

# ON THE STABILITY OF AROMATIC HYDROCARBONS. IV<sup>1</sup>

## ON THE LINEARITY OF THE DELOCALIZATION ENERGY RELATIONSHIPS

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Some formulas for the calculation of the delocalization energy of aromatic hydrocarbons are obtained using the perfect aromatic limit structure.

In a previous paper<sup>2</sup> a linear relationship has been established between the Hückel Molecular Orbital delocalization energy (HDE) of the *ortho*-condensed aromatic hydrocarbons and two parameters: the number of hexagonal rings and the number of non-Kekulé rings in the mesomeric limit structure with the maximum number of Kekulé rings. The aim of the present paper is to develop the mentioned procedure by obtaining the coefficients with a higher degree of accuracy and by the modification of the parameters.

### METHOD OF CALCULATION

We will consider a linear form for the delocalization energy (*DE*):

$$DE = aM + bN + c$$

where:

*M*, *N* are molecular parameters and

*a*, *b*, *c* are the coefficients which were obtained using the least-squares method to fit the *HDE* values of some hydrocarbons.\*

In order to estimate the precision of the results the following criteria were used:

a) the variance

$$d = \sum_{i=1}^n (DE_i - HDE_i)^2 / (n - 3)$$

where

*n* is the number of compounds used in parametrization,

\* The *HDE* values were found in reference.<sup>3</sup>

<sup>1</sup> Part III, V. E. SAHINI, *Rev. Chim.* (București), **1964**, 551.

<sup>2</sup> V. E. SAHINI, *J. Chim. phys.*, **59**, 177 (1962).

<sup>3</sup> E. HEILBRONNER and P. STRAUB, "Hückel Molecular Orbitals", Springer Verlag, Berlin, 1966.

shows the magnitude of the scattering of the  $DE$ , but is unit-dependent \*.  
 b) the determination coefficient ( $= 100 k$ , where

$$k = 1 - \frac{\sum_{i=1}^n (DE_i - HDE_i)^2}{\sum_{i=1}^n \left( DE_i - \sum_{j=1}^n HDE_j/n \right)^2};$$

a value close to 1 expresses a good relationship between the  $HDE$  and the parameters; the determination coefficient is not unit-dependent \*\*.

### SELECTION OF THE PARAMETERS

The parameters are found by using the mesomeric limit formula.<sup>2</sup>

We obtained  $M$  by using the number of single bonds  $M'$  ( $M = M'/3$ ; in *ortho*-condensed hydrocarbons  $M$  is the number of cycles). The second parameter,  $N$  was determined from the formula with maximum number of benzenoid rings (the formula which minimizes  $N$ )\*\*\*.  $N$  reflects the existence of subsystems in arenes. When  $c \neq 0$  they are not additive :

$$DE = aM + bN + c = a(M - N) + (a + b)N + c$$

(the energy is not a sum of terms corresponding to the energies of  $N$  subsystems with delocalization energy  $a + b$  and  $M - N$  subsystems with delocalization energy  $a$ ). Three cases were studied :

1) The original<sup>2</sup> choice of  $N$ , which is discussed on the basis of localized molecular orbitals in reference<sup>6</sup>;  $N$  is the number of rings that have not a perfect aromatic character. For *ortho*-condensed arenes\*\*\*\*  $N$  can be easily determined from the topology of the molecule, as shown by Balaban.<sup>7</sup>

\* In this paper we use  $\beta$  units.

\*\* The variance and the determination coefficient are similar to those used in statistics.

\*\*\* The formula with maximum number of perfect aromatic benzenoid rings is defined in reference.<sup>2</sup> It is known that it is the best picture of the molecule with localized bonds (from experiment: Fries'rule<sup>4</sup>; from theory: localized molecular orbitals<sup>5,6</sup>).

\*\*\*\* Exceptions are molecules such as pentaphene, where a ring with imperfect aromatic character is used by more than one group of three linearly condensed rings.

<sup>4</sup> L. F. FIESER and M. FIESER, "Textbook of Organic Chemistry", D. C. Heath, Boston, 1950.

<sup>5</sup> W. ENGLAND, S. SALMON and K. RUEDENBERG, *Fortschr. Chem. Forsch.*, **23**, 31 (1967).

<sup>6</sup> V. E. SAHINI and A. SAVIN, to be published.

<sup>7</sup> A. T. BALABAN, *Match*, **1**, 33 (1975) and references cited therein.

2) The value of  $N$  represents the number of rings that are not isolable benzenoid subsystems in arenes (e.g. in naphthalene there is only one such subsystem). It is related to Clar's ideas<sup>8</sup> and finds a theoretical basis in reference.<sup>9</sup>\*

3) The value of  $N$  represents the number of double bonds not included in rings with perfect aromatic character. This rests on the fact that localized molecular orbitals that belong to rings with perfect aromatic character have an energy that differs from that of the localized molecular orbitals which do not belong to these rings.<sup>6</sup>

The value of  $N$  as the number of double bonds not included in isolable benzenoid subsystems will not be discussed here independently, as it is connected with that determined in the second case.

The differences between the three choices of  $N$  are confirmed by the following example: for  $000^{00}$ ,  $000^0$ ,  $^000^0$ ,  $^000^0$   $N$  is (1, 3, 1), (1, 2, 0), (1, 2, 1), viz. (0, 2, 0) (the numbers show the values of  $N$  in the first, second, and third choice, respectively).

## RESULTS

Table 1 presents the formulas for the delocalization energies, the three choices corresponding to formulas 1–4, 5, 6 respectively. Benzene was not always used in interpolation, providing an exception in many cases. The analysis of the variance shows good results in all cases, the determination coefficients have very high values. If we consider as normal the distribution of the  $HDE$  we can define the probability of finding a  $HDE$  value in a domain bounded by  $M - a/2$  and  $M + a/2$  or  $N - b/2$  and  $N + b/2$ . The high value of  $a$  determines a probability of 1.0 in the former case; in the latter, it is of over 0.9 (formulas 1, 3, 4, 5), 0.8 (formula 2 with rounded coefficients), 0.6 (formula 8, because the coefficient  $b$  used in this formula is approximately one half of the one used in formulas 1–5; if we define the domain by the bounds  $N - b$  and  $N + b$ , the probability is of over 0.9).

Formula 4 shows that the use of a new type of molecules (*peri*-condensed hydrocarbons) does not modify essentially the values of the  $a$ ,  $b$ ,  $e$ , the variance or the determination coefficient.

\* A graphical method could be used here, based on the fact that two isolable benzenoid subsystems cannot be joined together.  $N$  is then obtained by subtracting from  $M$  the number of possible eliminations of cycles which are not connected with more than one cycle and the cycles linearly connected with the former.

<sup>8</sup> E. CLAR, "Polycyclic Hydrocarbons", Academic Press, London, 1964.

<sup>9</sup> O. E. POLANSKY and G. DERFLINGER, *Internat. J. Quantum Chem.*, **1**, 379 (1967).

The results obtained with formula 2 show that the rounding of the coefficients does not alter essentially the values of the variance and the determination coefficient. Formula 2 differs from the one obtained in the first paper of this series <sup>2</sup> only by the value of the last coefficient.

Table 1

The linear equations:  $DE = a.M - b.N + c$

	a	b	c	variance	determina- tion coeffi- cient
1 *	1.754	-.131	.201	.0016	99.97
2 **	1.75	-.15	.20	.0035	99.94
3 ***	1.761	-.132	.167	.0015	99.96
4 ****	1.757	-.129	.185	.0015	99.98
5 ***	1.813	-.165	.205	.0019	99.95
6 ***	1.737	-.070	.241	.0015	99.97

\* The 24 *cata*-annelated hydrocarbons of reference<sup>3</sup> were used in parametrization.

\*\* The coefficients of formula 1 were rounded to halves of tenths.

\*\*\* Benzene was not used in parametrization.

\*\*\*\* The 24 *cata*-annelated and the 6 *peri*-condensed hydrocarbons of reference<sup>3</sup> were included in parametrization.

As the formal analysis shows good results, it can be expected that the *HDE* could be calculated by using the linear relationship.

As *N* has the same meaning in formulas 1, 3 and 4 the differences between the coefficients **a**, **b**, **c** are small (also **a** and **c** are of opposite sign) only one value of the *DE* is presented in tables 2, 3 and 4 (that calculated with formula 4).

The values for the *DE* are listed in tables 2 and 3. Knowing the values of the variance, it is not surprising to find that there are only remarkably small errors for the energy values.

Table 4 presents the relative errors ( $100 (DE_i - HDE_i)/HDE_i$ ) for the first ten *n*-acenes. In this limit case the formula  $DE = 1.75 M - 0.13 N + 0.19$  (obtained by interpolation from the values of the *HDE* of the acenes) is remarkably close to formula 2.

The values presented in the tables prove that the linear equations can be used in order to determine the delocalization energies, having the same degree of confidence as the *HMO* values.

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Table 2

Delocalization energies of the cata-annulated molecules used in parametrization

Molecule	HDE	DE formula			
		1.34	2	5	6
O	2.00	1.94	1.95	2.02	1.98
OO	3.68	3.70	3.70	3.67	3.71
OOO	5.31	5.33	5.30	5.31	5.31
OO <sup>O</sup>	5.45	5.46	5.45	5.48	5.45
OOOO	6.93	6.95	6.90	6.96	6.91
OOO <sup>O</sup>	7.10	7.08	7.05	7.12	7.12
O <sup>O</sup> OO	7.19	7.21	7.20	7.12	7.19
OO <sup>OO</sup>	7.19	7.21	7.20	7.12	7.19
<sup>O</sup> OOO	7.27	7.21	7.20	7.29	7.19
OOOOO	8.54	8.58	8.50	8.61	8.59
OOOO <sup>O</sup>	8.73	8.71	8.65	8.78	8.71
OOO <sup>OO</sup>	8.76	8.84	8.80	8.78	8.85
<sup>O</sup> OO <sup>O</sup>	8.83	8.84	8.80	8.78	8.85
OOO <sup>OO</sup>	8.84	8.84	8.80	8.78	8.85
O <sup>OOO</sup> O	8.88	8.84	8.80	8.94	8.85
O <sup>OOO</sup> <sup>O</sup>	8.88	8.84	8.80	8.94	8.85
OOO <sup>O</sup> <sub>O</sub>	8.94	8.84	8.80	8.94	8.92
<sup>OO</sup> <sub>OO</sub>	8.94	8.97	8.95	8.94	8.92
O <sup>OO</sup> <sub>OO</sub>	8.94	8.97	8.95	8.94	8.92
OO <sup>OO</sup> <sup>O</sup>	8.94	8.97	8.95	8.94	8.92
<sup>O</sup> OOO <sup>O</sup>	9.00	8.97	8.95	8.94	8.92
OOOO <sup>OO</sup>	10.46	10.47	10.45	10.42	10.45
OOO <sup>OO</sup> <sup>O</sup>	10.59	10.60	10.55	10.59	10.59
<sup>OOO</sup> <sub>OOO</sub>	12.24	12.23	12.15	12.24	12.26

Table 3

Delocalization energy for not cata-condensed benzenoid hydrocarbons					
Molecule	HDE	DE calculated using formula			
		1, 3, 4	2	6	5
$\text{O}_6^{\text{O}}$	6.50	6.50	6.47	6.54	6.52
$\text{O}_6^{\text{O}_2\text{O}}$	8.25	8.26	8.22	8.35	8.17
$\text{O}_6^{\text{O}_2\text{O}_2\text{O}}$	9.25	9.30	9.23	9.36	9.22
$\text{O}_6^{\text{O}_2\text{O}_2\text{O}_2\text{O}}$	9.43	9.43	9.38	9.50	9.38
$\text{O}_6^{\text{O}_2\text{O}_2\text{O}_2\text{O}_2\text{O}}$	10.55	10.60	10.55	10.66	10.42
$\text{O}_6^{\text{O}_2\text{O}_2\text{O}_2\text{O}_2\text{O}_2\text{O}}$	14.50	14.46	14.33	14.57	14.32
$\text{O}_7^{\text{O}}$	4.38	4.28	4.28	4.29	4.44
$\text{O}_7^{\text{O}_2\text{O}}$	6.77	6.63	6.62	6.61	6.85
$\text{O}_7^{\text{O}_2\text{O}_2\text{O}}$	6.77	6.63	6.62	6.61	6.85

Table 4

Relative errors obtained for the delocalization energy of n-acenes				
No of rings	Relative errors, formula			
	1, 3, 4,	2	5	6
2 *	.4	.4	-.2	.4
3 *	.4	-.2	.0	.0
4 *	.3	-.4	.4	-.3
5 *	.5	-.5	.8	-.4
6	.4	-.6	1.0	-.6
7	.5	-.6	1.1	-.6
8	.5	-.6	1.3	-.6
9	.6	-.6	1.4	-.6
10	.6	-.6	1.5	-.6

\* Used in parametrization.