CROATICA CHEMICA ACTA CCACAA **57** (6) 1621—1628 (1984)

YU ISSN 0011-1643
*CCA-1545* UDC 541
*Original Scientific Paper*

# A Comparison of Pencil and Paper Procedures. PMO, Free Electron PMO, and Structure-Resonance Theory Calculations for Proton Affinities

*László v. Szentpály*

*Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 7000 Stuttgart 80, West Germany*

*William C. Herndon*

*Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79967, USA*

Received February 9, 1984

Pencil and paper quantum chemical procedures are applied to correlations of electrophilic substitution and proton affinity data. The data are also compared with other types of MO calculations, including SCF results, and simplified methods are found to give as satisfactory correlation as the more complex procedures.

## INTRODUCTION

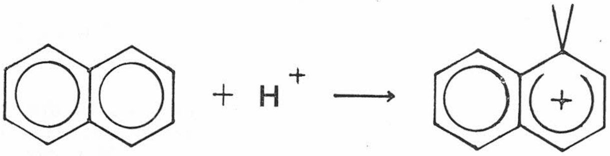
Quantum chemical pencil and paper procedures can be used to correlate kinetic and thermodynamic data, particularly for structurally related sets of $\pi$-system organic compounds. Methods are required that are widely applicable, easy to use, and that give quantitatively good results for correct physical reasons. Reactivity indices obtained from Hückel MO calculations of course lie in the pencil and paper category. Actual HMO calculations are seldom necessary since there are comprehensive tabulations of eigenvalues, eigenvectors, and derived indices for nearly all common $\pi$-systems with less than thirty *p*-orbitals.[1] However, the correlative ability of HMO calculations is generally worse than results from SCF-$\pi$ or all-valence-electron SCF methods. This can be seen in, *e. g.*, the work of Streitwieser, *et al.*,[2] in which rates of protodetritiation of aromatic hydrocarbons are compared with several types of localization energy calculations. Correlation coefficients with the log of the rate constant are 0.979, 0.970, and 0.893 for localization energies calculated by CNDO/2, SCF (Nishimoto-Mataga[3]), and HMO methods respectively.

The perturbational MO method of Longuet-Higgins[4] and Dewar[5], thoroughly reviewed by Dewar and Dougherty[6], has been the pencil and paper method of choice for most applications. Applied to the protodetritiation data referred to above there is some improvement (corr. coeff. 0.926) over the standard HMO method, but the quality of the correlation can still only be characterized as »fair«.[7] Since the protodetritiation reaction can be considered to be the prototype electrophilic substitution reaction, an argument against the use of the PMO procedure might be adduced from this example.

Recently, a modified free-electron MO approach[8-10] and a valence bond structure-resonance theory (SRT)[11-13] have been separately applied to several common organic structure and reactivity problems. A new perturbational variant of the free-electron MO method (PMO : F) has also been derived and reported.[14] Both PMO : F and SRT qualify as simple pencil and paper procedures. In this paper PMO : F and SRT localization energies will be compared with experimental electrophilic substitution parameters[2,15-19] and with proton affinities (PA) obtained by gas phase ion-equilibrium methods.[20,21] The theoretical methods predict gas phase values of PA, but previously the basicities of organic $\pi$ systems had only been estimated in solution. The experimental PA data should constitute an excellent test for theoretical calculations.

## CALCULATION PROCEDURES

Protonation of a $\pi$ organic base is presumed to lead to a delocalized even electron cationic species, the so-called Wheland intermediate in electrophilic substitution reactions. If the cation is an odd alternant $\pi$ system, the difference



(1)

between the $\pi$ energy of the cation and that of the neutral $\pi$ hydrocarbon can be estimated by perturbation theory. In both Hückel and the free-electron models, the odd alternant cation possesses a nonbonding orbital. The eigenvector coefficients of this NBMO can be written by inspection, since they must conform to the zero-sum rule.[4] Expositions of procedures for finding the coefficients are available[22-24], so details will not be given here. The important point is that the localization energy for reaction (1) can be estimated from the first order change[4-6] in energy given by Eq. (2),

$$\Delta E = 2 \left| c_r \beta_r + c_s \beta_s \right| \qquad (2)$$

where $c_r$ and $c_s$ are the NBMO coefficients adjacent to the site of protonation, and the $\beta$'s are the corresponding resonance integrals.

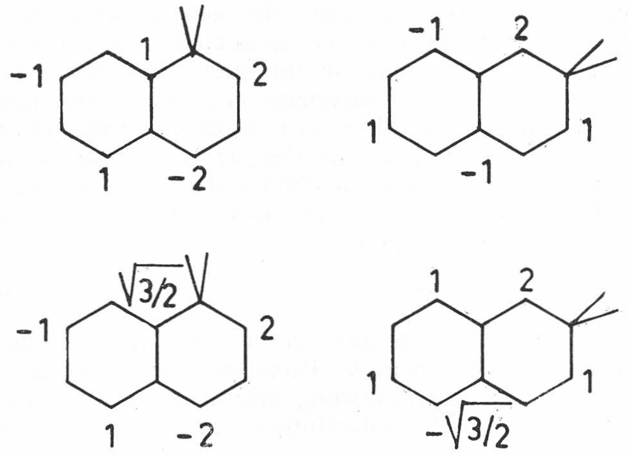
A free-electron topological matrix can be formulated in terms of an LCAO model with only nearest neighbor interactions using a procedure advanced by Ruedenberg and Scherr.[25] The FE topological matrix is identical to the Hückel topological matrix except for the fact that the FEMO method differentiates the values of off-diagonal resonance integrals involving $\pi$ bonds at branching points of the carbon skeleton. Atoms at branching points are called joints. The FEMO branching conditions[26,27] require the introduction of three related resonance integrals instead of the usual single resonance integral of HMO theory.

| | |
|---|---|
| $\beta$ | between a pair of nonjoints |
| $\sqrt{2/3}\ \beta$ | between a joint and a nonjoint |
| $2/3\ \beta$ | between a pair of joints |

Now, these are not additional parameters since their relationship to the HMO $\beta$ is a consequence of the branching conditions appropriate to FEMO's.[26,27]

The similarities between the FEMO and HMO models are reflected in the PMO : F and PMO methods. One finds that the amplitudes of the NB free-electron de Broglie wave are precisely given by the values of the Hückel NBMO coefficients. However, the FENBMO coefficients become different owing to the different number of branches connected to the atoms. In order to obtain correct normalization, the free-electron NBMO coefficient at a joint of the odd alternant cation contains a factor $\sqrt{3/2}$ which does not show up at nonjoints. After normalization all FENBMO coefficients for systems that contain joints must necessarily differ from their Hückel counterparts. Eq. 2, of course, remains valid for the PMO : F method.

The FENBMO coefficients of $\pi$ cations corresponding to $\alpha$ and $\beta$ protonations in naphthalene are derived in **1** to serve as examples. Note that in the case of $\alpha$ protonation, the FEMO model offers two possibilities for the effective potential. The bridge-head atom on the ring may be treated either as a joint or a nonjoint. In the first case, an appendix of the free-electron path is pointing towards the $\alpha$-position. In this paper, the bridge-head atom normally is taken as a joint.



unnormalized Hückel NBMO coefficients (zero sum rule)

unnormalized FENBMO coefficients

$$\frac{2\left(\sqrt{\frac{3}{2}\cdot\frac{2}{3}}+2\right)\beta}{\sqrt{11.5}} = 1.769\,\beta \qquad \frac{2\,(2+1)\,\beta}{\sqrt{8.5}} = 2.058\,\beta \qquad \Delta E\ \text{(localization)}$$

**1**

However, the strain in the case of other than six-membered rings needs special consideration. Generally, the $\alpha$ positions adjacent to a fused strained ring have reduced reactivity toward electrophilic substitution[28,29]. The increased strain in five- or four-membered rings adjacent to an $\alpha$ protonation site is modeled in the PMO : F-method by treating the bridge-head atom of the strained ring as a nonjoint. An increase in $\pi$-localization energy is obtained by the different normalization and by using the resonance integral $\beta$ between a pair of nonjoints. This is a quantitatively effective, but somewhat indirect modeling of the experimental results (Table I), because the NBMO energy of the FEMO and PMO : F models is independent of the assumption regarding the bridge-head atom. On the other hand, the NBMO's of all odd-alternants are regarded as degenerate, without inferring that the different Wheland intermediates had the same stability.

As a hydrocarbon with an odd-membered ring possesses at least a near-nonbonding orbital, the PMO-method has been successfuly extended to such systems[30]; in this paper, we extend PMO : F as well. The coefficients of the near-NBMO are obtained by severing the odd-membered ring in order to generate alternant systems. Contrary to the earlier recipe[30], the severing is not done at the bonds adjacent to a given atom, because this would sometimes create another odd-membered ring. As a rule, the odd-membered ring can be severed in two different ways, without at the same time severing an even-membered ring. The unnormalized coefficients of the NBMO's of each new system are found according to the zero-sum rule[4]. The new systems have identical coefficients in the protonated part of the connected ring systems, whereas even the starring of the atoms changes in the other part. Here, the unnormalized coefficients of the original non-alternant system are obtained by addition of the two severed systems. The identical coefficients of the other part must not be added, however. It is easily verified by comparison with HMO and FEMO calculations, that the normalized PMO and PMO : F orbitals are very similar to those of the parent models. The near-NBMO energy is obtained by first-order intramolecular perturbation

$$E = \alpha + c_o c_p \beta_{op} + c_t c_u \beta_{tu} \tag{3}$$

where the c's are the normalized coefficients adjacent to the severed bonds, and the $\beta$'s the corresponding resonance integrals. These perturbational energies are in good agreement with the corresponding orbital energies of the HMO and FEMO models. For electrophilic substitution, $\Delta E$ (localization) is calculated[30] as

$$\Delta E \text{ (localization)} = 2 \left| c_r \beta_r + c_s \beta_s + E - \alpha \right| \tag{4}$$

Procedures and results of VB structure-resonance calculations are detailed in a recent review article[12], so only a brief outline will be given. Referring to **1**, the number of resonance structures for the cations obtained by summing the absolute values of the NBMO coefficients, 7 and 6 for $\alpha$ and $\beta$ cations respectively. The number of Kekule structures for the original hydrocarbon is 3, given by the sum of the coefficients adjacent to the site of protonation. The $\pi$ energies in SRT have been precisely related to the logarithm of the number of structures in several investigations.[12] Therefore a reactivity index for protonation is related to the logarithm of the SC ratio, $\ln (7/3) = 0.847$ ($\alpha$ protonation) and $\ln (6/3) = 0.693$ ($\beta$ protonation).

## RESULTS AND DISCUSSION

A set of $\sigma^+$ constants from several investigations,[2,15–19] gas phase proton affinities,[20,21] and PMO : F, PMO, and SRT localization energies are summarized in Table I. The $\sigma^+$ values comprise a larger set of test data than the rate constants of Streitwieser *et al.*[2] mentioned above. The most significant differences are $\sigma^+$ values for anthracene derived from actual protodetritiation experiments and new values for biphenyl, recently reported by Taylor and his coworkers.[18,19] The experimental $\sigma^+$ values of fluoranthene[29] are included in order to test the methods on a non-alternant molecule. With the exception of the PMO : F values, many of the calculations have been previously published,[11] but are included here to facilitate comparisons. The values were newly calculated and checked with correction of the PMO value for benzo[*a*]pyrene. Each proton affinity is presumed to refer to a calculated most reactive position. This agrees in every case for all three types of calculations.

TABLE I

*$\sigma^+$, Proton Affinities, and Localization Energies*

| Compound | | PA | $\Delta E$ (Localization) | | |
|---|---|---|---|---|---|
| (Position of substitution) | $-\sigma^+$ | kJ mol$^{-1}$ | PMO : F | PMO | SRT |
| Benzene | 0.00 | 786.3 | 2.309 | 2.309 | 0.405 |
| Biphenyl (2) | 0.22 | 828.2 | 1.940 | 2.066 | 0.811 |
| Biphenyl (4) | 0.25 | | 1.940 | 2.066 | 0.811 |
| Naphthalene (1) | 0.35 | 821.9 | 1.769 | 1.809 | 0.847 |
| Naphthalene (2) | 0.25 | | 2.057 | 2.121 | 0.693 |
| Anthracene (1) | 0.45 | | 1.540 | 1.569 | 1.099 |
| Anthracene (2) | 0.32 | | 1.835 | 1.886 | 0.916 |
| Anthracene (9) | 0.82 | 876.8 | 1.206 | 1.265 | 1.386 |
| Phenanthrene (1) | 0.34 | | 1.782 | 1.857 | 0.956 |
| Phenanthrene (2) | 0.25 | | 2.063 | 2.182 | 0.788 |
| Phenanthrene (3) | 0.29 | | 1.943 | 2.041 | 0.875 |
| Phenanthrene (4) | 0.33 | | 1.873 | 1.961 | 0.875 |
| Phenanthrene (9) | 0.37 | 842.0 | 1.728 | 1.796 | 0.956 |
| Triphenylene (1) | 0.32 | 836.1 | 1.882 | 2.000 | 0.938 |
| Triphenylene (2) | 0.24 | | 1.982 | 2.121 | 0.894 |
| Pyrene (1) | 0.67 | 873.0 | 1.414 | 1.512 | 1.253 |
| Pyrene (2) | 0.22 | | 2.190 | 2.309 | 0.773 |
| Pyrene (4) | 0.36 | | 1.633 | 1.680 | 1.041 |
| Tetracene (5) | | 915.7 | 0.983 | 1.026 | 1.686 |
| Chrysene (6) | 0.47 | 851.2 | 1.569 | 1.668 | 1.179 |
| Perylene (3) | 0.74 | 891.8 | 1.244 | 1.334 | 1.492 |
| Coronene (1) | 0.44 | 866.7 | 1.667 | 1.796 | 1.224 |
| Benz(*a*)anthracene (7) | 0.64 | | 1.270 | 1.353 | 1.421 |
| Dibenz(*a,h*)anthracene (7) | 0.65 | | 1.393 | 1.511 | 1.386 |
| Benzo(*a*)pyrene (6) | 0.86 | | 1.069 | 1.155 | 1.609 |
| Anthanthrene (6) | 0.81 | | 0.962 | 1.026 | 1.758 |
| Picene (5) | | 861.7 | 1.566 | 1.668 | 1.242 |
| Benzo(1,12)perylene (4) | | 881.8 | 1.418 | 1.546 | 1.386 |
| Styrene ($\beta$) | | 855.8 | 1.512 | 1.512 | 0.916 |
| 1,1-Diphenylethylene ($\beta$) | | 897.3 | 1.155 | 1.265 | 1.386 |
| Biphenylene (1) | 0.23 | | 1.947 | 2.000 | 0.847 |
| Biphenylene (2) | 0.48 | 856.7 | 1.576 | 1.732 | 0.981 |
| Fluoranthene (1) | 0.29 | | 1.941 | 2.090 | 1.253 |
| Fluoranthene (2) | 0.22 | | 2.057 | 2.121 | 0.693 |
| Fluoranthene (3) | 0.46 | 844.5 | 1.617 | 1.833 | 1.344 |
| Fluoranthene (7) | 0.28 | | 1.934 | 1.947 | 0.981 |
| Fluoranthene (8) | 0.42 | | 1.830 | 1.947 | 0.981 |

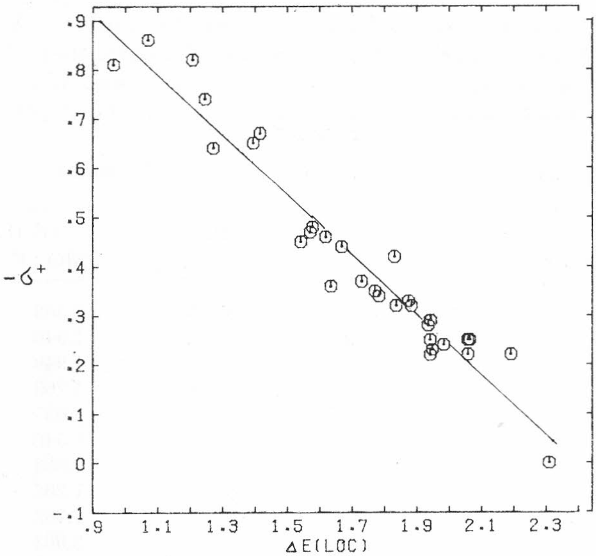


Figure 1. Correlation between —$\sigma^+$ for protodetritiation and $\Delta E$ (localization) calculated by PMO:F

We have carried out several pairwise linear regressions (Figure 1) of the data in Table I which are summarized in Table II. The experimental data have been compared with other types of MO calculations, and these results are also given in Table II. One concludes that the simple pencil and paper procedures are as satisfactory as SCF methods in correlating the experimental data. For alternants only, the correlation with $\sigma^+$ can be described as »very good« for the PMO : F, and as borderline »good« to »very good« for PMO and SRT. The PMO : F and PMO remain at the same level of consistency if fluoranthene is included, whereas the SRT and Hückel correlations drop to »fair« and »good« resp. A detailed analysis of biphenylene and fluoranthene shows that the strain effects are properly accounted for by the PMO : F method. The proton affinity data present a wider range of structural types than the

TABLE II

*Correlation Coefficients:[a] Theory with $\sigma^+$ and Proton Affinities*

| Expt. | PMO:F | PMO | SRT | HMO | PPP[b] | CNDO/2 |
|---|---|---|---|---|---|---|
| $\sigma^+$ (27)[d] | —0.973(27) | —0.960(27) | 0.959(27) | —0.954(27) | 0.932(22) | 0.961(20) |
| $\sigma^+$ (32)[e] | —0.972(32) | —0.956(32) | 0.918(32) | —0.940(32) | | |
| PA (17)[e] | —0.958(17) | —0.930(17) | 0.927(17) | —0.663(17) | 0.926(10) | 0.941(9) |

[a] The number of compounds in the correlation is given in parentheses.

[b] Ref. 2.

[h] Ref. 31.

[d] Alternants only

[e] Including fluoranthene

$\sigma^+$ data. The Hückel method is interdicted for these applications because of the very poor correlation ($r = 0.663$) with proton affinities. The performance of PMO : F seems to parallel that of the FEMO method itself, as demonstrated in recent FEMO calculations of ionization energies[8,9] and reactivities toward electrophilic substitution.[10]

The fact that the pencil and paper procedures give a satisfactory correlation of the data in Table I raises again the question as to why the HMO method fails. The lack of consideration of electron repulsion effects in the HMO-treatment was cited as the culprit in several previous works.[2,32,33] It has also been pointed out previously[10,11] that no explicit electronic charge effects are included in SRT, PMO, or free-electron MO calculations. The present work underlines the conclusion that inherent deficiencies of the HMO method are responsible, rather than a neglect of charge repulsion.

*Acknowledgment.* — William C. Herndon thanks the Robert A. Welch Foundation of Houston, Texas for financial support.

## REFERENCES

1. *Supplemental Tables of Molecular Orbital Calculations,* A. Streitwieser, Jr. and J. I. Brauman, Pergamon Press, New York, 1965.
2. A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, and A. Lewis, *J. Amer. Chem. Soc.* **92** (1970) 6529.
3. K. Nishimoto and N. Mataga, *Z. Phys. Chem.* **12** (1957) 335.
4. H. C. Longuet-Higgins, *J. Chem. Phys.* **18** (1950) 265, 275, 283.
5. M. J. S. Dewar, *J. Amer. Chem. Soc.* **74** (1952) 3341.
6. *The PMO Theory of Organic Chemistry,* M. J. S. Dewar and R. C. Dougherty, Plenum Press, New York, 1975.
7. We consider correlation coefficients larger than 0.99 excellent; 0.96—0.99 very good; 0.93—0.96 good; 0.90—0.93 fair; less than 0.90 poor.
8. L. v. Szentpály, *Chem. Phys. Lett.* **67** (1979) 63.
9. L. v. Szentpály, *J. Mol. Struct.* **60** (1980) 391.
10. L. v. Szentpály, *Chem. Phys. Lett.* **77** (1981) 352.
11. W. C. Herndon, *J. Org. Chem.* **40** (1975) 3583.
12. W. C. Herndon, *Isr. J. Chem.* **20** (1980) 270.
13. W. C. Herndon, *J. Phys. Chem.* **85** (1981) 3040.
14. L. v. Szentpály, *J. Photochem.* **17** (1981) 112; L. v. Szentpály, *29th International Congress of Pure and Applied Chemistry,* Cologne, FRG, June 5—10, 1983.
15. A. Streitwieser, Jr., A. Lewis, T. Schwager, R. W. Fish, and S. Labana, *J. Amer. Chem. Soc.* **92** (1970) 6525.
16. R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc., Perkin Trans.* **2** (1972) 97.
17. T. M. Krygowski, *Tetrahedron* **28** (1972) 4981.
18. H. V. Ansell, M. M. Hirschler, and R. Taylor, *J. Chem. Soc., Perkin Trans.* **2** (1977) 353.
19. Y. F. E. Shafig and R. Taylor, *J. Chem. Soc., Perkin Trans.* **2** (1978) 1263.
20. D. H. Aue and M. T. Bowers, in: M. T. Bowers (Ed.), *Gas-Phase Ion Chemistry,* Academic Press, New York 1979, Chapter 9.
21. M. Meot-Ner (Mautner), *J. Phys. Chem.* **84** (1980) 2716.
22. *Quantum Chemistry,* N. V. Riggs, Macmillan Publishing Co., Toronto, 1969.
23. T. Živković, *Croat. Chem. Acta* **44** (1972) 351.
24. W. C. Herndon, *J. Chem. Educ.* **51** (1974) 10.
25. K. Ruedenberg and C. W. Scherr, *J. Chem. Phys.* **21** (1953) 1565.
26. H. Kuhn, *Helv. Chim. Acta* **32** (1949) 2247.
27. K. Ruedenberg, *J. Chem. Phys.* **22** (1954) 1878.
28. H. V. Ansell and R. Taylor, *J. Chem. Soc., Perkin Trans.* **2** (1977) 866; with earlier Refs. cited therein.

29. K. C. C. Bancroft and G. R. Howe, *J. Chem. Soc., Perkin Trans.* **2** (1970) 1541.
30. W. C. Herndon, *Tetrahedron* **28** (1972) 3657.
31. M. J. S. Dewar and C. C. Thompson, Jr., *J. Amer. Chem. Soc.* **87** (1965) 4414.
32. C. Párkányi, Z. Dolejsak, and R. Zahradník, *Collect. Czech. Chem. Commun.* **33** (1968) 1211.
33. A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, J. R. Wright, P. H. Owens, and D. M. E. Reuben, *The Jerusalem Symposium of Quantum Chemistry and Biochemistry, II, Quantum Aspects of Heterocyclic Compounds in Chemistry and Biochemistry,* Israel Academy of Sciences and Humanities, Jerusalem, 1970. pp. 160—180.

## SAŽETAK

### Protonski afiniteti $\pi$-elektronskih molekula. Usporedba rezultata dobivenih s pomoću metoda PMO, PMO:F i SR

*László v. Szentpály i William C. Herndon*

Razmotreni su parametri elektrofilne suptsitucije i protonski afiniteti $\pi$-elektronskih ugljikovodika, i to primjenom perturbacijske metode molekulskih orbitala (PMO), perturbacijske metode slobodnih elektrona (PMO:F) i metode koja povezuje valentnu strukturu s rezonancijom (SR). Osnovna karakteristika primijenjenih metoda jest njihova krajnja jednostavnost, tako da se računi mogu izvesti s pomoću papira i olovke. Rezultati su uspoređeni s eksperimentalnim podacima i mnogo složenijim SCF računima. Postignuto je zadovoljavajuće slaganje, što opravdava uporabu spomenutih jednostavnih teorijskih postupaka.