*J. Serb. Chem. Soc.* *71* (10) 1039–1047 (2006)
*JSCS–3498*

UDC 539.194:541.6:547.53
*Original scientific paper*

# Dependence of Dewar resonance energy of benzenoid molecules on Kekulé structure count

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(Received 1 February 2006)

*Abstract:* The dependence of the Dewar resonance energy (*DRE*) on the Kekulé structure count ($K$) was found to be significantly different from that earlier anticipated. Within classes of benzenoid isomers, the *DRE* increases either as $K^{\lambda}$ for $\lambda \approx 0.3$ or as $(\ln K)^{\lambda}$ for $\lambda \approx 2$. Both functional dependencies result in approximate expressions for *DRE* of nearly equal accuracy. Approximations of the form $DRE \approx a\,K + b$ and $DRE \approx a' \ln K + b'$ are somewhat less accurate, but can still be used in usual practical applications of the Dewar resonance energy.

*Keywords:* Dewar resonance energy, resonance energy, Kekulé structure count, benzenoid hydrocarbons.

## INTRODUCTION

Resonance energies are used for rationalizing the peculiar chemical and physico chemical behavior of polycyclic conjugated molecules which are sometimes referred to as "aromaticity".[1–4] Dewar and de Llano[5] were the first to recognize that the early failures of resonance energy to correctly predict the stability of many polycyclic conjugated systems is due to an inadequately chosen reference structure. This led to an appropriate change in the definition of resonance energy, resulting in what was eventually named[6,7] "Dewar resonance energy", *DRE*. In fact, several variants of the *DRE* were proposed.[8–14] (all in the 1970s). In this paper, the most popular of these Dewar resonance energies, the variant introduced by Hess and Schaad,[8] is considered. According to it,

$$DRE = E - E^{\mathrm{ref}}$$

where $E$ is the total $\pi$-electron energy as calculated within the Hückel molecular orbital approximation. (For details on $E$ see the recent review.[15]) The reference energy $E^{\mathrm{ref}}$ in

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doi: 10.2298/JSC0610039G

the Hess–Schaad model is an additive function of bond increments $E_{ij}$ such that

$$E^{\mathrm{ref}} = \sum_{ij} E_{ij}$$

with the summation embracing all carbon–carbon bonds, and

$E_{ij} = 2.0699$ for a HC = CH bond
$E_{ij} = 2.1083$ for a HC = C bond
$E_{ij} = 2.1716$ for a C=C bond
$E_{ij} = 0.4660$ for a HC–CH bond
$E_{ij} = 0.4362$ for a HC–C bond
$E_{ij} = 0.4358$ for a C–C bond.

Above are listed only those bond energy terms which are required for the calculation of $E^{\mathrm{ref}}$ of benzenoid hydrocarbons. Recall that the Hess–Schaad reference energy is computed for a particular Kekulé structure, and thus slightly depends on the choice of this Kekulé structure. In the present calculations, the "best" Kekulé structure, as determined by the Fries rule was always employed.[16]

A detailed account of the Dewar resonance energy can be found in the reviews.[2,4]

An important factor influencing various energy related properties of benzenoid molecules, and thus also their *DRE*-value, is the Kekulé structure count *K*.[15,17–22] Based on the fact that for a conjugated molecule *M* containing two non-interacting conjugated π-electron systems $M_1$ and $M_2$,

$$DRE(M) = DRE(M_1) + DRE(M_2) \text{ and } K(M) = K(M_1) \cdot K(M_2)$$

Swinborne Sheldrake *et al.* concluded[23] that the *K*-dependence of the Dewar resonance energy must be logarithmic, *i.e.*, of the form

$$DRE \approx a_0 \ln K \tag{1}$$

where $a_0$ is a parameter determined by least squares fitting. Eq. (1) resonably well reproduced the Dewar–de Llano *DRE* values of benzenoid hydrocarbons existing in 1975.[23] In the years that followed, this approximation was assumed to be fully satisfactory, was often quoted, and was used in several subsequent researches.[24,25] Curiously, however, after more powerful computing machines became available its validity was never re-checked.

Here, it will be shown that the approximation (1) is only valid to a limited degree, and that the *K*-dependence of the *DRE* is much better reproduced by expressions having considerably different analytical forms.

Examining the structural factors that influence the value of *DRE* (and the "aromaticity" of the underlying conjugated compound), it was soon realized that the dominant factor is molecular size (in the case of hydrocarbons: the number of carbon atoms and carbon carbon bonds).[2]

A standard way to avoid size dependent effects in the topological theory of conjugated molecules is to restrict the consideration to groups of isomers.[15,20–22]

Such a strategy has also been adopted in the present work. The obtained results are based on the analysis of seven sets of isomeric benzenoids of different size, each set consisting of all possible isomers: the details are given below.

## A CASE STUDY: BENZENOID ISOMERS $C_{28}H_{16}$

The details of the examination of the *K*-dependence of the *DRE* of Kekuléan benzenoid molecules of the formula $C_{28}H_{16}$ are presented here. The number of Kekuléan isomers of this kind[26] is 62, and their *K*-values lie between 9 and 31. These benzenoid hydrocarbons are heptacyclic and possess two internal carbon atoms (carbon atoms simultaneously belonging to three six-membered rings).

The respective *DRE*-values of these benzenoid isomers are plotted versus *K* in Fig. 1, and versus the logarithm of *K* in Fig. 2.

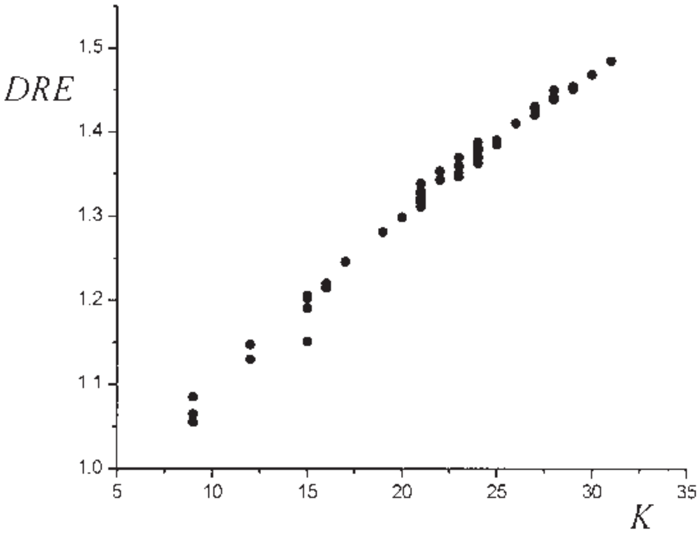

Fig. 1. The dependence of the Dewar resonance energies (*DRE*) of the $C_{28}H_{16}$ benzenoid isomers on the Kekulé structure count (*K*). The correlation is essentially linear, but a slight curvilinearity can be recognized. For details see text.

From Fig. 1, it can be seen that the correlation between the *DRE* and *K* is essentially linear, which contradicts the earlier postulated logarithmic *K*-dependence, Eq. (1). That the *K*-dependence is certainly not logarithmic is clearly seen from Fig. 2.

A detailed examination of the two correlations gave the following results. Although a slight curvature of the data points is "seen" in Fig. 1, no statistically significant curvilinearity could be confirmed by the *F*-test (at confidence levels of 90% and higher). The almost obvious curvilinearity of the data points in Fig. 2 was confirmed by the *F*-test, but only up to a 95 %, and not at a 99 % confidence level. For the data points in Figs. 1 and 2, the correlation coefficients (a measure of the quality of a linear correlation) were 0.9937 and 0.9884, respectively.

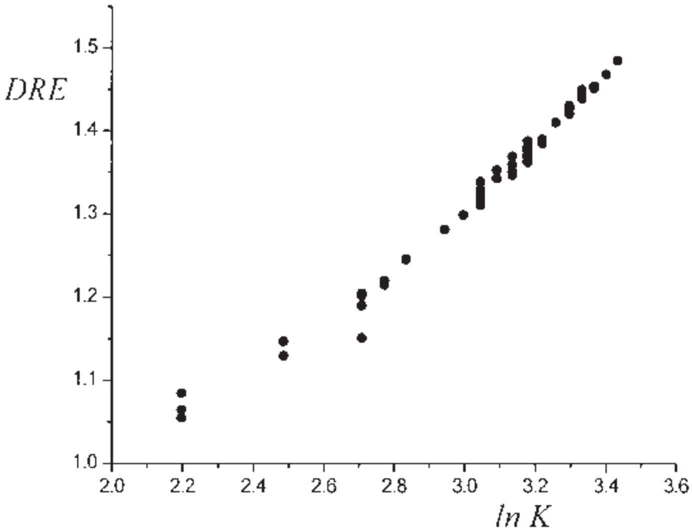

Fig. 2. The same *DRE*-values as in Fig. 1 plotted *versus* the logarithm of *K*. A pronounced curvilinearity is seen, inferring that the assumption that the *K*-dependence of the *DRE* is logarithmic is not correct.

Thus, from Figs. 1 and 2, it can be concluded that, at least in the case of the $C_{28}H_{16}$ benzenoid isomers, the dependence of the *DRE* on *K* is almost linear,

$$DRE \approx a\,K + b \tag{2}$$

and by no means logarithmic,

$$DRE \approx a' \ln K + b' \tag{3}$$

In formula (2), $a = 0.02$ and $b = 0.91$; in formula (3), $a' = 0.35$ and $b' = 0.26$ (for more details see Table II). Formula (2) reproduces the *DRE*-values of the $C_{28}H_{16}$ isomers with an average relative error of 0.63 %. Formula (3) yields a much greater (but still reasonably small!) average relative error of 0.90 %. Thus the $C_{28}H_{16}$ isomers provide a counterexample for the validity of formula (1) and of its slightly modified version Eq. (3). The fact that the coefficient $b'$ in formula (3) significantly differs from zero is one more argument against the validity of Eq. (1).

In order to take into account the small curvature seen in Fig. 1, formula (2) was modified to:

$$DRE \approx a\,K^{\lambda} + b. \tag{4}$$

Analogously, in order to "linearize" the correlation encountered in Fig. 2, the following modified version of formula (3) was considered:

$$DRE \approx a' (\ln K)^{\lambda} + b' \tag{5}$$

In (4) and (5), $\lambda$ is a variable parameter, the value of which is determined so as to minimize the average relative error. Obviously, for $\lambda = 1$, formulas (4) and (5) reduce, respectively, to (2) and (3).

Our expectation that the optimal values of $\lambda$ would be near to unity were not confirmed by numerical calculations. For the examined set of benzenoid isomers, it was found that $\lambda = 0.62$ for Eq. (4) and $\lambda = 2.81$ for Eq. (5). Using these values of the parameter $\lambda$, in Eq. (4), $a = 0.10$ and $b = 0.69$; in Eq. (5), $a' = 0.02$ and $b' = 0.89$ (for more details see Table II).

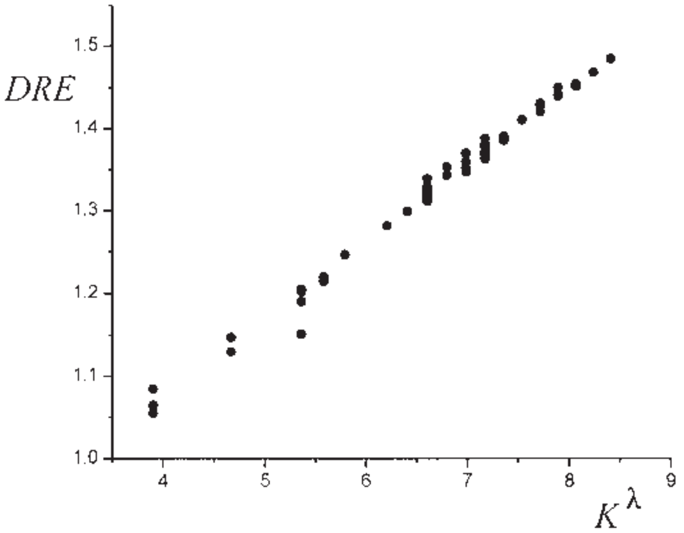

Fig. 3. The same *DRE*-values as in Fig. 1 plotted versus $K^{\lambda}$, $\lambda = 0.62$, according to Eq. (4). For details see text.

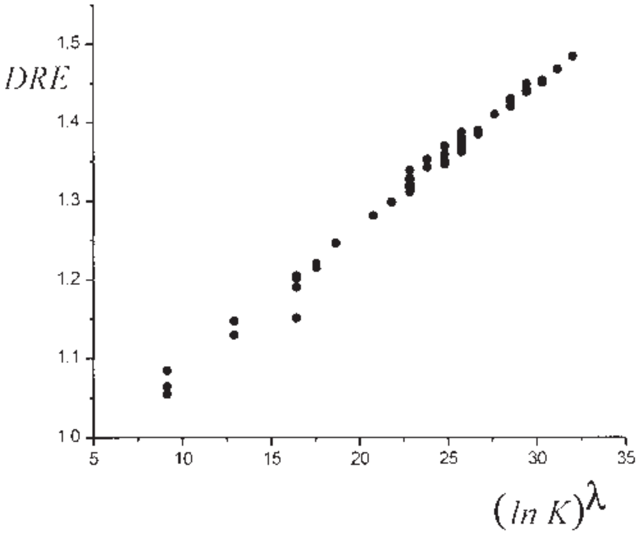

Fig. 4. The same *DRE*-values as in Fig. 1 plotted versus $(\ln K)^{\lambda}$, $\lambda = 2.81$, according to Eq. (5). For details see the text. Note that Figs. 3 and 4 appear almost identical.

Using the optimized values of $\lambda$, the average relative error of both Eq. (4) and (5) was found to be 0.50 %, which is significantly smaller than 0.63 % and 0.90 %

for $\lambda = 1$. It should be noted that in the case of the $C_{28}H_{16}$ isomers, as well as for all other examined groups of benzenoid isomers (see below), the optimized approximations (4) and (5) reproduce the *DRE* with nearly equal precision.

The *DRE* values of the considered benzenoid isomers versus $K^{\lambda}$ for $\lambda = 0.62$ are plotted in Fig. 3. The same *DRE*-values are plotted versus $(\ln K)^{\lambda}$ for $\lambda = 2.81$ in Fig. 4. Both correlations are linear and appear almost identical. This is in harmony with the fact that, in spite of their different analytical forms, the optimized Eqs. (4) and (5) yield equivalent numerical results.

## NUMERICAL WORK AND DISCUSSION

Investigations analogous to those outlined in the preceding section were undertaken for six additional sets of benzenoid isomers, each consisting of all possible Kekuléan species. The results obtained were fully analogous to those for the $C_{28}H_{16}$ isomers, except that the optimal $\lambda$-values varied significantly. These results are summarized in Table I.

TABLE I. Data on the dependence of the Dewar resonance energy on the Kekulé structure count, for seven sets of benzenoid isomers. N. I. = number of Kekuléan isomers of the benzenoid systems with the given formula; all these isomers were contained in the sets considered; *ARE*($\lambda$) = average relative error for the given (optimal) value of the parameter $\lambda$, *ARE*($\lambda = 1$) = average relative error of Eqs. (4) and (5) for $\lambda = 1$, *i.e.*, the average relative error of formulas (2) and (3)

| Formula | N.I. | Eq. | $\lambda$ | *ARE*($\lambda$) | *ARE*($\lambda = 1$) |
|---|---|---|---|---|---|
| $C_{18}H_{12}$ | 5 | (4) | 0.25 | 0.18 % | 0.65 % |
| | | (5) | 1.47 | 0.18 % | 0.24 % |
| $C_{22}H_{14}$ | 12 | (4) | 0.42 | 0.39 % | 0.76 % |
| | | (5) | 1.92 | 0.38 % | 0.58 % |
| $C_{24}H_{14}$ | 13 | (4) | 0.47 | 0.32 % | 0.51 % |
| | | (5) | 2.22 | 0.32 % | 0.49 % |
| $C_{26}H_{14}$ | 9 | (4) | 0.28 | 0.32 % | 0.47 % |
| | | (5) | 1.81 | 0.32 % | 0.36 % |
| $C_{26}H_{16}$ | 36 | (4) | 0.31 | 0.31 % | 0.84 % |
| | | (5) | 1.79 | 0.31 % | 0.49 % |
| $C_{28}H_{16}$ | 62 | (4) | 0.62 | 0.50 % | 0.63 % |
| | | (5) | 2.81 | 0.50 % | 0.90 % |
| $C_{30}H_{18}$ | 118 | (4) | 0.30 | 0.33 % | 0.74 % |
| | | (5) | 1.88 | 0.32 % | 0.44 % |

The coefficients *a, b, a', b'* in Eqs. (2)–(5) were calculated by least squares fitting. Their numerical values are found in Table II.

TABLE II. The coefficients in Eqs. (2) – (5), calculated by least squares fitting, using the $\lambda$-values given in Table I

| Formula | Eq. | *a* or *a*' | *b* or *b*' |
|---|---|---|---|
| $C_{18}H_{12}$ | 2 | 0.0650 ± 0.0025 | 0.429 ± 0.021 |
| | 3 | 0.4360 ± 0.0077 | 0.046 ± 0.015 |
| | 4 | 1.0860 ± 0.0160 | –0.875 ± 0.026 |
| | 5 | 0.2205 ± 0.0033 | 0.305 ± 0.001 |
| $C_{22}H_{14}$ | 2 | 0.0441 ± 0.0014 | 0.588 ± 0.017 |
| | 3 | 0.4236 ± 0.0097 | 0.069 ± 0.024 |
| | 4 | 0.3936 ± 0.0070 | 0.002 ± 0.020 |
| | 5 | 0.1057 ± 0.0019 | 0.513 ± 0.010 |
| $C_{24}H_{14}$ | 2 | 0.0287 ± 0.0005 | 0.748 ± 0.013 |
| | 3 | 0.3963 ± 0.0101 | 0.112 ± 0.027 |
| | 4 | 0.2480 ± 0.0045 | 0.297 ± 0.016 |
| | 5 | 0.0557 ± 0.0010 | 0.674 ± 0.009 |
| $C_{26}H_{14}$ | 2 | 0.0210 ± 0.0009 | 0.856 ± 0.018 |
| | 3 | 0.4016 ± 0.0126 | 0.078 ± 0.037 |
| | 4 | 0.6295 ± 0.0198 | –0.177 ± 0.045 |
| | 5 | 0.0928 ± 0.0028 | 0.604 ± 0.020 |
| $C_{26}H_{16}$ | 2 | 0.0268 ± 0.0007 | 0.793 ± 0.013 |
| | 3 | 0.4107 ± 0.0058 | 0.100 ± 0.017 |
| | 4 | 0.5784 ± 0.0058 | –0.133 ± 0.014 |
| | 5 | 0.1061 ± 0.0010 | 0.575 ± 0.007 |
| $C_{28}H_{16}$ | 2 | 0.0193 ± 0.0003 | 0.908 ± 0.006 |
| | 3 | 0.3495 ± 0.0069 | 0.264 ± 0.021 |
| | 4 | 0.0951 ± 0.0012 | 0.691 ± 0.008 |
| | 5 | 0.0186 ± 0.0002 | 0.894 ± 0.005 |
| $C_{30}H_{18}$ | 2 | 0.0167 ± 0.0003 | 0.989 ± 0.008 |
| | 3 | 0.4113 ± 0.0036 | 0.099 ± 0.012 |
| | 4 | 0.5357 ± 0.0032 | 0.010 ± 0.009 |
| | 5 | 0.0805 ± 0.0005 | 0.692 ± 0.004 |

The most remarkable feature that can be seen in Table I (*cf*. column $ARE(\lambda)$), is that the accuracy of Eqs. (4) and (5) is almost the same for all the seven studied cases (In Table I this is seen only from the $ARE(\lambda)$-values, but also the other statistical characteristics of the two approximations were found to coincide). This implies that the approximations (4) and (5) are of the same quality, irrespective of their significantly different analytical forms.

The values of $ARE(\lambda)$ for the optimal value of $\lambda$ are necessarily smaller than the corresponding values of $ARE(\lambda = 1)$. In the majority of cases, the decrease of

*ARE*($\lambda$) relative to *ARE*($\lambda = 1$) is significant. This implies that, in the majority of cases, Eqs. (4) and (5) are significantly more accurate than Eqs. (2) and (3). On the other hand, Eqs. (2) and (3) are also of similar quality and there is no reason to give preference to either.

Eqs. (2) and (3) are inferior to their optimized versions (4) and (5), but their precision is also not bad. In all examined cases, Eqs. (2) and (3) reproduce the *DRE* with an average relative error below 1 %. Such an accuracy would be sufficient for most chemical applications of the *DRE*, in particular in considerations pertaining to the "aromaticity" of benzenoid hydrocarbons.[2–4]

The optimal $\lambda$-values for Eq. (4) are always less than unity and, in most cases, are around 0.3. For Eq. (5), the $\lambda$-values are always much greater than unity, assuming values roughly around 2. However, as can be seen from Table I, the actual $\lambda$-values vary greatly and no monotonicity (or any other regularity) in their dependence on molecular size could be envisaged.

## CONCLUDING REMARKS

The examinations described in the preceding sections lead to the following conclusions concerning the dependence of the Dewar resonance energy on the Kekulé structure count:

* The Swinborne–Sheldrake formula,[23] Eq. (1), is not correct.

* Instead of Eq. (1), two simple approximations, Eqs. (2) and (3) can be used. Although the former assumes a linear and the latter a logarithmic dependence of the *DRE* on *K*, both yield results of comparable (yet not very high) accuracy.

* In order to improve the precision of Eqs. (2) and (3), their generalized forms, Eqs. (4) and (5), respectively, in which an adjustable parameter $\lambda$ was introduced, were examined.

* The optimal value of the parameter $\lambda$ is very different from unity. For Eq. (4), it is less than unity, whereas for Eq. (5) it is greater than unity. The actual $\lambda$-values vary from sample to sample in a (hitherto) unpredictable manner.

* The approximate Eqs. (4) and (5), when applied with the optimized values of the parameter $\lambda$, reproduce the *DRE* with a similar accuracy. This is a surprising finding, in view of the different analytical form of the *K*-dependence of the *DRE* assumed in Eqs. (4) and (5).

## ИЗВОД

# ЗАВИСНОСТ DEWAR-ОВЕ ЕНЕРГИЈЕ РЕЗОНАНЦИЈЕ БЕНЗЕНОИДНИХ МОЛЕКУЛА ОД БРОЈА KEKULÉ-ОВИХ СТРУКТУРА

ИВАН ГУТМАН и СЛАВКО РАДЕНКОВИЋ

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Нађено је да је зависност Dewar-ове енергије резонанције (*DRE*) од броја Kekulé-ових структура (*K*) значајно различита од онога што је до сада прихватано као тачно. У оквиру група изомерних бензеноидних молекула, *DRE* расте или kao $K^{\lambda}$ за $\lambda \approx 0.3$ или као $(\ln K)^{\lambda}$ за $\lambda \approx 2$. Обе ове функције доводе до апроксимативних формула за *DRE* које имају скоро подједнаку тачност. Апроксимација облика $DRE \approx a\,K + b$ и $DRE \approx a' \ln K + b'$ су нешто мање прецизне, али се ипак могу употребити у уобичајеним практичним применама Dewar-ове енергије резонанције.

(Примљено 1. фебруара 2006)

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