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Basicities of the Methyl Benzenes. I. Hyperconjugation in the LCAO-MO Framework

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The logarithms of the relative basicities of the methyl substituted benzenes have been assumed proportional to the changes in the π-electron resonance energies accompanying protonation of the neutral aromatics. These energies have been computed for the 13 members of the series and their carbonium ions by detailed semi-empirical self-consistent MO methods. Comparisons with experimental results obtained for the HF reactions indicate that hyperconjugative interactions between the reactant (protonation site) group and substituent methyls in the ions may be of dominant importance in determining the observed basicities. The importance of other effects, e.g., steric repulsions, are estimated. Linear free energy equations are used for comparisons with other experimental information on these systems. Correspondence between the theoretical results and such empirical results as C-H to C-C bond hyperconjugation effects, favored positions for electrophilic substitution, and meta- to para-resonance ratios ($\rho\sigma$ equation) is found to be generally good. Other theoretical quantities such as the hyperconjugation energies of the ions are also presented and discussed.

Introduction

1. General Discussion.—Aromatic molecules dissolve in strongly acidic media to form mono-protonated cations in a simple acid–base reaction.[2] Profound effects of structure on the equilibrium constants have been demonstrated for a variety of these molecules including the methyl substituted benzenes. The least and most basic members of the latter series (respectively, benzene and hexa-methylbenzene) differ by at least 10^6 in K_{eq} according to two independent studies of the entire series[3] and a third more careful study of selected members.[4]

Distinct effects of the number and positions of the methyl groups are clearly indicated by these studies. Viewed with regard to stabilization of the aromatic cations, the results are in agreement with empirical rules of organic reactivity. For example, an *ortho*

or *para* group appears to stabilize an electron deficient (protonated) site more than a *meta* methyl group. Rough logarithmic additivity of the effects per methyl group per position to K_{eq} is also apparent. However, while agreement exists between the experimental results and these qualitative rules, the mechanism of the substituent effects upon the measured position of equilibrium is still open to question.

Methyl hyperconjugative electron release, especially in the cations, was assumed by the early investigators[3b] to explain the observed basicity spread. To this date nothing more quantitative has been attempted in terms of hyperconjugation than an empirical "partial equilibrium factor" separation[5] of the different positional methyl group effects. Mackor, *et al.*,[4] on the other hand, have tested the idea of pure inductive release by methyl to account for the different basicities of five members of this series. They used the simple perturbation method developed by Longuet-Higgins[6] and found that very strong electron donation by methyl would be required to explain the observed spread in K_{eq}'s. Specifically, the coulomb integral α of any ring carbon to which a methyl group is attached

(1) (a) This work was assisted by the Office of Naval Research. (b) Computations carried out at Wright Air Force Development, Wright Patterson, Dayton, Ohio.

(2) For a relatively recent review, see K. L. Nelson and H. C. Brown, in "The Chemistry of Petroleum Hydrocarbons," **3**, 465, Reinhold Publishing Corp., New York, N. Y., 1955.

(3) (a) D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950). (b) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951). (c) M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(4) E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

(5) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959). The familiar partial rate factor method is modified here for use on equilibrium data.

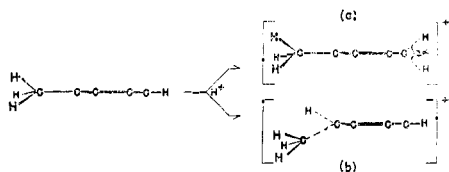(6) H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A207**, 121 (1951).

Fig. 1.—Formation of (a) 4H$^+$- and (b) 1H$^+$-toluenium ions.

would have to be changed by 0.6 to 0.8 e.v. This seems a quite unreasonably large inductive effect for the methyl group.

In the present paper a quantitative study of the effects of hyperconjugation has been made to see whether this effect can reasonably account for the experimental equilibrium results. The method involves computation and comparison of the π-electron energies of each methylated benzene and its carbonium ions by a modification of the Muller, Pickett and Mulliken LCAO–MO method.[7] Correlations then are drawn with the relative K_{eq}'s for the series through linear free energy relationships.

2. Theory A. Molecular Geometries.—The configurations assumed for the hydrocarbons and ions are exemplified for toluene viewed edgewise in Fig. 1. When the proton is attached to the *para* position, the ion is called the 4H$^+$-toluenium ion (a); when the attachment is to the methyl-bearing ring position, the 1H$^+$-toluenium ion (b). In general, the ions are named for the parent neutral aromatics by addition of -ium as suffix and with a prefix number indicative of the position of proton attachment. Details of the model for type (a) ions have been given in ref. 7 where the protonation of benzene was discussed. An additional feature is introduced by the presence of methyl groups at non-reactant sites. Here, one of methyl's two quasi-π MO's and two electrons are capable of conjugative interaction with the ring. (In the hydrocarbons themselves, each methyl also contributes a two-center MO and two electrons to the six AO's and π electrons of the benzene ring.)

In ion (b), the proton and the methyl group carbon attached to the reaction site are assumed to lie in a plane perpendicular to, but not necessarily equidistant from the ring plane. As in ion (a), a quasi-π group may be constructed (now of H and CH$_3$). It is easily shown moreover that this methyl group, attached to a ring position which is protonated, must lose virtually all its own conjugation with the ring by virtue of its displacement from the ring plane (likely on the order of 60°). This follows from the approximate cosine variation of overlap and resonance integrals between pπ orbitals bent with respect to one another. Therefore, the methyl group located at the reaction site is treated as if it were a single atom: its quasi-π-electrons are considered as localized.

B. Relation of Computed Energies to Equilibrium Constants.—We have adopted a modified version of Wheland's model[8] of the protonation proc-

ess which assumes that the free energy of protonation of an aromatic hydrocarbon is proportional to the difference in π-electron *delocalization* energies between the cation and parent hydrocarbon. Explicitly

$$\Delta F \propto E_\pi(\mathrm{ArH}^+) - E_\pi(\mathrm{Ar}) - E_{\mathrm{H}^+} = \Delta E_\pi - E_{\mathrm{H}^+} \quad (1)$$

where ΔF is the free energy change on protonation and E_{H^+} is the energy of the free proton in the reaction medium. Here, the E_π quantities are the π-electron *resonance* (not delocalization) energies.[9]

Relation of the theoretical quantities of equation 1 to terms of relative equilibrium constants is possible, *i.e.*

$$-RT \ln K/K_s = \Delta F - \Delta F_s = \Delta\Delta F = \mu\Delta\Delta E_\pi \quad (2)$$

The subscript s denotes an arbitrarily chosen standard protonation reaction and μ is the proportionality constant relating the π-electron resonance and free energy differences. In equations 1 and 2, proportionality of ΔF to ΔE_π imposes several important restraints upon ΔS and ΔE_σ (the energy term arising from σ-electron rearrangements upon reaction). Constancy, or at least proportionality, of ΔS to the corresponding enthalpy difference, ΔH, is demanded. At the same time, ΔE_σ must be equal or proportional to ΔE_π. There is some empirical justification for proportionality of ΔH and ΔS in the linear free energy correlations developed by Hammett[10] and Taft and Lewis[11] in conjunction with recognition of the small (although not negligible) steric effects for even larger groups in electrophilic aromatic substitutions.[12] The limitation of ΔE_σ is on much weaker ground, the usual π-electron approximation; it has been assumed initially as well, however. Further, as Hammett has pointed out,[10] if ΔS is constant over the series, $\Delta\Delta F$ reflects only the potential energy changes upon reaction *and*, then if ΔE_σ is also constant, the value of μ would be unity, *i.e.*, $\Delta\Delta F = \Delta\Delta E_\pi$. The value of μ for these reactions will be given further consideration.

The experimental K_{eq}'s are over-all equilibrium constants, *i.e.*, they refer to the sums of concentration of all isomeric ions. The relative equilibrium constants given directly[8a,b] or derivable from the individual K's[8c] of these studies are

$$K/K_s = \left[\frac{\sum_i [\mathrm{ArH}^+]_i}{\sum_i [\mathrm{Ar_sH}^+]_i} \right] \bigg/ \left[\frac{[\mathrm{Ar}]}{[\mathrm{Ar_s}]} \right]_{\mathrm{HF}} \quad (3)$$

(7) N. Muller, L. W. Pickett and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 4770 (1954).

(8) G. W. Wheland, *ibid.*, **64**, 900 (1942); see also V. Gold and F. L. Tye, *J. Chem. Soc.*, 2173, 2181, 2184 (1952); E. Heilbronner and M.

Simonetta, *Helv. Chim. Acta*, **35**, 1049 (1952); T. Morita, *Bull. Chem. Soc., Japan*, **32**, 893 (1959).

(9) This modification would not be necessary if we had considered only the ions formed by protonation at unsubstituted sites since $\Delta\Delta E_\pi$'s (*vide infra*) are ultimately to be used and these would be the same by either method. However, when protonation occurs at a ring carbon which carries a CH$_3$ group, the latter's quasi-π electrons are localized; their energy changes upon localization must be included if comparisons with the energies of ions protonated at unsubstituted sites are to be made.

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, and references given therein.

(11) *Cf.*, R. W. Taft. Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959); *J. Am. Chem. Soc.*, **80**, 2436 (1958).

(12) H. C. Brown and L. M. Stock, *ibid.*, **79**, 5175 (1957); G. Illuminati, *Chem. and Ind. (London)*, 917 (1958).

In terms of the individual thermodynamic constants

$$K/K_S = \left(\sum_i n_i k_i\right) \Big/ \sum_i (n_S)_i (k_S)_i \qquad (4)$$

Here, n_i is the number of equivalent isomers of type i, s again refers to the standard reaction and $n_i k_i = [ArH^+]_i/[Ar][H^+]$. The concentration of uncomplexed aromatic in the HF phase is $[Ar]$.

Therefore, since

$$k_i/k_S = \exp(-\mu \Delta \Delta E_i/RT) \qquad (5)$$

then

$$K/K_S = \frac{\sum_i n_i \exp(-\mu \Delta \Delta E_i/RT)}{\sum_i (n_S)_i \exp(-\mu \Delta (\Delta E_S)_i/RT)} \qquad (6)$$

3. Computations. A. LCAO-MO Formulation.—The carbonium ions are treated, respectively, as $(6 + 2n)$ or $(4 + 2n)$ π-electron delocalization systems depending whether protonation takes place at a hydrogen- or methyl-bearing ring position. The number of substituent methyl groups is n. These electrons are taken to occupy the MO's arising from linear combinations of the six ring $2p\pi$ CAO's with the quasi-π orbital of the reaction group (H,H or H,CH₃) and with one dimension of the quasi-π orbitals, say π_x, of the non-reaction-site methyl carbons and their hydrogens. In all cases, Slater AO's are used. In general, then, the ion will have a framework with one more center than the number of its π plus quasi-π_x delocalization electrons. The corresponding neutral aromatic will have the same number of delocalization electrons and sites. The localized models for the neutral aromatics have two π-electrons in each of the three two-center ring orbitals (benzene C–C distances) and two quasi-π_x electrons in each methyl group. If in the ion the positive charge is assumed to be in the ring, the ions have two occupied two-center ring orbitals, two quasi-π_x electrons in each methyl group and two π_x electrons in the reaction quasi-group. The resonance energies obtained by use of these models are vertical. Corrections due to compression are considered below (section 2B, Results and Discussion).

The secular equations are constructed in the usual manner. Overlap is included for nearest neighbors. Following the notation of Mulliken,[13] the diagonal elements are $x_j = \alpha_j - \epsilon$, where ε is the orbital energy and the Coulomb integral $\alpha_j = \int \psi_j H \psi_j d\tau$. The off-diagonal elements are $\gamma_{ij} = \int \psi_i H \psi_j d\tau = \beta_{ij} + (S_{ij}/2)(\alpha_i + \alpha_j)$. The resonance integral, β_{ij}, is taken proportional to the overlap integral, $S_{ij} = \int \psi_i \psi_j d\tau$.

Eigenvalue solutions of such secular equations are well known to yield charge densities and bond orders generally inconsistent with the original α's and β's assumed. This is especially true for ions in which the charge density difference from the initially-implied neutral atom state would have a profound polarizing effect upon α. Employing the empirical self-consistency scheme of Muller, Pickett and Mulliken,[7] iterative linear adjustments of α and S were made respectively with the charge densities (q) and bond orders (p)[14] to self-consistency in the latter quantities for all models considered. The additional adjustments of S_{quasi} (and thereby β_{quasi}, assumed proportional to the latter) were also made for all the conjugating quasi-π bonds.

To illustrate this adjustment for the CH₂ quasi-π bond

$$S_{quasi} = \sqrt{2} \sin \alpha \, S_{CH}/\sqrt{1 - S_{HH}} \qquad (7)^{[15]}$$

S_{CH} and S_{HH} are, respectively, the t_{eC} with $1s_H$, and $1s_{Ha}$ with $1s_{Hb}$ orbital overlap integrals. The HCH angle is 2α. S_{CH} and S_{HH} are both expressible as functions of ρ's $(=\frac{1}{2}(\zeta_a + \zeta_b)/R)$ and $R_{HH} = 2 \sin \alpha_{CH}$. If we assume the same quadratic bond order-length form for the quasi-π bonds as is often taken for carbon-carbon bonds[16] and further, that the bond order per C–H bond is one-half the sum of quasi-σ (taken as unity) and quasi-π bond orders then

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(13) R. S. Mulliken and C. A. Rieke, *J. Am. Chem. Soc.*, **63**, 1770 (1941); R. S. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

(14) The bond order, charge density definitions employed are from B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc. (London)*, **A201**, 196 (1950).

(15) A. Lofthus, *J. Am. Chem. Soc.*, **79**, 24 (1957).

(16) *Cf.*, C. A. Coulson, *Proc. Roy. Soc. (London)*, **A169**, 413 (1939).

$$S_{quasi} = 2 \sin \alpha \{1.6044 - [1.3095 \sin \alpha + 0.5191]\rho_{CH} + [0.5105 \sin^2\alpha + 0.4236 \sin \alpha]\rho_{CH}^2 - 0.1652 \sin^2\alpha\rho_{CH}^3\}$$

This expansion of equation 7 is good to 1% in the range of interest, $S_{quasi} = 0.575$ to 0.675. Here, $\rho_{CH} = 1.235 - 0.145 p_\pi - 0.01 p_\pi^2$.[17]

B. Choice of Semi-empirical Parameters.—The other self-consistency relationships employed were

$$\alpha_j = \alpha_j^0 + \omega \beta_0(1 - q_j)$$

$$S_{ij} = 0.080(p_\pi)_{ij} + 0.195$$

$$\beta_{ij} = \beta_0 \frac{S_{ij}}{S_0}$$

where α_j^0 is the initially chosen coulomb integral for site j (sp^2 carbon in benzene taken as zero). S_0 and β_0 were also referred to benzene and taken, respectively, as 0.248 and -2.6 e.v. The empirical overlap to bond order relation was taken from ref. 7. For the hydrogenic quasi-π groups, the coulomb integrals were assumed to be $\alpha^0 - 0.3\beta_0$ in line with the conclusions of I'Haya.[18] S_{quasi} was taken equal to 0.629.[19]

The carbons to which the hydrogenic quasi-groups are attached are assigned coulomb integrals equal to $\alpha^0 - 0.075\beta_0$ in recognition of their sp^3 character and because of some electropositivity they would derive from the quasi-group. The corresponding parameters for the (H,CH₃) quasi-group and the carbon to which it is attached were taken respectively as $\alpha^0 - 0.5\beta_0$, 0.629 and $\alpha^0 - 0.125\beta_0$. The $\alpha^0 - 0.5\beta_0$ value for (H,CH₃) is obtained by interpolation of the parameters for (H)₃ and (CH₃)₃ employed by I'Haya[20] in calculations on the dipole moments and spectra of the alkyl benzenes. While the absolute values for these parameters which he chose are open to the same criticism as those of Coulson and Crawford[21] (where hyperconjugation was assumed totally responsible for the dipole moment of toluene), the relative values seem reasonable. Hence the interpolated value has been put on the same scale with the hydrogenic value given above ($\alpha^0 - 0.3\beta_0$). The same factor (1/4) has been used here to relate quasi-α's to the α's of the attached ring carbon. While S_{quasi} might be somewhat lower here (~0.600, from an analogous treatment to that of equation 7), 0.629 is again taken for convenience. This difference should have little effect upon the final results.

The parameter ω originally taken as unity by Wheland and Mann[22] has been subjected to careful scrutiny.[7,23] The values 1.25 and 1.47 were adopted[23] for use with the respective (H,H) coulomb integral choices, $\alpha^0 - 0.5\beta_0$ and α^0 in computations on the stabilization energies of alkyl radicals and ions. Since the appearance of this paper, the mass spectrometrically obtained values of these energies have been revised[24] so that 1.25 seems most reasonable. This has been chosen. Recently, further use has been made of this coulomb integral adjustment scheme in somewhat simpler calculations. Ron, Halevi and Pauncz[25] have employed 1.30 and 1.35 for ω in calculations involving overlap while Streitweiser[26] chose 1.40 by fitting ionization potentials in calculations without overlap.

C. Computational Details.—A Remington Rand 1103A computer was programmed to solve automatically the original secular determinant provided as data, to regenerate the adjustable parameters and then to repeat iteratively this process until self-consistency in the charges and bond orders

(17) Overlap *versus* bond length values from, R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(18) Y. I'Haya, *ibid.*, **23**, 1165 (1955).

(19) The value 0.629 is obtained for the C=H₂ quasi-π bond from equation 7 assuming 2α = 120° and R_{CH} = 1.14 Å. The degeneracy in the methyl hydrogen orbitals leads to the same relationship but where 2α = 109° 28′ and R_{CH} = 1.10 Å. This yields S = 0.626. For convenience both are taken to be 0.629.

(20) Y. I'Haya, *Bull. Chem. Soc., Japan*, **28**, 376 (1955).

(21) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(22) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(23) N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.*, **80**, 3489 (1958).

(24) (a) F. W. Lampe and F. H. Field, *ibid.*, **81**, 3238 (1959). (b) F. P. Lossing and J. B. De Sousa, *ibid.*, **81**, 281 (1959). (c) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

(25) A. Ron, E. A. Halevi and R. Pauncz, *J. Chem. Soc.*, 630 (1960).

(26) A. Streitweiser, *J. Am. Chem. Soc.*, **82**, 4123 (1960).

TABLE I

SELF-CONSISTENT π-ELECTRON ENERGIES OF AROMATIC CARBONIUM IONS AND HYDROCARBONS

Hydrocarbons (methyl positions)	$(E - \alpha^0)/\beta_0$		Ions[a] position of protonation, number of equivalent isomers	$(E - \alpha^0)/\beta_0$[b]	
	$E_{deloc.}$	$E_{res.}$[d]		$E_{deloc.}$	$E_{res.}$[d]
Benzene	5.88478	1.07837	1,6	8.02482	2.02594
Toluene (1)	8.69980	1.09878	2,2	10.88634	2.09286
			3,2	10.84372	2.05024
			4,1	10.88667	2.09319
o-Xylene (1,2)	11.51488	1.11926	3,2	13.70540	2.11731
			4,2	13.70436	2.11627
			[1,2]	13.46496	2.12351
m-Xylene (1,3)	11.51474	1.11912	2,1	13.74461	2.15652
			4,2	13.74327	2.15518
p-Xylene (1,4)	11.51466	1.11904	2,4[c]	13.70396	2.11587
			[1,2]	13.46101	2.11956
Pseudocumene (1,2,4)	14.33058	1.14035	3,1	16.56114	2.17844
			5,1	16.56100	2.17830
			[1,1]	16.31512	2.17907
Hemimellitene (1,2,3)	14.33082	1.14059	4,2	16.56317	2.18047
			[2,1]	16.31754	2.18149
Durene (1,2,4,5)	17.14691	1.16208	3,2	19.37893	2.20163
			[1,4]	19.13260	2.20194
Prehnitene (1,2,3,4)	17.14564	1.16081	5,2	19.38044	2.20314
			[1,2]	19.13672	2.20606
			[2,2]	19.13875	2.20809
Mesitylene (1,3,5)	14.32959	1.13936	2,3	16.59499	2.21229
Isodurene (1,2,3,5)	17.14595	1.16112	4,2	19.41383	2.23653
			[2,1]	19.16464	2.23398
Pentamethylbenzene	19.96223	1.18279	6,1	22.23349	2.26158
			[2,2]	21.98375	2.25848
Hexamethylbenzene	22.77706	1.20302	[1,6]	24.80562	2.28575

[a] Isomers arising from methyl substituted ring site protonation indicated by brackets, [ ]. [b] For comparison, energies for the bracketed ions assuming $\alpha(H, CH_3)$ and α (reaction site bearing H, CH_3) equal to $\alpha^0 - 0.30\beta_0$ and $\alpha^0 - 0.075\beta_0$, respectively, are available from the energies of the appropriate one-fewer methyl substituted ions plus the energy of two electrons in localized $C\equiv H_3$ group (i.e., $2.79461\beta_0$). For example, for $1H^+$-pseudocumenium ion, see $4H^+$-m-xylenium. [c] The ion isomer arbitrarily chosen as standard. [d] Localization energies: $(E - \alpha^0)/\beta_0$ (two electrons). For $C\equiv H_2$ and $C\equiv H_3$ (x component only) = 2.79461; $C\equiv (H, CH_3)$ (bond specified only) = 2.54796; $C\equiv C$ (S = 0.2483$_3$) = 1.60214.

was obtained. The Jacobi–Schmidt orthogonalization diagonalization method[27] was employed yielding simultaneously the eigenvector and eigenvalue solutions. The program included a generation scheme for the Chirgwin-Coulson bond order, charge density matrix,[14] $\bar{P} = 1/2$ $(\overline{SXN\bar{X}^*} + \overline{XN\bar{X}^*S})$, where $\bar{X}$ and $\bar{X}^*$ are respectively the eigenvector matrix and its transpose, $\bar{N}$ is the diagonal matrix specifying the eigenvectors of the occupied MO's and $\bar{S}$ is the overlap matrix. The appropriate new integrals were obtained from the $\bar{P}$ elements.

In some runs convergence was oscillatory and slow. To hasten convergence, a geometric mean extrapolation procedure was built into the program. Employing the results of the last three of n iterations (n usually chosen as five), automatic extrapolation of the $\bar{P}$ elements was carried out and repeated until convergence was obtained.[26] With this improvement most cases were found to have converged to the determined limits (usually 0.001) in less than 8 iterations where more than 30 often were needed before.

Results and Discussion

1. Comparison of Theoretical and Experimental Results.—The self-consistent ion and neutral hydrocarbon delocalization energies and $E_{res.}$ values

(27) Cf. E. Bodewig, "Matrix Calculus," Interscience Publishers, Inc., New York, N. Y., 1956.

(28) The formula

$$X_{ext} = X_i + \frac{(X_{i+1} - X_i)^2}{(X_{i+1} - X_i) - (X_{i+2} - X_{i+1})}$$

which is applicable for either monotonic or oscillatory convergence was employed.

are given in Table I. Generally, only those ions with resonance energies less than 0.04 β_0 smaller than the most stable isomer from the same parent are included in this tabulation; the others would contribute negligibly to the computed over-all equilibrium constants. The computed results for $3H^+$-toluenium ion are provided for an uncomplicated illustration of the substituent effects from the *ortho, meta* and *para* positions. Several points of interest may be noted from this Table. Protonation invariably is accompanied by an increase in $E_{res.}$ of greater than 0.9β_0. Further, the energies of both the hydrocarbons and particularly the ions are found to increase with increased methylation. And, as expected, substitution *ortho* or *para* to the reaction site is always more effective than in a *meta* position in stabilizing the ions.

Table II contains the $\Delta\Delta E_{res.}$ values, the derived relative equilibrium constants, $(n_i k_i / n_s k_s)$, and these relative constants without the statistical factors for equivalent forms, i.e., (k_i / k_s). The reference ion is the $2H^+$-p-xylenium ion. All computations were made with μ assumed equal to unity at 0°. (The studies of McCaulay, et al.,[3a,b] were made at 0 and 20°, those of Kilpatrick and Luborsky[3c] at 20°.) The over-all constants ob-

TABLE II

$\Delta\Delta E_{res}$. AND INDIVIDUAL ION ISOMER EQUILIBRIUM CONSTANT VALUES

Hydrocarbon	Ion isomer[a] position of protona- tion	$10^2 \cdot \Delta\Delta E_{res}/\beta_0$	(k_i/k_s)	(n_ik_i/n_sk_s)
Benzene	1	−4.926	0.0043	0.006
Toluene	2	−0.275	.738	.369
	3	−4.537	.0066	.003
	4	−0.242	.765	.191
o-Xylene	3	.122	1.14	.57
	4	.018	1.02	.51
	[1]	.742	2.27	1.14
m-Xylene	2	4.057	88.7	22.2
	4	3.923	76.5	38.2
p-Xylene	2	0	1	1
	[1]	0.369	1.50	0.75
Pseudocumene	3	4.126	95.8	24.0
	5	4.112	94.2	23.6
	[1]	4.189	103	25.8
Hemimellitene	4	4.305	117	58.5
	[2]	4.407	135	33.8
Durene	3	4.272	112	56.0
	[1]	4.303	116	116
Prehnitene	5	4.550	153	76.5
	[1]	4.842	211	106
	[2]	5.045	265	132
Mesitylene	2	7.660	4500	3380
Isodurene	4	7.858	6000	3000
	[2]	7.603	4480	1120
Pentamethyl- benzene	6	8.196	8610	2150
	[2]	7.886	6120	3060
Hexamethyl- benzene	[1]	8.590	13300	20000

[a] Isomers arising from methyl substituted ring site protonation indicated by brackets, [ ]. [b] $\beta_0 = -2.6$ e.v. $\cong$ −60 kcal./mole.

TABLE III

OVER-ALL EQUILIBRIUM CONSTANTS

| Hydrocarbon | K_{eq}. (relative to p-Xylene) | | |
	Computed	McCaulay and Lien	Kilpatrick and Luborsky
Benzene	0.004	......	0.09
Toluene	0.32	∼0.01	0.63
o-Xylene	1.3	2	1.1
m-Xylene	34	20	26
p-Xylene	1	1	1
Pseudocumene	42	40	63
Hemimellitene	53	40	69
Durene	98	120	140
Prehnitene	180	170	400
Mesitylene	1900	2800	13000
Isodurene	2200	5600	16000
Pentamethylbenzene	3000	8700	29000
Hexamethylbenzene	11000	89000	97000

tained from equation 6 are presented in Table III along with the experimental results just mentioned.

The computed equilibrium constants are seen to be in good agreement with the experimental values. It is of interest that up to and including prehnitene the theoretical values agree as well quantitatively with the experimental results as the latter do with each other. For the stronger bases, mesitylene, isodurene, penta- and hexamethylbenzene, there is

some divergence of the calculated values from those of experiment as well as some between those of the two methods. The computed values are small with respect to either experimental result; those of Kilpatrick are up to five times greater than McCaulay's. The average factor necessary to bring the computed values into agreement with those of experiment (both sets) is 2.9. The factor between the experimental sets is 2.2. Variation in the value of μ does not improve the over-all agreement for the series. For $\mu = 1.1$, the computed constants for the stronger bases are closer to the experimental values but the xylene, pseudocumene and hemimellitene results are then too high. It would seem, in light of the differences between the experimental results themselves, knowledge of the approximations employed in their derivation, and several other factors to be discussed, that a μ value roughly equal to unity provides satisfactory agreement between the theoretically and experimentally determined equilibrium constants.

From these results it seems that not only is the hyperconjugation model employed capable of explaining the basicity order in the methylbenzenes but that, unless fortuitous cancellation occurred between the ΔE_σ and ΔS proportionality factors (to ΔE_π and ΔH, respectively, see section 2B), $\Delta\Delta F \cong \Delta\Delta E_\pi$. The former conclusion might be drawn if any constant and reasonable value of μ would provide agreement between the calculated and experimental K_{eq}'s.[29] The latter however implies, *assuming the model correctly represents the physical system*, that hyperconjugation is the main contributing effect in determining the basicities of the methyl benzenes. It would be of interest to see how this conclusion agrees with the other pertinent information available on these compounds.

2. Possible Effects of Geometry on Equilibrium.—With respect to structure, the assumptions have been made that the aromatics are planar and that the only carbons not in the ring plane in the ions are those attached to protonation sites. Direct structural information is available only for the hydrocarbons. There seems to be no reason however to question the qualitative model adopted for the ions. At the same time, all of the aromatics with the possible exception of hexamethylbenzene (HMB) almost certainly are planar. The latter which for some time had been the subject of considerable attention in this regard now seems from the work of Schnepp and McClure[30] to be planar, at least in the crystal. These workers, employing ultraviolet techniques, arrived at the conclusion that the molecule is of S_6 symmetry (gear-tooth methyl hydrogen arrangement) but suggest that there may be some strain and therefore the tendency to pucker because of the proximity of the methyl groups. Even though this puckering may be less than the zero point amplitude of the carbon motion it conceivably still might affect the conjugation energy. Certainly, the restriction of rotation of the

(29) To define a reasonable value of μ depends entirely upon how much of an effect ΔE_σ and ΔS might be expected to have. While the theory would perhaps retain a cataloging value if μ were much larger or smaller than unity, it would be difficult under these circumstances to see how the methyl substituent effects could be attributed to hyperconjugation to any significant degree.

(30) O. Schnepp and D. S. McClure, *J. Chem. Phys.*, **26**, 83 (1957).

methyl groups would make hexamethylbenzene less stable than the assumed model which implies free rotation. If the E_π of hexamethylbenzene is overestimated by the assumption of planarity and/or the total energy is in error by neglect of the methyl rotations *and* if the ion is better pictured (bending the reaction site CH$_3$ group out of plane should somewhat relieve the methyl–methyl strain), the computed energy difference and therefore the $K_{eq.}$ would be too small. Whatever similar effects are present in pentamethylbenzene, etc., should of course be considerably smaller. These steric effects are conceivably responsible for the more than additive methyl effects measured for the highly substituted members of the series.

3. Methyl Group Contributions to the Computed Energies.—From Table I, it is apparent that the effects of the methyl groups on the energies of the neutral aromatics are virtually additive. The average increases in the delocalization and resonance energies per methyl are, respectively, 2.81521 β_0 and 0.02059 β_0 with average deviations of 0.00019 β_0 over the twelve methyl benzenes. These results agree with those of calculations by simpler methods[21] and with expectations for systems where charge separated *sacrificial* hyperconjugation stabilization above and beyond Kekulé hyperconjugation is possible.[31]

For the ions, however, *isovalent* hyperconjugation structures may be written. Here the energies are strongly dependent upon the positions of the methyl substituents. Compared to the benzenium ions, the *ortho, meta* and *para* protonated toluenes are seen to have extra resonance (and delocalization) energies of 0.06692 (2.86152), 0.02430 (2.81890) and 0.06725 (2.86185), respectively, in β_0 units. These results are consistent with the empirically predicted enhancement for the *ortho* and *para* positions in toluene in nucleophilic reactions. An interesting extension of this result is possible. The $\Delta E_{res.}$ values for the formation of these toluenium ion isomers relative to that for the benzenium ion are *ortho*, 0.04650, *meta*, 0.00388 and *para*, 0.04683 β_0. These double differences should be, under the assumptions of section 2B of the Introduction, directly proportional to the Hammett $\rho\sigma$ product for this protonation reaction. Further, since the model is constructed explicitly to evaluate the π-electronic effects of the systems, it does not seem unreasonable to expect that this $\Delta\Delta E_{res.}$ proportionality would extend to the resonance effects within these Hammett $\rho\sigma$'s, as separated by Taft and Lewis.[11] It is noteworthy then that Taft and Lewis found a *meta-* to *para-* R ratio of $\sim$1/10 generally applicable for reactions where direct-conjugation (*i.e.*, isovalent conjugation) between the substituent and reaction site is possible. The equilibria under consideration are just such cases and this ratio is 1/12. This agreement is certainly satisfactory especially since the more naïve LCAO-MO treatments provide entirely different results. Without charge redistribution and other self-consistency adjustments the predicted *meta* and *para* effects are of the opposite sign.[32]

(31) For a detailed discussion of the types and importance of the various conjugation and hyperconjugation stabilized molecular structures see reference 5.

Still other comparisons with the Hammett and Taft equations are possible. Additivity of the effects within the linear free energy equations accompanying multiple substitution has long been recognized.[33] For example, for 4H$^+$-*o*-xylenenium ions, the $\Delta\Delta E_{res.}$ (referred to benzene) is 0.04944 β_0 and the $\Delta\Delta E_{res.}$ sum for 3H$^+$- and 4H$^+$-toluenium ions is 0.05071 β_0. These results agree within 2%. Similarly for 5H$^+$-hemimellitinium ions, the only other multiply-substituted ion without *ortho* position substitution, $\Delta\Delta E_{res.} = 0.05295$ β_0, compared to the sum, again obtained from the toluenium isomers, of 0.05495 β_0. Here again some slight levelling from exact additivity is noted. This deviation would be too small to detect experimentally by the usual techniques. Including the ions with *ortho* positions substituted, effective additivity is maintained upon multiple substitution.

Little explicit attention has been paid thus far to the ions formed by protonation of the methyl substituted ring sites. These are obviously important contributers to the over-all equilibrium constants as the strong basicity of hexamethylbenzene attests. Additional indirect evidence for their importance lies in the fact that the highly alkylated benzenes, with the exceptions of those with substituents solely *meta* to one another, rearrange in HF·BF$_3$.[34] Table II predicts protonation to be slightly favored at the substituted sites, all else being equal. While neither the isomerization phenomena nor the experimental equilibrium data can definitely substantiate this result it seems probable from the following considerations. Isodurene and hemimellitene have experimental K_{eq}'s twice as large as those for mesitylene and *m*-xylene, respectively. If protonation were just as favorable energetically at the methyl substituted as unsubstituted sites, this factor should be smaller than two (*viz.*, $\sim$ [2 × (0.0066/0.0043) + 1]/3 = 1.3). For the parameters chosen, the calculated ratio is [2 × (0.0066/0.0043) + 1 × (1.50/0.765)]/3 = 1.7.[35] It is doubtful that the experimental data are good enough for one to place too much faith in this numerical result, but it seems of some worth especially when coupled with the fact that the computed relative K_{eq}'s are generally much smaller when protonation at the substituted ring sites is ignored or assumed less important than at the unsubstituted sites.
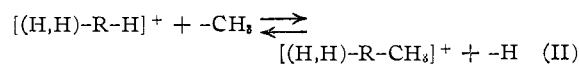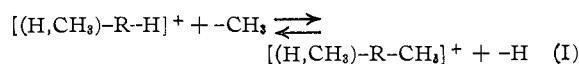
4. C–H *versus* C–C Bond Hyperconjugation.—From the computed results it is possible to estimate the relative C–H *versus* C–C bond hyperconjugation effects as these are found within Taft's analysis. The following hypothetical equilibria are assumed.

(32) First and second order perturbation yields a value of −1/11 for the *meta* to *para* ratio. It may also be noted that the computed *ortho* to *para* $\Delta\Delta E_{res.}$ ratio is approximately unity in agreement with the corresponding perturbation result. Unfortunately this is not experimentally verifiable at present.

(33) *Cf.*, H. H. Jaffé, *Chem. Revs.*, **53**, 253 (1953).

(34) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **74**, 6246 (1952).

(35) The ratios 0.0066/0.0043 and 1.50/0.765 are from values in Table II, column 2, respectively, for 3H$^+$-toluenium compared to benzenium ion. (covering the effect of the extra *meta* methyl group) and 1H$^+$-*p*-xylenium compared to 4H$^+$-toluenium ion (expressing the K_{eq} difference for protonation of a substituted *versus* unsubstituted site with the same environment).

$[(H,CH_3)-R-H]^+ + -CH_3 \rightleftarrows$
$$[(H,CH_3)-R-CH_3]^+ + -H \quad (I)$$

$[(H,H)-R-H]^+ + -CH_3 \rightleftarrows$
$$[(H,H)-R-CH_3]^+ + -H \quad (II)$$

The quasi-groups formed by protonation are now considered as the linear free energy equation substituents and R is the aromatic nucleus with whatever other methyl substituents apply. Since the quasi-groups may be viewed as $(H,H)^{+-}$ and $(H, CH_3)^{+-}$ (compare, for example, with NH_3^{+-}, or NO_2^-), the reference equilibrium would be of the type, benzene $\rightleftarrows$ toluene. To eliminate whatever small differences from additivity exist upon multiple substitution, the reference is perhaps better chosen as $H-R-H \rightleftarrows H-R-CH_3$. With $\rho_R\sigma_R = \Delta\Delta\bar{E}_\pi = \Delta E_{I \text{ or } II} - \Delta E_{\text{ref.}}$, the relative σ ratio for (H,H) and (H,CH_3) as substituents may be obtained, viz., $(\Delta E_{II} - \Delta E_{\text{ref.}})/(\Delta E_I - \Delta E_{\text{ref.}})$. Table IV contains the ΔE values and this ratio for the cases where the quasi-group "substituent" and "reaction groups" are ortho and para to one another. When the orientation is meta, $\Delta\Delta\bar{E}_\pi$ is extremely small, probably beyond the reliability of the energy values because of the convergence limits imposed in the self-consistency procedures.

TABLE IV

C–H versus C–C BOND CONTRIBUTIONS TO
HYPERCONJUGATION FROM COMPUTED $\Delta E_{\text{res.}}$[a]

R[b] Methyl positions	ΔE_I	ΔE_{II}	$\Delta E_{\text{ref.}}$	$\Delta\Delta\bar{E}_{II}/\Delta\Delta\bar{E}_I$
		$10^2 \times$		
"para" Reactions				
2	5.556	6.232	2.034	1.19
2,6	5.249	5.577	2.024	1.10
2,3,6	5.039	5.809	2.077	1.25
			Av.	1.18 ± 0.05
"ortho" Reactions				
2	5.798	6.366	2.034	1.15
2,4	5.491	5.711	2.024	1.07
2,3,4	5.242	3.606	2.053	1.12
			Av.	1.11 ± 0.03

[a] All energies in units of β_0. [b] Quasi-group (H,H) or (H, CH_3) always at ring position 1.

Examination of Table IV reveals the (H,H) to (H, CH_3) contributions to stabilization of the ions to be in the ratio of ~1.15 to 1. Per bond (C–H to C–CH_3) this ratio is ~1.3 to 1 if $\sigma_I/\sigma_{II} = \Delta\Delta\bar{E}_I/\Delta\Delta\bar{E}_{II} = 2h_H/(h_H + h_C)$, adopting the notation of Taft. The empirically derived values for this ratio from the data for many reactions is 1.3.[11]

5. Additional Considerations. A. Other Experimental Information.—Besides the two experimental studies cited and discussed, Mackor, et al.,[4] have examined several members of the series by vapor pressure and solution distribution techniques. The relative K_{eq}'s obtained were in qualitative agreement with those previously reported but are generally more widely spread. In Fig. 2, the log K_{eq} values reported in the Makor studies, adjusted to refer to a given isomer for each parent aromatic, are plotted versus the computed $\Delta\Delta E_{\text{res.}}$ values from Table II similarly adjusted by energy weighting. With the understandable excep-
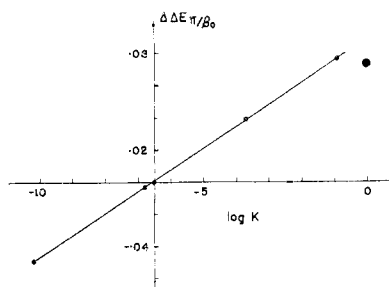

Fig. 2.—$\Delta\Delta E_\pi$ versus experimental (Mackor, et al.) log K.

tion of the hexamethylbenzene point the other aromatics are fit by a straight line corresponding to μ of 1.5_3. These data, measured by what appears to be somewhat more refined techniques than employed in the earlier studies of McCaulay, suggest that there are other energy contributions to the relative stabilities of the ions than are included in the theoretical model. These other contributions appear proportional to and on the order of one-half the importance of the $\Delta\Delta E_{\text{res}}$. The entropy measurements, also made during the course of the Mackor studies, are of further interest. Examination of these strengthens the conclusions that while hyperconjugation appears to be an important contributing effect to the basicities of the methyl benzenes, it is not the only one. The average value of $-T\Delta S$ for the protonation of toluene, meta- and para-xylene and mesitylene is 3.6 ± 0.4 kcal./mole with a maximum spread of 1.0 kcal./mole. If correct, these can hardly be construed as constant entropy effects, especially with regard to equilibrium constants. If one assumes that the more highly substituted members of the series are accommodated within this range, the K_{eq}'s which would be observed if the entropy changes were constant at the value for p-xylene, $T\Delta S = -4.1$ kcal./mole, would be from one-fifth to twice the experimental values reported. Correcting all the experimental data for the entropy effects in this way and applying the refinements suggested by Mackor to the earlier results (e.g., distribution coefficient differences for the hydrocarbons between HF and heptane as a function of the number of methyl substituents), overlapping is found among the three experimental sets of K_{eq}'s with limits covered by the theoretical treatment for μ between 0.9 and 1.6.

B. Theoretical Refinements.—Implicit in the assumptions from which the theoretical model was constructed are two points, rather closely connected, which deserve further attention now. The first involves the theoretical sigma bond reaction effects, arising from the changes in geometries (between the neutral aromatics and ions) determined solely by the different computed π-electron distributions in these species. Conventionally, a measure of these effects would be the differences in compression energies (c.e.) for the reactant and product pairs. These energy changes have been assumed unimportant in the double energy differences, from which the K_{eq}'s were computed, after the following results were considered. While we may not obtain unambiguous c.e.'s here because of the several localized structures of comparable energy which may be written, especially for the ions (viz.,
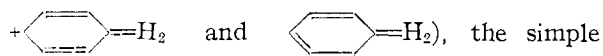
$+\langle\!\!\!\begin{array}{c}\end{array}\!\!\!\rangle{=}H_2$ and $\langle\!\!\!\begin{array}{c}\end{array}\!\!\!\rangle{=}H_2)$, the simple average c.e's for these structures as well as those for given structures are almost constant for the series of ions when referred to the pertinent parent aromatics. For example, the c.e. of the 4H⁺-toluenium ion where the positive charge is localized *para* to the reaction center is 11.24 kcal./mole less than that of toluene, while the corresponding value for the benzenium ion is 10.57 kcal./mole less than that for benzene, both neutral hydrocarbons taken to have Kekulé type localized structures. For the simple average, with the positive charge on the three ring positions which are stable by valence bond criteria, the corresponding differences are respectively −6.89 and −6.91 kcal./mole for the toluene and benzene cases. From these calculations then, and those of similar intent,[36] the sigma bond compression effects accompanying the π-electron redistribution between the aromatics and ions have been assumed negligible in comparison to the included theoretical effects and experimental uncertainties.

Second, it is well known that the value of β chosen in semi-empirical calculations depends sensitively among other things on whether or not this sigma bond compression energy effect is considered. Hydrocarbon molecule calculations which ignore it show need for a considerable variation in β depending upon the phenomenon to be examined. The value of −2.6 e.v. chosen here is in agreement with previous work employing similar models and interestingly enough seems generally applicable to a larger number of phenomena besides reactivity when the computations of the sort described above are made. Further attention will be paid to this problem, that is, constancy of semi-empirical parameters, in a later paper.

C. Semi-localized Models.—A measure of the hyperconjugation stabilizations due to the reaction quasi-groups is available for the ions of this series by computation of their semi-localization energies. Here, delocalization is restricted to the framework of the five ring carbons, other than that at the reaction site, and whatever methyl groups are attached to them.[37] This effectively open-chain fragment is taken to be unipositively charged. Two or four completely localized π-electrons (in one or two, two-center orbitals) respectively for unsubstituted or methyl substituted reaction sites are taken to occupy the reaction quasi-group. The sum of the energies of these electrons are the semi-localization energies for the ions. The differences between the delocalization energies, Table I, and the semi-localization energies are the hyperconjuga-

(36) Unpublished work of the author where a reaction compression energy defined as the energy necessary to distort the bonds of the reactant, which is taken as standard, to those of the product is computed. This method avoids the complications of the conventional c.e. calculations by not requiring assumption of hypothetical localized structures. The force constants are taken as those for the standard bonds (of the the neutral aromatics) and are computed by assuming a parabolic dependence upon bond order through the values known for the hydrocarbons, ethylene, acetylene and benzene. These energies while meaningless for a single reaction pair are useful for series comparisons and yield results effectively equivalent to those reported above.

(37) This model is an extension of those employed by G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942); M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949), among others.

TABLE V
SEMI-LOCALIZATION AND HYPERCONJUGATION ENERGIES

Hydrocarbon	Ion isomer[a] position of protonation	$(E - \alpha^0)/\beta$ $E_{semiloc}$	$10 \times E_{hyperconj}$[b]
Benzene	1	4.99611	2.3410
Toluene	2	7.88051	2.1122
	3	7.81613	2.3298
	4	7.88657	2.0549
o-Xylene	3	10.70069	2.1010
	4	10.70544	2.0431
	[1]	7.88051	2.4188
m-Xylene	2	10.75163	1.9837
	4	10.75955	1.8911
p-Xylene	2	10.69929	2.1006
	[1]	7.88657	2.3187
Pseudocumene	3	13.57233	1.9420
	5	13.57677	1.8926
	[1]	10.75955	2.1300
Hemimellitene	4	13.57943	1.8913
	[2]	10.75163	2.2334
Durene	3	16.39164	1.9268
	[1]	13.57677	2.1326
Prehnitene	5	16.39581	1.9002
	[1]	13.57943	2.1472
	[2]	13.57233	2.2385
Mesitylene	2	13.62106	1.7932
Isodurene	4	16.44216	1.7706
	[2]	13.62106	2.0101
Pentamethylbenzene	6	19.26009	1.7879
	[2]	16.44216	1.9902
Hexamethylbenzene	[1]	19.26009	2.0296

[a] Isomers arising from methyl substituted ring site protonation indicated by brackets, [ ]. [b] $E_{hyperconj.} = E_{deloc.} - (E_{semiloc.} + E_{C=H_2 \, or \, C=H,CH_3})$.

tion energies. Table V contains these $E_{semiloc}$ and $E_{hyperconj}$ values.

These results, while not simply applicable to the equilibrium constant comparison, provide further insights into the mechanism of substituent stabilization in the model chosen. In agreement with the conclusions reached from the resonance energy computations, methyl substituents in the "active" (*ortho* and *para*) positions have the greatest effect upon the hyperconjugation energy and much less from the *meta* position. In contrast however, the latter are generally *decreased* by *ortho* and *para* substitution indicating the semi-localization energies to be more sensitive to such substitution than are the delocalization energies. Considerable leveling is also noted, much greater than for the delocalization energies. Successive methyl substitution is thereby accompanied by smaller changes in the hyperconjugation energy. This is particularly striking in the *meta* substitution cases; some highly substituted ions are actually found to exhibit *increased* hyperconjugation energies upon further substitution in the *meta* positions. The generally greater hyperconjugation energies computed for the ions formed by protonation at methyl bearing, than at unsubstituted ring sites, all else being equal is also of interest.

In general, it would seem from these results that the hyperconjugation responsible for the basicity order of the methyl benzenes is a phenomenon involv-

ing the direct interactions of the reaction group, ring carbons and methyl groups together.

Conclusions

The semi-empirical self-consistent LCAO–MO method employed in this investigation seems capable of explaining the relative basicities of the methyl benzenes in strong acid solutions mainly on the basis of hyperconjugative stabilization of the cations by the substituent methyl groups. Equally consistent results would not be obtained from naïve molecular orbital treatments. The most important theoretical factor introduced by the improved methods is unquestionably charge redistribution, particularly in the ions.

The quantitative results obtained agree well with empirical expectations for electrophilic aromatic reactions and with predictions from simple valence bond theory. Agreement with the former extends from the qualitative notions of the effects of electron donors as functions of position of substitution, to the quantitative separations afforded by linear free energy equations, e.g., $\rho\sigma$ meta to para resonance ratios, and C–C bond, relative to C–H bond, hyperconjugation. The intermediate theoretical results, as well as the total equilibrium constants calculated therefrom, are found to be consistent with experiment wherever comparisons are available. The importance of C–C bond hyperconjugation is strongly indicated in this study, under acceptance of the model. Compared to the C–H bond effect, it appears to be about three-fourths as effective in para position hyperconjugation (and about the same in the ortho position) for a reaction series which may be derived from the theoretical data.

Extension of this model to test further the importance of hyperconjugation in molecules where it might be expected to contribute appreciably as a stabilizing effect would be desirable. Other methyl-substituted aromatics such as the naphthalenes and azulenes, for the ions of which isovalent hyperconjugation structures may be written, are of particular interest. Studies of these systems and an attempt to refine the inductive model for comparisons of the results by both methods are contemplated for the near future.

Electronic States in the C₄ Molecule[1a]

BY ENRICO CLEMENTI[1b]

An s.c.f.–l.c.a.o.–m.o. ground state wave function for the lowest $^3\Sigma_g^-$ and for an excited $^1\Sigma_g^+$ state of C₄ is reported. All twenty-four electrons are considered in this computation. The internuclear distance assumed for all the states is 1.28 Å. for the three bonds of C₄, following some earlier prediction. Diagrams are presented which give a pictorial representation of the molecular orbitals obtained. An l.c.a.o.–m.o. computation was done for the $^1\Delta_g$ and $^1\Sigma_g^+$ states and for a second $^1\Sigma_g^+$ excited state. A discussion is given on the expected bond variation for the different excited states, as compared with the ground state. Estimates are made of the centers of gravity for the two lowest $^3\Pi$ and $^1\Pi$ states. It is concluded that the $^3\Sigma_g^-$ should be the ground state as earlier suggested by Pitzer and the author.

Introduction

Some time ago Pitzer and the author[2] presented evidence that the C₄ molecule is linear and that its ground state should have $^3\Sigma_g^-$ symmetry. This conclusion was based on a refinement[2b] of the Hückel π-electron model.[3] The correct assignment is of importance, since all the C_n molecules with n even and > 2 were predicted as having the same species of ground state.

In the present paper we present a complete s.c.f.–l.c.a.o.–m.o. computation for the C₄ molecule. All the integrals for the 24 electrons were accurately computed using McLean's Linear Molecules Program. The basis set for the wave function consists for each atom of one 1s, one 2s, one 2pσ and one 2pπ Slater-type orbital (s.t.o.), with the same orbital exponents as were found best for the ground state of the C₂ molecule.[4] We examined several electronic configurations and thus we can present a theoretical computation for a discussion of the symmetry and the electronic configuration of the ground state for the C₄ molecule.

The internuclear distances were chosen as 1.28 Å., and these may be somewhat in error, since there should be bond alternation in various degrees in the different states. The value of 1.28 Å. was taken from the C₃ molecule[5] and is the same as that postulated for C₄ in the original work.[1]

Analysis of the Resulting Wave Functions.—The ground state electron configuration is supposed to be

$$1\sigma_g^2\,1\sigma_u^2\,2\sigma_g^2\,2\sigma_u^2\,3\sigma_g^2\,3\sigma_u^2\,4\sigma_g^2\,4\sigma_u^2\,5\sigma_g^2\,1\pi_u^4\,1\pi_g^2 \quad (a)$$

where clearly the electron pairs in the first four m.o.'s are expected to correspond essentially to atomic 1s² closed shells of the C atoms. The electrons in the remaining three σ_g and two σ_u m.o.'s provide for the σ bonds and two essentially non-

(1) (a) This work was supported by the National Science Foundation. (b) I. B. M. Research Laboratory, San Jose, California.

(2) (a) K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.*, **81**, 4477 (1959); (b) R. S. Mulliken, C. A. Rieke and W. G. Brown, *ibid.*, **63**, 41 (1941); A. Loftus, *ibid.*, **79**, 24 (1957).

(3) E. Hückel, *Z. Physik*, **70**, 204 (1931); **76**, 628 (1932).

(4) B. J. Ransil, *Revs. Modern Phys.*, **32**, 239 (1960).

(5) A. E. Douglas, *Astrophys. J.*, **144**, 466 (1951); K. Clusius and A. E. Douglas, *ibid.*, **32**, 319 (1954); G. Herzberg, *Mme. soc. roy. sci. liege*, **15**, 251 (1955); N. H. Kiess and H. P. Broida, *Can. J. Phys.*, **34**, 1971 (1956).