

# Topological Localized Molecular Orbitals

## II. Polycyclic Aromatic Hydrocarbons\*

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Localized molecular orbitals for the  $\pi$ -systems of a series of polycyclic aromatic hydrocarbons have been obtained by a topological procedure. These "topological localized molecular orbitals" (TLMO's) are shown to be in good accordance with those obtained using more sophisticated methods. TLMO's can be associated to the Kekulé structure of largest Kekulé index. Secondary Kekulé structures as well as excited valence bond ones are studied by means of an external variant of the localization procedure.

**Key words:** Topology – Localized molecular orbitals – Aromatic hydrocarbons.

### 1. Introduction

The characteristic stability and geometry of aromatic hydrocarbons, as well as their undesirable biological properties, have maintained the interest of theoretical chemists in those compounds since the very beginning of organic chemistry [1].

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An obvious way to approach the problem of bond delocalization in those systems is by using localized molecular orbitals (LMO's).

The first systematic study of  $\pi$ -LMO's in aromatic hydrocarbons was made by Ruedenberg and coworkers [2], who localized Hückel-Wheland canonical molecular orbitals (CMO's) using the self-energy maximization criterium [3]. Although their CMO's calculation was essentially topological, it did not make use of the zero differential overlap (ZDO) approximation and, for this reason, many bielectronic integrals had to be retained for effecting the localization [2a]. Some years later Lipscomb and coworkers [4] used Boys criterium [5] to analyze complete and  $\pi$ -only localization on some conjugated systems in the partial retention of diatomic differential overlap approximation [6].

In the present work, the Hückel molecular orbitals (HMO's) of a series of twenty-two polycyclic benzenoid hydrocarbons are localized according to the topological method introduced in the preceding paper [7], and the results are compared with those of the previous works. The relationship between the localized structures obtained and the valence bond (VB) theory is analyzed by means of the Kekulé index [8] of the Kekulé structure to which LMO's can be associated. LMO's corresponding to other VB structures are obtained via an external variant of the localization method and the results are analyzed in connection with the bond-order matrix.

## 2. Procedure

Let us consider an  $m$  carbon  $\pi$ -system with  $n$  electrons. A molecular orbital (MO),  $\phi_i$ , will be expressed as a linear combination of  $2p_z$  atomic orbitals (AO's),  $\chi_r$ ,

$$\phi_i = \sum_r^m C_{ri} \chi_r.$$

Localization is then achieved by maximizing the localization sum

$$S = \sum_i^n \sum_{rs}^m C_{ri}^2 L_{rs} C_{si}^2, \quad (1)$$

where  $L_{rs}$  are the elements of the localization matrix for which the following expression will be taken [7]

$$\mathbf{L} = \mathbf{1} + k\mathbf{T}, \quad (2)$$

$\mathbf{1}$  being the  $m \times m$  identity matrix and  $\mathbf{T}$  being the topological matrix:

$$T_{rs} = 1 \quad \text{if atoms } r \text{ and } s \text{ are } \sigma\text{-bonded, and} \\ = 0 \quad \text{otherwise.}$$

The LMO's thus obtained will be referred to as topological LMO's (TLMO's). Several values for parameter  $k$  have been tested and, for the family of compounds we are considering, the resulting TLMO's are not significantly affected by the

particular choice made, as illustrated in Table 1 for the molecule of naphthacene. Nevertheless we have used  $k = 1$  for the present calculations, since with this value non-bonding monocentric and bonding bicentric MO's are given the same weight [7].

**Table 1.** TLMO's populations for naphthacene

Bond <sup>a</sup>	Atom <sup>b</sup>	Orbital population		
		$L = \mathbf{1}$	$L = \mathbf{1} + \mathbf{T}$	$L = \mathbf{T}$
1-2	2	0.922	0.918	0.911
	1	0.796	0.803	0.814
	3	0.123	0.121	0.115
	4	0.043	0.043	0.044
	16	0.030	0.034	0.039
	15	0.035	0.032	0.029
	12	0.027	0.025	0.023
	14	0.011	0.011	0.011
3-4	4	0.929	0.926	0.920
	3	0.796	0.801	0.809
	15	0.123	0.119	0.123
	1	0.061	0.062	0.062
	2	0.053	0.054	0.057
	14	0.011	0.011	0.011
5-15	5	0.005	0.010	0.003
	5	0.974	0.969	0.961
	15	0.533	0.550	0.570
	14	0.284	0.276	0.264
	12	0.120	0.112	0.106
	3	0.027	0.028	0.029
	18	0.020	0.018	0.018
13-14	16	0.008	0.011	0.015
	13	0.983	0.980	0.977
	14	0.290	0.299	0.312
	11, 12	0.285	0.280	0.274
	15, 18	0.048	0.048	0.047
	1, 10	0.012	0.012	0.012
12-16	3, 8	0.011	0.011	0.011
	16	0.951	0.943	0.931
	12	0.533	0.549	0.569
	15	0.224	0.215	0.205
	1	0.123	0.115	0.103
	14	0.049	0.052	0.055
	3	0.034	0.031	0.028
	2	0.021	0.023	0.026
	11	0.020	0.020	0.020
	5	0.011	0.015	0.021
	18	0.013	0.013	0.014
4	0.011	0.012	0.015	

<sup>a</sup> Carbon atoms are numbered according to Fig. 1.

<sup>b</sup> Only atoms whose population is  $>0.010$  for  $L = \mathbf{1} + \mathbf{T}$  are considered.

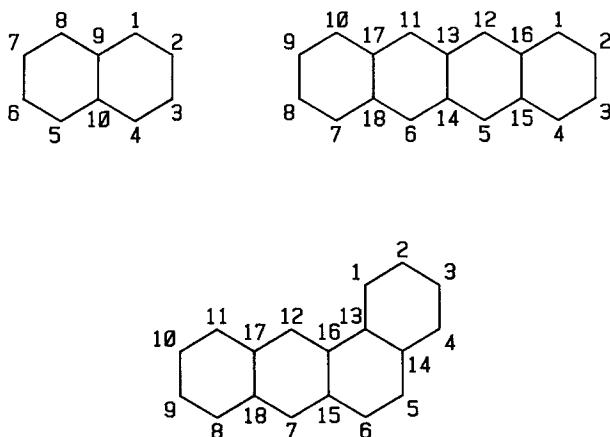


Fig. 1. Numbering of carbon atoms for naphthalene, naphthacene and benzenanthracene

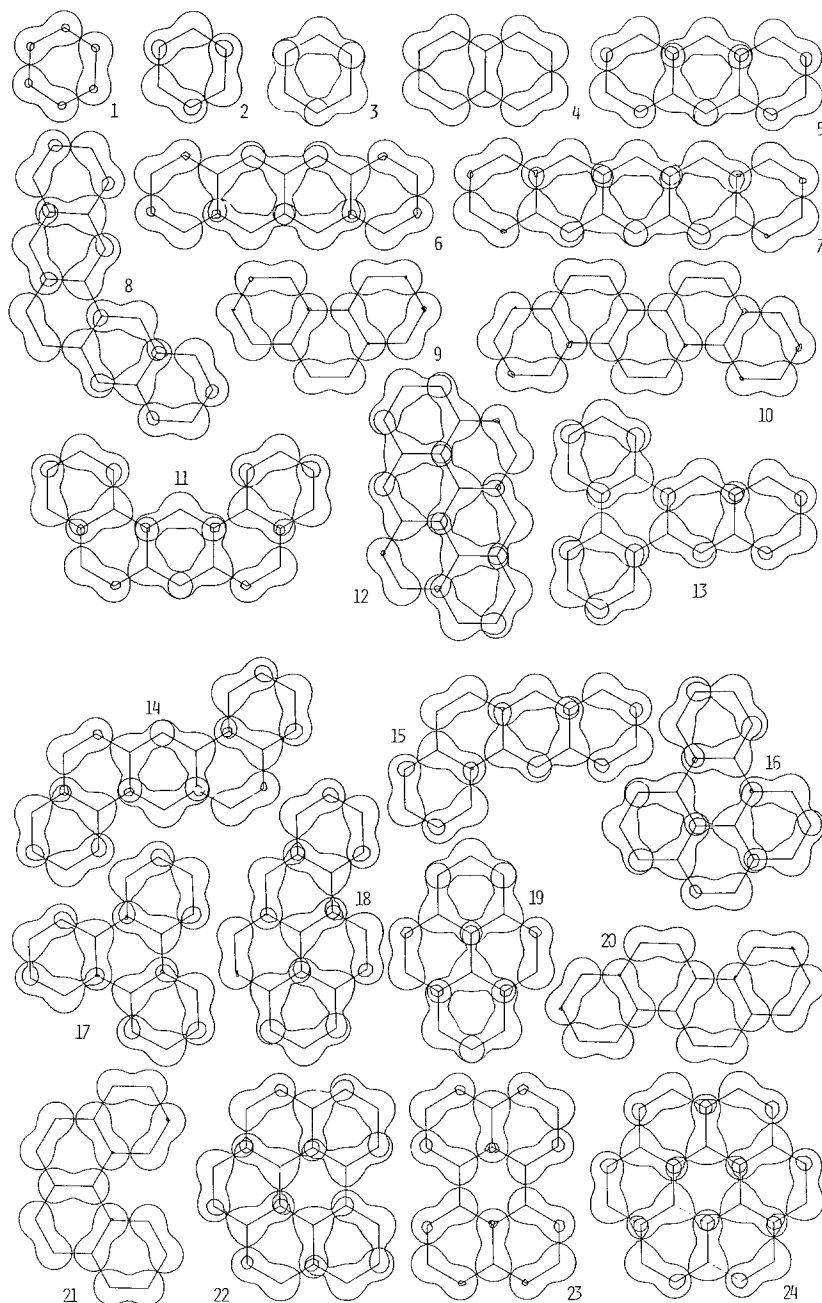
The maximization of  $S$  is effected through an iterative sequence of  $2 \times 2$  rotations [3a]. Since this process converges rather slowly for aromatic systems, we have adopted a mixed iterative scheme that has proven very efficient: pairwise rotations are effected in a cyclic order until every such step no longer produces any significant change in the localization sum; then a rotation is made within the pair of MO's producing the largest increase in  $S$ , followed by a new set of cyclically-ordered rotations. This process is repeated until the greatest increase in  $S$  in every pairwise rotation is smaller than the prescribed convergence criterion.

As the starting point for the iterative procedure we have taken the CMO's, although Kekulé-type MO's [2a] corresponding to different  $VB$  structures, as well as randomly-rotated CMO's, have also been localized in order to make sure that the true maximum has been reached.

### 3. Results

The molecules we have studied together with their TLMO's are shown in Fig. 2. For each orbital, the contour of constant value  $\phi_i = 0.1$  a.u. on a plane parallel to the molecular one passing through the point of maximum  $2p_z$  AO value has been plotted. Basis orbitals have been taken as  $2p_z$  STO's with the exponential coefficient given by the Slater rules ( $\zeta = 1.625$ ).

A qualitative comparison shows a great similarity between our plots and those of Ruedenberg et al. [2] on the one hand and Lipscomb et al. [4] on the other, although larger asymmetries and/or delocalization tails can be found in some of our LMO's. The greatest discrepancy appears in pyrene, for which the two previous calculations give different LMO's structures (see Fig. 3a, b) while ours shows an interesting peculiarity: the absolute maximum of  $S$  corresponds to structure a, but a secondary relative maximum is obtained for structure b. Although Ruedenberg did several calculations for each molecule starting from



**Fig. 2.** Contour plots of TLMO's of aromatic hydrocarbons. **1, 2, 3<sup>a</sup>:** 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

<sup>a</sup> The usual continuous degeneracy [4, 13] is found in benzene

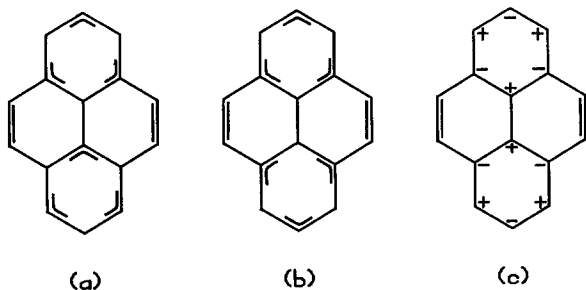


Fig. 3

different sets of Kekulé-type MO's while searching for secondary maxima, he found none. However we have verified that Kekulé-type MO's corresponding to classical Kekulé structures always converge to the main maximum, and a set of orbitals arranged according to a separated charge structure (Fig. 3c) is needed in order to reach the secondary maximum. One could expect, therefore, that this relative maximum also exists in the energy-localization sum hypersurface. In any case the assertion that, barring symmetry equivalences, no secondary LMO structures are found in  $\pi$ -localizations [2a, 4] is no longer true.

As Ruedenberg calculations use a non orthogonal AO basis [2a], a quantitative comparison cannot be made via the expansion coefficients. Therefore we have calculated the populations of Ruedenberg LMO's [2a] on the carbon atoms, which, including overlap, are given by

$$q_r^i = 2C_{ri} \sum_s^m S_{rs} C_{si}$$

Table 2 collects LMO populations for the three types of calculation in two extreme cases: naphthalene, for which the results are very similar, and benzanthracene whose LMO's, though representing the same Kekulé structure, show a rather different shape.

The degree of delocalization of an LMO is usually quantified by means of the delocalization index [9], which measures the magnitude of the LMO populations on atoms other than those bonded by that orbital. However this index is not very useful for aromatic  $\pi$ -systems, since multi-center LMO's are often encountered, and it may even be difficult to decide the atoms upon which a LMO is centered. On the other hand, it has been suggested [2] that the orbital energies

$$\varepsilon_i = \alpha + \beta \sum_{r,t}^m C_{ri} T_{rt} C_{ti}$$

should decrease as the LMO spreads over the molecule independently of the orbital shape, and therefore they can be used as an alternative delocalization index. Orbital energies in  $\beta$  units for the TLMO's plotted in Fig. 2 have been grouped following an orbital classification similar to that proposed by Ruedenberg [2] (see Fig. 4), and are reported in Fig. 5. This shows that three

**Table 2.** LMO populations for naphthalene and benzanthracene

Molecule	Bond <sup>a</sup>	Atom <sup>b</sup>	Orbital population			
			TLMO's	ELMO's <sup>c</sup>	BLMO's <sup>d</sup>	
naphthalene	7-8	8	0.86	0.87	0.88	
		7	0.85	0.86	0.87	
		6, 9	0.09	0.09	0.08	
		5	0.06	0.06	0.05	
		10	0.04	0.04	0.04	
	9-10	3	0.01	0.01	—	
		9, 10	0.75	0.75	0.78	
		1, 4, 5, 8	0.08	0.08	0.07	
		2, 3, 6, 7	0.05	0.04	0.04	
benzanthracene	1-2	1	0.93	0.87	0.87	
		2	0.74	0.81	0.83	
		13	0.18	0.12	0.11	
		4	0.07	0.06	0.05	
		3	0.05	0.08	0.09	
		14	0.02	0.04	0.05	
		12	0.01	0.01	—	
		6	—	0.01	—	
		3-4	3	0.92	0.87	0.85
			4	0.74	0.82	0.85
	2		0.17	0.12	0.10	
	13		0.07	0.05	0.05	
	14		0.04	0.08	0.10	
	1		0.03	0.05	0.05	
	12		0.01	—	—	
	5-6		6	0.94	0.86	0.92
			5	0.83	0.88	0.93
			15	0.10	0.07	0.04
		14	0.04	0.06	0.05	
		13	0.04	0.03	0.02	
		16	0.01	0.01	0.01	
		2, 7, 18	0.01	0.01	—	
		4	0.01	—	—	
		17	—	0.01	—	
		7-15	7	0.96	0.87	0.82
	15		0.58	0.74	0.84	
	18		0.27	0.14	0.08	
	12		0.10	0.10	0.06	
	5		0.03	0.03	0.02	
	6		0.02	0.04	0.03	
16	0.01		0.06	0.10		
9	0.01		0.01	—		
17	—		0.03	0.05		
13	—		0.01	0.01		
8-9	8	0.94	0.89	0.89		
	9	0.76	0.83	0.87		
	18	0.15	0.11	0.07		
	11	0.07	0.06	0.04		
	10	0.05	0.06	0.08		

**Table 2.** (cont.)

Molecule	Bond <sup>a</sup>	Atom <sup>b</sup>	Orbital population		
			TLMO's	ELMO's <sup>c</sup>	BLMO's <sup>d</sup>
		17	0.01	0.03	0.03
		15	0.01	—	—
	10-11	10	0.93	0.88	0.87
		11	0.77	0.84	0.90
		9	0.15	0.11	0.07
		18	0.05	0.04	0.03
		8	0.04	0.05	0.04
		17	0.03	0.08	0.08
		15	0.01	0.01	—
		12	0.01	—	—
	12-16	16	0.95	0.86	0.83
		12	0.59	0.76	0.83
		15	0.20	0.12	0.08
		13	0.10	0.06	0.02
		18	0.06	0.05	0.04
		5	0.02	0.01	—
		7	0.02	0.05	0.07
		17	0.01	0.06	0.09
		6, 14	0.01	0.01	0.01
		9, 11	0.01	—	—
	13-14	14	0.89	0.81	0.80
		13	0.61	0.73	0.80
		4	0.17	0.11	0.09
		5	0.10	0.07	0.04
		2	0.07	0.06	0.05
		1	0.04	0.07	0.08
		6	0.03	0.03	0.03
		3	0.03	0.04	0.05
		15	0.02	0.02	0.01
		16	0.02	0.04	0.04
		12	0.02	0.01	—
		18	0.01	0.01	—
	17-18	17	0.94	0.81	0.76
		18	0.44	0.67	0.78
		12	0.26	0.13	0.09
		11	0.15	0.10	0.06
		15	0.06	0.05	0.03
		9	0.05	0.05	0.03
		10	0.02	0.04	0.03
		8	0.02	0.06	0.06
		5, 13	0.01	0.01	—
		16	0.01	0.03	0.03
		7	0.01	0.06	0.11

<sup>a</sup> Carbon atoms are numbered according to Fig. 1.

<sup>b</sup> Only atoms whose population is >0.01 are considered.

<sup>c</sup> Energy LMO's (Ref. [2]).

<sup>d</sup> Boys LMO's (Ref. [4]).



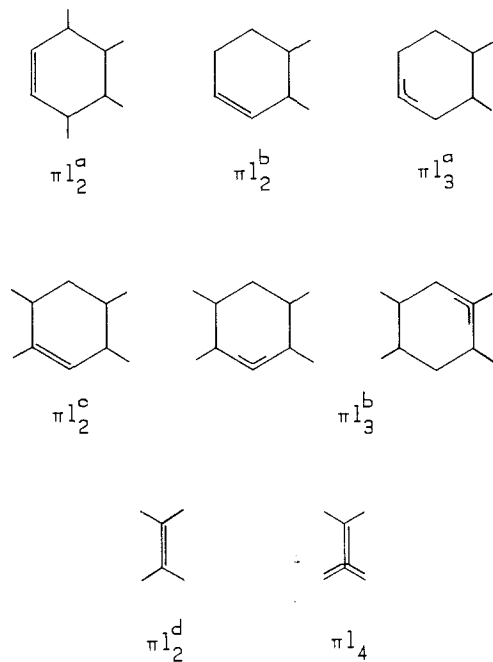


Fig. 4. Types of TLMO's appearing in aromatic hydrocarbons

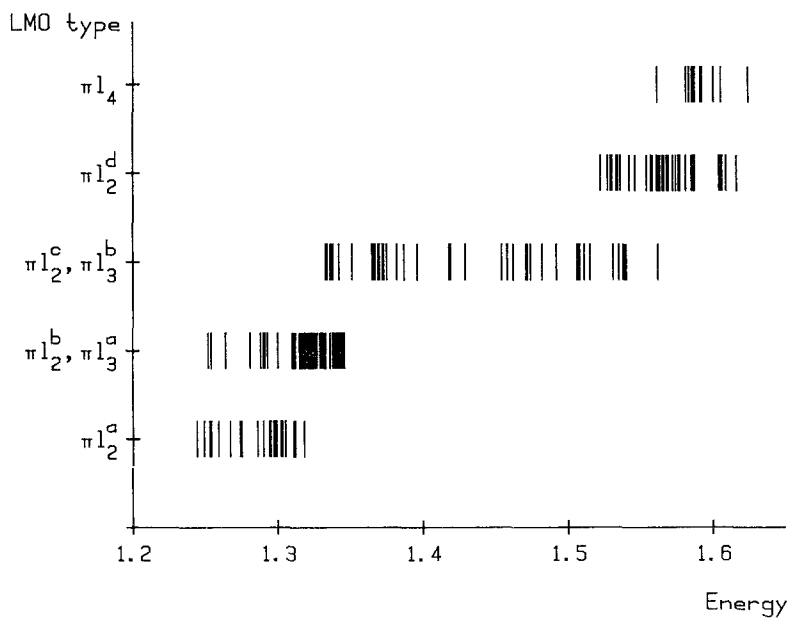


Fig. 5. Energy in  $\beta$  units for different types (see Fig. 4) of TLMO's of aromatic hydrocarbons

main types of orbitals can be distinguished according to their location in the molecule, having energy values ranging between the following limits:

- 1)  $\pi l_2^a, \pi l_2^b, \pi l_3^a$        $\alpha + 1.24\beta \leq \varepsilon_i \leq \alpha + 1.34\beta$
- 2)  $\pi l_2^c, \pi l_3^b$        $\alpha + 1.33\beta \leq \varepsilon_i \leq \alpha + 1.56\beta$
- 3)  $\pi l_2^d, \pi l_4$        $\alpha + 1.52\beta \leq \varepsilon_i \leq \alpha + 1.62\beta$ .

It follows that TLMO's are most localized when their main contributing atoms belong to only one ring and the degree of delocalization increases with the number of main contributing atoms shared by two or more cycles. This agrees with the increase in localization with increasing distance from the molecular center which Lipscomb et al. found by studying LMO delocalization indices [4].

### 3.1. TLMO's and Kekulé Structures

The manifest relationship between LMO's and VB structures makes the former a tempting starting point in the search for connections between MO and VB methods at a simple level. Lipscomb et al. [4] have already pointed out that the full localizations of aromatic systems yield LMO's arranged according to the most "stable" Kekulé structure as predicted by the empirical Fries rule [10]. In  $\pi$ -only localizations, LMO's corresponding to two-center bonds are not always obtained; however Ruedenberg et al. [2a] found some empirical rules for the occurrence of Kekulé-type LMO's structures using Pauling bond orders [11]. They also discovered that whenever such structures appear, they correspond to the set of conjugated double bonds for which the sum of Pauling bond orders is maximal.

From a different point of view Graovac and coworkers [8] have also considered the problem of connecting MO and VB theories: they have proposed a MO-based index in order to estimate the relative weights of different Kekulé structures in a VB calculation. For a  $2n$ -electron  $\pi$ -system, this "Kekulé index" (KI) is defined as the arithmetic mean of the norms of the CMO's projections on the space spanned by  $n$  strictly bicentric MO's<sup>1</sup> arranged according to a given Kekulé structure. In the case of alternant hydrocarbons it can be shown [8a] that, in the ZDO approximation,






















$$KI(K) = 1/2n \sum_{r,s}^{\pi-b} (2 + 2p_{rs})^{1/2} \quad (3)$$

where  $p_{rs}$  is the bond order between atoms  $r$  and  $s$ , and the summation extends over the pairs of  $\pi$ -bonded atoms in Kekulé structure  $K$ . As an extension of Fries rule, the KI should be useful to analyze LMO's in terms of VB concepts.

<sup>1</sup> The phrase "strictly bicentric MO" will henceforth refer to a normalized, symmetric, linear combination of two AO's:

$$1/\sqrt{2}(\chi_r + \chi_s)$$

**Table 3.** Kekulé indices and external localization sums for Kekulé structures of some aromatic hydrocarbons

Kekulé structure	KI	S	$S^{1a}$	
			LMO's	KMO's <sup>b</sup>
	0.9129	1.0516	0.7010	0.7010
	0.9171	1.7723	0.7089	0.7088
	0.9032	1.6691	0.6676	0.6675
	0.9117	2.4192	0.6912	0.6911
	0.8999	2.2955	0.6559	0.6557
	0.9129	2.4436	0.6959	0.6958
	0.9066	2.3652	0.6758	0.6757
	0.9002	2.3068	0.6591	0.6589
	0.8975	2.2610	0.6460	0.6455
	0.9054	2.6903	0.6726	0.6724
	0.9054	2.6750	0.6688	0.6686
	0.8957	2.5352	0.6338	0.6335
	0.9052	3.3525	0.6705	0.670 <sup>A</sup>
	0.9034	3.3183	0.6637	0.6636
	0.9026	3.3213	0.6643	0.6642
	0.9017	3.3091	0.6618	0.6617
	0.9009	3.2824	0.6565	0.6564
	0.8991	3.2637	0.6527	0.6526
	0.8963	3.1921	0.6384	0.6382
	0.8937	3.1221	0.6244	0.6237
	0.8937	3.1594	0.6319	0.6316

<sup>a</sup> External localization sum normalized to half the number of MO's.<sup>b</sup> Kekulé-type MO's.

With this aim the KI's for the Kekulé structures of the molecules shown in Fig. 2 have been calculated, and in every case it has been found that the Kekulé structure closest to the LMO's arrangement is that of greatest KI value (for KI's of Kekulé structures of some of these molecules see Table 3). This closest Kekulé structure should be found taking the following into consideration: 1) when there are two different symmetry-related Kekulé structures with maximal KI, tricentric LMO's are obtained in the benzenoid rings differing in both structures (e.g. anthracene); 2) 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; this kind of LMO appears when there are secondary Kekulé structures with KI differing only slightly from the maximal one, as is the case of 1,2-benzopyrene.

This result can be given a simple qualitative explanation: since localization tends to produce bicentric and/or monocentric MO's [7], the most localized MO's within the space spanned by the CMO's will tend to resemble the set of bicentric orbitals which overlaps most with that space, implying that the associated Kekulé structure is that with maximal KI.

Since  $\pi$ -MO localization generally leads to a unique maximum in the localization sum (barring symmetry degeneracies), the former relationship between LMO's and the KI cannot be extended to secondary Kekulé structures. However, an extension can be made by using an external localization procedure: introducing a localization matrix associated to a given VB structure as [7]

$$L_{rs} = 1 \quad \text{if atoms } r \text{ and } s \text{ are joined by a } \pi\text{-bond in the VB structure and} \\ = 0 \quad \text{otherwise}^2 \quad (4)$$

in Eq. (1), LMO's arranged according to that structure are obtained. These have been calculated for the Kekulé structures of the molecules in Fig. 2 and some of the corresponding localization sums and KI's are listed in Table 3.

As can be seen from this Table, the correlation between those two parameters can be extended to different Kekulé structures; moreover, a comparison between different molecules can be made if we normalize the localization sum to half the number of MO's, since it can be shown [7] that the maximal contribution of an MO to the localization sum is now  $1/2$ . Fig. 6 shows that a good linear correlation exists between normalized sums and KI's although some inversions take place when two Kekulé structures have very similar KI values. On the other hand, the localization sum resolves the KI degeneracies not due to symmetry equivalence.

The explanation given for the connection between intrinsic localized MO's and the KI can be extended to interpret this correlation: a large value for the localization sum associated with a Kekulé structure means that one can come very near to the corresponding set of strictly bicentric MO's within the CMO

<sup>2</sup> We only consider neutral VB structures without charge separation, so that lone pairs cannot appear.

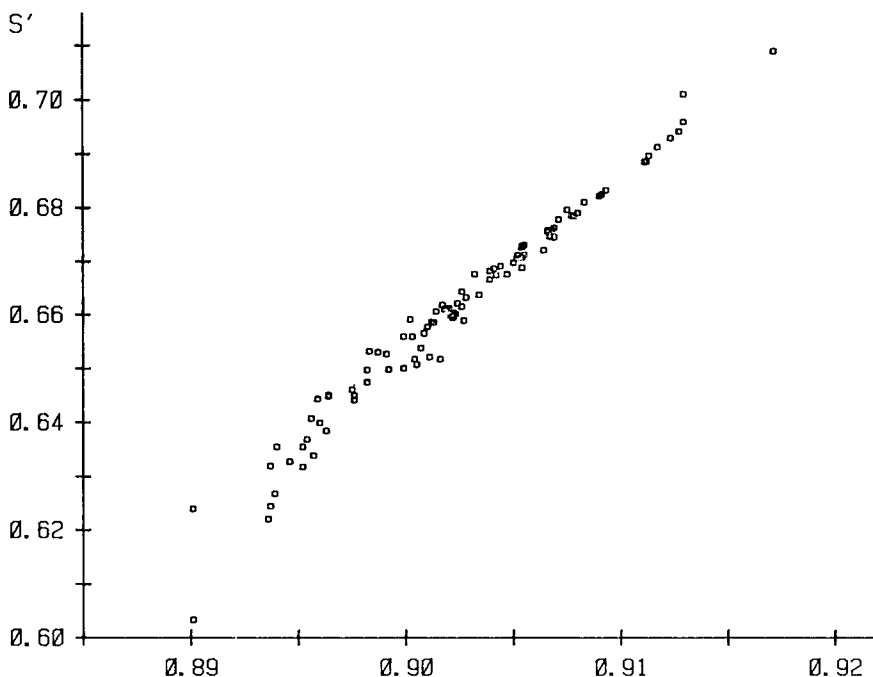


Fig. 6. Normalized external localization sums versus Kekulé index









space, so the KI will be large. This suggests that a good approximation to the LMO's should be obtained by projecting those strictly bicentric MO's on the CMO space and orthonormalizing the resulting projections, thus obtaining the Kekulé-type MO's introduced by Ruedenberg [2a]. The results shown in the fourth column of Table 3 confirm this hypothesis: the normalized external localization sum is, for Kekulé-type MO's, a few tenths below that of the LMO's, which amounts to about 99.9% of the localization sum increase in going from the CMO's to the LMO's.

The external localization procedure has also been applied to excited VB structures and some results for naphthalene are shown in Table 4: the first two columns list the structures used to build the external localization matrix and their KI's, while the third and fourth show a schematic representation of the LMO's and their respective normalized localization sums.

The first thing to note is that, in some cases, anti-bonding LMO's are obtained, i.e. LMO's whose two main contributions are of opposite sign. A look at the bond-order matrix of naphthalene (Table 5) shows that this happens whenever an LMO lies between carbon atoms whose bond order is negative. This can be understood by taking into consideration that bond orders are invariant under orthogonal transformations of the MO's and, in terms of LMO's, the bond order of a pair of atoms,  $r$  and  $s$ , joined by LMO  $\phi_i$  should be roughly given by

$$p_{rs} \approx 2C_{ri}C_{si}.$$

**Table 4.** Kekulé indices and external LMO's for some excited VB structures of naphthalene

VB structure	KI	LMO's	$S'^a$
	0.8567		0.6537
	0.8377		0.6516
	0.8762		0.5962
	0.7582		0.5916

<sup>a</sup> External localization sum normalized to half the number of MO's.

<sup>b</sup> The dashed line represents an antibonding LMO.

Therefore  $C_{ri}$  and  $C_{si}$  will be of the same or opposite sign depending on  $p_{rs}$  being positive or negative. Moreover, the localization sum depends on the square of the expansion coefficients, so that the localization process can lead to antibonding as well as to bonding LMO's<sup>3</sup>.

When antibonding LMO's appear, the linear relationship between normalized localization sums and KI's breaks down: the former are comparatively larger than the latter. This happens because the KI depends on the sign of bond orders (Eq. (3)) so that it will be relatively small for VB structures with bonds joining negative bond-order atoms. The question arises, as to which parameter gives a better appreciation of the weight of excited VB structures. The localization sum gives little weight to structures with long bonds, in accordance with chemical intuition, and on the other hand the weight of a structure in a VB calculation seems not to depend on whether pairs of atoms with positive or negative bond

Atoms <sup>b</sup>	Bond order
1-2	0.7246
1-4	-0.3623
1-5	0.0849
1-7	-0.1699
1-9	0.5547
2-3	0.6032
2-6	0.1560
2-10	-0.2409
9-10	0.5182

**Table 5.** Relevant bond orders of naphthalene<sup>a</sup>

<sup>a</sup> Only non-zero and non symmetry-equivalent bond orders are reported.

<sup>b</sup> Carbon atoms are numbered according to Fig. 1.

<sup>3</sup> Antibonding orbitals could in principle be also obtained as intrinsic LMO's; however, these tend to concentrate where the magnitude of the bond order is large, and negative bond orders are in general of little absolute value, so that the appearance of antibonding intrinsic LMO's is very improbable.

order are bonded [12]. However, it is not clear whether VB calculations do show a decrease in the structure weight for longer bonds [12], and further investigation is needed before a decision can be made.

#### 4. Conclusions

The topological localization procedure developed in the previous paper [7] has been applied to a series of polycyclic aromatic hydrocarbons, giving results in good agreement with other methods [2, 4]. This demonstrates that topology is sufficient, not only to give approximated  $\pi$ -CMO's, but also to effect the localization of these orbitals, so that it is not necessary to resort to additional information concerning neither molecular geometry nor even the explicit form of the AO basis to obtain a localized picture of the molecule.

The relationship between LMO's arrangement and the KI of the associated Kekulé structure has been studied in order to gain some insight into the relationship between MO and VB methods. It has been found that LMO's are always arranged according to the Kekulé structure of greatest KI. LMO's corresponding to other VB structures have been obtained by means of an external variant of the localization method, showing that a good linear correlation exists between KI's and normalized localization sum values, though some discrepancies are found for excited VB structures. Several facts suggest that this parameter could be a good alternative to the KI.

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