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On the Aromatic Character of some Ten π-Electron Systems

By

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The electronic structure of 1,4,5-triaza-cyclohepta-2,6-diene has been studied. The treatment accounts for the failure of detecting, by experiment, a cyclic conjugation in this and related seven membered ring systems.

Die Elektronenstruktur des 1,4,5-triaza-cycloheptadien-2,6 wurde theoretisch untersucht. Das Ergebnis erklärt das Mißlingen von Versuchen, in diesem und verwandten Siebenring-systemen zyklische Konjugation aufzufinden.

La structure électronique du 1,4,5-triaza-cycloheptadiène-2,6 a été étudiée. Le résultat explique pourquoi une conjugaison cyclique n'a pas été trouvée expérimentalement ni dans ce composé ni dans d'autres systèmes cycliques semblables à sept membres.

When two electrons are added to cyclooctatetraene a planar molecule with aromatic character is obtained [6, 8]. This is in accordance with Hückel's rule [5] that $(4n+2)$ π-electrons are required to give aromaticity in monocyclic cases. In an attempt to prepare other compounds fulfilling Hückel's rule with $n=2$, Allinger and Youngdale [2] recently synthesized some dibenzo derivatives of the structures represented by Fig. 1a to d. It was claimed that these structures which all contain ten π-electrons should be capable of planarity without undue strain.

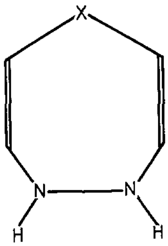


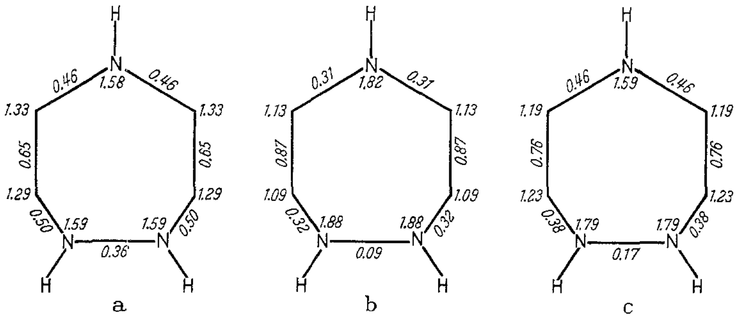
Fig. 1
Structures considered.
a) $X = NH$;
b) $X = NCH_3$;
c) $X = O$; d) $X = S$

In a previous communication [1] the same authors reported a molecular orbital calculation for the structure 1a using the simple Hückel method [3, 9]. The Coulomb parameter for nitrogen was chosen as $\alpha_N = \alpha + 0.5\,\beta$, where α is the Coulomb parameter for carbon and β is the usual resonance integral. The calculated resonance energy was $2.47\,\beta$, to be compared with the value of $2.12\,\beta$ for pyrrole when using the same set of parameters.

In Fig. 2a we present the π-electron density and bond orders as resulting from a HMO (Hückel molecular orbital) calculation, using the parameters chosen by Allinger and Youngdale. The bond orders are seen to be high for all bonds. The calculation therefore predicts a cyclic conjugation, since the electrons are able to migrate around the ring from atom to atom. An external magnetic field will produce cyclic currents, reinforcing the magnetic field outside the ring. Thus an attached proton should, in a nuclear magnetic resonance experiment, resonate at a lower applied field than if no cyclic conjugation was present [7]. Such experiments were carried out on the dibenzo derivatives of the structures shown in Fig. 1 by Allinger and Youngdale [2], but with a negative result: no shift of the above mentioned type was observed. Attempts to demonstrate cyclic conjugation by other means likewise failed, and the authors finally concluded that this type of 10 π-electron system did not have the character that might have been expected.

However, the $(4n+2)$ rule by Hückel is a necessary, not a sufficient condition for aromaticity, and the blame for the apparent discrepancy between theory and experiment is not to be laid on the HMO method. Indeed, the choice of parameters in the calculations carried out seems to have been an unfavourable one. The properties of compounds containing pyrrole nitrogen, i. e. nitrogen which contributes two electrons to the conjugated system, are now considered to be better predicted by using a value for α_N lying somewhere in between $\alpha + 1.5\,\beta$ and $\alpha + 2.0\,\beta$.

We have therefore carried out a HMO calculation with $\alpha_N = \alpha + 2.0\,\beta$. The resulting resonance energy was found to be $1.34\,\beta$ to be compared with the value



a b c

Fig. 2. Molecular diagrams. a) HMO with $\alpha_N = \alpha + 0.5\,\beta$; b) HMO with $\alpha_N = \alpha + 2\,\beta$; c) SCF LCAO MO method

of $1.47\,\beta$ for pyrrole with the same set of parameters. It is questionable whether this value is high enough to cause the system to flatten out, since three nitrogen atoms are present, in contradistinction to the single nitrogen atom in pyrrole. The π-electron density and bond orders found are set forth in Fig 2b. By considering that diagram it will be noticed that the bond order between the two *N-H* groups is very small. This means that the cyclic conjugation is interrupted. Thus, by introducing more realistic parameters in the HMO treatment the experimental findings can be accounted for. It is to be expected that similar results should be valid for the systems 1b to 1d.

Since the HMO method is so highly empirical, we have found it of interest to examine whether the small bond order between the two *N-H* groups is retained also after a more extensive treatment. We have therefore performed a SCF LCAO MO calculation for the system 1a, assuming the molecule to be a regular heptagon with bond distances equal to 1.38 Å. The course of proceeding was identical to the one used in a calculation of pyrrole [*4*], and thus the method will not be further described here. The molecular diagram of Fig. 2c shows our results. Although the bond order to be considered is somewhat higher in 2c than in 2b the amount of cyclic conjugation is still so small as to explain the experimental findings. Fig. 2c further shows that the electronic arrangement around the uppermost nitrogen atom is almost as in 2a, while the electronic distribution around the neighbouring

N-H groups is better represented by 2b. This means that inductive parameters [*9*] should be introduced into the HMO method in order to reproduce the diagram 2c.

The more laborious SCF calculation reported above served the purpose of arriving at an unambigious prediction with respect to the bond order between the two *N-H* groups. It is worth while to notice that the result obtained is in agreement with the predictions given by simple valence bond arguments. The only way in which a double bond may be introduced between the two *N-H* groups is through ionic structures where both of the two neighbouring nitrogen atoms carry a positive charge. Such structures have high energies, and thus their contribution to the resonating system should be small.

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