Quantitative Perturbational Molecular Orbital Calculations for Conjugated Hydrocarbons

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Two methods based on Dewar's perturbational molecular orbital approach are shown to be as quantitative for calculation of heats of atomization of conjugated hydrocarbons as the more sophisticated techniques, provided δE_{RS} is minimized according to Dewar's specification for predicting u.v. spectra. In addition, if this convention is adopted, Dewar's method for deriving the rules governing pericyclic reactions is shown not to be totally *equivalent* to the Woodward–Hoffman rules, explaining at least one Woodward–Hoffman violation.

Two methods based on Dewar's perturbational molecular orbital (PMO)[1] theory reproduce heats of atomization of conjugated hydrocarbons with accuracy comparable to the Pariser–Parr–Pople (PPP) method of Dewar and De Llano[2] and the Hückel techniques of Figeys[3] or

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[1] M. J. S. Dewar (*a*) *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3345, 3350, 3353, 3357; (*b*) ' The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969; (*c*) M. J. S. Dewar and R. C. Dougherty, ' The PMO Theory of Organic Chemistry,' Plenum, London–New York, 1975.

[2] M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, 1969, **91**, 789.

[3] H. P. Figeys, *Tetrahedron*, 1970, **26**, 4615.

Schaad and Hess.[4] One of these methods, termed here the direct RS technique, requires knowledge of the Hückel molecular energies[*] of the molecules comprising the R and S pair. The other, which actually yields greater accuracy, does not. Rather than obtain parameters directly from heats of atomization self-consistent field (SCF) values were used virtually without modification. This choice allows total quantitative resonance energies to be calculated by only two reference parameters, an advantage shared by the SCF calculations, but not by the Hückel calculations which require eight reference energies for reliable resonance energies. As the following examples demonstrate, the simplest molecular orbital technique can provide as accurate total ground state energies as those of more complicated techniques for both alternate and nonalternate systems. Admittedly some rather large differences do occur between the various methods, but unfortunately no experimental data is available for comparison.

The PMO Method.—By applying perturbation theory to Hückel wavefunctions, Dewar derived 74 theorems concerning the reactivities and stabilities of conjugated hydrocarbons. Compounds are classified as even alternant, odd alternant, and non-alternant by the familiar starring technique of Longuet-Higgins,[6] and their respective behaviour and properties evaluated. Since most of these theorems have been elaborated on in the previously cited PMO literature, only the few pertinent to this work will be reviewed here.[†]

Union of even alternant hydrocarbons. An even alternant hydrocarbon, RS, formed by union of one bond at atoms r and s of two other even alternant hydrocarbons, R and S, has the π-energy given by equation (1)

$$\begin{aligned} E_{\mathrm{RS}} &= E_{\mathrm{R}} + E_{\mathrm{S}} + \delta E_{\mathrm{RS}} \\ &= \sum_i E_i + \sum_j F_j + 4\sum_i^{\mathrm{occ}}\sum_j^{\mathrm{occ}} \frac{a_{i\mathrm{r}}{}^2 b_{j\mathrm{s}}{}^2 \beta_{rs}{}^2}{E_i + F_j} \end{aligned} \qquad (1)$$

where E_i and F_j are the energies of the molecular orbitals i and j in R and S respectively, $a_{i\mathrm{r}}$ and $b_{j\mathrm{s}}$ are the molecular orbital coefficients of atoms r and s, and β_{rs} is the resonance integral of the bond rs in the united molecule.

If it is assumed that $E_i + F_j$ can be replaced by some average value $2\bar{E}$, and by using other pertinent theorems for even alternant hydrocarbons, expression (1) becomes (2).

$$E_{\mathrm{RS}} = \sum_i E_i + \sum_j F_i + \beta_{\mathrm{rs}}{}^2/2\bar{E} \qquad (2)$$

Cyclic structures formed by union of even alternant hydrocarbons do not, however, have this simple additive relationship. Ring closure can be stabilizing, destabilizing, or inconsequential resulting in an aromatic, antiaromatic, or nonaromatic ring accordingly.

Union of odd alternant hydrocarbons (*direct RS technique*). Union between two odd alternant hydrocarbons produces an even alternant hydrocarbon whose π energy is given by equation (3) where E_i, F_j, and β_{rs} are as

$$\begin{aligned} E_{\mathrm{RS}} &= E_{\mathrm{R}} + E_{\mathrm{S}} + \delta E_{\mathrm{RS}} \\ &= \sum_i E_i + \sum_j F_j + 2\sum a_{0\mathrm{r}} b_{0\mathrm{s}} \beta_{\mathrm{rs}} \end{aligned} \qquad (3)$$

defined previously and $a_{0\mathrm{r}}$ and $b_{0\mathrm{s}}$ are the coefficients of the nonbonding molecular orbitals at atoms r and s in R and S respectively, found by the method of Longuet-Higgins. Usually no second-order terms are included, the assumption being that they are sufficiently small to be ignored in this qualitative method or that the molecules under comparison are of sufficient similarity that the second-order effects cancel.

Nonalternant hydrocarbons. The only nonalternant systems of interest here are those such as azulene, formed by intramolecular union of two atoms of like parity (either both starred or both unstarred) in an even alternant hydrocarbon. Such union produces no first-order perturbation and such compounds can justifiably be termed pseudomonocyclic.

Quantitative Application.—It had been believed until the work of Schaad and Hess that the PMO method was far superior to the Hückel method, and interestingly, it seemed to predict qualitatively what was later observed by experiment or predicted by PPP calculations. Extension was made toward non-planar systems of topological orbital equivalence to the corresponding planar conjugated systems allowing derivation of the Woodward–Hoffman rules without orbital correlation diagrams.[7] It was evidently assumed, however, as it was in the Hückel method that the assumptions were too drastic for quantitative prediction. The two methods given below, however, show that the method is as accurate for conjugated hydrocarbons as any other. As in the work of Schaad and Hess, σ compression energies are not calculated explicitly.[‡]

Direct RS technique. For the direct RS technique, Dewar provides an estimate of 1 eV for the value of β [8] and if SCF σ energies are used, the predicted heats of atomizations are, considering the crudity, surprisingly close.[9] Unfortunately, ambiguity exists as to how the division into R and S should be made. Dewar, using second-order effects as a guideline, suggests δE_{RS} should be minimized. Lehr and Marchand,[10] however, stress maximizing this term, though not citing any theoretical

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[*] Various compilations are available. The values used here for E_{R} and E_{S} are from ref. 5.

[†] Proofs are best found in ref. 1*b*, ch. 6.

[‡] Schaad and Hess demonstrated that CC bond energy was very nearly linear with π bond order of 0.3—0.9. This linear relation allows compensation of σ compression energies in the values of the π energy.

[4] (*a*) B. A. Hess, jun., and L. J. Schaad, *J. Amer. Chem. Soc.*, 1971, **93**, 305; (*b*) L. J. Schaad and B. A. Jess, jun., *ibid.*, 1972, **94**, 3068; (*c*) *J. Chem. Educ.*, 1971, **51**, 640.

[5] R. Zahradnik and J. Pancir, 'HMO Energy Characteristics,' IFI–Plenum, New York–Washington–London, 1970.

[6] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.

[7] M. J. S. Dewar, *Tetrahedron*, 1966, **8**, Supplement p. 75.

[8] Ref. 1*b*, p. 277.

[9] See for example ref. 1*c*, section 3.16, p. 104, β was assumed to be 1.00 eV and Dewar and De Llano σ values assumed.

[10] R. Lehr and A. P. Marchand, 'Orbital Symmetry—A Problem Solving Approach,' Academic Press, New York, 1972, p. 128.

reasoning. Although, Dewar's recommendation was put forward for predicting u.v. spectra, the crude approximations mentioned previously suggested this to be the correct choice for ground state properties, a somewhat interesting result. A second problem arises in determining the values for E_R and E_S. Since they are odd alternant hydrocarbons, no definite method of determining their energy is always possible. If Hückel values are used, only fair agreement is achieved, and higher aromatic compounds have H_a values too large, implying some reduction in E_R and E_S is needed [equation (4)]. Using this as a basis, equation (5) was

$$(E_R + E_S)_{PMO} = K(E_R + E_S)_{HMO} \qquad (4)$$

$$H_a = [(E_R + E_S)0.935\,89 + \delta E_{RS}]\beta + n_{CC\sigma}3.940\,9 + n_{CH\sigma}4.437\,5 \qquad (5)$$

devised where $\beta = 0.942\,56$, $n_{CC\sigma}$ and $n_{CH\sigma}$ are the number of CC and CH σ bonds respectively, and H_a is in eV.

Calculations using this relation are listed in Table 1. No attempt was made to estimate higher perturbations. Comparison is made with experimental values and those calculated by Dewar and De Llano and by method B of Schaad and Hess. As a check, H_a for linear polyenes less the C–H σ energy plotted against the n of Dewar and Gleicher[11] is linear, but the values appear to be too large by *ca.* 0.3 eV. Other polyenes, polyphenyls, and annulenes seem to have H_a slightly too large as well.*

TABLE 1

Heats of atomization for benzenoid hydrocarbons by direct RS technique

	E_π(eV)			H_a(eV)				Error (%)
Compound	(PMO)	PMO	Hückel	SCF *	Obs.	PMO	Hückel	SCF
Benzene	6.89	57.15	57.14	57.16	57.16	0.02	0.03	0.00
Naphthalene	11.70	90.55	90.59	90.61	90.61	0.07	0.02	0.00
Anthracene	16.46	123.89	123.95	123.89	123.93	0.03	0.02	0.03
Phenanthrene	16.73	124.16	124.14	124.22	124.20	0.03	0.05	0.02
Tetracene	21.28	157.29	157.30	157.11	157.56	0.17	0.17	0.29
Chrysene	21.75	157.76	157.67	157.77	157.73	0.02	0.04	0.03
Benzo[*c*]phenanthrene †	21.46	157.47	157.67	157.77	157.48	0.01	0.12	0.18
Benzo[*a*]anthracene	21.59	157.60	157.54	157.58	157.49	0.07	0.03	0.06
Pyrene	19.29	138.54	138.60	138.62	138.88	0.24	0.20	0.19
Triphenylene †	21.63	157.64	157.79	157.94	157.76	0.14	0.02	0.11
Benzo[*e*]pyrene	24.29	172.12	172.08	172.38				
Coronene	29.71	201.18	201.32	201.53				
Pentaphene	26.58	191.17	190.95	191.01				
Pentacene	26.12	190.71	190.90	190.29				
Dibenz[*a,h*]anthracene	26.70	191.29	191.12	191.24				
Dibenz[*a,j*]anthracene	26.74	191.33	191.12	191.24				
Biphenyl	14.16	109.77	109.68	109.75	109.76	0.01	0.07	0.01
Biphenylene	13.75	104.42	104.70	104.87	102.00	2.42	2.70	2.87
Styrene	9.12	76.14	75.85	75.91	75.83	0.41	0.03	0.11
Azulene	10.90	89.75	90.13	89.46	89.19	0.63	1.05	0.30

* SCF values from Dewar and De Llano, unless the calculation was not performed. In that case, the values are from D. H. Lo and M. A. Whitehead, *Canad. J. Chem.*, 1968, **46**, 2027, 2041. Observed values throughout are those listed by Dewar and De Llano, except as otherwise indicated. † Both these compounds were not divided according to Dewar's specifications (ref. 1*c*, p. 406) but in a manner which resulted in lower δE_{RS}. This resulted in better agreement with the observed u.v. spectra as well.

Reference structure method. The mixing of HMO π energies, SCF σ values, and the PMO method, together with the somewhat *ad hoc* correction needed if the points of union differ by two, may be less than satisfying. A much simpler method, which results in greater accuracy, consists of using the reference structure † as a starting point and calculating δE of ring closure, a technique much more in keeping with the spirit of the PMO method as originally envisioned. In this case, no empirical fit was needed and all parameters, including β,‡ are obtained from SCF theory virtually without modification.

In employing this method, heats of atomization are calculated by using the following guidelines. (1) An appropriate starting reference structure should be chosen in which the π energy .can be calculated from the additivity theorem. Such a calculation will result from union of even alternate hydrocarbons at single points of union. It is not necessary, nor in most cases desirable, for the compounds forming the reference structure to have additive π energies. In the example given in Figure 1, stilbene is the appropriate reference compound for calculation of the energy of phenanthrene, and whose

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* If the points of union differ by two the values of this method disagree with SCF values by *ca.* 0.3 eV per extra point of union; the PMO values being too large by 0.3 eV if one point of union and too small by 0.3 eV for each point of union >2. This correction does not necessarily increase the accuracy. In addition the values of large annulenes appear to be somewhat too large when comparison is made with SCF values.

† The reference structure of Dewar and De Llano, with some slight modification can be used. This is not the reference structure of the usual Hückel method which is, as pointed out by Schaad and Hess, unreliable as a criterion for determining aromaticity.

‡ The energy of the aromatization is the first-order perturbational energy of forming the cyclic structure from the open chain analogue. Therefore, while forming benzene from two allyl radicals has $\delta E_{RS} = 2\beta[(1/\sqrt{2})(1\sqrt{2}) + (-1/\sqrt{2})(-1\sqrt{2})]$ (this assures δE_{RS} is the minimum), the heat of aromatization of 'localized' cyclohexatriene forming benzene is half that. This value is equivalent to Dewar's resonance energy, which is 20.00 kcal mol^{-1} for benzene according to Dewar's SCF values. β is therefore easily calculated.

[11] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1965, **87**, 692. All other theories which do reproduce accurate heats of formation require this.

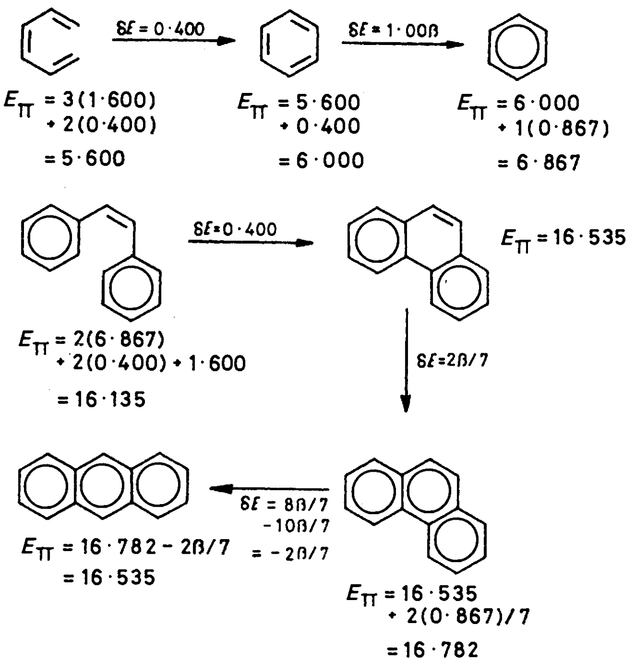

FIGURE 1 Scheme for benzenoid formation (energy in eV)

TABLE 2

Heats of atomization (eV) by the reference structure method

No.	Compound	E_π(PMO)	PMO	Hückel	SCF	Obs.
1	Benzene	6.87	57.14	57.14	57.16	57.16
2	Naphthalene	11.73	90.58	90.59	90.61	90.61
3	Anthracene	16.53	123.96	123.95	123.89	123.93
4	Phenanthrene	16.78	124.21	124.14	124.22	124.20
5	Tetracene	21.24	157.25	157.30	157.11	157.56
6	Chrysene	21.69	157.70	157.67	157.77	157.73
7	Benzo[*c*]phenanthrene	21.72	157.73	157.67	157.78	157.48
8	Perylene	24.26	172.09	172.12	172.15	172.04
9	Benzo[*a*]anthracene	21.52	157.53	157.54	157.58	157.49
10	Pyrene	19.43	138.68	138.60	138.62	138.88
11	Triphenylene	21.96	157.97	157.79	157.94	157.76
12	Pentacene	25.96	190.54	190.90	190.29	
13	Pentaphene	26.36	190.95	190.95	191.01	
14	Dibenz[*a,h*]anthracene	26.52	191.11	191.12	191.24	
15	Dibenz[*a,j*]anthracene	26.73	191.32	191.12	191.24	
16	Benzo[*e*]pyrene	24.24	172.07	172.08	172.38	
17	Dibenz[*a,c*]anthracene	26.78	191.37	191.21	191.35	
18	Dibenzo[*c,g*]phenanthrene	26.73	191.32	191.20		
19	Picene	26.61	191.20	191.21	191.39	
20	Benz[*ghi*]perylene	27.26	186.91	186.74	186.89	
21	Coronene	30.12	201.60	201.32	201.57	

π energy is given as the sum of two benzene energies, one double bond, and the two second-order perturbations corresponding to the π energy of a conjugated ' single ' bond. (2) To determine which is the correct initial additive compound, the first-order term $2a_0b_{0\beta}$ should be minimized in accord with determining the u.v. transition of the final compound. For this reason stilbene is chosen as the correct compound for phenanthrene calculations, rather than 2-butadienylnaphthalene or some similar compound. For reference compounds with nonadditive portions, calculations should be done on those portions as if they were separate molecules. (3) The final first-order term added is δE_{RS} of ring closure and not total δE_{RS}. The total δE_{RS} used in the phenanthrene u.v. transition calculation is $2\beta[(1/\sqrt{7})(1/\sqrt{7}) + (2/\sqrt{7})(2/\sqrt{7})]$, but the second is automatically included when the reference structure was calculated. The remaining first-order term of ring closure is therefore $2\beta(1/\sqrt{7})(1/\sqrt{7})$, to which the constant second-order term must be added. (4) Some complicated polynuclear systems must be analysed carefully to determine the appropriate reference compound. Often this compound is in itself quite complex requiring a separate calculation.

Aromatic hydrocarbons. All values in Table 2 and 3 were calculated using the parameters in Table 4 by the method stated above and illustrated in Figure 1. Some compounds, such as anthracene, must be calculated indirectly as shown if no convenient reference structure allowing minimum δE_{RS} is available. If this is not possible, δE_{RS} is chosen to be as low as possible from some convenient reference structure.

Nonaromatic hydrocarbons. By the PMO definition, a cyclic structure with no first-order energy change from the open chain structure is nonaromatic. The extra π energy of the ' single bond ' must be added, however. These compounds, such as fulvene and fulvalene, have simple additive energies if PMO analysis predicts the compound to be nonaromatic.

Antiaromatic hydrocarbons. Most antiaromatic compounds have $\delta E_{RS} = 0$ and often more than one possibility exists in choosing an RS pair each with different, negative, resonance energies (Figure 2). It is logical, as well as consistent with the above method, to choose the RS pair for which the resonance energy is the least negative. Since antiaromatic compounds tend to adopt bond lengths which reduce the destabilization of the system, this also seems to be realistic. Calculations for nonaromatic and antiaromatic compounds are provided in Table 5.

Methyl substitution. Often methyl substituents stabilize otherwise reactive compounds. Dewar's SCF values were used for the calculations in Table 6.† Again, not unexpectedly, agreement is quite good.

TABLE 3

Heats of atomization (eV) for polyenes and polyphenyls

No.	Compound	E_π	PMO	H_a Hückel	SCF	Obs.
22	Butadiene	3.60	42.05	42.02	42.05	42.05
23	Styrene	8.87	75.89	75.85	75.91	75.83
24	Stilbene	16.13	128.50	128.48	128.54	128.48
25	Biphenyl	14.13	109.74	109.68	109.75	109.76
26	Biphenylene	14.16	104.84	104.87	104.86	104.32
27	Acenapthylene	14.13	104.80	104.87	104.80	104.35
28	Fluoranthene	19.40	138.65	138.59	138.67	138.11
29	1,3,5-Triphenylbenzene	28.66	214.94	214.75	215.00	215.00
30	Hexatriene	5.60	60.80	60.86	60.81	61.10 *
31	Octatetrene	7.60	79.56	79.71	79.60	
32	Decapentaene	9.60	98.31	98.57	98.36	
33	1-Vinylnaphthalene	13.73	109.34	109.32		
34	1-Phenylnaphthalene	19.00	143.18	143.15	143.24	
35	2-Phenylnaphthalene	19.00	143.18	143.13	143.24	
36	2,2′-Binaphthyl	23.86	176.63	176.29	176.69	
37	1,1′-Binaphthyl	23.86	176.63	176.31		

* From ref. 3.

Ring strain. Dauben's calculations of ring strain ‡ allow strain energies to be determined by expression (6)

$$\Delta E_{\text{strain}}\ (\text{eV}) = \Sigma(0.00104)(\Delta\theta)^2/2 \qquad (6)$$

where $\Delta\theta$ is the deviation from the unstrained angle and the sum is over all internal angles except in triply substituted atoms where all three angles are independently calculated.

Some values are listed in Table 7. It is interesting that no other method using Dauben ring strain produces such close agreement with azulene. It should also be mentioned that no method accurately predicts H_a for biphenylene, even compensating for ring strain.

TABLE 4

Parameters for PMO calculations (eV)

σ Energy *			
C–C (sp^2–sp^2)	3.9409	C–C (sp^2–sp^3)	3.8745
C–H (sp^2)	4.4375	C–C (sp^3–sp^3)	3.6957
C–H (sp^3)	4.2816		
π Energy			
Localized bonds †			
C–C	0.400		
C=C	1.600		

In all calculations β was taken as 0.8673 eV (20.00 kcal mol^{-1}).

* The C–C (sp^2–sp^3) value is not listed in ref. 2 but is mentioned in ref. 12. The value listed here was determined by interpolation. The C–H sp^3 value is from ref. 12. † Since in conjugated molecules there is considerable double bond character even in single bonds, the assignment of a π energy to a conjugated single bond is not a contradiction. These parameters were obtained from the values of the bonds given by Dewar and de Llano, and subtracting the σ value of 3.9409. The resulting numbers were then rounded from 0.409 and 1.5969 to 0.400 and 1.600 respectively. This gave improved results.

Comparison with Other Methods.—All three methods, PPP, PMO, and HMO, are of comparable accuracy when experimental data are available. The HMO values for some nonaromatic compounds tend to be slightly larger than those of the PPP method, but the PMO method tends to underestimate the PPP values slightly. More serious discrepancies are *s*-indacene and calicene. The HMO method predicts *s*-indacene to have a low resonance energy of *ca.* 4 kcal mol^{-1}, but by necessity the PMO method predicts an antiaromatic destabilization of *ca.* 10 kcal mol^{-1}. Calicene, according to HMO theory has a large positive resonance energy of *ca.* 11 kcal mol^{-1}, but the compound according to the

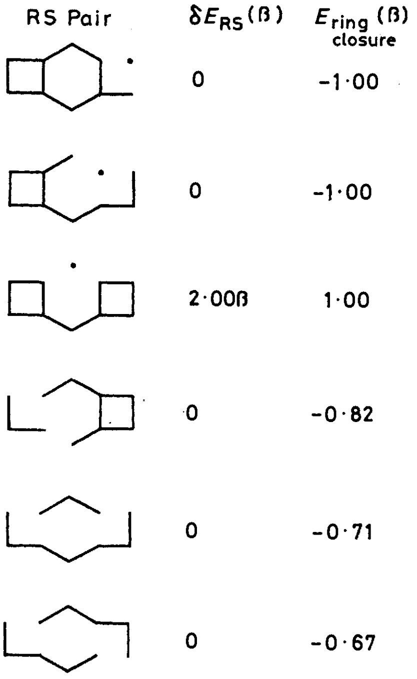

FIGURE 2 Alternative RS pairings for tricyclo[6.2.0.0^{2,5}]decapentaene

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† Ref. 2 and 12 list different values for the needed parameters.

‡ Unpublished, but explained in the Schaad and Hess papers.

[12] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 1968, **90**, 1953.

TABLE 5

Heats of atomization (eV) for cyclic nonalternant, nonaromatic, and antiaromatic compounds

No	Compound	E_π	H_a PMO	H_a Hückel	H_a SCF	H_a Obs.
38	Cyclobutadiene	2.77	36.29	36.20		
39	Benzocyclobutadiene	8.61	70.70	70.64		
40	Tricyclo[6.2.0.$0^{2,5}$]decapentaene *	10.22	84.14	84.01		
41	Butalene	6.40	51.74	51.51	51.47	
42	3,4-Dimethylenecyclobutadiene	6.00	56.27	56.02		
43	Methylenepropene	4.00	37.51	37.57		
44	Fulvene	6.00	56.27	56.37	56.34	
45	Heptafulvene	8.00	75.03	75.23		
46	Fulvalene	10.40	89.25	89.33		
47	Calicene	8.40	70.49	71.43		
48	Sesquifulvalene	12.40	108.01	109.04		
49	Heptafulvalene	14.40	126.76	127.23		
50	Bicyclo[3.2.1]hexatriene	7.27	52.60	52.55		
51	Pentalene	7.40	69.49	70.74	70.53	
52	Azulene	10.98	89.83	90.13	89.46	89.19
53	Heptalene	11.90	107.51	108.59	108.14	
54	Octalene	14.40	126.76	127.66	126.71	
55	*s*-Indacene	12.30	102.97	104.31		

* This is an interesting example of an antiaromatic compound with $4n + 2$ π electrons demonstrating as does pyrene that the number of electrons is not so important as the manner in which they are arranged if a compound is to be considered aromatic or not.

TABLE 6

Heats of atomization (eV) for methyl-substituted conjugated hydrocarbons *

No.	Compound	H_a PMO	H_a Obs.
56	Toluene	69.42	69.43
57	*o*-Xylene	81.70	81.68
58	*m*-Xylene	81.70	81.70
59	*p*-Xylene	81.70	81.69
60	1,2,3-Trimethylbenzene	93.98	93.91
61	1,2,4-Trimethylbenzene	93.98	93.95
62	1,3,5-Trimethylbenzene	93.98	93.98
63	Hexamethylbenzene	103.82	130.50
64	Dimethylfulvene	80.84	80.49
65	Propene	35.57	35.58
66	Isoprene	54.33	54.35

* Observed values taken from J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London and New York, 1970.

PMO method is nonaromatic. Dewar's calculations, however, predict a low resonance energy. The compound itself is unknown, but derivatives, which behave as aromatic compounds, undergoing substitution, do

TABLE 7

Heats of atomization of some nonalternant hydrocarbons corrected for ring strain

Compound	Strain energy (eV)	H_a(eV) uncorr.	H_a(eV) corr.	H_a(eV) obs.
Dimethylfulvene	0.41	80.84	80.43	80.49
Cyclopentadiene	0.30	49.49	49.19	49.23
Azulene	0.65	89.83	89.18	89.19
Acenapthylene	0.45	104.80	104.35	104.32
Fluoroanthene	0.60	138.65	138.05	138.11
Biphenylene	3.74	104.83	101.09	102.00

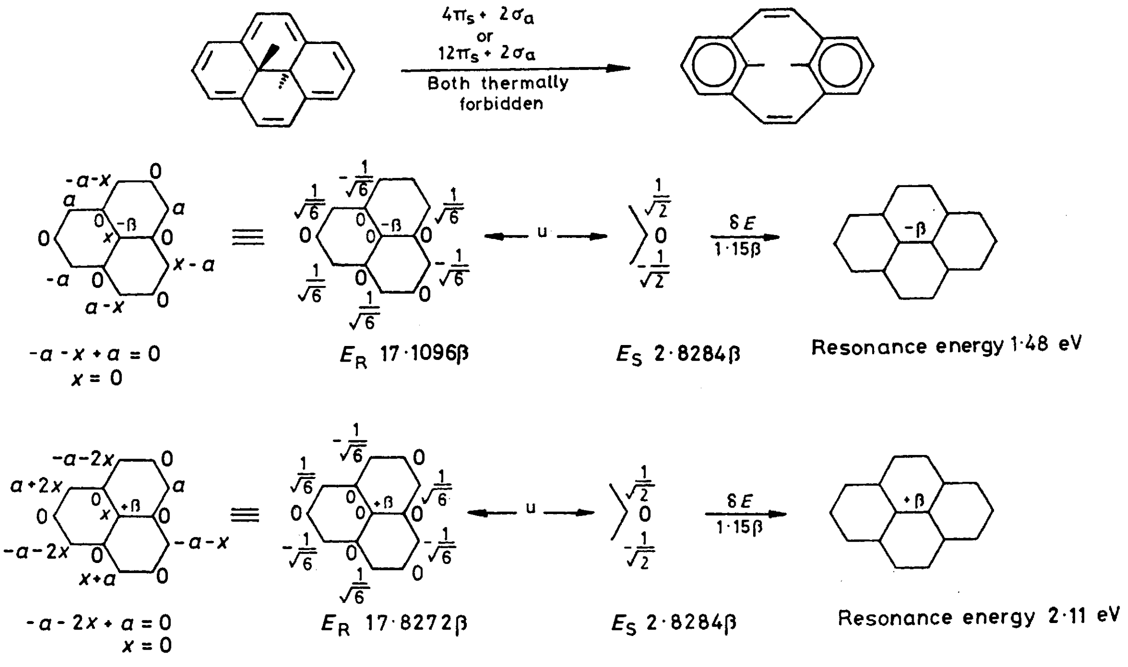

FIGURE 3 Woodward–Hoffman and PMO analysis of thermolysis of 15,16-*trans*-dimethyldihydropyrene

exist.[13] No definite conclusions can be made as to which method is the more accurate.

As a final note, the minimization of δE_{RS} as a basis for PMO calculations allows an unambiguous method for determination of the aromaticity, antiaromaticity, or nonaromaticity of transition states, when using Dewar's method for the derivation of the rules for pericyclic reactions, and in at least one case explains an apparent violation of the Woodward–Hoffman rules quite simply without invoking configurational interactions [14] (Figure 3). *trans*-15,16-Dimethyldihydropyrene undergoes either a 14 electron or 6 electron conrotatory ring opening, with a transition state isoconjugate with anti-Hückel pyrene. The PMO analysis demonstrates that while the compound is not as aromatic as pyrene, it is still quite aromatic and the analogous transition state is therefore aromatic as well. The extra stabilization comes of course from the formation of the aromatic rings, an effect not unambiguously determinable using the Woodward–Hoffman rules, but quite evident with the PMO analysis.

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