Multi-electron (12π–20π) pericyclic processes

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Abstract: Fulvadienes, sterically fixed conjugated polyenes with 12 to 24π electrons, have been investigated with respect to their ability to undergo the all-electron (α,ω) electrocyclization. It was directly or indirectly established, that the 12-,14-,16-,18- and 20π-cyclizations are sterically controlled and proceed via conrotatory ring closure. In the corresponding penta/heptafulvatrienes (14 to 18π) the electrocyclization was not an equally favoured process. The original goal, the use of the fulvadienes as precursors for the corresponding angularly annelated tricycloannulenes, was successfully achieved only in a single case (14π-phenazulene). Novel 14π-azulenoid tricycloannulenes were prepared by pericyclic pathways (14π) and were shown to be "aromatic". A (formal) [18+2]-cycloaddition has been observed between heptahendecafulvalene and tetracyanoethylene.

INTRODUCTION

The bridged annulenes I, which are composed of two odd membered rings (pentalene, azulene, heptalene...), as well as the, at least formally, quinoid systems II and III (m, n = 2, 3, 4, 5) which can be derived from I by linear and angular insertion of a six-membered ring, belong to the "evergreens" in the area of non-benzenoid π-perimeter-chemistry (ref. 1). The lasting
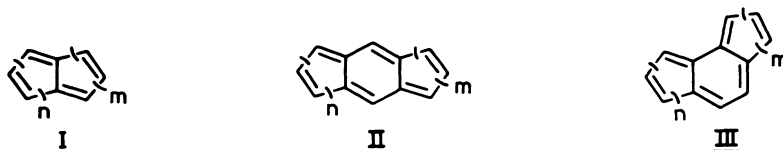
"flowering" of these systems has certainly been helped by the fact that many of the annellated compounds have not been made and therefore conflicting theoretical results have never been checked experimentally.

In Scheme 1 is summarized how my research group intended to make a preparative synthetic contribution, especially with respect to the angular systems III. Based on our early work concerning the cross-conjugated fulvalenes IV (ref. 2, 3), the construction of the latter systems

Scheme 1   α, ω - C y c l o a d d i t i o n s

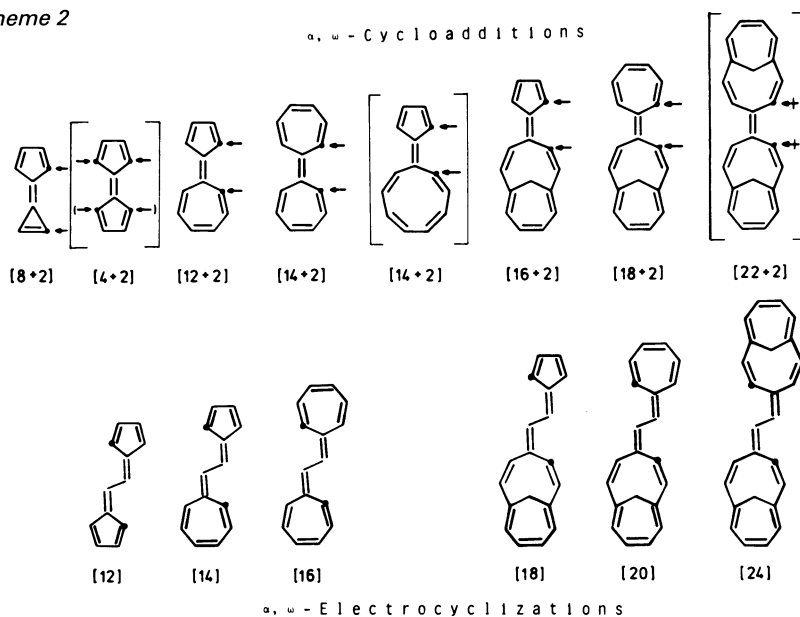α, ω - E l e c t r o c y c l i z a t i o n s
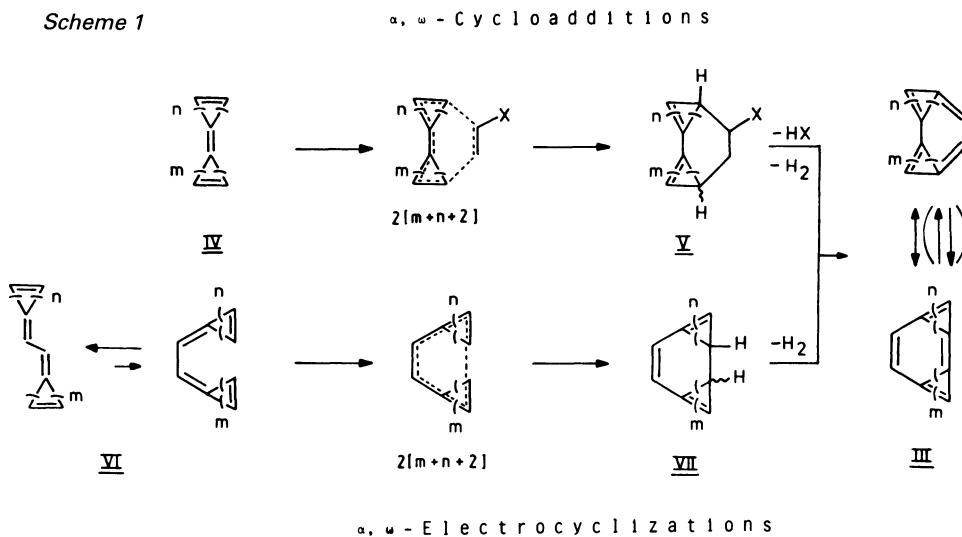
III was pursued in two ways:

    : α,ω-cycloaddition of di(poly)enophiles to fulvalenes (IV → V)

    : α,ω-electrocyclization of the corresponding fulvadienes (VI → VII)

The scope and limitations of route IV → V → III have already been discussed at length and were the subject of a previous lecture (ref. 3). The compilation given in Scheme 2 shows the α,ω-additions which have been realized with fulvalenes, processes that are not necessarily concerted. The types of the dienophiles involved were rather restrictive and did not allow useful access to the highly reactive basic skeletons III or to simple derivatives thereof. The [18+2] addition with the heptahendecafulvalene has only recently been discovered but still lacking are the ([14+2]) addition experiments to the recently published pentanonafulvadiene (Neuenschwander et al., ref. 4).

This paper deals primarily with our activities concerning the second route (VI → VII → III). In common to the cyclization steps VI → VII is the participation of all 2[m+n+2]perimeter π-electrons in the formation of a six-membered ring through Hückel and anti-Hückel transition states involving unusually high numbers of π-electrons. A prominent precursor of such electrocyclizations in cross-conjugated polyolefins is exemplified in the Ziegler-Hafner azulene synthesis (ref. 5).

In Scheme 2 are listed the fulvadienes which have been prepared for this study, ranging from the 12π pentafulvadiene to the 24π hendecafulvadiene. As a result, in parallel with the preparative-synthetic goals as outlined above, questions as to the importance of orbital-symmetry (ref. 2,6) for the periselectivity and stereoselectivity of the electrocyclization steps have emerged. Implicit in this project were several uncertainties. In view of the known propensity of the fulvalenes IV, in particular those containing a pentafulvene unit (ref. 2,7), for intermolecular reactions (di-, polymerization), it was uncertain to what extent intra- and intermolecular reactions of fulvadienes VI would compete. The possibility to isolate or identify directly the primary cyclization products would depend critically on the necessary thermal activation energy of the step VI → VII. The two aliphatic hydrogens in VII which serve as stereochemical indicators are doubly allylic and consequently highly sigmatropically active. On the other hand, it could be expected that the fulvadienes VI might easily switch from the practically planar s-transoid to helically twisted s-cisoid conformations, the prerequisites for α,ω-bond formation.

Scheme 2

α,ω-Cycloadditions

[8+2]   [4+2]   [12+2]   [14+2]   [14+2]   [16+2]   [18+2]   [22+2]

[12]   [14]   [16]   [18]   [20]   [24]

α,ω-Electrocyclizations

When it was found that the fulvadienes VI with n,m = 2,3 underwent exclusively the α,ω-cyclization, the analogous process of the Z-fulvatrienes VIII, in which eight-membered rings (VIII → IX) would be created, was investigated (Scheme 3). From the documented fast 8π-cyclizations in Z,Z-1,3,5,7-octatetraene (t½(25°C) = 23 s, ref. 8) and 1,8-dialkyl-derivatives (ΔG‡ = 20-25 kcal/mol, ref. 9) it was considered likely that electrocyclizations of this type might occur with sufficiently low activation barriers. The kinetics of similar examples are very dependent, however, upon the substitution pattern (ref. 10). As yet, any predictions as to the selectivity and ease of α,ω-bond formations in the substrates VIII have been only speculative.

Scheme 3

$$m = n = 2$$
$$14\,\pi$$

$$m = 2 \quad n = 3$$
$$16\,\pi$$

$$m = n = 3$$
$$18\,\pi$$
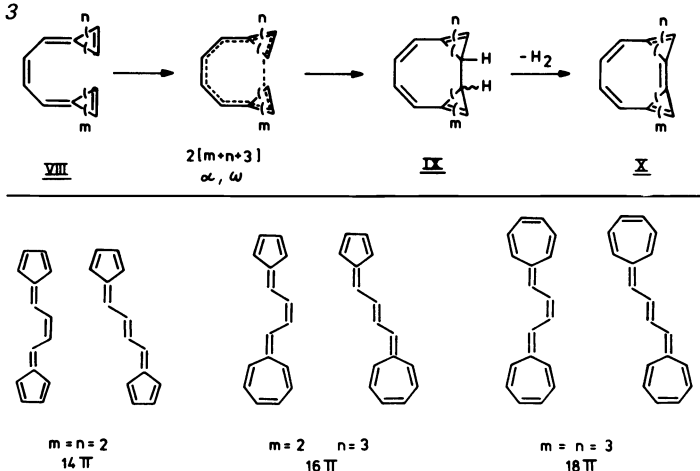
A 12π-ELECTROCYCLIZATION

A thermal 12π-electrocyclization of the pentafulvadiene A-1 -> A-2 was the proposed route to the as-indacene-skeleton A-4 (ref. 2,11). The risks involved in such a transformation were likely to be high, as pentafulvalene as reported by Doering and Matzner (ref. 7) and similarly the 2,3-diphenyl derivative (ref. 12) are extremely prone to polymerization. Pentafulvadiene requires significant steric protection in both rings to make the system kinetically stable and isolable (cf. the X-ray analysis of the tetra-tert-butyl-derivative, Hafner et al., ref. 13). Fortunately enough, A-1, which is available in low yields but nevertheless in g-quantities from cyclopentadiene and glyoxal sulfate, survived isolation in crystalline form and could be stored for months at temperatures below -10°C under an inert atmosphere. From the UV/VIS-spectrum and the shift differences measured for the 1(12)- and the 4(9)-proton pairs, a practically planar s-trans-conformation was deduced for A-1.
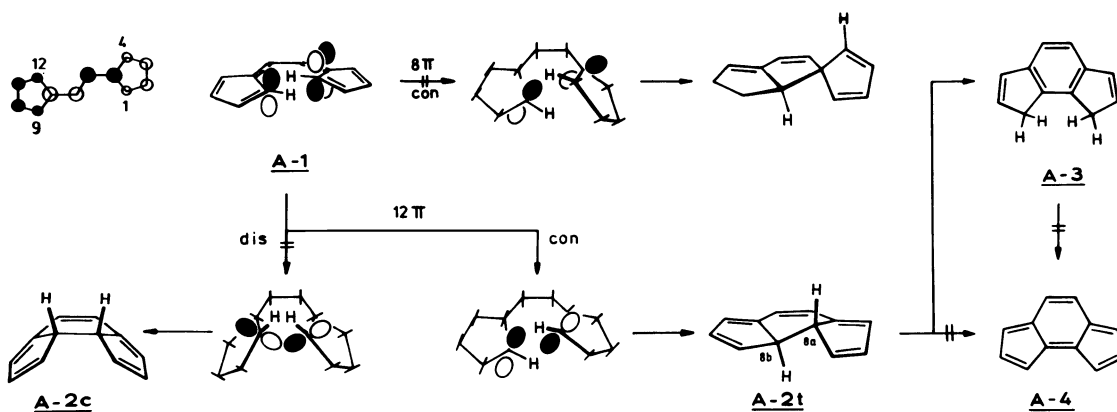
For a full appreciation of the experimental findings it should be pointed out that, on the basis of HOMO symmetry and HOMO coefficients and of the stereoelectronic situation as inferred from models with helically twisted s-cis-conformations of A-1, the five-membered ring formation via the conrotatory 8-electron pathway had to be considered as a serious competition to the desired six-ring formation A-1 -> A-2. In vinylogous pentafulvenes such 8π-reactions have been observed (ref. 14). As to the stereochemistry of the 6-membered ring formation, an early bonding interaction between the 1,12-positions is possible in the "symmetry-allowed" conrotatory mode by a slight twisting of the π-perimeter. In contrast, the "forbidden" disrotatory 1,12-interaction demands a rather severe distortion about the exocyclic double bonds. Clearly, the distinction between these two pericyclic alternatives depends upon the kinetic stability of the dihydro-as-indacene(s) A-2c/A-2t, or more exactly upon the relative rates of electrocyclization and subsequent sigmatropic H-migration.

Experimentally, it was found that the conrotatory reaction is favored to such an extent, that intermolecular processes at concentrations between 10^{-4}M(UV) and 10^{-2}M(^{1}H-NMR) and in the temperature range of -15° to +30°C did not interfere and the trans-dihydro-as-indacene A-2t was obtained in practically quantitative yield. The electronic spectra of A-1 and A-2t are sufficiently different for kinetic measurements. From these data (Ea = 20 ± 0.4 kcal/mol, log A = 11.3 ± 0.3; $\Delta H^{\ddagger}$ = 19.4 ± 0.4 kcal/mol; $\Delta S^{\ddagger}$ = -9 ± 1eu) it is understandable that the otherwise fast sigmatropic H-migrations in 5-alkyl-cyclopentadienes (Ea ca. 24 kcal/mol) do not interfere, a decisive point in the elucidation of the stereochemical aspect. On heating to 80°C A-3 is produced which, in the the presence of base (triethylamine), equilibrates with the other two benzenoid dihydro-as-indacenes.

Differentiation of the C$_2$-symmetrical **A-2t** from the C$_s$-symmetrical **A-2c**, with the H$_{8a}$-/H$_{8b}$-coupling constant not being available, was based on an opti-shift-study of the C$_2$-symmetrical bisadduct, which formed stereospecifically from the reactive bis-diene **A-2t** in the presence of a large excess of dimethylacetylenedicarboxylate. The structural details of this adduct, especially the trans orientation (torsional angle exactly 180°C) of **H-8/H-9** ($\equiv$ H$_1$,H$_1$' in fig.) have since been established by X-ray analysis.
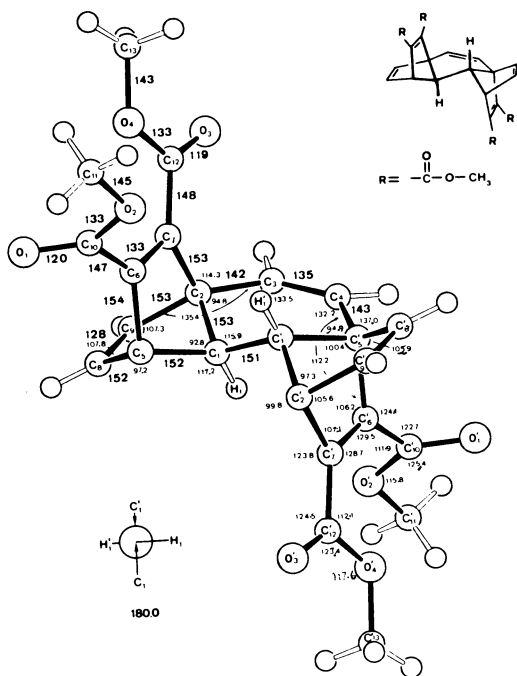

Efforts to induce in **A-1** a photochemical electrocyclization were not successful. **A-1** (ca. 10^{-4}M solutions in CH$_3$CN) is inert towards light of varying wave-length (-15°C, λ = 250, 290, 400nm, **A-2t** is virtually transparent at 400nm) as well as acetone-sensitized excitation. In daylight **A-2t** slowly reverts back to **A-1** and this 12π-retroelectrocyclization is complete after short irradiation with light of 280nm wave-length.

With g-amounts of **A-2t** in hand, we invested a lot of time and effort to bring about the dehydrogenation to the as-indacene **A-4**, directly or indirectly (e.g. radical bromination, dehydrobromination). In all cases there was no indication that **A-4** had been produced.

Substitution by tert-butyl groups, as successfully applied to relevant cases e.g. cyclopentadienone, calicene, sesquifulvalene and fidecene (ref. 2) is expected to confer the required stability upon **A-4**. The 2,2'-di and the 1,1', 3,3'-tetra-tert-butyl-pentafulvadienes have recently been shown also to undergo the 12π-electrocyclization (boiling xylene, tetralin, resp.) (ref. 13).

The ease of the transformation **A-1** $\rightarrow$ **A-2t** suggested that this type of process might be observable for the benzoannellated pentafulvadiene **A-6**. A rough estimate places the activation barrier for this 16-electron process to be ca. 35 kcal/mol. **A-6** (as well as the pure anti-dibenzofulvadiene) (ref. 15) was prepared conventionally from the known indenylidene-acetaldehyde and isolated in 55-60% yield as brown needles (J$_{1',2'}$ = 12.0 Hz). Each benzoannellation causes a redshift of ca. 30 nm in the otherwise very similar electron spectra. Dilute (10^{-2}M to 10^{-4}M) solutions of **A-6** in xylene are stable up to 140°C. After total consumption (2 hrs at 150°C), in addition to polymeric material, a 20-30 % yield of a single crystalline
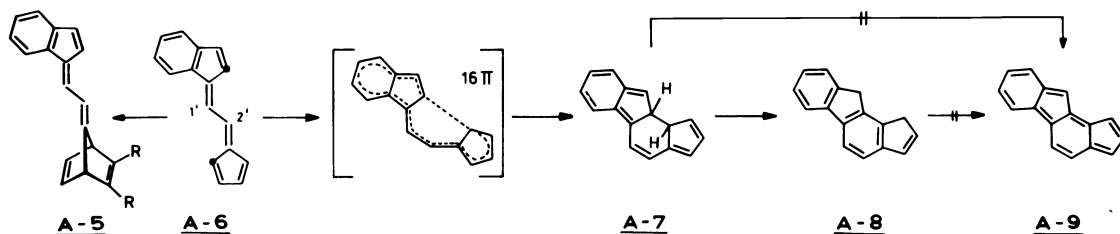

substance was isolated and characterized as **A-8** (1,10-dihydro-cyclopenta[b:a]fluorene), of which the 1,2,3,10-tetrahydro-derivative is known. **A-8** is in all probability formed via the antarafacial 16π-cyclization **A-6** $\rightarrow$ **A-7**. Thermolysis in the presence of various oxidizing agents did not provide any indication for the formation of the quinoid 16π-annulene **A-9**. It was also not possible to intercept the dihydro-annulene **A-7**, ([8+2], [4+2]) as was done successfully with **A-2**, by thermolyzing **A-6** in the presence of a vast excess of dimethylacetylenedicarboxylate. Under the conditions required for the electrocyclization, the addition to **A-6** to give the norbornadiene **A-5** is too fast. As expected, the anti-dibenzofulvadiene was stable up to 250°C and showed only unspecific decomposition above this temperature.

B 14π-ELECTROCYCLIZATION

"Phenazulene" (Cyclohept[e]indene) **B-5** was the ultimate goal in planning the 14π-electrocyclization of the pentaheptafulvadiene **B-1** $\rightarrow$ **B-2** (ref. 16). Calculations had given contradictory predictions as to the electronic nature of this "annulene". Stable derivatives of **B-5** have been obtained (ref. 17) via a [12+2]-addition to the dicyano-sesquifulvalene rather than via a [6+8]-addition between pentafulvenes and heptafulvenes (ref. 18).

The uncertainties and risks connected with the approach B-1 → B-2 → B-5 were similar to those cited at the beginning of the preceding chapter. Again there were serious doubts with respect to availability of the starting material and to the extent to which competing inter- molecular side reactions would occur. These were i.a. justified by our experience with the parent sesquifulvalene (ref. 2,3), a thermally highly labile and acid sensitive compound. Nevertheless we tackled this project when, in another context, we had found an efficient ac- cess to B-1 (ref. 19). Crystalline B-1 decomposes slowly at room temperature. In solution it is clearly more stable than A-1 (t½ of a ca. 10^{-2}M solution (isooctane, CDCl₃) at 25°C ca. 100 h). Marked shift differences for the 2'(5') and 2(7)-protons and the $J_{6',8}$-value of 12.8 Hz are again evidence for a planar s-trans-conformation. Since B-1 consists of a vinylogous
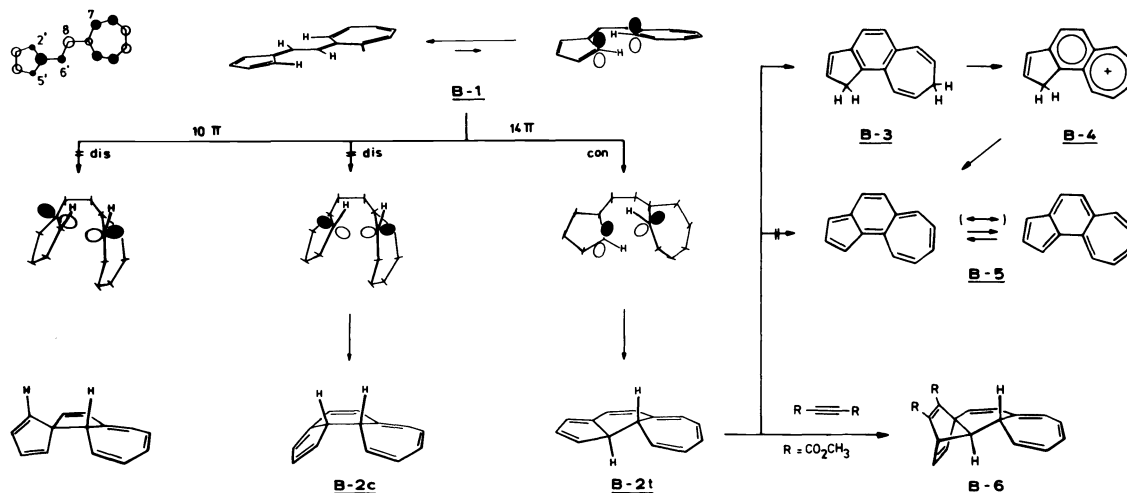

pentafulvene as well as of a vinylogous heptafulvene unit, a third alternative had to be considered in form of the 10π-route to the azulene skeleton (ref. 20) in addition to the all- electron (α,ω ;14π) and the 8π-cyclizations. A comparison of the stereoelectronic changes on going towards the sterically congested non-planar s-cis transition state led to the following conclusions: severe H-2/H-2' interactions and distortions of the π-perimeter are only avoided by antarafacial bond formation and the six-membered ring formation has a stereoelectronic ad- vantage over the two five-membered ring formations. The theoretically interesting aspect is that, according to the HOMO-symmetry of B-1, it is the disrotatory mode of the 14π-cycliza- tion (B-2c), which is symmetry-allowed.

The deeply coloured solutions of B-1 were rapidly decolourized when heated above 50°C. When the kinetics of the process were followed by UV/VIS-(ca. 10^{-4}M) or ¹H-NMR spectroscopy (ca. 10^{-2}M), a seemingly straightforward transformation was observed and indeed, an almost quanti- tative yield of a ca. 95:5-mixture of 1,8-dihydrocyclohept[e]indene (B-3) and its 3,8-dihy- dro-isomer was isolated. These two products do not equilibrate under the above conditions. The activation parameters (Ea = 23.9 ± 0.5 kcal/mol, log A = 12.0, $\Delta H^{\ddagger}$ = 23.4 ± 0.5 kcal/mol, $\Delta S^{\ddagger}$ = -6.2 ± 1.2 e.u.) were determined by ¹H-NMR in degassed benzene solution. The- se values undoubtedly must be assigned to the slow cyclization step B-1 → B-2 which is fol- lowed by rapid 1,5-H-migrations. The increase by ca. 3 kcal/mol as compared with the A-1 → A-2 reaction suffices to make the isolation or direct (spectroscopic) identification of the primary cyclization product(s) B-2t (B-2c) impossible, since the sequential [1,5]-sigmatropic hydrogen migrations in the cyclopentadiene and cycloheptatriene-units (leading to aromatiza- tion) become very rapid. The stereochemistry of the process could nevertheless be indirectly established when, after some tedious experimentation with varying dienophiles, a significant percentage of B-2 could be intercepted. It was found that dimethylacetylenedicarboxylate, in contrast to tetracyanoethylene and N-phenyltriazolinedione, discriminates sufficiently bet- ween B-1 and B-2. After thermolysis in a ca. 500 M excess of diester, in addition to a small amount of B-3 and ca. 30% of the [8+2]/[4+2]-bisadduct of B-1, a ca. 20% yield of the 1:1- adduct B-6 was separated. The latter structure was deduced originally from the NMR-data (i.a. $J_{10,11}$ = 10.0 Hz) and was finally proven by X-ray analysis. With the structure B-6 it is con- firmed, at least within the limits of the isolated yield, that the thermal 14π-electrocycli- zation in B-1 follows the symmetry-forbidden conrotatory mode. Arguments have been forwarded that the formation of B-2t from B-2c via equilibration is highly unlikely. As was observed for A-1, electrocyclization of B-1 either by direct or sensitized photo-excitation could not be achieved.

The phenazulenium salt B-4 proved to be rather reactive but was sufficiently stable to be analyzed by ¹H-NMR as the hexachloroantimonate (AsCl₃/CD₂Cl₂). For deprotonation, the more soluble although less stable BF₄⁻-salt had to be used. In highly dilute CH₂Cl₂ solutions (which guaranteed very fast deprotonation), the 14π-phenazulene B-5 (deep blue colour) was characterized by its UV/VIS-spectrum. B-5 survives as ca. 10^{-3}M solutions at -60°C but quickly polymerizes above -30°C. Upon adding such a solution to excess CF₃CO₂H the conjugate acid B-4 is selectively reformed. All efforts to concentrate such solutions of B-5 (for NMR) or to effect cycloadditions (e.g. with TCE) at necessarily low temp. (-60°C) were unsuccess- ful. B-5 is extremely sensitive towards electrophilic reagents and short contact with silica gel suffices to cause polymerization. The extreme thermal reactivity of B-5 is probably a re- sult of the highly strained non-planar quinoid structure.
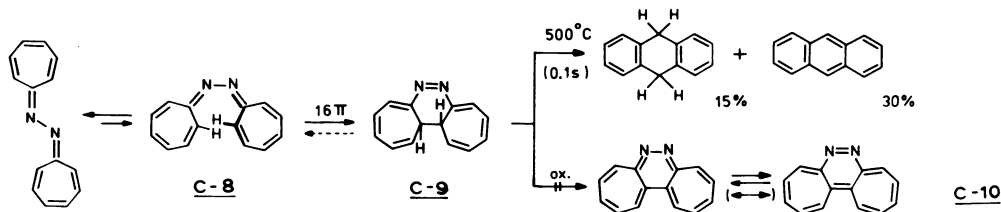
C 16π-ELECTROCYCLIZATIONS

From past reports on unsuccessful approaches towards the linear s-tropacene (ref. 21) and
from our experiences with A-4 and B-5, the prospects for a successful realization of the
sequence C-1 → C-2 → C-7 did not look very promising, at least insofar as the dehydrogena-
tion step was concerned. In this case, the availability and kinetic stability of the starting
material was no problem: heptafulvadiene C-1 had been described by Kitahara et al. (ref. 22),
who also mentioned its thermal transformation into a tricyclic isomer of unknown structure in
a later paper. After some optimization of the original protocol we had g-quantities of C-1 at
our disposal (ref. 23).
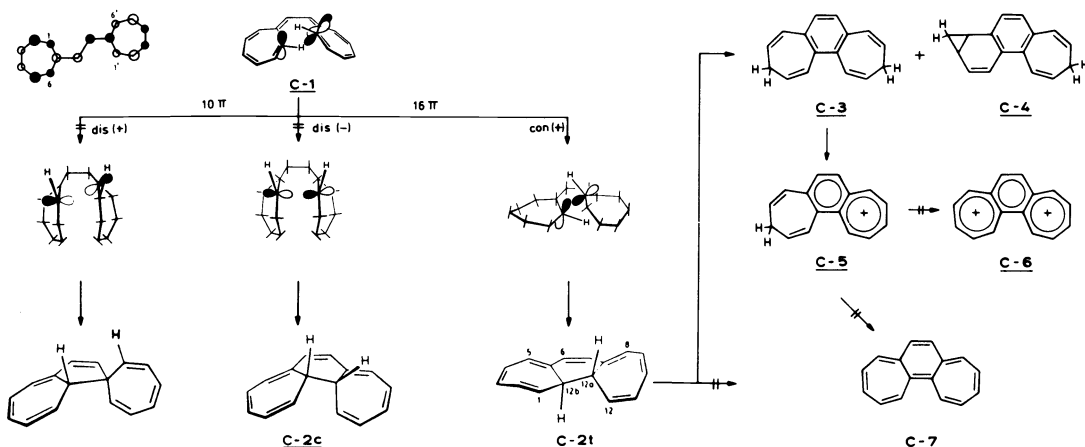
The rotation in the practically planar s-trans-conformation ($\Delta\delta(1(1')H/ 6(6')H) = 0.24$ ppm)
is even more hindered by H/H-compression than in the case of A-1 and B-1. The disrotatory
modes, allowed for the 10π-routes, and forbidden for the 16π-routes, were considered unlikely
for steric reasons. In the competition between the forbidden 10π- and the allowed 16π-con-
rotatory routes, the latter was considered more likely.

The tendency for polymerization of C-1 was much less pronounced than for A-1 and B-1 and more
concentrated solutions could be employed for the thermolysis studies. On heating ca. 10^{-2}M
degassed benzene solutions of C-1, the deep red colour slowly changed to yellow between 60-
100°C and a single isomer was produced (94% isolated), to which the C_2-symmetrical C-2t
structure was assigned. The differentiation from C-2c(C_s) rested primarily on the $J_{12a,12b}$-
value ≤ 2Hz (from ^{13}C-satellites) and was proven by the X-ray analysis. The kinetic data for
this 16π-electrocyclization were determined by ^{1}H-NMR between 60° and 90°C: Ea = 22 ± 1.5
kcal/mol; log A = 10.8; $\Delta H^{\ddagger}$ = 22 ± 2 kcal/mol, $\Delta S^{\ddagger}$ = -11 ± 2 e.u. Above 140°C, 1,5-sigma-
tropic migrations lead finally to a mixture of C-3/C-4 (90%, 7:3 at 165°C, 2:8 at 180°C). C-
2t was consumed under a variety of dehydrogenation conditions without any evidence for the
formation of the expected deeply coloured as-tropazene C-7. Conventional hydride elimination
from C-3 smoothly furnished the tropazenium conjugate acid C-5 which resisted a second H⁻-
elimination to give the bistropylium cation C-6 even under rigorous conditions (AsCl₃/
SbCl₅). When solutions of C-5 in CF₃CO₂D were kept for a few days at 20°C, no H/D-exchange
(via C-7) took place. Various attempts to deprotonate C-5 with strong and sterically hindered
bases resulted only in rapid decolourization and no C-7 was observed.

The ready access to the tropone azine C-8 (ref. 24), a diazaanalogue of C-1, made it another
preparatively attractive candidate for this study. It was understood that the azine → azo-
isomerization C-8 → C-9 would be endothermic (by 4-11 kcal/mol) and possibly reversible. The
chance was seen however to catalyze the electrocyclization. C-8 is more stable than C-1 and
degassed, ca. 10^{-2}M solutions (xylene, sulfolane) remained unchanged after heating at 140°C
for several hours. Above 160°C (H-migrations in C-9 should shift the equilibrium) polymeriza-
tion occured without the formation of a monomeric product and without any noticeable N₂-

elimination. Addition of oxidizing agents did not alter the situation. When intermolecular
reactivity was excluded by vapour phase flash thermolysis (500°C), significant amounts of
dihydroanthracene and anthracene (15%, 30% at 0.1s, no phenanthrene, no stilbenes) were
produced, depending upon contact-time. The intermediacy of the 16π-cyclized material C-9 was
nevertheless indicated.

In 10^{-3}M CH$_2$Cl$_2$ solution in the presence of 0.5 equiv. CF$_3$CO$_2$H, ca. 80% of a 4:1 mixture of
the dihydrodicycloheptapyridazines C-14/C-15 were isolated after slow and total conversion at
20°C. Mono-protonated C-11 is most certainly responsible for the acid-catalyzed reaction: At
lower temp. (-20°C) or with 2 equiv. of acid, no cyclization took place. As with C-2t, no
way was found to oxidize C-14 or C-15 to C-10. Evidence for the postulated mechanism came

C-11   C-12   C-13   C-14   C-15
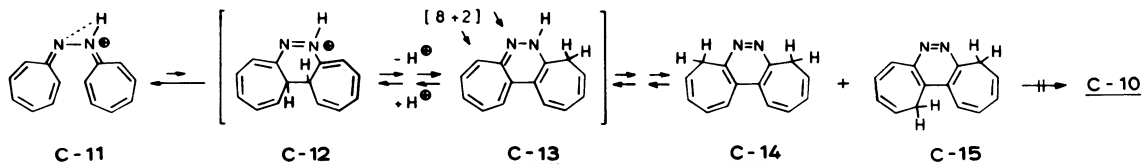
from experiments in higher concentrated solutions. At ca. 10^{-1}M concentration an additional
product was easily observed by its intense blue-green colour and was isolated as black-green
needles in 5-10% yield. The material presumably arose by way of an [8+2]-adduct of C-1 to C-
13 followed by elimination of troponehydrazone. Other [8+2]-adducts of C-13 with tropone and
chloranil could also be isolated.

D 18π-ELECTROCYCLIZATION

Substitution of the five- and seven-membered ring units in the bicycloannulenes of type III
with Vogel's CH$_2$-bridged 11-membered ring made an extension of these series feasible.

A first 18π pericyclic access to this angular annellated skeleton was realized by stereospe-
cific [16+2]-cycloaddition of TCE to the 16π 3,8-methanobridged pentahendecafulvalene
("fidecene") D-1. Of direct relevance to the results presented in this chapter are the find-
ings that the symmetry-allowed suprafacial addition to D-1 occurs on the side syn to the
methylene bridge and that the suprafacial 1,9-hydrogen shift in D-2 to yield D-3 is so fast,
that the primary adduct could not be observed at 0°C (ref. 25).


D-1   D-2   D-3
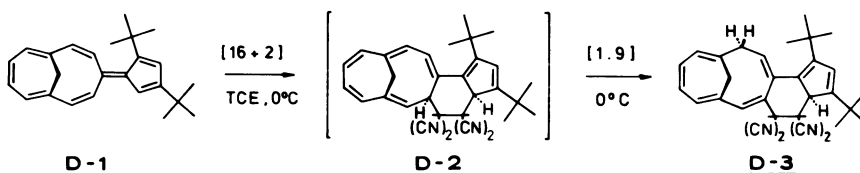
The violet crystalline pentahendecafulvadiene (vinylogous fidecene) D-6 was synthesized from
the ketone D-4 (ref. 26) via the aldehyde D-5 (ref. 27). D-6 added dimethylacetylenedicarbo-
xylate at 80°C to yield the 1:1-adduct D-7 (80%). The latter product was intended to provide
access to D-8, a substituted heptahendecafulvadiene (see E-1), but under no conditions could
the photo-rearrangement D-7 → D-8 be achieved. On account of the methylene bridge in D-6,
two sides for attack (syn-, anti-) have to be distinguished and the question of preferred
conformation was relevant in connection with the selectivity of electrocyclization reactions.
The expected s-trans-geometry of D-6 was revealed by $J_{1'',2'}$ = 12.5 Hz (practically constant
between -30° and +150°C). Since 2''-H is significantly deshielded with respect to 5''-H ($\Delta\delta$=
0.32ppm), although 1-H with respect to 10-H is not($\Delta\delta$= 0.07ppm), it was concluded that C-11
is displaced from the C1-C2-C9-C10 plane to an extent which excludes a sizable anisotropic
influence of the C1'' = C2' double bond upon the 1(10)-hydrogens. From the known geometry of
ketone D-4 (ref. 28) and of the heptahendecafulvalene E-10 (ref. 30) it was safely assumed
that this displacement of C11 in D-6 is in the direction of the CH$_2$-bridge (syn).

D-4   D-5   D-6   D-7   D-8
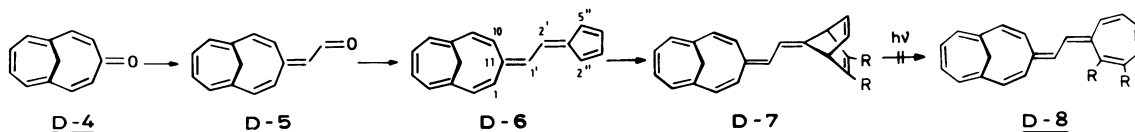
That D-6 melted without decomposition and 10^{-2}M degassed benzene solutions could be refluxed
for several hours without change was indicative of the relative stability of this fulvadiene.
On heating in degassed ca. 10^{-2}M xylene solution, D-6 remained unchanged up to 120°C and a
single monomeric product was observed (TLC, ^{1}H-NMR) and isolated in up to 55% yield at higher
temperatures (t$_½$ ca. 5 min, $\Delta G^{\ddagger}$(130°C) ca. 30 kcal/mol). This colourless, crystalline com-
pound (m.p. 72°C) was identified as D-12 (indeno [g-4,5]tricyclo [5.4.1.0^{1,3}]dodeca-4,6,8,10-
tetraene). The relative orientation of the three CH$_2$-units was confirmed i.a. by extensive
NOE-measurements. The assignment of D-12 was supported by the data which were obtained for
the benzylidene derivative D-15. The structure of D-12 and the selectivity of its formation
are consistent with the pericyclic reaction sequence D-6 → D-9 → D-10 → D-11 → D-12 which
includes a (forbidden) conrotatory 18π-cyclization, two ([1.9]; [1.5]) sigmatropic H-migra-
tions and an (allowed) disrotatory 14π-electrocyclization. As to the sequence of the
sigmatropic steps, the [1,9]-migration is considered to be faster because of its unusually
fast rate in the [16+2]-adduct D-2.

An effort was made to confirm the syn, trans-stereochemistry that was formulated for D-9 by attempting to form an adduct through the pentafulvene section of the molecule as was carried out with A-2t and B-2t. When D-6 was thermolysed in excess dimethylacetylenedicarboxylate at 150°C, the [4+2]-adduct D-7 was the only monomeric component. Thermolysis of D-6 in the

D-6 → [18 π] → D-9 → [1,9-H] → D-10 → [1,5-H] → D-11 → [14 π] → D-12

D-9 → D-13 ← -H- ← D-14

D-12 → D-15
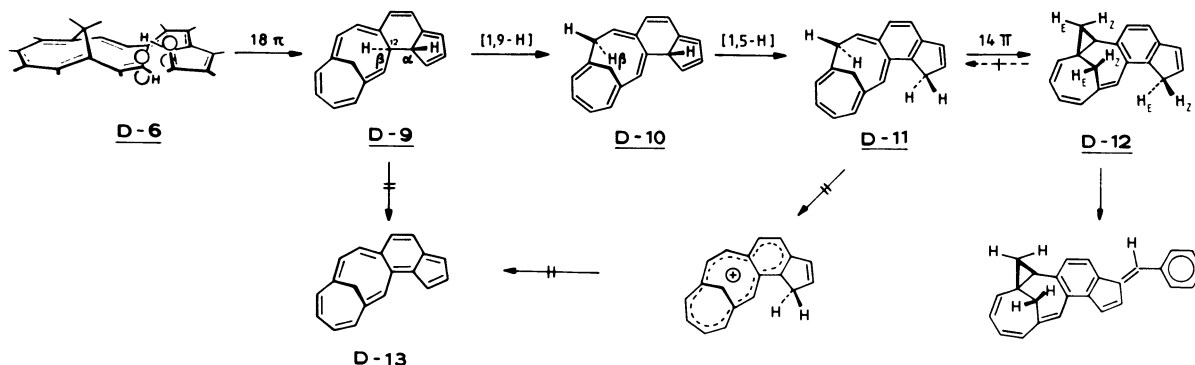
presence of various oxidizing reagents (e.g. MnO₂, ...) 14π-annulene F-19) gave no indication for the presence of the annulene D-13. In analogy to the successful preparation of phenazulene B-5 through deprotonation of B-4, access to D-14, a conjugate acid of D-13, was sought by H⁻-abstraction from D-11. Since D-11 is a potential though non-benzenoid equilibrium isomer of D-12, the latter was treated with trityl tetra-fluoroborate under a variety of conditions but no hydride elimination was achieved.

E   20π-ELECTROCYCLIZATION: A [18 + 2]-CYCLOADDITION REACTION?

The heptahendecafulvadiene E-1 was the candidate for the formation of the [20]-annulene E-6 (ref. 29). E-1 was prepared from aldehyde D-5 and the cycloheptatrienylidene-ketene. The syn-orientation of the heptafulvene-part in s-trans- E-1 (J₁',₂' = 12 Hz) was apparent from the shift-differences determined for the 2'' (7'')- and 3(5)-hydrogen pairs (Δδ = 0.28, 0.09 ppm).

E-1 → [20 π] → E-2 → E-3 → E-4 ⇌ E-5

E-2 → E-6

E-7   E-8 → E-9
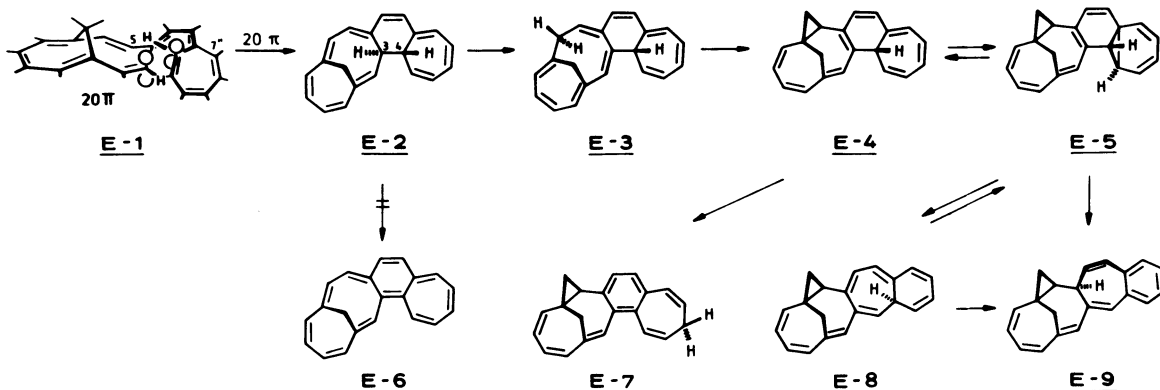
In degassed 5·10⁻³ molar xylene solutions E-1 remained practically unchanged up to 100°C for several hours. At 150°C the red-brown colour changed to yellow-brown (t₁ ca. 5 min). After partial (30%, 50%) as well as after total conversion two products (in addition to polymeric material) were formed in a practically constant 2:1 ratio (40%, not optimized) and were iden-tified by elaborate ¹H- and ¹³C-NMR analyses (with extensive NOE measurements) as E-7 (pentacyclo [14.4.1.0¹'³.0⁴'¹⁴.0⁷'¹³]heneicosa-4,6,8,11,13,15,17,19-octaene) and E-9 ((1α, 4β)-pentacyclo[14.4.1.0¹'³.0⁴'¹⁴.0⁷'¹²]heneicosa-5,7,9,11,13,15,17,19-octaene). In line with arguments presented above for the thermolysis of D-6, the formation of E-7/E-9 can be explained by the intervention of the common intermediates E-2 - E-4 which result from an initial 20π-electrocyclization via the syn-conrotatory transition state, followed by [1,9]-suprafacial H-migration, 10π-electrocyclization and [1,5]-H-migration in E-4 or homo-[1,5]-H-migration in its "bisnorcaradiene"-tautomer E-5. E-9 could also arise via E-8. The 3β,4α-configuration in the initial cyclization product E-2 and consequently the formally "symmetry-allowed" syn-conrotatory mode of cyclization in E-1 was firmly, albeit indirectly, estab-lished as follows: (i) the [1.9]-H-migration in E-2 is only possible anti to the CH₂-bridge, (ii) the β-orientation of 4-H in E-9 and consequently of the corresponding hydrogen in E-5 follows from the NOE-experiments and (iii) the two hydrogens in the cyclopropane ring of E-5 must be trans. Obviously, this peri- and stereospecificity was again proven only to the limited extent of isolated products.

The parent heptahendecafulvalene E-10 was still unknown and was prepared as a potential 18π-component for cycloaddition reactions. An 82% yield (red-brown crystals, m.p. 103°) was achieved by addition of the cycloheptatrienylidene ketene to ketone D-4. X-ray analysis revealed the extent of deviation from coplanarity in the direction towards the methylene

bridge (syn), a situation very similar to that in ketone D-4. Concerning the behaviour of E-10 in cycloaddition reactions, preliminary observations can be presented: E-10 reacts rapidly with TCE (the results of N-phenyltriazolinedione are comparable) at 20°C to give a ca. 10:10:1 mixture (84%) of the three crystalline 1:1-adducts E-11 - E-13, which could be separated chromatographically. The structural assignments were based on extensive ^{1}H- and ^{13}C-NMR measurements. The product composition obtained by reaction at -30°C was practically unchanged and on dissolving the individual adducts in benzene, the original product-ratio was restored. On long standing only E-12/E-13 (1:1) remained. The stereochemistry of the [18+2]-adduct E-11 is unambiguous only at C-3. 3-H shows a marked NOE with H-21 and does not undergo the fast sigmatropic migration as would be expected when anti-oriented (D-2). In view of both the syn-attack on the fidecene D-1 as well as of the geometry of E-10, a concerted formation of E-11 seems not very likely (ref. 30).
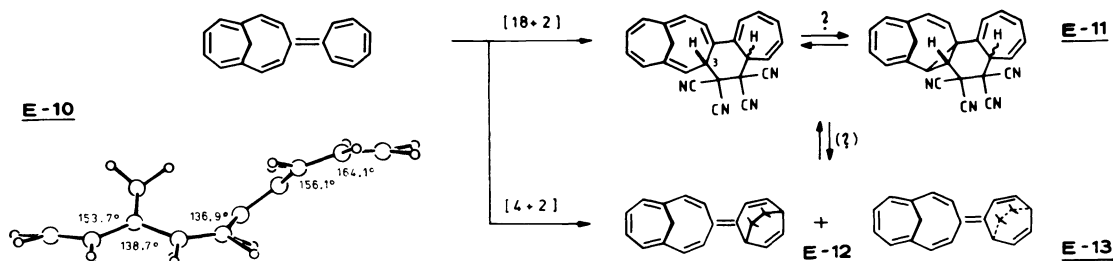
F AN (ATTEMPTED) 24π-ELECTROCYCLIZATION: AZULENOID 14π-TRICYCLOANNULENES

The longest polyene chain sterically fixed in the form of a fulvadiene for which a preparatively reasonable access seemed feasible was the dicyano-24π-hendecafulvadiene F-1 (ref. 31). Complications were introduced by the fact that anti-/syn-isomers (F-1a, F-1s) are possible. Synthesis of F-1 was accomplished along the lines for the corresponding dicyano-derivative of C-1. In solution (presumably under acid catalysis, slowly at 20°C, quickly at 140°C) or neat (short heating beyond the melting point) F-1a equilibrates with F-1s (ca. 9:1). Upon chromatography, pure solutions of F-1s can be separated. The ^{1}H-NMR spectra of F-1a (C_1) and F-1s (C_2) are very similar. Their differentiation was not possible with opti-shift reagents and rested mainly on the longest wavelength UV/VIS absorption of 468 and 408 nm resp. and a comparison of molecular models based on the geometry of D-4 and E-10.
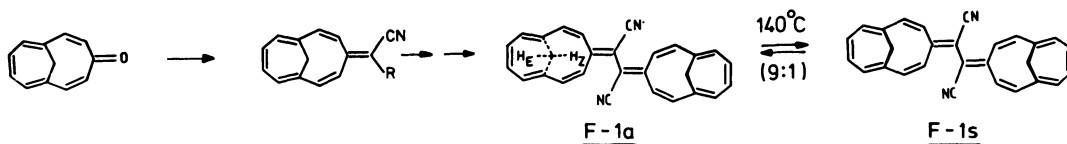
By inspection of models it was suggested that in both F-1a and F-1s, the orbital interaction in the α,ω(24π)-electron transition states are not as favourable as in the earlier cases and that the 14π-cyclizations (e.g. F-2) were serious alternatives. In fact, F-1a (F-1s) is kinetically much more stable than the lower vinylogues. In 10^{-2}M solutions (tetralin, triglyme) it remains unchanged up to 190°C. At temperatures between 200° and 500°C only polymerization occurred. Futhermore, in the presence of an oxidizing agent (chloranil, MnO2), no highly coloured component or any other monomer was seen (TCL, UV/VIS, ^{1}H-NMR). Only upon flash pyrolysis (400°C, 0.01 Torr, contact time ca. 0.1 s) very small amounts (3-5% each) of
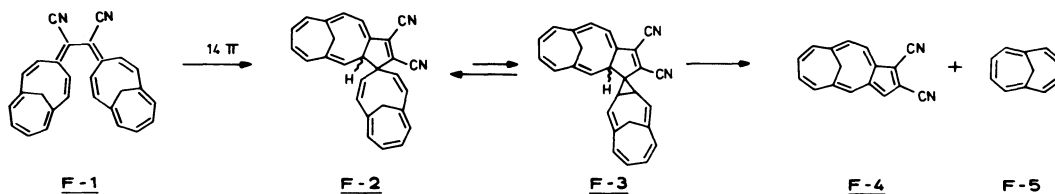

two monomeric products were isolated: the green crystalline F-4 (1,2-dicyano-5,10-methanocyclopentacycloundecaene (m.p. 206°C) and F-5. Their formation was ascribed to a 14π-cyclization (F-1 → F-2) followed by fragmentation of the valence isomer F-3 into the two stable ("aromatic") components. One might speculate whether the polymeric material comes from any of the products expected from 24π-cyclization. This latter mode would certainly have much better chances in the s-cis-fixed anhydride F-6 or in the (protonated) azine F-7. With respect to the latter, neither the ketone D-4 nor its alkoxonium-salts could be condensed with hydrazine even under severe conditions.

The novel 14π-perimeter molecule F-4 extends the series of the σ-bridged annulenes I. In the
context of formulating the 14π-transition state leading to F-2, the question arose as to the
electronic nature of this novel type of tricycloannulenes. In order to gain more information
regarding this point, the parent compound and several more or less substituted derivatives
were prepared - all via polyelectron-pericyclic approaches. It must be stressed, however,
that the individual compounds at this stage had only to provide physical data and that
therefore the yields were not optimized.

The earlier projected [12+2]-addition with hendecafulvenes and dienophiles (ref. 3) was suc-
cessfully realized with the fulvenic ester F-8 and dimethylacetylenedicarboxylate. At 80°C
(boiling benzene) the reaction had led only to polymeric material, but on addition of an oxi-
dizing agent (e.g. MnO₂), green crystals of F-10 were isolated in 25% yield as the only
monomeric component. One may well assume that the primary [12+2]-adduct F-9 undergoes fast
sigmatropic rearrangements with the resulting cyclopentadienes giving rise to polymerization.
Saponification and decarboxylation (100% phosphoric acid,   90°C) of F-10 led ultimately to

F-8   F-9   F-10   F-11
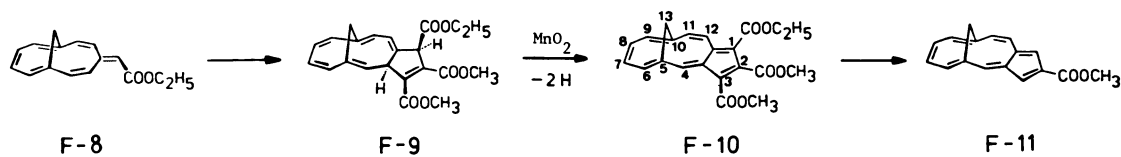
the monoester F-11 in 52% yield (green needles). Its relationship with 10π-azulene is
manifested i.a. by its fast and reversible (triethylamine, 100%) protonation (C1/C3)by tri-
fluoroacetic acid. F-14 (green crystals), the tricyano-anologue of F-10, was available from
the reaction between the cyanohendecafulvene F-12 and dichlorodicyanoquinone (DDQ, 20°C,
CH₂Cl₂). As in the first examples which utilized DDQ as a dicyanoacetylene equivalent in cy-
cloaddition reactions (ref. 17,32), yields under varied conditions remained very poor (≈
10%) and the mechanistic details (e.g. the intervention of the [12+2]-adduct F-13) obscure.
The reactivity of F-8 towards tetrachlorothiophenedioxide, applied e.g. as a 4π-component in
[6+4]-additions with pentafulvenes (ref. 33), was interesting primarily as a potential route
towards F-16, the derivative of the still unknown next higher (16π) member in the series of

F-12   F-13   F-14   F-15   F-16
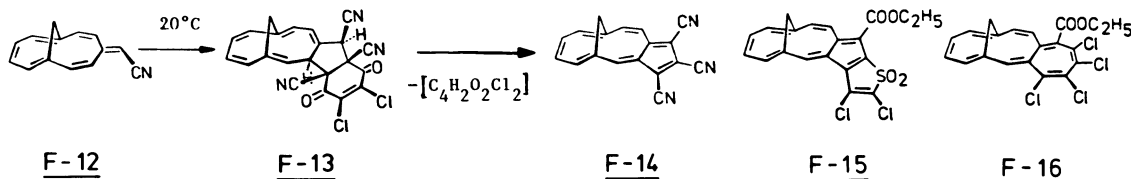
the σ-bridged annulenes I. The reaction turned out to proceed rather sluggishly and demanded
a relatively high reaction temperature (boiling xylene). Under varied conditions with and
without base (quinoline) no F-16 could be detected and instead the green-black F-15 was
isolated in very low yield (ca. 1-4%). The structural assignment, based on the ¹H- and ¹³C-
NMR analyses was ambiguous with respect to the alternative position of the SO₂-group in the
cyclopentadiene ring.

Efforts to realize α,ω(14π)-electrocyclizations in vinylogous hendecafulvenes of type F-17/F-
18, so far not documented, were intended to lead ultimately to alternatively substituted 14π-
tricycloannulenes and to provide information with regard to the problem of overruling the 1,9
H-migration by dehydrogenation in cases where a rather stable annulene can be expected.

Two examples, available from the aldehyde D-5, were checked. The dinitrile F-17 (86%, violet
needles) could not be cyclized. Highly dilute solutions (10⁻⁴M) were unchanged up to tempera-
tures > 160°C, where only decomposition was observed. The analogous heptafulvene-derivative

F-17: R = R´ = CN
F-18: R = H, R´ = COOC₂H₅   F-19   F-20   F-21/ F-22
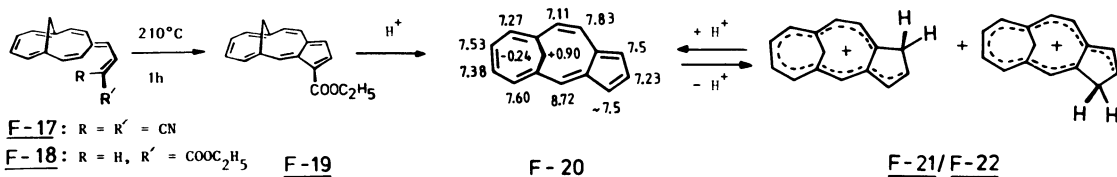
cyclizes between 400-500°C (ref. 34). Even F-18 remained unchanged up to 200°C, obviously
being kinetically more stable than the fulvalenes D-6/E-1 and at 210°C (ca. 10⁻²M tetralin
solutions, 1h), in the presence of MnO₂, a small amount of F-19 was formed and isolated (6-
8%) as a green oil (λₘₐₓ(ethanol) = 625nm (ε = 800); λₘₐₓ (CF₃CO₂H) = 442nm (ε = 6000)). F-19
was considered as a useful precursor to the parent compound F-20 in view of the behaviour of
triester F-10 under decarboxylation conditions. After heating F-19 in 100% H₃PO₄ (150°C), ca.
50% F-20   were separated chromatographically as a green oil (λₘₐₓ (ethanol) = 640, 426, 317,
270 (sh)). Its ¹H NMR spectrum was, as expected, very similar to that of the 2-ester F-11.
Since we had only mg-amounts, ¹³C-data were not obtained.

To better determine the electronic structure of the parent 14π-tricycloannulene <u>F-20</u>, a knowledge of the bond lengths would have been important. However, in spite of intensive efforts, crystals of sufficient quality of any of the crystalline derivatives could not be obtained. The close relationship to azulene, implicating an appreciable π-electron delocalization (aromaticity) (ref. 35) was firmly established by the following correlations (ref. 36):

i) The λ_{max} values of the esters <u>F-10</u>, <u>F-19</u> and <u>F-11</u> vary according to the substitution pattern (610, 634, 672 nm) in a way which has been theoretically explained for the analogous azulene esters (584, 645, 726 nm);

ii) The vicinal coupling constants measured for <u>F-10</u>, <u>F-11</u> and <u>F-19</u> in the eleven-membered ring, like those in the seven-membered ring of azulene, are of comparable magnitude and are not "alternating" to the extent seen in the annellated, more "localized" azulenes;
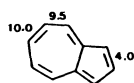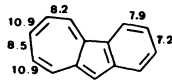
(Heilbronner)   (Bertelli)   (Takeuchi)
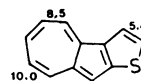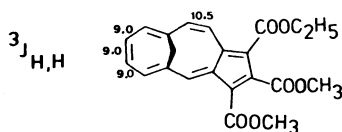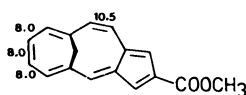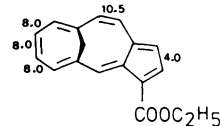
F-10   F-11   F-19

iii) The ^{1}H- and ^{13}C-chemical shifts of the eleven-membered ring moiety compare well with those of "delocalized" 10π-systems. The average of these ^{1}H- and ^{13}C-chemical shifts fall between the values of the delocalized 10π-cation and localized polyenes (Vogel, Masamune).
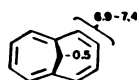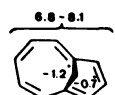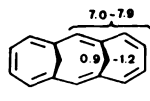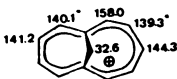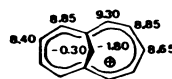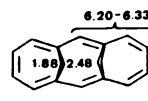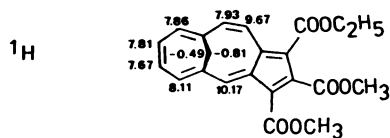

(Vogel)   (Scott)   (Vogel)
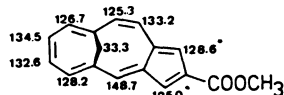

(Vogel, Masamune)

^{1}H

^{13}C
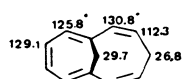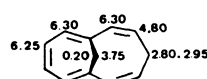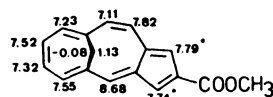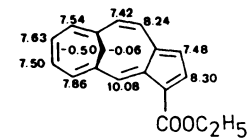
F-10   F-11   F-19
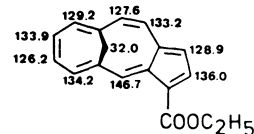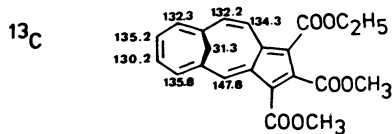
In the context of this chapter is the α, (24π)-cycloaddition with the hendecafulvalene <u>F-23</u> (ref. 37) pertinent. There are good reasons to assume that <u>F-23</u> has the anti-configuration and this would help to explain why <u>F-23</u>, as the only fulvalene of Scheme 2, resisted even TCE (up to 80°C, benzene). With N-methyltriazolinedione only decomposition occurred. In a configuration analogous to <u>E-10</u>, both sides of <u>F-23</u> are efficiently sterically shielded.
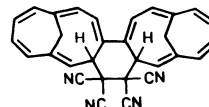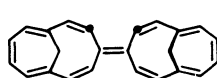
F-23

G ELECTROCYCLIZATIONS WITH THE FULVATRIENES

The comparison of transition state models for the α,ω-cyclization in the penta/heptafulva-
dienes and the cis-penta/heptafulvatrienes raised early doubts that the eight-membered ring
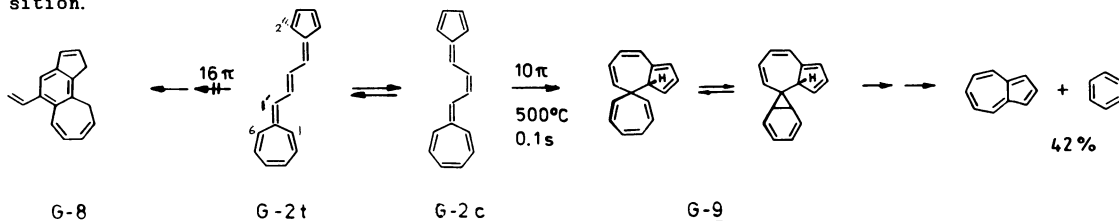formation VIII → IX would proceed with equal ease. Due to the inherent buildup of
considerable strain, it was not even clear whether the cyclization step would be exothermic.

     A-1   G-1   B-1   G-2   C-1   G-3
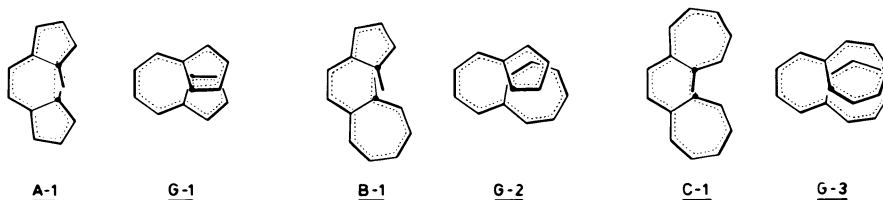
In fact, the cis-fulvatrienes G-1 - G-3 were in general kinetically much more stable than the
corresponding fulvadienes. In highly dilute, degassed solutions (ca. 10^{-4} M) between 100–
130°C, only cis/trans-isomerization occurred in addition to significant polymerization. No
primary cyclization product could be identified (e.g. G-5 by interception with a dienophile,
c.p. A-5, B-6). Flash pyrolysis conditions (0.1s contact time) were therefore applied as ex-
ercised with F-1. From G-1c (ref. 38), at around 500°C up to 64% (based on sublimed material)
of the vinyl dihydro as/s-indacenes G-4/G-7 (as tautomers) were isolated. G-4 most probably
arises via an initial 14π-cyclization G-1c → G-5 and G-7 presumably via an initial 8π-cy-
clization G-1c → G-1t → G-6. The final conversions G-5 → G-4 and G-6 → G-7 have preced-
ents in the literature.

     G-4   G-5   G-1c   G-1t   G-6   G-7
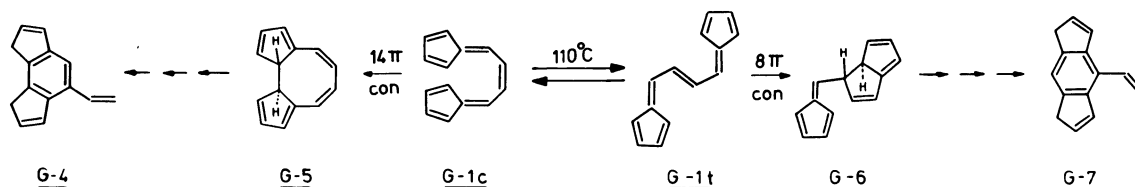
In the case of the pentaheptafulvatrienes G-2 (ref. 39) only the trans-isomer was at our dis-
posal. After pyrolysis (500°C), 42% monomeric material were identified as a ca. 1:1 mixture
of azulene and benzene. No G-8, the benzenoid isomer expected as final product of the α,ω-cy-
clization, was found. This result is reminiscent of the fragmentation observed for the hende-
cafulvadiene F-1. 10π-cyclization to G-9 and fragmentation of its norcaradiene-tautomer are
plausible intermediate stages. G-3 (ref. 40) could not be sublimed without extensive decompo-
sition.

     G-8   G-2t   G-2c   G-9   42%

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