Notes

On the Application of Dewar's Definition of Resonance Energy to the Hückel Method

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In the 1940's Hückel delocalization energy appeared to be a theoretical parameter that promised to correlate with the experimental chemist's concept of aromaticity. However, as more computations were made, it was found that almost all conjugated systems, even those such as fulvene which subsequently were determined not to be aromatic, have substantial Hückel delocalization energies. The Hückel method seemed therefore to fail in the prediction of aromatic character, and more elaborate schemes were investigated. Many of these failed too, but in 1969 Dewar and de Llano[1] published calculations based on the Pariser–Parr–Pople (PPP) method[2,3] which gave strikingly good predictions of aromaticity. However, in computing resonance energy, they made use of a polyene reference structure instead of the usual reference of isolated double bonds. It turns out that it is this change in reference rather than the switch to a more sophisticated computational method which is crucial. We have found[4–7] that, with a reference structure analogous to Dewar's, the simple Hückel method can make as accurate predictions of aromaticity as can Dewar's more elaborate procedure.

Use of a polyene reference structure goes back to the work of Dewar and Gleicher,[8] who found that the π energy of acyclic polyenes computed by the PPP method can be represented accurately as the sum of bond energy terms. Two such terms, one for double and one for single bonds, were found to be sufficient. Resonance energy was then defined as the difference between the calculated π energy and the sum of bond energy terms. This difference vanishes for acyclic polyenes, is positive for aromatics, and is negative for antiaromatics. For example, in the case of benzene, E (resonance) = E (PPP of benzene) − 3 [E (double bond) + E (single bond)].

In applying Dewar's idea of a polyene reference structure to Hückel calculations, we found that we were unable to reproduce the Hückel energies of the acyclics to a sufficient accuracy using only two bond-energy terms. Instead we required the eight listed in Table I.

Table I

π Bond Types and Energy Terms for Carbon–Carbon Double and Single Bonds

Bond	Type	E_{ij} (β)
$CH_2{=}CH$	23	2.0000
$CH{=}CH$	22	2.0699
$CH_2{=}C$	22′	2.0000
$CH{=}C$	21	2.1083
$C{=}C$	20	2.1716
$CH{-}CH$	12	0.4660
$CH{-}C$	11	0.4362
$C{-}C$	10	0.4358

Two papers similar to ours have also appeared recently. In the one by Milun, Sobotka, and Trinajstić[9] the simple Hückel method was used; the other by Figeys[10] employed an iterative modification (LCAO-BETA). Both used only two bond types. We wish to compare here the results of these two methods with ours and comment upon the problem of eight *vs.* two bond types.

In the bond energy terms of Table I, the subscript ij refers to a bond of nominal order i with j attached H atoms. Although for convenience we have classified bonds according to the number of attached hydrogens, a more significant index would probably be $(4 - j)$ = the number of links to the conjugated system. It is of course not surprising that we are able to fit the acyclic energies with eight parameters; the point is that the use of these bond energy terms, fit to the *total* π energy of *acyclics*, gives *resonance* energies for *cyclic* compounds that are in excellent agreement with the experimental properties of a wide range of both alternant and nonalternant hydrocarbons.[4–7] Further, there is evidence for more than two bond types from Dewar's own work. Computed bond lengths[1,11] for acyclic compounds are shown in Figure 1 grouped according to our bond types.[4] The double bonds do fall into five types of different lengths, although the single bond types overlap.

It is impossible to construct a compound with arbitrary numbers of each of the bond types in Table I. There are in fact two linear relations connecting the numbers of the various bond types.[4,7] It follows that two of the bond energy terms can be fixed arbitrarily. Therefore no attempt should be made to correlate bond length with bond energy term. Other, but equally valid, choices of the two arbitrary energies can reverse the order of bond energies, can give single bond energies greater than double, or can give negative bond energies. All choices lead to identical resonance energies for all molecules.

Aromatic Stabilities (A_s) of Trinajstić.—Trinajstić has reported the calculation of "aromatic stabilities" (A_s) using the Hückel method,[9] and two bond-energy terms obtained from the linear acyclic polyenes. While

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

[2] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[3] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[4] B. A. Hess, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 305 (1971).

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

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

[7] L. J. Schaad and B. A. Hess, Jr., *J. Amer. Chem. Soc.*, **94**, 3068 (1972).

[8] M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 692 (1965).

[9] M. Milun, Z. Sobotka, and N. Trinajstić, *J. Org. Chem.*, **37**, 139 (1972).

[10] H. P. Figeys, *Tetrahedron*, **26**, 5225 (1971).

[11] C. R. de Llano, Ph.D. Thesis, University of Texas, 1968.

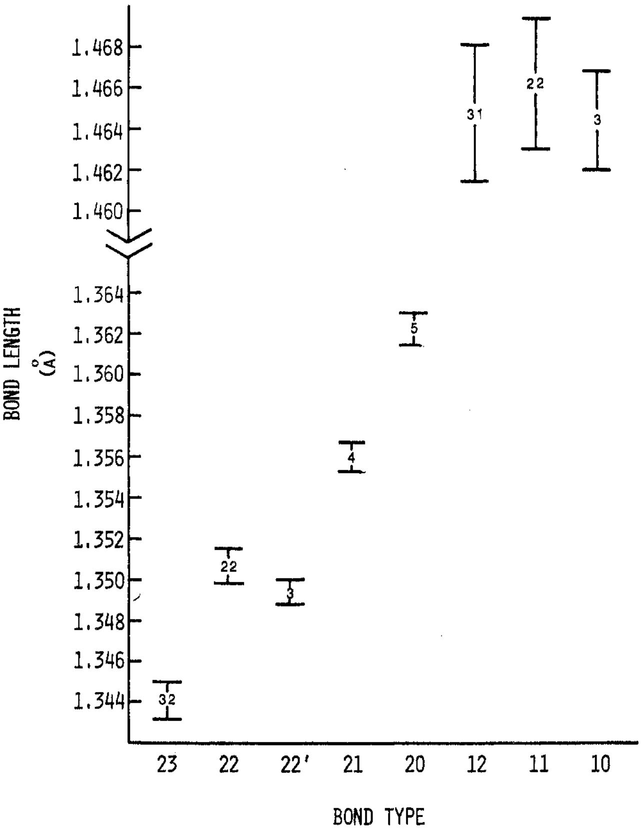
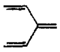
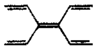


Figure 1.—Calculated bond lengths[1,11] in acyclic hydrocarbons. The bond types are those in Table I. The numbers between bars give the number of bonds of a type in the indicated range (*e.g.*, there are 32 bonds of type 23 computed to have length between 1.343 and 1.345 Å). Note the break in scale between 1.36 and 1.46 Å.

indeed these terms can be used to obtain the π energies of linear acyclic polyenes, they do not give additivity for many branched acyclic polyenes (see Table II).

TABLE II

COMPARISON OF ADDITIVITY OF BRANCHED ACYCLIC POLYENES USING TWO AND EIGHT BOND TYPES WITH THE HÜCKEL AND LCAO-BETA METHODS

Compd	Hückel REPE (β)		LCAO-BETA REPE (eV)	
	Two bond types[a]	Eight bond types[b]	Two bond types[c]	Eight bond types[d]
	−0.024	0.004	−0.012	0.004
	−0.029	0.003	−0.021	0.003
	−0.016	0.001	−0.011	0.001

[a] Bond energies in ref 9 used. [b] Reference 4. [c] Bond energies in ref 10 used. [d] Eight bond energies obtained using LCAO-BETA energies of 40 acyclics in ref 4.

Hence a basic premise of Dewar's definition—the additivity of all acyclic polyenes—does not hold. Furthermore, a comparison of our HMO resonance energies per π electron (REPE) with Trinajstić's aromatic stability per π electron (A_s/e) (see Table III) indicates that while for many compounds the two methods give very similar results there are notable exceptions. The REPE of fulvene suggests that it is nonaromatic, while the A_s/e indicates that it is antiaromatic. The same is true for methylenecyclopropene and trimethylenecyclopropane.

TABLE III

HÜCKEL RESONANCE ENERGY PER π ELECTRON (REPE), INDICIES OF AROMATIC STABILITIES PER π ELECTRON (A_s/e), AND LCAO-BETA RESONANCE ENERGIES PER π ELECTRON (LCAO-BETA REPE)

Registry no.	Compd	REPE (β)	A_s/e (β)	LCAO-BETA REPE (eV)[a]
71-43-2	Benzene	0.065	0.073	0.075
91-20-3	Naphthalene	0.055	0.056	0.064
129-00-0	Pyrene	0.051	0.049	0.060
83-32-9	Acenaphthalene	0.039	0.038	0.047
275-51-4	Azulene	0.023	0.024	0.027
3227-90-5	Trimethylenecyclopropane	−0.002	−0.043	−0.001
497-20-1	Fulvene	−0.002	−0.016	−0.002
250-25-9	Pentalene	−0.018	−0.018	−0.020
5291-90-7	Dimethylenecyclobutene	−0.028	−0.058	−0.028
6249-23-6	Calicene	0.043	0.043	0.050
4026-23-7	Benzocyclobutadiene	−0.027	−0.027	−0.020
4095-06-1	Methylenecyclopropene	0.005	−0.020	0.005

[a] Obtained using eight bond-energy terms calculated from the energies of the 40 acyclics in ref 4.

The LCAO-BETA Method of Figeys.—Using an iterative method to adjust the Hückel parameters Figeys has also determined that the energies of the linear acyclic polyenes are additive when only two bond energy terms are considered and has used these terms to obtain resonance energies of the annulenes.[10] However, as in the simple Hückel method, we have found that these terms do not give accurate additivity of branched acyclic polyenes (see Table II). We have carried out a treatment of the LCAO-BETA results in a fashion exactly analogous to our treatment of the simple Hückel results.[4] One is able to obtain eight bond-energy terms which do give additivity of all acyclic polyene energies. Furthermore, resonance energies obtained with these terms are almost exactly analogous to the Hückel resonance energies obtained by our method (Table III). Hence it appears that nothing is gained over the simple Hückel method in going to the more complex LCAO-BETA method.

Heterocycles Containing a d-Orbital Acceptor Atom. Consideration of the Dependence of Structural and Reactivity Effects on Whether the Number of Ring Atoms Is Odd or Even

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I wish to call attention to a ring-size effect upon the symmetry of planar cycloalkane filled molecular orbitals. The effect is such that heterocycles containing