aniline (p$K_a$ −6.68[42]). For each kinetic run a 55-ml aliquot of solvent I was syringed into a 100-ml long-necked flask, sealed with a serum cap, and maintained at 25.00 ± 0.02°. A solution of the hydrocarbon in 2 ml of $CCl_4$ was injected into the flask and shaken vigorously. At intervals, 10-ml aliquots were withdrawn and quenched with excess cold 2 *N* NaOH. The mixture was extracted with ether or cyclohexane, washed until neutral, and dried. In early runs the evaporated residues were sublimed but this procedure gave irreproducible results; subsequent control experiments showed that sublimation resulted in loss of tritium activity. Hence, the extracts were assayed spectrophotometrically and the samples for counting were prepared by diluting known volumes with scintillation solution.

**Solvent II.** A solution of 2–8 mg of tritiated hydrocarbon in 0.5 ml of $CCl_4$ was injected into 25 ml of trifluoroacetic acid and 8 aliquots were sealed in 5-ml ampoules with nitrogen flushing. The ampoules were maintained at 70.00 ± 0.06°; after thermal equilibrium was reached, points were removed at intervals and quenched in Dry Ice–acetone. The contents were worked up as above.

In the runs with pyrene-2-*t* the solutions were made up with vacuum line techniques and transferred with argon pressure to tubes which were sealed off with complete exclusion of air. For best results we recommend this type of procedure generally for studies of polycyclic hydrocarbons in trifluoroacetic acid. In several runs using the earlier procedures we noticed varying amounts of decomposition that probably result from radical cations produced by oxygen.

The data were handled as first-order kinetics using Perrin's program[7] or LSKIN[6] and were checked for quality with CalComp plots. A typical plot is shown in Figure 2.

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[42] M. J. Jorgenson and D. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 1963). The indicator was kindly supplied by Dr. Jorgenson.

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# Semiempirical SCF MO Calculations on Electrophilic Aromatic Substitution[1]

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**Abstract:** Various semiempirical MO methods have been applied to the extensive reactivity data now available from protodetritiation of polycyclic aromatic hydrocarbons in trifluoroacetic acid. In common with past experience the simple HMO method is totally inadequate to handle the wide range of structures available. The HMO-$\omega$ technique, however, is astonishingly satisfactory, undoubtedly because it is an approximation of SCF-$\pi$ methods. The latter methods are also satisfactory and do not depend in an important way on the specific model or parameter set used. The CNDO/2 method also gives a generally excellent correlation. The effect of methyl substituents is well accounted for by CNDO/2 although the resulting correlation differs from that of the unsubstituted polycyclic systems. None of the methods gives a satisfactory account of the strained biphenylene system; CNDO/2 also is useless in interpreting aromatic substitution reactivities in fluorene and benzocyclobutene.

Studies of protodetritiation of polycyclic aromatic hydrocarbons in trifluoroacetic acid pioneered by Eaborn and his research group[2,3] and extended by us[4] have provided data for many positions of a number of compounds covering a reactivity range of over six orders of magnitude. These data are unique because quantitative reactivity data are available not only for those positions normally reactive in aromatic substitution reactions but also for several positions which are too unreactive to be accessible in direct reactions—examples are the pyrene-2 and fluoranthene-2 positions; hence, these data are ideal for comparisons with molecular orbital models. Furthermore, the mechanism has been elucidated with adequate detail,[5] and has been shown to involve the formation of a symmetrical Wheland intermediate. The transition states leading to and from the intermediate are almost identical, differing only by the isotope effect of tritium and hydrogen. Problems such as free-radical formation[6] and oxidation[4] can be largely circumvented by use of pure trifluoroacetic acid[2] and careful technique.[4]

In this paper we apply several MO models to these data. First we review the use of the simple Hückel (HMO) method followed by the SCF methods: Pople's SCF-$\pi$ method and the all-valence-electron CNDO/2 procedure.

## HMO

Much has already been published on the HMO treatment of aromatic substitution.[7] Of the many indices proposed to determine reactivity in aromatic substitution the localization energy appears to be the most fundamental and reliable. Dewar's reactivity numbers, a perturbation approach to localization energies,[8] apply only to alternant systems; hence in order to include the nonalternant system, fluoranthene, cation localization energies, $L_r^+$, were used as determined from the usual HMO calculations. The HMO

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[1] This research was supported in part by Grants No. 1002-66 and 68-1364 of the Air Force Office of Scientific Research, U. S. Air Force, and by National Science Foundation grants. Many of the calculations were run with time donated by the Computer Center of the University of California, Berkeley, Calif.

[2] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 247 (1961).

[3] R. Baker, C. Eaborn, and J. A. Sperry, *ibid.*, 2382 (1962).

[4] A. Streitwieser, Jr., A. Lewis, I. Schwager, R. W. Fish, and S. Labana, *J. Amer. Chem. Soc.*, **92**, 6525 (1970).

[5] R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, New York, N. Y., 1965, Chapter 8.

[6] C. Eaborn, P. M. Jackson, and R. Taylor, *J. Chem. Soc. B*, 613 (1966).

[7] For example, see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 11.

[8] M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3357 (1952); *Rec. Chem. Progr.*, **19**, 1 (1958).

Table I. Calculated MO Quantities and Experimental Protodetritiation Reactivities

| Aromatic position | Symbol | HMO $L_r^+$ | HMO-ω $L_\omega''$ | SCF-π-NM $-\Delta E$, eV | CNDO/2 $-\Delta E$, eV | Log rel rate[a] $CF_3COOH$, 70° |
|---|---|---|---|---|---|---|
| Benzene | B | 2.536 | 1.490 | 1.5821 | 12.141 | −3.00 |
| Naphthalene-1 | 1N | 2.299 | 1.180 | 0.6708 | 13.115 | (0) |
| Naphthalene-2 | 2N | 2.480 | 1.358 | 1.1452 | 12.698 | −0.86 |
| Phenanthrene-1 | 1P | 2.217 | 1.133 | 0.5646 | 13.222 | −0.03 |
| Phenanthrene-2 | 2P | 2.497 | 1.328 | 1.0451 | 12.844 | −0.75 |
| Phenanthrene-3 | 3P | 2.453 | 1.257 | 0.8651 | 13.003 | −0.40 |
| Phenanthrene-4 | 4P | 2.365 | 1.215 | 0.7481 | 13.070 | −0.075 |
| Phenanthrene-9 | 9P | 2.298 | 1.175 | 0.5809 | 13.320 | 0.22 |
| Biphenylene-1 | 1Bi | 2.408 | 1.242 | 0.9500 | 12.780 | −0.97[b] |
| Biphenylene-2 | 2Bi | 2.352 | 1.194 | 0.7736 | 13.086 | 1.16[b] |
| Chrysene-6 | 6C | 2.254 | 1.042 | 0.2196 | 13.714 | 1.00 |
| Pyrene-1 | 1Py | 2.190 | 0.928 | −0.03481 | 14.093 | 2.91 |
| Pyrene-2 | 2Py | 2.549 | 1.351 | 1.1186 | 12.695 | −1.09 |
| Pyrene-4 | 4Py | 2.274 | 1.130 | 0.4342 | 13.438 | 0.15 |
| Fluoranthene-1 | 1F | 2.466 | 1.238 | 0.7635 | 13.054 | −0.52 |
| Fluoranthene-2 | 2F | 2.503 | 1.389 | 1.0944 | 12.795 | −1.14 |
| Fluoranthene-3 | 3F | 2.341 | 1.142 | 0.4724 | 13.489 | 0.96 |
| Triphenylene-1 | 1T | 2.378 | 1.192 | 0.6926 | 13.136 | 0.025 |
| Triphenylene-2 | 2T | 2.477 | 1.279 | 0.8829 | 13.040 | −0.77 |
| Perylene-3 | 3Pe | 2.140 | 0.869 | −0.2527 | 14.487 | 3.15 |
| Anthracene-1 | 1A | 2.231 |  | 0.3139 | 13.577 | 0.76[c] |
| Anthracene-2 | 2A | 2.423 |  | 0.8578 | 13.101 | 0.00[c] |
| Anthracene-9 | 9A | 2.013 |  | 0.3623 | 14.410 | 4.17[c] |
| Fluorene-1 | 1Fl |  |  |  | 12.878 | −1.68[b,d] |
| Fluorene-2 | 2Fl |  |  |  | 12.828 | 1.24[b,d] |
| Fluorene-3 | 3Fl |  |  |  | 12.864 | −0.90[b,d] |
| Fluorene-4 | 4Fl |  |  |  | 13.109 | 0.75[b,d] |

[a] Reference 4 except where noted. [b] Not included in least-squares correlations. [c] Derived from the deuterodeprotonation data of ref 13 using the correlation slope (1.08) to protodetritiation derived elsewhere (ref 4). [d] R. Taylor, *Chimia*, **22**, 1 (1968).

procedure gives π energies in the form of eq 1 and $L_r^+$ is defined as the difference in π-bonding energies between an aromatic hydrocarbon and the corresponding cation derived from removing position r and two electrons from the π system as in eq 2.[7] The localization energies were obtained from standard sources.[9]

$$E_\pi = n\alpha + M\beta \qquad (1)$$

$$L_r^+ = M - M^+ \qquad (2)$$

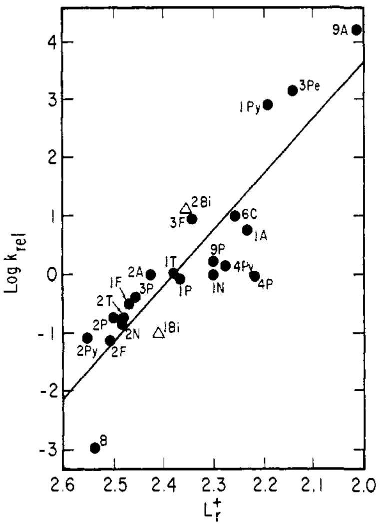

Figure 1. Correlation of protodetritiation reactivities with HMO localization energies, $L_r^+$. Symbols are defined in Table I. The least-squares line is shown for the circled points.

Table II. Summary of Correlations

| Method | Slope ± std dev | Std dev of fit | Corr coeff | No. of points |
|---|---|---|---|---|
| HMO | 9.72 ± 1.13 | 0.73 | 0.893 | 21 |
| HMO-ω | 8.75 ± 0.59 | 0.38 | 0.966 | 18 |
| SCF-π-NM | 3.17 ± 0.18 | 0.39 | 0.970 | 21 |
| CNDO/2 | 2.69 ± 0.13 | 0.32 | 0.979 | 21 |
|  | Dewar–Thompson[a] SCF-π Correlations |  |  |  |
| PPP | 3.18 ± 0.23 | 0.39 | 0.972 | 13 |
| SPO | 3.05 ± 0.23 | 0.41 | 0.969 | 13 |
| PPP-SCβ | 3.66 ± 0.31 | 0.45 | 0.962 | 13 |
| SPO-SCβ | 2.92 ± 0.82 | 1.13 | 0.732 | 13 |

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

The comparison with experimental protodetritiation reactivities summarized in Table I and plotted in Figure 1 shows a mediocre correlation (Table II) with substantial scatter. Párkányi, Dolejsek, and Zahradnik[10] have shown that such plots actually reveal separate linear correlations for like positions such as α-naphthyl, β-naphthyl, 9-anthracyl types, each having separate slopes and intercepts. This sort of dissection applies as well to Figure 1 and is undoubtedly a consequence of the neglect of electron-repulsion effects common in HMO methods.

The "ω-technique" modification of the HMO method has been shown to be an approximate SCF method;[11] a corresponding localization energy, $L_\omega''$, can be defined[12] and has been shown to give improved correlations with aromatic substitution reactions.[7,12] The

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[9] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965.

[10] C. Párkányi, Z. Dolejsek, and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **33**, 1211 (1968).

[11] A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

[12] A. Streitwieser, Jr., J. I. Brauman, and J. B. Bush, *Tetrahedron, Suppl.*, **19** (2), 379 (1963).

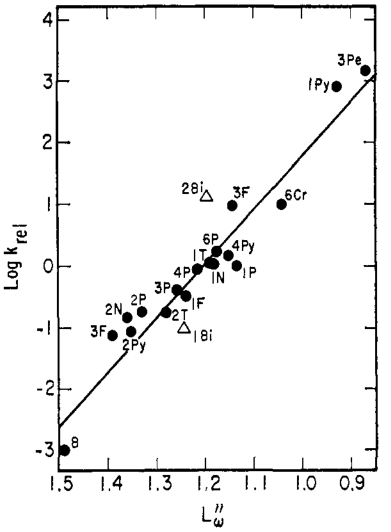

Figure 2. Correlation of protodetritiation reactivities with HMO-$\omega$ localization energies, $L_\omega''$. The least-squares line shown does not include the biphenylene points (triangles).

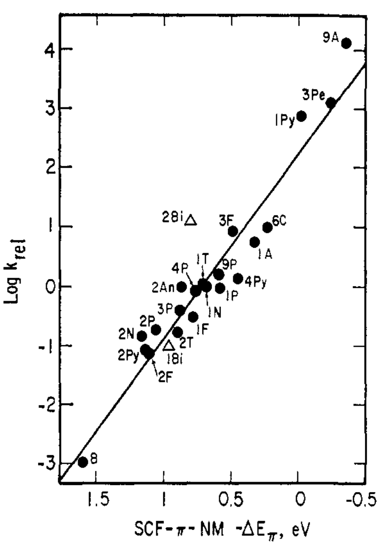

Figure 3. SCF-$\pi$-NM correlation of electrophilic aromatic protodetritiation reactivities. The least-squares line shown does not include the biphenylene points (triangles).

$L_\omega''$ values of ref 12 were augmented by additional calculations made by our research group at various times with the same program and are included in Table I. The comparison with experimental protodetritiations in Figure 2 shows a much improved correlation in which the least-squares correlation coefficient is now a respectable 0.966 (Table II). Furthermore, dissection into position types is no longer discernible. Clearly, the complete lack of explicit consideration of electron-repulsion effects is a major weakness of the HMO method in dealing with charged species and some form of SCF approach is necessary. This point has been emphasized repeatedly.[13] We have done nothing more with the HMO-$\omega$ method because more complete SCF-$\pi$ methods are now commonplace.

## SCF-$\pi$

In their deuterodeprotonation studies of aromatic hydrocarbons, Dallinga, *et al.*,[14] showed that an SCF-$\pi$ procedure based on Pople's[15] method gave a good correlation with experiment. Dewar and Thompson[16] have applied several modifications of the Pople SCF-$\pi$ method to nitration reactivities with generally successful results. The least-squares correlations between their calculated quantities and protodetritiation reactivities are summarized in Table II. These correlations are all satisfactory and show no advantage for the "self-consistent $\beta$" (SC$\beta$) method in which C–C bond lengths and the corresponding $\beta$ values are varied until self-consistency with bond orders is obtained; that is, equally good results are obtained by a "standard structures" procedure in which the benzenoid hydrocarbons and the localized cations are constructed from regular hexagons having a constant C–C bond length with a single value for $\beta$.

Since the Dewar and Thompson calculations omitted some significant structures for which data are now available (for example, fluoranthene and the pyrene-2 and -4 positions) we have contributed additional calculations using the SCF-$\pi$ approach which we have also applied to arylmethyl cations.[17] The structures were generated from hexagons with C–C bond lengths of 1.40 Å and repulsion integrals were evaluated by the Nishimoto–Mataga procedure[18] with $\gamma_{11}$ = 11.13 eV and $\beta$ = $-2.331$ eV.[17] The long bonds in biphenylene were set at 1.50 Å. The localized cations were obtained by deleting the localized position. Calculations were made with a modified version of program 71 of the Quantum Chemistry Program Exchange, Indiana University. We are indebted to Dr. James S. Wright for the preparation of this program and to Miss Lilly Wong for the calculations. The results are summarized in Table I and plotted in Figure 3. The resulting least-squares correlation (SCF-$\pi$-NM in Table III) is as good as the best of the Dewar and Thompson results but applies to a far wider range of structures. The same features are reproduced in all of the SCF-$\pi$ models. There is no dissection into position types. Expecially noteworthy is the agreement found for the phenanthrene-4 and triphenylene-1 positions for which steric-hindrance effects are frequently apparent in aromatic substitution reactions; the exact correspondence of these points with the correlation line demonstrates that protodetritiation in trifluoroacetic acid is a reaction with exceptionally low steric demands. Also significant is the demonstration in Figure 3 that the nonalternant fluoranthene positions are as well accommodated by the SCF-$\pi$ model as are normal alternant benzenoid hydrocarbons. These SCF-$\pi$ results have clear predictive utility and show that the specific parameter set used is not important. Only biphenylene is not well represented in the SCF-$\pi$ model but its four-membered ring represents unusual structure features (*vide infra*).

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(13) For example, M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(14) G. Dallinga, A, A. Verrijn Stuart, P. J. Smit, and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957).

(15) See Table II, footnote *a*.

(16) M. J. S. Dewar and C. C. Thompson, Jr., *J. Amer. Chem. Soc.*, **87**, 4414 (1965).

(17) A. Streitwieser, Jr., H. A. Hammond, R. H. Jagow, R. M. Williams, R. H. Jesaitis, C. J. Chang, and R. Wolf, *ibid.*, **92**, 5141 (1970).

(18) K. Nishimoto and N. Mataga, *Z. Phys. Chem.*, **12**, 335 (1957).

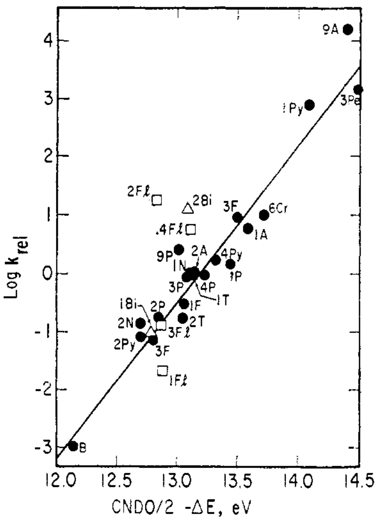

Figure 4. Correlation of electrophilic protodetritiation reactivities with CNDO/2 proton affinities. The least-squares line shown does not include the biphenylene (triangles) or fluorene (squares) points.

Finally we mention the localization model of Chalvet, Daudel, and Kaufman[19] which differs from the foregoing in that the core of the localized carbon is included as a part of the localized cation $\pi$ system; this model has been criticized[16] but still gives a reasonable correlation (correlation coefficient = 0.95).

## CNDO/2

In applying the semiempirical CNDO all-valence-electron SCF method we used the parameters of Pople and Segal[20] and the standard structure[21] approach in which the aromatic hydrocarbons were generated from hexagons with C–C bond lengths of 1.39 Å and C–H bond lengths of 1.08 Å. The Wheland intermediates were derived by adding a hydrogen to the reacting carbon to give a methylene group with $r$(C–H) = 1.10 Å and an H–C–H angle of 110°. The long bonds in biphenylene were set at 1.51 Å. These calculations, which give proton affinities rather than localization energies, made use of a modified version of QCPE 100 and correspond to our related treatments of arylmethyl cations.[17]

The results are summarized in Table I and plotted in Figure 4. The least-squares correlation is quite good; the correlation coefficient is 0.979 (Table II). Indeed, the results are similar in pattern and quality to the SCF-$\pi$ results. In both cases the 2 position of biphenylene is far more reactive than predicted; in other work[17,22,23] we have shown that CNDO/2 calculations of unsubstituted conjugated anions and cations parallel the corresponding SCF-$\pi$ calculations.

In principle, the CNDO method should be able to account for substituted aromatic systems; however, in our other studies of arylmethyl cations[17,22] and anions[23] we have found that such substituents are not correlated on the same basis as extended conjugation—the mechanism of charge delocalization is weighted differently by the CNDO approximations than the electrostatic interaction of a charge and a substituent dipole. Although substantial data are available for protodetritiation of substituted aromatics[24] we will restrict our attention here to alkyl substituents.

Protodetritiation results are available for all of the aromatic positions of fluorene.[25] Our corresponding CNDO/2 calculations were made on a model in which the benzene rings were the usual hexagons, the remaining C–C bonds in the five-membered ring were 1.48 Å, and the methylene group was given the tetrahedral HCH angle with $r$(C–H) = 1.09 Å. The results are summarized in Table I and are included in Figure 4. The reactivity of the 3-fluorene position fits the established correlation but the wide deviation of the other positions suggests that this one agreement is fortuitous. The 2 position, which is the most reactive position in fluorene in all electrophilic substitution reactions, is actually calculated to be the least reactive. Clearly, the CNDO calculations provide no insight into this chemistry of fluorene.

The effect of methyl substituents[24,26] was handled differently. The CNDO/2 calculations on the methyl-substituted systems used a tetrahedral methyl group with $r$(C–C) = 1.52 Å and $r$(C–H) = 1.09 Å. To isolate the methyl group effects the log $k_{rel}$ for the parent hydrocarbon was subtracted from that for the substituted hydrocarbon to give a Δ log $k$ which was compared to the $\Delta\Delta E$ obtained from subtraction of the CNDO $\Delta E$ of the parent from that of the substituted compound. This procedure isolates the experimental and calculated substituent effects; results for several systems are summarized in Table III and plotted in Figure 5. A fair correlation is obtained having a slope substantially different from that in Figure 4. Such correlations should be useful in estimating reactivities of polymethylated systems—note that both benzene and naphthalene systems are included in this correlation.

Table III. Effect of Methyl Substituents

| Protodetritiation position | $-\Delta$ log $k^a$ | CNDO/2 $\Delta\Delta E$, eV |
|---|---|---|
| Toluene-2 | 2.36 | 0.363 |
| Toluene-3 | 0.70 | 0.056 |
| Toluene-4 | 2.65 | 0.455 |
| $o$-Xylene-3 | 3.12$^b$ | 0.443 |
| $o$-Xylene-4 | 3.28$^b$ | 0.534 |
| 2-Methylnaphthalene-1 | 2.46 | 0.389 |
| 4-Methylnaphthalene-1 | 1.92 | 0.426 |
| 1-Methylnaphthalene-2 | 2.43 | 0.401 |
| 3-Methylnaphthalene-1 | 0.56 | 0.174 |
| 4-Methylnaphthalene-1 | 0.47 | 0.048 |
| 6-Methylnaphthalene-1 | 1.29 | 0.218 |

$^a$ Reference 23. $^b$ Reference 25.

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(19) O. Chalvet, R. Daudel, and J. J. Thompson, *J. Phys. Chem.*, **68**, 490 (1964).

(20) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 43, S136 (1965); **44**, 3289 (1966).

(21) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(22) A. Streitwieser, Jr., and R. G. Jesaitis in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 197.

(23) A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, J. R. Wright, P. H. Owens, and D. M. E. Reuben, The Jerusalem Symposia on Quantum Chemistry and Biochemistry, II, The Israel Academy of Sciences and Humanities, Jerusalem, 1970, p 160.

(24) See Table I, footnote *d*.

(25) K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 4806 (1964).

(26) R. Taylor, G. J. Wright, and A. J. Holmes, *J. Chem. Soc. B*, 780 (1967).

## Strained Systems

The inadequacy of the CNDO treatment of the reactivity of biphenylene and fluorene prompted a further study of strained systems. Calculations on benzocyclobutene used a structure having a 95° fusion angle with the aromatic ring. The calculated proton affinities of the 3 and 4 positions were compared with those of *o*-xylene and with the protodetrimethylsilylation results of Bassindale, Eaborn, and Walton[27] in Table IV. There is no correlation at all between calculation and experiment. The CNDO procedure is clearly of limited effectiveness in strained compounds. The semiempirical treatments give no insight into two recent interpretations of the aromatic chemistry of such strained hydrocarbons, the bond order–bond length argument[26,28] and the explanation based on hybridization of small rings.[29] This inadequacy of the CNDO/2 procedure is clearly pointed up by the fluorene and biphenylene results (*vide supra*). The observed coincidence of the biphenylene-1 point on the protodetritiation correlation (Figure 4) is undoubtedly fortuitous and without significance.

**Table IV.** Reactivities of Benzocyclobutane

| Position | Rel reactivity[a] | CNDO/2 proton affinity $\Delta E$, eV |
|---|---|---|
| *o*-Xylene-3 | 71 | 12.584 |
| *o*-Xylene-4 | 56 | 12.675 |
| Benzcyclobutene-3 | 5.9 | 12.611 |
| Benzcyclobutene-4 | 56.5 | 12.721 |

[a] Rate relative to benzene for protodetrimethylsilylation in aqueous $HClO_4$–methanol at 0° (ref 26).

We now must ask whether the present limitations of CNDO/2 result from the particular parameter set used. Other parameter sets have been suggested[30] but it would take extensive calculation and expensive computer time to check them all; however, the SCF-π results suggest that much the same pattern would emerge from any internally consistent parameter set that the limitations are inherent in the fundamental approximations of the CNDO framework. Certainly, the theory has major approximations such as the zero differential overlap approximation, the treatment of p orbitals as spherical for calculation of electron-repulsion integrals, and the general crudeness with which interactions with neighboring atoms are included. These approximations are internally consistent and are necessary to permit SCF-like calculations on large molecules without the much longer computer times required for complete *ab initio* SCF calculations.[31] Nevertheless, the extreme nature of the CNDO approximations has been criticized[32] and the limitations in the applications to organic reactivities demonstrated in this and previous[17,22,23] papers greatly restrict the usefulness of CNDO and the theoretical conclusions derived from it.

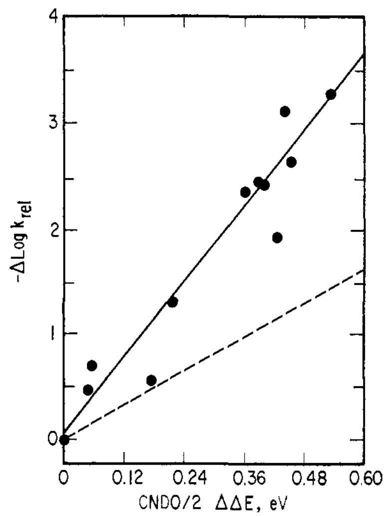

Figure 5. Effect of methyl substituents on protodetritiation compared to the effect on CNDO/2 proton affinities. The data plotted refer to Table III. The slope is 5.85 ± 0.54; correlation coefficient 0.96. The dotted line shows the slope of the CNDO correlation in Figure 4.

Other related semiempirical valence-electron SCF procedures have been suggested recently.[33] In general the input parameters are derived from "normal" systems and these methods may be expected to give more or less satisfactory results for related normal systems. Their possible application to strained molecules will require extensive testing of the type outlined in this paper.

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(27) A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc., B*, 12 (1969).

(28) J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, **21**, 1665 (1965); J. Vaughan and G. J. Wright, *J. Org. Chem.*, **33**, 2580 (1968).

(29) A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).

(30) For example, K. B. Wiberg, *ibid.*, **90**, 59 (1968).

(31) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

(32) D. B. Cook, P. C. Hollis, and R. McWeeny, *Mol. Phys.*, **13**, 553 (1967).

(33) For example, MINDO: N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).