

## 220. The Dianions of Pyrene and Pyrene Isomers as $(4n)\pi$ -Perimeters<sup>1)</sup>

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### Summary

Metal reduction of pyrene and of pyrene isomers under carefully controlled conditions yields the corresponding dianions. The properties of the neutral compounds and of the dianions are studied via <sup>1</sup>H-NMR. spectroscopy. Whereas the former exhibit similar behaviour, the charge distribution within the dianionic species proves to be very different. As a consequence, some of the polycyclic dianions can be regarded essentially as  $(4n)\pi$ -perimeters, an approach which is satisfactorily rationalized by simple MO-models. Further evidence in favour of this bonding scheme comes from the ESR. spectroscopic measurement of the spin density distribution within the corresponding radical anions.

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**1. Introduction.** - Due to the simple topology of annulenes their eigenvalues within a HMO-model can be determined in a closed form [1]. It is well known that the resulting orbital patterns exhibit certain regularities which allow a straightforward interpretation of various spectroscopic properties [2]. Thus, as the annulenes constitute suitable probes for the ascertainment of theoretical predictions [1] [2] it is not surprising that they also have been invoked as model compounds for more complicated  $\pi$ -species. Typical examples are represented by the transition states of electrocyclic rearrangements [3] or by unsaturated polycycles.

When depicting the possible *Kekulé*-structures for an unsaturated polycycle one can well raise the question whether perimeter-type structures contribute to the ground-state of the molecule. Various molecular properties have been referred to in order to estimate the importance of perimeter structures in polycycles. The charge distribution, e.g. within porphyrin systems, which represent potential [18]annulenes [4] [5], has been determined from <sup>13</sup>C-chemical shifts and from MO-calculations or characteristic ring current effects have been evaluated from <sup>1</sup>H-NMR. data in corannulenes [6] and annuleno-annulenes [7].

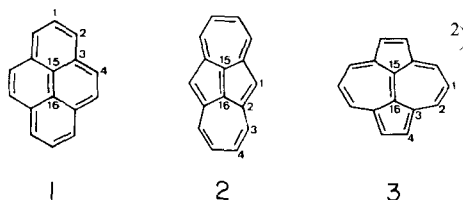
The spectroscopic characterization of  $\pi$ -systems does not necessarily provide a clear-cut conclusion about the specific bonding situations. This short-coming can in part be attributed to the fact that the resulting data depend on geometrical factors such as the configuration or conformation of the rings. However, when transforming

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<sup>1)</sup> In part reported at the «Chemiedozenten-Tagung» held at Marburg, Germany, 1977.

a neutral molecule into its ionic derivatives, the comparison of spectroscopic properties and the subsequent interpretation in terms of bond theory become much more straightforward. Thus, the parallel inspection of a  $(4n)\pi$ -system and its corresponding  $(4n+2)\pi$ -dianion provides a test for *Hückel's* rule, but within the same molecular framework [8].

This work is devoted to testing the validity of the above mentioned principles: the importance of perimeter structures in polycycles and the theoretical significance of dianion generation. Therefore, we compare here the bonding situations within



the neutral species, the radical anions and dianions of polycyclic  $\pi$ -systems. As appropriate models we have selected pyrene (1) and the 'isopyrenes' bis(cyclohepta)[*cd, gh*]pentalene (2) [9] as well as bis(cyclopenta)[*ef, kl*]heptalene (azupyrene) (3) [10] [11].

**2. Structural features of pyrene and isopyrenes.** - The molecular frameworks of the isomers 1-3 exhibit some structural features which will become essential when discussing the charge distribution in the dianions.

In each isomer the 5-, 6- and 7-membered rings are condensed in such a way as to maintain a plane of symmetry through the central C-atoms C(15) and C(16).

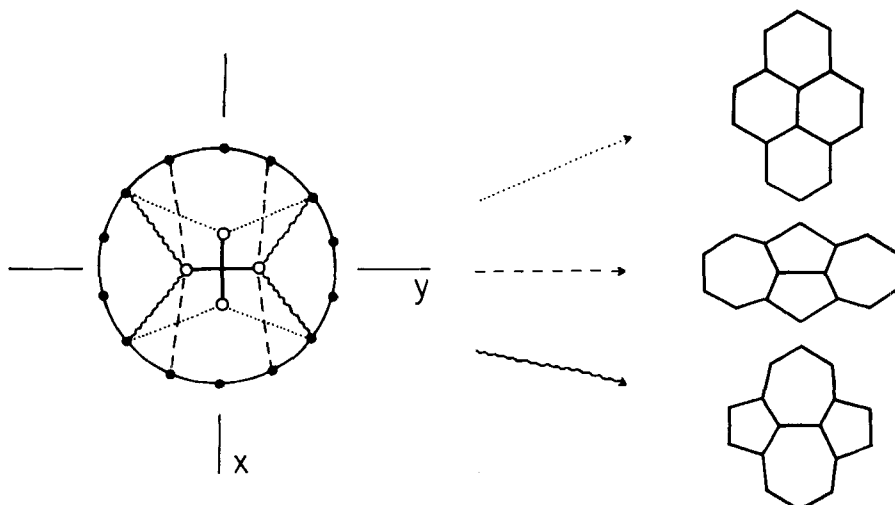
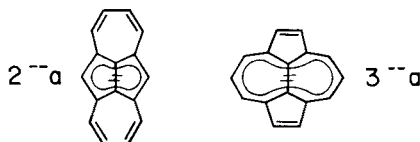


Fig. 1. Building up of the three isomeric polycycles 1-3 by differently bridging a 14-membered perimeter

<sup>2)</sup> The numbering of the centers has been chosen in such a way as to allow a simple comparison within the series.

This plane of symmetry in **1** runs through two opposite centers of the ring (see *Fig. 1*), in **2** and **3**, however, it bisects two peripheral bonds. Within the isomers **2** and **3**, on the other hand, the central ethylene bridge is differently bonded to the  $14\pi$ -perimeter. By simple application of *Hückel's* rule one might well expect the dominance of a bridged  $14\pi$ -perimeter structure for the neutral compounds. Consequently, for the corresponding dianions one will have to consider those structures which involve a charge separation between the bridge and the perimeter. In an alternative interpretation one can consider structures **2<sup>2-</sup>a** and **3<sup>2-</sup>a** as adequate representations of the dianions **2<sup>2-</sup>** and **3<sup>2-</sup>**, respectively, since it is well known that pentalene [12] and heptalene [13] form very stable dianions.



**3. Experimental and results.** - In *Figures 2* and *3* we present the  $^1\text{H-NMR}$ . spectra of the neutral isomers **1-3** as well as those of the corresponding dianions **1<sup>2-</sup>-3<sup>2-</sup>**. The dianionic species have been prepared by reduction of the neutral compounds with lithium in absolute tetrahydrofuran- $d_8$ . Thereby a technique could advantageously be applied which has been developed recently [13]. In a typical experiment one introduces with a specially constructed press a wire of pure lithium into the upper part of an NMR. tube containing the degassed frozen solution of the starting material. After sealing the tube one sublimates the metal by means of an induction furnace. Simply by turning the tube one can bring the solution into contact with the metal mirror for controlled periods of time. Moreover, this arrangement allows one to control the kinetics of the reduction, *i.e.* the appearance and disappearance of the intermediate radical anions and the final formation of the dianions, by ESR. and NMR. spectroscopy. Already at low radical concentrations the  $^1\text{H-NMR}$ . signals of **1-3** are broadened beyond detection. This observation, which is a consequence of the fast electron exchange between the neutral and radical species, is in contrast with the observation made during the metal reduction of heptalene [13]. In the latter case the reduction is accompanied by a significant change in the molecular geometry which tends to slow down the electron exchange. Such a situation is unlikely to be encountered in the rigid polycycles **1-3**. The resulting dianions are identified on the basis of their  $^1\text{H-NMR}$ . splitting patterns (see *Fig. 2* and *3*) and by chemical evidence: bubbling dry oxygen through the solutions of the dianions yields the starting materials as only products.

The most significant outcome which can be derived from inspection of the spectra in *Figures 2* and *3* is the great difference in the chemical shifts of the dianions **1<sup>2-</sup>-3<sup>2-</sup>**, while the neutral compounds all absorb at similarly low field. Therefore one calculates the following upfield shifts for the centers of gravity of the  $^1\text{H-NMR}$ . signals (see also the *Table*): 7.2 ppm, **1<sup>2-</sup>**; 3.2 ppm, **2<sup>2-</sup>**; 1.3 ppm, **3<sup>2-</sup>**.

Quite naturally, when discussing these features in terms of bond theory one will essentially have to compare the similar behaviour of the neutral compounds with the deviations among the dianion series. The following procedure might therefore

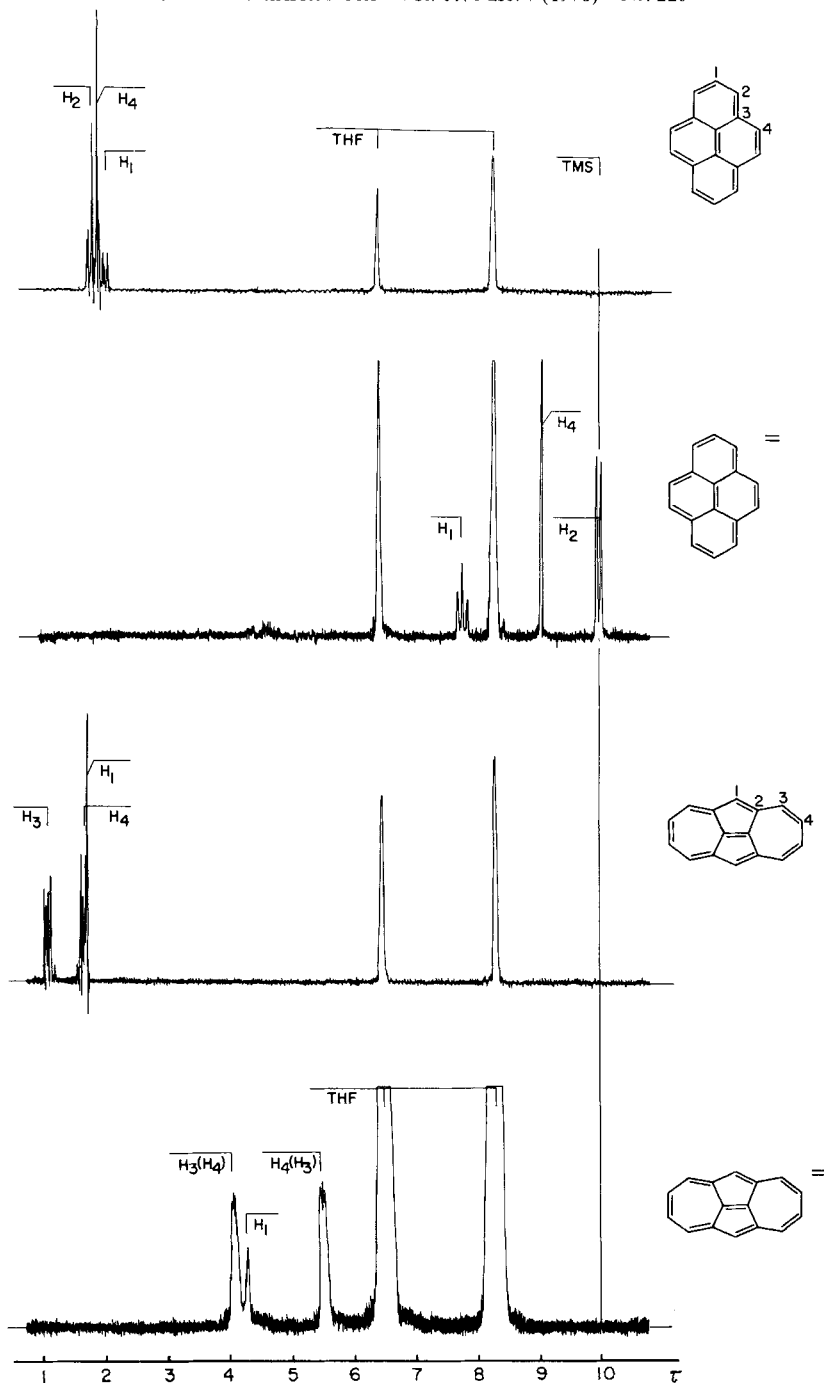


Fig. 2 and 3. The  $^1\text{H-NMR}$  spectra (100 MHz, CW-mode, solvent  $\text{THF-d}_8$ ,  $-40^\circ$ ) of the neutral isomers 1-3 as well as of their corresponding dianions 1<sup>2-</sup>-3<sup>2-</sup> (as lithium salts). The proposed signal assignments are based on relative intensities and on the obvious splitting patterns (as simplified by H,H-decoupling experiments)

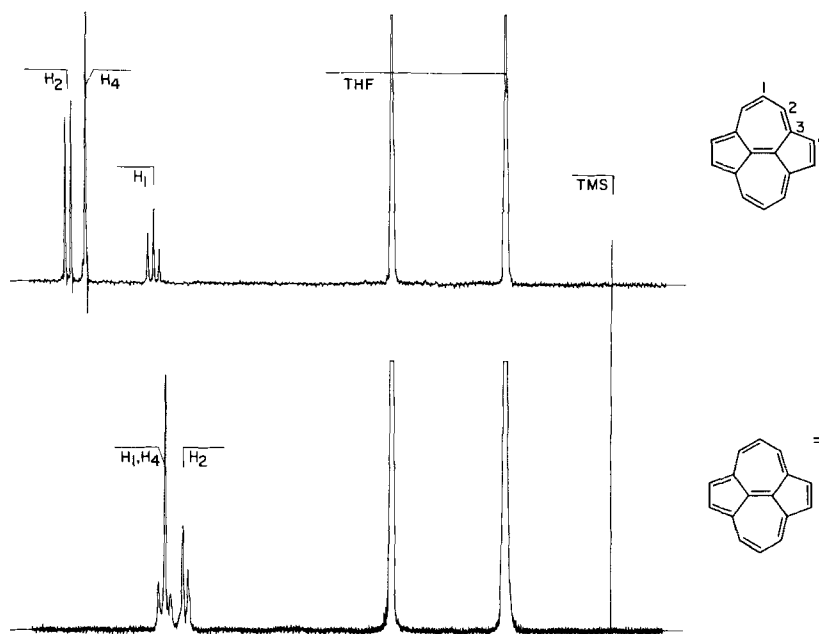


Fig. 3

be a useful approach: one considers, first, the bonding situation of the neutral molecules and then proceeds by examining the spin density distribution within the intermediate radical anions. The latter information can then be taken as a first working hypothesis for the distribution of the excess charge in the dianions.

Table.  $^1\text{H-NMR}$ . chemical shifts of the isopyrenes 1-3, of the corresponding dianions  $1^{2-}$ - $3^{2-}$  as well as of the pyrene dication  $1^{4+}$ )

	H-C(1)	H-C(2)	H-C(3)	H-C(4)	
$\tau(1^{2-})$	7.78	9.99		9.06	
$\tau(\mathbf{1})$	2.10	1.92		2.02	
$\Delta\tau[(1^{2-})-(\mathbf{1})]$	5.68	8.07		7.04	$\Delta\langle\tau\rangle = 7.18$
$\tau(2^{2-})^b)$	4.19		3.99 <sup>d)</sup>	5.43 <sup>d)</sup>	
$\tau(\mathbf{2})$	1.70		1.05	1.64	
$\Delta\tau[(2^{2-})-(\mathbf{2})]$	2.49		2.94	3.79	$\Delta\langle\tau\rangle = 3.19$
$\tau(3^{2-})$	2.79	3.13		2.79	
$\tau(\mathbf{3})$	2.58	1.21		1.49	
$\Delta\tau[(3^{2-})-(\mathbf{3})]$	0.21	1.92		1.30	$\Delta\langle\tau\rangle = 1.33$
$\tau(1^{4+})^c)$	2.59	1.62		1.87	
$\Delta\tau[(1^{4+})-(\mathbf{1})]$	0.49	-0.30		-0.15	$\Delta\langle\tau\rangle = -0.08$

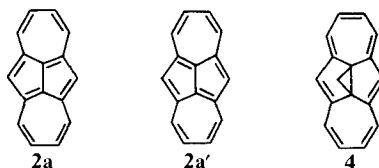
a) The chemical shifts (in  $\tau$  [ppm]) are measured with respect to the solvent signals and then referred to TMS.

b) An ESR. signal and, thus, a residual concentration of radicals can be detected even after prolonged contact with the metal. This induces some line broadening in the  $^1\text{H-NMR}$ . spectrum of the dianion.

c) Chemical shifts have been measured with respect to external TMS.

d) This assignment is not based on experimental evidence but has been deduced from comparison with the corresponding ESR. coupling constants.

**4. The neutral compounds. Importance of perimeter-type conjugation.** - The low-field absorption of the protons in **1-3** can well be accounted for by the assumption of a diamagnetic ring current in the perimeter. Even in **1**, whose diatropism will naturally be ascribed to the existence of the benzene fragments,  $^{13}\text{C-NMR}$ . investigations point towards the existence of an additional diamagnetic ring current in the periphery [14]. Furthermore, when correlating  $\pi$ -bond orders and vicinal H,H-coupling constants [15], one can easily demonstrate for compound **2** that resonance structures incorporating a formal C(15),C(16)-single bond (**2a**, **2a'**) do not contribute significantly to the ground-state of this molecule. In the situation described by structures **2a** and **2a'** the formation of two diene fragments at C(3)-C(6) and at C(10)-C(13) would result and  $\pi$ -bond localization would occur. In contrast, the experimental H,H-coupling constants indicate that compound **2**



has its  $\pi$ -bonds delocalized [16] and, thus, exhibits a close relationship with its homo-analogue, the bridged [14]annulene **4** [17]. One can therefore conclude, in accordance with various other spectroscopic and theoretical results, that compounds **1-3**, to a first approximation, can well be represented as bridged annulenes [17-19].

In his early 'perimeter-concept' *Platt* pointed out that certain polycyclic species possess a stable peripheral 'shell' which is isolated from an inner fragment by circular nodes [20]. Since then various other models have been proposed which are dedicated to make *Hückel's* rule applicable for polycycles [21-23].

Although we will not dwell on the classification of polycyclic compounds, *e.g.* as being 'aromatic' or not, one point in the present context deserves further comment. As has already been emphasized by *Randic* [23], these theoretical concepts are based merely on structural features such as the number and size of the rings or the number of possible *Kekulé*-structures<sup>3)</sup>. In contrast, the above characterization of **1-3** is deduced from molecular properties, *e.g.* the ring currents or the charge distribution as derived from NMR. spectroscopic data. The latter procedure will not necessarily lead one to conclusions being compatible with the 'structural' description; but it constitutes the only reasonable approach for a comparison of the neutral and the corresponding ionic species.

**5. The radical anions. Interaction of annulene- and bridge-MO's.** - As the radical anion **1<sup>-</sup>** [24] [25] has been described in the literature, only **2<sup>-</sup>** [16] and **3<sup>-</sup>** remain to be characterized in this work<sup>4)</sup>. A schematical representation

<sup>3)</sup> In a recent approach it has been pointed out by *Randic* [23] that, although mostly dominant, not only the peripheral circuit will control the properties of the molecules. He therefore proposed to consider all 'conjugated circuits' (either of  $4n$ - or  $4n+2$ -type) occurring within the *Kekulé*-structures of the molecules. Applying this procedure he succeeded in specifying the relative stabilities of **1-3**.

<sup>4)</sup> A brief description of **3<sup>-</sup>** has already been given in [11].

of the two lowest antibonding Hückel-MO's for any of the three isomers involved is given in Figure 4. This Figure also comprises the experimental ESR. hyperfine coupling constants for the individual ring protons. From the observation of a small coupling constant for a pair of two equivalent protons in  $1^{\dot{-}}$  and  $2^{\dot{-}}$  one can readily conclude that the unpaired electron occupies the MO  $\psi_{AA}$  which possesses a nodal plane through the ring centers C(1) and C(8).

If the spin density were distributed over the  $\pi$ -system according to  $\psi_{SS}$ , this coupling would be expected to be large. Such a situation is, indeed, encountered in the [14]annulene **4**. The observed sequence of the molecular orbitals can thereby be understood on the basis of a simple perturbation model [26]. This straightforward argument is not valid in  $3^{\dot{-}}$  since the two lowest-lying HMO's exhibit a nodal plane through the ring atoms C(1) and C(8). However, a calculation of the expected spin densities by the *McLachlan*-method [27] and subsequent correlation with the experimental data indicates that the unpaired electron occupies the  $\psi_{AS}$ -orbital. There is, thus, evidence for the assignment of the individual coupling constants as proposed in Figure 4. The above interpretation of the ESR. data leads one to an important conclusion: in  $1^{\dot{-}}$  and  $2^{\dot{-}}$ , respectively, the molecular orbitals which are occupied by the unpaired electron represent pure annulene MO's with a nodal plane through the bridge. This is no longer true for the radical anion  $3^{\dot{-}}$  since in this case the corresponding orbital possesses a high probability for the charge to reside on the bridge centers C(15) and C(16). Therefore, it cannot be regarded as a perimeter MO.

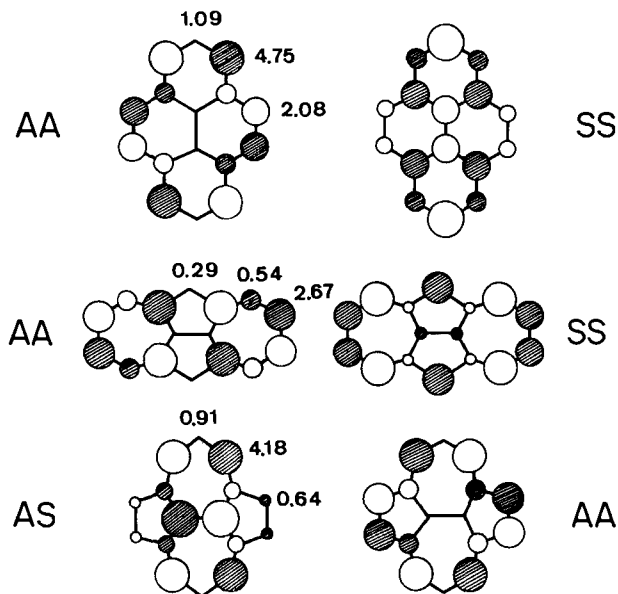


Fig. 4. Schematic representation of the two low-lying antibonding Hückel MO's of 1-3. The areas of the circles are proportional to the squares of the LCAO-coefficients, dotted and blank circles symbolize different signs. The symmetry of the orbitals has been classified with respect to the two mirror planes perpendicular to the molecular plane. The numbers represent the experimental ESR. hyperfine coupling constants (absolute values in Gauss) determined for the individual positions

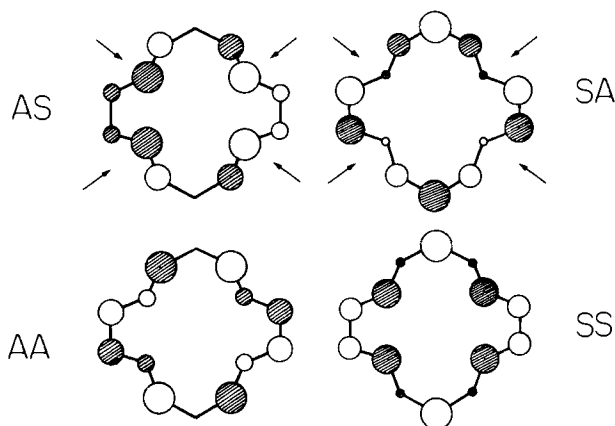


Fig. 5. Schematic representation of the two pairs of low-lying antibonding Hückel MO's of an idealized [14]annulene. The consequences of the bridging process leading to either **1** or **3** are described in the text. Note that the  $\pi^*$ -orbital of the bridge has SA-symmetry during the formation of **1** and AS-symmetry during the formation of **3** (see also Fig. 4).

In order to illustrate this basic difference one can simply refer to the introductory model considerations in which the three isomeric polycycles have been constructed from the combination of a [14]annulene and an ethylene bridge. As is well known, an in-plane deformation of the idealized  $D_{14h}$ -perimeter which gives rise to a  $D_{2h}$ -configuration of *e.g.* pyrene type or anthracene type leaves the energy of the corresponding Hückel-MO's unaltered [1] [2]. This is no longer true for the bridging process which, clearly, affects different positions of the 14-membered ring. As is readily deduced from inspection of Figure 5, none of the two lowest-lying annulene orbitals ( $\psi_{AA}$ ,  $\psi_{SS}$ ) possesses the proper symmetry for a substantial interaction with the  $\pi^*$ -orbital of the bridge (AS in **2** and **3**, SA in **1**). The interaction of the  $\pi^*$ -orbital with one orbital of the next higher pair of annulene MO's is, however, symmetry-allowed. But only in **3** is this function characterized by a large AO-coefficient at the bridgehead centers of the ring. Consequently, the MO  $\psi_{AS}$  is in **3** - and only in **3** - stabilized to such an extent that it achieves a lower energy than the two perimeter orbitals  $\psi_{AA}$  and  $\psi_{SS}$  (see also Fig. 4). This interpretation is in perfect agreement with the ESR. experiment<sup>5</sup>).

#### 6. The dianions. Charge distribution as a probe for the bonding situation. -

Having in mind the different situations being considered in **3<sup>+</sup>** on the one hand and in **1<sup>+</sup>** and **2<sup>+</sup>** on the other hand one can now proceed to analyse the charge distribution in the corresponding dianions. It has become clear from the introduction that a precise knowledge of the charge distribution in the ions allows a ready assignment of the structure. Not surprisingly, the shielding of the ring protons is enhanced due to the effect of the excess charge. In the particular case of the dianions **1<sup>2-</sup>** and **3<sup>2-</sup>** where the signal assignments can simply be deduced from the

<sup>5</sup>) Although this perturbational model is restricted to 'first-order-effects' only one has to be aware of the fact that other annulene MO's are to a minor extent also affected by the bridging.



splitting patterns, the amount of the upfield shift of the proton signals parallels the corresponding ESR. coupling constants. This is actually what one would have predicted on the basis of a simple MO-model. Moreover, one can deduce from the shift differences within the spectra of  $2^{--}$  and  $3^{--}$  that the excess charge is not localized in the 5- and 7-membered rings, respectively. Therefore, those structures involving the pentalene or heptalene dianion do not constitute an adequate representation of  $2^{--}$  and  $3^{--}$ , respectively. According to *Schaefer & Schneider* [28] the upfield shift of the  $^1\text{H-NMR}$ . signals is proportional to the change in the  $\pi$ -charge densities of the corresponding carbon centers. For two extra charges being uniformly distributed over a 16-membered  $\pi$ -system one will, thus, expect the following shift of the center of gravity of the signals:

$$\Delta\langle\tau\rangle = 10.7(18 - 16)/16 = 1.34 \text{ ppm.}$$

Taking a common proportionality factor of 10.7 [ppm/per unit charge] throughout the series one has to conclude that only the chemical shifts of  $3^{--}$  are in accordance with this equation. This outcome which corresponds with the analysis of the ESR. data implies that only in  $3^{--}$  one can expect a uniform charge distribution including the bridge centers. Further support in favour of this interpretation comes from SCF-(PPP, CNDO)-MO-calculations [29] of the  $\pi$ -charge densities. The same calculations for the dianions  $1^{--}$  and  $2^{--}$  predict that the two extra charges are distributed exclusively on the perimeter. This can - at least in part - explain the pronounced upfield shift of the  $^1\text{H-NMR}$ . signals. It is therefore tempting to characterize the dianions  $1^{--}$  and  $2^{--}$  as bridged  $16\pi$ -perimeter systems although a structure of that type is expected to be unfavourable in terms of *Hückel's* rule.

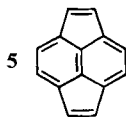
The existence of a charge separation between bridge and perimeter, alone, does not provide sufficient explanation for the observed upfield shifts in  $1^{--}$  and  $2^{--}$ . As a further possibility one might consider the quaternary carbon atoms (at the bridge and the bridgeheads) as accepting no negative or even a positive charge. Although this assumption is, e.g. in  $1^{--}$ , supported by calculations, our results indicate the dominance of yet another effect. If, indeed,  $1^{--}$  and  $2^{--}$  represent perturbed  $16\pi$ -perimeter systems one will expect the occurrence of a paramagnetic ring current in the periphery and, as a consequence, a further upfield shift of the proton signals. In the same respect one should point out that the SCF-calculations predict a higher degree of  $\pi$ -bond alternation within the non-alternant  $\pi$ -system  $2^{--}$  than within  $1^{--}$ . Increasing  $\pi$ -bond fixation is expected to quench to a certain extent a paramagnetic ring current [30], which might provide an explanation for the significantly higher upfield shift in  $1^{--}$  than in  $2^{--}$ .

When dealing with the potential overlap of charge effects and ring current effects it turns out to be a useful approach to compare the dianion of pyrene  $1^{--}$  with its corresponding dication  $1^{++}$ . The latter can easily be prepared from pyrene by oxidation with antimony pentafluoride in fluorosulfonyl chloride [31]. According to the well known pairing properties of the molecular orbitals in alternant hydrocarbons the highest occupied MO as well as the lowest unoccupied MO of pyrene possess a nodal plane through the bridging group. One should therefore expect similar properties for the dianion and the dication; namely, that no charge, negative or positive, is accepted by the bridge. Our experimental results (see *Table*) fit these

assumptions quite well: the sequence of the  $^1\text{H-NMR}$ . signals in  $\mathbf{1}^{++}$  is reversed with respect to the one in  $\mathbf{1}^{--}$ , or in other words, those protons experiencing the strongest deshielding in  $\mathbf{1}^{++}$  are most shielded in  $\mathbf{1}^{--}$ . These features provide an experimental verification of the pairing-properties of MO's in alternant  $\pi$ -systems, a finding that has already been well documented by a comparison of the corresponding radical anions and radical cations in this class of compounds [32].

The center of gravity of the  $^1\text{H-NMR}$ . signals remains in nearly the same position when going from pyrene to its dication. According to the model proposed above this finding implies that the expected downfield shift - being due to the charge - is compensated by an upfield shift which can be ascribed to a paramagnetic ring current in the  $(4n = 12)\pi$ -perimeter. One can, thus, safely conclude that a paramagnetic ring current is present both in the dianion  $\mathbf{1}^{--}$  and the dication  $\mathbf{1}^{++}$ . And this finding, in turn, provides supporting evidence in favour of the proposed perimeter model.

**7. Conclusion. Importance of the highest occupied MO.** - As we have recently deduced from the  $^{13}\text{C-NMR}$ . spectra of diamagnetic ions the charge distribution within these  $\pi$ -systems can be highly non-uniform [33]. In addition, from the present  $^1\text{H-NMR}$ . spectroscopic study we can now make the following statement: due to the nodal properties of the highest occupied MO a perimeter-type conjugation is to be preferred in the ions of polycyclic  $\pi$ -systems although this situation seems unlikely for electrostatic reasons and although *Hückel's* rule predicts an electronic destabilization<sup>6)</sup>.



The symmetry of the 'frontier-orbitals' has also been invoked to explain the bonding structure of the neutral polycycle pyracyclene (**5**) [34]. In close analogy with the situation in the isopyrene dianions two alternative models have been proposed to describe compound **5**: one taking into account a perturbed  $(4n)\pi$ -perimeter and the other considering a vinyl bridged naphthalene [34-36]. The observed paratropism of **5** strongly supports the former interpretation [34-37]. From that point of view the  $(4n)\pi$ -perimeters  $\mathbf{1}^{--}$  and  $\mathbf{2}^{--}$  can be regarded as ionic analogues of the neutral  $\pi$ -system pyracyclene.

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<sup>6)</sup> A bonding situation similar to the one in the dianions  $\mathbf{1}^{--}$  and  $\mathbf{2}^{--}$  is encountered in the cyclo-octa[de]fluorenyl anion which can be regarded as a vinyl bridged [15] annulenyl anion [38].

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