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PERTURBATIONAL MO THEORY AND REACTIVITY OF NON-ALTERNANT HYDROCARBONS

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Abstract—The wave-functions for zero-energy levels or approximate wave-functions for near zero-energy levels of odd non-alternant molecular fragments can be obtained by inspection using simple arithmetic. Consequently, the perturbational MO approach to structure-reactivity relationships may be applied to non-alternant molecules. Examples of the correlative ability of this approach are given. An excellent correlation of the acidities of hydrocarbon acids with π-energy changes is developed.

CALCULATIONS of reactivities of aromatic hydrocarbons and their derivatives occupy a main position in the body of physical-organic chemical theory. Several reactivity indices have been developed out of molecular orbital (MO) theory, the localization energy (L_r) concept being consistently reliable.[1-8] To define L_r, a deleted or extended orbital structure is chosen as a model for the transition state of an addition or substitution reaction. The difference in π-energy between parent hydrocarbon system and the odd transition state species is L_r. In most cases, L_r has been calculated using Hückel MO theory.[3, 7, 8] Failures of L_r to correlate reactivity data could be due to poor choices of models for transition intermediates, or to defects in the theory itself. To investigate the latter possibility, there are recent computations of L_r that employ SCF-π[9-13] and all-valence-electron[11-13] MO programs.

Estimates of L_r can be quickly calculated by hand using the perturbational MO (PMO) formalisms,[15, 16] and the PMO values correlate reactivity data as well as full computations. However, in the past, a disadvantage of the PMO method has been its *assumed*[17] limitation to alternant hydrocarbons. The purpose of this paper is to show how one can use the properties of zero-energy or near-zero energy wave functions of non-alternant odd hydrocarbon fragments to extend PMO theory to non-alternant systems. To be useful, one must be able to obtain the require wave-functions and energies quickly, without the aid of digital computers. A simple procedure with this character is outlined below. and applications to some extensively studied reactions are summarized.

EIGENFUNCTIONS OF ODD NON-ALTERNANTS

A non-alternant radical or ion possesses at least one zero-energy or near-zero-energy level. The associated wave-function for a structure containing one odd membered ring can be deduced by inspection if the odd membered ring is severed at the bonds adjacent to any position in such a way as to create two new alternant systems. The unnormalized coefficients of the zero-energy level of each alternant system are found by carrying out the alternant starring process, and writing coefficients which sum to zero around every orbital position in the structure (zero-sum rule).[18-20]

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The unnormalized coefficients in the original non-alternant system are a composite of the two severed systems coefficients. The procedure is exemplified in Fig. 1 for Wheland intermediates derived from fluoranthene.

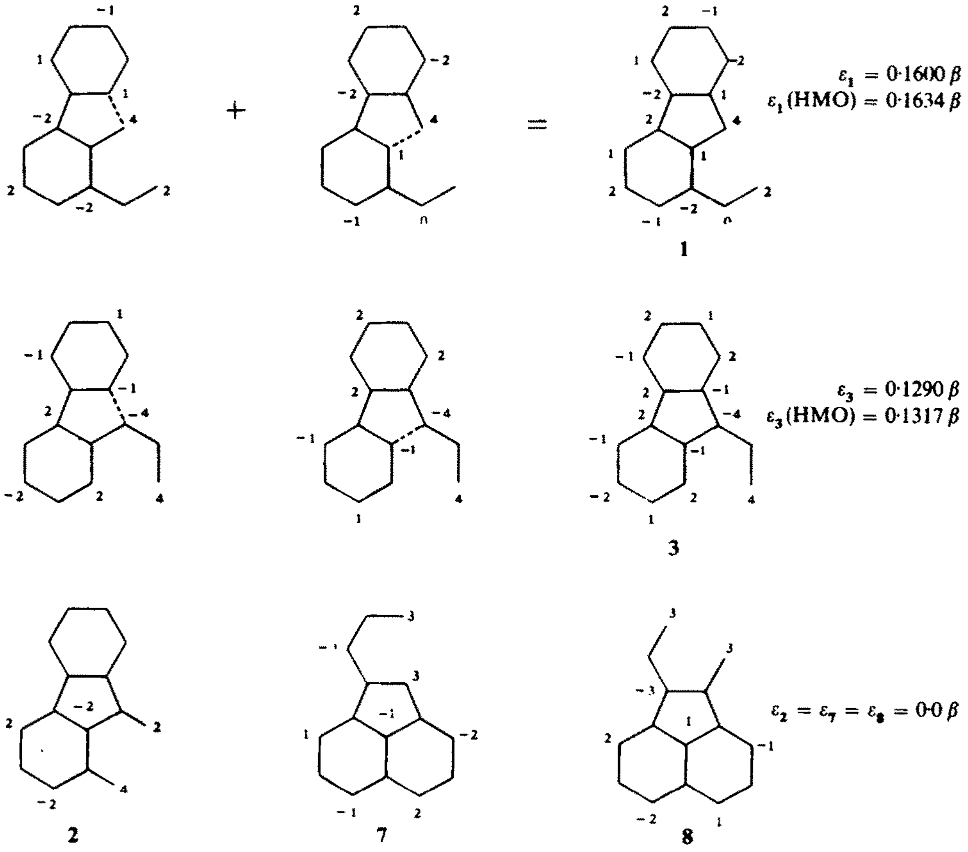


FIG 1. Frontier orbitals of Wheland intermediates derived from fluoranthene.

Application of the procedure immediately reveals zero-energy levels for the non-alternant structures **2**, **7**, and **8**, since the zero-energy level for the severed system must remain if the structure is reunited at positions where there are vanishing coefficients.[7, 15] Alternatively, one could use the zero-sum rule to reach the same conclusions, even though the systems are not alternant. Of course, the depicted wave functions for **2**, **7**, and **8** are the exact HMO functions.

The wavefunctions obtained for intermediates **1** and **3** are approximate wave functions whose eigenvalues can be calulated using simplified MO theory.[21] All bonding or antibonding interactions sum to zero except around the atom, r, isolated by severing the odd membered ring. The energy of the level is given by eq. 1, where s and t are the adjacent neighbors to r, and the sum is over all unnormalized coefficients.

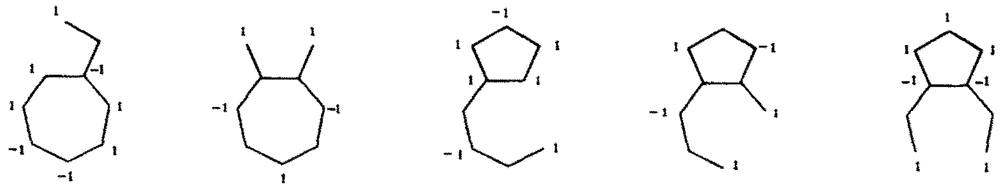
$$E = (u_r u_s + u_r u_t) \div \sum_i u_i^2 \qquad (1)$$

An interesting aspect of these wave functions is that the absolute value of the unnormalized coefficient at any position is the number of resonance structures that one can write with charge or odd electron localized at the point. If one is adept at writing resonance structures, this correspondence can be helpful in obtaining the required wave function. The procedure for determining the wave-functions was discovered empirically after deducing that the relationship between resonance structures and coefficients should hold for non-alternants in analogy to the known correspondence[16, 20] in alternant systems.

LOCALIZATION ENERGIES FOR NON-ALTERNANTS

Transition complexes for substitution in even alternant hydrocarbons have the same localization energy, regardless of the nature of the attacking reagent. The deleted atom structure has a zero-energy level that is empty in a carbonium ion, half-filled in a radical, and doubly-filled in an anion. Relative rates are predicted to be, and actually are independent of the type of reaction.[3, 6, 7] However, L_r^+, L_r^-, and L_r° may differ in non-alternant systems since the frontier orbital may be bonding or antibonding. The PMO method can now be used to calculate these quantities.

Reactivity indices for azulene have been studied in detail,[22] so we will use it as an example. Frontier orbital MO's are depicted in Fig. 2, and the L_r of different types are tabulated and compared with HMO values. The PMO L_r are calculated in the usual way as first-order perturbation energies with the addition of an energy term whose sign depends on the reaction type, and on whether the near-zero-energy orbital of the intermediate is bonding or antibonding. Fig. 3 gives the equations used to find the values of L_r. In Fig. 3, c_s and c_t are the normalized coefficients adjacent to the site of substitution.



	1	2	4	5	7
E	−0·2500	0·0	+0·2857	0·0	+0·2857
L_r^+	0·914	1·788	2·083	1·788	2·083
	(1·924)	(2·362)	(2·551)	(2·341)	(2·930)
L_r°	1·164	1·788	1·226	1·788	1·226
	(2·262)	(2·362)	(2·240)	(2·341)	(2·559)
L_r^-	1·914	1·788	0·940	1·788	0·940
	(2·600)	(2·362)	(1·929)	(2·341)	(2·188)

FIG 2. Localization energies for azulene.

There is a congruity of the two theoretical approaches and experimental results. Electrophilic substitution occurs at position 1,[23] and nucleophilic reaction at position 4[24] in harmony with the calculations, although the PMO L_r^- result does suggest that

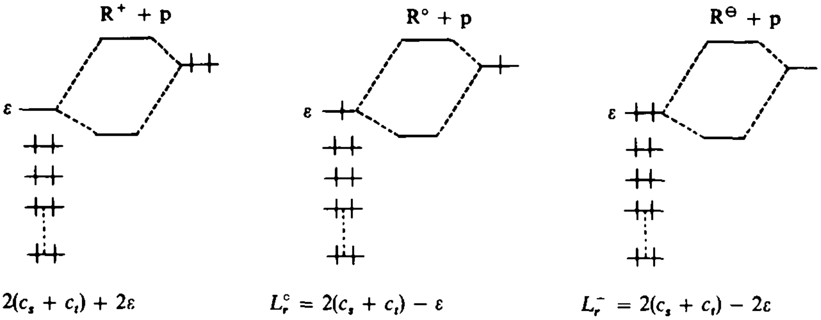


FIG 3. Localization energies calculated as first-order perturbations.

some nucleophilic substitution at position 6 is to be expected. The two theories disagree on the preferred site of radical substitution. The approximate PMO result predicts reaction at position 1 in agreement with the experimental fact.[25]

ELECTROPHILIC SUBSTITUTION

Extensive and precise experimental data are available for the relative rates of protodetritiation of aromatic hydrocarbons in trifluoroacetic acid,[26] eq. 2. The reaction

$$\mathrm{ArT} + \mathrm{CF_3COOH} \rightarrow \mathrm{ArH} + \mathrm{CF_3COOT} \qquad (2)$$

mechanism involves formation of a symmetrical positively charged Wheland intermediate, and rates should therefore correlate with L_r^+. HMO, SCF-π, and CNDO-2[27] calculations of L_r^+ have been compared with the experimental data.[12] PMO values of L_r^+ have not been tested because the compounds investigated included fluoranthene, a non-alternant hydrocarbon.

Table 1 is a list of the PMO L_r^+ values, including fluoranthene, and the experimental rates relative to that of 1-naphthalene substitution. Table 2 gives correlation coefficients of theory with data, and of the PMO values with HMO and CNDO/2 values. The correlation coefficients differ slightly from previously reported values[27] which excluded the biphenylene data.

HMO localization energies are more highly correlative if a disection into types of position such as α-naphthyl or β-naphthyl-types is carried out.[8] There is no dissection into position types for the SCF methods or for the PMO method. The PMO method also accommodates the fluoranthene data and the biphenylene data satisfactorily. The absence of explicit consideration of electron-repulsion effects does not seem to have any significant effect on the correlative ability of the PMO approach. If a cost factor is applied to the calculations, one might decide that the PMO method provides the better correlative theory. However, an advantage of the CNDO/2 method is that it might handle substituents on the aromatic system with proper parameterization.[26]

For all positions in fluoranthene, the relative rates are predicted to be 3 > 8, 7 > 1 > 2 (L_r^+ for both positions 7 and 8 is 1·945), in reasonable agreement with the experimental order for nitration 3 > 8 > 7 > 1 > 2.[28] The PMO method and CNDO/2 correctly predict the correct order of reactivity for positions within a single molecule in every case in Table 1. HMO theory fails in the case of phenanthrene.

TABLE 1. L_r^+ (PMO) FOR AROMATIC HYDROCARBONS

Aromatic position	L_r^+	Log rel rate[a]
Benzene	2·310	−3·00
Naphthalene-1	1·808	(0·00)
Naphthalene-2	2·120	−0·86
Phenanthrene-1	1·856	−0·03
Phenanthrene-2	2·182	−0·75
Phenanthrene-3	2·042	−0·40
Phenanthrene-4	1·960	−0·075
Phenanthrene-9	1·796	0·22
Biphenylene-1	2·000	−0·97
Biphenylene-2	1·734	1·16
Fluoranthene-1	2·017	−0·52
Fluoranthene-2	2·120	−1·14
Fluoranthene-3	1·782	0·96
Chrysene-6	1·668	1·00
Pyrene-1	1·512	2·91
Pyrene-2	2·310	−1·09
Pyrene-4	1·680	0·15
Triphenylene-1	2·000	0·025
Triphenylene-2	2·120	−0·77
Perylene-3	1·332	3·15
Anthracene-1	1·568	0·76
Anthracene-2	1·884	0·00
Anthracene-3	1·264	4·17

[a] 70°C, ref. 26.

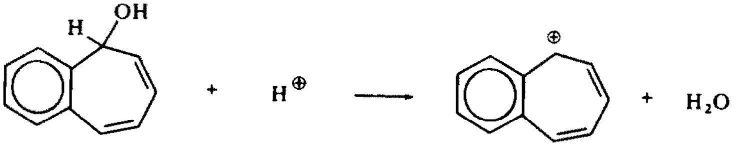
TABLE 2. CORRELATION COEFFICIENTS. TRITIUM EXCHANGE AND L_r^+

Comparison	Corr. coeff.
Expt.—PMO (Fluoranthene excluded)	0·926
Expt.—PMO (all compounds)	0·929
Expt.—HMO	0·884
Expt.—SCF-π	0·952
Expt.—CNDO/2	0·960
PMO—HMO	0·954
PMO—CNDO/2	0·940

The basicities of aromatic hydrocarbons[29] can also be correlated with L_r^+. Plots of pK_B values against L_r^+ (most basic position) are linear using either HMO values or SCF-π calculations,[13, 30, 31] although the SCF plots show less scatter. This is considered to be support for the necessity of using an MO method which includes electron interaction terms. Since the only non-substituted non-alternant molecule which has been investigated is azulene, the question will not be discussed further, except to note that azulene is more basic than naphthalene[29] in agreement with their relative L_r^+ as calculated by any technique.

NON-ALTERNANT CARBONIUM IONS FROM CARBINOLS

The carbonium ion-forming equilibrium depicted in eq. 2 is typical of aryl carbinols



(2)

that can give resonance-stabilized carbonium ions. The alcohol is designated as a "pseudo" or "secondary" base, and the extent of equilibrium is measured by a pK_{R^+} in analogy to the pK_b of a normal base. Several cycloheptatrienyl, cyclopropenyl, and indenyl alcohols which lead to non-alternant carbonium ions have been studied.[32] Since some different solvent systems are represented, it is difficult to judge the correlation between experiment and theory. Nevertheless π-energy changes, $\Delta\pi$ for eq. 2, calculated by the HMO method have been stated to correlate the available data in a reasonable manner.[33]

PMO estimations of $\Delta\pi$ are obtained by calculating the first-order π-energy change, L_r^+, when one extends the odd carbonium ion by one orbital, and subtracting it from the constant increment[34, 35] of energy for the addition of a double bond to the parent molecular π system. As illustrated in eq. 3, the larger L_r^+, the more negative the pK_{R^+} should be.

$$\begin{tikzcd}
\mathrm{R{-}OH} \arrow[r, "\Delta\pi"] \arrow[rr, bend right, "\Delta E = \text{constant (C)}"'] & {[\mathrm{R}]^+} \arrow[r, "L_r^+"] & \mathrm{R{=}CH_2}
\end{tikzcd}$$

$$\Delta\pi = C - L_r^+ \qquad (3)$$

HMO and PMO results are compared with the pK_{R^+} data in Table 3. The list does not contain values for tribenzocycloheptatrienol or dibenzo[a.c.]cycloheptatrienol, both of which deviate substantially from either the PMO or the HMO least squares regression line. Severe overcrowding in a planar cation could be a contributing factor,[33] but this does not seem to be a discernable phenomena in anions (see later discussion). Also, the recently measured value of pK_{R^+} for unsubstituted cyclopropenyl cation, $-7{\cdot}4$,[36] is not included. In this molecule, the inadequacies of a perturbation theory which assumes a relatively constant sigma system are apt to be exposed to the largest degree, and the theory predict a very high positive pK_{R^+} in disagreement with experiment.

The HMO calculations are nicely correlative within a certain structural type, but the overall correspondence of theory and experiment is poor. In contrast, the PMO results give a high correlation coefficient, even including the noncyclic benzyl, benzhydryl, and triphenylmethyl cases. If the PMO results are meaningful, then the π-energy changes are the controlling factors in the measured equilibria, in agreement with an original suggestion by Wheland.[37]

The acetolysis of arylmethyl p-toluenesulfonates also produces carbonium ion intermediates, and kinetic studies can be used to establish the relative stabilities of the ions. The rate data for 17 arylmethyl compounds, has been compared with several kinds of MO calculations.[11, 13] Only two of the compounds are non-alternant system, and none of the theories are outstanding in their correlative ability, so the experimental and theoretical results will not be reproduced here. However, CNDO/2

TABLE 3. CARBONIUM IONS, pK_{R^+} AND $\Delta\pi$ VALUES

Carbonium ion precursor	pK_{R}^{+}	PMO (L_r^+)	HMO ($\Delta\pi$)
Benzyl alcohol	−19·0[a]	1·512	0·721
Benzhydrol	−13·3[b]	1·265	1·301
Triphenyl carbinol	− 6·6[b]	1·109	1·800
9-Fluorenol	−14·0[c]	1·527	1·161
9-Phenyl-9-fluorenol	−10·8[d]	1·326	1·698
Dibenzo[a,e]cycloheptatrienol	− 3·7[e]	0·792	1·544
Naphtho[2',3',a]cycloheptatrienol	0·8[f]	0·694	1·724
Benzo[a]cycloheptatrienol	3·7[f]	0·494	1·772
Naphtho[1',2',a]cycloheptatrienol	4·7[f]	0·594	1·830
Cycloheptatrienol	4·7, 9·9[g]	0·185	2·000
Diphenylcyclopropenol	0·3[h]	0·498	1·903
Triphenylcyclopropenol	3·2[h]	0·111	2·309
	correlation coefficient	(0·950)	(0·853)

[a] N. C. Deno, P. T. Groves, J. J. Jaruzelski and M. N. Lugesch, *J. Am. Chem. Soc.* **82**, 4719 (1960); [b] N. C. Deno and A. Schriesheim, *Ibid.* **77**, 3051 (1955); [c] A. Streitwieser, Jr., ref. 3, p. 365; [d] R. Breslow, *Chem. Eng. News* **43**, No. 26, 90 (1965); [e] C. Berti, *J. Org. Chem.* **22**, 230 (1957); [f] G. Naville, H. Strauss and E. Heilbronner, *Helv. Chim. Acta* **43**, 1221 (1960); values modified by A. Streitwieser, Jr., see footnote *c*; [g] Average used, see footnote *c* and W. E. Doering and L. H. Know, *J. Am. Chem. Soc.* **76**, 2303 (1954); [h] R. Breslow, J. Lockhart and H. W. Chang *Ibid.* **83**, 2375 (1961)

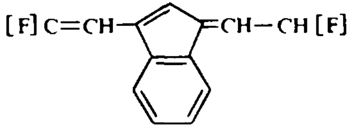
and SCF-π calculations are better for correlating the data than HMO or PMO results. Correlation coefficients are CNDO/2 (12 compounds, 0·867), SCF-π (17 compounds, 0·883), HMO (17 compounds, 0·770), and PMO (17 compounds, 0·768). This reaction deserves further theoretical study.

ACIDIC HYDROCARBONS

The relative acidities of aryl and unsaturated alkanes can be determined by studies of equilibria or by kinetic experiments.[38–41] Whatever the method, the final objective is to establish values of pK_a for the carbon acids. For comparison with other kinds of acids, one would like values referred to water as a common solvent. The pK_a data in Table 4 are mostly taken from a recent compilation,[39] and are the results of an attempt to define a consistent scale of relative acidities of hydrocarbon acids. Several assumptions are made in assembling an acidity scale of this type, particularly with regard to acidity functions in nonaqueous solvents.[41–44] The data in table 4 has been listed uncritically, but it is doubtful whether any adjustment of the pK's of standard compounds would greatly affect the relative acidicities.

Many of the compounds in table 4 yield non-alternant carbanions containing a fluorenyl or indenyl group which incorporates a cyclopentadienyl moiety. Both simple HMO theory and the empirical Hückel 4n + 2 rule of resonance theory predict a relatively high stability for the cyclopentadienyl anion. The table also contains data for both condensed polycyclic and open-chain alternant carbanions, and for several compounds which must lead to substantially non-planar anions. One might feel that this circumstance would preclude correlating the data with theoretical calculations which do not take the actual geometry of the anion into account. In apparent confirmation of this supposition, hydrocarbon acids in which a planar anion would be

TABLE 4. HYDROCARBON ACIDS, $L_r^{\ominus}$ and $\Delta\pi$ VALUES

No.	Compound[a]	pK[b]	$L_r^{\ominus}$ (PMO)	$\Delta\pi$ (HMO)
1	(3,4,5,6-dibenzo[F]C=CH)$_3$CH	5·9	0·1246	—
2	(3.4.5.6-dibenzi[F]C=CH)$_2$CH$_2$	8·2	0·2620	2·01
3	(3,4,5,6-dibenzo[F])C=CH—CH—3,4,5,6-dibenzo[F]	9·1	0·2468	2·33
4	([F]C=CH)$_3$CH	9·4	0·3117	2·50
5	3.4.5.6-dibenzo[F]C=CH—CH$_2$—CH=C[F]	9·8	0·3598	—
6		10·0	0·2278	2·35
7	([F]C=CH)$_2$C = CH—CH[F]	10·4	0·3117	2·34
8	([F]C=CH)$_2$C=CH—CH=CH—CH[F]	11·2	0·3253	—
9	3,4,5,6-dibenzo[F]CH—CH=C[F]	11·2	0·3562	2·29
10	([F]C=CH)$_2$—CH$_2$	11·8	0·4735	1·93
11	[F]C=CH—CH=CH—CH[F]	12·2	0·4735	2·23
12	[P]C=CH—CH[P]	13·6	0·5461	2·21
13	[P]CH—CH=C[F]	13·6	0·5173	2·21
14	Fluoradene	13·9	0·5577	2·12
15	[F]C=C(C$_6$H$_5$)CH[F]	14·0	0·4685	2·18
16	[F]CH—CH=C[P]	14·0	0·5173	2·21
17	[F]CH—CH=C[F]	14·3	0·4685	2·23
18	[F]C=CH—CH(C$_6$H$_5$)CH=C[F]	14·8	0·4636	2·34
19	9-phenyl-3,4,5,6-dibenzofluorene	15·9	0·5523	2·06
20	3,4,5,6-dibenzofluorene	16·8	0·5613	1·63
21	[F]C=CH—CH$_2$C$_6$H$_5$	16·9	0·7138	1·66
22	[F]CH—CH=C(C$_6$H$_5$)$_2$	17·1	0·6498	2·15
23	[F]C=C—CH(C$_6$H$_5$)$_2$	17·5	0·6498	2·12
24	9-phenyl-1,2,7,8-dibenzofluorene	17·3	0·5462	2·11
25	1,2,7,8-dibenzofluorene	17·5	0·5577	1·69
26	9-phenylfluorene	18·5 (18·5)	0·7746	1·98
27	3,4-benzofluorene	19·6 (19·5)	0·6979	1·58
28	1,2-benzofluorene	— (20·1)	0·6880	1·62
29	indene	20·1 (19·9)	0·7070	1·75
30	benzanthrene	— (21.2)	0·8165	1·50
31	4,5-methylenephenanthrene	21·2 (22·6)	0·8799	1·51
32	2,3-benzofluorene	— (23·2)	0·9391	1·49
33	2,3,6,7-dibenzofluorene	21·4	1·0101	1·45
34	fluorene	22·4 (22·7)	0·8317	1·52
35	(C$_6$H$_5$—C$_6$H$_4$)$_3$CH	26·3	1·024	1·86
36	1,1,3-triphenylpropene	— (26·6)	0·970	—
37	*p*-biphenylyldiphenylmethane	28·8 (30·2)	1·050	—
38	triphenylmethane	30·7 (31·5)	1·109	1·80
39	9-methylanthracene	31·2	1·069	0·95
40	diphenylmethane	32·1 (33.1)	1·265	1·30
41	toluene	— (35·0)	1·512	0·72
42	propene	— (35·5)	1·414	1·41

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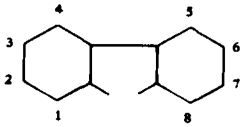
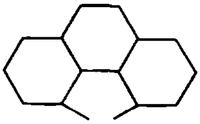
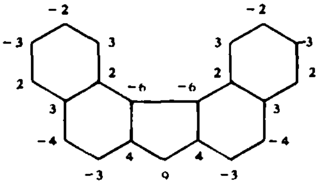
[a] Abbreviations 

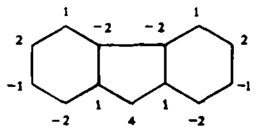
= F;  = P highly hindered have been found to deviate (pK[expt.] > pK[calc.]) from linear plots of changes in π-localization energy as calculated using the HMO method.[39, 45]

PMO calculations of L_r^-, eq. 4 (cf. Fig. 3 and eq. 3), for the compounds in Table 4

$$L_r^- = 2c_s - 2\varepsilon \qquad (4)$$

were carried out in one evening. The approximate wavefunctions of 3,4,5,6-dibenzofluorenyl, fluorenyl, and 4,5-methylenephenanthryl shown below were useful in obtaining composite wave functions of near-zero-energy orbitals for larger systems. The HMO values of $\Delta\pi$ were taken from the literature.[39, 41, 45, 46] Correlation coefficients are listed in Table 5. The high correlation coefficients for the PMO calculations indicate a significant correspondence of the experimental data with theory.





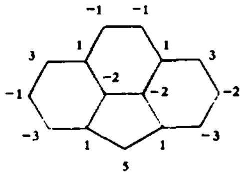


TABLE 5. CORRELATION COEFFICIENTS, DATA OF TABLE 4

Comparison	Compounds	Corr. Coeff.
Expt.—HMO	39 compounds	0·859
Expt.—HMO	12 compounds[a]	0·626
Expt.—PMO	42 compounds	0·977
Expt.—PMO	14 compounds[a]	0·961

[a] pK values in parentheses, Table 4.

An idea of the maximum accuracy of the PMO calculations can be obtained by observing that isomeric systems, compounds **4** and **7**, **10** and **11**, **13** and **16**, and **22** and **23**, must give the same calculated value of $\Delta\pi$ if the perturbational approach used here is adopted. The average difference in pK for these four pairs is 0·6 pK units.

$$pK\,(\text{calc.}) = 22{\cdot}68\,L_r^- + 2{\cdot}98 \qquad (5)$$

The average deviation for all the compounds in Table 4 can be calculated from the PMO least squares regression line, eq. 5, and the value obtained, ±1·3 pK units, is about twice the 0·6 estimate of minimum error calculated above.

It is of interest to see if any common structural feature are characteristic of those compounds which deviate strongly from the correlation line. Only compounds **37**, **38**, and **39** are calculated to be more acidic than experimentally determined by 2·0 pK

TABLE 4—*continued*

[b] Figures in parentheses are from Streitwieser, *et al.*, ref. 41. All other values are from the review by Fischer and Rewicki, ref. 39. pK values in the first column are in solvents of high dielectric constant. Those in the second column are in nonpolar solvents.

units or more, 39 deviating by 4·0 *pK* units. No cogent argument for a steric factor opposing ionization is discernable. Compounds **21** and **41** deviate in the opposite direction by 2·3 *pK* units, compound **33** by 4·5 units. Again, no apparent structural feature could account for these results.

Comparisons of pairs of closely related molecules do perhaps provide an argument for steric effects of overcrowding in anions. Compare fluorene and diphenyl methane, compounds **34** and **40**, expt. $\Delta pK = 12{\cdot}2$, calc. $\Delta pK = 7{\cdot}6$. Previously,[47] about 1/3 of the pK_a difference between the two compounds had been assigned to the increased coplanarity of the fluorenyl system and 2/3 to the anion-stabilizing ability of the 5-membered ring. This argument could still be valid. However, the most important overall factor in determining acidity is obviously the π-stabilization energy on going to the anion. In general, overcrowding and non-planarity in the anions produced does not decrease the effects of delocalization in a significant relative manner. Also the relative effects of electron repulsion must be constant from compound to compound.

CONCLUSIONS

The PMO method, even starting with approximate wave functions and energies, has been shown to be capable of correlating several different kinds of organic reactivity in a quantitative manner. Results are better than if one used HMO calculations, and in general are as good as SCF computations. The charge nature of the intermediates does not require that one use an SCF approach, and the PMO calculations seem to approximate SCF-π methods. The reason for the validity of the PMO approach lies in the nature of perturbation theory itself. One is calculating directly small energy differences, rather than trying to obtain these differences by subtracting one large inaccurate π-energy from another.

The correlations demonstrated help to reinforce the belief that perturbation theory is a useful and logical method for treating chemical reactivity. Perturbational methods using SCF wave equations should be the next stage of theoretical development.

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