Hückel Molecular Orbital π Resonance Energies. The Question of the σ Structure

L. J. Schaad* and B. Andes Hess, Jr.*

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203. *Received June 21, 1971*

Abstract: Examination of changes in the σ electronic structure of conjugated hydrocarbons shows that for each bond both σ compression energy and π bonding energy are approximately linear functions of π bond order. It follows that σ contributions to resonance energy are proportional to π contributions, thus providing a rationalization for the simple HMO method which takes into account only the latter. Heats of atomization computed by the HMO method are found to be accurate to 0.1%, implying an accuracy of $\pm 0.005\beta$ in resonance energy per π electron.

The concept of aromaticity has produced a large literature. In spite of this it is a property with no generally agreed upon quantitative experimental definition.[1] The consensus seems to be that aromatic molecules are unusually stable and that typically they react by electrophilic substitution. Beyond this there is not agreement. Theoreticians have examined the correlation of aromaticity with various computed molecular indices. Without a precise experimental definition there can of course be no precise correlation, but until recently theory could not make correctly even the rough distinctions that are apparent from experiment. In particular the failure of Hückel delocalization energy is well known. Almost all compounds, even ones that are very unstable, have significant delocalization energy. Further, the computed delocalization energies are not in the observed experimental order.

A new approach by Dewar seems to have overcome these faults. Dewar and Gleicher[2] first noted that plots of computed total C–C bonding energy *vs.* number of C–C bonds give very accurate straight lines for acyclic polyenes. The bonding energy of such a polyene therefore equals the sum of empirical bond energy terms. For cyclic molecules this is not true, and the theoretical resonance energy was defined as the difference between the calculated energy and the sum of bond energy terms. An important point is that even in the polyenes, "single" bonds have considerable double bond character. Total binding energy of a reference polyene is therefore larger than earlier reference binding energies, and as a result, computed resonance energies are in general smaller than by earlier methods. More important is that these smaller resonance energies turn out to be in proper experimental order.[3]

Dewar's calculations were done by the Pariser–Parr–Pople method for the π electrons with σ electrons being taken into account empirically. We have shown that equally good results can be obtained from the simple HMO method if, following Dewar, one uses a polyene reference structure.[4,5] The resonance energies per π electron (REPE) so obtained correlate with experiment for nonalternants,[4,6] where delocalization energy is notoriously poor, as well as for alternants. These conclusions are illustrated by the ten compounds listed in Figure 1.

The success of our treatment of simple HMO calculations in the prediction of aromaticity of cyclic conjugated hydrocarbons raises several questions. In this paper we examine two of these relating to the σ electron structure of aromatics. First, why does our model which neglects the σ electrons entirely work as well as Dewar's more elaborate model which treats them explicitly? We shall show that this is explained by a linear relation between σ and π resonance energies.

Second, can the simple HMO model be employed to calculate accurate heats of atomization? Dewar has used the accuracy of computed heats of atomization as a test of his method. We shall show that the HMO method does as well.

The σ Structure

Our definition of resonance energy is modeled after Dewar's, except that we consider the π electrons only, and calculate their energy with the elementary HMO method. We find, as does Dewar, that acyclic conjugated polyenes have no resonance energy; *i.e.*, the calculated HMO energy is the same as the energy of the localized model. In general our resonance energies of cyclic compounds agree with Dewar's, with the simpler method occasionally giving results in better agreement with experiment. Note that our bond energy terms for calculating the energy of the localized structure (Table I, ref 4) refer to π energies only. In particular, the single bond energies refer to the π parts of the "single" bonds. There is thus a certain amount of delocalization even in the localized model. "Additive" might be a better adjective than "localized" here, but we shall follow Dewar and continue to use "localized." Section 5.5 of ref 7 contains a further discussion of this point.

Figeys[8] has recently published a treatment of conjugated systems that is in many ways intermediate between ours and Dewar's. Figeys calculates π energies with an iterative Hückel method in which the resonance integral is a function of calculated bond length.[9] σ

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[1] A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968).

[2] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685, 692 (1965).

[3] M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969).

[4] B. A. Hess, Jr., and L. J. Schaad, *ibid.*, **93**, 305, 2413 (1971).

[5] B. A. Hess, Jr., and L. J. Schaad, *Tetrahedron Lett.*, 17 (1971).

[6] B. A. Hess, Jr., and L. J. Schaad, *J. Org. Chem.*, **36**, 3418 (1971).

[7] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[8] H. P. Figeys, *Tetrahedron*, **26**, 4615, 5225 (1970).

[9] H. P. Figeys and P. Dedieu, *Theor. Chim. Acta*, **9**, 82 (1967).

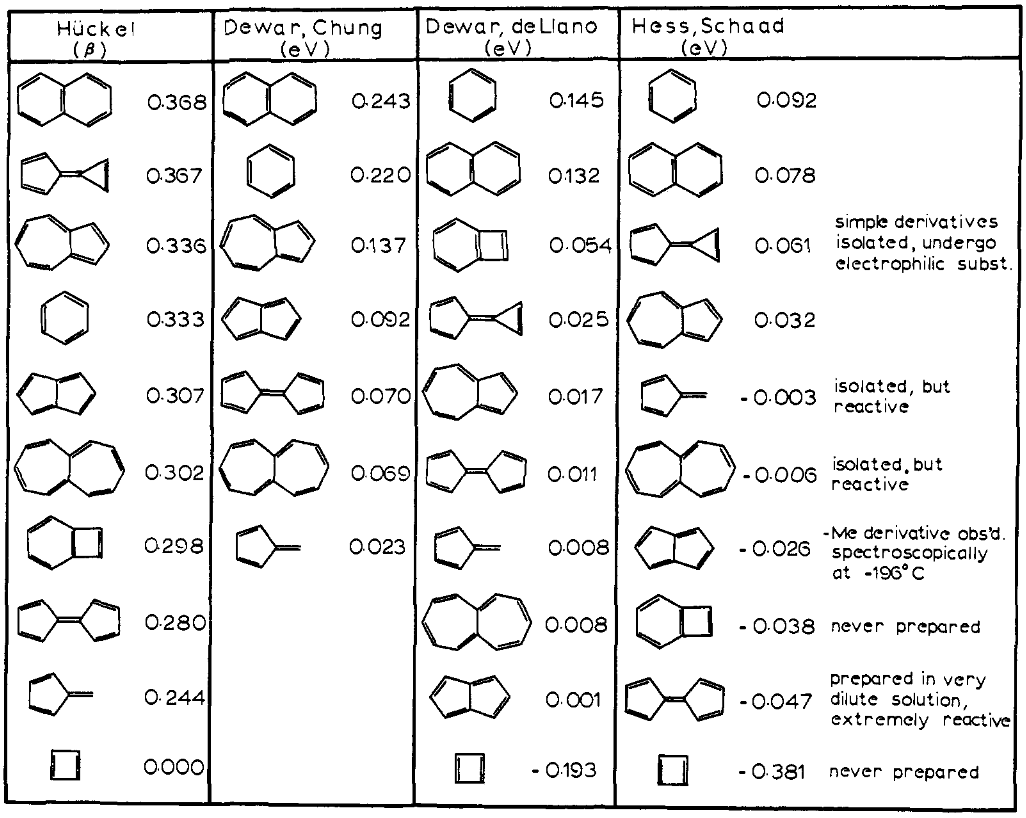

Figure 1. A comparison of resonance energies per π electron. The Hückel results in the first column are delocalization energies. The Pariser–Parr–Pople results in the second column are from ref 14; those in the third column are from ref 3 except for calicene, cyclobutadiene, and fulvalene, which are from C. de Llano, Ph.D. Dissertation, The University of Texas, 1968, and benzcyclobutadiene, from N. C. Baird, *J. Chem. Educ.*, **48**, 509 (1971). The Hückel results in the fourth column are REPE's from ref 4 using the value of β obtained from method B of the present paper. Experimental properties are from: calicene, A. S. Kende, P. T. Izzo, and P. T. MacGregor, *J. Amer. Chem. Soc.*, **88**, 3359 (1966), A. S. Kende, P. T. Izzo, and W. Fulmore, *Tetrahedron Lett.*, 3697 (1966), E. K. v. Gustorf, M. C. Henry, and P. V. Kennedy, *Angew. Chem., Int. Ed. Engl.*, **6**, 627 (1967); fulvene, J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.*, 177 (1956); heptalene, H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 4569 (1961); pentalene, R. Bloch, R. A. Marty, and P. de Mayo *ibid.*, **93**, 3071 (1971); benzcyclobutadiene and cyclobutadiene, M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y. 1967, G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, 1969; fulvalene, W. von E. Doering, "Theoretical Organic Chemistry, The Kekulé Symposium," Butterworths, London, 1959, p 35.

energies were computed in Dewar's fashion, but using a harmonic potential rather than Dewar's tractrix equation. This seems to give equally good computed heats of atomization.

One might imagine that neglect of σ energy does not affect computed resonance energies because both the actual structure and the localized structure have the same σ energy which then cancels in taking the difference. However, this is not true. The energy of each bond type in the localized model is fixed with no allowance for variation of energy with length. Hence, there can be no canceling of the σ compression energy of the actual molecule. Alternatively, σ compression energies might be small compared to π energies, and their neglect insignificant. We shall see that this is not true either.

To examine this problem in more detail let us start with the Hückel approximation of σ–π separability

$$E = E_\pi + E_\sigma \tag{1}$$

In the Hückel treatment one ignores the σ energy and considers only

$$E_\pi = E(\text{HMO}) = \sum_k n_k \epsilon_k \tag{2}$$

where ϵ_k is the orbital energy of the kth MO and n_k is the number of electrons it contains. Let the normalized MO's be

$$\psi_k = \sum_i c_{ik}\phi_i \tag{3}$$

where the ϕ's are the basis AO's. Then

$$E_\pi = \sum_k n_k \sum_{ij} c_{ik}c_{jk}H_{ij} \tag{4}$$

With the usual approximations this simplifies to

$$E_\pi = \alpha\sum_k n_k \sum_i c_{ik}^2 + 2\beta\sum_m \rho_m \tag{5}$$

The last sum in eq 5 goes over all bonds, and ρ_m is the π bond order of the mth bond. Because of normalization the double sum in (5) simplifies still further to give

$$E_\pi = N\alpha + 2\beta\sum_m \rho_m \tag{6}$$

where N is the number of π electrons in the system. The first term in (6) is the energy of the π electrons in the field of infinitely separated nuclei. The second term is the bonding energy. Empirical bond energies were obtained[4] from a least-squares fit to this term for 40 acyclic hydrocarbons. With the bond energies thus obtained, the energy of the localized structure of butadiene, for example, is

$$E_{\text{loc}} = 2\bar{E}_{23} + \bar{E}_{12} = 4.4660\beta \tag{7}$$

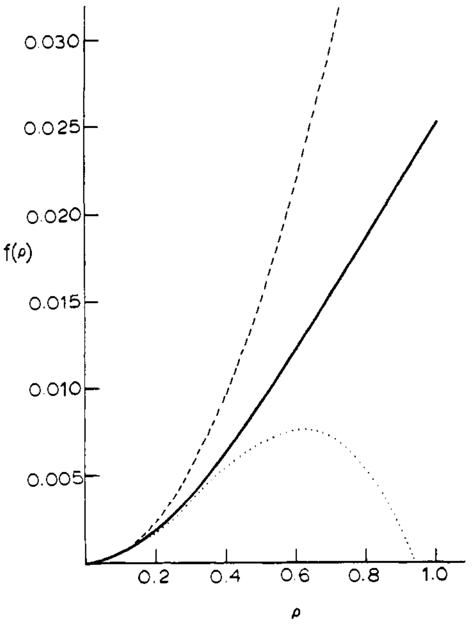

Figure 2. Solid line, the function f(ρ); dotted and dashed lines, first and first plus second terms in the expansion of f(ρ) about $\rho = 0$.

where $\bar{E}_{23}$ and $\bar{E}_{12}$ are the bond energy terms for the double and single bonds in butadiene. Measuring the Hückel E_π relative to α in the usual way (*i.e.*, dropping the first term in eq 6), one has $E_\pi = 4.472\beta$. The difference, $E_\pi - E_{\text{loc}} = 0.006\beta$, is the π resonance energy and is essentially zero in this case.

The σ energy may be written approximately

$$E_\sigma = n_C E^\sigma{}_C + n_H E^\sigma{}_H + \sum_i E^\sigma{}_{CH}(i) + \sum_j E^\sigma{}_{CC}(j) \quad (8)$$

The first two terms, with n_C = the number of carbon atoms, $E^\sigma{}_C$ = the σ energy of an isolated carbon atom, and n_H and $E^\sigma{}_H$ = the analogous quantities for hydrogen, will cancel in computations of heats of atomization or binding energies and need be examined no further. All CH bonds will be assumed identical, reducing the third term in eq 8 to $n_{CH}E^\sigma{}_{CH}$, with n_{CH} = the number of CH bonds. $E^\sigma{}_{CC}(j)$ is the σ energy of the jth CC bond. Assuming a harmonic potential, this becomes

$$E^\sigma{}_{CC}(j) = E^0{}_{CC} + {}^1\!/_2\epsilon(x_j - s)^2 \quad (9)$$

Here x_j is the length of the jth bond, s is the length of a pure sp^2–sp^2 single bond, ϵ is the stretching force constant for such a bond, and $E^0{}_{CC}$ is its energy.

Changes in σ energy can now be related to changes in π energy using the bond orders from (6) to compute bond lengths to be substituted into (9). We have used the bond-order–bond-length relation suggested by Figeys and Dedieu[9]

$$x = \frac{\epsilon s - 1.5(\epsilon s - 1.397\delta)\rho}{\epsilon - 1.5(\epsilon - \delta)\rho} \quad (10)$$

The bond length x is given in Å with $\epsilon = 5.6 \times 10^5$ dyn cm^{-1}, $\delta = 7.6 \times 10^5$ dyn cm^{-1}, and $s = 1.517$ Å. The σ compression energy is then proportional to

$$f(\rho) = (x - s)^2 = \left[\frac{1.5\delta(1.397 - s)\rho}{\epsilon - 1.5(\epsilon - \delta)\rho}\right]^2 \quad (11)$$

Note that the π binding energy (second term in eq 6) is linear in the various ρ's. The σ compression energy ${}^1\!/_2\epsilon f(\rho)$ is not at first sight linear in ρ; in fact the leading term in the expansion of f(ρ) about $\rho = 0$ is quadratic. Nevertheless, a plot of f(ρ) shows (Figure 2) that the function is practically linear over the range ρ = 0.3–0.9 where most bonds occur.

Thus for a given bond the σ and the π contributions to the binding energy are both linear functions of the bond order. It follows than that the π contribution to resonance energy is proportional to the σ contribution. In the next section we evaluate these quantities using experimental heats of atomization and see that this expected proportionality does hold. *This linear correlation gives a rational basis for the calculation of resonance energies of cyclic conjugated hydrocarbons using only the simple HMO π energies since any set of compounds arranged in order of increasing π resonance energy is automatically in order of increasing total resonance energy.*

Heats of Atomization

Dewar's theoretical definition of resonance energy suggests a corresponding experimental definition. If experimental binding energies of acyclic polyenes are accurately given by summing individual bond energy terms, experimental resonance energy can be defined as the difference between experimental binding energy and the sum of bond energy terms. This difference would vanish for acyclics, but not necessarily for cyclics. Resonance energy would then give a measure of the binding energy of a molecule compared to that of an acyclic polyene. Those with more would be called aromatic; those with less would be antiaromatic, and the acyclic polyenes themselves nonaromatic. If the acyclics do not have this additive property, resonance energy could still be defined in the same way with some arbitrary set of bond energy terms. But in this case there would be no group of real molecules with zero resonance energy, and the definition would lose some of its physical appeal.

At present there are three difficulties in carrying out a comparison of experimental and theoretical resonance energies based on this definition. First, the molecular energies from a variational calculation refer to molecules at the bottom of their potential curves. Even at 0°K correction for the zero-point vibrations must be made, and at any other temperature one must allow for the spread of molecules through excited translational, rotational, and vibrational states. This can be done to an accuracy of approximately 1 kcal/mol when complete configuration interaction wave functions are known.[10] Similar accuracy can also be obtained from good SCF wave functions of somewhat larger systems for processes in which correlation energy does not change significantly.[11,12] In semiempirical work it is usual to ignore these corrections or to hope that they are automatically taken into account by the adjustable parameters of the method used.[13,14]

(10) M. E. Schwartz and L. J. Schaad, *J. Chem. Phys.*, **47**, 5325 (1967).

(11) L. C. Snyder, *ibid.*, **46**, 3602 (1967).

(12) L. C. Snyder and H. Basch, *J. Amer. Chem. Soc.*, **91**, 2169 (1969).

(13) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, Chapter 7.

(14) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965).

Table I. Observed and Calculated Heats of Atomization (eV)

Compound	Obsd[a]	Method A	Method B	Dewar	Figeys[b]	A diff	B diff	Dewar diff	Figeys diff
1 Benzene	57.16	57.14	57.14	57.16	57.09	0.02	0.02	0.00	0.07
2 Naphthalene	90.61	90.59	90.59	90.61	90.60	0.02	0.02	0.00	0.01
3 Phenanthrene	124.20	124.14	124.14	124.22	124.20	0.06	0.06	−0.02	0.00
4 Anthracene	123.93	123.95	123.95	123.89	124.04	−0.02	−0.02	0.04	−0.11
5 Pyrene	138.88	138.60	138.60	138.62	138.72	0.28	0.28	0.26	0.16
6 Triphenylene	157.76	157.79	157.79	157.94	157.86	−0.03	−0.03	−0.18	−0.10
7 Benz[*a*]anthracene	157.49	157.54	157.54	157.58	157.67	−0.05	−0.05	−0.09	−0.18
8 Benz[*c*]phenanthrene	157.48	157.67	157.67	157.77	157.77	−0.19	−0.19	−0.29	−0.29
9 Chrysene	157.73	157.67	157.67	157.77	157.78	0.06	0.06	−0.04	−0.05
10 Perylene	172.04	172.12	172.12	172.15	172.29	−0.08	−0.08	−0.11	−0.25
11 Tetracene	157.56	157.30	157.30	157.11	157.47	0.26	0.26	0.45	0.09
12 Butadiene	42.05	42.01	42.02	42.05	42.07	0.04	0.03	0.00	−0.02
13 Hexatriene	61.10	60.84	60.86	60.81	60.93	0.26	0.24	0.29	0.17
14 Azulene	89.19	90.13	90.13	89.46	90.22	−0.94	−0.94	−0.27	−1.03
15 Acenaphthylene	104.32	104.86	104.87	104.86	104.99	−0.54	−0.55	−0.54	−0.67
16 Fluoranthene	138.11	138.58	138.59	138.67	138.71	−0.47	−0.48	−0.56	−0.60
17 Fulvene		56.37	56.39	56.34	56.51				
18 Pentalene		70.74	70.74	70.53	70.92				
19 Heptalene		108.60	108.60	108.15	108.78				
20 Pyracyclene		118.92	118.94	119.05	119.25				
21 Acepleiadylene		138.24	138.24	137.93	138.43				
22 Biphenylene		104.67	104.70	104.87	104.88				
23 Fulvalene		89.29	89.33	89.40	89.66				
24 3-Radialene		56.12	56.15	56.19	56.35				
25 4-Radialene		74.70	74.76	74.94	75.07				
26 Benzcyclobutadiene		70.57	70.64		70.92				
27 Sesquifulvalene		109.04	109.04	108.23	109.14				
28 Dimethylenecyclobutene		55.98	56.02		56.26				
29 *s*-Indacene		104.32	104.31		104.52				
30 Calicene		71.43	71.43	70.72	71.48				
31 Cyclobutadiene		36.20	36.20		36.53				

[a] Reference 8. [b] These numbers have been recalculated by us using Figeys' method. They agree with his published results for the alternants, but there are small differences for the nonalternants. Professor Figeys has himself now recalculated these and agrees with our numbers. We are grateful to him for correspondence on this point.

Second, the Gibbs free energies that one really wants for comparisons of stability are not commonly available and one identifies theoretical energies with enthalpies instead.[7,14]

Third, experimental heats of atomization are not available for enough acyclic polyenes to test whether or not they are accurately given as the sum of bond energy terms. As Dewar explains (ref 7, p 176), his experimental resonance energies are obtained using bond energies from calculated rather than experimental polyene results. The plausible, but not yet experimentally verified, justification is that if one is able to get calculated heats of atomization that are in good agreement with experiment for cyclic compounds, the same should be true for acyclics, and the calculated bond energy terms should then agree with the experimental when they become available. Consequently, in this approach it is important to show that a suggested computational method can yield sufficiently accurate heats of atomization.

We shall present in this section two methods based on HMO calculations, one with and one without explicit inclusion of σ effects, for the computation of heats of atomization of conjugated hydrocarbons. Results will be compared with those of more complex calculations by Dewar[3] and Figeys.[8]

Method A. Combining the σ- and π-energy expressions, eq 6 and 8–10, and subtracting the result from the energy of the isolated atoms give the heat of atomization as approximately

$$\Delta H_a = -[n_{CH}E^{\sigma}{}_{CH} + n_{CC}E^{0}{}_{CC} + \sum_{j} {}^1\!/_2\epsilon(x_j - 1.517)^2 + 2\beta\sum_{m}\rho_m] \quad (12)$$

The three unknowns ($E^{\sigma}{}_{CH}$, $E^{0}{}_{CC}$, and β) were determined by using the experimental heats of atomization for compounds **1–10** (see Table I) and the least-squares method. The values obtained are $E^{\sigma}{}_{CH} = -4.2599$ eV, $E^{0}{}_{CC} = -3.2613$ eV, and $\beta = -1.6911$ eV. These values were in turn used in eq 12 to calculate the heats of atomization of **11–31** (Table I). The experimental heats of atomization in Table I are those used by Figeys.[8] They are the same as the set used by Dewar and de Llano[3] except in the case of hexatriene where these authors listed no experimental number. For the unstrained compounds **1-13** our computed ΔH_a's

Table II. Empirical Total ($\sigma + \pi$) Carbon–Carbon Bond Energies Obtained from Acylic Conjugated Olefins

Type of bond	Designation	Calculated ($\sigma + \pi$) bond energy, eV
$H_2C{=}CH$	23	6.0000[a]
$HC{=}CH$	22	5.9041
$H_2C{=}C$	22′	6.0000[a]
$HC{=}C$	21	5.9619
$C{=}C$	20	6.0574
$HC{-}CH$	12	4.4389
$HC{-}C$	11	4.2920
$C{-}C$	10	4.1891

[a] Arbitrarily assigned.

Table III. Total Resonance Energies as Calculated by Method A

Compd	π energy, β	$\epsilon/2\sum_i(x_j - s)^2$, eV	C—C energy ($\sigma + \pi$), eV	Additive C—C energy, eV	TRE, eV	TREPE, eV	REPE, β	SREPE, eV
1	8.000	1.511	−31.586	−31.029	−0.577	−0.0927	0.0654	0.0179
2	13.683	2.506	−56.508	−55.724	−0.784	−0.0784	0.0553	0.0150
3	19.448	3.524	−81.546	−80.461	−1.085	−0.0775	0.0555	0.0150
4	19.314	3.487	−81.355	−80.420	−0.935	−0.0668	0.0471	0.0128
5	22.505	4.025	−95.998	−94.854	−1.144	−0.0715	0.0505	0.0139
6	25.274	4.558	−106.670	−105.242	−1.428	−0.0793	0.0563	0.0157
7	25.101	4.511	−106.424	−105.157	−1.267	−0.0704	0.0498	0.0137
8	25.187	4.533	−106.548	−105.197	−1.351	−0.0750	0.0526	0.0146
9	25.192	4.534	−106.555	−105.197	−1.358	−0.0754	0.0533	0.0147
10	28.245	5.036	−121.000	−119.637	−1.363	−0.0681	0.0483	0.0135
11	24.931	4.463	−106.184	−105.116	−1.068	−0.0593	0.0417	0.0113
12	4.472	0.899	−16.448	−16.439	−0.009	−0.0022	0.0016	0.0004
13	6.988	1.362	−26.761	−26.782	0.021	0.0035	−0.0023	−0.0004
14	13.364	2.419	−56.053	−55.726	−0.327	−0.0327	0.0231	0.0064
15	16.619	2.978	−70.784	−70.118	−0.666	−0.0555	0.0394	0.0111
16	22.500	4.028	−95.986	−94.900	−1.086	−0.0679	0.0483	0.0138
17	7.466	1.379	−30.814	−30.831	0.017	0.0029	−0.0020	−0.0006
18	10.456	1.848	−45.185	−45.383	0.198	0.0247	−0.0176	−0.0050
19	15.618	2.808	−66.001	−66.069	0.069	0.0057	−0.0042	−0.0013
20	19.416	3.430	−84.845	−84.512	−0.333	−0.0238	0.0181	0.0068
21	22.252	3.955	−95.638	−94.856	−0.782	−0.0489	0.0346	0.0096
22	16.505	2.983	−70.587	−70.161	−0.426	−0.0355	0.0275	0.0111
23	12.799	2.307	−55.212	−55.720	0.508	0.0508	−0.0329	−0.0048
24	7.301	1.355	−30.558	−30.567	0.009	0.0015	−0.0011	−0.0004
25	9.657	1.801	−40.620	−40.756	0.136	0.0171	−0.0108	−0.0012
26	10.381	1.900	−45.007	−45.381	0.374	0.0468	−0.0267	0.0016
27	15.931	2.894	−66.442	−66.063	−0.379	−0.0316	0.0222	0.0060
28	7.208	1.340	−30.416	−30.677	0.261	0.0435	−0.0284	−0.0045
29	16.231	2.866	−70.240	−70.080	−0.160	−0.0134	0.0092	0.0022
30	10.939	1.981	−45.869	−45.377	−0.492	−0.0615	0.0434	0.0118
31	4.000	0.649	−19.160	−20.686	1.526	0.3815	−0.2680	−0.0716

agree slightly better with experiment than do Dewar's, the sum of absolute errors being 1.37 and 1.77 eV, respectively. As expected, since angle strain has not been taken into account, heats of atomization of compounds with five- or seven-membered rings are not computed as accurately.

We now have the parameters needed to examine both the σ and the π contributions to the resonance energy. Total ($\sigma + \pi$) binding energies were computed using (6) and (8) for the 40 acyclic hydrocarbons in Table II of ref 4, and empirical bond energies were fit by least squares to these (Table II). As before, two of the eight bond types must be assigned arbitrarily due to linear dependence. These bond energies were then used to calculate the total resonance energies (TRE) of compounds **1**–**31** by subtracting the total ($\sigma + \pi$) carbon–carbon localized energy, obtained in an additive fashion using the bond energies given in Table II, from the total carbon–carbon energy obtained by method A (see Table III). Total resonance energies per π electron (TREPE) were also calculated for comparison with the previously calculated[4] π resonance energy per π electron (REPE).

σ resonance energy per π electron (SREPE) was obtained as the difference between TREPE and REPE. Figures 3 and 4 show the expected linear relation between the σ and π contributions to the resonance energy. The σ effect is smaller than the π, but it is not negligible. Note that the two are of opposite sign. That is, what we have called "σ resonance energy" by analogy with the π resonance energy is actually a destabilization energy due to compression and stretching of the σ framework.

Method B. Since σ compression terms are approximately linear in π binding energies, one can combine the two and write

$$\Delta H_a = -[n_{CH}E^{\sigma}_{CH} + n_{CC}E^{0}_{CC} + 2\beta\sum_m p_m] \quad (13)$$

The β in eq 13 is, of course, not the same as in eq 12 since the last term in eq 13 is the sum of the last two terms in eq 12. Fitting the three parameters in eq 13 to the experimental heats of atomization of compounds **1**–**10** one obtains $E^{\sigma}_{CH} = -4.2606$ eV, $E^{0}_{CC} = -3.3702$ eV, and $\beta = -1.4199$ eV. These parameters give computed heats of atomization (Table I) as accurate as those from any of the more elaborate methods. The β (= −1.4199 eV = −32.74 kcal/mol) is appropriate for simple HMO work since it automatically takes into account changes in the σ skeleton.

The computed heats of atomization above appear to be satisfyingly accurate with average error being under 0.1%. However, the heats of atomization are themselves large numbers, and a small per cent error may lead to large errors in quantities such as resonance energies which are differences between two large heats of atomization. It is true that a method with even larger error might, by cancellation, give accurate resonance energies. But this cannot be checked until experimental ΔH_a's are available for the acyclics. Are the ΔH_a's by method B accurate enough to ensure reliable resonance energies? The standard deviation of the fit of observed to calculated ΔH_a per electron for the unstrained compounds (**1**–**13**) in Table I is 0.0037 eV. REPE is the difference between two such quantities, and should therefore have a standard deviation of $\sqrt{2}$ ×

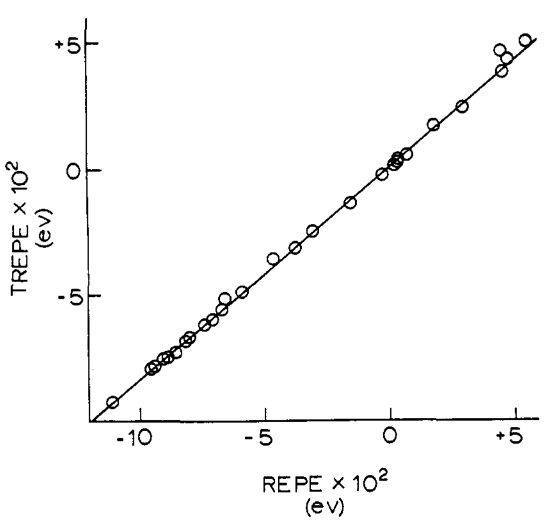

Figure 3. Total resonance energy per π electron (TREPE) *vs.* the π resonance energy per π electron.

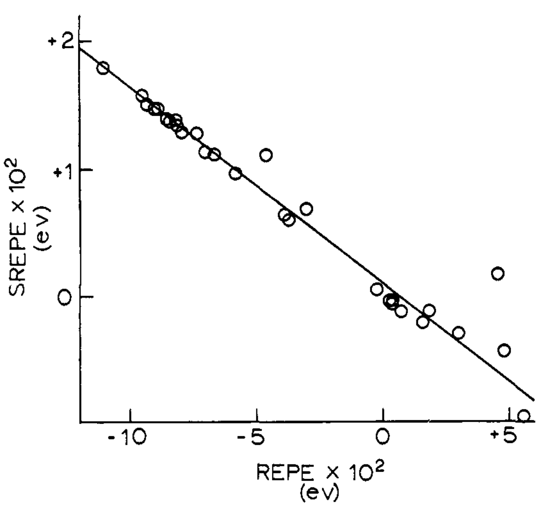

Figure 4. π resonance energy per π electron (REPE) *vs.* σ resonance energy per π electron (SREPE).

$0.0037\beta/1.4199 = 0.004\beta = 0.12$ kcal/mol. Molecules we have studied typically have REPE's lying between $+0.05$ and -0.05β. An accuracy of $\pm 0.005\beta$ seems sufficient to make REPE a useful index.

Strain Energies

In all the methods above, computed ΔH_a's are significantly worse for the nonalternants **14–16**. This is not surprising since these compounds contain strained rings and none of the methods took angle strain into account. Note that all errors are in the correct direction to be explained by angle strain; *i.e.*, **14–16** are computed to be more stable than observed.

To obtain a quantitative estimate of angle strain we have used a method developed by Dauben.[15] This work was never published but appears to have been widely circulated and has been quoted in the literature.[16] We are indebted to Professor K. B. Wiberg who suggested the method to us and sent us a copy of Dauben's notes. Dauben assumed the strain energy to be of the form $\frac{1}{2}A(\Delta\alpha)^2$, where $\Delta\alpha$ is the strain angle. The value $A = 0.024$ kcal deg^{-2} gave good results for both CC single and double bonds. In the case of angle deformation about a triply substituted C atom, as in the ring junctions of azulene, Dauben summed the contribution of all three angle distortions. It seems to us somewhat more reasonable not to do this. The value of A was obtained by considering experimental energies of monocyclic olefins and paraffins. For such olefins, the internal angles of the ring were considered, but distortion of external CCH angles was not. The external CH bond presumably adjusted itself to bisect the internal CCC angle, and any energy changes were counted with the CCC bend. For a triply substituted carbon atom it seems more consistent to count one of the angle distortions from 120° plus the angle of distortion of the remaining bond from the bisector of the first angle. The resulting energy depends upon which angle one chooses first. We take as the first angle that closest to 120°. This gives the minimum distortion energy. For example, in azulene assuming, as Dauben does, regular polygons for the two rings, the angle internal to the five-membered ring at the ring junction is 108°; that of the seven-membered ring is 128.5714°; and the external angle is 123.4286°. Dauben gives for the strain around this atom $\frac{1}{2}A[(120-108)^2 + (120-128.5714)^2 + (120-123.4286)^2] = 2.75$ kcal. We get instead $\frac{1}{2}A[(120-123.4286)^2 + (\frac{1}{2}[360-123.4286]-108)^2] = 1.41$ kcal. There are no experimental data to choose between these two. Table IV shows the computed strain energies and errors in revised heats of atomization. It is seen that strain energy corrections make the nonalternant results as accurate as those for the alternants.

Table IV. Strain Energies

	Compound	Strain energy, kcal	Error in computed ΔH_a corrected for strain, eV Method A	Method B	Dewar
14	Azulene[a]	12.41	−0.40	−0.40	0.27
		(16.4)	(−0.23)	(−0.23)	(0.44)
15	Acenaphthylene	12.81	−0.02	−0.01	−0.02
16	Fluoranthene	12.81	0.09	0.08	0.00

[a] The numbers in parentheses are obtained with Dauben's value of the azulene strain energy.

Conclusions

Dewar's definition of aromaticity seems to us very appropriate since extra stability, compared to an open chain polyene, is a property that most would agree compounds called aromatic possess. Others might prefer another definition, but if one does agree upon this definition, two questions remain. First, how well do other physical properties such as substitution *vs.* addition, nmr chemical shift, and bond alternation correlate with aromaticity? Second, how well do various theoretical methods compute aromaticity? If one has accepted Dewar's definition, and if a method computes accurate heats of atomization for a compound and its corresponding localized polyene, and if the compound is thus computed to be aromatic, then by definition it is

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(15) H. J. Dauben, Notes on Hydrocarbon Strain Energies.

(16) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 244.

aromatic. If, for example, the nmr spectrum then does not show low-field protons, this concerns the first question, not the second.

Fewer experimental heats of atomization of conjugated hydrocarbons are available than one would like, but for those available we have shown that the simple HMO method gives as accurate results, and therefore as accurate predictions of aromaticity, as Dewar's Pariser–Parr–Pople method. Note again that in this work we have not modified the Hückel method itself. We have used it in the familiar simple version, and have changed only the reference structure to accord with Dewar's definition of aromaticity. It remains to be seen how far this success of the simple Hückel method can be extended. Preliminary work on heterocycles is encouraging.

Application of the Principle of Least Motion to Organic Reactions. II.[1] Molecular Rearrangements

Oswald S. Tee*[2a] and Keith Yates[2b]

Contribution from the Department of Chemistry, Sir George Williams University, Montreal 107, Quebec, Canada, and the Department of Chemistry, University of Toronto, Toronto 181, Ontario, Canada. *Received June 21, 1971*

Abstract: Calculations using the principle of least motion have been extended to cover a variety of molecular rearrangements: cyclopropyl–allyl, butadiene–cyclobutene, hexatriene–cyclohexadiene, cyclohexane–cyclohexane, Cope, methylcarbene–ethylene. Despite the assumptions inherent in the approach, there is remarkable concordance with experimental observations and the predictions of more sophisticated theoretical models. The relation between the predictions of the present approach and those arising from consideration of orbital symmetry is discussed.

In the previous paper[1] a generalized method of calculation using the principle of least motion (PLM) was outlined. This approach, which is an extension of that used previously by Hine,[3] was applied to a variety of systems in order to gain insight into the types of reactions to which it might be usefully applicable. The present paper outlines calculations carried out on several molecular rearrangements. Since the PLM approach neglects those atoms not common to the reactant and the product,[1,3] such reactions should be particularly amenable to study.

Concern has been expressed[4] because the calculations consider only the motions of nuclei explicitly. However, the electronic structures of the reactant and the product are implicit in their geometries. For instance, the choice of a planar geometry for ethylene with equilibrium bond lengths and bond angles implies that the electronic structure corresponds to that of the ground state. To require that the geometry of the reactant change smoothly to that of the product implies that their electronic structures interchange smoothly also. The conservation of orbital symmetry[5] also requires that electronic structure and molecular geometry change smoothly from reactant to product.

The understanding of the stereochemical courses of many rearrangements has been greatly enhanced by the invocation of orbital symmetry and, in particular, by the work of Woodward and Hoffmann.[5] However, not all systems of interest can be treated by such an approach. In some instances there may not be suitable elements of symmetry present to enable the correlation of energy levels. In other cases, symmetry arguments may not be able to distinguish between two allowed processes having different stereochemical consequences. It is hoped that PLM calculations may prove to be of value in such cases.

Method of Calculation

The minimum sum of the squares of the atomic displacements ($E_{\min}$)[1] between reactant and product was calculated using the program LESMOT, the basis of which was described earlier.[1,6] For systems where many different conformers of the reactant and/or product were considered, a program LESMOT/2 was utilized which incorporates LESMOT as a subroutine and which evaluates the desired conformations from given initial geometries of the reactant and the product.

The geometries of the molecules studied were calculated[7] either from their published molecular parameters, or from estimates based upon suitable models.[8] The parameters used are listed in Table I.

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[1] Part I: O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969).

[2] (a) Author to whom correspondence should be addressed at Sir George Williams University; (b) University of Toronto.

[3] J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

[4] In particular by one of the referees.

[5] R. B. Woodward and R. Hoffmann, "The Conversation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, and references therein.

[6] The mathematical approach described earlier[1] is very similar to that used for least-squares fitting to nonlinear functions. See, for example: (a) J. B. Scarborough, "Numerical Analysis," John Hopkins Press, Baltimore, Md., 1958; (b) H. Kim, *J. Chem. Educ.*, **47**, 120 (1970); (c) N. R. Draper and H. Smith, "Applied Regression Analysis," Wiley, New York, N. Y., 1968, Chapter 10.

[7] Calculation was either by hand or using the program CORCAL (Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., 1970, program no. 130).

[8] "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18** (1965).