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KEKULÉ STRUCTURES AND RESONANCE ENERGIES OF BENZENOID HYDROCARBONS

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In this paper we show that resonance energies and localization energies of benzenoid hydrocarbons can be obtained by counting resonance structures, and that results are tantamount to the best obtainable from highly parameterized SCF-LCAO-MO calculations.

The number of Kekulé structures for a benzenoid hydrocarbon is accepted to be an approximate empirical measure of resonance stabilization.[1] However, resonance energies are usually estimated as delocalization energies obtainable from Hückel molecular orbital (HMO) or semi-empirical self-consistent-field (SCF) calculations. The extensive variable bond-length SCF results that have been obtained by Dewar and co-workers[2] can be taken to provide a reliable reference set of resonance energies. Recent modified HMO procedures that use open-chain π-systems as reference structures[3,4] give resonance energies for aromatic hydrocarbons that correlate closely with the Dewar SCF results.

A parameterized structure-resonance theory based solely on covalent Kekulé structures has also been developed that precisely duplicates the Dewar resonance energies.[5] During the course of that development we noted the correlation between the Kekulé structure count[6] (SC) and Dewar resonance energy illustrated in the Table. Since the average difference between the SCF resonance energies and those calculated from the algorism is only ±0.04 eV, this procedure is a very simple and convenient method to calculate resonance energies and ortho or para localization energies of SCF quality. The quantities so obtained allow one to calculate accurate experimental heats of formation[7] and to correlate various kinds of reactivity including carcinogenicities.[8]

In equations (1) and (2) we give algebraic equalities which give at least a partial understanding of the results delineated in the Table. Equation (1) expresses the fact

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Resonance Energies of Aromatic Hydrocarbons

Compound	SC[a]	SCF-MO (eV)[b]	1.185 ln SC	Difference
Benzene	2	0.869	0.821	0.048
Naphthalene	3	1.323	1.302	0.021
Anthracene	4	1.600	1.643	-0.043
Phenanthrene	5	1.933	1.907	0.026
Pyrene	6	2.098	2.123	-0.025
Benzo[c]phenanthrene	8	2.478	2.464	0.014
Benz[a]anthracene	7	2.291	2.306	-0.015
Chrysene	8	2.483	2.464	0.019
Triphenylene	9	2.654	2.604	0.040
Perylene	9	2.619	2.604	0.015
Naphthacene	5	1.822	1.907	-0.085
Pentacene	6	2.004	2.123	-0.119
Dibenz[a,c]anthracene	13	3.058	3.040	0.018
Dibenz[a,h]anthracene	12	2.948	2.945	0.003
Dibenz[a,j]anthracene	12	2.948	2.945	0.003
Benzo[a]pyrene	9	2.584	2.604	-0.020
Benzo[d]pyrene	11	2.853	2.842	0.011
Benzo[1,12]perylene	14	3.128	3.127	0.001
Coronene	20	3.524	3.550	-0.026
Benzo[1,14]bisanthene	30	3.862	4.031	-0.169
Ovalene	50	4.539	4.636	-0.097
Zethrene	9	2.694	2.604	0.090
Quaterrylene	81	5.309	5.208	0.101
Fluoranthene	6	2.141	2.123	0.018
Biphenyl	4	1.699	1.643	0.056
Styrene	2	0.858	0.821	0.037
Stilbene	4	1.712	1.643	0.069

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[a] Reference 6. [b] Reference 2.

that resonance energies (structure-resonance theory) for π-system composed of aromatic fragments connected by essential single bonds are additive whereas equation (2) shows that the SC

$$RE(A\text{-}B\cdots\cdots Z) = RE(A) + RE(B) + \cdots\cdots + RE(Z) \qquad (1)$$

$$SC(A\text{-}B\cdots\cdots Z) = [SC(A)][SC(B)]\cdots\cdots[SC(Z)] \qquad (2)$$

are multiplicative. The relationship between the ln SC and resonance energy is therefore exact for such systems. In SCF calculations, the absence of resonance stabilization through essential single bonds has also been pointed out.[2]

One should note also the relationships given by equations (3) and (4). The square of the SC is the product of the eigenvalues (absolute values) of the HMO adjacency

$$(SC)^2 = \prod_{j=1}^{j=N} |x_j| \qquad (3)$$

$$2 \ln SC = \sum_{j=1}^{j=N} \ln |x_j| \qquad (4)$$

matrix,[9] equation (3), and the logarithm of the SC is therefore half of the sum of the logarithms of the HMO eigenvalues, equation (4). Incorporating the results given in the Table, equation (4) implies an exact linear equality of the SCF resonance energies and the sum of the logarithms of the HMO eigenvalues, equation (5). Furthermore, since the sum term in equation (4) has been shown to be a function of topological invariants[10] (bonds,

$$RE_{SCF} = 1.185 \ln SC = 0.5925 \sum_{j=1}^{i=N} \ln |x_j|_{HMO} \qquad (5)$$

atoms, number and types of rings, etc.) the SCF resonance energy is also only a function of these same topological quantities. These latter relationships remain to be clarified.

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