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(14) Use, instead, of the Slater–Kirkwood–Hellmann–Margenau equation [H. Margenau, *Rev. Mod. Phys.*, **11,** 1 (1939)], with the effective number of oscillating electrons per electron pair being taken as 2 throughout (and with the values of α and R unchanged), yields somewhat higher values of E_L than does eq 1. The spacings among the substituents look seriously distorted, and understandably[2d,e] so, but the sequence of substituents is still F < Cl < Br < H $\simeq$ I ≪ Me.

(15) E.g., it is not practicable to estimate by calculation the extent to which the inductomeric effect of Hal and the effect of Hal on ΔE_L^* contribute to the gas-phase acid strength sequence[16] $H-CH_2CO_2H \ll F-CH_2CO_2H < Cl-CH_2CO_2H < Br-CH_2CO_2H$ (in principle, both contribute to the observed halogen order, even though the inductomeric effect is expected to be the more important here). (NB The "anti-inductive" order is less prominent in $HalCH_2COOH$ than in $HalC_6H_4OH$ acidities.)

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Resonance Theory. VIII. Reactivities of Benzenoid Hydrocarbons

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An algorithm, logarithm of the number of Kekulé structures, gives resonance energies for benzenoid hydrocarbons that are equivalent to results of highly parameterized SCF–LCAO–MO calculations. The relationship also holds for odd alternant cationic and anionic species. Reactivity indices based on the structure count algorithm correlate with various types of experimental reactivity data.

A simple parameterized structure–resonance theory has recently been developed[1,2] that allows one to calculate resonance energies for many types of π-molecular systems that correlate precisely with the results of semiempirical SCF–MO (Dewar[3]) calculations, or with those obtained from open chain reference structure modified Hückel MO (Hess and Schaad[4]) procedures. During the course of that development an exponential relationship between the Kekulé structure count (SC) and the Dewar resonance energy was noted.[5] The purpose of this paper is to show that this relationship extends to cations and anions postulated as intermediates in reactions of benzenoid aromatic hydrocarbons. Consequently, accurate correlations and predictions of reactivities are quickly and precisely obtainable.

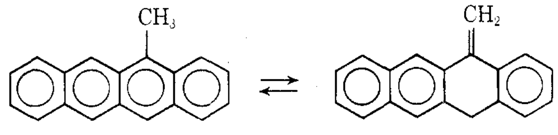
No attempt will be made here to give a quantum mechanical interpretation of the relationships described. A sufficient justification is the excellent quantitative agreement of experimental and theoretical data with the empirical SC function. However, it should be noted that the high correlative accuracy cannot arise from accidental or mathematical congruities[6] of resonance theory with the HMO formulation. HMO reactivity indices have been shown in most cases to yield poor correlations of reactivity data in comparison to the results of SCF calculations. Some illustrations of this fact will be given in tables to follow.

Resonance Energies of Benzenoid Hydrocarbons. The variable β and bond length SCF calculations, parameterized with thermochemical data, of Dewar and coworkers[3] can be taken to provide a reliable reference set of resonance energies. As shown previously,[5] there is an exact linear relationship between the logarithm of the SC and the Dewar[3b] resonance energy (RE) given in eq 1. Alternant and nonalternant benzenoid hydrocarbons, including compounds with essential single bonds, are included in the correlation.

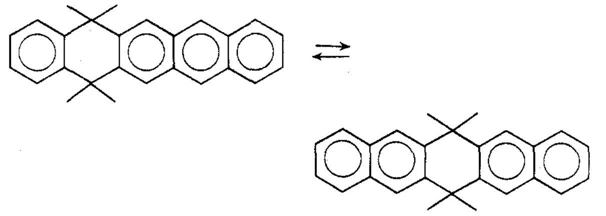
$$\text{RE (eV)} = 1.185 \ln \text{SC} \qquad (1)$$

Their structures were enumerated using the graph-theoretical methods described previously.[7] The correlation coefficient of the calculated resonance energies is 0.998, and the average deviation of the SC algorithm from the SCF result is ±0.042 eV, less than 1 kcal.

The calculations for acene derivatives summarized in Table I provide a stringent test of the SC algorithm. The SCF results were obtained by Herr[8] in an attempt to understand tautomeric equilibria of the types shown in eq 2 and 3. Assuming that the enthalpy differences between pairs of molecules are constant except for π energy differences, the energy of reaction, ΔE_π, should be a linear function of the logarithm of the ratio, SC of product P to SC of reactant R; cf. eq 4.



(2)



(3)

$$E = a(\ln \text{SC}_P - \ln \text{SC}_R) + b = a \ln (\text{SC}_P/\text{SC}_R) + b \qquad (4)$$

The structure count function parallels the calculated SCF energy differences very closely as evidenced by the correlation coefficients for the two groups of reactions, 1.000 and 0.990, respectively.

Some kinetic data suitable for testing eq 1 and 4 have been published by Dewar and Pyron.[9] They determined the rate of Diels–Alder addition of maleic anhydride to the aromatic compounds listed in Table II. The logarithm of the SC ratio is obviously a paralocalization energy and is highly correlated with the logarithm of the second-order rate constant, supporting the postulation of a cyclic transition state for the cycloaddition reaction. A calculation based on the assumption of rate-determining formation of a biradical intermediate (see next section) only gives a correlation coefficient of 0.738, in complete agreement with the prior SCF calculations and conclusions.[9]

Aromatic Substitution Reactions. Electrophilic Sub-

Table I
π Energy Differences for Acene Derivatives

Registry no.	Compd	SC	$\Delta H_a(R)-\Delta H_a(P)$, eV[a]	ln (SC_P/SC_R)
108-88-3	Toluene[b]	2	−1.400	−0.693
3217-87-6	3-Methylene-1,4-cyclohexadiene	1		
90-12-0	1-Methylnaphthalene	3	−0.998	−0.405
40476-27-5	1,1-Dihydro-4-methylenenaphthalene	2		
610-48-0	1-Methylanthracene	4	−0.821	−0.288
40476-28-6	1,1-Dihydro-4-methyleneanthracene	3		
779-02-0	9-Methylanthracene	4	−0.428	0.0
40476-29-7	9,9-Dihydro-10-methyleneanthracene	4		
40476-21-9	1-Methylnaphthacene	5	−0.745	−0.223
40476-30-0	1,1-Dihydro-4-methylenenaphthacene	4		
14214-56-3	5-Methylnaphthacene	5	−0.179	+0.182
40476-31-1	5,5-Dihydro-12-methylenenaphthacene	6		
40476-23-1	1-Methylpentacene	6	−0.702	−0.182
40476-32-2	1,1-Dihydro-4-methylenepentacene	5		
40476-24-2	5-Methylpentacene	6	−0.061	+0.288
40476-33-3	5,5-Dihydro-14-methylenepentacene	8		
40476-25-3	6-Methylpentacene	6	+0.111	+0.405
40476-34-4	6,6-Dihydro-13-methylenepentacene	9		
		corr coeff 1.000		
20244-36-4	5,14-Dihydropentacene[c]	8	+0.165	+0.118
13574-08-3	6,13-Dihydropentacene	9		
40476-37-7	5,16-Dihydrohexacene	10	+0.237	+0.182
40476-38-8	6,15-Dihydrohexacene	12		
40476-39-9	5,18-Dihydroheptacene	12	+0.276	+0.223
40476-40-2	6,17-Dihydroheptacene	15		
	6,17-Dihydroheptacene	15	+0.072	+0.065
40476-41-3	7,16-Dihydroheptacene	16		
40476-42-4	6,19-Dihydrooctacene	18	+0.110	+0.105
40476-43-5	7,18-Dihydrooctacene	20		
40476-44-6	7,20-Dihydrononacene	24	+0.039	+0.041
40476-45-7	8,19-Dihydrononacene	25		
		corr coeff 0.990		

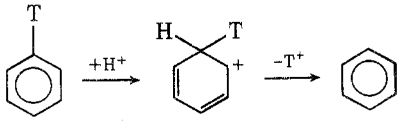
[a] Reference 8. [b] Reactions analogous to eq 2. The second compound in each pair is taken to be the product of the reaction. [c] Reactions analogous to eq 3.

Table II
Diels-Alder Reactions of Aromatic Compounds[a]

Registry no.	Reactant	SC_P/SC_R	ln (SC_P/SC_R)	ln ($k \times 10^4$)[b]
120-12-7	Anthracene	4/4	0.0	4.324
56-55-3	Benz[*a*]anthracene	6/7	−0.154	1.934
92-24-0	Naphthacene	6/5	+0.182	7.230
215-58-7	Dibenz[*a,c*]anthracene	10/13	−0.262	1.275
53-70-3	Dibenz[*a,h*]anthracene	9/12	−0.287	−0.293
224-41-9	Dibenz[*a,j*]anthracene	9/12	−0.287	−0.393
			corr coeff 0.989	

[a] Reference 9. Reaction with maleic anhydride, diethyl succinate solution at 129.7°C. [b] Rate constant *k* in l. $mol^{-1}\ sec^{-1}$.

stitution. A set of σ^+ constants that are generally applicable to electrophilic aromatic substitution reactions have been derived from extensive studies of rates of protodetritiation of polycyclic aromatic hydrocarbons.[10] These data have also been used to test various types of MO calculations,[11-13] with the assumption that the reaction involves the formation of a symmetrical Wheland transition intermediate; cf. eq 5.



(5)

Table III lists σ^+ values and several types of calculated localization energies, i.e., the π energy differences between cationic intermediates and the neutral reactant aromatic molecule. Some of the σ^+ values are estimated from older reactivity data.[10c] The most reliable HMO reactivity indices are the localization energy, L_r^+,[14] and Dewar's perturbational MO reactivity number, N_R.[14,15] They do not correlate with the σ^+ values as well as do the calculations that use SCF-MO procedures. The CNDO/2 calculations of Streitwieser et al.[12] are highly correlative but only 18 of the 26 listed compounds have been investigated. It should be pointed out that the CNDO/2 method also handles some substituted and nonalternant aromatic hydrocarbons in a satisfactory manner.[12]

The SC ratio in Table III is simply the ratio of Kekulé structures for the postulated cation and the neutral reactant. The structures for the cations were enumerated by

Table III
Localization Energies and σ^+

Registry no.	Compd (position of substitution)	σ^+	SC ratio[a]	ln (SC ratio)	L_r^+ (HMO)[b]	N_R (Dewar)[c]	ΔE (CNDO/2)[d]	ΔE[e] (PPP)
71-43-2	Benzene	0.00	3/2	0.405	2.54	2.31	12.141	0.00
92-52-4	Biphenyl (2)	0.24	9/4	0.811	2.40	2.07		0.199
	Biphenyl (4)	0.24	9/4	0.811	2.45	2.07		0.198
91-20-3	Naphthalene (1)	0.35	7/3	0.847	2.30	1.81	13.115	0.907
	Naphthalene (2)	0.25	6/3	0.693	2.48	2.12	12.698	0.498
	Anthracene (1)	0.41	12/4	1.099	2.25	1.57	13.577	1.304
	Anthracene (2)	0.36	10/4	0.916	2.40	1.89	13.101	0.832
	Anthracene (9)	0.72	16/4	1.386	2.01	1.26	14.410	1.870
85-01-8	Phenanthrene (1)	0.34	13/5	0.956	2.32	1.86	13.222	1.057
	Phenanthrene (2)	0.25	11/5	0.788	2.50	2.18	12.884	0.653
	Phenanthrene (3)	0.29	12/5	0.875	2.45	2.04	13.003	0.831
	Phenanthrene (4)	0.33	12/5	0.875	2.37	1.96	13.070	0.881
	Phenanthrene (9)	0.37	13/5	0.956	2.30	1.80	13.320	1.060
217-59-4	Triphenylene (1)	0.32	23/9	0.938	2.38	2.00	13.136	0.962
	Triphenylene (2)	0.26	22/9	0.894	2.48	2.12	13.040	0.849
129-00-0	Pyrene (1)	0.67	21/6	1.253	2.19	1.51	14.093	1.465
	Pyrene (2)	0.22	13/6	0.773	2.55	2.31	12.695	
	Pyrene (4)	0.36	17/6	1.041	2.28	1.68	13.438	
	Tetracene (5)	0.80	27/5	1.686	1.93	1.02		
218-01-9	Chrysene (6)	0.46	26/8	1.179	2.25	1.67	13.714	1.451
198-55-0	Perylene (3)	0.74	40/9	1.492	2.14	1.33	14.487	1.886
191-07-1	Coronene (1)	0.44	68/28	1.224	2.31	1.80		1.430
	Benz[*a*]anthracene (7 or 12)	0.64	29/7,27/7	1.386[f]	2.10	1.43		
	Dibenz[*a*,*h*]anthracene (7)	0.65	48/12	1.386	2.13	1.51		
50-32-8	Benzo[*a*]pyrene (9)	0.86	45/2	1.609	1.96	1.51		2.273
191-26-4	Anthanthrene (7)	0.81	58/10	1.758	1.93	1.03		2.453
			corr coeff	0.977	−0.873	−0.900	0.987	0.932

[a] See text. [b] Units of β, ref 14. [c] Reference 15. [d] eV, ref 12. [e] eV relative to benzene, ref 11. [f] Average value.

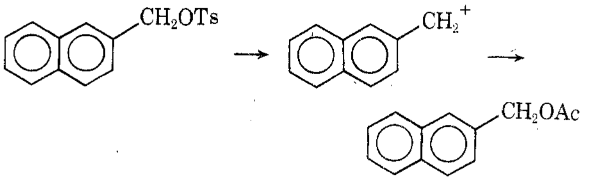
summing the absolute values of the unnormalized coefficients of eigenvectors of the nonbonding orbital for each cation.[6,7] The ln (SC ratio) is a really excellent reactivity index for electrophilic substitution as indicated by the correlation coefficient with σ^+ of 0.977. A comparison of the ln (SC ratio) with the SCF-MO calculations gives the following correlation coefficients: CNDO/2,[12] 0.989, and PPP,[11] 0.993.

Additional tables detailing the congruence of ln SC functions with theoretical and experimental results for many types of chemical reactions could be given. However, the same molecular π systems are repeatedly used in most investigations, so I have chosen to summarize results by giving only the reaction type, correlations, number of compounds considered, and brief comments. In each case the ln (SC ratio) function compared is the same as that given in Table III, or, for arylmethyl systems, is calculated in an analogous manner.

Nucleophilic Substitution. Rates of deuterium exchange with lithium cyclohexylamide in cyclohexylamine at 50°C,[16] polycylic aromatic reactants, carbanion intermediates. Expt: CNDO/2, nine compounds, corr coeff 0.930. Expt: PPP,[17] 0.844. Expt: ln (Sc ratio), 0.863. CNDO/2: ln (SC ratio), 0.980. PPP: ln (SC ratio), 21 compounds,[11] 0.992.

None of the experimental–theoretical correlations are outstandingly good. The SCF–MO calculations again show almost perfect correlations with the SC algorithm. The Dewar–Thompson[11] variable β PPP results exhibit the best correlations with ln (SC ratio) as in the previous calculations on electrophilic substitution.

Solvolytic Reactions, Arylmethyl Systems. σ^+ constants derived from rates of acetolysis of polycyclic arylmethyl tosylates and other derivatives,[18-20] arylmethyl carbonium ion intermediate; cf. eq 6. σ^+: CNDO/2,[19] nine compounds, corr coeff 0.930. σ^+: PPP,[11] 13 compounds, 0.919. σ^+: ln (SC ratio), 14 compounds, 0.937. CNDO/2:[19] ln (SC ratio), nine compounds, 0.986. PPP:[11] ln (SC ratio), 16 compounds, 0.993. The remarks regarding the correlations for aryl carbanions in the previous paragraph also apply to this series.



(6)

Acidities of Methylarenes. Rates of hydrogen isotope exchange, catalyzed by lithium or cesium cyclohexylamide in cyclohexylamine, arylmethyl carbanion intermediate.[17,21] Expt: CNDO/2,[17] nine compounds, corr coeff 0.940. Expt: PPP,[11] 0.988. Expt: ln (SC ratio), 0.976. Expt: HMO,[21] 0.757. CNDO/2:[17] ln (SC ratio), ten compounds, 0.954. PPP:[11] ln (SC ratio), 12 compounds, 0.996. The lower correlation of CNDO/2 calculations with the SC function, coupled with the excellent agreement of PPP results, the SC function, and the experimental data, may indicate some error in the CNDO/2 calculations.

Summary

An extended discussion is not warranted in view of the empirical nature of the algorithm that has been tested in this work. The most significant results are the astonishingly precise agreements of sophisticated semiempirical MO calculations with the SC algorithms. The high correlation coefficients, from 1.000 to as low as 0.980 (for exception see previous paragraph), should not be accidently obtainable. In any event, a quantitative relationship between numbers of structures and SCF–MO calculations has now been established, and a theoretical explanation is desirable.

The failures of the HMO method to correlate the data reviewed were attributed[12,17] to the lack of consideration of electron repulsion effects in the HMO treatment. If the SC algorithm is justified in future theoretical work, that previous conclusion may require modification. No explicit electronic charge effects are included in a structure–resonance theory that only includes Kekulé resonance structures.

At present, the efficacy of the SC approach has only been demonstrated for alternant π systems, and this may constitute a limit to use of this idea. The extension to nonalternant systems is under investigation.

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Synthesis of Arylphosphonous Dichlorides, Diarylphosphinous Chlorides, and 1,6-Diphosphatriptycene from Elemental Phosphorus

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Reaction of elemental white phosphorus with aryl halides at temperatures ranging from 280 to 350°C in the presence of Lewis acid catalysts gave arylphosphonous dichlorides and diarylphosphinous chlorides. Reaction of white phosphorus with *o*-dichlorobenzene in the presence of $FeCl_3$–$TiCl_4$ produced in addition to *o*-chlorophenylphosphonous and di(*o*-chlorophenyl)phosphinous chloride 1,6-diphosphatriptycene, a novel, phosphorus-containing heterocyclic compound.

The preparation of phenylphosphonous dichloride (**1a**) and diphenylphosphinous chloride (**1b**) has been investigated earlier by several research groups. One of the best routes to **1a** developed previously involved the reaction of benzene with phosphorus trichloride in the presence of aluminum chloride in stoichiometric quantities.[1]

$$C_6H_6 + PCl_3 \xrightarrow{AlCl_3} \underset{\mathbf{1a}}{C_6H_5PCl_2} + HCl$$

The resulting phenylphosphonous dichloride (**1a**) forms strong complexes with the aluminum chloride catalyst. The extraction of the product is therefore difficult. An improvement of the isolation procedure was introduced by adding phosphorus oxychloride in stoichiometric quantities as a complexing agent to remove the aluminum chloride.[2,3]

Since phenylphosphonous dichloride (**1a**) disproportionates in the presence of aluminum chloride to yield diphenylphosphinous chloride (**1b**) and phosphorus trichloride[4–6]

$$\underset{\mathbf{1a}}{2C_6H_5PCl_2} \xrightarrow{AlCl_3} \underset{\mathbf{1b}}{(C_6H_5)_2PCl} + PCl_3$$

the reaction of benzene with phosphorus trichloride and aluminum chloride may be used to produce diphenylphosphinous chloride directly without isolating phenylphosphonous dichloride. The complex of diphenylphosphinous chloride with aluminum chloride formed during the disproportionation may be split by addition of potassium chloride.[4]

In this paper we wish to report the synthesis of phenylphosphonous dichloride and diphenylphosphinous chloride in high yield by a new and simple method from chlorobenzene and elemental white phosphorus.[7]

Results and Discussion

The subject reaction is carried out by heating elemental phosphorus in an excess of the chlorobenzene in a sealed