

## Quantitative Perturbational Molecular Orbital Calculations. Part 2.<sup>1</sup> Radicals and Heterocycles

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Parameterization of PMO theorems pertaining to radicals and heterocycles has allowed quantitative reproduction of total electronic ground state energies. Results are comparable to the more complicated semi-empirical self-consistent field or Hückel molecular orbital methods.

In Part 1<sup>1</sup> it was shown that Dewar's perturbational molecular orbital (PMO) method not only is an excellent qualitative tool as has been demonstrated repeatedly,<sup>2</sup> but is also capable of quantitative accuracy for calculating heats of atomization of conjugated hydrocarbons. The accuracy, despite the ease of the calculations, is as precise as the self-consistent field (SCF) technique of Dewar and de Llano,<sup>3</sup> the modified Hückel calculations of Figeys,<sup>4</sup> or the unaltered Hückel method of Schaad and Hess.<sup>5</sup> In this paper the earlier hydrocarbon calculations are extended to radicals and heterosubstituted compounds. Proofs of the needed theorems are best found in ref. 2b and only those portions relevant to this work will be reviewed below.

*Conjugated Radicals.*—Dewar originally derived a theorem for calculating the energy of union of an R,S pair where R is an even alternate hydrocarbon and S is a lone  $p$  orbital. The calculation is an indirect one involving a thermocycle in which R is united with the ethylene  $\pi$  system and the resulting first-order term evaluated in back-calculating to the desired radical. The net result is that RS will possess an energy increase over R,  $\delta E_{RS}$ , given by equation (1) where  $E_D$  is the conjugated double

$$\delta E_{RS} = E_D - 2a_0\beta \quad (1)$$

bond energy,  $a_0$  the nonbonding molecular orbital coefficient at the  $p$  orbital after union (obtained easily by the familiar starring technique), and  $\beta$  the resonance (off-diagonal) integral. The extension to larger and more complicated radicals is trivial.

In most qualitative PMO calculations, second-order terms are ignored. This was found to be an unacceptable approximation for quantitative application<sup>1</sup> but fortunately such terms are constant, not only for intramolecular unions (*i.e.*, cyclizations), but for intermolecular unions as well. A more general equation for radicals which would account for these effects is (2) where  $E_{\pi, \text{Rad}}$

$$E_{\pi, \text{Rad}} = \sum_i^{R,S,T} E_i + E_D + (n-1) E_{\pi, c-c} - 2a_0\beta \quad (2)$$

is the total radical  $\pi$  energy,  $E_i$  the energies of the appropriate even alternate systems,  $E_{\pi, c-c}$  the second-order term (equivalent to the  $\pi$  energy of a conjugated single bond †),  $n$  the number of bonds directly attached to the odd  $p$  orbital, and  $a_0$ ,  $E_D$ , and  $\beta$  are as defined previously.

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<sup>‡</sup> All formal conjugated single bonds contain significant  $\pi$  density. As a result,  $\pi$  energy of such a bond is not contradictory.

Any new parameterization is unnecessary if the earlier PMO parameters are employed [equation (2a)].

$$E_{\pi, \text{Rad}} = \sum_i^{R,S,T} E_i + 1.600 + 0.400(n-1) - 2(0.8673)a_0 \quad (2a)$$

Using  $E_i$  values obtained in the earlier calculations, the energies in Table I were determined. Though

TABLE I  
Heats of atomizations for conjugated radicals

Radical	$H_A/eV$			
	PMO	HMO	SCF <sup>a</sup>	Obs. <sup>a</sup>
Allyl	32.04	32.06	32.08	31.92
Benzyl	65.80	65.80	65.64	65.78
$\alpha$ -Phenylethyl	78.05	78.05	77.89	78.19
Cyclohexenyl	63.67	63.68	63.71	63.54
Cyclohexadienyl	58.40	58.38	58.30	58.14
$\alpha$ -Naphthyl	99.40	99.37		
$\beta$ -Naphthyl	99.30	99.27		
Cyclopentadienyl	46.49	46.47		

<sup>a</sup> M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 1968, **90**, 1953. Methyl and methylene energy contribution were also obtained here. Although some alterations were required for the HMO  $\sigma$  values, these were trivial.

adequate experimental values are meagre, the agreement between the calculated and observed values is quite comparable with the other methods.

*Heterosubstituted Hydrocarbons.*—Substitution of a heteroatom into a carbon framework can be looked upon, at least as far as the electronic system is concerned, as introducing a perturbation at that atom by inducing changes in electronegativity and overlap properties. The basic PMO theorems pertaining to heteroatomic compounds traditionally employed are as follows. (1) Heterocyclic compounds with orbital topology equivalent to polynuclear hydrocarbons or with lone electrons as part of the  $\sigma$  system will have a resonance energy identical with the associated hydrocarbon, although the reference energies may vary. (2) If the compound is isoconjugate with a hydrocarbon anion or cation,<sup>§</sup> the energy difference,  $\delta E_{X,A/C}$ , over the anion or cation is given by equation (3) where  $\delta\alpha_X$  is an electro-

$$\delta E_{X,A/C} = (1 - a_0^2) \delta\alpha_X \quad (3)$$

negativity difference between the heteroatom X and a carbon atom in a similar environment. (3) Nonalternate anions or the analogous heterocycles have an energy

<sup>§</sup> In HMO and PMO (but not SCF) calculations, acyclic and benzylic type anions and cations have energies identical to those of the radicals.

change  $\delta E_{NA}$ , over the open chain systems given by equation (4) where  $a_0$  and  $b_0$  are the NBMO coefficients

$$\delta E_{NA} = 2a_0b_0\beta \quad (4)$$

involved in the intramolecular union. If both coefficients are of identical algebraic sign stabilization results upon ring closure; opposite signs indicate destabilization.\* Although the heterosystems do not necessarily possess the same  $a_0$  and  $b_0$  values as the appropriate anions, generally no modification is attempted and none will be done so here. (4)  $\beta_{XC}$  is usually assumed equal to  $\beta_{CC}$ .

To turn the above theorems to quantitative utility, it is necessary to realize that they in essence define two classes of compounds, one with the lone pair of the heteroatom orthogonal to the  $\pi$  system and the other with the lone pair forming part of the  $\pi$  electrons.

As long as the compounds contain no heteroatom lone pair in the  $\pi$  system, the difference between the  $\pi$  energies of the heteroatom and the related hydrocarbon energy is simply given by equation (5) where  $\delta E_{\pi,C=X}$  and

$$\delta E_{\pi} = \sum_{C=X}^{\text{all}} \delta E_{\pi,C=X} + \sum_{C-X}^{\text{all}} \delta E_{\pi,C-X} \quad (5)$$

$\delta E_{\pi,C-X}$  are merely the differences between the carbon-carbon and carbon-heteroatom double and single bonds. Since theorem (1) assures that the resonance energy of the hydrocarbon and the heteroanalogue will be identical, the above equation is valid for aromatic, nonaromatic, and antiaromatic compounds provided they meet the stated lone pair criterion. In addition, SCF bond values

TABLE 2

Bond strengths (all values, except for oxygen values are from previous SCF determinations)

Bond type	$E/eV$
$\sigma$ C-C	3.9409
C-N	3.3463
C-O	4.0000
C-S	3.2780
C-H	4.4375
N-H	4.0420
O-H	4.8008
S-H	3.5258
$\pi$ C=C	1.6000
C-C <sup>a</sup>	0.4000
C=N <sup>b</sup>	1.8191
C-N <sup>a</sup>	0.4880
C=O <sup>b</sup>	2.8350

<sup>a</sup> Some  $\pi$  overlap occurs in conjugated single bonds. <sup>b</sup> Uncharged.

work perfectly for evaluating the terms as they did in the PMO calculations for hydrocarbons, making it unnecessary to obtain them from total ground state energies, although of course this would have been possible as well. The compounds to which equation (5) would be commonly applied are those with pyridine nitrogen, ketones, imines, and thioketones although no experimental values are available for the last two.

If on the other hand, a heterosubstituted hydrocarbon does possess a lone pair as part of the  $\pi$  system, the com-

\* The reverse rules apply for cationic systems, but for most common organic heterocycles these systems are not important.

pound will have an orbital topology of a hydrocarbon anion and theorems (2) and (3) must be used. In addition equation (3) must be modified slightly to (6) to account both for the effect that in the thermocycle  $E_D$  will be for a carbon-heteroatom bond and for second-order effects. In principle, the first two terms are the

$$\delta E_{\pi,X} = \delta E_{\pi,C=X} + (n-1)\delta E_{\pi,C-X} + (1-a_0^2)\delta\alpha_N \quad (6)$$

same as above and should have identical values.  $\delta\alpha_N$  might also be obtained from SCF values but both these

TABLE 3

Additive perturbation terms for lone pair  $\pi$  contributions

Heteroatom	Environment	$\delta E_{\pi,C=X} + (n-1)\delta E_{\pi,C-X}/eV$
N (amines)	Primary	0.2191
	Secondary	0.0000
	Tertiary	-0.2247
O (phenols and others)	Primary	0.6964
	Secondary	0.6615
S (sulphides)	Primary	0.4140
	Secondary	0.0499

assumptions in fact provide quite poor energies, and empirical adjustments, albeit perhaps justifiable ones, are required.

TABLE 4

Other parameters

Heteroatom	$\delta\alpha_X$ (eV)
N	-0.7592
O	-2.0632
S	-1.1568

$\beta = 0.8673$  eV in all cases.

By using aniline as a model and the SCF value for  $\delta E_{\pi,C=N}$  of 0.2191 eV,  $\delta\alpha_N$  was set at *ca.* 0.76 eV. Such a value did indeed provide excellent agreement for other primary amines. However, if the appropriate value of  $\delta E_{\pi,C-N}$  (0.088 eV) is used in calculations for secondary amines, the agreement is far poorer, the sum  $\delta E_{\pi,C=N} + \delta E_{\pi,C-N}$  needing to be very nearly zero if the desired accuracy is to be achieved. In addition it appeared that for a tertiary amine the sum would require a negative value. This descending trend is not unique for nitrogen but also characteristic of oxygen and sulphur.

It is possible in such an approximate method to accept this as purely a needed empirical adjustment, but it can also perhaps be rationalized as having some physical meaning by considering that only in the case of a primary amine will the thermocycle proceed through an uncharged imine structure. The smaller  $E_D + \delta E_{\pi,C=X}$  value would be expected with increasing charge with all heteroatoms studied, and it appears this trend is therefore not qualitatively incorrect. On the other hand trying to assign some absolute interpretation onto the magnitude of these values is probably meaningless.

All parameterization was performed on compounds with the heteroatom in an acyclic environment. Stability of ring closure (or lack of it) can be calculated by theorem (3). In the light of the above discussion if the system contains a particular substitution at the heteroatom (primary, secondary, or tertiary) this should remain

unchanged in proceeding from the acyclic to the cyclic structure. Rigorous arguments also indicate heterocyclic and anion coefficients should vary somewhat but

TABLE 5

Heats of atomizations for heterosubstituted compounds

Compound	$E_{\pi}$	$\sigma$ Strain	$H_a/eV$	
			Calc.	Obs. <sup>a</sup>
Pyridine	7.17	0.00	51.82	51.80
Quinoline	12.04	0.00	85.26	85.18
Acridine	16.84	0.00	118.64	
Pyrrole	4.67	0.30	44.68	44.72
Indole	9.65	0.45	78.09	78.07
Diphenylamine	14.18	0.00	116.58	116.53
Carbazole	14.76	0.60	111.63	111.99
Aniline	7.05	0.00	64.31	64.27
1-Naphthylamine	11.97	0.00	97.81	97.71
2-Naphthylamine	11.93	0.00	97.77	97.78
Vinylamine	1.81	0.00	30.50	
Divinylamine	3.69	0.00	48.93	
Trivinylamine	5.54	0.00	67.34	
Divinyl ether	3.48	0.00	45.99	45.92
Furan	4.46	0.30	41.74	41.62
Phenol	6.97	0.00	61.60	61.60
1-Naphthol	11.73	0.00	94.94	94.97 <sup>b</sup>
2-Naphthol	11.79	0.00	95.01	95.05 <sup>b</sup>
Benzofuran	9.17	0.45	83.75	
Diphenyl ether	14.06	0.00	113.72	113.73
Hydroquinone	7.07 <sup>c</sup>	0.00	66.06	66.04
Dibenzofuran	14.63	0.60	108.76	108.72
Formaldehyde	2.83	0.00	15.71	15.69
Benzaldehyde	10.01	0.00	68.31	68.39
Benzophenone	17.37	0.00	120.91	120.89
Divinyl sulphide	3.48	0.00	44.54	
Benzenethiol	7.07	0.00	59.71	59.71
Thiophen	4.46	0.30	40.28	40.32

<sup>a</sup> Experimental values were recalculated from data provided in J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London-New York, 1970, except in the case of quinoline which was from ref. 3c. <sup>b</sup> Heats of sublimations taken from 'Handbook of Chemistry and Physics,' Chemical Rubber Company, Cleveland, 1970-1971, 51st edn., p. C 716. <sup>c</sup>  $E_{\pi}$  determined by assuming two delocalized orthogonal nonbonding molecular orbitals whose coefficients are determined by starring the structure as would be done for an odd alternate system. In such cases where two nonbonding orbitals occur it is assumed that in one orbital the starred atoms will have nonzero coefficients and in the other orbital the unstarred atoms will. The coefficients are approximated as usual after ignoring the oxygen atom with the zero valued coefficient so that an odd alternate system is formed. In this case, both orbitals have identical coefficients with the benzyl anion, but are offset by one atom. Unfortunately, no further experimental confirmation is available as an additional check for this method for diamino-, dihydroxy-, and dialkoxy-benzenes except for systems such as veratrole, which has a  $\pi$  energy identical to hydroquinone. When proper values are chosen for the additional  $\sigma$  energies agreement is quite good, however.

corrections for this results in unnecessary complexity due to additional  $\beta$  values. In addition, results are not necessarily improved.

These nonalternate systems will also inevitably suffer from  $\sigma$  strain. Although in some instances SCF and HMO values seem somewhat insensitive to this effect, PMO values in almost all these cases manifested evidence of ring destabilization. Dauben<sup>6</sup> has proposed an empirical equation for correcting these effects, the

energy of ring strain  $\Delta E_{\text{strain}}$  (eV) being given by  $0.001\ 04\ \Sigma (\Delta\theta)^2/2$  where  $\Delta\theta$  is the difference of the normal angle for the particular hybridization of the atom and the observed value. The sum is taken over all internal angles except for triply substituted centres in which the contribution from all three angles is determined. Usually regular polyhedra are assumed.

Unfortunately the amount of ring strain contribution at a heteroatom centre is not as easily determined as for carbon atoms since the planarity of the heteroatom cannot necessarily be assumed. Rather than attempt a reparameterization of Dauben's equation, it was assumed that the heteroatoms contribution to  $\sigma$  strain was small. Somewhat surprisingly, this initial assumption worked perfectly. It should be emphasized that Dauben strain was not included to obtain the parameters in any manner and the excellent agreement of the calculated values with experiment followed independently.

**Conclusion.**—All values for heterocompounds are listed in Table 5. The agreement is as good as the other methods but as mentioned in the HMO work the limited number of experimental values is a handicap for any comparison with the calculated values. A 'best' set of parameters can only be reliably evaluated when new experimental values are available and the older ones redetermined as well.

It might appear that the added element of empiricism present for heterocompound calculations (but absent for radical energies) is unfortunate, but the simplicity involved is certainly some compensation. The ease of the calculations in fact allows the PMO method to be used as a quantum mechanically based alternative to the totally empirical group additivity methods when the more complex calculations are, for one reason or another, not available. Also additivity methods do not account for the extra stability of the non-alternate systems unless a totally *ad hoc* correction is included. Such effects are not a problem in the PMO calculations since any such correction is determined explicitly by the method itself.

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