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# On the Relationship Between Localized Molecular Orbitals and Kekulé Structures*

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Localized molecular orbitals for π-systems of conjugated polycyclic hydrocarbons have been calculated using both intrinsic and external localization criteria relying only on molecular topology. For benzenoid aromatic compounds the intrinsic localized molecular orbital arrangement can always be associated to the Kekulé structure of maximal Kekulé index value. However hydrocarbons containing four-membered rings show some exceptions to this correspondence, though the localized orbital array always corresponds to the most important Kekulé structure as predicted by the extended Fries rule. External localization sums show a good linear correlation with the Kekulé index, though different slopes are found for benzenoid and cyclobutadiene-containing systems. The results obtained for the canonical valence bond structures of naphthalene suggest that the external localization sum could be a good alternative to the Kekulé index.

## INTRODUCTION

Many of the characteristic properties of conjugated hydrocarbons are considered to be related to their peculiar π-molecular orbital (MO) system and, in particular, to the delocalization of these orbitals over the molecule. This and other aspects of π-systems can conveniently be analyzed through their localized molecular orbitals (LMO's).

LMO's of benzenoid polycyclic hydrocarbons have been studied using both, the Edmiston-Ruedenberg[1] (ER) and the Foster-Boys[2] (FB) criteria. In the first case Hückel-Wheland MO's were employed for the calculation[3] and the bielectronic integrals necessary for the localization process were approximated following a suggestion by Mulliken[4], which implies the evaluation of Coulomb repulsion integrals for every interatomic distance. FB localization

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was carried through at a more sophisticated semi-empirical level[5], including $\sigma$ and $\pi$ MO's both with and without the constraint of $\sigma$-$\pi$ separation.

In the present work the $\pi$-LMO's of benzenoid as well as cyclobutadiene-containing polycyclic hydrocarbons have been calculated at the Hückel level using a localization procedure which is strictly topological[6] in the sense that it does not resort to additional molecular information other than the topology of the system. The results agree with previous calculations whenever these are available. The connection between the LMO structures, the Kekulé index[7] (KI) and the Fries rule[8] is considered. An external variant of the localization procedure is used to study secondary LMO structures, leading to a good linear correlation between localization sums and KI's. For naphthalene excited valence bond (VB) structures are also considered in order to analyze the utility of the corresponding external localization sums as an estimate of the weight of the structures in a VB calculation.

## LOCALIZATION PROCEDURE

Let us consider a $n$ carbon, $^{2}m$ electron closer shell $\pi$-system and let $\chi_r$ be a $2\,p_z$ atomic orbital (AO) centered on carbon $r$. A MO, $\varphi_i$, will be expressed as

$$\varphi_i = \sum_{r}^{n} C_{ri}\,\chi_r$$

Topological localized molecular orbitals (TLMO's) are defined as those maximizing the localization sum

$$S = 1/m \sum_{i}^{m} \sum_{r,s}^{n} C_{ri}^{2}\,L_{rs}\,C_{si}^{2}$$

where 1/m is a normalization factor introduced in order that localization sum values for different molecules be comparable, and the $L_{rs}$ are the elements of the topological localization matrix:[6c]

$$L = 1 + kT$$

$T$ being the topological or adjacency matrix and k being a parameter which should be given a value of 0 if density-localized MO's[9] are to be obtained and some value between 0 and 1 if the LMO's are to be similar to energy-localized MO's[1].

For external localization processes matrix $L$ is substituted by a localization matrix $K$ associated to a given VB structure of elements

$K_{rs} = 1$ if atoms $r$ and $s$ are joined by a $\pi$-bond in the VB structure and
$= 0$ otherwise.

The normalization factor shall now be 2/m since the maximal contribution of a MO to the localization sum is now half its value in the case of the external localization.

The maximization of $S$ is effected through an iterative sequence of $2 \times 2$ rotations[1a]. This process has been repeated taking as starting point canonical MO's (CMO's) as well as Kekulé-type MO's[3a] obtained by projecting a set of strictly bicentric MO's adapted to a given Kekulé structure onto the space spanned by the CMO's and orthogonalizing the result by the Löwdin procedure.

## INTRINSIC LOCALIZATION RESULTS

TLMO's have been calculated for a series of twenty-two benzenoid hydrocarbons and the results obtained taking $k = 1$ in the localization matrix $L$ are shown in Figure 1. For each orbital, the contour of constant value $\varphi_i = 0.1$ a. u. on a plane paralell to the molecular one passing through the point of maximum $2p_z$ STO value has been plotted. The TLMO's structures show a great similarity with the LMO's obtained using the ER criterium[3], although the former are in some cases slightly more delocalized than the latter. FB $\pi$-LMO's also coincide except for a few differences already pointed out[5].

Since LMO's often extend considerably over more than two centers it is not always trivial to associate them to a Kekulé structure. However this can be done taking the following into consideration:

— the LMO's corresponding to a pair of symmetry-related Kekulé structures are tricentric for the rings differing in both structures, and

— asymmetric tricentric or tetracentric LMO's not included in the previous case should be considered as bonds between the two carbon atoms of greatest orbital population.

A numerical way of applying this receipt could be to select the Kekulé structure $K$ which maximizes the quantity

$$\sum_{(r_2,\, r_1) \varepsilon K} C_{r_1 r}\, C_{r_2 r}$$

where the sum runs over the pairs of atoms ($r_1$, $r_2$) $\sigma$-bonded in $K$, and index $r$ refers to the LMO for which the product of coefficients from atoms $r_1$ and $r_2$ is maximal.

In this way it is found that LMO's always correspond to the Kekulé structure with larger number of benzenoid rings, according to the predictions of the empirical Fries rule[8] for the Kekulé structure with largest weight in a VB calculation. Notwithstanding, the latter is sometimes ambiguous, since there can be distinct structures with the same number of benzenoid rings. In this respect it has been introduced a MO based index with the aim of quantifying in a simple manner the relative importance of different VB structures. The Kekulé index[7] is defined as the arithmetic mean of the norms of the CMO's projections on the space spanned by a set of strictly bicentric MO's arranged according to a given Kekulé structure. For a 2m-electron alternant hydrocarbon the KI of Kekulé structure $K$ can be expressed in the form[7]

$$\mathrm{KI\,(K)} = 1/2\mathrm{m} \sum_{(\mathrm{r},\, \mathrm{s}) \varepsilon \mathrm{K}} (2 + 2\mathrm{p}_{\mathrm{rs}})^{1/2}$$

where $p_{rs}$ is the bond order between atoms $r$ and $s$. For all of the benzenoid hydrocarbons considered in this work the LMO's arrangement corresponds to the Kekulé structure of maximal KI value. Moreover, when there is a secondary Kekulé structure with KI differing little (less than ca. 0.003) from the maximal one, distorted bicentric or asymmetric tricentric LMO's are generally obtained for the bonds differing in both structures.

The topological localization procedure has also been applied to a series of eighteen conjugated hydrocarbons containing four- and six-membered rings. These are the molecules shown in Figure 1 of Ref. 7b excluding the open

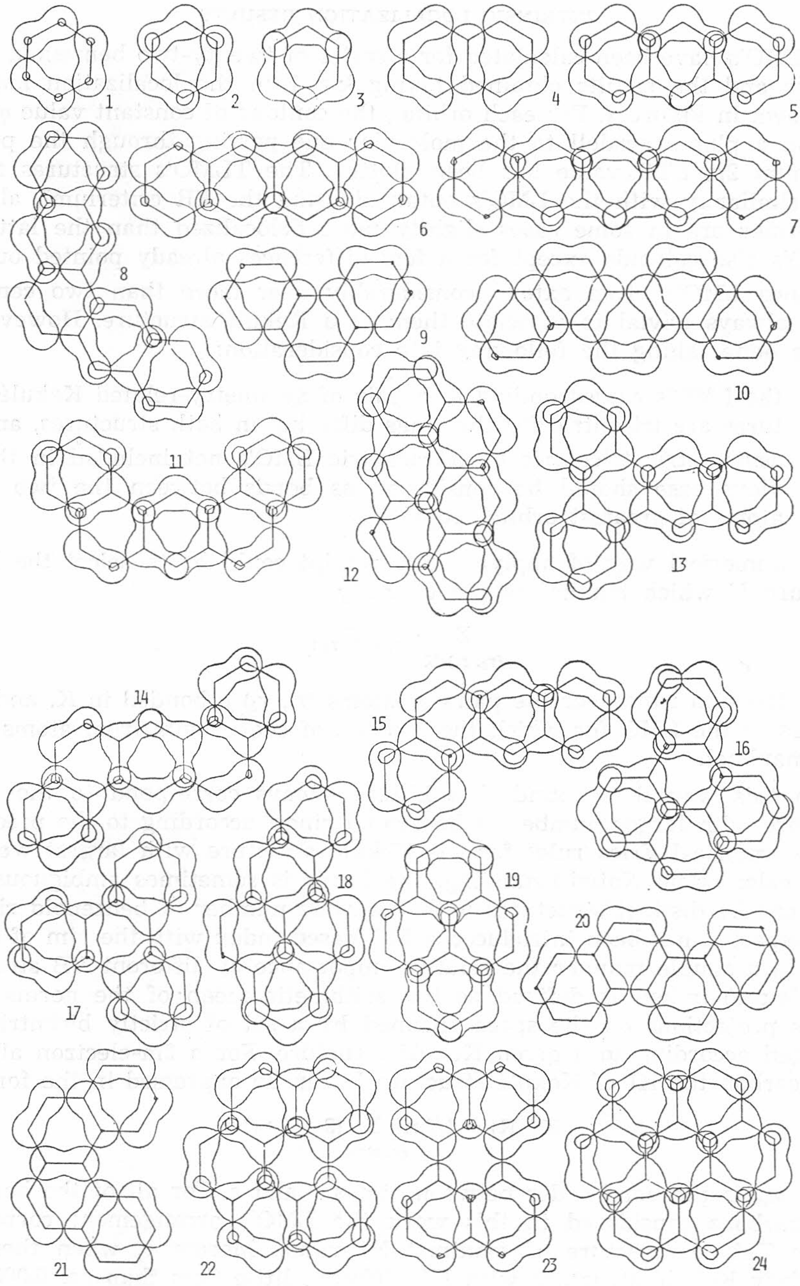

**Figure 1.** Contour plots of TLMO's of benzenoid polycyclic hydrocarbons. **1**, **2**, **3**[a]: Benzene; **4**: Naphthalene; **5**: Anthracene; **6**: Naphthacene; **7**: Pentacene; **8**: Pentaphene; **9**: Phenanthrene; **10**: Picene; **11**: 1,2,7,8-Dibenzanthracene; **12**: Anthanthrene; **13**: 1,2,3,4-Dibenzanthracene; **14**: 1,2,5,6-Dibenzanthracene; **15**: Benzanthracene; **16**: 1,2-Benzopyrene; **17**: Triphenylene; **18**: 3,4-Benzopyrene; **19**: Pyrene; **20**: Chrysene; **21**: Benzophenanthrene; **22**: Benzoperylene; **23**: Perylene; **24**: Coronene.

[a] The usual continuous degeneracy[4,13] is found in benzene.

shell systems III and VIII. The TLMO's obtained fit to the same conclusions drawn from the study of benzenoid systems except for the following remarks:

i) the Fries rule should be extended to include fourmembered rings as follows: the most important Kekulé structure(s) should give the maximum value to F(K) = number of benzene rings — number of cyclobutadiene rings.

ii) although the Kekulé structure associated to the TLMO's has always the largest F value, there are three cases for which it does not coincide with that of largest KI; these are shown in Figure 2.

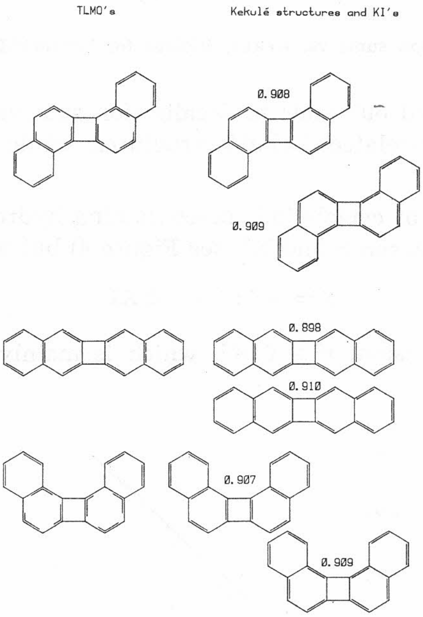

Figure 2.

## EXTERNAL LOCALIZATION RESULTS

In order to study secondary Kekulé structures from the viewpoint of LMO's the external localization procedure previously introduced has been applied to every Kekulé (non excited) structure of the molecules considered in the previous section. It is to be expected that some correlation exists between the KI's and the external localization sums of the respective Kekulé structures a large value of the former means that one can approach much a set of strictly bicentric MO's disposed according to the corresponding Kekulé structure without leaving the CMO space, and therefore external LMO's will be very localized. Certainly the S and KI values found for the Kekulé structures of benzenoid hydrocarbons show that a good linear correlation exists between both parameters (see Figure 3). A least-squares fit gives the following result:

$$S = -2.42 + 3.42\,\mathrm{KI}$$

with a correlation coefficient $r^2 = 0.989$

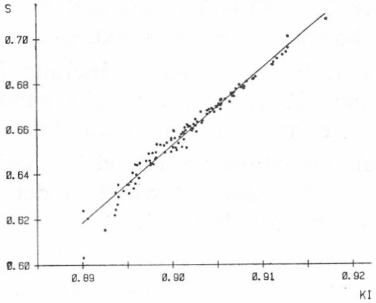

Figure 3. External localization sums vs. Kekulé indices for benzenoid polycyclic hydrocarbons.

It should be pointed out that the localization sum values differ for every pair of non symmetry-related Kekulé structures, while several degeneracies are found in the KI's.

A similar analysis of cyclobutadiene-containing hydrocarbons shows again a linear correlation between S and KI (see Figure 4) but with a different slope:

$$S = -1.98 + 2.93\,\mathrm{KI}$$

and some larger disperision: $r^2 = 0.948$, which is mainly due to the smallest pairs of values.

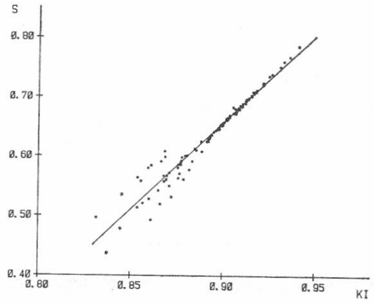

Figure 4. External localization sums vs. Kekulé indices for cyclobutadiene-containing polycyclic hydrocarbons.

While for benzenoid systems the external localization always leads to a set of bicentric LMO's disposed according to the Kekulé structure used for building matrix K, this does not always happen to cyclobutadine-containing systems: when a Kekulé structure has a four-membered ring with two double bonds exocyclic to the six-membered ring to which it is attached, the external localization yields in the former ring a pair of delocalized MO's analogous to the occupied CMO's of cyclobutadiene, as can be seen in Figure 5a for benzocyclobutadiene. Moreover, if there is another four-membered ring in position 3,4 relative to the first one, asymmetric delocalized orbitals are obtained in this ring and part of the six-membered one (see Figure 5b).

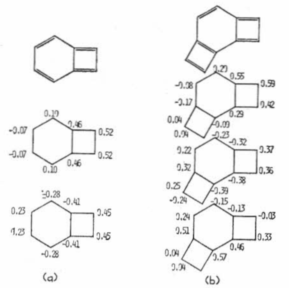

**Figure 5.** »Non localizable« Kekulé structures and the corresponding delocalized orbitals.

This agrees with the fact that Kekulé-type MO's cannot be obtained for such structures: the projection of strictly bicentric MO's adapted to the Kekulé structure onto the CMO's space produces a set of linearly dependent orbitals so that they cannot be orthogonalized.

## EXCITED VB STRUCTURES

The study of the preceding section has been extended to the complete set of canonical VB structures of naphthalene, for wich extensive VB calculations are available.[10] The TLMO's obtained in each case are schematically represented in Figure 6.

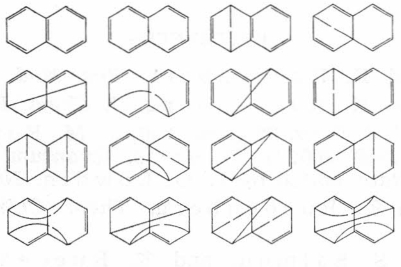

**Figure 6.** External LMO's for the canonical VB structures of naphthalene. The broken lines represent »anti-bonding« LMO's.

The most striking result is that »antibonding LMO's« (i. e., LMO's with a nodal plane between its main contributing atoms) are obtained whenever the associated Kekulé structure has a π-bond between atoms whose bond order is negative. This is a consequence of the localization sum depending on the squared expansion coefficients, so that it is indifferent to the sign inversion. This fact makes the linear correlation between S and KI break down: since this index depends on the sign of bond orders, it will be small compared with S when antibonding LMO's appear. In order to decide which of the parameters gives a better estimate of the structure weight (W) we have confronted their values with the coefficients of the structure wave functions in a VB calculation including all of the canonical structures of the molecule.[10]

Figure 7 shows that for both parameters an approximately linear correlation exists with the logarithm of the structure weight.

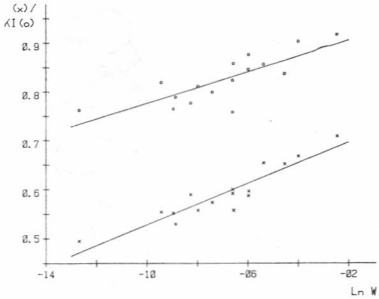

Figure 7. External localization sums and Kekulé indices vs. the logarithm of the weights of the VB canonical structures of naphthalene.

However a least-squares fit reveals that the correlation is somewhat better for the localization sum:

$$\mathrm{KI} = 0.937 + 0.016\ \mathrm{Ln}\ W; \quad r^2 = 0.637$$

$$S = 0.738 + 0.021\ \mathrm{Ln}\ W; \quad r^2 = 0.859$$

Although none of the correlation coefficients is really good, it is certainly encouraging that simple topology-based indices can afford some information concerning the results of cumbersome VB calculations which include a large number of configurations.

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## SAŽETAK

### O vezi lokaliziranih molekularnih orbitala s Kekuléovim indeksom

*J. C. Paniagua i A. Moyano*

Koristeći intrinsiktne i vanjske kriterije za lokalizaciju temeljene jedino na molekularnoj topologiji, izračunate su lokalizirane pi-molekularne orbitale (LMO) za konjugirane policikličke ugljikovodike. Za benzenoidne aromatičke spojeve raspored intrinsiktnih LMO dade se povezati s Kekuléovom strukturom najvećeg Kekuléovog indeksa (KI). Ova veza pokazuje neka odstupanja kod sustava s četveročlanim prstenovima, međutim tu se raspored LMO dobro slaže s proširenim Friesovim pravilom. Vanjska lokalizacijska suma dobro se korelira s KI, pa rezultati dobiveni za naftalen sugeriraju da bi ova suma mogla poslužiti kao dobra alternativa za KI.