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QUANTUM-CHEMICAL STUDIES ON THE AROMATICITY OF CONJUGATED SYSTEMS

RE-EVALUATION OF THE "THERMODYNAMICAL" VALUE OF β AND CALCULATION OF THE HEAT OF ATOMIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY THE IMPROVED HUCKEL-METHOD*†

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Abstract—The total π-energy and σ-compression energy of a series of benzenoid aromatic hydrocarbons have been calculated by the iterative β-procedure developed recently.[13] By regression analysis of the relation between the experimental and calculated heats of atomization ΔH_f°, we have obtained the following values:

$$E^{\sigma}(C_{sp_2}\text{—H}) = 4{\cdot}314\,\text{eV}$$

$$E^{\sigma}(C_{sp_2}\text{—}C_{sp_2}) = 3{\cdot}726\,\text{eV, for } R(C_{sp_2}\text{—}C_{sp_2}) = 1{\cdot}517\,\text{Å}$$

$$\beta^{\pi}_{CC} = 1{\cdot}292\,\text{eV, for } R_{CC} = 1{\cdot}40\,\text{Å}$$

The method was then used to calculate ΔH_f°-values for a series of open-chain as well as cyclic, alternant and non-alternant, fully conjugated hydrocarbons: agreement with experimental values is very good.

I. INTRODUCTION

IN RECENT years, several authors emphasized the importance of hybridization on bond lengths and bond energies[1–7] and its effect on the thermochemical properties of organic compounds. In the field of planar fully conjugated molecules, the inaccessibility of the necessary bond energy values, due to the absence of suitable model molecules, led quantum organic chemists to compare calculated π-bonding energies to vaguely defined experimental quantities, such as "resonance energies". Dewar[8–11] was the first to realize the unsound basis of such confrontations and proposed as a test for any thoretical approach the calculation of the *heat of atomization*, i.e. the heat of formation ΔH_f° from atoms in the gas phase. He showed that the results obtained by a semi-empirical SCF–MO treatment based on the Pople method[12] and a thermocycle[1] determining the one-electron core resonance integrals (β^c), agreed with experiment to within the limits of experimental error in almost every case.

Careful analysis of the approximations and assumptions involved in his calculations led Dewar[10] to the conclusion that the early successes of the HMO method in interpreting "resonance energies" were due essentially to chance; in fact, the only series of molecules where "reasonable" results might be expected by the HMO method

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* For a detailed description of this theory, see Ref 13.

† Throughout this paper, the conversion factor of electron-volts to SI-units is: 1 eV = $1{\cdot}6021.10^{-19}$ J.

should be the benzenoid aromatic hydrocarbons. This conclusion emerged by considering that in this series of compounds:

1. No extra π-charge is accumulated on any one carbon atom;
2. The bond-lengths vary little from the mean "aromatic" value ($\sim 1{\cdot}40$A°).

The original HMO method should thus be unable to predict accurate thermodynamic properties of e.g. open chain polyenes (where the bond-lengths vary greatly) or non-alternant aromatic compounds (where the π-charge distribution is not uniform).

The aim of this paper is to show that promising accurate results can be obtained by the improved semi-empirical Hückel method[13] where the variations of the exchange integrals β_{ij} with bond-lengths are taken into account by an iterative procedure.

II. THEORY*

(a) *The thermochemical problem.* If we assume that in a fully conjugated hydrocarbon the total electronic bonding energy E_b° can be divided into contributions from the σ-framework and the π-system, then

$$E_b^\circ = E_\sigma^\circ + E_{\pi b}^\circ \tag{1}$$

Now, E_b° is related to ΔH_f^T, the heat of atomization, i.e. formation of the molecule from atoms in the gas phase at T°K, by:[8]

$$\Delta H_f^T = E_b^\circ - \sum_i 1/2 h\nu_i + \int_0^T \Delta C_p \cdot \mathrm{d}T \tag{2}$$

where ν_i is the vibration frequency of the molecule according to the ith normal mode and C_p is the specific heat at constant pressure. However, as was pointed out by Dewar and Chung,[8] the fact that in the case of saturated molecules, we can express heats of atomization quite accurately as additive sums of bond energies suggests that a correction for the terms in ν_i and C_p can be included in the empirical bond energies.

If we suppose that the same conclusions hold for a fully conjugated molecule, then we have:

$$\Delta H_f^\circ = E_{\sigma b} + E_{\pi b} \tag{3}$$

with

$$E_{\sigma b} = \sum_i E_{CC}^\sigma(i) + n_{CH} E_{CH} \tag{4}$$

In these equations, ΔH_f° is the standard heat of atomization, $E_{CC}^\sigma(i)$ the σ-energy of a C_{sp_2}—C_{sp_2} bond of length r_i, E_{CH} that of a C_{sp_2}—H bond and n_{CH} the number of the latter bonds. If σ-compression energy is taken into account, we have:

$$E_{CC}^\sigma(i) = E_{CC}^\sigma - 1/2.k_{CC}(r_i - 1{\cdot}517)^2 \tag{5}$$

where E_{CC}^σ is the σ-energy of C_{sp_2}—C_{sp_2} bond at its "natural" length of 1·517A°,[14] and k_{CC} the appropriate force constant (5,5.10^5 dynes/cm).[15] According to Eqs 4 and 5, Eq. 3 may be written:

$$\Delta H_f^\circ = n_{CC} \cdot E_{CC}^\sigma - V + n_{CH} \cdot E_{CH} + E_{\pi b} \tag{6}$$

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* All energy symbols used in this paragraph have a positive value.

where V is the total molecular compression energy and is given by:

$$V = \sum_i 1/2\, k_{CC}(r_i - 1{\cdot}517)^2 \tag{7}$$

(b) *The quantum-chemical problem.* As has been said before, the aim of this paper is to see whether the heats of atomization of a wide variety of fully conjugated hydrocarbons can be predicted correctly when $E_{\pi b}$ is estimated by the improved iterative Hückel-method (called LCAO–BETA) we have previously described.[13] As in the original HMO theory, the total π-energy E_π of the molecule is given as a sum of orbital energies E_j, i.e.

$$E_\pi = \sum^{occ} \cdot E_j \tag{8}$$

where n_j is the number of π-electrons occupying orbital j. E_j can be written in the form:

$$E_j = \alpha_C + m_j \cdot \beta_{CC} \tag{9}$$

and substitution in Eq. 8 gives:

$$E_\pi = \alpha_C \cdot \sum_j^{occ} n_j + \beta_{CC} \cdot \sum_j^{occ} n_j \cdot m_j, \quad \text{or} \quad E_\pi = \alpha_C \cdot N_C + \beta_{CC} \cdot \sum_j^{occ} n_j \cdot m_j \tag{10}$$

since in any neutral unsaturated hydrocarbon,

$$\sum_j^{occ} n_j = N_C$$

the total number of carbon atoms implied in the π-system.

According to current SCF theory, it can be shown however[10, 16, 17] that the total electronic energy is *not* a sum of orbital energies; in fact, one has to subtract the total electronic interaction energy and to add the total internuclear repulsion. In particular, in the LCAO–BETA method, the diagonal elements of the hamiltonian matrix for a carbon atom are given by:[13]*

$$\alpha_C \equiv H_{CC} = W_C - 1/2 \cdot J_{CC}. \tag{11}$$

where W_C is the valence-state π-ionisation potential of a carbon atom and J_{CC} is the monocentric coulomb repulsion integral (J_{CC} = 11,13 eV by Pariser's approximation[18]).

The term in J_{CC} arises from an intra-orbital π-electron repulsion; indeed, in an unsaturated hydrocarbon with an even number of π-electrons, the distribution of α- and β- spin electrons is the same and thus the charge density present in a $2p_z$ orbital will have half α-spin and half β-spin. Let us now suppose that we "atomize" our molecule in one step, hybridization being conserved; all the electrons of the atoms obtained will of course have random spins relative to each other and the total π-energy will be the sum of the valence state ionisation potentials $W_C \neq \alpha_C$.

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* In agreement with our convention throughout this paper, α_C has a positive value; this explains the somewhat unusual signs which appear in Eq. 11.

It should also be emphasised that in the thermocycle used to calculate the "*experimental*" atomization energy, the molecule is decomposed to C atoms which we may presume to be in the normal ^{3}P ground state.[19] However, as far as π-electrons alone are concerned, we calculated here the π-bonding of our molecule from the appropriate hybridized valence-state of the C atoms involved.

The π-ionization potential of this valence-state however ($C_{trtrtr\pi}$), i.e. W_C, is about 0·1 eV smaller than for the ground state.[20] Thus in the case of anthracene, an error of ~1·4 eV (32 Kcal/M) is automatically introduced in this type of confrontation with experiment.

These electron repulsion—and spin rearrangement—corrections should of course be taken into account when calculating atomization energies. However, in order to make the LCAO–BETA method the closest possible to the original Hückel method (corrected for unequal bond lengths), all these terms will be formally neglected.

Accordingly, we obtain for the π-bonding energy and atomization energy respectively:

$$E_{\pi b} = \beta_{CC} \cdot \sum_{j}^{occ} n_j \cdot m_j \tag{12}$$

and

$$\Delta H_f^\circ = n_{CC} \cdot E_{CC}^\sigma - \sum_{j} 1/2\, k_{CC}(r_i - 1{\cdot}517)^2 + n_{CH} \cdot E_{CH} + \beta_{CC} \cdot \sum_{j} n_j \cdot m_j \tag{13}$$

It should however be emphasised that, due to the approximations made throughout this paper, this last relation is largely empirical and that it cannot be considered as theoretically established, even if exceedingly good agreement between calculated and "measured" heats of atomization is reached. In fact, the necessary corrections for the severe approximations tolerated in this paper should be included in the *empirical values* of the three adjustable parameters E_{CC}^σ, E_{CH} and β_{CC}.

III. RESULTS AND DISCUSSION

The total π-bonding energy $E_{\pi b}$ and the σ-compression energy V were calculated according to Eqs 12 and 7 respectively by the LCAO–BETA method for the hydrocarbons listed in Table 1; the bond-lengths used in the calculation of V were those obtained at self-consistency of the iterative procedure.

Once the experimental value of ΔH_f° is known and the value of V is calculated, Eq. 13 may be set in the form:

$$w = a.x + b.y + c.z \tag{14}$$

with

$$w = \Delta H_f^\circ + V, a = n_{CH}, b = n_{CC}, c = \sum_{j}^{occ} n_j \cdot m_j$$

and the unknown

$$x = E_{CH}, y = E_{CC}^\sigma \text{ and } z = \beta_{CC}.$$

TABLE 1. EXPERIMENTAL AND CALCULATED HEATS OF ATOMIZATION OF CONJUGATED HYDROCARBONS

Compound	ΔH°_{f},[a] observed (eV)	ΔH°_{f} calculated (eV) This work	Dewar[11]	Differences (eV) This work	Dewar
(a) *Alternant*					
1. Benzene	57·16	57·09	57·16	0·07	—
2. Naphthalene	90·61	90·60	90·61	0·01	—
3. Phenanthrene	124·20	124·20	124·22	—	−0·02
4. Anthracene	123·93	124·04	123·89	−0·11	0·04
5. Pyrene	138·88	138·72	138·62	0·16	0·26
6. Triphenylene	157·76	157·86	157·94	−0·10	−0·18
7. Tetracene	157·56	157·47	157·11	0·09	0·45
8. Benz[*a*]anthracene	157·49	157·67	157·58	−0·18	0·09
9. Benzo[*c*]phenanthrene	157·48	157·77	157·77	−0·29	−0·29
10. Chrysene	157.73	157·78	157·77	−0·05	−0·04
11. Perylene	172·04	172·29	172·15	−0·25	−0·11
12. Butadiene (*trans*)	42·05	42·07	42·05	−0·02	—
13. Hexatriene (*trans*)	61·10[b]	60·93	—	0·17	—
	±0·13			±0·13	
(b) *Non-alternant*					
1. Azulene	89·19	89·65	89·46	−0·46	−0·27
2. Acenaphthylene	104·32	104·27	104·86	0·05	−0·54
3. Fluoranthene	138·11	137·83	138·67	0·28	−0·56
4. Fulvene	—	56·18	56·33	−0·15	
5. Pentalene	—	70·47	70·53	−0·06	
6. Heptalene	—	108·11	108·14	−0·03	

[a] Ref 11, unless otherwise stated.

[b] Calculated from the heat of combustion given in Ref 25.

These parameters were determined by a computer regression analysis of the known data for compounds 1–6 of Table 1. This gives us the following results:

$$\begin{aligned} E_{\mathrm{CH}} &= 4{\cdot}314\ \mathrm{eV}\ (99{\cdot}40\ \mathrm{Kcal/M}) \\ E^{\sigma}_{\mathrm{CC}} &= 3{\cdot}726\ \mathrm{eV}\ (85{\cdot}85\ \mathrm{Kcal/M}) \\ \beta_{\mathrm{CC}} &= 1{\cdot}292\ \mathrm{eV}\ (28{\cdot}77\ \mathrm{Kcal/M}) \end{aligned} \qquad (15)$$

The values for E_{CH} and E^{σ}_{CC} are in fair agreement with those proposed by Dewar and de Llano,[11] i.e. 4·4375 and 3·9409 eV respectively, although their theoretical approach for calculating π-bonding energy (the improved β-iterative Pople method) is much more sophisticated than ours.

Eq. 13 was then used to calculate atomization energies of six other alternant hydrocarbons; as can be seen from Table 1, the differences between the experimental and theoretical values are of the same order of magnitude as those obtained for the "adjusted" molecules; the agreement is at least as good as in the case of Dewar's calculations.[11]

Even for non-alternant hydrocarbons the agreement is fairly good, although the too high values calculated by Dewar could be more nicely explained in terms of ring-strain.

Some explanation for this surprisingly good result can be found in the fact that the energy is a rather insensitive criterion for testing wave-functions.[21]

A much greater sensitivity to error will be present in the estimation of any other molecular property if the wave-functions are not eigenfunctions of the operator for this property, and indeed, dipole moments and accordingly charge density distributions are wrongly predicted by the LCAO–BETA method for the non-alternant hydrocarbons, e.g. for azulene.[22]

It should however be emphasised that by the method outlined in this work, heats of atomization of cyclic as well as open chain polyenes (e.g. butadiene) are correctly calculated, and this is indeed an important progress with regard to the original Hückel method.[23] As it was applied, the treatment looks essentially like a Hückel method where allowance is made for variation of β with molecular geometry. It should be noticed that the value of the "thermodynamical β" we obtain (28·77 Kcal/M) is substantially higher than the one generally proposed in recent text books ($\sim$ 16 Kcal/M),[23,24] which is based on empirical resonance energies and includes σ-compression and -rehybridization contributions.

In forthcoming publications, this theory will be applied to investigate the aromaticity and the validity of Hückel's 4n + 2-rule in cyclic polyolefines.

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