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Heteropentalenes and Heterocyclic Ferrocenes

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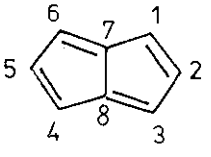
The synthesis and properties of heteropentalene anions with one heteroatom and heterocyclic ferrocenes with a fused π-heterocycle have been reviewed.

Introduction:

In 1922 Robinson and Armitt [1] considered the possibility that pentalene (1) might be an aromatic hydrocarbon. Three years later the same authors [2] pointed out that this was unlikely since sextets of electrons could not develop in each ring.

Simple MO calculations [3] predict that the eight π-electrons in pentalene occupy the four bonding orbitals and that the non-bonding orbital remains unoccupied. So the question was raised whether pentalene is an open shell molecule. As pentalene is a nonalternant hydrocarbon calculations by the Wheland-Mann-method (ω-technique) with inclusion of alternating bond lengths [4] gave improved values for pentalene. Due to this self-consistent method symmetrical pentalene is an open shell molecule. Calculations by the method of Hess and Schaad [5] gave a resonance energy RE= - 0.14 ß and a resonance energy per electron REPE = -0.018ß, which means that pentalene is a polyene or an antiaromatic compound.



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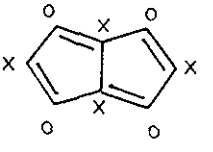
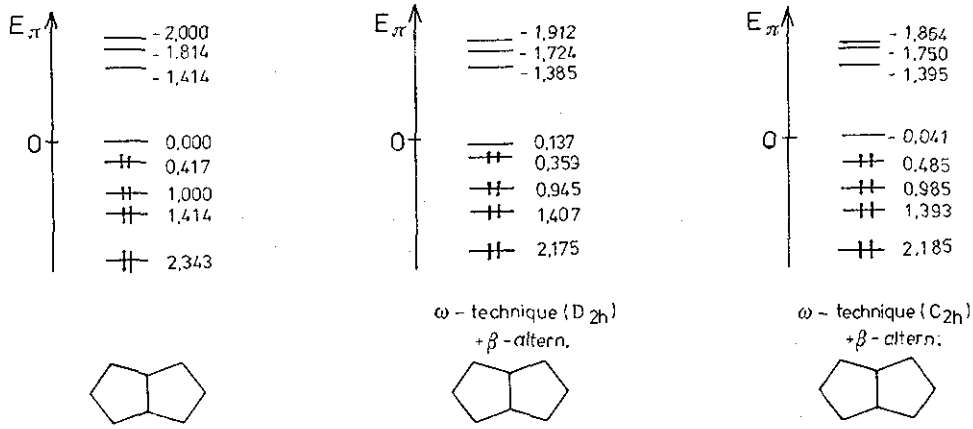
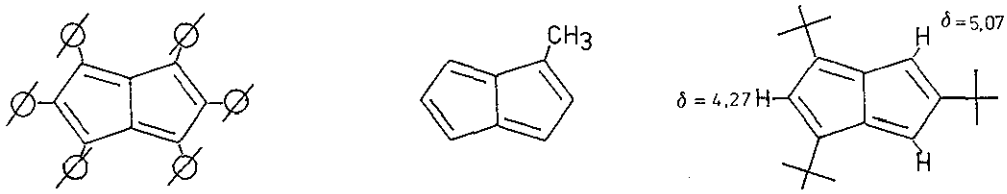


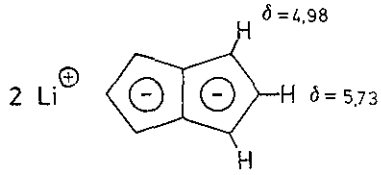


In agreement with the theoretically deduced instability of pentalene were the many unsuccessful attempts to synthesize pentalene. Only quite recently, however, the following three *derivatives of pentalene* (2) [6], (3) [7] and (4) [8] could be synthesized.



2 3 4

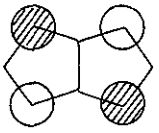
On the basis of comparative nmr studies an antiaromatic character was deduced for (4). Pentalene could be converted to an aromatic system by the addition of two electrons. And Katz and Rosenberger [9] obtained the pentalene dianion (5) by the action of butyllithium on a dihydropentalene.



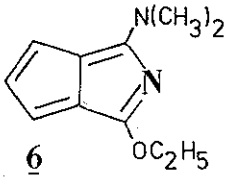
5 δ = 4,98

1-, 2- and 7-Azapentalenes

Pentalene is, as shown before, an open shell molecule and its properties are greatly determined by its lowest unoccupied orbital (LUMO).



Heteroatoms which are more electronegative than carbon should destabilize a heteropentalene when they are in 1-, 3-, 4- and 6- position and their influence can be neglected when they are in 2-, 5-, 7- and 8- position. In agreement with this 2- and 7- azapentalene derivatives with electron-donating substituents, which stabilize even the parent pentalenes, (6) [10], (7) [11] and (8) [12] could have been synthesized and are relatively stable.



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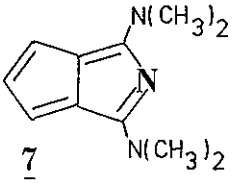

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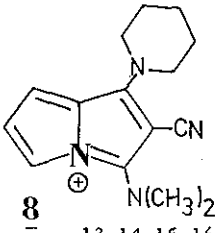
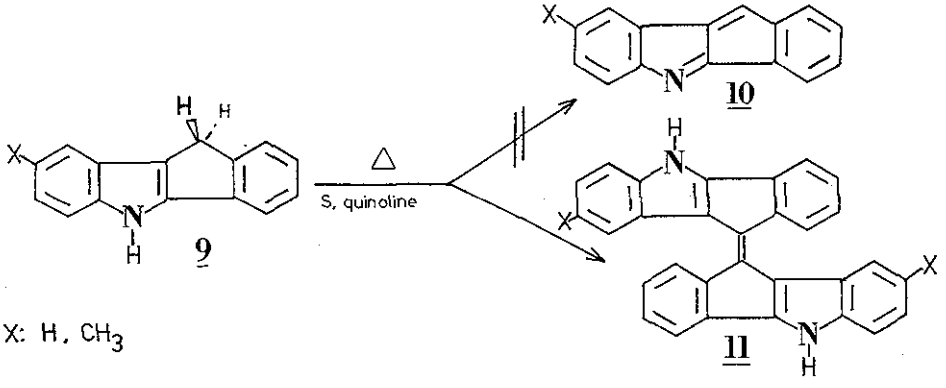


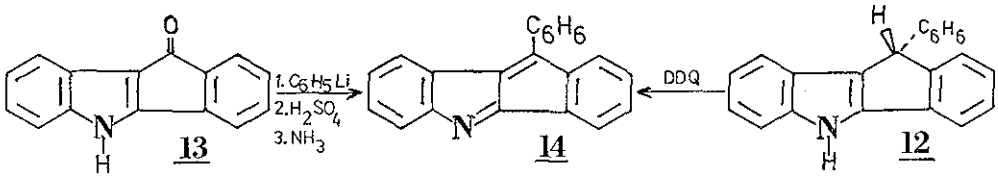
8

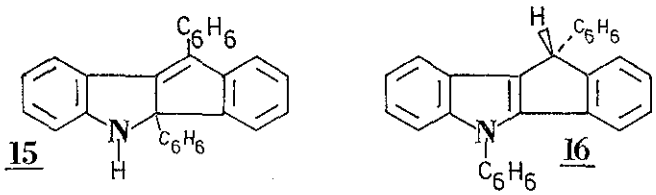
There were some reports on benz- and dibenz-azapentalenes in the literature [13, 14, 15, 16] which have been discredited [15, 17, 18]. It could be shown by spectroscopic studies and independent synthesis of the reaction products that the sulfur dehydrogenation of 2, 3-dihydrocyclopent[b] indoles (9) does not yield dibenz-1-azapentalenes (10) but bis-indenoindoles (11) [17].



The dibenz-1-azapentalene (14) was prepared quite recently by two different routes: either by the DDQ dehydrogenation of (12) or by the addition of phenyllithium to ketone (13) and subsequent dehydration [19].

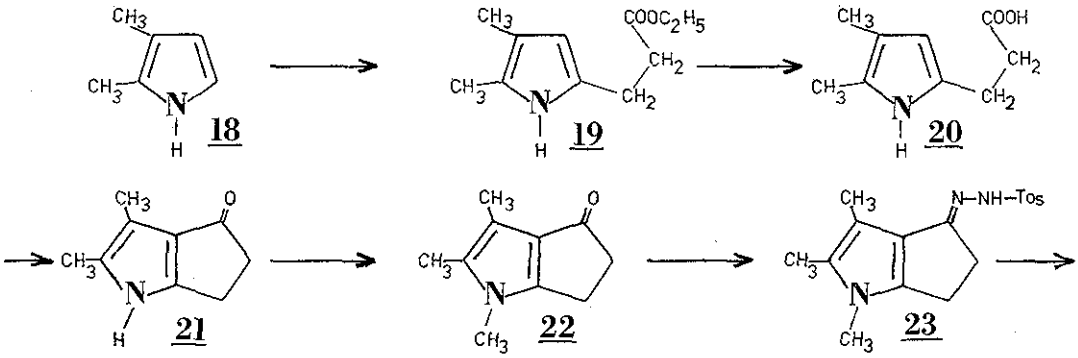
Treatment of (14) with an excess of phenyllithium in ethyl ether yielded the two compounds (15) and (16).

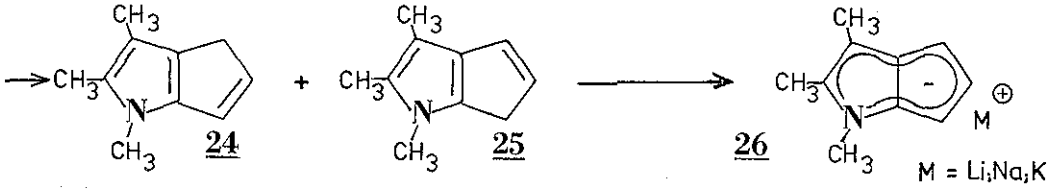




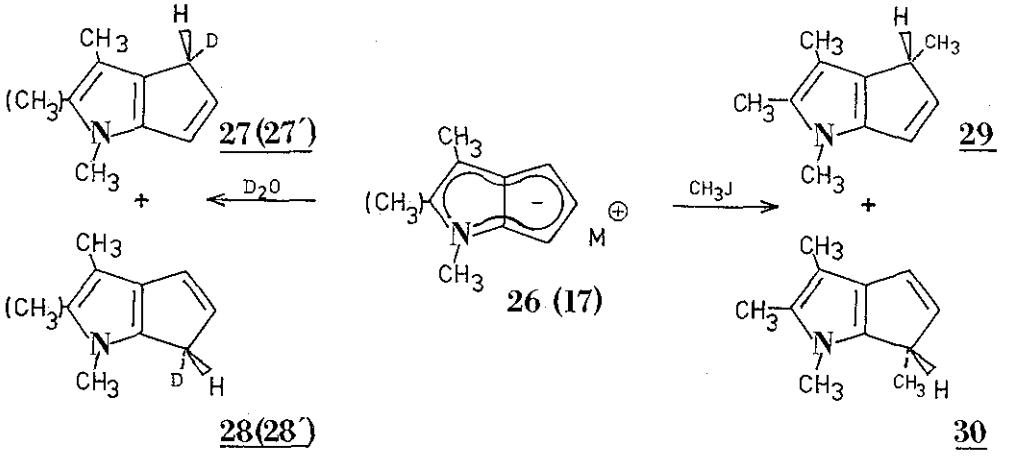
1-Azapentalene Anions

The addition of phenyllithium to (14) documents the open shell character of 1-azapentalenes. *The 1-azapentalene anion, however,* should be a stable aromatic 10 π-electron system. The 1-azapentalene anion (17) was prepared by a 12-step synthesis starting from Knorr's pyrrole [20] and (26) could be received starting from 2, 3-diemthyl pyrrole (18) by a 7-steps synthesis [21].

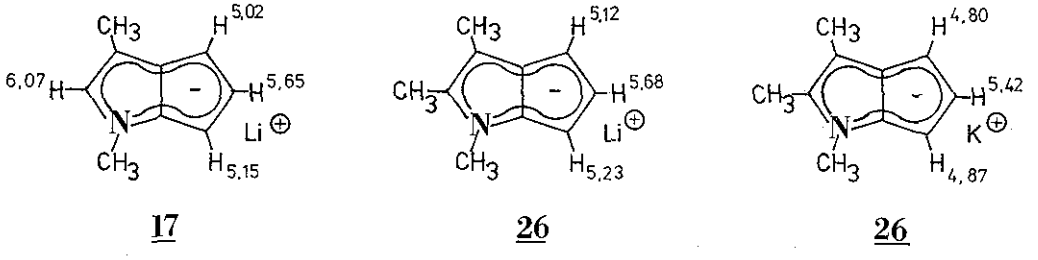




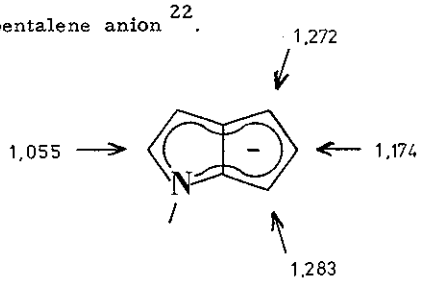
Quenching of the anions (17) and (26) with deuterium oxide led to the monodeutero olefins (27)/(27'), and (28)/(28'). Alkylation of (26) with methyl iodide gave the methyl olefins (29) and (30)



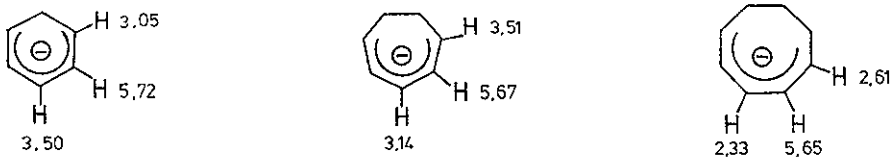
^{1}H-chemical shifts of (17) and (26) in THF resp. THF-d_8, δ rel. TMS:



The chemical shifts of the methine protons correlate good with the respective HMO-π-electron densities of the 1-azapentalene anion [22].

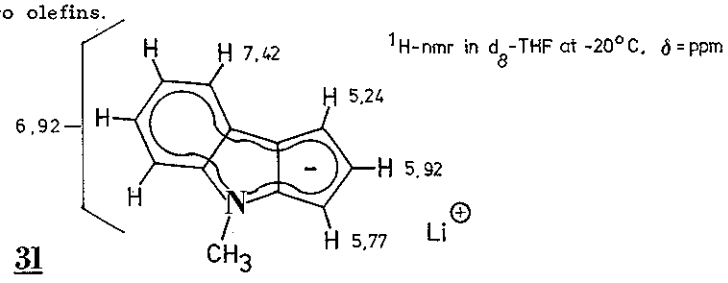


The nmr signals of the protons of the carbocyclic ring in (17) and (26) appear in a relatively narrow range, whereas the chemical shifts of the protons of unsaturated carbanions without cyclic conjugation normally differ much more. And a diamagnetic ring current for (17)



and (26) is indicated by the deshielding of the protons H-4, H-5 and H-6. Five membered unsaturated ring compounds are considered aromatic if there are small differences in the vicinal spin-spin coupling constants of their ring protons [23, 24]. In conformity with the ΔJ values of (26), $\Delta J = 0.4$ Hz for the lithium salt and $\Delta J = 0.25$ Hz for the potassium salt, the 1-azapentalene anion is an aromatic compound. The shift of the ^{1}H-nmr signals of (26) to somewhat higher field by going from the lithium salt to the potassium salt is certainly produced by the different interaction of the ions in the contact ion pair [25].

Starting from 1-keto-2, 3-dihydrocyclopentindole the 1-methyl-benz [b] -1-azapentalene anion (31) was prepared in a 4-step synthesis [26]. According to its ^{1}H-nmr spectrum (31) is an aromatic azapentalene derivative. Quenching of (31) with deuterium oxide gave the two corresponding monodeutero olefins.



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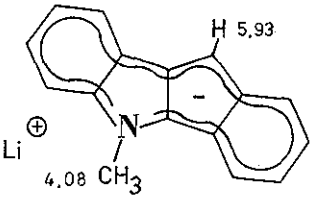
Deprotonation of N-methyl-indeno-indole with butyllithium produced in THF the orange and in ether the yellow solution of the 1-methyl-dibenz [b, f] -1-azapentalene anion (32) [27].

On cooling the solution the lithium salt of (32) precipitates as yellow crystals.

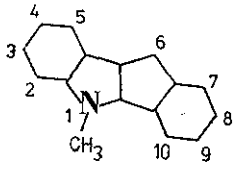
^{1}H-nmr in THF at - 20°C, δ ppm:

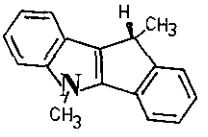


benzo protons: 6.45-7.72 ppm

32

Alkylation of (32) with methyliodide gave in 86 % yield the 1.6-dimethyl-indeno-indole (33). Addition of benzophenone to (32) and subsequent dehydration resulted in the formation of the yellow diphenyl fulvene derivative (34) which has a long wave length absorption at λ_{max} 448 nm.





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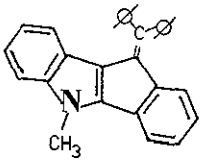

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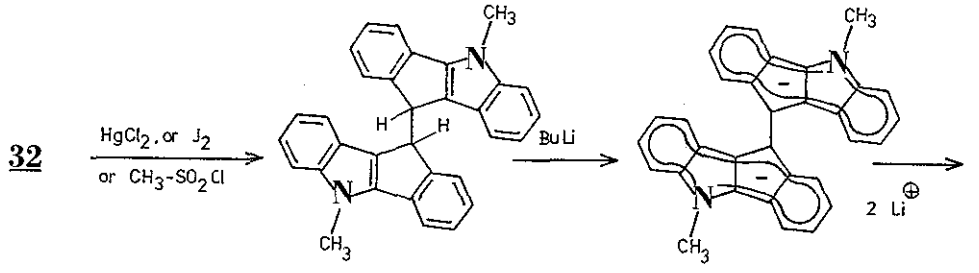
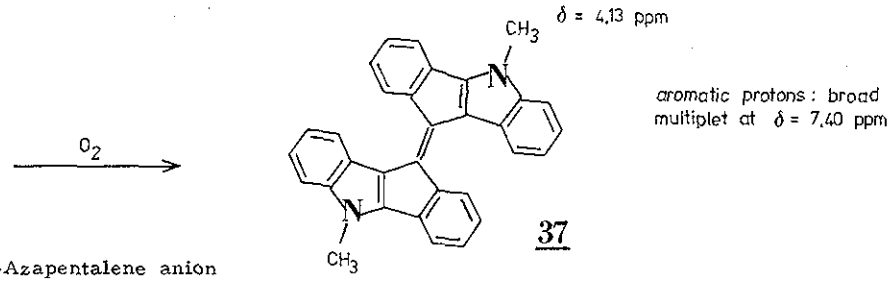
The reaction of $HgCl_2$, or J_2, or methyl sulfochloride with (32) produces the dimer N-methyl-indeno-indole (35). Deprotonation of (35) with butyllithium yielded the dark blue dianion (36). Treatment of (36) with dry oxygen gave the fulvalene (37). Whether only the trans isomer of (37) or a mixture of cis and trans isomers is formed in the above reaction has still to be clarified. The isolated fulvalene (37) has in CH_2Cl_2 a long wave length absorption at 550 nm.



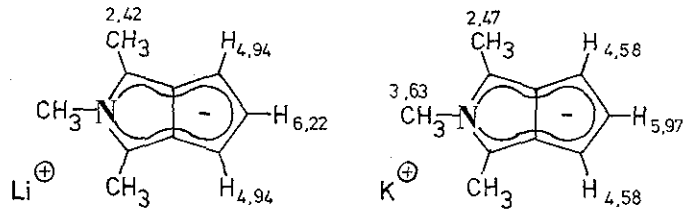
35 **36**



The 2-Azapentalene anion

The 1. 2. 3-trimethyl-2-azapentalene anion (38) was prepared in a 9-step synthesis starting from 2. 5-dimethyl-pyrrole [28]

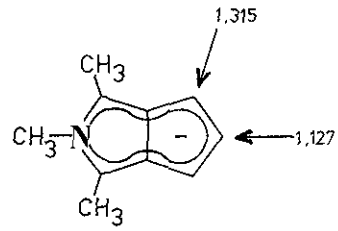
^1H-nmr spectrum δ ppm *rel. TMS:*



38 in THF (-20°C)

38 in THF-d_8 (-20° C)

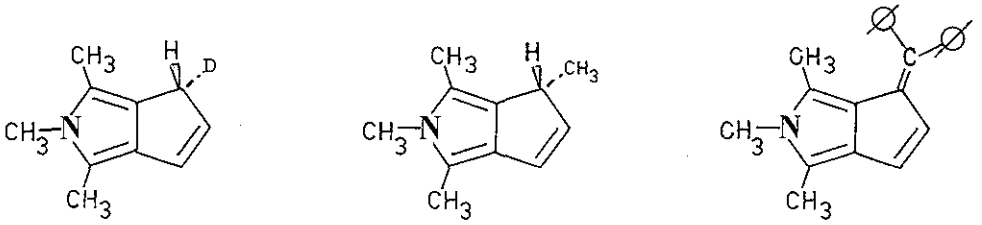
HMO-π-electron densities of (38) [29]:



The simplicity of the nmr spectrum of (38) shows that it is indeed the symmetrical, delocalized species shown and not a covalent lithium compound. In analogy to the 1-aza-pentalene anion (26) the deshielding of the protons H-4, H-5 and H-6 indicates a diamagnetic ring current in (38).

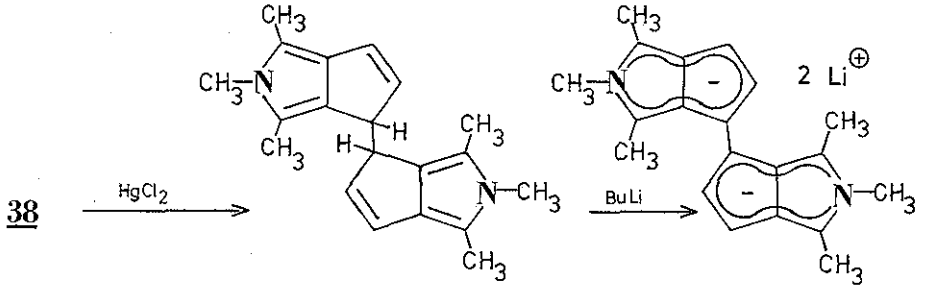
Addition of deuterium oxide to a solution of (38) gave the monodeuterated olefin (39).

Alkylation with methyl iodide yielded the 1. 2. 3. 4-tetramethyl olefin (40). The reaction with benzophenone and subsequent dehydration produced the di-phenyl-pyrrolo-fulvene (41) [30].

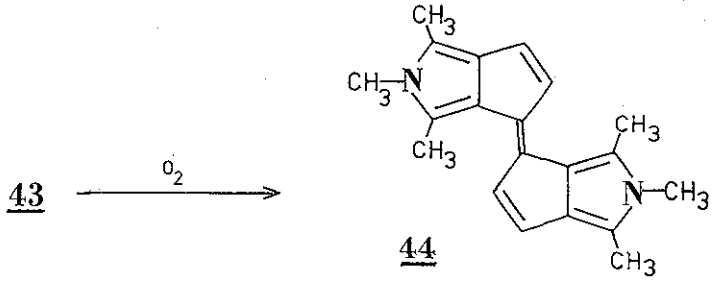


39 **40** **41**

Treatment of (38) with $HgCl_2$ gave the dimer olefin (42) which was deprotonated to the dark red dianion (43) by butyllithium. The dianion (43) was oxidized to the fulvalene (44) by dry oxygen[31].



42 **43**

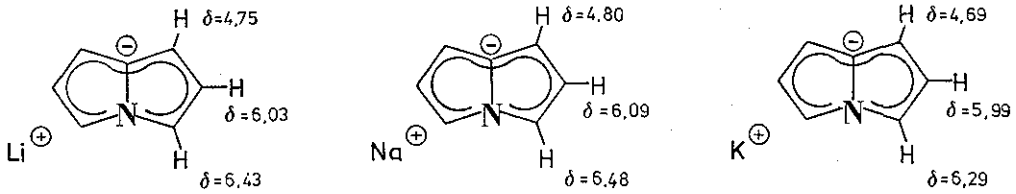


44

A comparison of the ^{1}H-chemical shifts of the protons H-4, H-5 and H-6 in (38) and H-4 in (43) shows that there is practically no charge transfer from one half to the other half in the dianion (43). On the basis of HMO calculations the 2-azapentalene anion (38) should be less stable than the 1-azapentalene anion (26). The determination of the rate of exchange of the protons of the corresponding olefins with D_2O in DMF containing triethylamine (method of R. Dessy [32]) is in good agreement with the theoretical prediction [33].

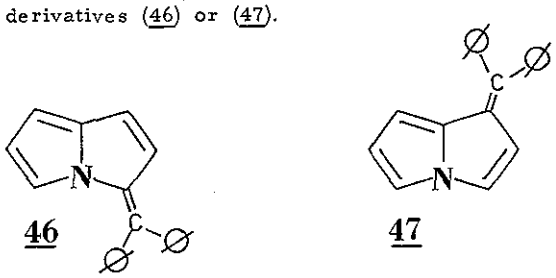
The 7-Azapentalene Anion

The 7-azapentalene anion (45) was prepared by treating 3-H-pyrrolizine in THF at -78°C either with n-butyllithium or with potassium or sodium [34].



45 45 45

The long-wave length maximum of (45) in THF is λ_{max} 295 nm. (45) reacts with benzophenone to give the fulvene derivatives (46) or (47).

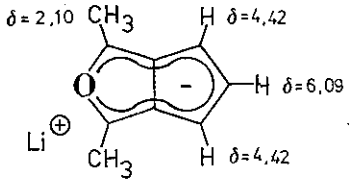


46 47

The pK_a of 3-H-pyrrolizine was determined as 29 (pK_a-Indene 18.2).

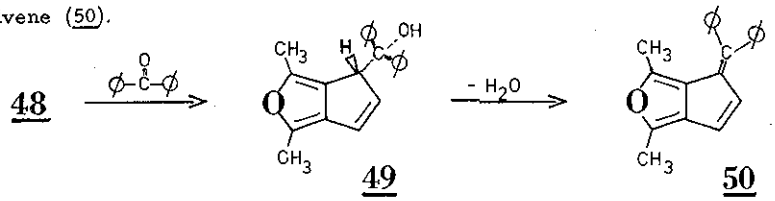
The 2-Oxapentalene Anion

Starting from t-butyl acetoacetate the 2-oxapentalene anion (48) was prepared in a eight-step synthesis [35].



48

Quenching of (48) with deuterium oxide gave the monodeutero olefin and alkylation with methyl iodide gave the 1,3,4-trimethyl olefin. Addition of benzophenone to (48) produces alcohol (49) which loses water by warming in benzene in the presence of a trace of toluenesulfonic acid to form the fulvene (50).



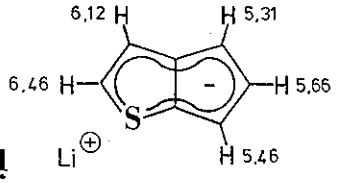
The upfield shift of the nmr signals of (48) in comparison with the 2-azapentalene anion (38) and the 2-thiapentalene anion (57) could be accounted for by a weaker ring current effect in the 2-oxapentalene anion (48).

The 1-oxapentalene anion has not yet been synthesized.

The 1-Thiapentalene anions

The 1-thiapentalene anion (51) was prepared in a seven-step synthesis [36] and the 5-methyl-1-thiapentalene anion (52) in a four-step synthesis [37] starting from thiophene. Both anions form yellow solutions in THF and can be precipitated at -78°C as pale yellow lithium salts.

^{1}H- and ^{13}C-nmr spectra of (51), (52) and (55) δ ppm rel. TMS:



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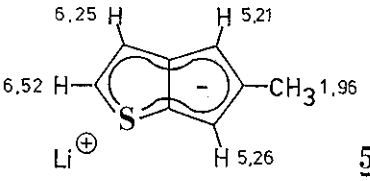

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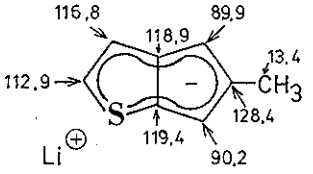

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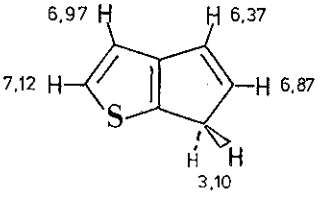

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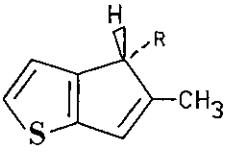
Quenching of (52) with deuterium oxide yields a mixture of 4-deutero- and 6-deutero-olefin (53a) resp. (54a). Alkylation with methyl iodide gave a mixture of two olefins (53b) and (54b).

a) R = D
b) R = CH_3



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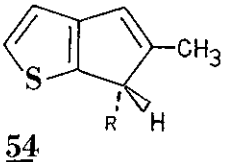


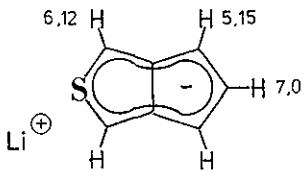
54

Because of the ring current in (51) and (52) the nmr-signals of H-4, H-5 and H-6 appear at relatively low field. The signals of the thiophene protons of (51) and (53) are shifted upfield by 0..6 - 0.85 ppm relative to the thiophene protons of the olefin (55). This indicates that negative charge is delocalized to some extent into the thiophene ring of (51) and (52). This charge delocalization is also documented by the ^{13}C-nmr-spectrum of (52). The signals of C-2 and C-3 of (52) are shifted upfield by 10-12 ppm relative to thiophene (C_α 125.4; C_β 127.2 ppm [38]). Furthermore, the ^{13}C-chemical shifts of C-4 and C-6 of (52) are of the same order as those of C-1 and C-3 of the indenyl anion [39].

The 2-Thiapentalene anion

Starting from thiophene the 2-thiapentalene anion (56) was prepared in a 10-step synthesis[40]. The 1.3-dimethyl-2-thiapentalene anion (57) could have been synthesized in 7 steps starting from 2.5-dimethyl-thiophene[41]. The nmr spectra show that the anions (56) and (57) have a

^{1}H-chemical shifts of (56) and (57) δ ppm rel. TMS:



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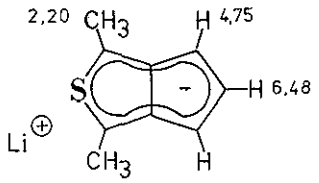
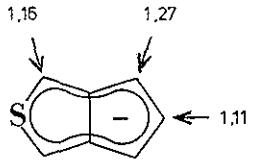


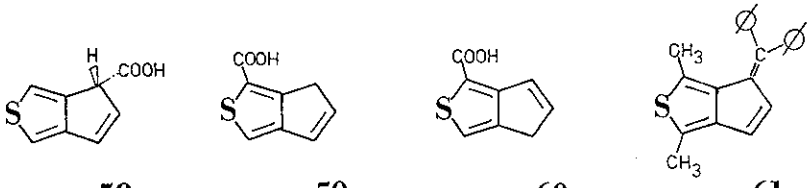
57

symmetrical ionic structure.

π-electron density (ω-technique):



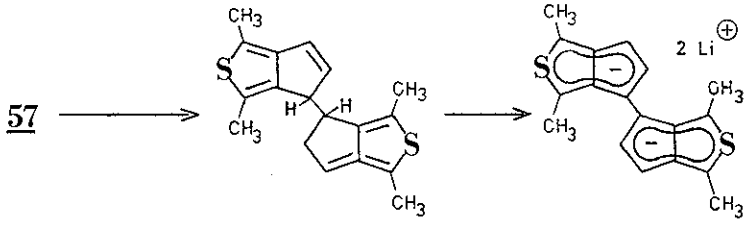
By treatment of (56) with carbon dioxide at -10° to 0°C and immediate acidification with dilute hydrochloric acid one obtains a mixture of acids. The major component of this mixture was according to nmr of 4-carboxy-4-H-cyclopenta[c]thiophene (58). However, carboxylation of (56) occurs also in the positions 1 and 3 forming the acids (59) and (60). Addition of benzo-



58 **59** **60** **61**

phenone to (57) followed by dehydration produces the fulvene (61).

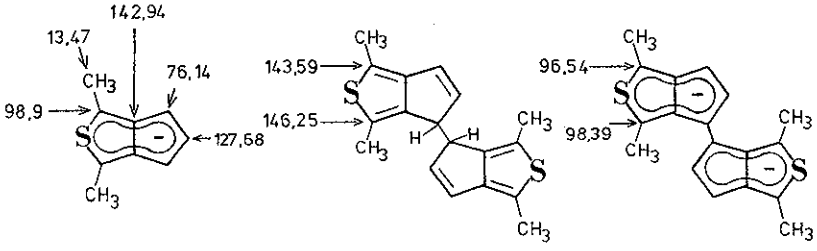
The reaction of iodine or $FeCl_2$ with (57) yielded the dimeric olefin (62), which was converted to the dark red dianion (63) [42].



62 **63**

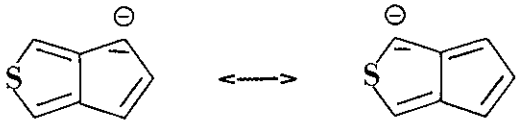
The comparison of the ^{13}C-nmr spectra of (57), (62) and (63) shows that there is also delocalization of negative charge into the thiophene ring of the anions (57) and (63). Which means

^{13}C-chemical shifts of (57), (62) and (63) δ ppm rel. TMS:



57 **62** **63**

that structure (65) makes some contribution to the total resonance structure of the 2-thiapentalene anion. And this is in good agreement with the experimental finding that carboxylation occurs also to some extent in the thiophene moiety of (56).



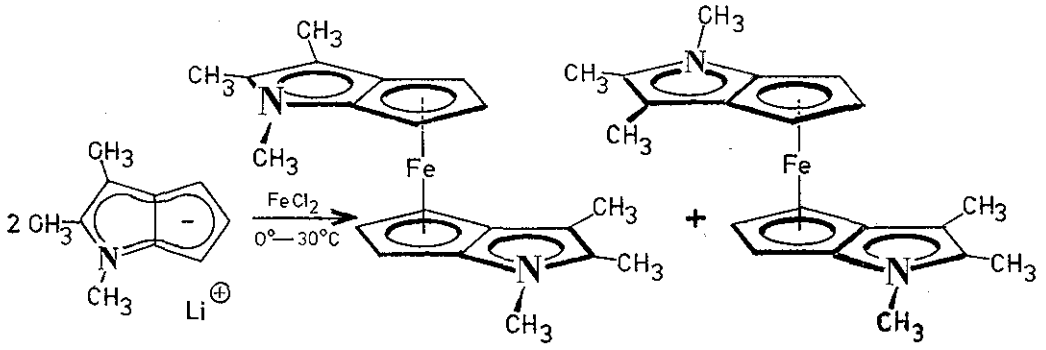
64 **65**

Heterocyclic Ferrocenes

Since the discovery of ferrocene there has also appeared an immense body of literature concerning the chemistry of heterocyclic ferrocenes [43]. However, there was no report on heterocyclic ferrocenes with a fused π-heterocycle until quite recently. And it is this later type of heterocyclic ferrocenes we want to deal with in this review.

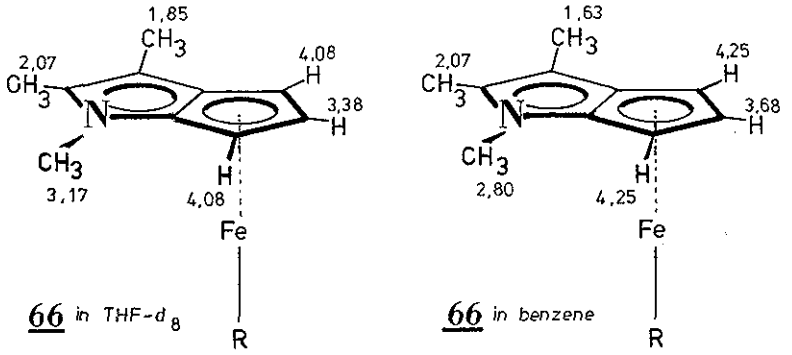
The Bis(1. 2. 3-Trimethyl-Pyrrolo (b))Ferrocene.

The bis(1. 2. 3-trimethyl-pyrrolo (b))ferrocene (66) was received as dark red crystals by reacting the 1-azapentalene anion (26) with $FeCl_2$ in THF [44]. It could not be clarified until now whether one isomer or a mixture of the two isomers (66) and (66') is formed in the above reaction. The long wave-length absorption of (66) is at λ_{max} 493 nm.



(66) is less stable than the isoelectronic di-indenyl-iron. Relative to (26) the signals of the protons of the carbocyclic rings in (66) are shifted upfield by more than 1 ppm.

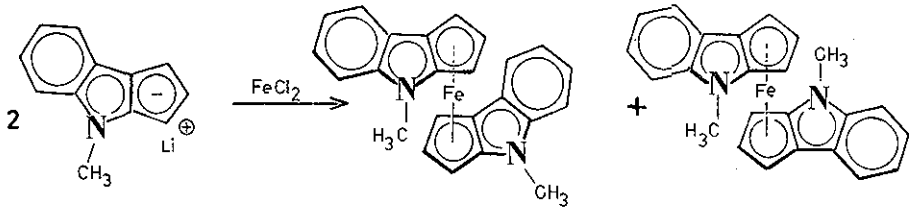
^{1}H-chemical shifts of (66) δ ppm rel. TMS:



The catalytic hydrogenation of (66) in methanol over platinum is very slow and leads to the bis (1. 2. 3-trimethyl-pyrrolino (b)) ferrocene.

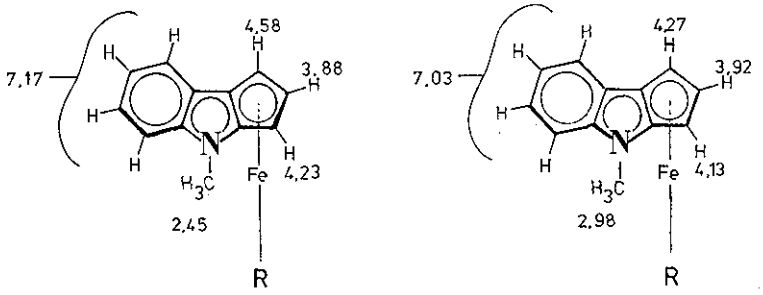
The Bis(N-Methyl-Indolo (b)) Ferrocene

The reaction of the benz-1-azapentalene anion (31) with $FeCl_2$ gives a mixture of the two dark red isomeric bis-indolo-ferrocenes (67) and (67')[45]. The isomer (67) could be received in pure form by fractionated crystallization, whilst (67') remains always contaminated with some (67). Both isomers are sensitive to air oxidation.



31 67 (λ_{max} 491,5 nm) 67' (λ_{max} 496 nm)

^{1}H-chemical shifts of (67) and (67') δ ppm rel. TMS:



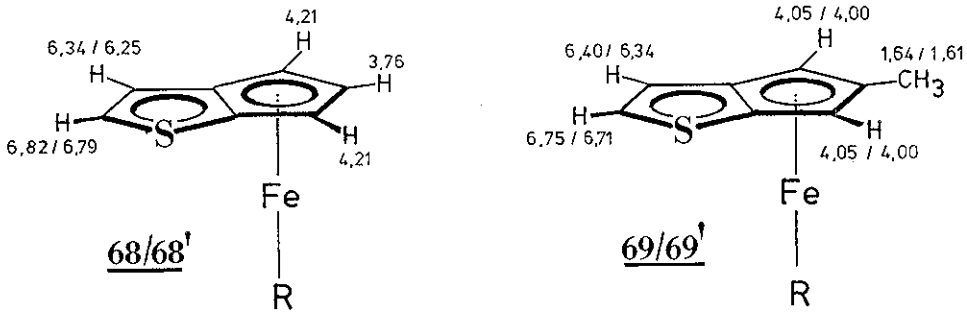
67 67'

In the nmr spectra of (67) and (67') we observe an upfield shift of the signals of the carbocyclic ring protons relative to the anion (31).

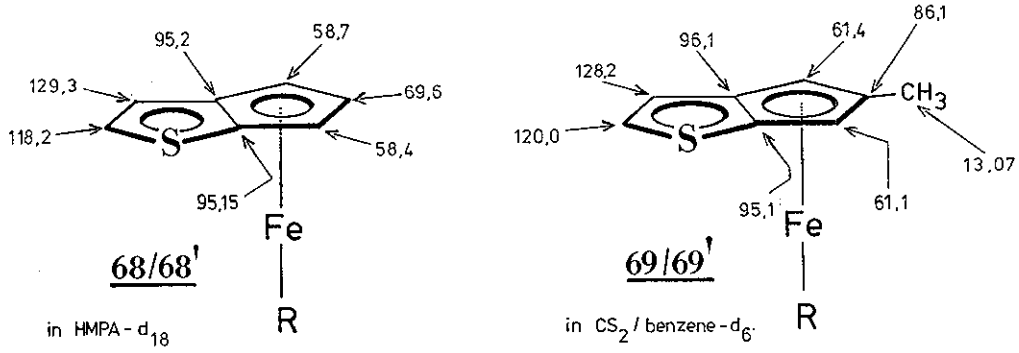
The Bis(Thiopheno (b)) Ferrocenes

In each case mixtures of the two isomeric red bis-thiopheno-ferrocenes (68/68')[46] and (69/69')[47] were prepared reacting the anions (51) and (52) with $FeCl_2$. Both mixtures of isomers could not be separated until now. The formation of two isomers in the respective reactions can be proved by nmr however.

^{1}H-chemical shifts of (68/68') and (69/69') in benzene-d_6 δ ppm rel. TMS:



^{13}C-chemical shifts of (68/68') and (69/69') δ ppm rel. TMS:



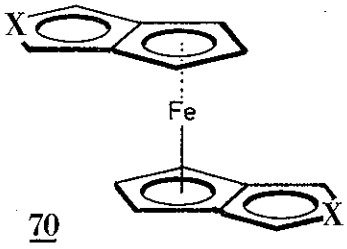
As in the case of the ferrocenes (66/66') and (67/67') one observes also an upfield shift of the nmr signals of the protons of the carbocyclic rings by going from (51) to (68/68') or (52) to (69/69'). Comparing the ^{13}C-nmr spectra of (52) and (69/69') an even more dramatic shift of signals can be observed. The signals of the carbon atoms of the carbocyclic rings in (69/69') are shifted upfield by 23-42 ppm whereas the signals of the thiophene ring carbon atoms are shifted downfield by 7.10-11.90 ppm relative to (52).

The red bis-thiopheno ferrocene (69/69') can be easily oxidized to the green ferricinium ion by Fe (III) or dil. HNO_3 and the ferricinium ion can be reduced back to (69/69') by dithionite. The easier oxidizability of (68/68') and (69/69') relative to ferrocene itself is demonstrated by cyclic voltammetry.

	ferrocene	68/68'	69/69'
E_o(V):	0.480	0.330	0.299

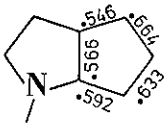
Heterocyclic ferrocenes of type (70)

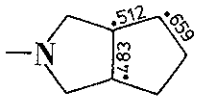
Heterocyclic ferrocenes with the heteroatom in the 2-position could not have been prepared by the reaction of the respective 2-heteropentalene anions with $FeCl_2$. The reason therefore may be for instance the relatively low π-bond order of bond 7-8 in 2-azapentalene.



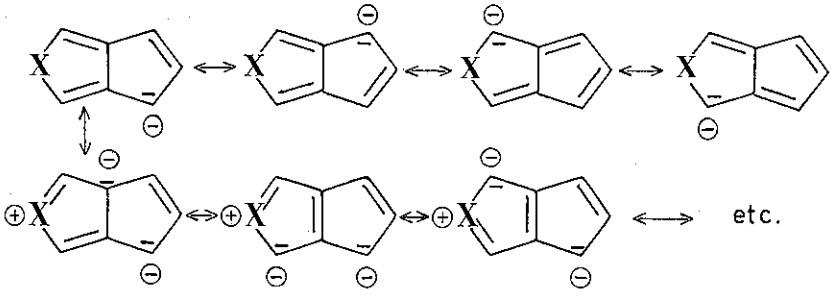
70

HMO-π-bond orders of the 1- and the 2-azapentalene anion:





Resonance structures of the 2-hetero-pentalene anion:



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++) Dedicated with best wishes to Prof. Dr. R. B. Woodward on the occasion of his 60th birthday

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