169. Photoelectron-spectroscopic Evidence Concerning "Homo-aromaticity" 1)

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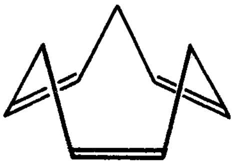
Summary. The first of the two π-bands in the photoelectron spectrum of *cis-cis-cis*-1,4,7-cyclononatriene (I, symmetry C_{3v}) shows a *Jahn-Teller* split. This is consistent with the prediction of molecular orbital theory that the top occupied orbitals of I are $\boldsymbol{e}(\pi)$ and $\boldsymbol{a}_1(\pi)$ respectively. From the difference $\varepsilon(\boldsymbol{e}(\pi)) - \varepsilon(\boldsymbol{a}_1(\pi)) = 0.90$ to 0.97 eV a value of $\beta_{1,3} = -0.68$ eV $= 0.27\beta$ ($\beta = -2.5$ eV) is obtained for the homoconjugative interaction of two π-orbitals in I. This value represents almost exclusively through-space interaction between the π-orbitals. Through-bond interaction (hyperconjugation) is a minor effect in I. A comparison of the photoelectron data of bicyclo[4.2.1]nonatriene with those of norbornene and cycloheptadiene shows that homoconjugation (homo-aromaticity) can only be detected by photoelectron spectroscopy if the interacting π-bonds (basis orbitals) are symmetry equivalent or have accidentally (almost) degenerate energies.

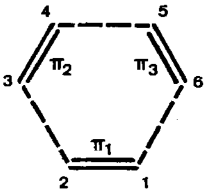
One of the most intriguing ideas concerning the delocalisation of π-electrons among weakly interacting double bonds is that covered by the catchword 'homo-aromaticity' [2]. This concept, due to *Winstein* [3], assumes that homoconjugative interaction among π-bonds, separated from each other by sp^3-hybridised centers, should give rise to large first-order effects if the following conditions are fulfilled:

a) The π-bonds have to be arranged in such a way that homoconjugation between nearest neighbours leads to a closed loop over which the π-electrons can be formally delocalised.

b) The number of interacting π-bonds must be $1 + 2n$ ($n = 1, 2, 3, \ldots$), so that the number of the delocalisable π-electrons satisfies *Hückel*'s rule. The classical example of such a neutral system is *cis-cis-cis*-1,4,7-cyclononatriene (I), which was synthesized independently by three groups [4] [5].



I



II

The structure of I has been determined by X-ray analysis at $-35°$ [6] and that of the silver nitrate adduct of I at $-125°$ [7]. Both determinations lead to pratically the same results for the conformation of I. (For a discussion see ref. [8].)

Neither the interatomic distances (R(C=C) $= 1.34$ Å) nor the bond angles ($\sphericalangle$ (C–CH$_2$–C) $= 108°$) are indicative of any significant departure from a model which

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1) Part 13 of «Applications of Photoelectron-Spectroscopy». Part 12: [1].

assumes three non-interacting double bonds. The same is true for the NMR. data (vinylic hydrogens: $\tau = 4.44$; methylenic hydrogens: $\tau = 6.05$ (endo), $\tau = 7.74$ (exo) [9]), and for the heat of hydrogenation ($\Delta Hh = -76.9$ kcal mole^{-1}, as compared to -23.6 kcal mole^{-1} for *cis*-cyclononene [6]). Indeed, the heat of hydrogenation of I suggests a small amount of strain in the molecule.

The reason for the failure of these measurements to yield an indication for the presence, let alone the extent, of an interaction between the three double bonds in the molecule I can be illustrated by the following naïve molecular orbital argument (cf. also [4] [9]).

To each of the double bonds $j = 1,2,3$ (see formula II) we assign a bonding (π_j) and an antibonding (π_j^*) linear combination of $2p$-atomic orbitals in ZDO-approximation (*e.g.* $\pi_1 = 1/\sqrt{2}\,(\phi_1 + \phi_2)$; $\pi_1^* = 1/\sqrt{2}\,(\phi_1 - \phi_2)$). The corresponding orbital energies are $\varepsilon_j = \alpha + \beta$ and $\varepsilon_j^* = \alpha - \beta$ respectively. ($\alpha = \langle\phi_\mu \mid \mathcal{H} \mid \phi_\mu\rangle$; $\beta = \langle\phi_\varkappa \mid \mathcal{H} \mid \phi_\lambda\rangle$ with $\varkappa, \lambda = 1,2;\ 3,4;\ 5,6$). The interaction between pairs of bonds shall be described by a resonance integral $\langle\phi_\mu \mid \mathcal{H} \mid \phi_\nu\rangle = \beta_{\mu\nu} = m\beta$ ($\mu, \nu = 2,3;\ 4,5;\ 6,1$) where $0 \leq m \leq 1$. For $m = 0$ we have three independent double bonds and for $m = 1$ the situation would be formally identical with that prevailing in benzene. It is easy to show that the total π-electron energy $E_\pi(m)$ for the independent electron model of I is given by:

$$E_\pi(m) = 6\alpha + 2\beta\left(1 + m + 2\,(1 - m + m^2)^{1/2}\right) \tag{1}$$

The ratio of the delocalisation energies (DE) defined in the usual way for a model of I (with parameter m) and for benzene ($m = 1$) is

$$\frac{\mathrm{DE(I)}}{\mathrm{DE(benzene)}} = m - 2 + 2\,(1 - m + m^2) \tag{2}$$

with $\mathrm{DE(I)} = E_\pi(m) - E_\pi(0)$ and $\mathrm{DE(benzene)} = E_\pi(1) - E_\pi(0) = 2\beta$. The dependence of this ratio on m is shown in fig. 1a. It is seen that for $m < 0.3$, which, as we shall see, is the order of magnitude for homoconjugative interaction, we expect DE(I)/DE(benzene) < 0.08. With DE(benzene) $\approx$ 30 kcal mole^{-1} [10] this leads to DE(I) $<$ 2.4 kcal mole^{-1}, a quantity much too small to be detectable, in view of the steric and conformational strain present in I [6] [8].

The bond orders $p_{1,2} = p_{3,4} = p_{5,6}$ and $p_{2,3} = p_{4,5} = p_{6,1}$ can be derived from the linear combinations

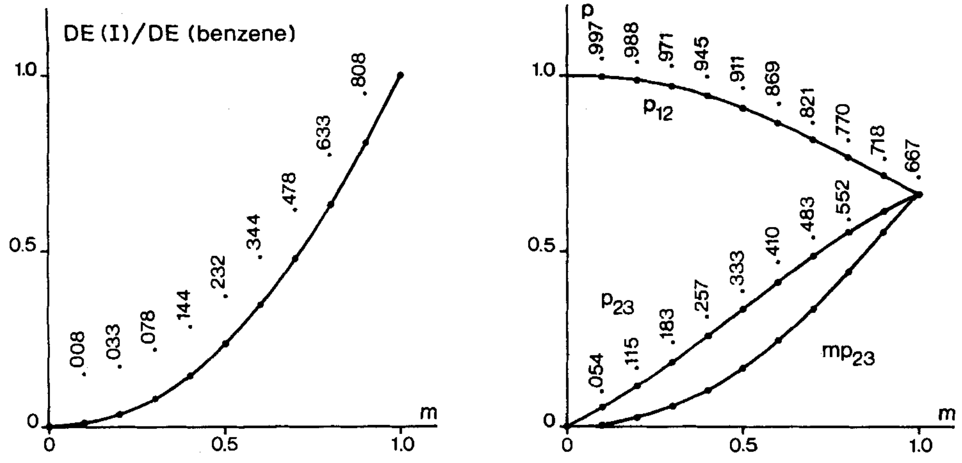
$$\psi_J = \sum_{j=1}^{3} \left(c_{Jj}\,\pi_j + c_{Jj}^*\,\pi_j^*\right). \tag{3}$$

Their dependence on m is shown in fig. 1b. It is evident that for $m < 0.3$ the bond order alternation is too large to allow for a noticable ring current [10]. This predicted bond order alternation would be even more pronounced if we had included second order bond fixation, since the total π-electron energy E_π depends on $mp_{2,3}$ rather than on $p_{2,3}$ (cf. Fig. 2):

$$E_\pi = 6\alpha + 6\beta\,(p_{1,2} + m\,p_{2,3})\,. \tag{4}$$

On the other hand the split between the orbital energies $\varepsilon(\boldsymbol{a}_1(\pi))$ and $\varepsilon(\boldsymbol{e}(\pi))$ of the lowest occupied orbital $\psi_1 = \boldsymbol{a}_1(\pi)$ and the degenerate highest occupied orbital pair $\psi_2, \psi_3 = \boldsymbol{e}(\pi)$ (assuming C_{3v} symmetry) is, according to our model,

$$\varepsilon\big(\boldsymbol{e}(\pi)\big) - \varepsilon\big(\boldsymbol{a}_1(\pi)\big) = \mid \beta \mid \left(1 + m - \sqrt{1 - m + m^2}\right). \tag{5}$$



a) b)

Figure 1. a) *Ratio DE(I)/DE(benzene) as a function of the parameter* m (*formula* (*2*); b) *Dependence of the bondorders* p_{12} *and* p_{23} *on the paramter* m.

The curve $m\,p_{2,3}$ corresponds to the contribution of the homoconjugative interaction to the total π-energy (see formula (4))

For small values of m, *i.e.* $m < 0.3$, this split is approximately $3m\,|\,\beta\,|/2$. We conclude that for 'homo-aromatic' systems such as I photoelectron spectroscopy is the method of choice for the direct determination of the magnitude of homoconjugative interaction, characterised by the parameter m in our model.

The photoelectron spectrum (PE. spectrum) of cyclononatriene (I) is reproduced in Fig. 2, and the relevant data are given in the table. In the following we shall concentrate on the first two bands 1 and 2. In accordance with the simple model given above these bands correspond to ionisation processes for which the electron leaves either the degenerate $e(\pi)$ orbitals (band 1) or the orbital $a_1(\pi)$ (band 2). The ionisation potentials found for the first band ($(I(1)_{ad.} = 8.45$ eV; $I(1)_{vert.} = 8.77$ eV) are in excellent agree-

Table. *Vertical ionisation potentials* (*band maxima*)

All values are given in eV; the orbital type is given in brackets

		π-bands			σ-band[a]
		1	2	3	
I	*cis-cis-cis*-Cyclonona-1,4,7-triene	8.77 (e)[b]	8.9–9.0 (e)[b]	9.80 (a_1)	11.32
	Cyclopentene [11]	9.02 (b_1)[c]			12.12
VII	Norbornene [16]	8.97 (a')			10.55
	Cyclohepta-1,3-diene	8.30 (a'')[d]	10.60 (a')[d]		11.16
VI	Bicyclo[4.2.1]nonatriene	8.36 (a'')	9.02 (a')	10.55 (a')	11.28

[a] Only the position of the first maximum is given.

[b] *Jahn-Teller*-split.

[c] Assuming C_{2v} symmetry.

[d] Assuming C_s symmetry.

ment with those obtained by *Demeo & El-Sayed* ($I(1)_{ad.}$ = 8.42 eV [11]) and by *Winstein & Lossing* ($I(1)_{vert.}$ = 8.72 eV [12]). Only the vertical ionisation potentials will be used as a basis for the subsequent discussion in this paper. The main reason for this is that the positions of the band maxima are much easier to locate than the positions of the 0–0 transitions. This is especially true for overlapping bands, whose *Franck-Condon* envelopes are difficult to assess. In this respect the situation encountered in photoelectron spectroscopy of larger molecules is rather similar to that prevailing in electronic spectroscopy.

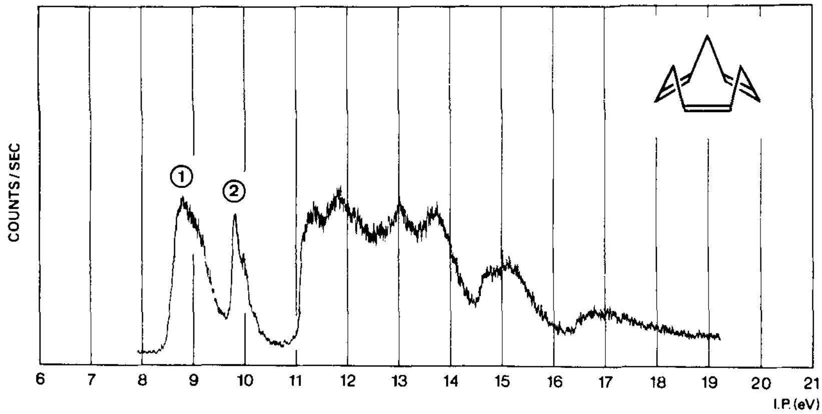


Figure 2. *PE.-spectrum of* cis-cis-cis-*1,4,7-cyclononatriene* (*I*)
Abscissa: ionisation potential in eV; ordinate: intensity in arbitrary units (see experimental section)

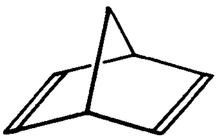
The complex structure of the first band in the PE.-spectrum of I, especially its shape with a flattened top, suggests strongly that the radical cation I^+ undergoes a *Jahn-Teller* splitting in its ^2E ground state. Such situations have been previously encountered in photoelectron spectroscopy *e.g.* in allene [13] and in cyclopropane [14]. However, the second of the two overlapping bands is rather difficult to locate and the value given in the Table (~8.9 to 9.0 eV) is somewhat uncertain.

The second band at 9.90 eV has to be ascribed to I^+ in its first electronically excited $^2A_1$ state.

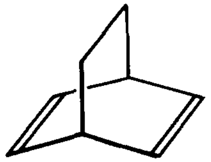
Assuming the validity of *Koopmans*'s theorem and that the *Jahn-Teller* effect leads to a symmetrical split of the ^2E state of I^+ we obtain:

$$E(^2\boldsymbol{E}) - E(^2\boldsymbol{A}_1) = \varepsilon(\boldsymbol{e}(\pi)) - \varepsilon(\boldsymbol{a}_1(\pi)) \approx 0.90 \text{ to } 0.97 \text{ eV}. \qquad (6)$$

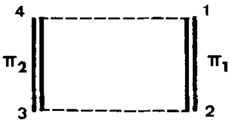
Using a conservative value of $\beta = -2.5$ eV [15] in formula (5) we obtain m = 0.26 to 0.28. (For $\beta = -3.0$ eV the corresponding values would be m = 0.21 to 0.23.)



III (C_{2v})



IV (C_{2v})



V

We now compare this result with those obtained for the two 'antihomo-aromatic' systems norbornadiene (III) and bicyclo[2.2.2]octadiene (IV) [16]. (See table). In these cases the observed split between the orbitals $\boldsymbol{b}_2(\pi)$ (highest occupied) and $\boldsymbol{a}_1(\pi)$ (second highest occupied) amounts to 0.85 eV (III) and 0.6 eV (IV) respectively. If, in analogy to our model II, we assume the interaction between the pair of double bonds to be a pure through-space interaction (V with $\beta_{2,3} = \beta_{4,1} = m\beta$), then the split would be given by the expression

$$\varepsilon(\boldsymbol{a}_1(\pi)) - \varepsilon(\boldsymbol{b}_2(\pi)) = 2\, m\beta \tag{7}$$

leading to $m = 0.17$ for III and $m = 0.12$ for IV. These values are only about half of that obtained for I. The reason for this reduction of the parameter m is evident from the results obtained from an extended *Hückel* model [17]: In I the interaction of the three double bonds is predicted by such a model to be indeed almost pure homoconjugation, *i.e.* through-space as postulated in the naïve treatment characterised by II. It is true that, in addition, the resulting orbitals $\boldsymbol{e}(\pi)$ and $\boldsymbol{a}_1(\pi)$ can mix with those lower-lying σ-orbitals of the methylene C–H bonds that belong to the same irreducible representations of C_{3v}. (This through-bond interaction could be called hyperconjugation. As shown in the diagram of Fig. 3, the orbitals $\boldsymbol{e}(\sigma)$ and $\boldsymbol{a}_1(\sigma)$ are linear combinations of the locally antisymmetric methylene orbitals, *i.e.* $a\,2\boldsymbol{p}(C) + b\,[1\boldsymbol{s}(H_{\text{endo}}) - 1\boldsymbol{s}(H_{\text{exo}})]$). However, the interaction of $\boldsymbol{e}(\pi)$ with $\boldsymbol{e}(\sigma)$ and of $\boldsymbol{a}_1(\pi)$ with $\boldsymbol{a}_1(\sigma)$ is small and does not result in a significant reduction of the original split $\varepsilon(\boldsymbol{e}(\pi)) - \varepsilon(\boldsymbol{a}_1(\pi))$. In contrast, the mixing of the π-orbitals in III and IV with lower-lying σ-orbitals will affect mainly the $\boldsymbol{a}_1(\pi)$ orbitals, as indicated in the orbital diagram of Fig. 4. The interaction of $\boldsymbol{b}_2(\pi)$ is much smaller, and as a result we observe a reduction of the difference $\varepsilon(\boldsymbol{b}_2(\pi)) - \varepsilon(\boldsymbol{a}_1(\pi))$ as calculated according to model V (formula (7)). This explains

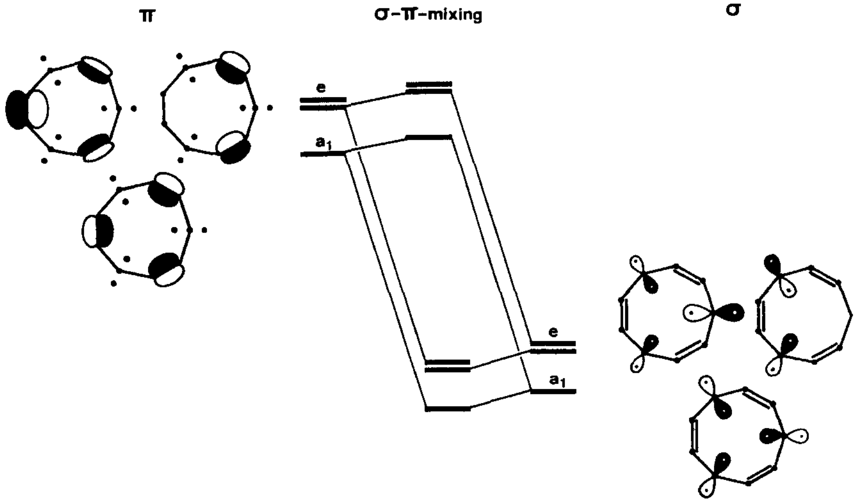


Figure 3. *σ-π-interaction diagram for* cis-cis-cis-*1,4,7-cyclononatriene* (*I*)
The σ-orbitals shown correspond to the locally antisymmetric combinations of the C–H-σ-orbitals (the dots signify the hydrogen nuclei)

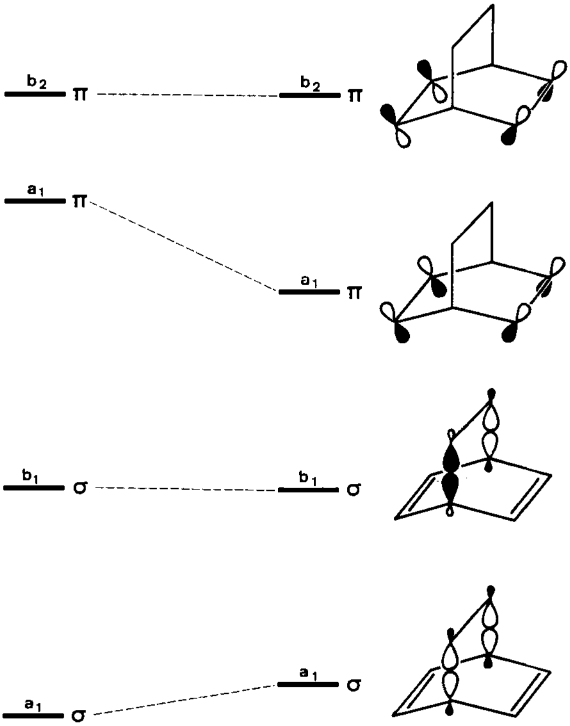


Figure 4. *Schematic representation of the interaction of σ- and π-orbitals in bicyclo[2.2.2]octadiene (IV)* Right: non-interacting orbitals. Left: orbitals after interaction. The symmetry classification is with respect to the group C_{2v}

why we obtain a smaller value of m with (7) than with (5) using the observed ionisation potentials. However, through-space interaction in III and IV still dominates the situation, as has been discussed in a previous note [18] (see also [19]).

An extended *Hückel* calculation [17] yields a split $\varepsilon(\boldsymbol{b}_2(\pi) - \varepsilon(\boldsymbol{a}_1(\pi))$ of 0.43 eV for III and of 0.23 eV for IV if it is assumed that the distance between the axes of the π-bonds in III is 2.39 Å [20] and 2.51 Å in IV. A similar calculation for I, based on the structure determined by *X*-ray analysis [6], predicts a split $\varepsilon(\boldsymbol{e}(\pi))) - \varepsilon(\boldsymbol{a}_1(\pi))$ of 0.59 eV. Furthermore, these calculations show that $\sigma - \pi$ interaction is about the same magnitude in III and IV, but that it is much smaller in I. Even though such calculations, based on a one-electron approximation, are necessarily rather crude, the results are surprisingly good in reproducing the magnitude and especially the relative size of the splits. One may therefore conclude that the values $m = 0.26$ to 0.28 ($\beta = -2.5$ eV) or $m = 0.21$ to 0.23 ($\beta = -3.0$ eV) obtained from the PE.-spectrum of I are representative for the homoconjugative, through-space interaction of two π-bonds in a relative conformation such as present in I.

Our value of $m \approx 0.3$ ($\beta = -2.5$ eV) is difficult to compare with previous estimates. Only a few examples will be given. *Simonetta* & *Winstein* [21] suggested $m = 0.28$ for the description of homoconjugation in homoallylic systems, whereas *Piccolini* & *Winstein* [22] derived 0.38 for the resonance integral of the 1,3-interaction in III. Later

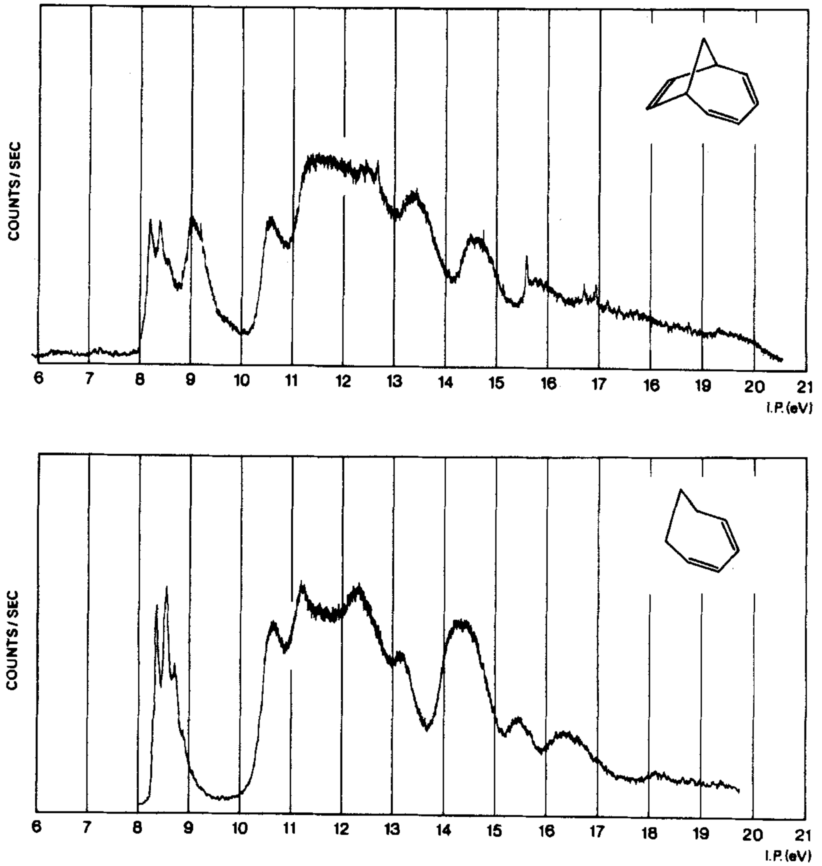
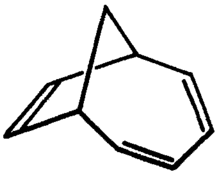


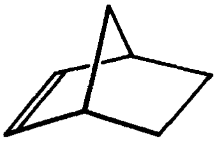
Figure 5. *PE.-spectra of bicyclo[1.2.4]nonatriene (VI) and of cyclohepta-1,3-diene (VIII)*
(See legend to Fig. 2)

a value of $m = 0.5$ was used in a systematic survey of homoaromatic systems [2] [3]. It should be noted that all these values are based on the assumption that β has its 'thermochemical' value of $\beta = 20$ kcal mole$^{-1} \approx -1$ eV. From a comparison of the electronic spectra with the relevant molecular orbital data the following calibration of m was obtained: $m = 0.73$ for the homotropylium cation [2] and $m = 0.33$ for the pentamethylcyclobutenyl cation [2] [22].

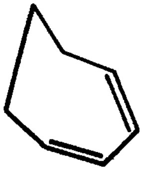
To conclude we wish to discuss the PE.-spectrum of bicyclo[4.2.1]nona-2,4,7-triene (VI) [23], shown in Fig. 5a (*c.f.* Table). For comparison we shall refer to the PE.-



VI (C_s)



VII (C_s)



VIII (C_s)

spectra of norbornene (VII) [11] [16] and of cyclohepta-1,3-diene (VIII) (Fig. 5b, Table 1).

In VI we are again in the presence of three interacting double bonds but in contrast to the situation in I homoconjugative interaction occurs only between $\boldsymbol{\pi}_1$ on the one hand and $\boldsymbol{\pi}_2$, $\boldsymbol{\pi}_3$ on the other. The interaction between $\boldsymbol{\pi}_2$ and $\boldsymbol{\pi}_3$ corresponds to normal conjugation, which in the case of VIII leads to a split $\varepsilon(\boldsymbol{a}''(\pi)) - \varepsilon(\boldsymbol{a}'(\pi)) = 2.30$ eV between the orbital energies of the symmetric linear combination $\boldsymbol{a}'(\pi) = (\boldsymbol{\pi}_2 + \boldsymbol{\pi}_3)/\sqrt{2}$ and the antisymmetric one $\boldsymbol{a}''(\pi) = (\boldsymbol{\pi}_2 - \boldsymbol{\pi}_3)/\sqrt{2}$.

As far as the π-bands are concerned it is evident from the correlation diagram in Fig. 6 that the PE.-spectrum of VI is essentially the superposition of the PE.-spectra of VII and VIII. At first sight this is surprising, as it seems to suggest that in VI there is no homoconjugative interaction between the π-orbitals of the diene system and those of the isolated double bond. However, this was to be expected. Indeed, the following application of our simple model shows that no significant departure from the observed additivity should occur even if the size of the parameter m describing the through-space interaction between the homoconjugated orbitals is the same as in I.

In the absence of interaction with $\boldsymbol{\pi}_1$ the energies of the orbitals $\boldsymbol{a}'(\pi)$ and $\boldsymbol{a}''(\pi)$ of the diene moiety in VI may be assumed to have the values deduced from the PE.-spectrum of VIII: $\varepsilon(\boldsymbol{a}'(\pi)) = -10.6$ eV, $\varepsilon(\boldsymbol{a}''(\pi)) = -8.3$ eV. As $\boldsymbol{\pi}_1$ belongs to the irreducible representation A', it can only interact with $\boldsymbol{a}'(\pi)$, while $\boldsymbol{a}''(\pi)$ remains unaffected. From the PE.-spectrum of VII we have $\varepsilon(\boldsymbol{\pi}_1) = -9.0$ eV. If $\boldsymbol{a}'(\pi)$ is approximated by a linear combination of $2p$-atomic orbitals as obtained from a *Hückel* treatment of a diene ($\boldsymbol{a}'(\pi) = 0.372\,(\phi_1 + \phi_4) + 0.602\,(\phi_2 + \phi_3)$ [24]), then the interaction between $\boldsymbol{a}'(\pi)$ and $\boldsymbol{\pi}_1$ is given by

$$\langle \boldsymbol{a}'(\pi) \mid \mathcal{H} \mid \boldsymbol{\pi}_1 \rangle = 0.526\, m\beta\,. \tag{7}$$

This interaction will give rise to second order shifts $\delta\varepsilon$ of the orbital energies $\varepsilon(\boldsymbol{a}'(\pi))$ and $\varepsilon(\boldsymbol{\pi}_1)$ which for $m = {}^1\!/_4$ and $\beta = -2.5$ eV amounts to

$$\mid \delta\varepsilon \mid = \frac{\langle \mathbf{a}'(\pi) \mid \mathcal{H} \mid \boldsymbol{\pi}_1 \rangle^2}{\varepsilon(\boldsymbol{\pi}_1) - \varepsilon(\mathbf{a}'(\pi))} = \frac{(0.526\, m\beta)^2}{-9.0 - (-10.6)} = 0.07 \text{ eV}\,. \tag{8}$$

This is too small to lead to a significant departure from additivity, especially as it will be partially obliterated by the effect of through-bond interactions, which we have neglected.

From this we conclude that even the use of PE.-spectroscopy for the assessment of homoconjugative interaction or of 'homo-aromaticity' is tied to special conditions: Only when the basis orbitals $\boldsymbol{\pi}_j$ of the molecule under consideration are symmetry-equivalent or if their orbital energies $\varepsilon_j = \alpha + \beta$ are accidentally (almost) degenerate, will large first order changes be observable in the PE.-spectra of such compounds.

In conclusion it might be added that the concept of homo-aromaticity or anti-homo-aromaticity is only meaningful if the interaction of the π-orbitals with the orbitals of the σ-bonds is negligible or the same for all π-orbitals. If the $\sigma - \pi$-interaction is of the same magnitude as the homoconjugative $\pi - \pi$-interaction and if, for reasons of symmetry, this interaction favours one of the linear combinations over the others, then homoconjugation as well as homo-aromaticity are no longer important factors for the description of the electronic structure of such molecules.

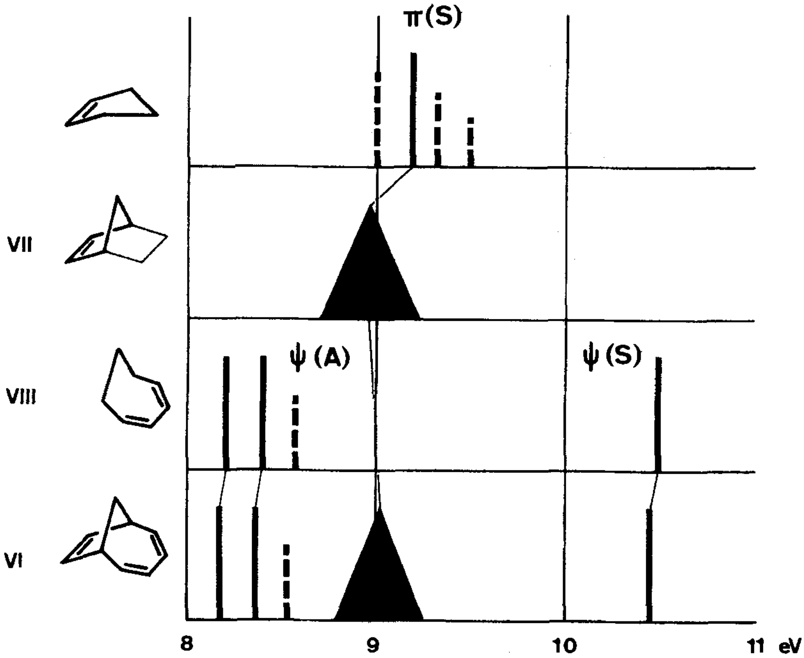


Figure 6. *Schematic diagram of the PE.-spectra of cyclopentene, norbornene (VII), cyclohepta-1,3-diene (VIII) and of bicyclo[4.2.1]nonatriene (VI)*

Only the π-bands are shown. The solid lines (maximum) and broken lines represent the vibrational fine structure of the corresponding band. A triangle is used to characterise a broad band with unresolved fine structure. *A* and *S* refer to the antisymmetric and symmetric behaviour of the corresponding orbital with respect to a plane of symmetry. The symbol ψ is used for the linear combinations of the two-center π-orbitals ($\psi(S) = \boldsymbol{a}'(\pi)$; $\psi(A) = \boldsymbol{a}''(\pi)$)

Experimental. – The PE.-spectra have been recorded on a modified PS-15 spectrometer from *Perkin-Elmer Ltd.* (Beaconsfield, England) which corresponds essentially to the type of instrument described by *Turner* [25]: Open He-discharge (584 Å, 21.21 eV), electrostatic focussing sector (radius 5 cm, sector angle $\pi/\sqrt{2}$, resolution 0.02 eV at 5.46 eV kinetic energy of the photoelectrons). The ordinate of our spectra (counts per second) are in arbitrary units. The falloff in intensity towards higher potentials is an artefact due in part to the design of the spectrometer. All spectra are calibrated relative to the signals of an Ar/Xe mixture, which is added to the sample as an internal standard.

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170. Über Pterinchemie

33., vorläufige Mitteilung [1]

Luftoxydation von 6,6-disubstituierten Tetrahydropterinen, ein Beitrag zur Frage der Existenz von Parachinoid-dihydropterinen

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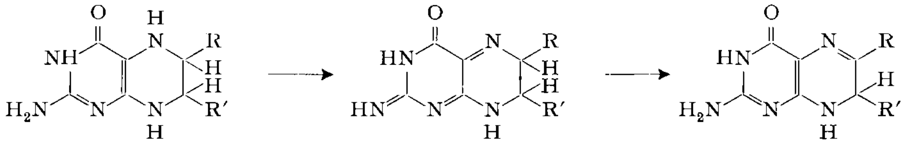
(7. VII. 70)

Zusammenfassung. Die Luftoxydation von 6,6-disubstituierten Tetrahydropterinen führt nicht, wie vermutet, zu Parachinoid-dihydropterinen, sondern unter Verlust einer der beiden Seitenketten zu 7,8-Dihydropterinen. Dieses Ergebnis wird im Zusammenhang mit der existierenden Theorie der Tetrahydropterin-Oxydation kurz diskutiert.

Bei der Luftoxydation der Tetrahydropterine (I) in wässerigen Lösungen von physiologischem pH lassen sich als erste fassbare Produkte 7,8-Dihydropterine (III) nachweisen bzw. isolieren. In ganz bestimmten Fällen können intermediäre Produkte der Dihydrostufe zwischen I und III nachgewiesen werden [2]. Die Vermutung, dass



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