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Note

Simple Topological Formula for Dewar Resonance Energies of Benzenoid Molecules

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In this note we show that the Dewar resonance energies, *DRE*'s, of benzenoid hydrocarbons are well reproduced by the simple topological expression:

$$DRE = 2.233\ (n)^{1/6}\ (\ln\ K)^{5/6} - 0.329 \qquad (1)$$

where n and K are the number of hexagons and Kekulé structures, respectively, in a benzenoid hydrocarbon.

Dewar and co-workers[1] have reinvestigated the classical concept of resonance energy, *CRE,* and by making use of a polyene reference structure instead of the ethylene reference structure they were able to obtain good agreement between the SCF pi-MO calculations and experimental findings for both benzenoid and non-benzenoid molecules. This new concept, later named[2] »Dewar resonance energy«, was used with equal success within the framework of Hückel theory[3]. Extensive tables of *DRE* value of benzenoid hydrocarbons have been published[3a].

It is of evident chemical importance not only to calculate resonance energy, but also to understand its dependence on molecular structure. From this point of view *CRE* was studied for benzenoid hydrocarbons in several papers[4]. No analogous results are known for *DRE* except that the *DRE*'s of benzenoid hydrocarbons can be reproduced with a fair accuracy using a naive valence bond calculation scheme[5]. In the present work we wish to give a further contribution towards the understanding of the structural dependence of *DRE* in benzenoid hydrocarbons.

Recently[6] an integral formula for *DRE* has been derived based on earlier result of Coulson[7]:

$$DRE = (1/\pi) \int_{-\infty}^{+\infty} F(x)\, dx \qquad (2)$$

$$F(x) = \ln \left| P(G,\ ix)/\bar{P}(G,\ ix) \right| \qquad (3)$$

In the above formulae $i = \sqrt{-1}$, $P(G, x)$ and $\bar{P}(G, x)$ are the characteristic polynomial[8] and the acyclic polynomial[6], respectively, of the molecular graph.[8] For alternant hydrocarbons with N carbon atoms,

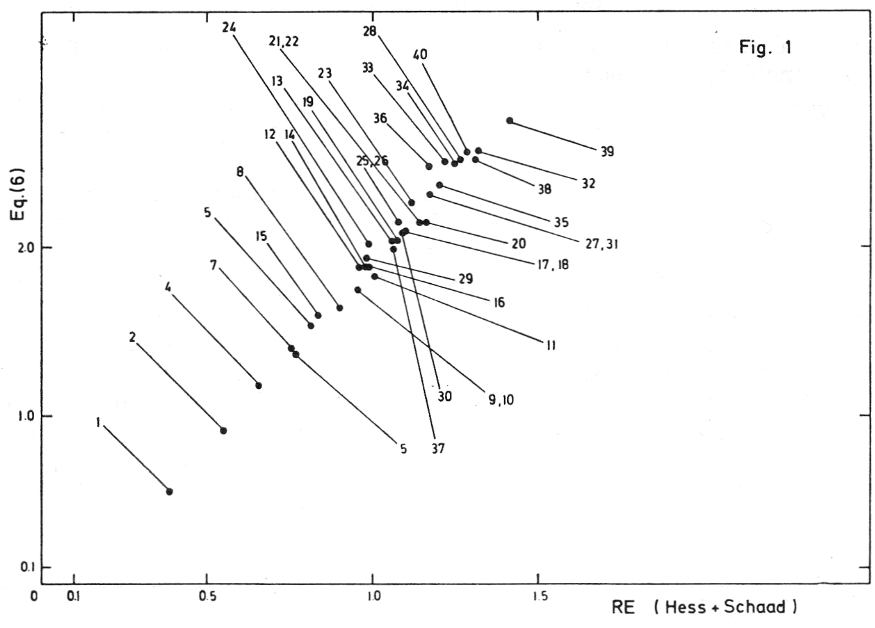
$$P(G,\ x) = \sum_{j=0}^{N/2} (-1)^j\, b_j\, x^{N-2j} \qquad (4)$$

$$\bar{P}(G,\, x) = \sum_{j=0}^{N/2} (-1)^j\, p_j\, x^{N-2j} \tag{5}$$

with p_j being the number of choices of j non-incident edges in G, whilst the coefficients b_j are discussed in details elsewhere[9]. According to Ref. 9, in benzenoid hydrocarbons $b_0 = p_0$, $b_1 = p_1$, $b_2 = p_2$, and $b_3 = p_3 + 2\,n$. Besides, $b_{N/2} = K^2$, $p_{N/2} = K$, and, excluding the cases of benzene and naphthalene, $K \geqslant 4$. Utilizing these relations and the fact $b_3/p_3 \approx 1 \ll b_{N/2}/p_{N/2} = K$, one can show that $F(x)$ is a bell-shaped function with $F_{max} = F(0) = \ln K$ and $F(x) \approx 2n\, x^{-6}$ for large x. Since the function $F_1(x) = (2\,n \ln K)/(2\,n + x^6 \ln K)$ has analogous properties, one may expect that

$$(1/\pi \int_{-\infty}^{+\infty} F_1(x)\,\mathrm{d}x = (2/3)\,(2n)^{1/6}\,(\ln K)^{5/6} \tag{6}$$

will result in good approximate formula for *DRE*.



In Figure 1 is plotted eq. (6) *vs.* *DRE* values of Hess and Schaad[3b] for 39 benzenoid hydrocarbons. The numbering of compounds follows that one of Ref. 3b. One sees that there is a good linear correlation between eq. (6) and *DRE*, the correlation coefficient being 0.989. Finally, eq. (1) follows from a least-squares fitting of Eq. (6) and the *DRE* values of Ref. 3b. Hence, eq. (1) is not only very convenient for the »pencil and paper« estimation of *DRE*'s, but gives also a topological insight into the reasons of particular aromatic character of benzenoid molecules.

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SAŽETAK

Jednostavna topološka formula za Dewarovu rezonancijsku energiju benzenoidnih ugljikovodika

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Izvedena je jednostavna topološka formula za Dewarovu rezonancijsku energiju, *DRE,* benzenoidnih ugljikovodika. Pokazano je da *DRE* kod te klase konjugiranih struktura ovisi jedino o broju šesteročlanih prstenova i o broju Kekuléovih struktura. To je još jedan doprinos ideji da je naročita topologija benzenoidnih ugljikovodika odgovorna za njihova posebna fizikalna i kemijska svojstva.

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