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An Attempt to Predict the Relative Resonance Stabilization of Some Non Benzenoid π-electron Systems with the Perimeter Model

By

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The π-electron systems of cata condensed aromatic hydrocarbons containing 4ν carbon atoms are viewed as perturbed perimeters. The influence of the geometry of crosslinks or of hetero-atoms on the resonance stabilization is assessed. The model is limited to cases in which changes in σ-strain energy are unimportant.

Les electrons π des hydrocarbures aromatiques cata-condensés contenant 4ν atomes de carbone sont considérés comme périmètres perturbés. L'on estime ainsi l'influence de la géometrie des liaisons transversales ou de l'introduction d'hétéro-atomes. Le modèle est limité à des cas où la difference relative d'énergie σ est négligeable.

Die π-Elektronen-Systeme kata-kondensierter aromatischer Kohlenwasserstoffe mit 4ν Kohlenstoffatomen werden als gestörte Perimeter betrachtet. Der Einfluß der Geometrie von Kreuzverbindungen oder die Einführung von Hetero-Atomen werden beurteilt. Die Anwendung des Modells ist auf Fälle beschränkt, in welchen Unterschiede der σ-Energie vernachlässigbar sind.

The perimeter model has been quite successfully applied to interpret the electronic spectra of various benzenoid and non benzenoid cata condensed aromatic hydrocarbons containing $4\nu + 2$ carbon atoms [*4*, *7*, *10*]. The aim of this note is to use the perimeter model to make some qualitative predictions on the relative resonance stabilization of cata condensed aromatic hydrocarbons containing 4ν carbon atoms, that is, on systems which do not obey Hückel's rule. The model has already been applied to classify the magnetic properties of such compounds [*13*]. It is well known that many of these molecules are very difficult to synthesize and that they may show marked instability. The question which we ask is the following: In what way does the geometry of the molecule, such as the position of crosslinks, affect the stability of the π-electron system? We will, for simplicity, neglect here the influence of the σ-frame. This will, however, limit our model to cases where the difference in σ-strain energy is unimportant.

We consider a ring of 4ν sp^2 hybridized carbon atoms of effective symmetry $D_{(4\nu)h}$. In the HÜCKEL scheme the ground state consists of a degenerate set of three singlets and one triplet. We designate the closed-shell part of the wave function times the normalization constant by N and write for the three singlets:

$$S\,(+\,+) = N\,|\,\nu^+\,\overline{\nu}^+\,|$$

$$S\,(-\,-) = N\,|\,\nu^-\,\overline{\nu}^-\,|$$

$$S\,(+\,-) = (N/\sqrt{2})\,\{\,|\,\nu^+\,\overline{\nu}^-\,| + |\,\nu^-\overline{\nu}^+\,|\,\}$$

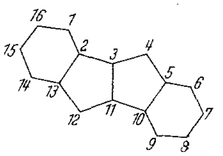
where

$$\nu^{\pm} = (4\nu)^{-\frac{1}{2}} \sum_{m=1}^{4\nu} \exp\,(\pm 2\pi i \nu m / 4\nu) \cdot \Phi_m$$

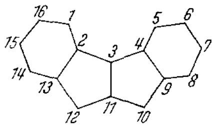
Φ_m being the $2p_z$ orbital of the mth carbon atom. If such a system actually existed it would be prone to JAHN-TELLER distortion, *i. e.* it would be geometrically deformed. Electron repulsion lifts the degeneracy and makes the ground state a triplet (if one neglects differential overlap the triplet is still degenerate with one singlet), which implies that the system may be chemically unstable. For the existence of a stable π-electron system with a 4ν-perimeter to be conceivable, the perimeter must get perturbed in such a way as to make the ground state a, preferably nondegenerate, singlet and the further this singlet lies below the triplet, the greater will the stabilization of the system then be. One possible perturbation is a distortion of the peripheral geometry, such as bond alternation. This aspect of the problem has been discussed in a variety of compounds [*1, 3, 6, 8, 12*]. It will not be dealt with further here. The type of perturbation which we wish to investigate is mainly the formation of crosslinks. The crosslink perturbation mixes the states $S\,(++)$ and $S\,(--)$ with $S\,(+-)$ and thereby pushes one of the singlet states below the triplet. We thus focus our attention on the magnitude of the matrix elements responsible for this mixing of states. Supposing that we form a bond between atoms k and l, p and q, we get

$$\langle S\,(++) \mid H' \mid S\,(+-)\rangle = \langle S\,(--) \mid H' \mid S\,(+-)\rangle =$$
$$= \frac{\sqrt{2}}{2\nu}\,\beta \left\{ i^{(k+l)} + i^{(p+q)} \right\}; \qquad i \equiv \sqrt{-1}$$

H' is the perturbation operator, β the crosslink resonance integral. The bigger the (absolute) value of these matrix elements, the bigger is the stabilizing effect. As an example, let us take the isomeric dibenzpentalenes I and II:



I



II

In the case of I we obtain the value $-(\sqrt{2}/8)\,\beta\,(1+2i)$, in the case of II $-(\sqrt{2}/8)\,\beta$. Consequently, the crosslinks of I are more effective than those of II in pushing down the lowest singlet state, that is, in stabilizing the π-system. To the author's knowledge II has, as a matter of fact, not yet been synthesized, whereas compound I exists [*9*]. Similarly, among the six possible dibenzheptalenes three isomers, namely, II, IV, VI (see Fig. 1) should be significantly more stable than the remaining three other ones.

Recently attempts [*2, 11*] have been made to synthesize various aza-pentalenes and -heptalenes. Such a hetero-atom as nitrogen may be considered to increase the respective Coulomb integral α by an amount $\delta\,\alpha$. This perturbation acts analogously to the crosslinks and mixes $S\,(++)$, $S\,(--)$ with $S\,(+-)$. Assuming atom k to be the nitrogen atom we find:

$$\langle S(++) \mid H'' \mid S(+-)\rangle = \langle S(--) \mid H'' \mid S(+-)\rangle = \\ = \frac{\sqrt{2}}{4\nu}(-1)^k\,\delta\,\alpha$$

If we introduce a second hetero-atom at position $k+1$, say, the perturbation due to the first hetero-atom is canceled. If, however, we introduce the second hetero-atom at position $k+2$, the effects are additive and stabilize the π-electron system. Here again, our model gives us a simple relationship between geometry and π-electron stabilization. As an example we can say that III should be more stable than IV. However, we must always be aware of the crudeness of our model; perhaps even more so here than in the case of cross-link perturbations.

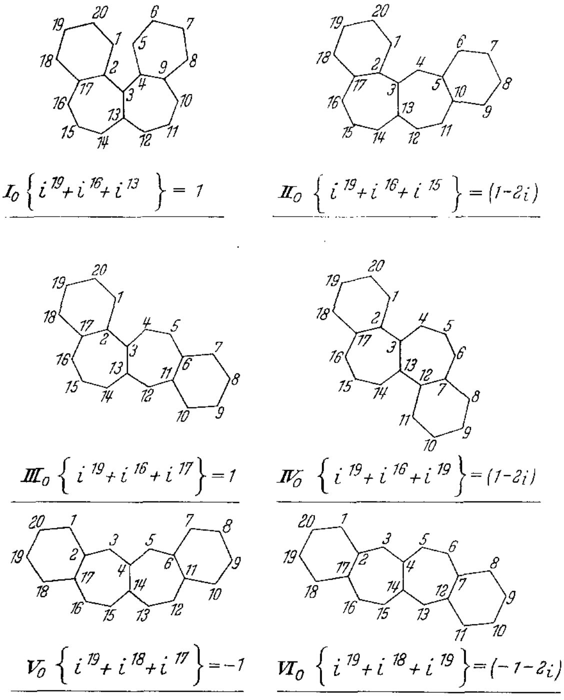
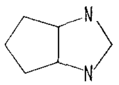
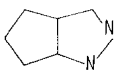


Fig. 1



III



IV

The relationship between the diamagnetic susceptibility perpendicular to the π-electron plane and the property of "aromaticity" is well known. Calculations by London's [5] method, assuming complete planarity and all bond lengths being equal, show an unperturbed cyclic π-electron system with 4ν carbon atoms to be paramagnetic. However, the more stable a molecule becomes by the criteria discussed above, the more highly diamagnetic will it then also be [13].

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[*] 1. 3a. 4. 6a-tetraaza-pentalene, the structure wich is discussed in this publication, is a 10 π-electron system and is therefore, from our point of view, benzenoid.
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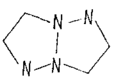

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