Excited-State Reactivities. III. Use of Configuration Interaction to Calculate Excited-State Localization Energies

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Abstract: Localization energies for calculating aromatic substitution reactions in lowest excited singlet and triplet states have been calculated for the methylbenzenes by using ground-state SCMO wave functions and interaction of all singly excited configurations. The triplet-state results are compared with previous open-shell results. A least-squares comparison of the values for the 40 unique positions in this series of compounds gives a standard deviation of ±0.154 ev. (A comparison of the ground-state localization energies calculated on the two different programs used yields a standard deviation of ±0.047 ev.) The excited singlet-state localization energies are compared with the spectroscopically determined experimental excited-state basicities of the polymethylbenzenes. A good linear fit is obtained between ΔE_{loc} and log K^*/K^*_{s}.

Among the quantum chemical methods employed in predicting reactivity toward aromatic substitution, the localization energy approximation has perhaps been the most successful.[1] This method has been applied extensively, both within the Hückel approximation[1] and within the more sophisticated self-consistent molecular orbital (SCMO) formalism to predict reactivities of π-electron systems in their ground electronic states. Although most quantum chemical predictions of excited-state reactivity have been based on arguments involving charge densities,[2] direct localization energy calculations have been made for excited triplet states by using an open shell SCMO program[3] based on Roothaan's formalism.

The present work presents the results of a configuration interaction calculation of localization energies for both excited singlet and excited triplet states of the methylbenzenes. The triplet results are compared with the open-shell SCMO results from ref 3. The singlet results are compared with the experimental results of Flurry and Wilson.[4]

Method

The calculations were performed on an IBM 1620 computer with disk pack. A Fortran II-D program based on Pople's formulation of the SCMO equations[5] for closed-shell systems was used. Once the ground-state wave functions were obtained, all singly excited configurations were used to calculate the energies of the excited singlet and triplet states by standard configuration interaction (CI) methods.[6] Only the results for the lowest singlet and triplet are reported since, because of the extreme rapidity of internal conversion processes from higher excited states, these will undoubtedly be the only states important in the excited-state reactions.

The localization energy as used in the present work is defined as the difference in total π-electron energy between the neutral molecule and the fragment remaining after removing one center and the appropriate number of π electrons from the system. For example, for benzene, the neutral molecule would contain six π centers and six electrons. The localization structure would contain five π centers and four electrons (two electrons being removed for cation localization energies). The magnitude of the localization energy should thus be roughly equivalent to twice the magnitude of the core α term plus the magnitude of two core β terms, representing the two bonds broken, plus the electronic repulsion for two electrons located on the same center plus the difference in delocalization energy of the cyclic six-atom system and the noncyclic five-atom system. Note that this should have a significantly larger value than localization energies as calculated in simple Hückel theory where the α term is usually the reference point and consequently has a value of zero and where interelectronic repulsions are completely neglected.

The basic empirical parameters used in the present work were the same as those used in ref 3. There were, however, slight differences in the calculations which produced some unexpected results. The main difference was in the method of evaluating the two-

Table I. Comparison of Theoretical and Pariser–Parr Values of Two-Center, Two-Electron Integrals for *o*-Xylene

Integral[a]	Theoretical, ev	P–P,[b] ev	Difference, ev
(11/11)	10.19[c]	10.19	0
(11/22)	7.26	7.14	−0.12
(11/33)	5.25	5.42	+0.17
(11/44)	4.68	4.85	+0.17
(11/66)	7.46	7.26	−0.20
(33/33)	10.84	10.84	0
(33/44)	7.70	7.38	−0.32
(33/55)	5.32	5.45	+0.13
(33/66)	4.72	4.87	+0.15

[a] Methyl-bearing positions are positions 1 and 2. [b] Pariser–Parr. [c] Owing to an error in the program used for the calculations in ref 3, this integral was consistently assigned the erroneous value of 10.19 ev. The correct value, using the parameters as presented in the previous work, should be 9.66 ev. For consistency in comparison the erroneous value was used throughout the present work.

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[1] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 11.

[2] For a review, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 550.

[3] R. L. Flurry, Jr., and P. G. Lykos, *J. Am. Chem. Soc.*, **85**, 1033 (1963), paper I of this series.

[4] R. L. Flurry, Jr., and R. K. Wilson, *J. Phys. Chem.*, submitted, paper II of this series.

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

[6] C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, Chapter 10.

Table II. Localization Energies for All Positions for All Methylbenzenes[a]

			State				
			N[b]		V[c]	T[d]	
Point no.[e]	Molecule[f]	Position	This work	Previous[g]	This work[h]	This work[h]	Previous[g,i]
1	Benzene	1	56.2354	56.8948	54.7746	54.5095	54.7458
2	Toluene (1)	1	55.7569	56.0019	54.2104	53.9226	53.7996
3	Toluene	2	56.1155	56.6134	54.5938	54.4308	54.5650
4	Toluene	3	56.2073	56.8550	54.6732	54.3262	54.5266
5	Toluene	4	56.1128	56.7146	54.7015	54.4143	54.7028
6	*o*-Xylene (1,2)	1	55.6415	55.7681	54.0332	53.4884	53.0212
7	*o*-Xylene	3	56.0909	56.5724	54.4917	54.2502	53.7232
8	*o*-Xylene	4	56.0856	56.6628	54.5993	54.2325	53.8238
9	*m*-Xylene (1,3)	1	55.7311	55.9623	54.1058	53.7196	53.3761
10	*m*-Xylene	2	56.0033	56.3351	54.4125	54.3705	54.2077
11	*m*-Xylene	4	55.9952	56.4311	54.5233	54.3208	54.3125
12	*m*-Xylene	5	56.1801	56.8061	54.5688	54.1198	54.0990
13	*p*-Xylene (1,4)	1	55.6322	55.8211	54.1369	53.8423	53.7953
14	*p*-Xylene	2	55.9914	56.5700	54.3953	53.9849	54.3841
15	Hemimellitene (1,2,3)	1	55.6192	55.7453	53.9271	53.6444	53.3543
16	Hemimellitene	2	55.5338	55.5554	53.8547	53.7853	53.4447
17	Hemimellitene	4	55.9709	56.3936	54.4194	54.1385	54.1920
18	Hemimellitene	5	56.0591	56.6201	54.4934	54.0265	54.3254
19	Pseudocumene (1,2,4)	1	55.5190	55.5946	53.9626	53.7498	53.0588
20	Pseudocumene	2	55.5196	55.7344	53.8318	53.3793	52.8872
21	Pseudocumene	3	55.9770	56.2993	54.3098	54.2043	53.6498
22	Pseudocumene	4	55.6072	55.7789	54.0318	53.6409	52.9632
23	Pseudocumene	5	55.9662	56.3856	54.4201	54.1609	53.7239
24	Pseudocumene	6	56.0622	56.5296	54.3864	54.0635	53.5833
25	Mesitylene (1,3,5)	1	55.7064	55.9314	53.9968	53.4803	53.2168
26	Mesitylene	2	55.6995	56.1679	54.5719	54.0420	54.2266
27	Prehnitene (1–4)	1	55.4971	55.5754	53.8551	53.5481	53.3197
28	Prehnitene	2	55.5099	55.5379	53.7484	53.5997	53.2693
29	Prehnitene	5	55.9430	56.3576	54.3130	53.9552	53.9766
30	Isodurene (1,2,3,5)	1	55.5928	55.7116	53.8173	53.4250	53.1416
31	Isodurene	2	55.2276	55.3880	53.6141	53.4720	53.4123
32	Isodurene	4	55.8590	56.1272	54.2389	54.0738	54.0475
33	Isodurene	5	55.5829	55.7454	53.9214	53.4022	53.1797
34	Durene (1,2,4,5)	1	55.4924	55.5497	53.8570	53.5697	53.0809
35	Durene	3	55.9519	56.2553	54.2048	54.0151	53.6978
36	Pentamethylbenzene (1–5)	1	55.4713	55.5396	53.7443	53.3302	52.8201
37	Pentamethylbenzene	2	55.3896	55.3658	53.6979	53.4827	52.8370
38	Pentamethylbenzene	3	55.4869	55.5117	53.6379	53.3767	52.9687
39	Pentamethylbenzene	6	55.8341	56.0989	54.1317	53.8829	53.5966
40	Hexamethylbenzene (1–6)	1	55.3673	55.3353	53.5658	53.2543	52.8477

[a] In electron volts. [b] Ground state. [c] First excited singlet state. [d] First excited triplet state. [e] Numbering for figures. [f] Methyl-bearing positions given in parentheses. [g] Reference 3. [h] Calculated by CI method. [i] Calculated by open-shell SCMO method.

center, two-electron integrals. In the previous work these were evaluated completely theoretically, using Roothaan's master formulas.[7] In the present work they were estimated using a Pariser–Parr-type parabolic interpolation.[8] Although the numerical values of the differences (Table I) are relatively small in comparison with the usual uncertainty of the parameters used in semiempirical methods, there were some important consequences in predicted reactivities and especially in predicted orientation within a given molecule. This point will be discussed more fully later. It was verified that the differences were, in fact, due primarily to the differences in integral values calculated by the two methods by feeding into the program the values of the theoretical integrals for several molecules. In these cases, the final results were essentially the same as the previous results for the ground-state calculations.

Footnote *c* of Table I requires some comment. The value of the one-center, two-electron integral involving a substituted center was consistently assigned an erroneous value in the calculations performed for ref 3. This was not detected until after the work was published. A repeat of a random sampling of the calculations using the correct value of this integral revealed that the over-all results for relative basicities were not changed. The absolute values of the localization energies were different, but the differences were consistent within the series. Since the relative basicities were the properties under consideration, the differences in localization energies between the two series of calculations in effect cancelled out. If some

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(7) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).
(8) R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).

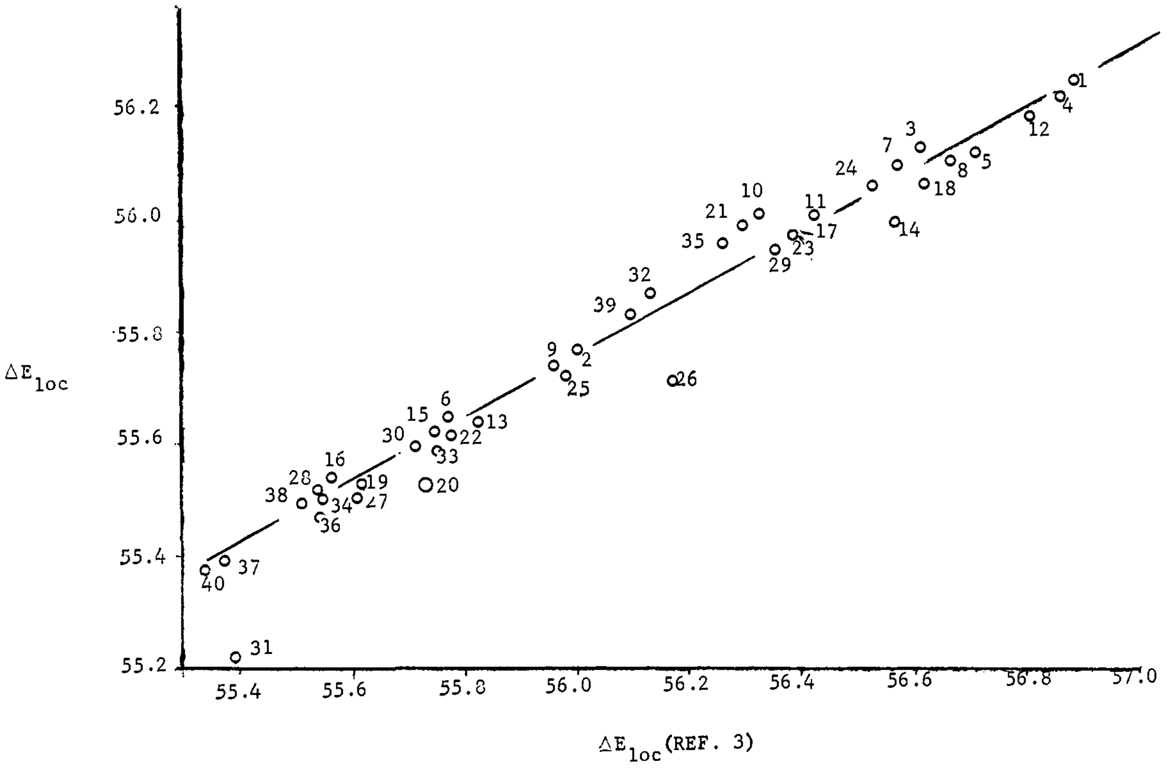

Figure 1. Comparison of ground-state localization energies from the present work with those of ref 3.

property of the individual molecule such as spectra or ionization potential had been the property under consideration, this error would have greatly affected the over-all results. These properties depend very strongly upon the differences between one-center and two-center two-electron integrals.[9]

Results and Discussion

The results for the localization energies for the ground, first singlet, and first triplet states for all unique positions of each of the molecules in the series are presented in Table II. For comparison, the ground- and triplet-state results from the calculations performed for ref 3 are included. The values presented are not corrected for either substitution at a methyl-bearing position[10] or for the number of equivalent reactive positions. Figures 1 and 2 present a graphical comparison of the present results with the previous results for the ground and triplet states. The slopes of the lines are not unity, but are approximately equal at a value of 0.57 for both figures. The intercepts are also approximately equal. The standard deviation[11] for the ground-state calculations is ±0.047 ev. The most serious deviations are point 31 corresponding to localization at position 2 in isodurene and point 26 corresponding to position 2 in mesitylene. For the triplet states, the standard deviation for the CI calculations *vs.* the open-shell calculations is ±0.154 ev. The scatter between the values is greater, but the qualitative agreement is still satisfactory. The results from ref 3 correlated well with the experimental values for ground-state basicities.[12] The correlation of the ground-state localization energies from the present work with the experimental basicities should thus also be good. Unfortunately, there are no experimental values to compare with the triplet-state localization energies.

Excited singlet-state basicities of the polymethylbenzenes in a trifluoroacetic acid–boron trifluoride mixture have been determined experimentally.[4] This determination was based on the Förster cycle.[13] Results were presented as obtained from both absorption and fluorescence measurements. Since electronic transitions are usually assumed to obey the Franck–Condon principle,[14] the results from the absorption spectrum should agree with the excited-state localization energies corresponding to the most basic positions in the ground-state molecules. This is shown graphically in Figure 3. There is good agreement between the logarithm of the relative excited state basicity and the localization energy for all molecules except mesitylene. In Figure 1 it was seen that the calculation for mesitylene in this work did not correlate well with those from the previous work. (The other poor correlation, position 2 of isodurene, is not for the most basic position in that molecule.)

It is especially satisfying that there is such good agreement for the excited singlet-state basicities since the parameters chosen in ref 3 yield poor spectral predictions. In fact, the trend on increasing methyl substitution predicted with the present parameters is the opposite of the observed trend of a shift to longer

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[9] P. G. Lykos, *J. Chem. Phys.*, 35, 1249 (1961).

[10] Reference 3, footnote 19.

[11] Defined as follows: $\sigma = [\Sigma(X_1 - X_2)^2/n]^{1/2}$, where X_2 is calculated from the least-squares fit and n is the number of points.

[12] D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, 73, 2013 (1951); M. Kilpatrick and F. E. Luborsky, *ibid.*, 75, 577 (1953); E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, 54, 186 (1958).

[13] T. Förster, *Z. Elektrochem.*, 54, 42 (1950).

[14] J. Franck, *Trans. Faraday Soc.*, 21, 536 (1926).

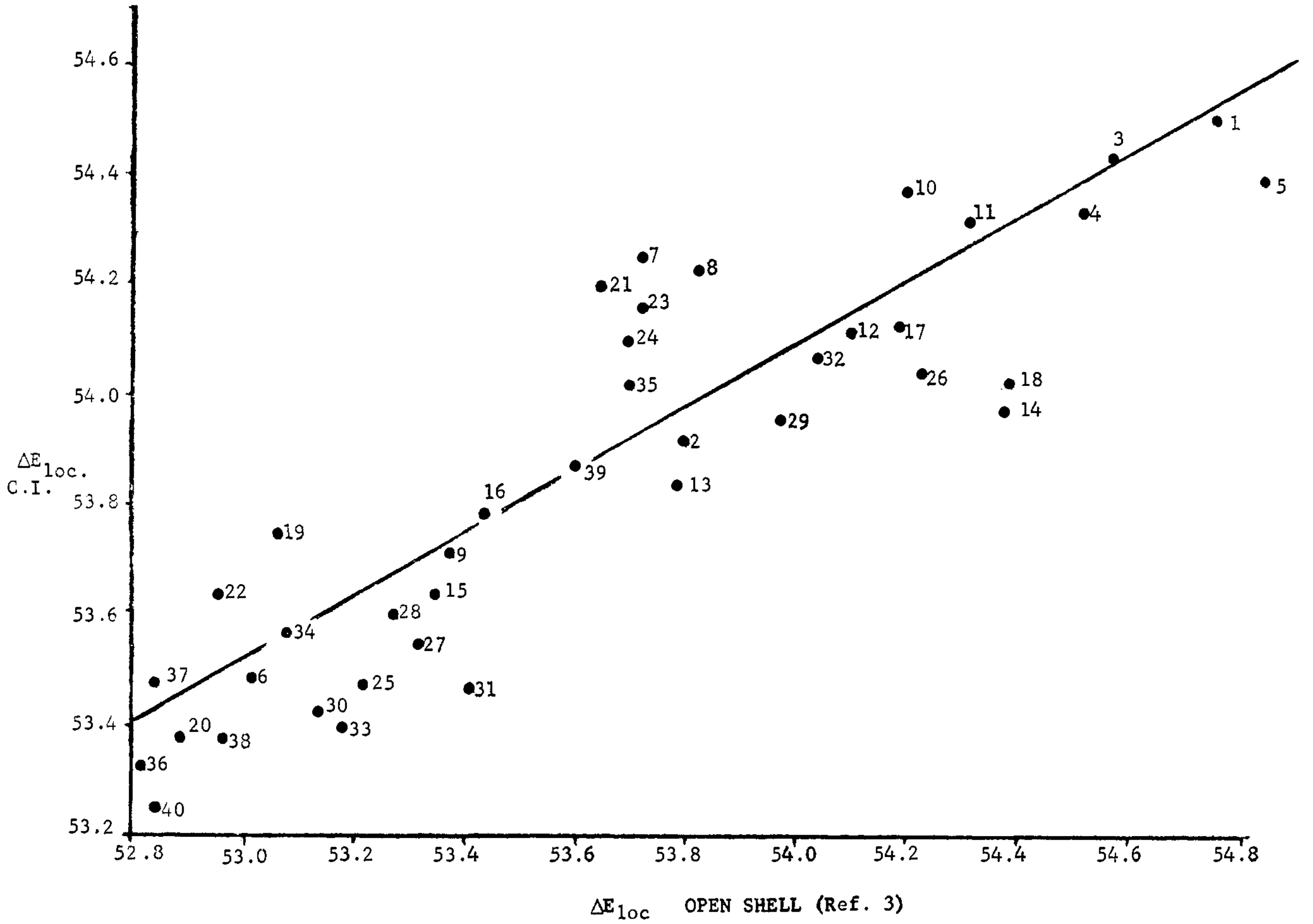

Figure 2. Comparison of triplet-state localization energies calculated by a CI method in the present work with those calculated by an open-shell method in ref 3.

wavelength with an increasing number of methyl substituents.[15]

A comparison of the excited singlet-state and triplet-state localization energies from Table II shows that the triplets have lower localization energies, and hence should be more basic than the excited singlets. This is somewhat contrary to what might have been intuitively expected. First of all, the excited singlet state is the state of higher energy and consequently would be expected to be more reactive. A second consideration is the "diradical" character of the triplet state. Radicals are normally thought of as electron-deficient species; consequently the greater "diradical" character of the triplet state might be expected to make it less reactive toward positively charged species.

The ground-state localization energies calculated in the present work and in the previous work, while numerically similar, predict some important differences in reactivity. This is especially noticeable in the position of attack within a given molecule. In eight of the eleven molecules with more than one equivalent position, the position of lowest localization energy differs in the two sets of calculations. This can be attributed almost entirely to the differences in the two-center integrals used in the two methods. Table III compares the results of the previous work with calculations done with the present program for

Table III. Comparison of Integral Evaluation Methods for Some Ground-State Localization Energies[a]

		Present program		
Molecule	Position	P-P integrals[b]	Theoretical integrals	Previous work[c]
Toluene	1	55.7569	55.6579	56.0019
	2	56.1155	56.2645	56.6131
	3	56.2073	56.4788	56.8550
	4	56.1128	56.3391	56.7146
m-Xylene	1	55.7311	55.6148	55.9623
	2	56.0033	56.0095	56.3351
	4	55.9952	56.0788	56.4311
	5	55.1801	56.4375	56.8061
p-Xylene	1	55.6322	55.4997	55.8211
	2	55.9914	56.2330	56.5700
Durene	1	55.4924	55.2115	55.5497
	3	55.9519	55.9128	56.2553

[a] Energies in electron volts. [b] Pariser and Parr triangle. [c] Taken from work done for ref 3.

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(15) This is due to the chosen method of estimating the β integral in ref 3. A straight proportionality to overlap was assumed. The inductive treatment of the methyl group made the effective nuclear charge of a substituted carbon smaller than that of an unsubstituted carbon. This, in turn, increased the value of the overlap integral, and, consequently, the absolute magnitude of the β integral for bonds involving a substituted carbon. It has been shown that in order to get spectral agreement for an inductive model, the β integral involving substituted centers must be smaller than that involving only unsubstituted centers.[16] If one were to assume that the β integral is proportional to both overlap and the valence-state ionization potentials of the atoms involved (R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941)), then they would be smaller when substituted centers were involved.

(16) J. Labarre, A. Julg, and F. Crasnier, *Compt. Rend.*, **261**, 4419 (1965).

several molecules using both Pariser–Parr and theoretical integrals. It is seen that the results when the same integrals are used are essentially the same. The differences between the localization energies from the present program and the previous work are essentially constant at 0.3–0.4 ev. The bulk of this difference is due to the fact that the previous program included a compensation for the distortion of the bond lengths in the molecule from the value for an isolated carbon–carbon bond.[17] The principal point is that the localization energy differences, both within a given molecule and within the series, are the same in the two cases using the same integrals.

Conclusions

It has been shown that qualitative agreement between open-shell calculations and CI calculations of excited triplet-state localization energies is obtained. This agreement is far from quantitative, however. The methods do not predict the same positions of reaction within a molecule or even the same over-all reactivity within a series. The excited singlet-state basicities calculated by the CI method give satisfactory agreement with experiment; hence, this implies that the CI results might be preferable to the open-shell results for the triplet states. This, however, can only be conjecture, in the absence of confirming experimental evidence.

It has also been shown that the predicted position of attack in SCMO calculations is dependent upon the method of evaluating two-center, two-electron repulsion integrals. This is a factor which should be investigated in detail.

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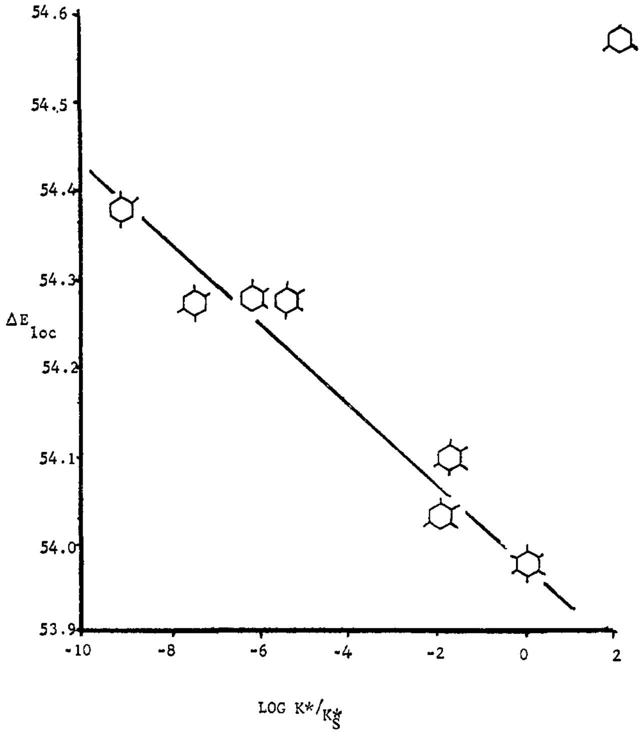

Figure 3. Plot of ΔE_{loc} for excited singlet states calculated by the CI method with experimental relative excited singlet-state basicities[4] (localization energies corrected for the number of equivalent reactive positions and for attack at a methyl-bearing position where appropriate; basicities referred to hexamethylbenzene as a standard).

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[17] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

Carbon-13 Magnetic Resonance. VI.[1a] Theory of Carbon-13 Magnetic Resonance Shifts in Aromatic Molecules[1b]

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Abstract: The 15.1-Mcps carbon-13 nuclear magnetic resonance spectra of biphenyl, naphthalene, phenanthrene, and pyrene have been obtained, and with the exception of the two bridgehead peaks in phenanthrene all of the resonance peaks have been assigned. An extension to the theory of chemical shifts for aromatic carbons is proposed which considers both σ- and π-electron density terms as they alter a proposed effective nuclear charge parameter for each bond. The theory is applied to toluene, chlorobenzene, and the above four alternant aromatic compounds.

Carbon-13 chemical shift values of aromatic compounds have been studied[2–5] with the purpose of illucidating additional details of the electronic structure in this interesting class of compounds. Empirically, it has been found that carbon-13 shifts vary

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[1] (a) Previous paper in this series: W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, **88**, 1496 (1966); (b) taken in part from the Ph.D. dissertation of T. D. Alger, University of Utah, Aug. 1966.

[2] P. C. Lauterbur, *J. Chem. Phys.* **26**, 217 (1957); *J. Am. Chem. Soc.*, **83**, 1838 (1961).

[3] H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

[4] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

[5] P. C. Lauterbur, *ibid.*, **43**, 360 (1965).