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Heats of Atomization of Conjugated Hydrocarbons by a New Semiempirical Method

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Heats of atomization of a range of conjugated hydrocarbons are calculated by a semiempirical method which combines characteristic features of the MO and the VB theory. The π-ground state of each hydrocarbon is represented as a linear combination of Kekulé structures where, unlike the VB theory, each Kekulé structure is a determinant containing bond orbitals. In this approach only the Hückel parameter has to be adjusted. Experimental heats of atomization are by this method reproduced approximately equally well as by the more sophisticated SCF-MO approach. The use of this method is however much simpler since it amounts to a single diagonalization of a matrix of the order equal to the number of Kekulé structures only.

Key words: Heats of atomization – Conjugated hydrocarbons – Semiempirical method.

By combining characteristic features of the MO and VB theory one can formulate a new semiempirical approach. This approach retains the concept of the resonance structure from the VB theory, while it treats each particular bond in the MO sense. We propose this approach to be called Molecular Orbital Resonance Theory (MORT). In MORT each resonance structure is a determinant containing bond orbitals, either excited or nonexcited. There is a formal resemblance in the evaluation of matrix elements between MORT resonance structures on one hand, and VB resonance structures on another. The details of the calculation of those matrix elements will be given elsewhere [1].

Here are presented some results of the simplest variant of the MORT approach. This variant retains only MORT Kekulé structures and it uses the Hückel

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Hamiltonian. Spin separation is assumed, i.e. each eigenstate is of the form

$$\Psi = \mathscr{A}\Phi_a\bar{\Phi}_b \tag{1}$$

where $\mathscr{A}$ is the antisymmetrisation operator while Φ_a and $\bar{\Phi}_b$ are spin-up and spin-down substates, respectively. One easily finds $\langle\Psi|\Psi\rangle = \langle\Phi_a|\Phi_a\rangle\langle\Phi_b|\Phi_b\rangle$ where $\langle\Psi|\Psi\rangle = \int \Psi^*\Psi d\tau$. Further, if H is the one-particle operator $\langle\Psi|H|\Psi\rangle = \langle\Phi_a|H|\Phi_a\rangle\langle\Phi_b|\Phi_b\rangle + \langle\Phi_a|\Phi_a\rangle\langle\bar{\Phi}_b|H|\bar{\Phi}_b\rangle$ and hence

$$\begin{aligned} E &= \langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle \\ &= \langle\Phi_a|H|\Phi_a\rangle/\langle\Phi_a|\Phi_a\rangle + \langle\bar{\Phi}_b|H|\bar{\Phi}_b\rangle/\langle\Phi_b|\Phi_b\rangle = E_a + E_b \end{aligned} \tag{2}$$

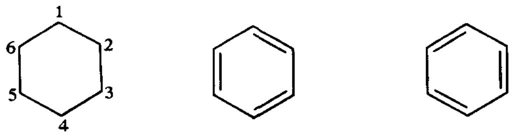
Both, Φ_a and Φ_b are expressed as linear combinations of Kekulé structures. Unlike the VB theory, the term "Kekulé structure" (and more generally "resonance structure") refers now separately to the spin-up and spin-down subspaces. According to Eq. (2) there are two secular equations, one referring to the spin-up and another to the spin-down state. Since the Hückel Hamiltonian is a spin independent operator, those two equations are identical, and hence for the ground state $\Phi_a = \Phi_b$. In the case of hydrocarbon molecules the Hückel Hamiltonian can be written as $H_{\text{Hück}} = \alpha I + \beta A$ where α and β are Hückel parameters while A is adjacency matrix. Instead of this operator we observe the operator

$$H = A - nI \tag{3}$$

which has the same eigenstates. In this equation n is the number of particles in the state Φ. Eigenvalues of the operator H give the energy in β units. This energy is shifted in such a way that each Kekulé structure possesses energy zero. As a first approximation one assumes that the Kekulé structure represents the referent classical structure. Accordingly $\text{RE} = \text{E} = 2\text{E}_\text{a}$ is interpreted as a resonance energy [2, 3]. We propose this approach to be called MORT-1 approximation.

As an example of the MORT-1 calculation consider the benzene molecule. There are two Kekulé structures K_1 and K_2 (Fig. 1). Those structures are antisymmetrised products of three bond orbitals

$$\begin{aligned} K_1 &= \mathscr{A}\phi_{12}\phi_{34}\phi_{56} \\ K_2 &= \mathscr{A}\phi_{23}\phi_{45}\phi_{61} \end{aligned} \tag{4}$$



G $\qquad K_1 = \mathscr{A}\phi_{12}\phi_{34}\phi_{56}$ $\qquad K_2 = \mathscr{A}\phi_{23}\phi_{45}\phi_{61}$

a b c

Fig. 1

where $\phi_{ij}=(\chi_i+\chi_j)/\sqrt{2}$ and χ_i are atomic orbitals. One easily finds

$$\begin{aligned}\langle K_1|K_2\rangle &= \int \phi_{12}(1)\phi_{34}(2)\phi_{56}(3)\mathscr{A}\phi_{23}(1)\phi_{45}(2)\phi_{61}(3)\,d1\,d2\,d3\\ &=(12|23)(34|45)(56|61)+(12|61)(34|23)(56|45)=\tfrac{1}{4}\end{aligned}$$

where $(ij|kl)=\int \phi_{ij}\phi_{kl}\,d\tau$.

Similarly

$$\begin{aligned}\langle K_1|A|K_2\rangle &= (12|A|23)(34|45)(56|61)+(12|A|61)(34|23)(56|45)\\ &\quad+\cdots+(12|61)(34|23)(56|A|45)=\tfrac{6}{4}.\end{aligned}$$

Also $\langle K_1|K_1\rangle=\langle K_2|K_2\rangle=1$ and $\langle K_1|A|K_1\rangle=\langle K_2|A|K_2\rangle=3$.

Hence $\langle K_1|H|K_1\rangle=\langle K_2|H|K_2\rangle=0$ i.e. the energy of each Kekulé structure vanishes. Further $\langle K_1|H|K_2\rangle=\frac{3}{4}$. The secular equation is a 2 by 2 matrix equation with the eigenvalues $\frac{3}{5}$ and -1. The corresponding eigenstates are $\Phi_1=K_1+K_2$ and $\Phi_2=K_1-K_2$, respectively. Since the energy is expressed in negative β units the ground state is the state $\Psi=\Phi_1\bar{\Phi}_1$ with the energy 1.2β. Similarly one can obtain resonance energies for other conjugated hydrocarbons. The calculation of the overlaps and matrix elements of the Hamiltonian H between different Kekulé structures can be sometimes very timeconsuming. However, one can devise a simple and efficient method to calculate those elements [1].

Table 1 shows experimental and calculated heats of atomization for a range of hydrocarbons. All compounds are taken from the Table 5.2 in the Ref. [3]. Heats of atomization, as calculated by the SCF-MO theory, are taken from the Ref. [2] where they are given to three decimal places. MORT-1 heats of atomization are calculated by the formula

$$-\Delta H = E_{\text{bond}}+\text{RE} \tag{5}$$

where E_{bond} is the energy of the corresponding classical structure with "localised" bonds as defined by Dewar [2, 3], and RE is the resonance energy calculated by the MORT-1 method. Eq. (5) is in accord with the Dewar definition of the resonance energy as a difference between the heat of formation and the energy E_{bond} of the referent classical structure. The energy E_{bond} is [2, 3]

$$E_{\text{bond}}=n_{\text{CH}}E_{\text{CH}}+n_{\text{C}-\text{C}}E_{\text{C}-\text{C}}+n_{\text{C}=\text{C}}E_{\text{C}=\text{C}}$$

where n_{CH}, $n_{\text{C}-\text{C}}$ and $n_{\text{C}=\text{C}}$ is the number of CH bonds, the number of CC "single" bonds and the number of CC "double" bonds, respectively. Bond energies E_{CH}, $E_{\text{C}-\text{C}}$ and $E_{\text{C}=\text{C}}$ are [2]

$$E_{\text{CH}}=4.4375\text{ eV}\qquad E_{\text{C}-\text{C}}=4.3499\text{ eV}\qquad E_{\text{C}=\text{C}}=5.5378\text{ eV}.$$

Resonance energy RE is obtained as the eigenvalue of the secular equation containing MORT Kekulé type structures. In the case of the Hückel Hamiltonian a matrix element between MORT Kekulé structures is expressed in terms of the Hückel integral β. This should be contrasted to the VB theory where the resonance between different Kekulé structures gives rise to several types of

Table 1. Heats of atomization and MORT-1 resonance energies of conjugated hydrocarbons

Compound[a]	$-\Delta H$ Obs[b] eV	SCF-MO[c] Calc eV	SCF-MO[c] Error eV	MORT-1 Calc ($\beta = -0.7091$ eV[d]) eV	MORT-1 Error eV	MORT-1 RE[e] ($-\beta$-units)
1. Benzene	57.16	57.157	0.00	57.139	−0.02	1.2
2. Naphthalene	90.61	90.612	0.00	90.584	−0.03	1.8271
3. Anthracene	123.93	123.889	−0.04	123.849	−0.08	2.2
4. Phenanthrene	124.20	124.222	0.02	124.203	0.00	2.6997
5. Pyrene	138.88	138.624	−0.26	138.640	−0.24	2.9802
6. Perylene	172.04	172.146	0.11	172.118	0.08	3.6542
7. Triphenylene	157.76	157.943	0.18	157.943	0.18	3.7423
8. Benzo(c)phenanthrene	157.48	157.767	0.29	157.741	0.26	3.4585
9. Chrysene	157.73	157.772	0.04	157.741	0.01	3.4585
10. 1,2-Benzanthracene	157.49	157.580	0.09	157.556	0.07	3.1970
11. Naphthacene	157.56	157.112	−0.45	157.019	−0.54	2.4400
12. 1,3-Butadiene	42.05	42.054	0.00	42.050	0.00	0.0
13. Biphenyl	109.76	109.751	−0.01	109.753	−0.01	2.4
14. Styrene	75.83	75.909	0.08	75.902	0.07	1.2
15. Stilbene	128.48	128.526	0.05	128.516	0.04	2.4
16. Acenaphthene	104.32	104.861	0.54	104.822	0.50	1.8271
17. Fluoranthene	138.11	138.668	0.56	138.673	0.56	3.0271
18. Azulene	89.19	89.458	0.27	89.706	0.52	0.5882
19. Biphenylene	102.00	104.873	2.87	105.228	3.23	2.4

[a] Structures of compounds 1—19 are given in Ref. [3]. Those compounds are identical with compounds in Ref. [2] for which an experimental value is given, except compounds XXXVII and XLVI in this reference

[b] Taken from Ref. [2]

[c] Predicted heats of atomization are from Ref. [2]. Errors are rounded to two decimal places

[d] The value $\beta = -0.7091$ eV is obtained as the best fit to experimental values for the first 15 compounds (all unstrained compounds)

[e] RE is the eigenvalue of the MORT-1 secular equation involving MORT Kekulé type resonance structures

exchange integrals. Accordingly, in MORT-1 the bonding is due to the one-particle integral β, while in the VB theory it is mainly due to the two-particle resonance integrals.

The agreement between calculated and observed heats of atomization is excellent, there being only five compounds for which the difference is significantly greater than the claimed limits of the experimental errors. For three of those (16, 17, 18) the discrepancies can be attributed to the ring strain which is neglected in the MORT-1 treatment. The differences for those compounds (~ 0.53 eV) are in the right sense, they are almost identical, and their values are close to the one which might be expected for the ring strain of the five-membered ring. The seven-membered ring in azulene (compound 18) should not contribute to the heat of atomization, since the ring strain can be easily avoided by a slight nonplanarity. The difference for biphenylene (3.23 eV) seems to be too large to be attributed to the ring strain alone. However, a more elaborate SCF-MO method also overestimates the difference for this molecule (2.87 eV) [2]. Concerning compound (11), there are good reasons for doubting the reliability of the thermochemical data for this compound, as discussed by Dewar [2].

The value $\beta = -0.7091$ eV is obtained as the best fit for the first 15 (all nonstrained) compounds in the Table 1. Hence one might speculate that the discrepancies for the compounds (16, 17, 18) and to the lesser extent for the compound (19), which are attributed to the ring strain are accidental, due to the fact that those compounds are not taken into account in the estimation of the best fit for the parameter β. However, the best fit to the first 18 compounds (all compounds in the Table 1 except biphenylene) produces discrepancies 0.46, 0.49, 0.50 and 3.17 eV for the compounds 16, 17, 18 and 19, respectively. Those values are close to the discrepancies obtained from the 15-point fit. The discrepancies for all other compounds do not change appreciably either. Similar result, though to the lesser extent, is obtained if parameter β is estimated as the best fit to all 19 compounds. In this case however the relatively large discrepancy for biphenylene tends to obscure much smaller discrepancies of other compounds. Hence the calculated discrepancies should be considered genuine, and can be attributed to the ring strain, except for the compound (11) where the thermochemical data are probably in error [2].

SCF-MO calculations give similar results [2]. Only the predicted difference for azulene (0.27 eV) seems to be too small to be attributed to the strain in the five-membered ring. Here MORT-1 predicts discrepancy of 0.52 eV, which is more in accord with the predicted discrepancies for acenaphthene (0.50 eV) and fluoranthene (0.56 eV).

Another measure of the correlation between experimental and theoretical results is the correlation coefficient. Here it is better to correlate resonance energies than heats of atomizations in order to eliminate the significant contribution to the correlation due to E_{bond}. Taking into account all nonstrained (first 15) compounds in the Table 1, the correlation coefficient between MORT-1 resonance energies and experimental (in Dewar's sense) resonance energies is 0.9695.

The correlation between MORT-1 and SCF-MO resonance energies for the same set of compounds is significantly better, the correlation coefficient being 0.9995. As expected, the correlation coefficient decreases if compounds containing strained rings are included. However, the correlation of MORT-1 resonance energies with the SCF-MO values remains always significantly better than the correlation between MORT-1 resonance energies with experimental (in Dewar's sense) resonance energies. In conclusion, MORT-1 approach essentially reproduces SCF-MO heats of atomization and resonance energies. Both approaches reproduce approximately equally well experimental heats of atomization. The MORT-1 approach is however significantly simpler. It uses essentially one parameter (Parameters E_{CH}, E_{C-C} and $E_{C=C}$ are taken from Ref. [2]) and the use of this method amounts to a single diagonalization of a matrix of the order equal to the number of Kekulé structures [1]. For example, in the case of naphthalene the SCF-MO method involves iterative diagonalization of a 10 by 10 matrix, while the MORT-1 method involves a single diagonalization of a 3 by 3 matrix etc.

MORT-1 method can equally well be applied to compounds containing heteroatoms [1]. Hence this method does not suffer from a drawback of other simple approaches which are usually applicable only to a very limited class of conjugated compounds. For example Herndon's method [4], which is essentially a naive resonance theory based on VB Kekulé structures, is unable to produce meaningful quantitative results for conjugated compounds containing 4-membered rings and/or heteroatoms. A simplest example is cyclobutadiene for which the resonance theory predicts stabilization due to the resonance between two Kekulé structures. In his paper Herndon fails to include the result for biphenylene, a compound which is present in the original Ref. [2]. In MORT-1 there is no resonance stabilization in the case of cyclobutadiene [1]. Concerning biphenylene, the difference between MORT-1 and experimental heat of atomization can be mainly attributed to the ring strain, and moreover the agreement with the SCF-MO result is relatively good (difference is 0.35 eV).

Besides heats of atomization, other ground state properties, like bond lengths, bond orders etc. can also be obtained by the MORT-1 method [1].

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