Revue Roumaine de Chimie, **24**, *1*, 165—169 (1979).

ON THE STABILITY OF AROMATIC HYDROCARBONS. V [1]

USE OF LOCALIZED MOLECULAR ORBITALS IN DELOCALIZATION ENERGY RELATIONSHIPS

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Received April 24, 1978

Molecular orbitals that minimize the bond resonance energy are defined and used as a foundation for the perfect aromatic limit structure and for some linear relationships of the delocalization energy.

INTRODUCTION

It was shown in a previous paper [1] that the Hückel molecular orbital delocalization energy (HDE)[2] can be approximated by a value (DE) obtained by using a linear relationship :

$$DE = aM + bN + c$$

where a, b, c are coefficients with values 0.6, −0.15, viz. 0.2, obtained by the least squares fit to HDE's,
M, N are molecular parameters, obtained from the formula with localized bonds and maximum number of Kékulé rings (the "perfect aromatic" limit structure [3]) : the number of CC single bonds, viz. the number of "imperfect aromatic" rings [3].

This paper demonstrates that the parameters M, N can be used for the classification of localized molecular orbitals (LMO's) from which the values of the coefficients a and b can be obtained.

THE LOCALIZATION METHOD

LMO's were obtained by a modification of the Magnasco-Perico [4] method of transforming canonical molecular orbitals : the LMO's are defined by the minimization of the resonance energy (RE) contained in

[1] Part IV, V. E. Sahini and A. Savin, *Rev. Roumaine Chim.*, **22**, 39 (1977).
[2] E. Heilbronner and P. A. Straub, "Hückel Molecular Orbitals", Springer Verlag, Berlin, 1966.
[3] V. E. Sahini, *J. Chem. Phys.*, **59**, 177 (1962).
[4] V. Magnasco and A. Perico, *J. Chem. Phys.*, **47**, 971 (1967).

the bonds (similar to McWeeny and Del Re's "optimum hybrids" [5]):

$$\sum_i RE_i \text{—minimum}$$

where

$$RE_i = \sum_{m,n}^{i} P_{mn}H_{mn},$$

H_{mn} is the resonance integral in the basis of the atomic orbitals,
$P_{mn} = 2\sum_i c_{mi}c_{ni}$ is an element of the charge density and bond order matrix (for closed shell systems),
c_{mi} are LCAO coefficients
the sum is performed only over the atomic orbitals contributing to the bond (in particular the pair of atomic orbitals centered at the same atom is not involved in the sum).

This localization is particularly suitable for the Hückel approximation (HMO), where the molecular orbitals are obtained by the minimization of the resonance energy of the whole molecule. The fact that the bonds are fixed prior to localization is in our case an advantage, as it can serve to the comparison of different localized structures. The method was preferred to the Magnasco-Perico and Edminston-Ruedenberg localization procedures [6], because there are no quantities which are not defined in the HMO approximation (as would be the overlap and bielectronic integrals). The formulas used to obtain the LMO's are similar to Magnasco and Perico's and will not be presented here.The localization procedure is iterative and the convergence is good : after each cycle the difference between the resonance energies contained in the bonds decreases by 1 — 2 orders of magnitude. The time necessary for a localization is shorter than that required by a Jacobi diagonalization.

The localization procedure presented here has been tested with sigma systems (within the MINDO/2 approximation [7]), where an overlap of over 0.9999 with Edminston-Ruedenberg LMO's was obtained. For pi systems the HMO method was used to generate molecular orbitals. The overlap with truncated and renormalized LMO's is of over 0.99 for sigma systems, but only about 0.90 — 0.95 for pi systems. About 96% of the resonance energy can be concentrated in the bonds in sigma systems (ethane, propane), 80% in pi systems with low delocalization (as butadiene, hexatriene), 60% for pi systems with strong conjugation (as benzene, naphthalene, pyrene).

THE USE OF LMO'S IN THE ANALYSIS OF THE DELOCALIZATION ENERGY RELATIONSHIP

It was mentioned [1,8] that "perfect aromatic" limit structures are supported by experimental and theoretical evidence. The present localization method confirms this, because the mentioned structures show the

[5] R. Mc Weeny and G. Del Re, *Theor. Chim. Acta*, **10**, 13 (1968).
[6] C. Edminston and K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 457 (1963).
[7] N. Bodor, M. J. S. Dewar, A. Harget and E. Hasselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).
[8] W. England, S. Salmon and K. Ruedenberg, *Fortschr. Chem. Forsch.*, **23**, 31 (1971).

highest degree of localization. Thus, for anthracene the Kékulé structure with two "perfect aromatic" rings concentrates 60% of the resonance energy in the bonds; the structure with one "perfect aromatic" Kékulé ring 58%; and the structures with "Dewar" cycles less than 51%.

In Table 1 some values of the LMO "bond resonance energies" (BE) are listed for "perfect aromatic" limit structures. The BE's are defined (for closed shell systems) as:

$$BE_i = 2 \sum_{m,n} c_{mi} c_{ni} H_{mn}$$

the total energy of the molecule being:

$$E = \sum_i BE_i$$

Table 1

Bond resonance energies

Number of substituents at the double bond	Molecule	Bond*	Energy (β units)
0	ethylene	1.2	2.00
1	butadiene	1.2	2.24
	hexatriene	1.2	2.25
2	hexatriene	3.4	2.49
	benzene	1.2	2.67
	naphthalene	1.2	2.62
	anthracene	1.2	2.61
		6.7	2.52
	phenantrene	1.2	2.63
		3.4	2.63
		9.10	2.57
	pyrene	1.2	2.66
		9.10	2.57
		4.5	2.47
3	anthracene	5.13	2.91
	pyrene	3.12	2.89
4	naphthalene	9.10	3.19
	anthracene	11.12	3.23
	phenanthrene	11.12	3.17
	pyrene	11.16	3.19

* Atoms numbered as in reference[2]

By inspection, one can deduce a contribution of about 0.3β to the delocalization energy for each substitution of a CH bond by a CC bond, explaining the first term (a M) in the linear relationship (1). The absolute

value of the BE decreases for the pair of electrons on LMO's localized in "imperfect aromatic" cycles with 0.1—0.15β per "imperfect aromatic" cycle, in agreement with the value of the coefficient b in equation (1).

In order to verify the correctness of the statements made above, the HDE is compared to the DE calculated by using the relationships :

$$DE = 0.6\text{M} \tag{2}$$

$$DE = 0.6\,\text{M} - 0.15\ \text{N} \tag{3}$$

Table 2

Delocalization energies*

M	N	HDE[2]	DE (equation 2)	DE (equation 3)
3	0	2.00	1.8	1.8
6	0	3.68	3.6	3.6
9	1	5.33	5.4	5.25
9	0	5.45	5.4	5.4
11	1	6.51	6.6	6.45
12	2	6.93	7.2	6.9
12	1	7.10	7.2	7.05
12	0	7.18— 7.27	7.2	7.2
14	1	8.25	8.4	8.25
15	3	8.54	9.0	8.55
15	2	8.73	9.0	8.7
15	1	8.76—8.94	9.0	8.85
15	0	8.94—9.00	9.0	9.0
16	2	9.25	9.6	9.3
16	1	9.42	9.6	9.45
18	2	10.46	10.8	10.5
18	1	10.57—10.59	10.8	10.65
21	2	12.24	12.6	12.3
25	3	14.50	15.0	14.55

* condensed benzenoid hydrocarbons from reference[2]

Such equations can be deduced from a perturbational treatment [9,10] up to the second and third order, respectively explaining the importance of the parameters M and N. Nevertheless, higher order corrections modify the values of the coefficients, as can be observed from a comparison of equations (2) and (3) with their perturbational analogues.

The results presented in Table 2 are much nearer the HMO values than the *DE* obtained from the proportionality between the *DE* and the number of pi electrons, [11] a relationship also based on LMO's. Therefore the analysis made in this paper can be considered as a second step in the study of the relationship between LMO's and HDE's.

[9] S. Diner, J. P. Malrieu, F. Jordan and P. Claverie, *Theor. Chim. Acta*, **13**, 1 (1969).
[10] J. P. Malrieu in O. Chalvet, R. Dandel, S. Diner, J. P. Malrieu, ed., "Localization and Delocalization in Quantum Chemistry", Vol. I, D. Reidel, Dodrecht, 1975, p. 335.
[11] W. England and K. Ruedenberg, *J. Amer. Chem. Soc.*, **95**, 8769 (1973).