ESR STUDIES OF SOME NONBENZOID RADICAL IONS*

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ABSTRACT

Two classes of nonbenzoid compounds have been considered in this lecture: (1) nonalternant hydrocarbons, and (2) bridged [10]- and [14]-annulenes.

(1) The radical anion and cation of a nonalternant hydrocarbon should exhibit dissimilar e.s.r. spectra, in contrast to the two corresponding radical ions of an alternant system. This prediction of a simple MO model has been verified for four nonalternant compounds: acepleiadylene (I), acenaphth-[1,2-a]acenaphthylene (II), acepleiadiene (III), and 3,5,8,10-tetramethylcyclo-penteno[ef]heptalene (IV). In all cases there is an excellent agreement between experiment and theory.

(2) The degeneracies of both the lowest antibonding and the highest bonding perimeter orbitals are removed in a bridged [10]- or [14]-annulene. The resulting energy sequence can be inferred from an MO perimeter model, if an adequate substituent effect is assumed for the bridging group. Since the e.s.r. spectra of the radical ions of bridged annulenes are determined by the energy sequence in question, they offer an experimental test of such an assumption. The substituent effect has been discussed for the bridging groups in 1,6-methano[10]annulene (V), its imino- and oxido-analogues (VI and VII), *syn*-1,6:8,13-bisoxido[14]annulene (VIII), *trans*-15,16-dimethyl-15,16-dihydro-pyrene (IX), and cycl[3,2,2]azine (X).

INTRODUCTION

Electron spin resonance (e.s.r.) spectroscopy is a powerful tool for testing the reliability of current π-electron models. With the exception of a few cases, only minor changes in the π-electron structure result, when an electron is added to or removed from an extended aromatic system. The radical ions can therefore be described by the same kind of π-electron models as the parent neutral compounds, and the information extracted from the e.s.r. spectra of the radical ions will in general also be characteristic of the neutral compounds[1,2].

Since the benzoid compounds are readily available, and their radical ions usually enjoy a remarkable stability, numerous studies of such radicals have been reported. In contrast, the number of radical ions derived from nonbenzoid aromatics is relatively modest[1]. A few examples will be presented in this lecture which attempts to give some insight into the potential of e.s.r. spectroscopy in the studies of interesting π-electron systems.

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* The topics dealt with in this lecture have been recently reviewed in ref. 1.

The nonbenzoid compounds, the radical ions of which will be considered here, are divided into two classes: (1) Nonalternant hydrocarbons; (2) Bridged [10]- and [14]-annulenes.

NONALTERNANT HYDROCARBONS

These hydrocarbons represent a general type of aromatic compounds, whereas alternant ones must be regarded as a special type of such compounds. MO models of nonalternants thus do not exhibit the regularities which are characteristic of alternants and known as pairing properties of orbitals.

In particular, the *lowest antibonding* orbital, ψ_a, and the *highest bonding* orbital, ψ_b, which are '*paired*' in alternants, are '*non-paired*' in nonalternants. The squared LCAO coefficients at the centres μ of the two 'frontier' orbitals, $c_{a,\mu}^2$ and $c_{b,\mu}^2$, are therefore *equal* for the former, but *different* for the latter.

$$\text{Alternants}: \; c_{a,\mu}^2 = c_{b,\mu}^2$$

$$\text{Nonalternants}: \; c_{a,\mu}^2 \neq c_{b,\mu}^2$$

ψ_a and ψ_b are the singly occupied orbitals in the radical anion and the radical cation, respectively. In the simple model, the values $c_{a,\mu}^2$ and $c_{b,\mu}^2$ represent the π-spin populations ρ_μ at the centres μ of the corresponding radical ions. They are connected by linear relationship[3] with the coupling constants of the ring protons attached to the centres μ.
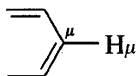
$$\text{Radical anion}: \; a_{H\mu}^{\ominus} = Q \cdot \rho_{\mu_-}^{\ominus} \approx Q \cdot c_{a,\mu}^2$$

$$\text{Radical cation}: \; a_{H\mu}^{\oplus} = Q \cdot \rho_{\mu}^{\oplus} \approx Q \cdot c_{b,\mu}^2$$

(Q is a proportionality factor.)

The absence or presence of pairing properties should therefore be reflected in the coupling constants $a_{H\mu}$. These values are predicted to be *nearly equal* for the radical anion and the radical cation of an alternant hydrocarbon, but *different* for those of a nonalternant one.

$$\text{Alternants}: \; a_{H\mu}^{\ominus} \approx a_{H\mu}^{\oplus}$$

$$\text{Nonalternants}: \; a_{H\mu}^{\ominus} \neq a_{H\mu}^{\oplus}$$

Consequently, the e.s.r. spectra of the two corresponding radical ions are expected to be *similar* for the former, but *dissimilar* for the latter.

A linear relationship should also exist between the sums of the ring proton coupling constants and the sums of the squared coefficients at the proton-bearing centres μ.

$$\text{Radical anion}: \; \sum_\mu a_{H\mu}^{\ominus} \approx Q \cdot \sum_\mu c_{a,\mu}^2$$

$$\text{Radical cation}: \; \sum_\mu a_{H\mu}^{\oplus} \approx Q \cdot \sum_\mu c_{b,\mu}^2$$

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The sum $\sum\limits_{\mu} a_{H\mu}$ which is here denoted as spectral range, can be readily determined from the e.s.r. spectrum as the distance between the two outermost hyperfine lines. Because the spectral range is a conspicuous feature of the spectrum and because it does not depend on the assignment of the coupling constants to individual protons, I shall preferentially make use of this quantity in the discussion. It is obvious that our model predicts *nearly equal* and *different* spectral ranges for the two corresponding radical ions of an alternant and a nonalternant hydrocarbon, respectively.

$$\text{Alternants:} \qquad \sum_{\mu} a_{H\mu}^{\ominus} \approx \sum_{\mu} a_{H\mu}^{\oplus}$$

$$\text{Nonalternants:} \quad \sum_{\mu} a_{H\mu}^{\ominus} \neq \sum_{\mu} a_{H\mu}^{\oplus}$$

For numerous alternant hydrocarbons the prediction was confirmed by experiment as long as ten years ago[4]. For example, the e.s.r. spectra of perylene radical ions, shown in *Figure 1*, are very similar and have almost equal spectral ranges.
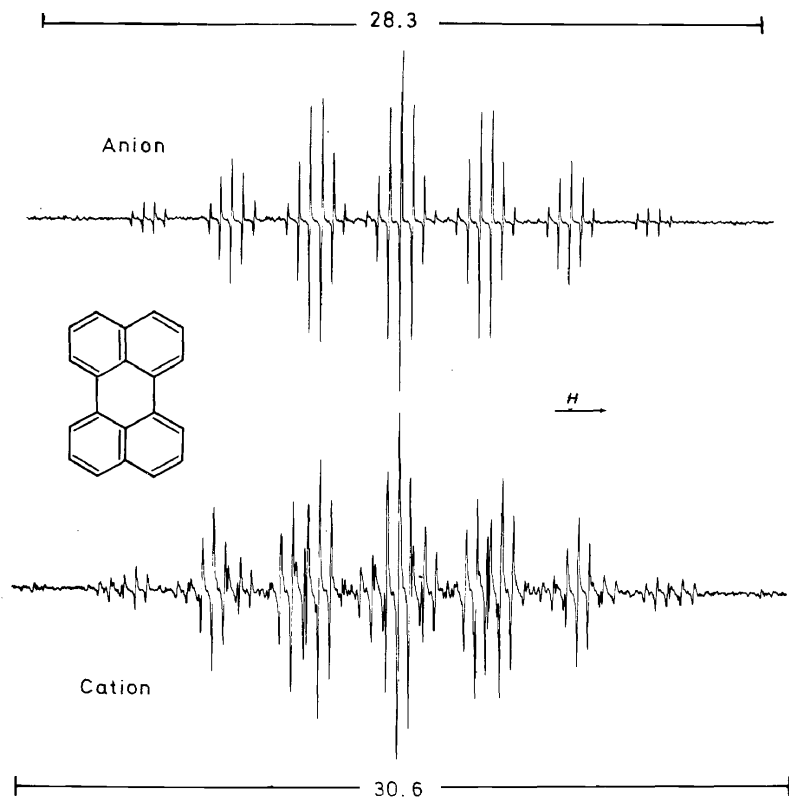

Figure 1. The e.s.r. spectra of perylene radical ions. The spectral ranges are given in gauss. Due to the superposition of some hyperfine components, the spectrum of the anion exhibits an apparently smaller number of lines than that of the cation.

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However, the complementary experimental test for nonalternant systems was lacking until 1965, since nonalternant hydrocarbons which would yield both radical ions are rather rare. We have been successful with four non-alternant hydrocarbons. Two of them are unsubstituted: acepleiadylene (I) and acenaphth[1,2-a]acenaphthylene (II); the remaining two bear alkyl substituents: acepleiadiene (III) and 3,5,8,10-tetramethyl-cyclopenteno[ef]-heptalene (IV). The compounds were first synthesized by Boekelheide (I[5] and III[6]), Letsinger (II[7]) and Hafner (IV[8]).
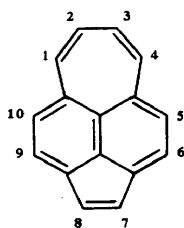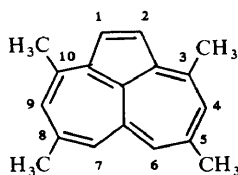

(I)
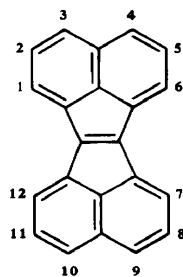
(II)
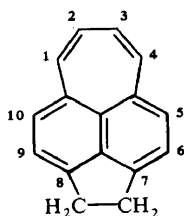
(III)

(IV)

Acepleiadylene (I) and acenaphth[1,2-a]acenaphthylene (II)

The lowest antibonding orbital ψ_a and the highest bonding orbital ψ_b of I are schematically depicted in *Figure 2*. As expected for a nonalternant system, the squared coefficients of the two orbitals are distinctly different. This is in particular true for the $c_{a,\mu}^2$ and $c_{b,\mu}^2$ values at the proton-bearing centres $\mu = 1$ to 10. The sum $\sum_\mu c_{a,\mu}^2 = 0.67$ at these centres is *smaller* than the corresponding sum $\sum_\mu c_{b,\mu}^2 = 0.76$.

Accordingly, the spectral range of the radical anion $I^\ominus$ is markedly *narrower* than that of the corresponding cation $I^\oplus$ (*Figure 3*)[9]. It is also noteworthy that the two spectra exhibit less similarity than those of the perylene radical ions.

The agreement between theory and experiment is even more impressive in the case of acenaphth[1,2-a]acenaphthylene (II). On looking at the diagrams of ψ_a and ψ_b which are presented for II in *Figure 4*, an interesting feature of the electron distributions in the two orbitals becomes evident. In contrast to the diagram of ψ_a, that of ψ_b is dominated by large circles at the
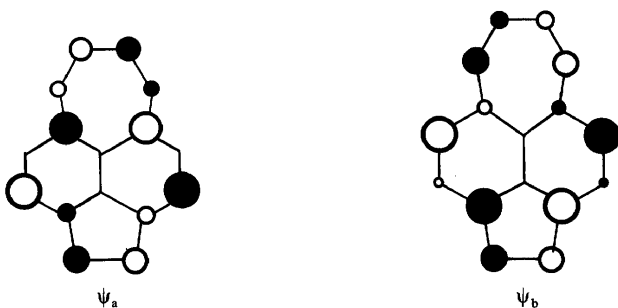
ψ_a $\qquad\qquad$ ψ_b

Figure 2. Lowest antibonding (ψ_a) and highest bonding (ψ_b) orbitals of acepleiadylene (I). The surfaces of the circles are proportional to the squared coefficients $c_{a,\mu}^2$ and $c_{b,\mu}^2$; the full and blank circles refer to different signs of these coefficients.

inner, 'blind' centres which are void of protons. Correspondingly, the squared coefficients $c_{b,\mu}^2$ at the outer, proton-bearing centres $\mu = 1$ to 12 are quite small. For these centres the sum $\sum_\mu c_{a,\mu}^2 = 0.78$ is *three times larger* than $\sum_\mu c_{b,\mu}^2 = 0.27$.

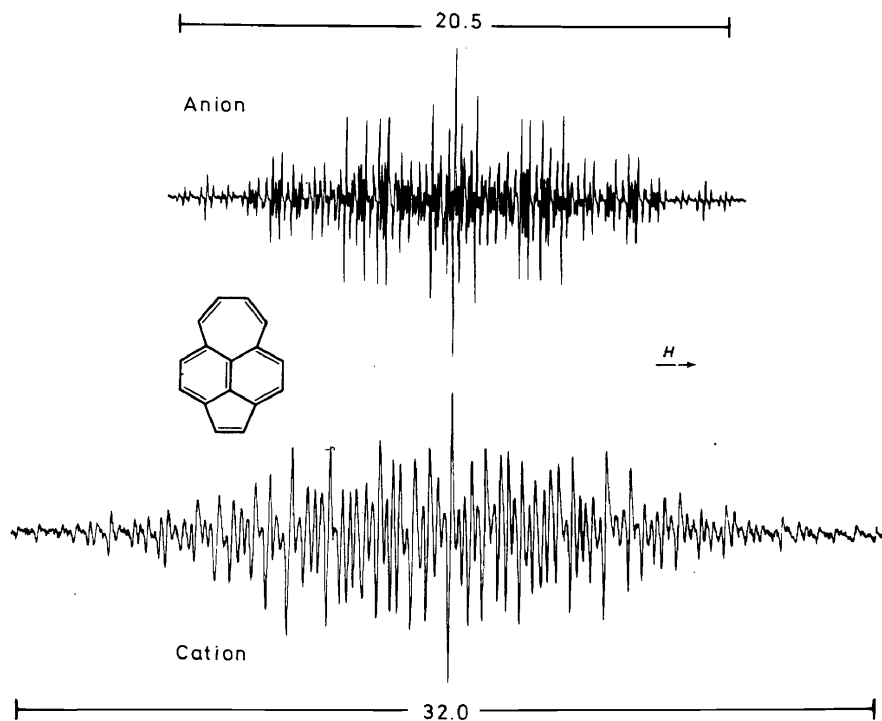This ratio is reflected in the spectral ranges of the radical ions $II^\ominus$ and $II^\oplus$

Figure 3. The e.s.r. spectra of acepleiadylene radical ions (anion $I^\ominus$ and cation $I^\oplus$). The spectral ranges are given in gauss.
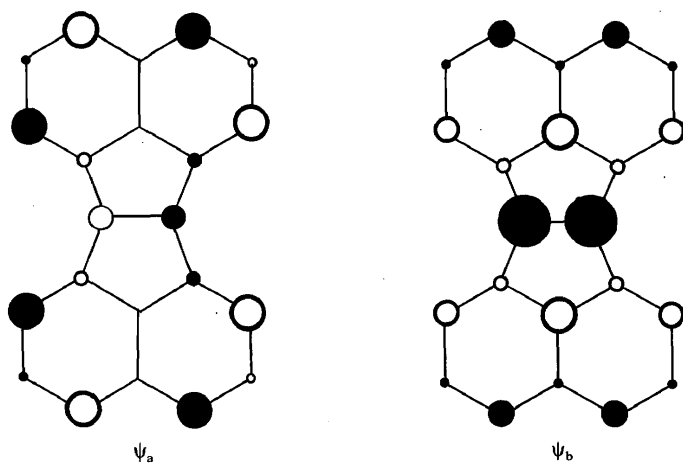
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Figure 4. Lowest antibonding (ψ_a) and highest bonding (ψ_b) orbitals of acenaphth[1,2-a] acenaphthylene (II). Schematic representation as in *Figure 2*.
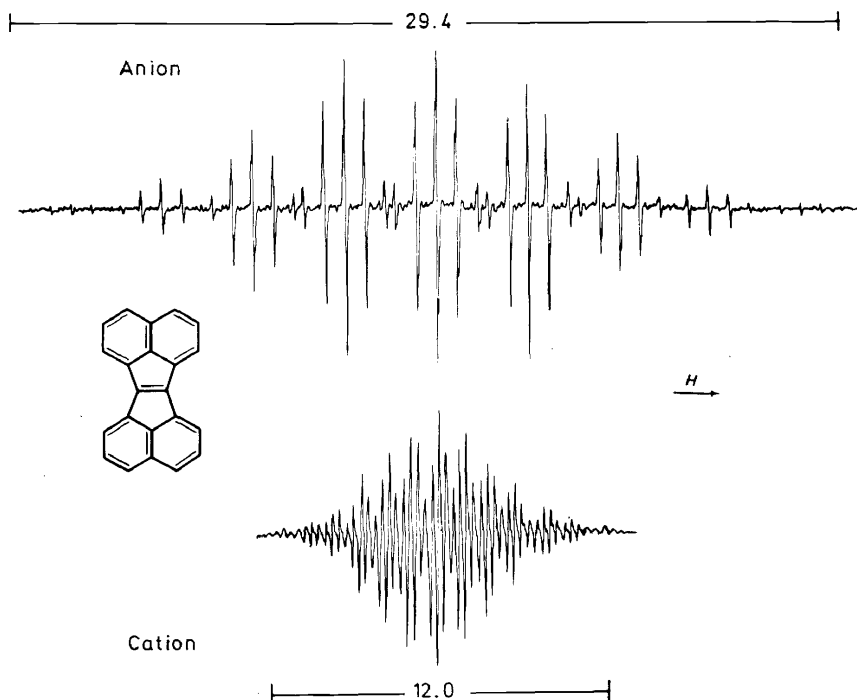

Figure 5. The e.s.r. spectra of acenaphth[1,2-a]acenaphthylene radical ions (anion II$^\ominus$ and cation II$^\oplus$). The spectral ranges are given in gauss.

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(*Figure 5*)[9]. The range of the anion *exceeds* that of the cation almost by a factor of three.

Acepleiadiene (III) and 3,5,8,10-tetramethyl-cyclopenteno[ef]heptalene (IV)

In the discussion of the two alkyl substituted nonalternant hydrocarbons III and IV one may disregard the perturbation due to the alkyl groups and use MO models of the unsubstituted systems. However, a replacement of a ring proton by an alkyl group has a striking effect on the spectral ranges of the radical ions. A methyl proton in a freely rotating substituent like those of IV or a methylene proton in a chain like that of III has an *equal* or a *larger* coupling constant than the ring proton which was replaced. Moreover, per one π-electron centre, there are *two* protons in a methylene and *three* in a methyl group instead of a *single* ring proton. The contribution of such sub-stituents to the spectral ranges is thus several times larger than that of corresponding ring protons. In other words: an alkyl substitution at a π-centre $\bar{\mu}$ greatly increases the effectiveness of the relevant spin population $\rho_{\bar{\mu}}$ with respect to the spectral range. The squared coefficients $c_{a,\bar{\mu}}^2$ and $c_{b,\bar{\mu}}^2$ at the substituted centres $\bar{\mu}$ are thus expected to play a major role in deter-mining the spectral ranges of the radical ions of III and IV.
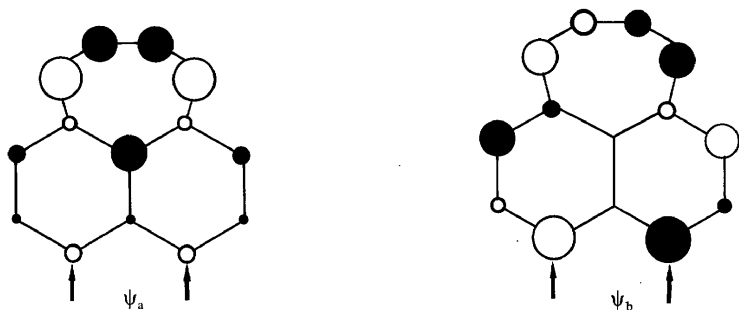

Figure 6. Lowest antibonding (ψ_a) and highest bonding (ψ_b) orbitals of pleiadiene. Schematic representation as in *Figure 2*. The centres 7 and 8 which are substituted in acepleiadiene (III) have been marked by arrows.

Figure 6 shows the lowest antibonding orbital ψ_a and the highest bonding orbital ψ_b of pleiadiene, the parent π-electron system of acepleiadiene (III). The squared coefficients at the two, in III substituted centres $\bar{\mu} = 7$ and 8 are much *smaller* for ψ_a than for ψ_b. The sum $\sum_{\bar{\mu}} c_{a,\bar{\mu}}^2$ amounts to 0.07, whereas the corresponding sum $\sum_{\bar{\mu}} c_{b,\bar{\mu}}^2$ is 0.30. For the proton-bearing centres $\mu = 1$ to 6, and 9,10 the analogous numbers are $\sum_{\mu} c_{a,\mu}^2 = 0.77$ and $\sum_{\mu} c_{b,\mu}^2 = 0.63$.

The e.s.r. spectra of the radical ions III$^{\ominus}$ and III$^{\oplus}$ (*Figure 7*)[10] attest the importance of the squared coefficients at the substituted centres $\bar{\mu}$ with regard to the spectral ranges. As predicted from the sums $\sum_{\bar{\mu}} c_{a,\bar{\mu}}^2$ and $\sum_{\bar{\mu}} c_{b,\bar{\mu}}^2$, the range of the anion is considerably *narrower* than that of the cation.
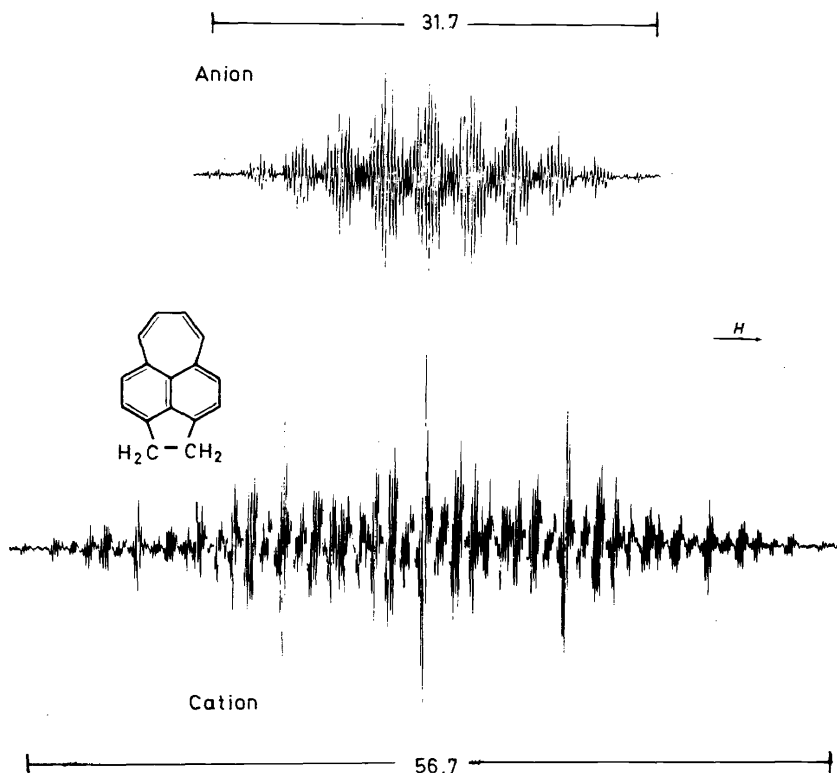
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Figure 7. The e.s.r. spectra of acepleiadiene radical ions (anion III$^{\ominus}$ and cation III$^{\oplus}$). The spectral ranges are given in gauss.

A contrary prediction is made for the radical ions of 3,5,8,10-tetramethyl-cyclopenteno[ef]heptalene (IV). The orbitals ψ_a and ψ_b of the parent π-system are depicted in *Figure 8*. The squared coefficients $c_{a,\bar{\mu}}^2$ at the four substituted centres $\bar{\mu} = 3, 5, 8$ and 10 are very *large*, whereas the corresponding values $c_{b,\bar{\mu}}^2$ are quite *small*. The reverse is true for the squared coefficients
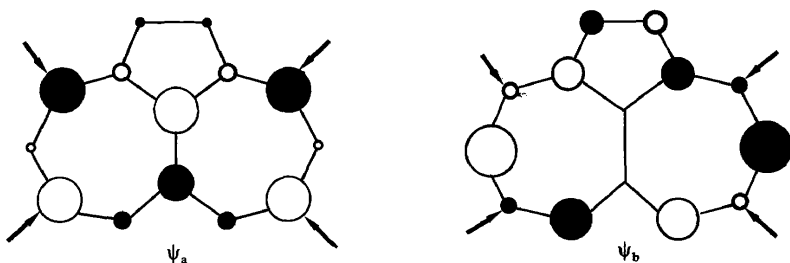

Figure 8. Lowest antibonding (ψ_a) and highest bonding (ψ_b) orbitals of cyclopenteno[ef]heptalene. Schematic representation as in *Figure 2*. The centres 3, 5, 8 and 10 which are substituted in the tetramethyl-derivative IV have been marked by arrows.

$c_{a,\mu}^2$ and $c_{b,\mu}^2$ at the proton-bearing centres $\mu = 1, 2, 4, 6, 7$ and 9. The relevant numbers are: $\sum_{\bar{\mu}} c_{a,\bar{\mu}}^2 = 0.61$ and $\sum_{\bar{\mu}} c_{b,\bar{\mu}}^2 = 0.09$ as compared with $\sum_{\mu} c_{a,\mu}^2 = 0.07$ and $\sum_{\mu} c_{b,\mu}^2 = 0.71$.

Since again the spectral ranges are much more affected by the squared coefficients at the substituted centres $\bar{\mu}$ than by those at proton-bearing centres μ, the radical anion $IV^\ominus$ greatly *surpasses* the cation $IV^\oplus$ in the spread of such a range (*Figure 9*)[10].

Concluding remark. In this brief discussion of e.s.r. results for the non-alternant radical ions I have not considered the values of coupling constants assigned to individual protons. The agreement between these values and the squared coefficients $c_{a,\mu}^2$ or $c_{b,\mu}^2$ is as good as for the radical ions of alternant hydrocarbons. In general, the radical anions and cations of nonalternant hydrocarbons exhibit a more even distribution of π-electron charges and
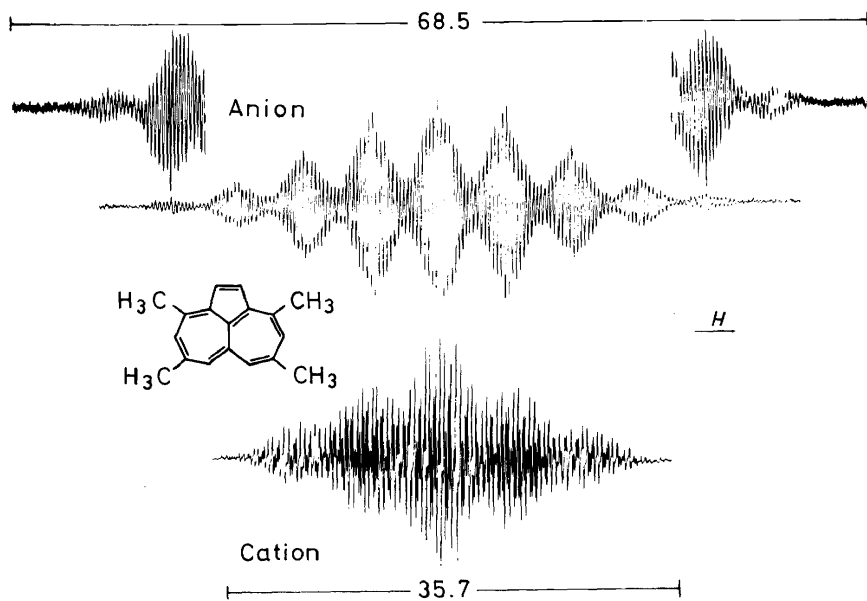

Figure 9. The e.s.r. spectra of 3,5,8,10-tetramethyl-cyclopenteno[ef]heptalene radical ions (anion $IV^\ominus$ and cation $IV^\oplus$). The spectral ranges are given in gauss. The outermost parts in the spectrum of the anion have been reproduced at higher amplification.

smaller differences in π-bond orders than the neutral compounds. In this sense, such radical ions may be considered to be more aromatic than the corresponding neutral systems, and simple MO models may well be more adequate for the former than the latter.
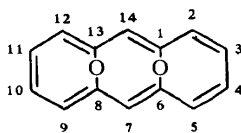
BRIDGED [10]- AND [14]-ANNULENES

The radical ions of the following compounds will be the subject of the second part of this lecture: 1,6-methano-, imino-, and oxido[10]-annulenes
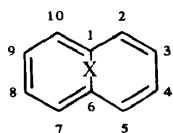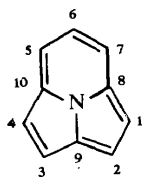
(V), X = CH$_2$
(VI), X = NH
(VII), X = O
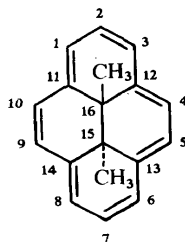
(VIII)

(X)

(IX)

(V, VI and VII, respectively), *syn*-1,6;8,13-bisoxido[14]annulene (VIII), *trans*-15,16-dimethyl-15,16-dihydropyrene (IX), and cycl[3,2,2]azine (X). They were synthesized by Vogel (V[11], VI[12], VII[13] and VIII[14]) and Boekelheide (IX[15] and X[16]).
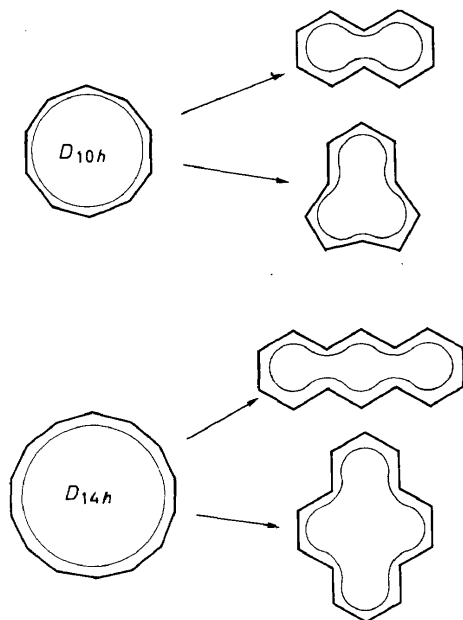

Figure 10. Ten- and fourteen-membered perimeters of the highest (D_{nh}) and of the lower symmetry forms.

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Although in the bridged annulenes V, VI, VII and VIII the π-electron systems deviate markedly from coplanarity[17, 18], the cyclic conjugation is not seriously inhibited[19]. All the compounds V to X can therefore be treated as substituted π-perimeters, and—with the exception of cycl[3,2,2]azine · (X)—the substituent effect of the bridging group may well be regarded as a perturbation of the perimeter orbitals.

Ideal n-membered perimeters have the symmetry D_{nh}. In our bridged annulenes V to X, however, the ten- and fourteen-membered peripheral π-systems do not possess this highest symmetry, but adopt approximately one of the lower symmetry forms shown in *Figure 10*.

For a perimeter of symmetry D_{nh}, the lowest antibonding and the highest bonding orbitals are both *doubly degenerate*. They can be classified as $\psi_{a\pm}$ and $\psi_{b\pm}$, respectively. 'Plus' signifies *symmetric* and 'minus' *antisymmetric* relative to a mirror plane which passes through two opposite centres and is perpendicular to the plane of the perimeter (*Figure 11*).
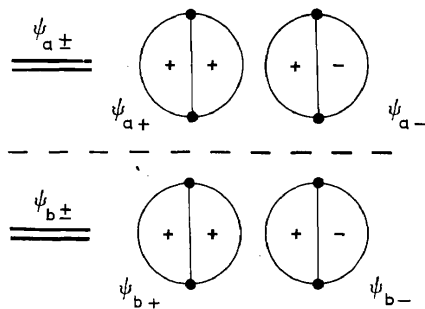

Figure 11. Classification of the degenerate lowest antibonding ($\psi_{a\pm}$) and highest bonding ($\psi_{b\pm}$) perimeter orbitals.

When the highest symmetry of the perimeter is reduced and/or a perturbation due to the substitution is introduced, the orbital degeneracy is removed; the two effects are inseparable experimentally in our bridged annulenes V to X. The relative energies of $\psi_{a\pm}$ and $\psi_{b\pm}$, which result from the removal of the degeneracies, determine the e.s.r. spectra of the radical ions, obtained
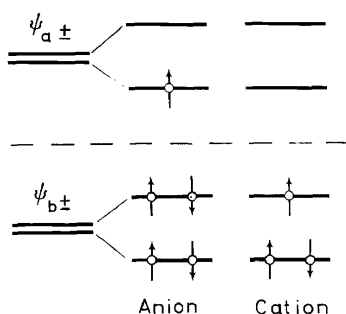

Anion   Cation

Figure 12. Occupancy of the lowest antibonding ($\psi_{a\pm}$) and highest bonding ($\psi_{b\pm}$) orbitals in the radical ions obtained from a deformed and/or perturbed perimeter.

from the deformed and/or perturbed perimeter system. The singly occupied orbital of the *anion* will resemble that of the *lowest antibonding* orbitals, ψ_{a+} or ψ_{a-}, which has the *lower* energy. On the other hand, the analogous orbital of the *cation* will be similar to that one of the *highest bonding* orbitals, ψ_{b+} or ψ_{b-}, which lies energetically *higher* (*Figure 12*).

An inspection of the coefficients $c_{a\pm,\bar{\mu}}$ and $c_{b\pm,\bar{\mu}}$ at the bridged centres $\bar{\mu}$ and a correct assumption with regard to the substituent effect of the bridging group allow one in general to predict the relative energies in question. This prediction can be tested by the e.s.r. spectra of the radical ions. Conversely, when the substituent effect of the bridging group is open to discussion, the e.s.r. spectra should inform us of the character and direction of such an effect.

1,6-Bridged [10]annulenes (V, VI and VII)

Applying the treatment to the lowest antibonding orbitals ψ_{a+} and ψ_{a-} of the ten-membered perimeter in 1,6-methano[10]annulene (V) one has to examine the coefficients $c_{a+,\bar{\mu}}$ and $c_{a-,\bar{\mu}}$ at the two bridged centres $\bar{\mu} = 1$ and 6. *Figure 13* presents the two orbitals in the conventional way; the perimeter is drawn in a form suitable for the compounds V, VI and VII. The coefficients $c_{a+,\bar{\mu}}$ of the symmetric orbital ψ_{a+} are *large* in magnitude and *opposite* in sign. The corresponding $c_{a-,\bar{\mu}}$ values are *zero*, since the bridged centres $\bar{\mu}$ lie in the nodal plane of the antisymmetric orbital ψ_{a-}.
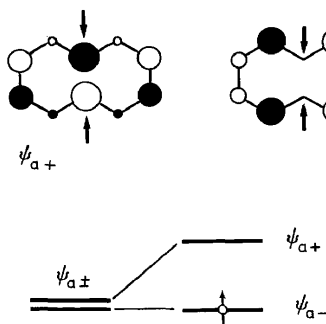

Figure 13. Top: Degenerate lowest antibonding orbitals ($\psi_{a\pm}$) of the ten-membered perimeter. Schematic representation as in *Figure 2*. The centres 1 and 6 which are bridged in the methano-, imino- and oxido[10]annulenes (V, VI and VII, respectively) have been marked by arrows. Bottom: Splitting and occupancy of the orbitals $\psi_{a\pm}$ in the radical anions $V^\ominus$, $VI^\ominus$ and $VII^\ominus$.

A substantial destabilization is predicted for ψ_{a+} relative to ψ_{a-} when the ten-membered perimeter is distorted from its highest symmetry to its actual form. This destabilization arises from the spatial proximity of the centres $\bar{\mu}$ in V[17] and can be rationalized by the MO theory in terms of Coulomb and resonance interactions. The Coulomb interaction is the mutual repulsion of the partial π-electron charges $c_{a+,1}^2$ and $c_{a+,6}^2$ at the two close centres $\bar{\mu}$; the resonance interaction is an antibonding contribution of $-c_{a+,1} \cdot c_{a+,6}$ to the potential C1–C6 linkage between the two centres. These interactions do not affect the orbital ψ_{a-} for which $c_{a-,1} = c_{a-,6} = 0$.

The electron-repelling substituent effect of the bridging methylene group

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works in the same direction. Since the perturbation due to this effect is proportional to the squared coefficients at the bridged centres $\bar{\mu}$, the symmetric orbital ψ_{a+} with its large $c^2_{a+,\bar{\mu}}$ values, is expected to be strongly destabilized. In contrast, its antisymmetric counterpart ψ_{a-}, for which the squared coefficients $c^2_{a-,\bar{\mu}}$ vanish, remains unaffected in first approximation.

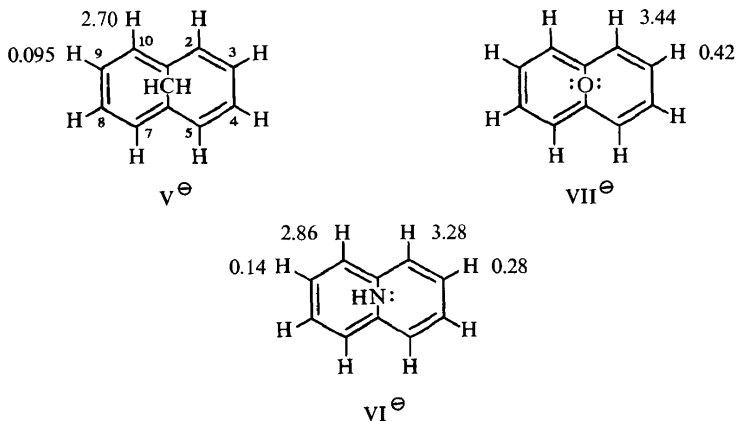Therefore, ψ_{a-} should have a *lower* energy than ψ_{a+} and it should become

Figure 14. Coupling constants (in gauss) of the ring protons in the radical anions of 1,6-bridged [10]annulenes ($V^\ominus$, $VI^\ominus$ and $VII^\ominus$). For each set of equivalent protons only one value is given. Note the lower symmetry of $VI^\ominus$ relative to that of $V^\ominus$ and $VII^\ominus$. The assignments are based on the comparison with the data of the corresponding 2,5,7,10-tetradeuterio derivatives[20, 21].

the singly occupied orbital in the radical anion $V^\ominus$ (*Figure 13*). From relative values of the squared coefficients $c^2_{a-,\mu}$ at the proton-bearing centres μ one concludes that in the case of the predicted occupancy of ψ_{a-} the coupling constant $a_{H\mu}$ of the four ring protons at $\mu = 2, 5, 7$ and 10 must be *larger* than that of the four ring protons at $\mu = 3, 4, 8$ and 9. The opposite would be required
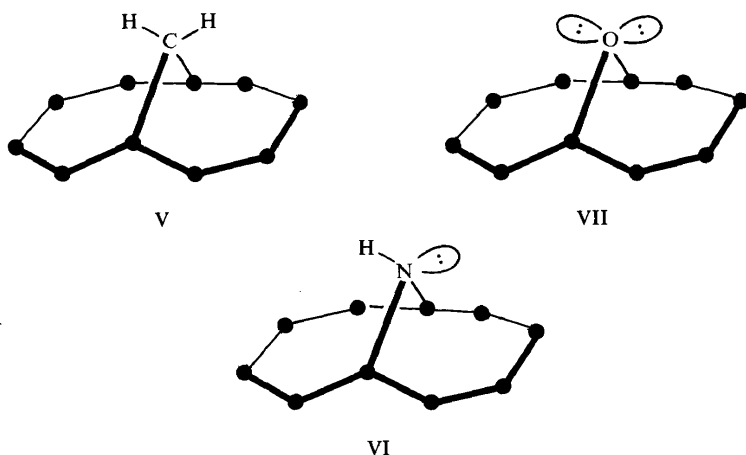

Figure 15. Molecular models of 1,6-bridged[10]annulenes (V, VI and VII).

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by the corresponding $c_{a+,\mu}^2$ values if—contrary to the prediction—ψ_{a+} were singly occupied.

The experimental data confirm the prediction (*Figure 14*)[20]. Moreover, the coupling constants $a_{H\mu}$ of the ring protons in $V^\ominus$ are not greatly changed when the methylene bridge is replaced by an imino- or an oxido-bridge to yield $VI^\ominus$ and $VII^\ominus$, respectively[20, 21]. This result indicates that ψ_{a-} is the singly occupied orbital in the radical anions of all three 1,6-bridged [10]annulenes. It also suggests that the overall substituent effect of the heteroatom bridges in VI and VII is similar in character and direction to the electron-repelling effect of the methylene bridge in V. The substituent effect of the imino- and oxido-bridges in VI and VII, respectively, is probably dominated by the repulsion between the lone pairs of the heteroatoms and the π-electrons of the perimeter, since the geometry of the bridges impedes the conjugation of the lone pairs with the π-system (*Figure 15*). Such a repulsion can override the attraction of the electronegative heteroatoms which is propagated through the σ-bonds[22].
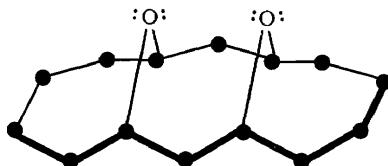

Figure 16. Molecular model of *syn*-1,6;8,13-bisoxido[14]annulene (VIII).

Syn-1,6;8,13-bisoxido[14]annulene (VIII)

Each of the two bridging oxygens resembles the single bridge of 1,6-oxido-[10]annulene (VII) in its geometrical arrangement relative to the respective π-electron perimeter (*Figure 16*)[18]. An assumption of an overall repelling effect of the two bridging oxygens seems therefore justified.

Figure 17 shows the two lowest antibonding orbitals ψ_{a+} and ψ_{a-} of the
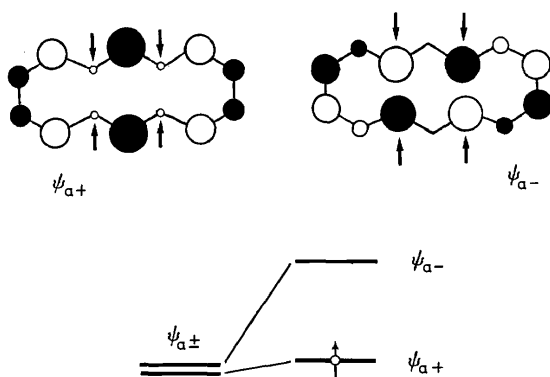

Figure 17. Top: Degenerate lowest antibonding orbitals ($\psi_{a\pm}$) of the fourteen-membered perimeter. Schematic representation as in *Figure 2*. The centres 1,6 and 8,13 which are bridged in *syn*-bisoxido[14]annulene (VIII) have been marked by arrows. Bottom: Splitting and occupancy of the orbitals $\psi_{a\pm}$ in the radical anion $VIII^\ominus$.

fourteen-membered perimeter which has a form appropriate for VIII. Again examination of the coefficients $c_{a+,\bar{\mu}}$ and $c_{a-,\bar{\mu}}$ at the two pairs of bridged and closest centres $\bar{\mu} = 1,6$ and $8,13$ should enable one to predict the relative energies of ψ_{a+} and ψ_{a-}. The π-electron distribution at each pair of the centres $\bar{\mu}$ in the antisymmetric orbital ψ_{a-} is very much like that at the corresponding two centres 1 and 6 in the symmetric orbital ψ_{a+} of the ten-membered perimeter considered before. This similarity holds for both the magnitude and relative sign of the relevant coefficients $c_{a-,\bar{\mu}}$ (ψ_{a-}; *Figure 17*) and $c_{a+,\bar{\mu}}$ (ψ_{a+}; *Figure 13*). Moreover the vanishingly small $c_{a+,\bar{\mu}}^2$ values in the symmetric orbital of the fourteen-membered perimeter (ψ_{a+}; *Figure 17*) are comparable to the zero values $c_{a-,\bar{\mu}}^2$ in the antisymmetric orbital of the ten-membered perimeter (ψ_{a-}; *Figure 13*).

Analogous arguments to those previously used for the 1,6-bridged [10]annulenes (V, VI and VII) lead therefore to the conclusion that in the case of 1,6;8,13-bridged [14]annulene (VIII) both the deformation of the perimeter and the electron-repelling substituent effect of the bridging oxygens should energetically *favour* the *symmetric* orbital ψ_{a+} relative to its antisymmetric counterpart ψ_{a-}. The former is thus expected to be the singly occupied orbital in the radical anion VIII$^\ominus$. As indicated by the squared coefficients $c_{a+,\mu}^2$ at the proton-bearing centres μ (*Figure 17*), such an occupancy should result in *large* coupling constants $a_{H\mu}$ of the six ring protons at $\mu = 2, 5, 7, 9, 12$ and 14: those of the four protons at $\mu = 3, 4, 10$ and 11 ought to be considerably *smaller*. A glance at the corresponding $c_{a-,\mu}^2$ values makes it obvious that the reverse would be found for the single occupancy of ψ_{a-}.

The experimental data agree with the prediction: the singly occupied orbital in VIII$^\ominus$ is ψ_{a+}, as made evident by the coupling constants $a_{H\mu}$ (*Figure 18*)[23].
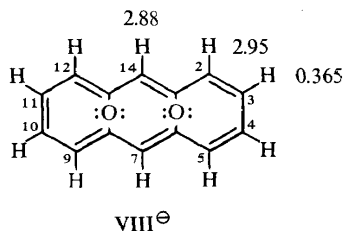

Figure 18. Coupling constants (in gauss) of the ring protons in *syn*-1,6; 8,13-bisoxido[14]annulene radical anion (VIII$^\ominus$). For each set of equivalent protons only one value is given. The assignment is based on the comparison with the data of the 2,5,9,12-tetradeuterio derivative[23].

Trans-15,16-dimethyl-15,16-dihydropyrene (IX)

This compound is another representative of bridged [14]annulenes. Since both of its radical ions, IX$^\ominus$ and IX$^\oplus$, are known, the relative energies can be verified not only for the lowest antibonding orbitals ψ_{a+} and ψ_{a-}, but also for the highest bonding orbitals ψ_{b+} and ψ_{b-}. The four orbitals are depicted in *Figure 19*, in which the fourteen-membered perimeter displays the form of the peripheral ring in IX. It is evident that the symmetric orbitals ψ_{a+} and ψ_{b+} on one hand, and the antisymmetric orbitals ψ_{a-} and ψ_{b-} on the other hand, have the same squared coefficients. (This equality is a consequence of
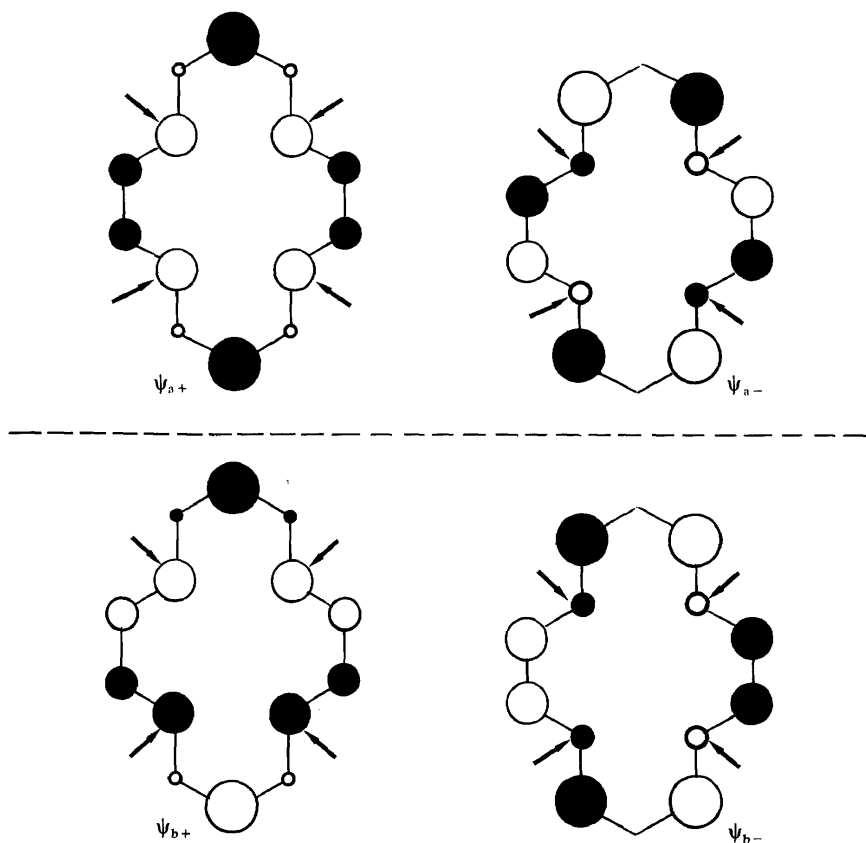
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Figure 19. Degenerate lowest antibonding ($\psi_{a\pm}$) and highest bonding ($\psi_{b\pm}$) orbitals of the fourteen-membered perimeter. Schematic representation as in *Figure 2*. The centres 11, 12, 13 and 14 which are bridged in *trans*-15,16-dimethyl-15,16-dihydropyrene (IX) have been marked by arrows.
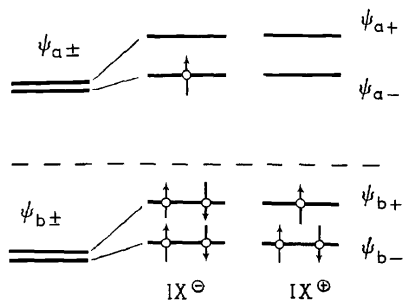

Figure 20. Splitting of the degenerate perimeter orbitals $\psi_{a\pm}$ and $\psi_{b\pm}$ by an inductive electron-repelling effect of the bridging group in *trans*-15,16-dimethyl-15,16-dihydropyrene (IX). Occupancy in the radical ions (anion IX$^{\ominus}$ and cation IX$^{\oplus}$).

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the pairing properties which hold for the orbitals of the fourteen-membered perimeter, an alternant system.)

The bridged centres $\bar{\mu} = 11, 12, 13$ and 14 in IX are not as close to each other as the corresponding centres $\bar{\mu}$ in the derivatives of [10]- and [14]- annulenes, V to VIII, discussed so far. Therefore, the change of the perimeter from the highest symmetry to its actual form (*Figure 10*) has in the case of IX only a small influence on the orbital energies, and the considerations can be restricted to the substituent effect of the bridging group. Comparison of the squared coefficients at the bridged centres $\bar{\mu}$, $c_{a+,\bar{\mu}}^2 = c_{b+,\bar{\mu}}^2 > c_{a-,\bar{\mu}}^2 = c_{b-,\bar{\mu}}^2$, indicates that the symmetric orbitals ψ_{a+} and ψ_{b+} should be *more strongly* perturbed by this effect than their antisymmetric counterparts ψ_{a-} and ψ_{b-}.

If the alkyl bridging group is taken for an electron-repelling substituent, ψ_{a+} and ψ_{b+} will be thus *less* stable than ψ_{a-} and ψ_{b-}, respectively. As a result, ψ_{a-} would be the singly occupied orbital in the radical anion $IX^{\ominus}$, whereas ψ_{b+} would represent such an orbital in the corresponding cation $IX^{\oplus}$ (*Figure 20*).

The most informative experimental data are the *large* coupling constants $a_{H\mu}$ found for the ring protons at the two centres $\mu = 2$ and 7 in both radical ions, $IX^{\ominus}$ and $IX^{\oplus}$ (*Figure 21*)[24]. The diagrams in *Figure 19* give evidence

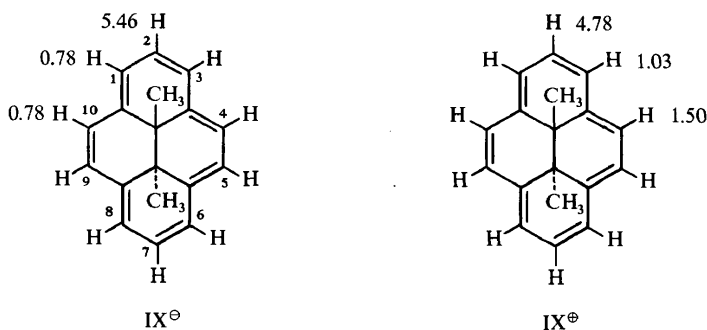*Figure 21.* Coupling constants (in gauss) of the ring protons in *trans*-15,16-dimethyl-15,16-dihydropyrene radical ions (anion $IX^{\ominus}$ and cation $IX^{\oplus}$). For each set of equivalent protons only one value is given. The assignment made for the coupling constants of 1.03 and 1.50 gauss ($IX^{\ominus}$) is uncertain; in the absence of evidence, the reverse assignment must be considered as equally probable[24].

that *both* singly occupied orbitals are *symmetric*, since only ψ_{a+} and ψ_{b+} exhibit *large* squared coefficients $c_{a+,\mu}^2 = c_{b+,\mu}^2$ at the two proton-bearing centres $\mu = 2$ and 7. In the antisymmetric orbitals ψ_{a-} and ψ_{b-} on the other hand, there is a nodal plane passing through these centres, so that the corresponding coefficients $c_{a-,\mu}^2 = c_{b-,\mu}^2$ are *zero*. The experimental evidence is thus partly disappointing. It confirms the prediction for the radical cation in that the singly occupied orbital should be ψ_{b+}. However, it disagrees with the prediction for the radical anion, since in this case the singly occupied orbital is clearly ψ_{a+}, and not ψ_{a-} as expected.
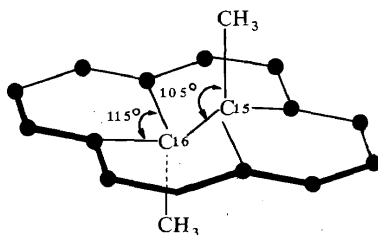
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Figure 22. Molecular model of *trans*-15,16-dimethyl-15,16-dihydropyrene (IX).

In order to account for the disagreement between theory and experiment, the geometry of IX must be considered in more detail. The x-ray analysis[25] shows that the C—C—C angles at the alkyl bridge deviate significantly from the normal values for sp^3-hybridized carbon atoms (*Figure 22*). The deviations suggest an attenuation of the inductive electron-repelling effect of the bridging group. Moreover, the bonds C15—C(methyl) and C16—C(methyl) are nearly perpendicular to the plane of the fourteen-membered perimeter so that the hyperconjugation of the σ-electrons in these bonds with the π-system should be favoured. For symmetry reasons, such a hyperconjugation affects only the symmetric orbitals ψ_{a+} and ψ_{b+}. In particular, it can stabilize ψ_{a+} relative to ψ_{a-} and thus lead to an agreement with experiment for the radical anion IX$^\ominus$ as well (*Figure 23*).
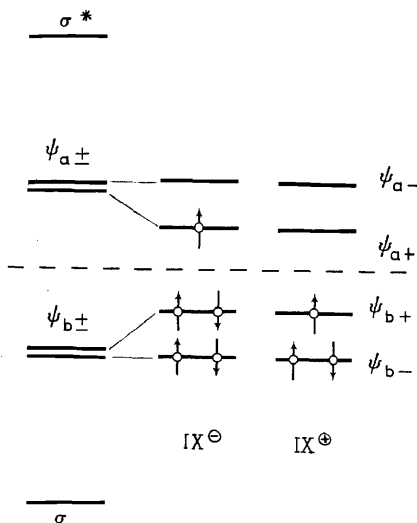

Figure 23. Splitting of the degenerate perimeter orbitals $\psi_{a\pm}$ and $\psi_{b\pm}$ by a hyperconjugative effect of the C15—C(methyl) and C16—C(methyl) bonds in *trans*-15,16-dimethyl-15,16-dihydropyrene (IX). Occupancy in the radical ions (anion IX$^\ominus$ and cation IX$^\oplus$).

Cycl[3,2,2]azine (X)

In this last compound of the series, the bridging nitrogen is nearly coplanar

with the peripheral π-electron system. The compound X can be regarded either as an iso-π-electronic derivative of aceindylenyl anion (Xa) or as an amino-substituted [10]annulene (Xb)[26, 27].

(Xa)   (Xb)

Large coupling constants a_{H_μ} of the four ring protons at the centres $\mu = 2, 3, 5$ and 7 are characteristic of the radical anion $X^\ominus$ (*Figure 24*)[28]. They compare favourably with the squared coefficients $c^2_{a-,\mu}$ at the corresponding proton-bearing centres μ in the antisymmetric perimeter orbital ψ_{a-}. This orbital is presented, along with its symmetric counterpart ψ_{a+}, in *Figure 25*; the ten-membered perimeter has been given the form of the peripheral ring in X.

Figure 24. Coupling constants (in gauss) of the ring protons in cycl[3,2,2]azine radical anion ($X^\ominus$). For each set of equivalent protons only one value is given. The assignment is based on the comparison with the data of the 1,4-deuterio derivative[28] and on MO calculations including Configuration Interaction[27].

$X^\ominus$

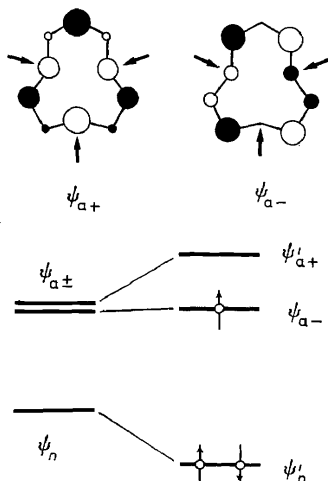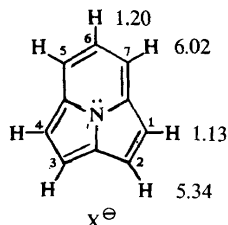

ψ_{a+} ψ_{a-}

Figure 25. Top: Degenerate lowest antibonding orbitals ($\psi_{a\pm}$) of ten-membered perimeter. The centres 8, 9 and 10 which are bridged in cycl[3,2,2]azine (X) have been marked by arrows. Bottom: Correlation diagram for the perimeter orbitals $\psi_{a\pm}$ and the lone pair orbital ψ_n in cycl[3,2,2]azine (X). Occupancy in the radical anion $X^\ominus$.

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The experimental data thus indicate that the singly occupied orbital in $X^{\ominus}$ is very similar to ψ_{a-}. This result can be rationalized by a simple correla- tion diagram (*Figure 25*). It is true that the amino substitution is by no means a mere perturbation. However, for symmetry reasons, the orbital ψ_n of the nitrogen lone pair 'mixes' only with the symmetric perimeter orbital ψ_{a+}. Of the two resulting modified orbitals ψ'_n and ψ'_{a+} the former is stabilized and the latter is destabilized relative to ψ_n and ψ_{a+}, respectively. In contrast, the presence of ψ_n does not essentially affect the antisymmetric perimeter orbital ψ_{a-}, so that the energy and the coefficients of this orbital remain unchanged in first approximation. It is evident that ψ_{a-} should lie energetically *lower* than ψ'_{a+} and thus become the singly occupied orbital of the radical anion $X^{\ominus}$, in accordance with the experimental findings.

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