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An Alternative Approach to the Problem of Assessing Stabilization Energies in Cyclic Conjugated Hydrocarbons

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Reactions are described that provide an alternative basis for evaluating stabilization energies of cyclic conjugated hydrocarbons. These reactions involve no changes in hybridization of carbon atoms and minimal changes in the nature of the carbon-hydrogen bonds. Such reactions exemplify those structural features that lead to stabilization. Theoretical and experimental molecular indices are introduced as a measure of these stabilizing effects. Calculated values of these indices are compared to experimental results.

Key words: Cyclic conjugated hydrocarbons – Hydrocarbons, cyclic conjugated ~, stabilization energy of ~

1. Introduction

The empirical resonance energy, as determined either from heats of combustion [1], heats of hydrogenation [1], or ethane reduction [2], actually includes contributions from (1) changes in hybridization as well as (2) changes in σ bond compression energies in reactants and products which have nothing to do with electron delocalization. In fact, Dewar and Schmeising [2, 3] have estimated that only about a quarter of the resonance energy observed in the ethane reduction of benzene is due to electron delocalization. Furthermore, when the theoretical resonance energy is defined as the difference between the energy of a molecule and the energy of some appropriate localized structure [4–8], it can not be equated directly to the empirical resonance energy. Essentially, this is due to the fact that the empirical resonance energy, as obtained from the conventional procedures, corresponds to ΔH^0 for a real chemical reaction, whereas the theoretical resonance energy, as defined above, is ΔH^0 for the conversion of a hypothetical structure with localized bonds into the actual molecule [9].

It is the purpose of this paper to consider an alternative molecular index with which to gauge the enhanced stability of conjugated cyclic hydrocarbons and similar structures. This index has the following features: (1) the theoretical index is defined as a reaction parameter which facilitates direct comparison between theory and experiment; (2) energy contributions due to changes in hybridization of carbon atoms in reactants and products are eliminated; (3) energy contributions due to changes in the nature of carbon-hydrogen bonds in reactants and products are minimized.

2. General Definitions

We define an homodesmotic reaction as one in which (1) there are equal numbers of carbon atoms in their various states of hybridization in reactants and products and (2) there is a matching of carbon-hydrogen bonds in terms of the number of hydrogen atoms joined to individual carbon atoms in reactants and products. For example, benzene can, in principle, be formed from 1-3 butadiene[1]

$$3CH_2{=}CH{-}CH{=}CH_2 \rightarrow C_6H_6 + 3CH_2{=}CH_2 . \tag{1}$$

In this reaction all carbon atoms are sp^2 hybridized and the carbon-hydrogen bonds are matched in that there are equal numbers of such bonds with one and two hydrogen atoms joined to the carbon atoms in reactants and products. Similar reactions can be established for all the annulenes using only butadiene and ethylene. Such reactions are special cases of isodesmic reactions introduced by Pople *et al.* [10, 11][2,3].

It is not possible, however, to construct an homodesmotic reaction for the polycyclic hydrocarbons, using only butadiene and ethylene. For example, if we attempt to form naphthalene as

$$6CH_2{=}CH{-}CH{=}CH_2 \rightarrow C_{10}H_8 + 7CH_2{=}CH_2 \tag{2}$$

or, in general, any polycyclic hydrocarbon C_aH_b as

$$\left(\frac{2a-b}{2}\right) CH_2{=}CH{-}CH{=}CH_2 \rightarrow C_aH_b + \left(\frac{3a-2b}{2}\right) C_2H_4 , \tag{3}$$

there are unequal numbers of carbon atoms with either zero, one, or two hydrogen atoms attached in reactants and products which violates the definition of an homodesmotic reaction. However, all carbon atoms are sp^2 hybridized and the reaction is isodesmic. An homodesmotic reaction can be established by using different reactants. For example, divinyl-ethylene (DVE, 2-vinyl-butadiene) [12] or tetravinyl-ethylene (TVE, 2, 3-divinyl-hexatriene) can be used to make naphthalene

$$2DVE + 2CH_2{=}CH{-}CH{=}CH_2 \rightarrow C_{10}H_8 + 5CH_2{=}CH_2 , \tag{4}$$

$$TVE + 2CH_2{=}CH{-}CH{=}CH_2 \rightarrow C_{10}H_8 + 4CH_2{=}CH_2 . \tag{5}$$

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[1] Trans-butadiene has been used throughout this work.

[2] Hehre *et al.* [10] match formal single and double bonds.

[3] While homodesmotic reactions may be regarded as a special case of isodesmic reactions, as defined in [10], the matching, not only of the hybridization but also the bonded atoms, puts them in a class of their own. All homodesmotic reactions are isodesmic but few isodesmic reactions are homodesmotic.

Here all carbon atoms are still sp^2 hybridized, but there are now equal numbers of carbon atoms with zero, one, and two hydrogen atoms attached in reactants and products as required by the definition. By appropriately adjusting the stoichiometry, similar homodesmotic reactions can be established for the other polycyclic hydrocarbons.

We emphasize that, if one assumes the stability of the polycyclic hydrocarbons is predominantly due to electron delocalization then it is more appropriate to base measurements and calculations of stability on either of the homodesmotic reactions (4) or (5) rather than the isodesmic reactions (3), since (3) involves the conversion of $(C_d\text{–}H)_2$ bonds into $(C_d\text{–}H)_1$ bonds [13], which would entail an energy change and has nothing to do with electron delocalization. However, it must be noted that stability considerations based on reaction (3) are still a significant improvement over the conventional reduction reactions, e.g. by cyclohexane or ethane [1, 2], that involve further changes in carbon-carbon bonds.

Next we define the experimental homodesmotic stabilization energy (HSE) as ΔH^0 for the homodesmotic reaction, with the necessary change of sign so as to refer to a positive quantity. HSE is easily obtained once ΔH_f^0 has been determined for each molecule in the reaction. Finally, we define the theoretical molecular orbital stabilization energy (HMOSE) as the difference in the total energy of the reactants and products in an homodesmotic reaction. HMOSE is easily obtained once the ground state energy of each molecule in the reaction has been calculated. The corresponding quantities for the isodesmic reaction (3) will be labeled ISE and IMOSE respectively.

We realize that the energy change in an homodesmotic reaction is not due solely to electron delocalization[4], nor is it solely a property of the molecule being investigated. For example, the homodesmotic reactions (4) and (5) for the polycyclic hydrocarbons involve either DVE or TVE, which in all probability are non-planar[5]. Structural features of this kind would certainly be reflected in the numerical values of HSE and HMOSE. However, DVE and TVE were chosen because they are the smallest acyclic structures that provide us with the necessary sp^2 carbon atom with no hydrogen atoms attached, in order to achieve exact matching in the types of C–H bonds in reactants and products.

Inevitably a proper comparison of a stabilization energy calculated from theory with the value obtained from experimental thermochemical data depends upon the theoretical calculation utilizing whatever geometry is appropriate for the reactant and product species. Hence in using butadiene as the acyclic polyene the *trans* conformation is required, since this is by far the predominant form at 298 °K. Likewise when the heats of formation for DVE and TVE have been determined, enabling the evaluation of HSE values based on reactions (4) and (5), it will be necessary for the theoretical calculations of their energies, from which

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[4] In fact it is impossible to write down a chemical reaction involving cyclic and acyclic structures in which the energy difference between reactants and products is due only to electron delocalization. For example, although the C–H bonds in benzene are matched as closely as they can be, according to chemical type, with the C–H bonds on C_2 and C_3 in butadiene, it cannot be maintained that the contributions of these bonds to the total molecular energies are identical.

[5] In computing HMOSE in later sections of this paper, we have taken DVE to be planar.

the HMOSE values are obtained, to reflect whatever the individual geometries may be.

DVE, TVE, ethylene and butadiene simply serve to set a reference level from which we measure the enhanced molecular stability of the polycyclic hydrocarbons. If a molecule other than DVE or TVE (which includes the necessary sp^2 carbon atom with no hydrogen atoms attached) were chosen as the reactant species, the reference level would be correspondingly shifted. But this in no way detracts from the usefulness of the homodesmotic reaction concept. In the last analysis all evaluations of stabilization energies from thermochemical data are reaction parameters and consequently depend on the choice of comparison molecules. Homodesmotic reactions serve to minimize extraneous structural effects contributing to the quantity identified as the stabilization energy.

In the next section we use the results of calculations of ground state energies that have appeared in the literature to calculate HMOSE and IMOSE for a few representative cyclic hydrocarbons. Unfortunately since no ΔH_f^0 data are presently available for TVE or DVE, HSE values cannot be included[6].

3. Calculation of HMOSE and IMOSE

3.1. *Ab initio*

Using the ground state energies currently available from *ab initio* calculations, the HMOSE of benzene can be calculated from reaction (1), where, for consistency we have evaluated HMOSE within a fixed basis. Only the STO-3G basis of Hehre *et al.* [14, 15], and the Gaussian lobe basis of Buenker and Peyerimhoff [6] have been used on all three molecules necessary to determine this index for benzene[7]. The results, see Table 1, are in substantial agreement with the experimental HSE, with the more flexible STO-3G basis yielding a somewhat better result. Apparently no *ab initio* results are available for the ground state energy of DVE or TVE and hence no HMOSE for the polycyclic hydrocarbons can be calculated. However, IMOSE values for naphthalene and azulene can be determined in the Gaussian lobe basis, see Table 1. For these considerably larger molecules the results show the correct qualitative behavior but are not in quantitative agreement with the corresponding ISE. This is to be expected for these isomers since the calculation of the necessary ground state energies was made possible only by utilizing a rather inflexible basis set [17]. Unfortunately, sufficiently accurate *ab initio* values of ground state energies of these and other large conjugated hydrocarbons, that would allow a further quantitative comparison to be made are not currently available.

3.2. *Semiempirical*

We calculate the total molecular energy in semiempirical theories under the usual assumption of separability of the π and σ energy contribution. Thus

$$E = E_\pi + E_\sigma , \tag{6}$$

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[6] Work is currently in progress to determine ΔH_f^0 for DVE.

[7] We thank Dr. W. J. Hehre for supplying us with some necessary data.

Table 1. *Ab initio* evaluations (kcal/mol)[e]

	HMOSE in basis		IMOSE in basis		
Molecule	STO-3G[a]	FGGL[b]	FGGL[b]	HSE[c]	ISE[c]
Benzene[d]	35.9	39.7	39.7	21.17	21.17
Naphthalene	—	—	66.4	—	30.82
Azulene	—	—	16.1	—	0.83
Cyclobutadiene	—	—	−70.0	—	—

[a] Ground state energy of benzene from: Hehre, W.J., Radom, L., Pople, J.A.: J. Am. Chem. Soc. **94**, 1496 (1972). Butadiene; Radom, L., Pople, J.A.: J. Am. Chem. Soc. **92**, 4786 (1970). Ethylene; Hehre, W.J., Ditchfield, R., Radom, L., Pople, J.A. [10].

[b] Fixed Group Gaussian Lobe Function basis, ground state energy of benzene from: Buenker, R.J., Whitten, J.L., Petke, J.D.: J. Chem. Phys. **49**, 2261 (1968). Naphthalene and Azulene; Buenker, R.J., Peyerimhoff, S.C.: Chem. Phys. Letters **3**, 37 (1969). Cyclobutadiene; Butadiene; Buenker, R.J., Whitten, J.L.: J. Chem. Phys. **49**, 5381 (1968). Ethylene; Buenker, R.J., Peyerimhoff, S.D., Whitten, J.L.: J. Chem. Phys. **46**, 2029 (1967)

[c] See footnotes to Table2.

[d] The homodesmotic and isodesmic reactions for benzene are the same.

[e] 1 a.u. ≡627.261 kcal/mol.

where E_π is the total π electron energy calculated using either SCF or HMO theories, and E_σ is the total energy of all the σ bonds in the molecule calculated in some approximation. Thus we express the HMOSE and IMOSE as

$$\Delta E_\pi + \Delta E_\sigma \tag{7}$$

where ΔE_π and ΔE_σ are the difference in total π energy and total σ energy respectively of reactants and products.

The isodesmic reaction (3) for the formation of polycyclic hydrocarbons yields for ΔE_π

$$\begin{aligned}\Delta E_\pi = E_\pi(\mathrm{C_aH_b}) + \left(\frac{3a-2b}{2}\right) E_\pi(\mathrm{C_2H_4}) \\ - \left(\frac{2a-b}{2}\right) E_\pi(\mathrm{C_4H_6}),\end{aligned} \tag{8}$$

while that for the homodesmotic reaction (4) yields

$$\begin{aligned}\Delta E_\pi &= E_\pi \text{ (polycyclic)} + Z E_\pi \text{ (ethylene)} \\ &- X E_\pi \text{ (divinyl-ethylene)} - Y E_\pi \text{ (butadiene)}.\end{aligned} \tag{9}$$

with X, Y, Z chosen to fit the stoichiometry of the reaction.

3.2.1. HMO Theory

The π energy difference ΔE_π is easily evaluated using simple HMO theory. To account for the σ energy we follow the recent work of Schaad and Hess [18–21] and write for the σ energy contribution

$$\begin{aligned}E_\sigma &= \sum_i E^\sigma_{\mathrm{CC}}(i) + \sum_i E^\sigma_{\mathrm{CH}}(i) \\ &= \sum E^\sigma_{\mathrm{CC}}(i) + N_{\mathrm{CH}} E^\sigma_{\mathrm{CH}}\end{aligned} \tag{10}$$

such that $E_{\mathrm{CC}}^{\sigma}(i)$ is the σ energy of an sp^2-sp^2 carbon-carbon bond of length r, E_{CH} the energy of an sp^2-s carbon-hydrogen bond and N_{CH} is the number of such bonds. Imagining these σ bonds to be compressed "pure" sp^2-sp^2 bonds, then

$$E_{\mathrm{CC}}^{\sigma}(i) = E_{\mathrm{CC}} - \tfrac{1}{2}\varepsilon(r_i - r')^2 \tag{11}$$

in the harmonic approximation of Figeys and Dedieu [22–24] and Schaad and Hess. We take the equilibrium bond length $r' = 1.517$ Å and $\varepsilon = 5.5 \times 10^5$ dyn cm^{-1} [22], recognizing the approximation involved in assuming the same force constant for every bond. The harmonic potential compression energies E_h^{σ} are determined by making use of the analytic relation between bond length r_{ij} and bond-order P_{ij} found by Figeys and Dedieu, [22] namely

$$r_{ij} = \frac{\varepsilon r' - 1.5(\varepsilon r' - \delta r'')P_{ij}}{\varepsilon - 1.5(\varepsilon - \delta)P_{ij}} \tag{12}$$

obtained by minimizing the total molecular energy with respect to the bond length. The bond length is given in Å, $\delta = 7.6 \times 10^5$ dyn cm^{-1} and $r'' = 1.397$ Å [22]. Thus, the IMOSE is given for reaction (3) by

$$\Delta E_\pi - E_h^{\sigma}(\mathrm{C_aH_b}) - \left(\frac{3a-2b}{2}\right)E_h^{\sigma}(\mathrm{C_2H_4}) + \left(\frac{2a-b}{2}\right)E_h^{\sigma}(\mathrm{C_4H_6}) \tag{13}$$

with

$$E_h^{\sigma}(X) = \tfrac{1}{2}\varepsilon\sum_i (r_i - r')^2$$

the summation being carried out over all bonds in molecule X, ΔE_π is given in Eq. (8). The HMOSE for reaction (4) is given by a similar expression. Results calculated in this fashion for a number of cyclic hydrocarbons appear in Table 2.

Inspection of Table 2 shows that the HMOSE and IMOSE have different values, which is to be expected even in HMO theory where all carbon-hydrogen bonds are treated identically, since different reactions are involved. For the benzenoid hydrocarbon series (1–8) there is moderate agreement between IMOSE and ISE values where experimental results are available. Agreement is not as good for the non-alternates, as would be expected, since the assumption that the coulombic integral in HMO theory is a constant of the molecule in which it appears is not valid for the non-alternates [25].

In the Schaad and Hess calculations of resonance energies, the bond energies and the value of β were evaluated by a regression analysis [18] on the calculated and experimental heats of atomization via a series of constraints. However, if the atoms in acyclic conjugated olefins are to be specified according to whether they are singly or doubly bonded, and according to the number of hydrogen atoms connected, it is not possible to avoid some arbitrary π or $(\pi + \sigma)$ bond energy assignments [18, 20].

The present alternative approach to stabilization avoids this problem. The parameters E_{CC}^{0} and E_{CH}^{σ}, which cannot be conveniently evaluated, have canceled between reactants and products in either the homodesmotic reaction (4) or the isodesmic reaction (3).

Table 2. HMO[a] evaluations (kcal/mol)

Molecule	IMOSE[b]	ISE[c]	HMOSE[d]	TRE[e]
1. Benzene	21.17	21.17	21.17	13.31
2. Naphthalene	30.78	33.46	34.29	18.08
3. Anthracene	38.52	42.84	45.56	21.56
4. Biphenyl	38.91	41.04[f]	42.43	—
5. Phenanthrene	43.28	49.24[f]	50.31	25.02
6. Tetracene	45.79	56.77	53.98	24.63
7. Pyrene	47.30	62.97	57.85	26.38
8. Coronene	74.61	—	95.70	—
9. Fulvene	1.87	3.65[g,h]	3.59	− 0.39
10. Azulene	21.72	− 3.99	22.93	7.54

[a] HMO values from Coulson, C. A., Streitwieser, A.: Dictionary of π-electron calculations. San Francisco, California: W. H. Freeman 1965.

[b] The value of β was taken to be 41.83 kcal/mol. This value was found by equating the $(\pi+\sigma)$ energy for benzene to the ISE.

[c] Heat of formation values from Cox and Pilcher [13]. No adjustments have been made for zero point energy differences or corrections to 0 °K.

[d] The value of β was again taken to be 41.83 kcal/mol.

[e] Total resonance energy from Schaad and Hess [18].

[f] ΔH_f^0 corrected for steric hindrance; biphenyl 1.4, phenanthrene 0.7 kcal/mol respectively. George, P.: A critique of the resonance energy concept with particular reference to nitrogen-heterocycles, especially porphyrins, Chem. Rev. **75**, 85 (1975).

[g] ΔH_f^0 calculated from the value for dimethyl fulvene, +32.1 kcal/mol, using the increment [ΔH_f^0 (toluene) $-\Delta H_f^0$ (isopropylbenzene)] = 11.03 kcal/mol.

[h] Value includes a correction of 5.8 kcal/mole for the strain energy in the 5-membered ring [13], see also George, P. *loc. cit.*

The total resonance energies (TRE) of Schaad and Hess [18] have also been included in Table 2 for purposes of comparison. It should be noted that the IMOSE, HMOSE, and TRE values are not the same but do follow, in most cases, the same general trend.

3.2.2. SCF

Several semiempirical SCF calculations of the ground state energy of various conjugated hydrocarbons have appeared in the literature. Among the more successful of these, particular in predicting heats of atomization, has been the series of papers by Dewar *et al.* [8, 26–28]. This treatment is essentially a version of the Pople method [29, 30], i.e., an SCF-LCAO-MO approximation on the π electrons in which differential overlap is neglected, and the one electron core resonance integrals (β) are estimated using the thermocycle of Dewar and Schmeising [2]. The σ bond energies were automatically estimated in the course of determining β from this same thermocycle. Using the procedure of Dewar and de Llano [28], the HMOSE and IMOSE can be evaluated for many cyclic hydrocarbons. Some representative results are given in Table 3. The predicted values for IMOSE are in quite good agreement with the corresponding ISE for reaction (3). For purposes of comparison we have also included in Table 3 the resonance energy, RE of these molecules calculated by Dewar and de Llano [28]. Although superficially there is some resemblance between Dewar and de Llano's use of a

Table 3. SCF evaluations (kcal/mol)

Molecule	IMOSE	HMOSE[a]	RE[a]
1	21.33	21.33	20.04
2	33.62	34.08	30.51
3	41.81	42.73	36.90
4	42.73	43.19	39.18
5	49.49	50.41	44.57
6	—	—	—
7	54.66	56.04	42.02
8	93.16	94.89	81.26
9	2.28	2.61	1.08
10	7.10	7.47	3.09

[a] Calculated heats of atomization and resonance energies (RE) from Dewar and de Llano [28].

linear polyene structure in their calculations of a resonance energy for benzene and other polycyclic hydrocarbons and our use of butadiene in the calculation of HMOSE (IMOSE), there is the fundamental difference that in their treatment averaged properties are employed in the evaluation of the energy of their reference structure, whereas in our homodesmotic reaction approach the reference structure is a real molecule, 1-3 butadiene with its own unique physical properties. Again it should be noted that the HMOSE, IMOSE, and RE values are not identical but do follow in most cases the same general trend.

Unfortunately most other semiempirical SCF evaluation of molecular energies have included only the contribution from the π electrons or at most the π electrons and a core repulsion, which does not represent the entire ground state energy of the molecule. However, if it is assumed that the difference in the remaining contributions to the ground state energy between reactants and products is small, the HMOSE or IMOSE can be approximately calculated. Preliminary results using the parametrization of Simmons[8] [31], indicate that if only the total π energy is used, theory and experiment are in poor agreement. If both the π energy and a framework repulsion energy are included, agreement is greatly improved.

4. Concluding Remarks

We have proposed an alternative molecular index – the energy change in an homodesmotic reaction, HMOSE – to serve as a *quantitative* measure of stability in conjugated organic systems. This index contains no energy contribution from changes in hybridization of carbon atoms, and a minimal contribution from changes in the nature of C–H bonds. As such, it provides an excellent practical measure of those structural features that lead to molecular stabilization.

Furthermore an inspection of Tables 2 and 3 show clearly that the *qualitative* features of HMOSE are quite similar to those of the theoretical resonance energy as defined by Dewar and also employed by Schaad and Hess. This is important since these authors have shown a significant *qualitative* correlation between their theoretical values and experimental considerations of aromaticity.

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[8] We thank Dr. H. E. Simmons and Dr. M. D. Gordon for some necessary data.

Since HMOSE (1) possess qualitative features similar to the theoretical resonance energy; (2) has the distinct advantage of being unambiguously comparable to experimental results, and (3) contains a minimum of extraneous energy contributions, it is most appropriate to define molecular stabilization in terms of homodesmotic reactions.

Note Added in Proof. In reactions involving combinations of *sp*, sp^2 and sp^3 hybridized carbon atoms the definition of an homodesmotic reaction requires more stringent condition than those given in this paper. These will be treated in a forthcoming publication.

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