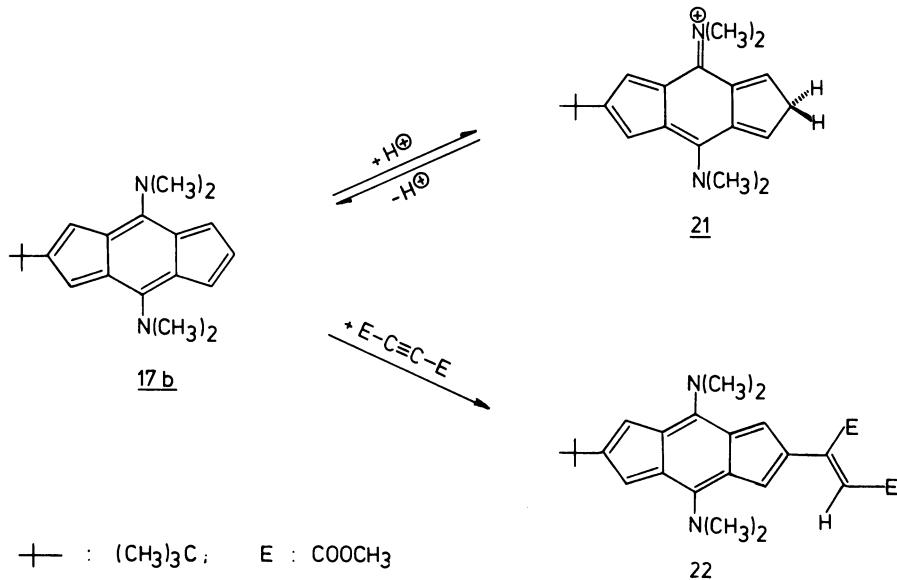


Figure 4. Molecular geometry of 2,4,6-tri-t-butyl-8-dimethylamino-s-indacene (19a).

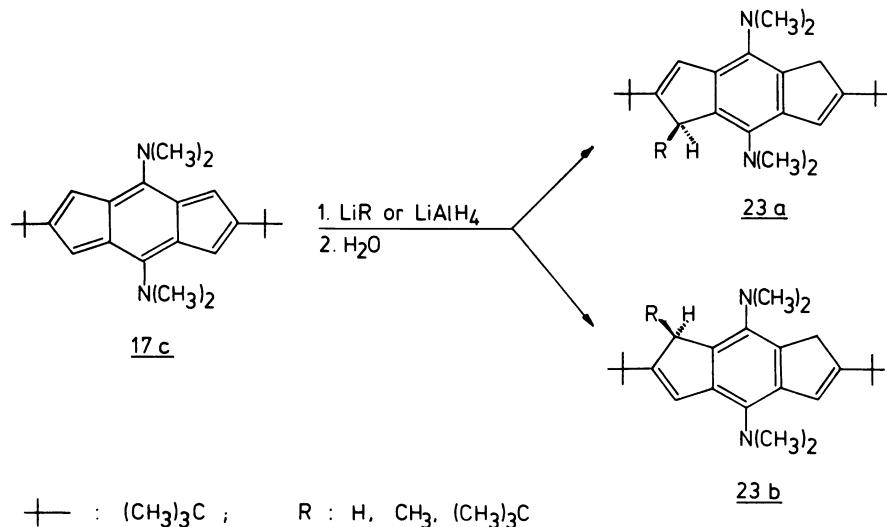
These findings show clearly that electron-donating substituents exert an important influence on the bonding nature of  $4n$   $\pi$ -electron systems. Quantum chemical calculations by means of MINDO/3 and MNDO on pentalene and s-indacene have shown a stabilization of the delocalized structures in the case of substitution by two dimethylamino groups. The same trend has been observed in the case of electron-withdrawing substituents. The theoretical background is similar in both examples as the two substitution patterns result into a transition to aromatic ( $4n+2$ )  $\pi$ -electron systems. In the unsubstituted s-indacene the aforementioned semiempirical MO calculations predicted energy differences between the localized and delocalized structure of about 8–10 kcal·mol<sup>-1</sup>. Substitution by two dimethylamino groups in any case leads to the delocalized structure. Theoretical findings in the pentalene series are in agreement with those of the s-indacene series (Ref. 22).

The difference in the bonding character of the  $12\pi$ -electron systems of s-indacene and its 4,8-bis(dimethylamino) derivatives 17 as borne out by quantum chemical data manifests itself just as impressively in the chemistry of these compounds. Chemically these tricyclic systems differ most markedly in their behavior towards electrophilic reagents, in particular with proton acids. While e.g., 2-t-butyl-4,8-bis(dimethylamino)-s-indacene (17b) can be reversibly protonated in 6-position by formation of the conjugated acid 21, the parent hydrocarbon decomposes immediately, even at low temperatures and in high dilution. Furthermore 17b reacts in contrast to s-indacene with



dimethyl acetylenedicarboxylate to the dimethyl 3-t-butyl-4,8-bis(dimethylamino)-s-indacene-6-yl maleate (22) (Ref. 18).

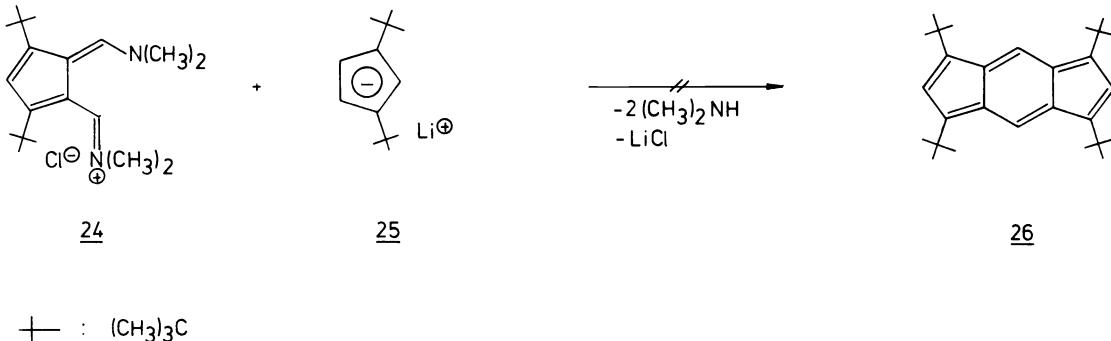
On the other hand 17c reacts with strong nucleophiles, as lithium aluminum hydride or lithium alkyls by addition to form the corresponding 1,5- and 1,7-dihydro-s-indacenes 23a and b in a 1:1 ratio, whereas it is inert towards weaker nucleophiles as sodium hydroxide or piperidine. Obviously the driving



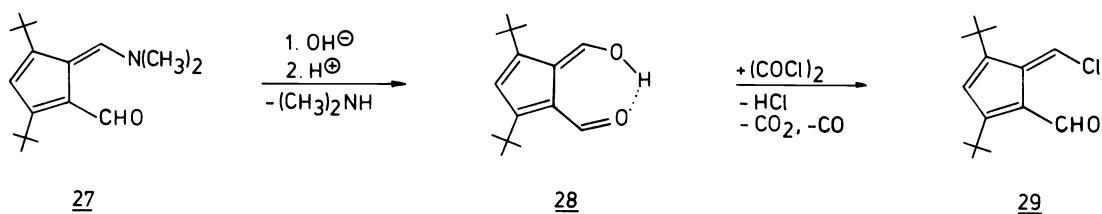
force for the addition reactions is the conversion of the tricyclic p-quinoid system 17c into the benzenoid structure of 23 (Ref. 18).

These findings challenged us to tackle next the more demanding synthesis of s-indacenes without strong electron-donating substituents to learn more about the electronic structure and chemical properties of the parent tricyclic  $12\pi$ -electron system. As our efforts to isolate the thermally extremely unstable parent hydrocarbon have so far not met with success, it was our aim to synthesize simple alkyl derivatives. Quantum chemical calculations have shown that the energy difference between the localized and delocalized structure of s-indacene can also be reduced due to alkyl groups in positions of low electron density (Ref. 22). Furthermore the  $12\pi$ -perimeter should be protected by means of bulky alkyl groups. As expected, again it proved most advantageous to stabilize the s-indacene molecule by introduction of t-butyl groups.

First attempts, however, to construct the 1,3,5,7-tetra-*t*-butyl-1-s-indacene (26) by cyclizing condensation of 2,4-di-*t*-butyl-6-dimethylaminopentafulvenyl-1-dimethylaldiminium chloride (24) (Ref. 18) with lithium 1,3-di-*t*-butylcyclopentadienide (25) (Ref. 23) took a disenchanted course. Even at elevated



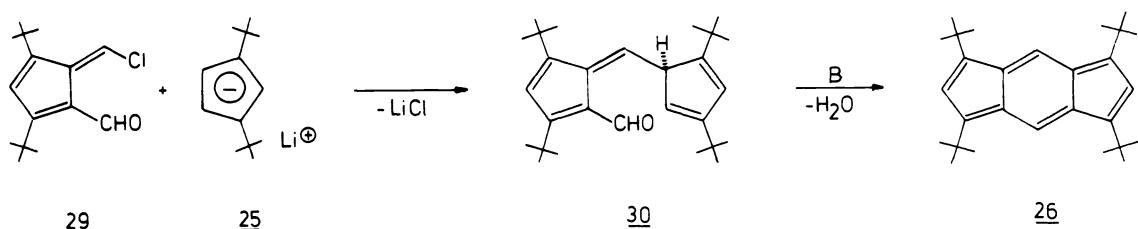
temperatures the desired ring closure reaction could not be achieved. Apparently the pentafulvenoid starting material lacks the desired reactivity due to the resonance stabilization of its vinylogous amidinium salt moiety. To overcome this difficulty it seemed promising to transform the 6-aminopentafulvene-1-aldiminium salt 24 into a more reactive species, e.g., a pentafulvene with a vinylogous acid chloride moiety. Like 6-chloropentafulvene, already prepared in very low yields (3-10%) as a thermally unstable and air-sensitive compound by Bergman et al. (Ref. 24) and just recently by Neuenschwander et al. (Ref. 25), 6-chloropentafulvene-1-carbaldehydes should exhibit a similar or even excel the former in reactivity towards nucleophiles. In order to prove this assumption, we hydrolysed 2,4-di-t-butyl-6-dimethylaminopentafulvene-1-carbaldehyde (27) to the corresponding yellow crystalline 6-hydroxypentafulvene-



$$+ : (\text{CH}_3)_3\text{C}$$

1-carbaldehyde 28 and reacted the latter with oxalyl chloride. By this route the desired 2,4-di-*t*-butyl-6-chloropentafulvene-1-carbaldehyde (29) is obtained as a highly reactive orange oil in about 70 % yield. In the meantime the reaction of 6-hydroxypentafulvenes with oxalyl chloride, oxalyl bromide or with phosgene turned out to be a general procedure for the preparation of 6-chloro- or 6-bromopentafulvenes, which display a pronounced tendency for substitution reactions even with weak nucleophiles (Ref. 18).

As expected, 2,4-di-*t*-butyl-6-chloropentafulvene-1-carbaldehyde (29) reacts with lithium 1,3-di-*t*-butylcyclopentadienide (25), probably via the unstable intermediate 30 (or tautomers), to the desired 1,3,5,7-tetra-*t*-butyl-s-



$\text{---} \text{+} \text{---} : (\text{CH}_3)_3\text{C}$

indacene (26), which could be isolated as red needles in a 30 % yield (Ref. 18).

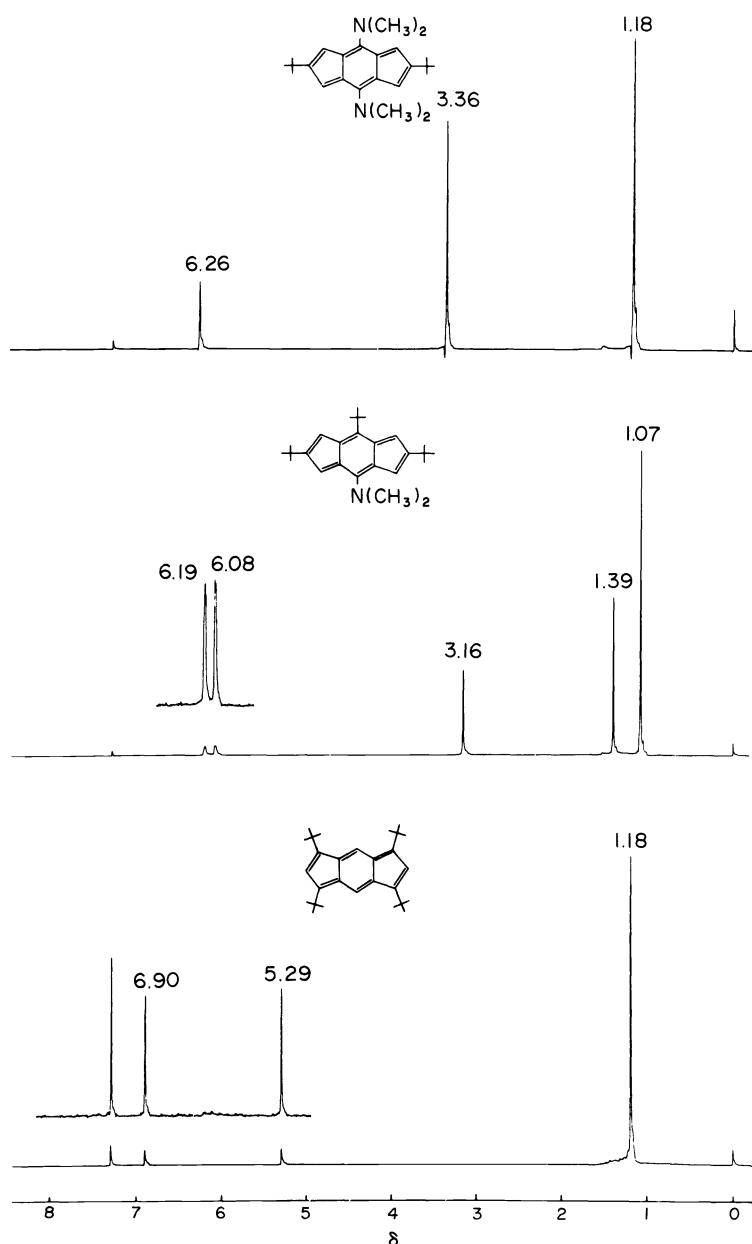


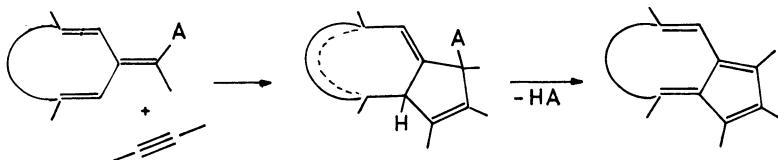
Figure 5. The n.m.r. spectra of 2,6-di-t-butyl-4,8-bis(dimethylamino)-s-indacene (17c), 2,4,6-tri-t-butyl-8-dimethylamino-s-indacene (19a), and 1,3,5,7-tetra-t-butyl-s-indacene (26) (in  $\text{CDCl}_3$ ; 100 MHz).

In striking contrast to 4,8-bis(dimethylamino)-*s*-indacenes 17 the new tetraalkyl-*s*-indacene 26 turned out to be a highly reactive polyolefine, reminiscent in its chemical behavior of pentafulvene and related substances, but due to the steric influence of the four bulky *t*-butyl groups less reactive than the unsubstituted *s*-indacene. The olefinic nature of the isolated tetraalkyl-*s*-indacene 26, indicated by its thermal instability and sensitivity towards proton acids, air and light is just equally borne out by its spectra, especially by its simple n.m.r. spectrum in comparison with those of the delocalized bis(dimethylamino)-*s*-indacene 17c and the mono-dimethylamino derivative 19 (Fig. 5). The signals of the 5-membered ring protons of 26 are significantly shifted to higher field as those of 17 and 19, due to a localized bond structure or even a small induced paramagnetic ring current in the tetraalkyl-*s*-indacene 26.

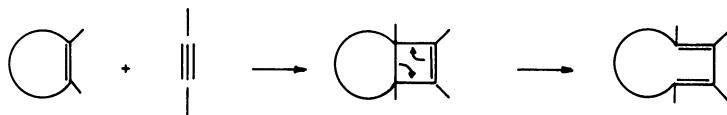
#### CYCLOADDITION REACTIONS OF AZULENES

The second above mentioned unexpected facile entry to new or so far difficult accessible nonbenzenoid cyclic conjugated  $\pi$ -electron systems are cycloaddition reactions. They allow either an annelation of a further 5- or 7-membered ring by [2+X]-cycloaddition and subsequent 1,γ-elimination or a homologization of a cyclopolyolefine by a [2+2]-cycloaddition with an activated alkyne or corresponding equivalents and subsequent valence isomerization of the primary formed adduct to the homologues ring system as shown

#### ANNELATION

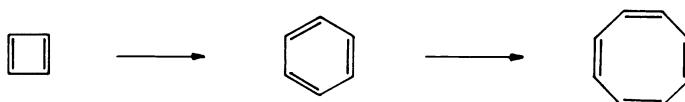


#### HOMOLOGIZATION

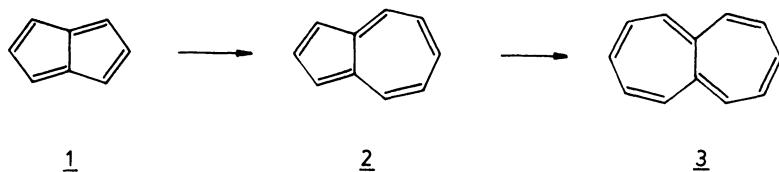


in the general scheme. About the synthetic potential of the annelation reactions, e.g., for the construction of pentalenes from pentafulvenes (Ref. 26) or of dicyclopent[ef,kl]heptalene (7) from aceheptylene (5) (Ref. 7, 27) as well as of penta- and hexacyclic conjugated hydrocarbons (Ref. 7), we have already reported. Doering et al. (Ref. 28), Houk et al. (Ref. 29), Leaver et al. (Ref. 30), and Sato et al. (Ref. 31) used this strategy for elegant syntheses of azulenes.

By the homologization method the simplest annulene, cyclobutadiene, could be transformed thermally into a benzene derivative (Ref. 32) and the classical aromatic compound photochemically induced into the next higher homologue,



cyclooctatetraene (Ref. 33). A similar transformation is feasible in the homologues series of the simplest bicycloannulenes, pentalene (1), azulene (2), and heptalene (3), as we showed recently (Ref. 6b).

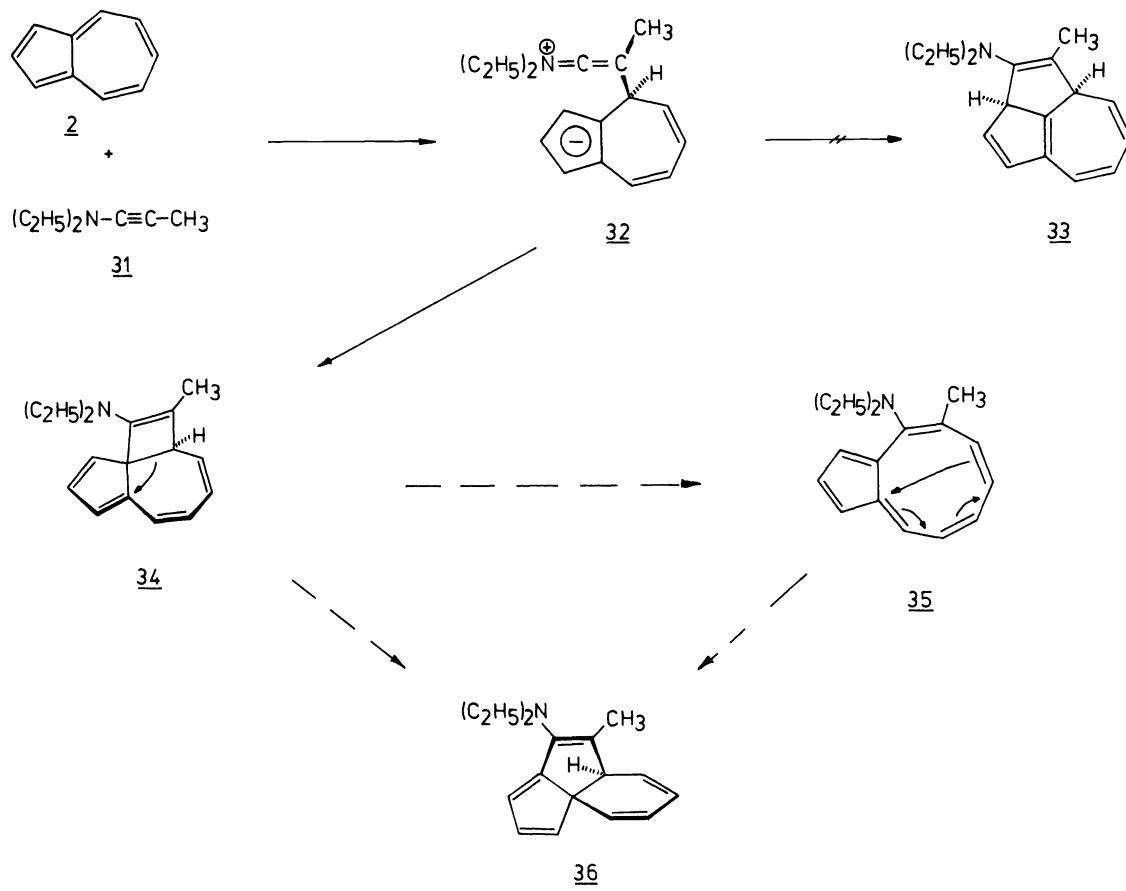


Among the homologization reactions of bicyclic hydrocarbons the transformation of azulene and a variety of its alkyl derivatives with dimethyl acetylenedicarboxylate into the corresponding dimethyl 1,2- as well as 2,3-heptalene-dicarboxylates is of particular interest. This method offers for the first time a general, rational and most simple synthesis for a great number of substituted heptalenes in yields up to 65 % (Ref. 6b, 34). This azulene homologization route to heptalenes together with the elegant but multistep syntheses for the parent hydrocarbon by Dauben, Jr. et al. (Ref. 6a), Vogel et al. (Ref. 6a), and Paquette et al. (Ref. 6a) now permit a detailed study of the bicyclic  $12\pi$ -electron system 3.

After having obtained these results it was of particular interest to study reactions of azulene with electron-rich alkynes e.g., 1-diethylaminopropyne (31) in order to achieve a peri-annelation or a homologization of the 7-membered ring.

In the following I would like to outline some of the progress which has recently been accomplished in this area of cycloaddition reactions in our laboratory.

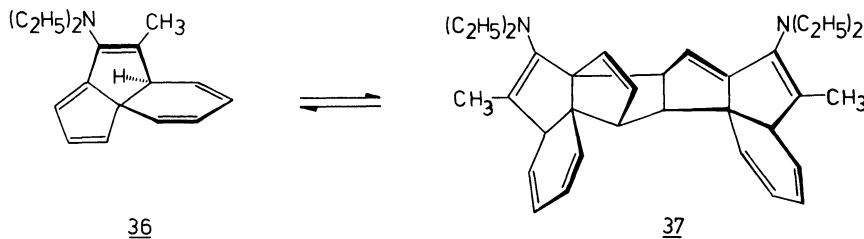
As with other nucleophiles, a primary attack of the ynamine 31 at the position of lowest electron density of azulene (2) should lead to the dipolar intermediate 32 which could stabilize itself by annelation to the tricyclic



adduct 33 or by a formal [2+2]-cycloaddition to the cyclobutene derivative 34. Its valence isomerization should produce the hitherto unknown cyclopentacyclononene system 35.

Contrary to our expectation the experimental examination of the reaction of azulene and several of its derivatives with the ynamine 31 furnished however rather remarkable results.

Surprisingly, azulene (2) and the ynamine 31 react within several days even at room temperature to a thermally stable colorless crystalline 1:1-adduct in 83 % yield. The structure of the product could be established by <sup>1</sup>H- and <sup>13</sup>C-n.m.r. spectra as well as an x-ray analysis as that of 3-diethylamino-

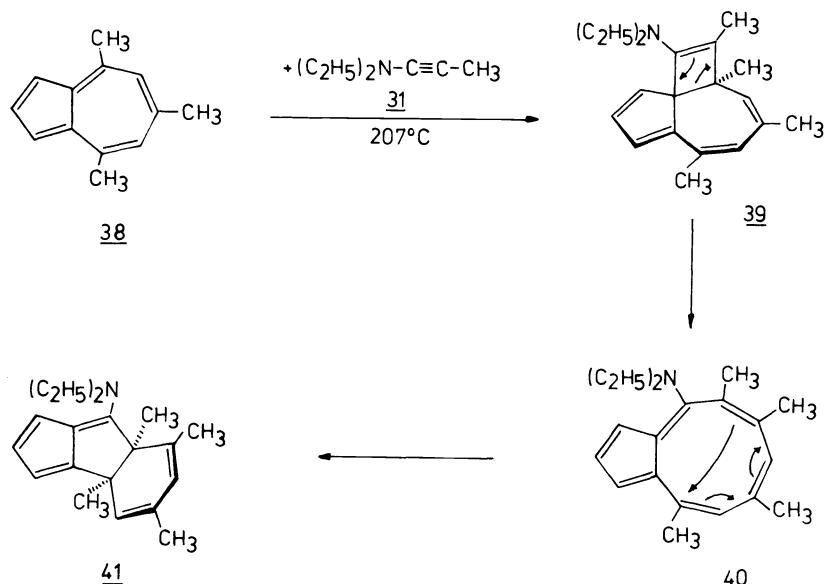


5-methyl-5a,9a-dihydrocyclopent[c]indene (36), which exist as dimer 37 in the crystal and as the monomer 36 in solution. The dimer is formed by a [4+2]-cycloaddition of the cyclopentadiene moiety whereas a rapid retro-Diels-Alder reaction occurs in solution, indicating a low activation energy (less than 25 kcal·mol<sup>-1</sup>) for the dimerization of the spiroadduct 36 as well as for the cycloreversion of its dimer. At elevated temperatures or in the presence of proton acids already at 25 °C the spiroadduct 36 smoothly isomerize to dihydrocyclopent[cd]azulene derivatives (Ref. 35).

Although a final experimentally proven explanation for the formation of the bridged spiro[4.5]decatetraene 36 is still missing, probably the expected primary adduct 34 is involved. This contains the structural unit of the spiro-[3.4]octa-1,5,7-triene, which has been shown by Miller et al. (Ref. 36) to resist isolation at -10°C, partly due to a presumed [1,5]sigmatropic ring expansion to form a dihydropentalene. An analogous rearrangement of the 1,3-diene-bridged derivative 34 could lead to 36. Due to theoretical considerations more probable however a valence isomerization of the cyclobutene derivative 34 to the cyclopentacyclononene 35 and subsequent electrocyclic 6π-electron reaction to the isolated adduct 36 - characteristic for cyclo-nonatetraene derivatives (Ref. 37) - has to be expected. Cycloaddition reactions of azulenes with electron-rich or electron-deficient alkynes as well as valence isomerizations of the first formed adducts can be rationalized on the basis of frontier orbital arguments and MO calculations. The observed product distributions can be explained by means of modifications of the frontier orbitals as well as the charge distribution in the cycloaddition partners (Ref. 22, 34).

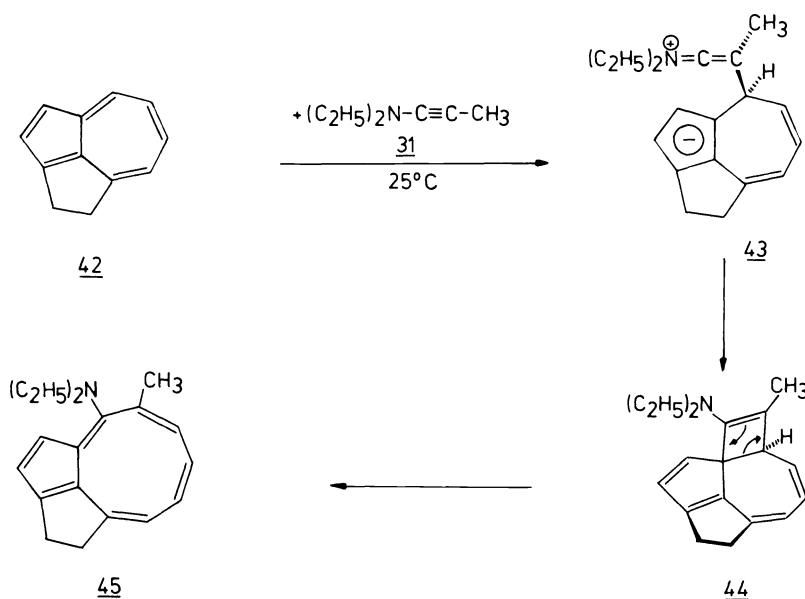
In accordance with this, substituents at the azulene system have a pronounced influence on the rate of the cycloaddition with the ynamine 31 as well as on the subsequent rearrangement reactions of the first formed adducts.

In contrast to azulene (2), e.g., its 4,6,8-trimethyl derivative 38 reacts with the ynamine 31 only at elevated temperatures, obviously due to a steric hinderance of a cycloaddition reaction by the alkyl groups in 4- and 8-position. The major product formed by reaction in boiling tetraline was



found to be the 8-diethylamino-3b,5,7,7a-tetramethyl-3b,7a-dihydrocyclopent-[a]indene (41), containing a resonance stabilized 6-aminopentafulvene moiety. The structure of 41 was established by n.m.r. spectra as well as an x-ray analysis (Ref. 38). Probably also this thermally induced cycloaddition reaction involves the primary adduct 39. Subsequent valence isomerizations via the unstable cyclopentacyclononene system 40 ultimately will lead to the isolated tricyclic system 41 (Ref. 35). The different route of the valence isomerization of the 9-membered ring compared to that of the reaction of azulene (2) with the ynamine is in agreement with MO calculations. Four alkyl groups in the 9-membered ring lead to a significant charge reorganization in this moiety (Ref. 22, 34).

These results prompted a study of cycloaddition reactions of the ynamine 31 with azulenes bearing substituents which hinder or rule out a valence isomerization of the 9-membered ring in the probably first formed cyclopentacyclononene system. Inspection of models suggested that the readily accessible 1,2-dihydrocyclopent[cd]azulene (42) (Ref. 7) should be particularly suitable for this purpose. It was anticipated that the cyclopentacyclononene derivative 45 possibly formed by the reaction of 42 with the ynamine 31 would resist further valence isomerization, as this should lead to an intermediate with a nearly planarized central  $sp^3$ -C-atom.



That these considerations do come quite close to reality is impressively demonstrated by our recent efforts to synthesize the cyclopentacyclononene system 45. As already reported (Ref. 39), the bridged azulene 42 reacts with the ynamine 31 like azulene (2) already at room temperature probably via 43 and 44 to 43 % of the desired 1,10-ethano-4-diethylamino-5-methylcyclopentacyclononene (45), which is obtained as brilliant reddish-brown crystals. This is the first cyclononatetraene derivative not stabilized by benzo-annelation, which proved to be perfectly stable towards heat, air and proton acids. The structure convincingly borne out by its n.m.r. spectra and other spectral data was also confirmed by an x-ray analysis (Fig. 6) (Ref. 39, 40). The  $12\pi$ -electron system consists of a nearly planar 6-aminopentafulvene moiety with bond length typical for this system (Ref. 41) and a non-planar polyene system in the 9-membered ring with double-bond fixation and high torsion angles of the single bonds ( $53-93^\circ$ ).

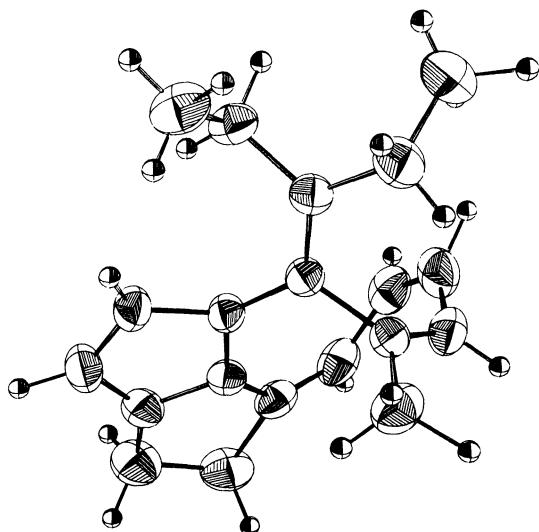
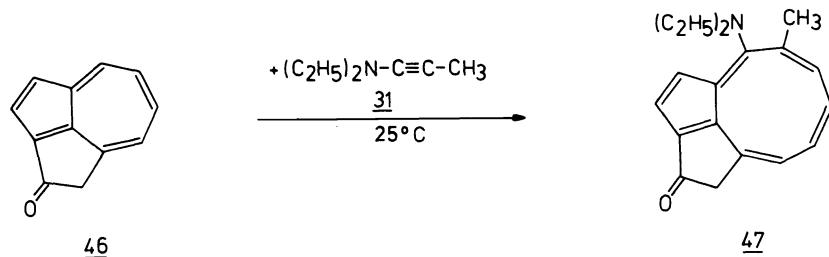


Figure 6. Molecular geometry of 1,10-ethano-4-diethylamino-5-methylcyclopentacyclononene (45).

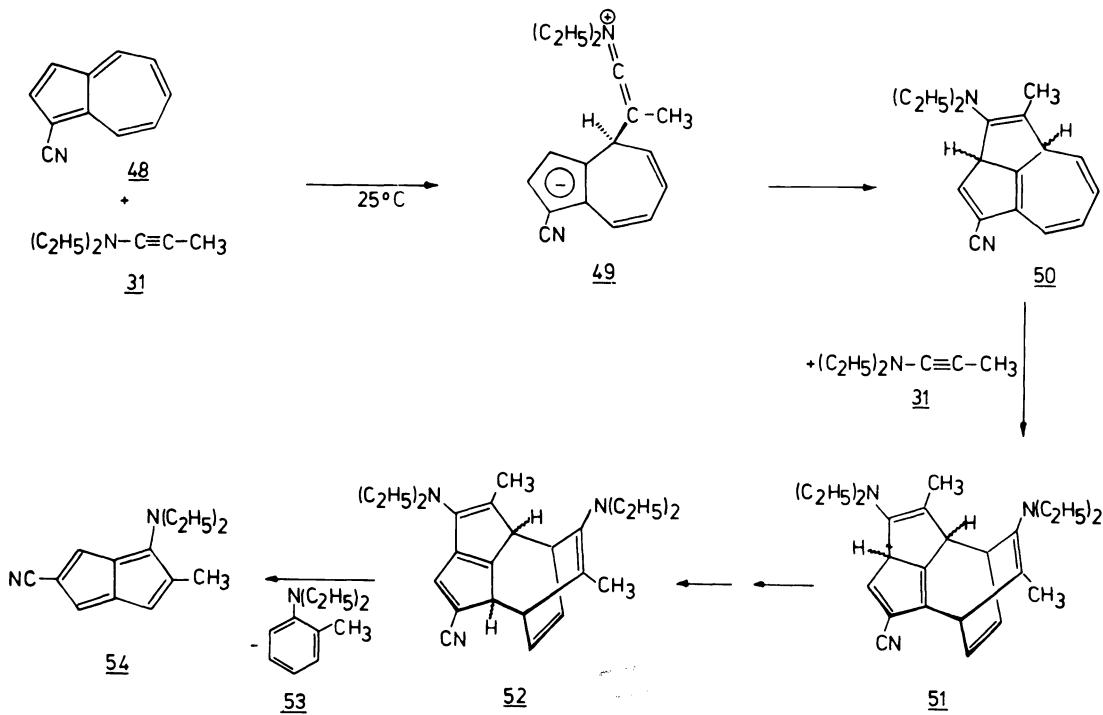
The weakening of the exocyclic pentafulvene double bond is manifested by the rather long bond ( $1.398\text{\AA}$ ) and a torsion angle of  $30^\circ$ . The conformation of the 9-membered ring corresponds to that of 1-(dimethylcarbamoyl)azonine (Ref. 42) and is similar to the tube form of cyclooctatetraene. In accordance with this the  $^1\text{H-n.m.r.}$  spectrum of 45 consists of an AB-system for the two ring protons of the pentafulvene moiety in a region characteristic for this species ( $\delta=6.20-6.50$ ) and a multiplett centered at  $\delta=5.5$  for the 4 olefinic protons of the 9-membered ring. The u.v. spectrum resembles those of 6-aminopentafulvenes.

Our efforts to introduce the missing double bond into the 5-membered ring of 45 in order to prove if the expected tricyclic  $14\pi$ -electron system - a homologue of cyclopent[cd]azulene (4) and aceheptylene (5) - exhibit aromaticity, have so far not met with success. Nevertheless, we are hopeful to obtain the fully unsaturated system soon, since we could show that 2-oxo-1,2-dihydrocyclopent[cd]azulene (46) (Ref. 7) reacts with the ynamine 31 already in a few hours at room temperature to 60 % of the likewise thermally



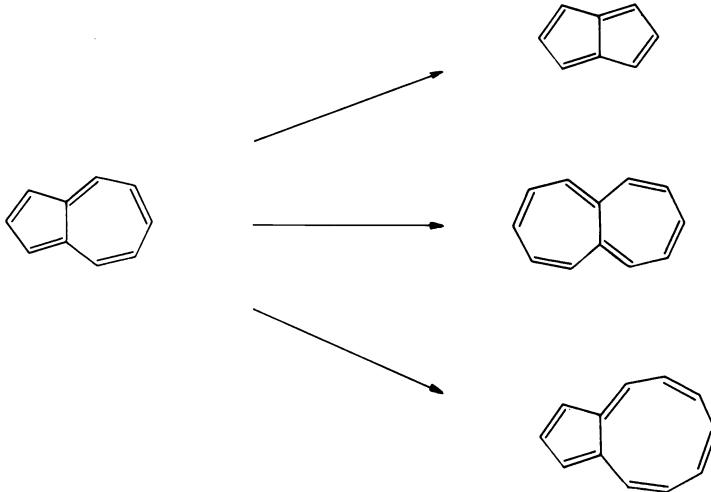
stable tricyclic ketone 47, obtained as brilliant yellow crystals (Ref. 43). Obviously the electron-attracting carbonyl group in 1-position of the azulene moiety of 46 favours the nucleophilic attack of the ynamine 31 at the 7-membered ring.

This observation encouraged us a few months ago to study also the behavior of 1-cyanoazulene (48) towards the ynamine 31. As anticipated, the reaction



proceeds rapidly already at room temperature, but surprisingly enough, instead of an expected 1:1-adduct we isolated besides N,N-diethyl-o-toluidine (53) 30 % of the 5-cyano-1-diethylamino-2-methylpentalene (54) as green compound showing remarkable stability (Ref. 43). All attempts to isolate or trap intermediates of this reaction sequence were so far unsuccessful. Mechanistic considerations however let assume that the two isolated products may be formed again via the resonance stabilized dipol 49, which results from a nucleophilic attack of the ynamine 31 on the azulene 48. Contrary to the aforementioned corresponding reactions of other azulenes, the dipolar intermediate probably stabilizes itself by periannelation to the dihydrocyclopent[cd]azulene 50. This contains in the 7-membered ring an electron-deficient cis-fixed 1,3-diene system, which may react with excess of ynamine by a Diels-Alder reaction with inverse electron demand to the 1:2-adduct 51. Two [1,5] H-shifts afford 52, which may experience a spontaneous Alder-Rickert cleavage producing the isolated compounds 53 and 54. It remains to further

studies to prove this proposition and to explore scope and limitation of this fascinating reaction of the azulene system, which now can be transformed not only into the heptalene and cyclopentacyclononene systems, but also into pentalenes.



#### CONCLUSION

In summary our studies on cyclizing condensation reactions of new highly reactive pentafulvenes as well as on cycloaddition reactions of polycyclic conjugated  $\pi$ -electron systems opened a versatile entry to several new or until now difficult to obtain polycyclic  $\pi$ -electron systems, which offer interesting information for a better understanding of the relations between structure and physical as well as chemical properties of these systems. The observed new cycloaddition reactions can be explained by means of frontier orbital arguments, charge distributions and modifications of the properties due to substituent effects on the perimeter. At the same time they furnish additional insights into the nature of polycyclic  $\pi$ -electron systems.

Acknowledgement - The co-operation of able young associates is gratefully acknowledged; M. Goltz, H.-P. Krimmer, and W. Ude participated in the experimental efforts which I have discussed. Furthermore I wish to thank Dr. M.C. Böhm for quantum chemical calculations and Prof. Dr. H.J. Lindner for x-ray analyses. Our work was generously supported by the Fonds der Chemischen Industrie, the Degussa, Frankfurt/Main, and the Dr. Otto-Röhm-Gedächtnisstiftung, Darmstadt.

#### REFERENCES

1. E. Hückel, Z. Phys. 70, 204 (1931); E. Hückel, Grundzüge der Theorie ungesättigter und aromatischer Verbindungen, Verlag Chemie, Berlin (1938).
2. F. Sondheimer, Acc. Chem. Res. 5, 81 (1972); Chimia 28, 163 (1974) and earlier papers; E. Vogel, Pure Appl. Chem. 28, 355 (1971); Top. Nonbenzenoid Aromat. Chem. 2, 243 (1977); Isr. J. Chem. 20, 215 (1980); E. Vogel, H.M. Dreger, P. Hebel, and J. Lex, Angew. Chem. 92, 943 (1980); Angew. Chem. Int. Ed. Engl. 19, 913 (1980), and earlier papers; M. Nakagawa, Angew. Chem. 91, 215 (1979); Angew. Chem. Int. Ed. Engl. 18, 202 (1979); V. Boekelheide, Top. Nonbenzenoid Aromat. Chem. 1, 47 (1973); Pure Appl. Chem. 44, 751 (1975); Y. Mao and V. Boekelheide, J. Org. Chem. 45, 2746 (1980), and earlier papers.

3. a) K. Hafner, Pure Appl. Chem. 28, 153 (1971); b) K. Hafner, Pure Appl. Chem., Suppl. 2, 1 (1971); P.J. Garrat, Aromaticity, McGraw Hill, London (1971); Ch. Jutz, Top. Curr. Chem. 73, 125 (1978).
4. R. Dönges, K. Hafner, and H.J. Lindner, Tetrahedron Lett. 1345 (1976); K. Hafner, Nachr. Chem. Tech. Lab. 28, 222 (1980).
5. T. Nozoe and Sh. Ito, Fortschr. Chem. Org. Naturstoffe 19, 32 (1961); V.B. Mochalin and Y.u.N. Porshner, Russian Chem. Rev. 46, 530 (1977); Uspekhi Khimii 46, 1002 (1977).
6. a) H.J. Dauben, Jr. and D.J. Bertelli, J. Am. Chem. Soc. 83, 4659 (1961); E. Vogel, H. Königshofen, J. Wassen, K. Müllen, and J.F.M. Oth, Angew. Chem. 86, 777 (1974); Angew. Chem. Int. Ed. Engl. 13, 732 (1974); E. Vogel and J. Ippen, Angew. Chem. 86, 778 (1974); Angew. Chem. Int. Ed. Engl. 13, 734 (1974); E. Vogel and F. Hogrefe, Angew. Chem. 86, 779 (1974); Angew. Chem. Int. Ed. Engl. 13, 735 (1974); L.A. Paquette, A.R. Browne, and E. Chamot, Angew. Chem. 91, 581 (1979); Angew. Chem. Int. Ed. Engl. 18, 546 (1979); b) K. Hafner, H. Diehl, and H.U. Süss, Angew. Chem. 88, 121 (1976); Angew. Chem. Int. Ed. Engl. 15, 104 (1976); W. Bernhard, H.-R. Zumbrunnen, and H.-J. Hansen, Chimia 33, 324 (1979).
7. Compound 4: K. Hafner, K.-P. Meinhardt, and W. Richarz, Angew. Chem. 86, 235 (1974); Angew. Chem. Int. Ed. Engl. 13, 204 (1974); compounds 5 and 8: Ref. 3a; compound 6: K. Hafner, H.D. Diesel, and W. Richarz, Angew. Chem. 90, 812 (1978); Angew. Chem. Int. Ed. Engl. 17, 763 (1977); compound 7: K. Hafner, H. Diehl, and W. Richarz, Angew. Chem. 88, 125 (1976); Angew. Chem. Int. Ed. Engl. 15, 108 (1976); A.G. Anderson, Jr., G.M. Masada, and G.L. Kao, J. Org. Chem. 45, 1312 (1980); Ch. Jutz and E. Schweiger, Synthesis 193 (1974).
8. K. Hafner and H.U. Süss, Angew. Chem. 85, 626 (1973); Angew. Chem. Int. Ed. Engl. 12, 575 (1977); B. Kitschke and H.J. Lindner, Tetrahedron Lett. 2511 (1977).
9. G. Maier and F. Köhler, Angew. Chem. 91, 327 (1979); Angew. Chem. Int. Ed. Engl. 18, 308 (1979), and earlier papers; S. Masamune, F.A. Souto-Bachiller, T. Machiguchi, and J.E. Berti, J. Am. Chem. Soc. 100, 4889 (1978), and earlier papers.
10. J.F.M. Oth and K. Müllen, unpublished results; P. Bischof, R. Gleiter, K. Hafner, K.H. Knauer, J. Spanget-Larsen, and H.U. Süss, Chem. Ber. 111, 932 (1978).
11. D. Jung, Tetrahedron 25, 129 (1969).
12. M.J.S. Dewar, Aromaticity, Chem. Soc. Spec. Publ. No. 21, 177 (1967); M.J.S. Dewar, The Molecular Orbital Theory of Organic Chemistry, McGraw-Hill, New York (1969).
13. K. Hafner, J. Heterocycl. Chem. 13, Suppl. Vol. III, S-33 (1976).
14. H.G. Viehe and Z. Janousek, Angew. Chem. 85, 837 (1973); Angew. Chem. Int. Ed. Engl. 12, 806 (1973); Z. Janousek and H.G. Viehe in H. Böhme and H.G. Viehe, Iminium Salts in Organic Chemistry, Part I, 343, Wiley, New York 1976.
15. K. Hafner and H.-P. Krimmer, Angew. Chem. 92, 202 (1980); Angew. Chem. Int. Ed. Engl. 19, 199 (1980).
16. H.-J. Gais and K. Hafner, Tetrahedron Lett. 771 (1974); K. Hafner, H.-G. Kläs, and M.C. Böhm, Tetrahedron Lett. 41 (1980).
17. K. Hafner, Angew. Chem. 75, 1041 (1963); Angew. Chem. Int. Ed. Engl. 3, 165 (1964).
18. Unpublished results with H.-P. Krimmer.
19. T. Nakajima, Top. Curr. Chem. 32, 1 (1972).
20. K. Hafner, K.F. Bangert, and V. Orfanos, Angew. Chem. 79, 414 (1967); Angew. Chem. Int. Ed. Engl. 6, 451 (1967).
21. H.J. Lindner, unpublished results.
22. M.C. Böhm, unpublished results.
23. L. Knothe, H. Prinzbach, and E. Hadicke, Chem. Ber. 114, 1656 (1981).
24. M.B. D'Amore and R.G. Bergman, J. Chem. Soc., Chem. Comm. 461 (1971).
25. J. Krebs, A. Weber, and M. Neuenschwander, Chimia 35, 55 (1981).
26. K. Hafner and M. Suda, Angew. Chem. 88, 341 (1976); Angew. Chem. Int. Ed. Engl. 15, 314 (1976); M. Suda and K. Hafner, Tetrahedron Lett. 2449 (1977); ibid 2453 (1977).
27. 7 is obtained in 80 % yield from dimethyl 1,2-dicyclopent[ef,k1]heptalene-dicarboxylate (7) by hydrolysis and thermal decarboxylation (unpublished results with G. Knaup).
28. W. v. E. Doering and D.H. Wiley, Tetrahedron 11, 183 (1960); W.K. Schenck, R. Kyburz, and M. Neuenschwander, Helv. Chim. Acta 58, 1099 (1975).
29. D. Mukherjee, L.C. Dunn, and K.N. Houk, J. Am. Chem. Soc. 101, 251 (1979), and earlier papers.
30. D. Copland, D. Leaver, and W.B. Menzies, Tetrahedron Lett. 639 (1977).

31. M. Sato, S. Ebine, and J. Tsunetsugu, Tetrahedron Lett. 2769 (1974).
32. L. Watts, J.D. Fitzpatrick, and R. Pettit, J. Am. Chem. Soc. 87, 3253 (1965); G. Maier, Angew. Chem. 86, 491 (1974); Angew. Chem. Int. Ed. Engl. 13, 425 (1974).
33. D. Bryce-Smith, A. Gilbert, and J. Grzonka, J. Chem. Soc., Chem. Comm. 498 (1970).
34. Unpublished results with W. Ude (Ph.D. Thesis, Darmstadt 1980).
35. K. Hafner, H.J. Lindner, and W. Ude, Angew. Chem. 91, 173 (1979); Angew. Chem. Int. Ed. Engl. 18, 161 (1979).
36. R.D. Miller and H.J. Schneider, Tetrahedron Lett. 1557 (1975).
37. K. Hafner and H. Tappe, Angew. Chem. 81, 564 (1969); Angew. Chem. Int. Ed. Engl. 8, 593 (1969); G. Boche, F. Heidenhain, and B. Staudigl, Tetrahedron Lett. 4201 (1979), and earlier papers.
38. H.J. Lindner, B. Kitschke, K. Hafner, and W. Ude, Acta Cryst., B36, 758 (1980).
39. K. Hafner, H.J. Lindner, and W. Ude, Angew. Chem. 91, 175 (1979); Angew. Chem. Int. Ed. Engl. 18, 162 (1979).
40. H.J. Lindner, B. Kitschke, K. Hafner, and W. Ude, Acta Cryst., B36, 756 (1980).
41. H.L. Ammon and G.L. Wheeler, J. Chem. Soc., Chem. Comm. 1032 (1971).
42. C.C. Chiang, I.C. Paul, A.G. Anastassiou, and S.W. Eachus, J. Am. Chem. Soc. 96, 1636 (1974).
43. Unpublished results with M. Goltz.