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Aromaticity vs Stoichiometry

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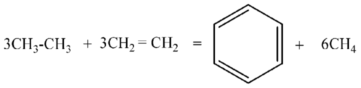
The reference species used to evaluate the resonance energy (RE) are optimized so as to make them completely free of any type of resonance, strain, hyperconjugation, differences in the types of bonds and hybridization, etc. This is achieved by introducing a fictive set of energies of the reference species referred to as the "equilibrium" energies. The latter are determined by requiring the energy change of any conceivable reaction involving the reference species to be zero and employing an optimization procedure similar to the least-squares method. It is shown further that the RE defined in terms of "equilibrium" energies of the reference species have the remarkable property of being independent of the stoichiometry of the reactions used to evaluate the RE.

Introduction

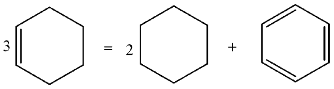
Energetically, aromaticity is characterized by the resonance energy (RE). The difficulties in defining and estimating this quantity are well-known.[1] Broadly, the RE of a given species is defined as the difference between an energetic characteristic of the species and the same energetic characteristic estimated via an additive scheme.[2] Thus, for benzene, the resonance energy is often defined as[1]

$$\mathrm{RE} = E(\mathrm{C_6H_6}) - 6E(\mathrm{C{-}H}) - 3E(\mathrm{C{-}C}) - 3E(\mathrm{C{=}C}) \quad (1)$$

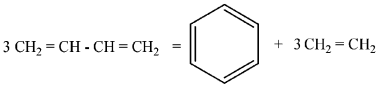
where $E(\mathrm{C_6H_6})$ is any energetic characteristic of the benzene (such as enthalpy of formation, atomization enthalpy, total energy, etc.) and $E(\mathrm{C{-}H})$, $E(\mathrm{C{-}C})$, and $E(\mathrm{C{=}C})$ are the bond energies estimated using various reference species and additive schemes. Clearly, because the selection of the reference species and additive schemes is not unique, so is the RE. For this reason numerous types of RE have been defined and estimated.[1] The most rigorous (and successful) selection of the reference species and structures are those proposed by Dewar[3] and Hess−Schaad.[4] These approaches employ a large number of reference species, thus allowing an accurate estimation of the group values energies. Concomitantly, a large variety of reaction schemes have been proposed to estimate different types of RE. The main advantage of these reaction schemes is their simplicity. In particular, within this approach the RE is always equal to the enthalpy change of the reaction scheme.[2] For instance, in the literature, the RE of benzene has been associated with the enthalpy change of various reactions:



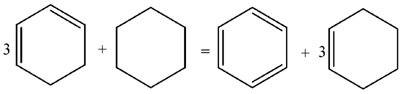
$$\mathrm{RE} = \Delta H_r = -64.8\ \mathrm{kcal/mol} \quad (2)$$



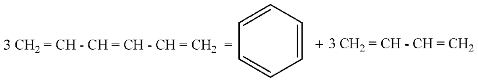
$$\mathrm{RE} = \Delta H_r = -36.0\ \mathrm{kcal/mol} \quad (3)$$



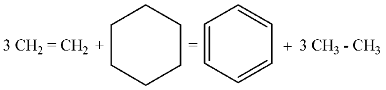
$$\mathrm{RE} = \Delta H_r = -20.7\ \mathrm{kcal/mol} \quad (4)$$



$$\mathrm{RE} = \Delta H_r = -29.2\ \mathrm{kcal/mol} \quad (5)$$



$$\mathrm{RE} = \Delta H_r = -63.0\ \mathrm{kcal/mol} \quad (6)$$



$$\mathrm{RE} = \Delta H_r = -48.6\ \mathrm{kcal/mol} \quad (7)$$

These reaction schemes result in different types of RE that are referred to as isodesmic[5] (reaction 2), homodesmotic[6] (reaction 4), hyperhomodesmotic[7] (reaction 6), and homonuclear[8] (reaction 7). Reaction 5[10] is an extension of the well-known Kistyakowski[9] definition of RE and expressed by reaction 3.

Although, by its very essence the RE is a relative quantity, the dependence of the RE on the choice of the reaction is confusing. First, because all of the above reactions formally preserve the number of C−H, C−C, and C═C bonds and, hence, according to eq 1 should result in the same value of the RE. Second, it looks like more rigorous methods of estimating

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the RE, such as Dewar's or Hess and Schadd's methods, are completely different; i.e., these methods have nothing in common with the methods based on various reaction schemes. The aim of this work is to present a new approach to the evaluation of the RE that, for a given set of reference species and additive scheme, have the remarkable property of being independent of the choice of reactions, i.e., independent of stoichiometry. More generally, on the basis of the proposed approach, it is proved that, energetically, the RE can be always uniquely expressed as the energy change of an arbitrary reaction, independently on the choice of reference species and group addivity scheme.

Notation and Definitions

Consider a set of n reference species $B_1, B_2, ..., B_n$ that are used to estimate the RE of a presumably aromatic species B_{n+1}. Consider next a set of m linearly independent chemical reactions among the reference species

$$\boldsymbol{\rho} = \boldsymbol{\nu}\mathbf{B} = \mathbf{0} \tag{8}$$

where

$$\boldsymbol{\rho} = (\rho_1, \rho_2, ..., \rho_m)^{\mathrm{T}} \tag{9}$$

$$\mathbf{B} = (B_1, B_2, ..., B_n)^{\mathrm{T}} \tag{10}$$

and

$$\boldsymbol{\nu} = \begin{bmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1n} \\ \nu_{21} & \nu_{22} & \cdots & \nu_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ \nu_{m1} & \nu_{m2} & \cdots & \nu_{mn} \end{bmatrix} \qquad \text{rank } \boldsymbol{\nu} = m \tag{11}$$

The matrix $\boldsymbol{\nu}$ is normally referred to as the *stoichiometric* matrix.[11] Reactions $\boldsymbol{\rho}$ may be defined in different ways, e.g., as conventional reactions[12] (preserving mass balance only), isodesmic reactions[13] (preserving the number and type of bonds), group additivity (GA) reactions[14] (preserving the number and type of groups in Benson's sense[15]), etc. Our analysis is general and, therefore, valid for any type of reaction. Because the stoichiometric formalism is the same for any type of reaction and because a group can always be formally assumed to be an element or a bond, we consider only the most general case of GA reactions.[14] Let thus $g_j (j=1,2,...,s)$ be a set of groups from which the species can be assembled. Let further g_{ji} be the number of groups g_j in species B_i. We thus can define the matrix

$$\mathbf{g}' = \begin{bmatrix} g_{11} & g_{12} & \cdots & g_{1s} \\ g_{21} & g_{22} & \cdots & g_{2s} \\ \cdots & \cdots & \cdots & \cdots \\ g_{n1} & g_{n2} & \cdots & g_{ns} \end{bmatrix} \tag{12}$$

Often rank $\mathbf{g}' = q < s$. In such cases, the linearly independent columns in $\mathbf{g}'$ may be dropped so that we can define a matrix

$$\mathbf{g} = \begin{bmatrix} g_{11} & g_{12} & \cdots & g_{1q} \\ g_{21} & g_{22} & \cdots & g_{2q} \\ \cdots & \cdots & \cdots & \cdots \\ g_{n1} & g_{n2} & \cdots & g_{nq} \end{bmatrix} \tag{13}$$

such that rank $\mathbf{g} = q$. In what follows the matrix $\mathbf{g}$ is referred to as the group matrix. By analogy with chemical stoichiometry the stoichiometric matrix $\boldsymbol{\nu}$ may be derived from

$$\boldsymbol{\nu}\mathbf{g} = \mathbf{0} \tag{14}$$

In other words the GA reactions ρ are required to preserve the type and number of groups. As well-known from linear algebra, the number of linearly independent solutions of eq 14, i.e., the number of linearly independent GA reactions, $\boldsymbol{\rho}$, is equal to $m = n - \text{rank } \mathbf{g} = n - q$. For our purposes it is necessary to generate a particular set of linearly independent GA $\boldsymbol{\rho}$. This can be done as follows. Let, for instance

$$\begin{vmatrix} g_{11} & g_{12} & \cdots & g_{1q} \\ g_{21} & g_{22} & \cdots & g_{2q} \\ \cdots & \cdots & \cdots & \cdots \\ g_{q1} & g_{q2} & \cdots & g_{qq} \end{vmatrix} \neq 0 \tag{15}$$

Then, a set of m linearly independent GA reactions ρ_j-$(j=1,2,...,m)$

$$\rho_j = \nu_{j1}B_1 + \nu_{j2}B_2 + ... + \nu_{jn}B_n = 0 \qquad j = 1, 2, ..., m \tag{16}$$

may be generated as[14]

$$\nu_{jk} = \begin{vmatrix} g_{11} & g_{12} & \cdots & g_{1q} & 0 \\ g_{21} & g_{22} & \cdots & g_{2q} & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_{k-1,1} & g_{k-1,2} & \cdots & g_{k-1,q} & 0 \\ g_{k1} & g_{k2} & \cdots & g_{kq} & 1 \\ g_{k+1,1} & g_{k+1,2} & \cdots & g_{k+1,q} & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_{q1} & g_{q2} & \cdots & g_{q} & 0 \\ g_{q+j,1} & g_{q+j,2} & \cdots & g_{q+j,q} & 0 \end{vmatrix} \qquad k = 1, 2, ..., q \tag{17}$$

$$\nu_{j,q+h} = \delta_{j,q+h} \begin{vmatrix} g_{11} & g_{12} & \cdots & g_{1q} & 0 \\ g_{21} & g_{22} & \cdots & g_{2q} & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_{q1} & g_{q2} & \cdots & g_{qq} & 0 \\ g_{q+h,1} & g_{q+h,2} & \cdots & g_{q+h,q} & 1 \end{vmatrix} = \delta_{j,q+h} \begin{vmatrix} g_{11} & g_{12} & \cdots & g_{1q} \\ g_{21} & g_{22} & \cdots & g_{2q} \\ \cdots & \cdots & \cdots & \cdots \\ g_{q1} & g_{q2} & \cdots & g_{qq} \end{vmatrix} \qquad h = 1, 2, ..., m \tag{18}$$

where

$$\delta_{j,q+h} = \begin{cases} 1 & \text{if} \quad j = h \\ 0 & \text{if} \quad j \neq h \end{cases}$$

Using the properties of the determinants, the set of m linearly independent GA reactions obtained above may be presented in a more compact form as

$$\rho_j = \begin{vmatrix} g_{11} & g_{12} & \cdots & g_{1q} & B_1 \\ g_{21} & g_{22} & \cdots & g_{2q} & B_2 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_{q,1} & g_{q,2} & \cdots & g_{q,q} & B_q \\ g_{q+j,1} & g_{q+j,2} & \cdots & g_{q+j,q} & B_{q+j} \end{vmatrix} = 0 \qquad j = 1, 2, ..., m \tag{19}$$

Define further the vectors

$$\mathbf{E} = (E_1, E_2, ..., E_n)^{\mathrm{T}} \tag{20}$$

$$\mathbf{\Delta E} = (\Delta E_1, \Delta E_2, ..., \Delta E_m)^{\mathrm{T}} \tag{21}$$

where $E_i(i=1,2,...,n)$ is any appropriate thermochemical quantity of species B_i that may be used to characterize the RE, e.g., experimental enthalpy of formation, atomization energy, total energy, or enthalpy from ab initio calculations, HMO energy, etc., and $\Delta E_j(j=1,2,...,m)$ is the change in quantity E of the GA reactions $\rho_j(j=1,2,...,m)$. To avoid confusion, in what follows, the quantity E is simply referred to as energy. According to the conventional thermodynamic formalism the vectors **E** and **ΔE** are interrelated via

$$\mathbf{\Delta E} = \boldsymbol{\nu}\mathbf{E} \tag{22}$$

or

$$\Delta E_j = \nu_{j1}E_1 + \nu_{j2}E_2 + ... + \nu_{jn}E_n \qquad j = 1, 2, ..., m \tag{23}$$

Inserting here the stoichiometric coefficients of the GA reactions, eqs 17 and 18, we obtain

$$\Delta E_j = \begin{vmatrix} g_{11} & g_{12} & \cdots & g_{1q} & E_1 \\ g_{21} & g_{22} & \cdots & g_{2q} & E_2 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_{q,1} & g_{q,2} & \cdots & g_{q,q} & E_q \\ g_{q+j,1} & g_{q+j,2} & \cdots & g_{q+j,q} & E_{q+j} \end{vmatrix} \qquad j = 1, 2, ..., m \tag{24}$$

Preliminary Considerations

As shown below, the reason the RE depends on the stoichiometry of the reactions is that energy changes **ΔE** of the GA reactions $\boldsymbol{\rho}$ are different from zero. These quantities, however, can be made equal to zero by allowing the species energies $E_i(i=1,2,...,n)$ to vary. Thus, we introduce a fictive set of species energies $E_i^{\mathrm{eq}}(i=1,2,...,n)$ that are referred to as “equilibrium” energies

$$\mathbf{E}^{\mathrm{eq}} = (E_1^{\mathrm{eq}}, E_2^{\mathrm{eq}}, ..., E_n^{\mathrm{eq}})^{\mathrm{T}} \tag{25}$$

The “equilibrium” energies of the reference species are chosen so that the energy changes of the GA reactions ρ are precisely equal to zero, i.e.,

$$\mathbf{\Delta E}^{\mathrm{eq}} = \boldsymbol{\nu}\mathbf{E}^{\mathrm{eq}} = \mathbf{0} \tag{26}$$

In other words, the “equilibrium” energies of the reference species imply an absolute lack of any type of resonance, strain, hyperconjugation, differences in the type of bonds and hybridization, etc. The “equilibrium” energies may be evaluated as follows. Define the vector

$$\mathbf{e} = \mathbf{E} - \mathbf{E}^{\mathrm{eq}} \tag{27}$$

Subtracting eq 26 from eq 22 we have

$$\boldsymbol{\nu}\mathbf{e} = \mathbf{\Delta E} \tag{28}$$

Now, the vector **e** may be evaluated by minimizing the product $\mathbf{e}^{\mathrm{T}}\mathbf{e}$ subject to the constraints given by eq 28. For this purpose we employ the method of Lagrange’s undetermined multipliers and minimize the Lagrangean function

$$F = \mathbf{e}^{\mathrm{T}}\mathbf{e} + \lambda^{\mathrm{T}}(\boldsymbol{\nu}\mathbf{e} - \mathbf{\Delta E}) \tag{29}$$

with respect to **e** and $\boldsymbol{\lambda}$. The procedure results in a system of linear equations

$$2\mathbf{e} + \boldsymbol{\lambda}^{\mathrm{T}}\boldsymbol{\nu} = \mathbf{0} \tag{30}$$

$$\boldsymbol{\nu}\mathbf{e} = \mathbf{\Delta E} \tag{31}$$

The solution of eqs 30 and 31 is[16]

$$\mathbf{e} = \boldsymbol{\nu}^{\mathrm{T}}(\boldsymbol{\nu}\boldsymbol{\nu}^{\mathrm{T}})^{-1}\mathbf{\Delta E} \tag{32}$$

Notice that although the stoichiometric matrix $\boldsymbol{\nu}$ is generated arbitrarily, **e** is unique. That is, **e** is independent of the choice of $\boldsymbol{\nu}$.[16] Once **e** is known, the “equilibrium” energies of the reference species $\mathbf{E}^{\mathrm{eq}}$ are obtained from eq 27, i.e.,

$$\mathbf{E}^{\mathrm{eq}} = \mathbf{E} - \mathbf{e} \tag{33}$$

The Main Result

We are now in a position to formulate our main finding. Consider an arbitrary GA reaction ρ involving the reference species B_1, B_2, ..., B_n and the aromatic species B_{n+1}

$$\rho = \sum_{i=1}^{n}\nu_i\mathrm{B}_i + \nu_{n+1}\mathrm{B}_{n+1} = 0 \tag{34}$$

We define the RE of the species B_{n+1} as the energy change of reaction 34 (per 1 mol of B_{n+1}) as

$$\mathrm{RE} = \frac{1}{\nu_{n+1}}\sum_{i=1}^{n}\nu_iE_i^{\mathrm{eq}} + E_{n+1} \tag{35}$$

Our main result may be formulated as *the RE defined by eq 35 is independent of the choice of GA reactions*. The proof of this statement entirely follows the lines described in our previous work[16] and is not given here. Concomitantly, eq 35 may be considered as the stoichiometric formulation of the RE for a particular selection of reference species, groups and species energies. In particular, the RE given by eq 35 is equivalent to Dewar’s and Hess−Schaad’s RE.

Because the GA reaction, eq 34, may be selected arbitrarily, it is convenient to choose this reaction as a GA response reaction (RER).[14] We remind the reader that a GA RER is a reaction involving no more than $q + 1$ species. In our case, one of the species should always be B_{n+1} and the remaining q species may be arbitrarily selected from the set of reference species. Let the q reference species involved in a GA RER be B_{i_1}, B_{i_2}, ..., B_{i_q}, where i_1, i_2, ..., i_q is a set of integers satisfying the condition $1 \le i_1 < i_2 < ... < i_q \le n$. Let further the determinant of order q formed from the rows B_{i_1}, B_{i_2}, ..., B_{i_q} of the group matrix **g** be different from zero

$$\Delta = \begin{vmatrix} g_{i_1,1} & g_{i_2,2} & \cdots & g_{i_1,q} \\ g_{i_2,1} & g_{i_2,2} & \cdots & g_{i_2,q} \\ \cdots & \cdots & \cdots & \cdots \\ g_{i_q,1} & g_{i_q,2} & \cdots & g_{i_q,q} \end{vmatrix} \neq 0$$

TABLE 1: Experimental Enthalpies of Formation and Total Enthalpies at the G3 Level of the Reference Species Used To Evaluate of the RE of Benzene

	$\Delta H_{f,i}^{exp}$, kcal/mol[a]	H_i^{G3}, hartree[b]
1. CH_4	−17.9	−40.453813
2. C_2H_6	−20.1	−79.718912
3. C_2H_4	12.5	−78.503424
4. C_4H_6 (1,3-butadiene)	26.0	−155.840336
5. C_6H_{12} (cyclohexane)	−29.4	−235.615985
6. C_6H_{10} (cyclohexene)	−1.0	−234.40711
7. C_6H_8 (1,3-cyclohexadiene)	25.0	−233.200736
8. C_6H_8 (1,3,5-hexatriene)	40.1	−233.176173
9. C_6H_6 (benzene)	19.8	−232.046743

[a] Reference 17. [b] Reference 18.

Then, an arbitrary GA RER involving the species B_{n+1} and q reference species is given by[14]

$$g(B_{i_1}, B_{i_2}, ..., B_{i_q}, B_{n+1}) = \begin{vmatrix} g_{i_1,1} & g_{i_1,2} & \cdots & g_{i_1,q} & B_{i_1} \\ g_{i_2,1} & g_{i_2,2} & \cdots & g_{i_2,q} & B_{i_2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_{i_q,1} & g_{i_q,2} & \cdots & g_{i_q,q} & B_{i_q} \\ g_{n+1,1} & g_{n+1,2} & \cdots & g_{n+1,q} & B_{n+1} \end{vmatrix} = 0 \quad (36)$$

whereas the RE of the species B_{n+1} is

$$RE = \frac{1}{\Delta}\begin{vmatrix} g_{i_1,1} & g_{i_1,2} & \cdots & g_{i_1,q} & E_{i_1}^{eq} \\ g_{i_2,1} & g_{i_2,2} & \cdots & g_{i_2,q} & E_{i_2}^{eq} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ g_{i_q,1} & g_{i_q,2} & \cdots & g_{i_q,q} & E_{i_q}^{eq} \\ g_{n+1,1} & g_{n+1,2} & \cdots & g_{n+1,q} & E_{n+1} \end{vmatrix} \quad (37)$$

Example 1

Next, we illustrate the application of the proposed approach to the estimation of the RE of benzene employing the set of reference species involved in reactions 2−7. It should be noticed that the below calculations are presented for purely illustrative purposes and are not intended to provide a “better” value for the RE of benzene. First, we generate an arbitrary set of linearly independent GA reactions involving the reference species $B_1 = CH_2{=}CH_2$, $B_2 = CH_2{=}CH{-}CH{=}CH_2$, $B_3 = C_6H_{12}$ (cyclohexane), $B_4 = C_6H_{10}$ (cyclohexene), $B_5 = C_6H_8$ (1,3-cyclohexadiene), $B_6 = CH_4$, $B_7 = CH_3{-}CH_3$ and $B_8 = CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$. Because all of the reactions 2−7 are isodesmic, the natural choice of groups is the type of bond, i.e., g_1(C−H), g_2(C−C), and g_3(C=C). Thus, the group matrix is

$$\mathbf{g} = \begin{array}{c} \\ \\ \end{array}\begin{array}{ccc|c} g_1 & g_2 & g_3 & \\ \hline 4 & 0 & 1 & B_1 \\ 6 & 1 & 2 & B_2 \\ 12 & 6 & 0 & B_3 \\ 10 & 5 & 1 & B_4 \\ 8 & 4 & 2 & B_5 \\ 4 & 0 & 0 & B_6 \\ 6 & 1 & 0 & B_7 \\ 8 & 2 & 3 & B_8 \end{array}$$

Because rank $\mathbf{g} = 3$, the number of linearly independent GA (isodesmic) reactions is equal to $m = 8 - 3 = 5$. Employing the stoichiometric formalism described above, an arbitrary set of linearly independent GA reactions may be generated, for instance, as

$$\rho_1 = 3B_1 - 3B_2 - 2B_3 + 3B_4 = 0$$
$$\rho_2 = 6B_1 - 6B_2 - B_3 + 3B_5 = 0$$
$$\rho_3 = -6B_1 + 3B_2 - {}^1/_2\, B_3 + 3B_6 = 0$$
$$\rho_4 = -6B_1 + 3B_2 - B_3 + 3B_7 = 0$$
$$\rho_5 = -B_1 + 2B_2 - B_8 = 0$$

Thus, the stoichiometric matrix is

$$\boldsymbol{\nu} = \begin{array}{cccccccc|c} B_1 & B_2 & B_3 & B_4 & B_5 & B_6 & B_7 & B_8 & \\ \hline 3 & -3 & -2 & 3 & 0 & 0 & 0 & 0 & \rho_1 \\ 6 & -6 & -1 & 0 & 3 & 0 & 0 & 0 & \rho_2 \\ -6 & 3 & -{}^1/_2 & 0 & 0 & 3 & 0 & 0 & \rho_3 \\ -6 & 3 & -1 & 0 & 0 & 0 & 3 & 0 & \rho_4 \\ -1 & 2 & 0 & 0 & 0 & 0 & 0 & -1 & \rho_5 \end{array}$$

(a) Experimental RE. In this case E_i = experimental enthalpy of formation of the species $\Delta H^{\circ}_{f,i}$, kcal/mol (Table 1). The energy (enthalpy) changes of the GA reactions ρ_1, ρ_2, ρ_3, ρ_4, and ρ_5 may be easily evaluated thus resulting into the following vector $\mathbf{\Delta E}$

$$\mathbf{\Delta E} = (15.3, 23.4, -36.0, -27.9, -0.6)^T$$

Substituting $\boldsymbol{\nu}$ and $\mathbf{\Delta E}$ into eq 32 we obtain

$$e_1 = 4.9 \text{ kcal/mol} \qquad e_5 = -0.2 \text{ kcal/mol}$$
$$e_2 = 0.9 \text{ kcal/mol} \qquad e_6 = -3.0 \text{ kcal/mol}$$
$$e_3 = 0.0 \text{ kcal/mol} \qquad e_7 = -0.4 \text{ kcal/mol}$$
$$e_4 = 1.1 \text{ kcal/mol} \qquad e_8 = -2.5 \text{ kcal/mol}$$

whereas from eq 33

$$E_1^{eq} = 7.6 \text{ kcal/mol} \qquad E_5^{eq} = 25.2 \text{ kcal/mol}$$
$$E_2^{eq} = 25.1 \text{ kcal/mol} \qquad E_6^{eq} = -14.8 \text{ kcal/mol}$$
$$E_3^{eq} = -29.4 \text{ kcal/mol} \qquad E_7^{eq} = -19.7 \text{ kcal/mol}$$
$$E_4^{eq} = -2.1 \text{ kcal/mol} \qquad E_8^{eq} = 42.6 \text{ kcal/mol}$$

Now, with these “equilibrium” energies (enthalpies of formation) of the reference species and experimental enthalpy of formation of benzene any conceivable GA (isodesmic) reaction involving the reference species and benzene will result in precisely the same RE. For instance, according to eq 35 the experimental RE of benzene obtained from reactions 2−7 is

$$RE^{exp}(2) = -3E_7^{eq} - 3E_1^{eq} + 6E_6^{eq} + E_{C_6H_6}^{exp} = -3*(-19.7) - 3*(7.6) + 6*(-14.8) + 19.8 = -32.7 \text{ kcal/mol}$$

$$RE^{exp}(3) = -3E_4^{eq} + 2E_3^{eq} + E_{C_6H_6}^{exp} = -3*(-2.1) + 2*(-29.4) + 19.8 = -32.7 \text{ kcal/mol}$$

$$RE^{exp}(4) = -3E_2^{eq} + 3E_1^{eq} + E_{C_6H_6}^{exp} = -3*25.1 + 3*7.6 + 19.8 = -32.7 \text{ kcal/mol}$$

etc.

(b) Ab Initio, G3 Level RE. In this case E_i = total enthalpy at 298 K of the species, hartree/mol (Table 1). Hence, the vector of the energy changes $\mathbf{\Delta E}$ of the GA reactions ρ_1, ρ_2, ρ_3, ρ_4, and ρ_5 is

$$\mathbf{\Delta E} = (0.021376, -0.041215, 0.035249, -0.001075, -0.0539105)^{\mathrm{T}}$$

Inserting $\boldsymbol{\nu}$ and $\mathbf{\Delta E}$ into eq 32 and evaluating further $\mathbf{E}^{\mathrm{eq}}$ from eq 33 we obtain

$$E_1^{\mathrm{eq}} = -78.510735 \text{ hartree/mol} \qquad E_5^{\mathrm{eq}} = -233.200924 \text{ hartree/mol}$$

$$E_2^{\mathrm{eq}} = -155.841654 \text{ hartree/mol} \qquad E_6^{\mathrm{eq}} = -40.449171 \text{ hartree/mol}$$

$$E_3^{\mathrm{eq}} = -235.616130 \text{ hartree/mol} \qquad E_7^{\mathrm{eq}} = -79.718526 \text{ hartree/mol}$$

$$E_4^{\mathrm{eq}} = -234.408339 \text{ hartree/mol} \qquad E_8^{\mathrm{eq}} = -233.172573 \text{ hartree/mol}$$

Using these "equilibrium" ab initio total enthalpies of the species in eq 35 results in a theoretical RE that, again, is independent of the choice of the GA (isodesmic) reactions. Indeed, employing reactions 2, 3, etc., we obtain

$$\begin{aligned}\mathrm{RE}^{\mathrm{G3}}(2) &= -3E_7^{\mathrm{eq}} - 3E_1^{\mathrm{eq}} + 6E_6^{\mathrm{eq}} + E_{\mathrm{C_6H_6}} \\ &= -3*(-79.718526) - 3*(-78.510735) + 6*(-40.449171) + (-232.046743) \\ &= -0.053986 \text{ hartree/mol} = -33.9 \text{ kcal/mol}\end{aligned}$$

$$\begin{aligned}\mathrm{RE}^{\mathrm{G3}}(3) &= -3E_4^{\mathrm{eq}} + 2E_3^{\mathrm{eq}} + E_{\mathrm{C_6H_6}} \\ &= -3*(-234.408339) + 2*(-235.616130) + (-232.046743) \\ &= -0.053986 \text{ hartree/mol} = -33.9 \text{ kcal/mol}\end{aligned}$$

etc. It is seen that the experimental RE and the theoretical RE at G3 levels differ by 1.2 kcal.

TABLE 2: Group Matrix, HMO, and "Equilibrium" π Energies (β Units) of the Reference Species in Hess−Schaad's RE Model

	g_1	g_2	g_3	g_4	g_5	g_6	g_7	g_8	E_j	e_i	E_j^{eq}
B_1	2	0	0	0	0	1	0	0	4.472	0.006	4.466
B_2	2	1	0	0	0	2	0	0	6.988	−0.014	7.002
$B_2(2)$	2	2	0	0	0	3	0	0	9.518	−0.020	9.538
$B_2(3)$	2	3	0	0	0	4	0	0	12.053	−0.021	12.074
$B_2(4)$	2	4	0	0	0	5	0	0	14.592	−0.017	14.609
$B_2(5)$	2	5	0	0	0	6	0	0	17.134	−0.011	17.145
$B_2(6)$	2	6	0	0	0	7	0	0	19.676	−0.005	19.681
$B_2(7)$	2	7	0	0	0	8	0	0	22.219	0.002	22.217
$B_2(8)$	2	8	0	0	0	9	0	0	24.763	0.010	24.753
$B_2(9)$	2	9	0	0	0	10	0	0	27.307	0.018	27.289
$B_2(10)$	2	10	0	0	0	11	0	0	29.852	0.027	29.825
B_3	2	0	1	0	0	0	2	0	6.899	0.027	6.872
$B_3(2)$	2	0	2	0	0	0	2	1	9.332	0.024	9.308
$B_3(3)$	2	0	3	0	0	0	2	2	11.764	0.020	11.744
$B_3(4)$	2	0	4	0	0	0	2	3	14.196	0.016	14.180
$B_3(5)$	2	0	5	0	0	0	2	4	16.628	0.012	16.616
$B_3(6)$	2	0	6	0	0	0	2	5	19.060	0.009	19.051
$B_3(7)$	2	0	7	0	0	0	2	6	21.492	0.005	21.487
$B_3(8)$	2	0	8	0	0	0	2	7	23.924	0.001	23.923
$B_3(9)$	2	0	9	0	0	0	2	8	26.356	−0.003	26.359
$B_3(10)$	2	0	10	0	0	0	2	9	28.788	−0.007	28.795
B_4	2	1	2	0	0	0	4	0	11.831	0.016	11.815
B_5	2	2	3	0	0	0	6	0	16.763	0.006	16.757
B_6	2	3	4	0	0	0	8	0	21.694	−0.005	21.699
B_7	2	4	5	0	0	0	10	0	26.625	−0.017	26.642
B_8	3	0	0	1	0	1	2	0	9.446	−0.001	9.447
B_9	4	0	0	0	1	0	4	0	11.925	0.009	11.916
B_{10}	5	0	0	1	1	1	4	1	16.908	−0.018	16.926
B_{11}	5	0	0	1	1	0	6	0	16.920	0.023	16.897
B_{12}	6	0	0	0	2	0	6	1	19.394	−0.002	19.396
B_{13}	3	0	1	1	0	1	2	1	11.875	−0.007	11.882
B_{14}	3	0	2	1	0	1	2	2	14.302	−0.016	14.318
B_{15}	3	1	1	1	0	2	2	1	14.385	−0.033	14.418
B_{16}	2	3	2	0	0	3	2	1	16.913	−0.003	16.916
B_{17}	6	0	0	2	1	0	8	0	21.906	0.028	21.878
B_{18}	7	0	0	1	2	0	8	1	24.385	0.008	24.377
B_{19}	3	1	1	1	0	1	4	0	14.388	−0.001	14.389
B_{20}	3	1	2	1	0	1	4	1	16.814	−0.011	16.825
B_{21}	4	1	1	0	1	1	4	1	16.881	−0.007	16.888
B_{22}	4	3	2	0	1	2	6	1	24.319	−0.047	24.366

Example 2

Consider next the Hess−Schaad RE.[4] According to this model the set of reference species comprises 40 acyclic polyenes and the energies of the species E_i are equal to the Hückel molecular orbital (HMO) π energies in units of β. Hess and Schaad further consider 8 types of groups (bonds), namely, $g_1(\mathrm{H_2C{=}CH})$, $g_2(\mathrm{HC{=}CH})$, $g_3(\mathrm{H_2C{=}C})$, $g_4(\mathrm{HC{=}C})$, $g_5(\mathrm{C{=}C})$, $g_6(\mathrm{HC{-}CH})$, $g_7(\mathrm{HC{-}C})$, and $g_8(\mathrm{C{-}C})$. The group matrix $\mathbf{g}$ and the HMO π energies of the reference species are presented in Table 2. It is immediately deduced that rank $\mathbf{g} = 6$, and hence, two groups are redundant, that is, may be dropped out, for example, g_1 and g_3. The number of linearly independent GA reactions is, consequently, equal to $m = n - \text{rank } \mathbf{g} = 40-6 = 34$. An arbitrary set of linearly independent GA reactions, $\boldsymbol{\rho}$, and their energy changes, $\mathbf{\Delta E}$, obtained using eqs 19 and 24, is presented in Table 3. Inserting $\boldsymbol{\nu}$ and $\mathbf{\Delta E}$ in eq 32 readily yields the vector $\mathbf{e}$ (Table 2). As can be seen, $\mathbf{e}$ coincides with the difference between the HMO π energies of the reference species and their additive values, as evaluated by Hess and Schaad.[4] This is an illustration of the proof that the RE given by eq 35 is equivalent to Hess and Schaad's RE. Solving further eq 33 for $\mathbf{E}^{\mathrm{eq}}$ the RE may be evaluated employing an arbitrary GA reaction involving the reference species and B_{n+1}. As an example, consider the RE of benzene. In Hess and Schaad's notation this is species B_{23}. Because rank $\mathbf{g} = q = 6$, a GA RER in this system involves $q + 1 = 6 + 1 = 7$ species, that is, 6 arbitrarily selected reference species plus species B_{23}. For instance, selection of B_1, B_3, $B_3(8)$, B_8, B_{17}, and B_{20} is appropriate because the respective determinant from $\mathbf{g}$ is different from zero

$$\Delta = \begin{array}{c} \begin{array}{cccccc} g_2 & g_4 & g_g & g_6 & g_7 & g_8 \end{array} \\ \left[\begin{array}{cccccc} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 2 & 7 \\ 0 & 1 & 0 & 1 & 2 & 0 \\ 0 & 2 & 1 & 0 & 8 & 0 \\ 1 & 1 & 0 & 1 & 4 & 1 \end{array}\right] \end{array} \begin{array}{l} \\ B_1 \\ B_3 \\ B_3(8) \\ B_8 \\ B_{17} \\ B_{20} \end{array} = -14$$

According to eq 36 the respective GA RER is

$$g(\mathrm{B}_1, \mathrm{B}_3, \mathrm{B}_3(8), \mathrm{B}_8, \mathrm{B}_{17}, \mathrm{B}_{20}, \mathrm{B}_{23}) = \begin{vmatrix} 0 & 0 & 0 & 1 & 0 & 0 & \mathrm{B}_1 \\ 0 & 0 & 0 & 0 & 2 & 0 & \mathrm{B}_3 \\ 0 & 0 & 0 & 0 & 2 & 7 & \mathrm{B}_3(8) \\ 0 & 1 & 0 & 1 & 2 & 0 & \mathrm{B}_8 \\ 0 & 2 & 1 & 0 & 8 & 0 & \mathrm{B}_{17} \\ 1 & 1 & 0 & 1 & 4 & 1 & \mathrm{B}_{20} \\ 3 & 0 & 0 & 3 & 0 & 0 & \mathrm{B}_{23} \end{vmatrix}$$

$$= -14(-3\mathrm{B}_1 + {}^{18}/_{7}\mathrm{B}_3 + {}^{3}/_{7}\mathrm{B}_3(8) + 3\mathrm{B}_8 - 3\mathrm{B}_{20} + \mathrm{B}_{23}) = 0$$

This gives the RE

$$\mathrm{RE} = -\frac{1}{14}\begin{vmatrix} 0 & 0 & 0 & 1 & 0 & 0 & E_1^{\mathrm{eq}} \\ 0 & 0 & 0 & 0 & 2 & 0 & E_3^{\mathrm{eq}} \\ 0 & 0 & 0 & 0 & 2 & 7 & E_3(8)^{\mathrm{eq}} \\ 0 & 1 & 0 & 1 & 2 & 0 & E_8^{\mathrm{eq}} \\ 0 & 2 & 1 & 0 & 8 & 0 & E_{17}^{\mathrm{eq}} \\ 1 & 1 & 0 & 1 & 4 & 1 & E_{20}^{\mathrm{eq}} \\ 3 & 0 & 0 & 3 & 0 & 0 & E_{23} \end{vmatrix} = -\frac{1}{14}\begin{vmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 4.466 \\ 0 & 0 & 0 & 0 & 2 & 0 & 6.872 \\ 0 & 0 & 0 & 0 & 2 & 7 & 23.923 \\ 0 & 1 & 0 & 1 & 2 & 0 & 9.477 \\ 0 & 2 & 1 & 0 & 8 & 0 & 21.878 \\ 1 & 1 & 0 & 1 & 4 & 1 & 16.875 \\ 3 & 0 & 0 & 3 & 0 & 0 & 8.00 \end{vmatrix} = 0.39$$

This is precisely the same RE as estimated by Hess and Schaad.[4]

Discussion and Concluding Remarks

The dependence of the RE on the type of reaction schemes is due to the fact that the reference species are not entirely free of resonance, strain, hyperconjugation, differences in the types of bonds and hybridization, etc. Enforcing a given set of reference species to be free of any type of resonance or strain completely eliminates the dependence of the RE on the choice of reactions. In this work we proposed a new approach to the complete elimination of the energetic differences among the reference species that represents a modification of the ordinary least-squares method. More specifically, the ordinary least-squares method is reformulated in terms of specially defined, GA reactions. As a result, any energetic formulation of the RE may be explicitly associated with the energy change of an arbitrarily selected GA reaction.

TABLE 3: Set of Linearly Independent GA Reactions and Their HMO π Energy Changes (β Units) for the Hess−Schaad RE Model

	ΔE_j
$\rho_1 = \mathrm{B}_1 - 2\mathrm{B}_2 + \mathrm{B}_2(2) = 0$	0.014
$\rho_2 = 2\mathrm{B}_1 - 3\mathrm{B}_2 + \mathrm{B}_2(3) = 0$	0.033
$\rho_3 = 3\mathrm{B}_1 - 4\mathrm{B}_2 + \mathrm{B}_2(4) = 0$	0.056
$\rho_4 = 4\mathrm{B}_1 - 5\mathrm{B}_2 + \mathrm{B}_2(5) = 0$	0.082
$\rho_5 = 5\mathrm{B}_1 - 6\mathrm{B}_2 + \mathrm{B}_2(6) = 0$	0.108
$\rho_6 = 6\mathrm{B}_1 - 7\mathrm{B}_2 + \mathrm{B}_2(7) = 0$	0.135
$\rho_7 = 7\mathrm{B}_1 - 8\mathrm{B}_2 + \mathrm{B}_2(8) = 0$	0.163
$\rho_8 = 8\mathrm{B}_1 - 9\mathrm{B}_2 + \mathrm{B}_2(9) = 0$	0.191
$\rho_9 = 9\mathrm{B}_1 - 10\mathrm{B}_2 + \mathrm{B}_2(10) = 0$	0.220
$\rho_{10} = -2\mathrm{B}_3 + \mathrm{B}_8 + \mathrm{B}_9 - \mathrm{B}_{10} + \mathrm{B}_3(2) = 0$	−0.003
$\rho_{11} = -3\mathrm{B}_3 + 2\mathrm{B}_8 + 2\mathrm{B}_9 - 2\mathrm{B}_{10} + \mathrm{B}_3(3) = 0$	−0.007
$\rho_{12} = -4\mathrm{B}_3 + 3\mathrm{B}_8 + 3\mathrm{B}_9 - 3\mathrm{B}_{10} + \mathrm{B}_3(4) = 0$	−0.011
$\rho_{13} = -5\mathrm{B}_3 + 4\mathrm{B}_8 + 4\mathrm{B}_9 - 4\mathrm{B}_{10} + \mathrm{B}_3(5) = 0$	−0.015
$\rho_{14} = -6\mathrm{B}_3 + 5\mathrm{B}_8 + 5\mathrm{B}_9 - 5\mathrm{B}_{10} + \mathrm{B}_3(6) = 0$	−0.019
$\rho_{15} = -7\mathrm{B}_3 + 6\mathrm{B}_8 + 6\mathrm{B}_9 - 6\mathrm{B}_{10} + \mathrm{B3}(7) = 0$	−0.023
$\rho_{16} = -8\mathrm{B}_3 + 7\mathrm{B}_8 + 7\mathrm{B}_9 - 7\mathrm{B}_{10} + \mathrm{B}_3(8) = 0$	−0.027
$\rho_{17} = -9\mathrm{B}_3 + 8\mathrm{B}_8 + 8\mathrm{B}_9 - 8\mathrm{B}_{10} + \mathrm{B}_3(9) = 0$	−0.031
$\rho_{18} = -10\mathrm{B}_3 + 9\mathrm{B}_8 + 9\mathrm{B}_9 - 9\mathrm{B}_{10} + \mathrm{B}_3(10) = 0$	−0.035
$\rho_{19} = 2\mathrm{B}_1 - \mathrm{B}_2 - 2\mathrm{B}_3 + \mathrm{B}_4 = 0$	−0.011
$\rho_{20} = 4\mathrm{B}_1 - 2\mathrm{B}_2 - 3\mathrm{B}_3 + \mathrm{B}_5 = 0$	−0.022
$\rho_{21} = 6\mathrm{B}_1 - 3\mathrm{B}_2 - 4\mathrm{B}_3 + \mathrm{B}_6 = 0$	−0.034
$\rho_{22} = 8\mathrm{B}_1 - 4\mathrm{B}_2 - 5\mathrm{B}_3 + \mathrm{B}_7$	−0.046
$\rho_{23} = \mathrm{B}_1 - \mathrm{B}_8 - \mathrm{B}_9 + \mathrm{B}_{11} = 0$	0.021
$\rho_{24} = \mathrm{B}_8 - \mathrm{B}_9 - \mathrm{B}_{10} + \mathrm{B}_{12} = 0$	0.007
$\rho_{25} = -\mathrm{B}_3 + \mathrm{B}_9 - \mathrm{B}_{10} + \mathrm{B}_{13} = 0$	−0.007
$\rho_{26} = -2\mathrm{B}_3 + \mathrm{B}_8 + 2\mathrm{B}_9 - 2\mathrm{B}_{10} + \mathrm{B}_{14} = 0$	−0.016
$\rho_{27} = \mathrm{B}_1 - \mathrm{B}_2 - \mathrm{B}_3 + \mathrm{B}_9 - \mathrm{B}_{10} + \mathrm{B}_{15} = 0$	−0.013
$\rho_{28} = 3\mathrm{B}_1 - 3\mathrm{B}_2 - 2\mathrm{B}_3 + \mathrm{B}_8 + \mathrm{B}_9 - \mathrm{B}_{10} + \mathrm{B}_{16} = 0$	0.030
$\rho_{29} = 2\mathrm{B}_1 - 2\mathrm{B}_8 - \mathrm{B}_9 + \mathrm{B}_{17} = 0$	0.033
$\rho_{30} = \mathrm{B}_1 - \mathrm{B}_9 - \mathrm{B}_{10} + \mathrm{B}_{18} = 0$	0.024
$\rho_{31} = 2\mathrm{B}_1 - \mathrm{B}_2 - \mathrm{B}_3 - \mathrm{B}_8 + \mathrm{B}_{19} = 0$	−0.001
$\rho_{32} = 2\mathrm{B}_1 - \mathrm{B}_2 - 2\mathrm{B}_3 + \mathrm{B}_9 - \mathrm{B}_{10} + \mathrm{B}_{20} = 0$	−0.011
$\rho_{33} = \mathrm{B}_1 - \mathrm{B}_2 - \mathrm{B}_3 + \mathrm{B}_8 - \mathrm{B}_{10} + \mathrm{B}_{21} = 0$	0.004
$\rho_{34} = 4\mathrm{B}_1 - 3\mathrm{B}_2 - 2\mathrm{B}_3 + \mathrm{B}_8 - \mathrm{B}_{10} + \mathrm{B}_{22} = 0$	−0.017

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