Correlation of the Hydride Affinities of Substituted Aromatic Carbocations and the Proton Affinities of Substituted Benzenes Calculated by MNDO with σ^+ Substituent Constants

Rafik Karaman,* Jun-Tsu Luke Huang, and James L. Fry*

Bowman-Oddy Laboratories, Department of Chemistry, The University of Toledo, Toledo, Ohio 43606-3390

Received June 8, 1990

MNDO-calculated heats of formation and ionization potentials of 248 structures involving substituted toluenes, diphenylmethanes (DPMH), xanthenes (XAN), 9*H*,10*H*-acridines (ACR), 9*H*-10-*N*-methylacridines (*N*-MACR), benzenes, and the corresponding carbocations are reported. Brown σ^+ constants have been successfully correlated with the energies (ΔH_r) of the isodesmic processes of bromination and protonation of substituted benzenes, solvolyses (dissociation) of substituted benzyl and benzhydryl (DPMCl) chlorides, hydride affinities of substituted aryl carbocations (benzyl, benzhydryl, etc.) as well as ionizations of substituted benzenes, toluenes, and diphenylmethanes. Comparisons of these results with experimental data and some ab initio theoretical calculations are also made.

Introduction

It was the purpose of this work to see if readily available semiempirical molecular orbital methods would provide calculated properties of neutral and charged species that could be used to make useful comparisons with experimental information about some commonly studied chemical phenomena. In particular, we wished to see if this approach could give reliable correlations and predictions of substituent effects for selected processes resembling simple solvolysis and electrophilic aromatic substitution reactions.

The study of gas-phase ion chemistry, in particular carbocation chemistry, is of considerable importance since it permits investigation of intrinsic molecular properties of ionic species in the absence of complex interactions with the solvent. Solution-phase carbocation chemistry has enjoyed a great advance since the development of thermochemical methods by Arnett and co-workers that afforded a direct measurement of heats of ionization of appropriate precursors to carbocations studied at low temperatures in superacidic media using NMR techniques.[1] In the gas phase, carbocations are readily produced by electron impact (EI) ionization of halide precursors,[2] ion cyclotron resonance (ICR) techniques that permit the determination of the relative stabilities of gas-phase carbocations by examining the preferred direction and equilibrium in reactions,[3] collisional activation (CA),[4] photoionization (PI),[5] photoelectron photoion coincidence (PEPICO),[6] and high-pressure mass spectrometry.[7] Although these methods are a stepping stone to the understanding of the chemistry of the carbocations, the theory is still of considerable interest in the question of the correlation of carbocation stability data with solution studies. For example, the lack of reliable heats of formation of a variety of compounds such as alkyl halides limits their use in the determination of halide affinities.[8] These give a convenient basis for the comparison of relative carbocation stabilities analogous to that from solvolysis of alkyl halides in solution.

Coincident with the progressive increase in availability of sophisticated computers, theoretical methods have become very important tools for investigation of the structure and reactivity of molecules. Disch and co-workers[9] and Wiberg[10] used ab initio methods to predict heats of formation using homodesmic and isodesmic reactions. Holmes and co-workers suggested a procedure based upon experimental data to estimate heats of formation of unknown cations that gave impressive results and have become an alternative way to estimate heats of formation theoretically.[11] Although reasonable estimates of the properties and reactivities of a variety of species can be obtained by ab initio self-consistent-field molecular orbital (SCF-MO) procedures, the use of such methods so far has been limited to very small systems.

There is therefore a pressing need for a general procedure for studying the properties of large molecules. An obvious candidate is the semiempirical MNDO method[12] which has been shown to reproduce the ground-state properties of a very wide variety of compounds such as cations and neutral species in a satisfactory and generally economical and convenient manner.[12,13] The only serious reservation of this method is the somewhat limited scope of tested applications to date. Although there are some systematic studies for excited states,[14] electron affinities, anions,[15] cations, and radical cations[13] the interpretation of electronic effects of substituents in quantitative terms by the MNDO method has remained unexplored.[16]

---

(1) Arnett, E. M.; Petro, S. C. *J. Am. Chem. Soc.* **1978**, *100*, 2563, 5402, 5408. Arnett, E. M.; Petro, S. C.; Pienta, N. *J. Am. Chem. Soc.* **1980**, *102*, 3329. Arnett, E. M.; Petro, S. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522. Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 3522; **1983**, *105*, 2889.

(2) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*; Holden-Day: San Francisco, 1967.

(3) Blint, R. J.; McMahon, T. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1269. Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. Solomon, J. J.; Field, F. H. *J. Am. Chem. Soc.* **1975**, *97*, 2625.

(4) McLafferty, F. W.; Proctor, C. J. *Org. Mass Spectrom.* **1983**, *18*, 193 and references therein.

(5) Lifshitz, C.; Goldenberg, M.; Malinovich, Y.; Peres, M. *Org. Mass Spectrom.* **1982**, *17*, 453 and references therein.

(6) Baer, T.; Morrow, J. C.; Shao, J. D.; Olesik, S. *J. Am. Chem. Soc.* **1988**, *110*, 5633 and references therein.

(7) Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(8) In some cases, quantitative and semiquantitative halide affinities were determined directly. For further information, see: (a) Abboud, J.-L. M.; Hehre, W. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 6072. (b) Wieting, R. D.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7552. (c) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964.

(9) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

(10) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 197.

(11) (a) Holmes, J. L.; Fingas, M.; Lossing, F. P. *Can. J. Chem.* **1981**, *59*, 80. (b) Holmes, J. L.; Lossing, F. P.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 133. (c) Holmes, J. L.; Lossing, F. P. *Can. J. Chem.* **1982**, *60*, 2365.

(12) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(13) Halim, H.; Heinrich, N.; Koch, W.; Schmidt, J.; Frenking, G. *J. Comput. Chem.* **1986**, *7*, 93.

(14) Dewar, M. J. S.; Fox, M. A.; Campbell, K. A.; Chen, C. C.; Friedheim, J. E.; Holloway, M. K.; Kim, S. C.; Liescheski, P. B.; Pakiari, A. M.; Tien, T. P.; Zoebisch, E. G. *J. Comput. Chem.* **1984**, *5*, 480.

(15) Olivella, S.; Urpi, F.; Vilarrasa, J. *J. Comput. Chem.* **1984**, *5*, 230.

0022-3263/91/1956-0188$02.50/0 © 1991 American Chemical Society

Table I. MNDO, STO-3G, and Experimental Data for Some Monosubstituted Benzenes

	relative energies				barrier to rotation		
substituent	conformation	MNDO	STO-3G[a]	exp[a]	MNDO	STO-3G[a]	exp[a]
OH	CCOH orthogonal	1.9	5.15	3.28, 3.36, 3.47	1.9	5.15	3.28, 3.36, 3.42
	CCOH planar	0	0	0			
OCH_3	CCOC orthogonal	0	0.23	6.	0.4	0.23	6
	CCOC planar	0.4	0	0			
NH_2	pyramidal	0	0	0	4.2[b]	2.72[b]	1.61[b]
	planar	4.2	2.72	1.61			
CH_3	CCCH planar	0	0	–	0	0.006	0.014
	CCCH orthogonal	0	0	–			
CH_2CH_3	CCCC planar	2.2	2.43	–	2.2	2.2	1.3
	CCCC orthogonal	0	0	–			
$CH(CH_3)_2$	CCCC planar	3.4	–	–	4.9	–	–
	CCCC orthogonal	0.6	–	–			
	CCCC $\phi = -30°$	4.9	–	–			
	CCCC $\phi = -120°$	0	–	–			
$C(CH_3)_3$	CCCC planar	0	–	–	0.2	–	–
	CCCC orthogonal	0.2	–	–			

[a] Experimental and STO-3G data taken from Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496. [b] Inversion barrier.

Interest in the use of substituent constants for correlating structure with reactivity continues to grow rapidly, especially in the solution chemistry of organic molecules.[17] By contrast, gas-phase data correlations still remain undeveloped. Thus, we sought to study the relationships between substituent constants (Hammett-constant type) and calculated properties of a variety of compounds by MNDO.

We have chosen for our investigations two different systems which have been studied extensively in solution. They are aromatic electrophilic substitution (bromination and protonation) of arenes and solvolysis (dissociation) of benzyl halides and related derivatives. We then compare our MNDO results with those obtained in earlier experimental studies. Our choice is justified by the fact that both systems are of considerable interest in the examination of the intrinsic substituent effects on the stabilities of carbocations and on the basicity of arenes.

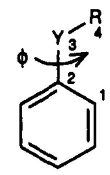
Methods

The MNDO calculations for toluene, diphenylmethane (DPMH), and benzene systems were conducted using the standard MNDO method,[12] as implemented in the MOPAC 5.0 semiempirical molecular orbital package[18] running on a CRAY X-MP/28 at the Ohio Supercomputer Center. The MNDO calculations for xanthene (XAN), 9*H*,10*H*-acridine (ACR), and 9*H*-10-*N*-methylacridine (*N*-MACR) systems were carried out on a DEC VAX 6420 computer using the AMPAC package[19] with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimization procedure.[20]

The starting geometries were created by the PCMODEL program.[21] The energies for substituted tolyl radical cations were calculated by both the restricted and unrestricted Hartree–Fock methods (RHF and UHF, respectively).[12] All other calculations were performed with closed-shell structures using the restricted Hartree–Fock (RHF) method with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles) without imposition of symmetry restrictions. Since an optimized geometry may turn out to be a local minimum, the global minima of monosubstituted benzenes were verified by using the "reaction coordinate" method.[22]

Results and Discussion

General Considerations. Because the energy of an organic molecule is strongly dependent on its conformation, we were concerned with the identification of the most stable conformation of each of the monosubstituted derivatives studied here. This was accomplished by rotation of the substituent about the bond leading to the phenyl ring (i.e., variation of the dihedral angle ϕ defined by atoms 1–4) and calculation of the attendant conformational energies. The relative energies of selected important conformations for some mono-substituted benzenes along with the associated barriers to rotation are given in Table I. Also included in this table are the energies for these rotamers derived from earlier work by others using the ab initio method with the STO-3G basis set and from experimental studies.



In the MNDO calculations for the *m*-OH derivatives of toluene, benzyl chloride, benzyl cation, diphenylmethane, benzhydryl chloride, and the diphenylmethyl cation, two types of conformations in particular were considered: the one where the hydroxy proton is coplanar to the phenyl ring and syn to the substituent and the other where it is coplanar to the phenyl ring and anti to the substituent. In the cases of the para derivatives, the starting geometries were begun where the hydroxy proton is coplanar to the phenyl ring. In all the cases, it was found that the conformation with a planar hydroxy group is the more stable one.

In the calculations of meta and para aminoarenes, two particular types of conformations were examined: one where the amine moiety is pyramidal and the other where it is planar. In all cases, it was found that the global minimum conformation is with a pyramidal amino group.

---

(16) There are few cases in the literature describing the treatment of Hammett constants with calculated heats of formation by semiempirical methods. For examples, see the use of the correlation analyses to protonic acidity of substituted benzoic acids: Gilliom, R. D.; Beck, J. P., Purcell, W. P. *J. Comput. Chem.* **1985**, *6*, 437. Sotomatsu, T.; Murata, Y.; Fujita, T. *J. Comput. Chem.* **1989**, *10*, 94.

(17) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247.

(18) Stewart, J. J. P. QCPE 455.

(19) Dewar, M. J. S. QCPE 506.

(20) Cioslowski, J.; Kertesz, M. *QCPE Bull.* **1987**, *7*, 159.

(21) The PCMODEL program was obtained from Serena Software, Box 3076, Bloomington, IN 47402.

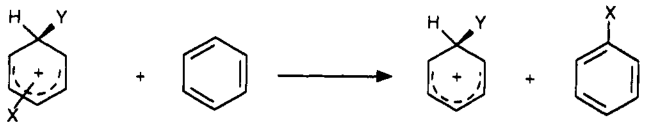
(22) Goldblum, A.; Loew, G. H. *J. Am. Chem. Soc.* **1985**, *107*, 4265. Müller, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1. Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1971**, *93*, 4290.

Table II. MNDO-Calculated Energies (kcal/mol) for Process 1

substituent X	$\Delta H_f°(XC_6H_5)^a$	$\Delta H_f°(XC_6H_5H^+)$	$\Delta H_f°(XC_6H_5Br^+)$	$(\Delta H_r)_{1a}{}^b$	$(\Delta H_r)_{1b}{}^b$	$\Delta E_1{}^c$	$\Delta E_2{}^d$	PA[e]	σ^{+f}
p-NMe$_2$	33.8	193.5	202.5	27.5	29.3	-	-	207.4	-1.7
p-NH$_2$	22.0 (20.8)	187.2	196.6	22.0	23.4	27.2	27.7	201.9	-1.3
p-OH	-26.6 (-23)	148.6	158.8	12.0	12.7	16.0	13.4	191.8	-0.92
p-OMe	-17.6 (-17.3)	154.4	164.3	15.2	16.2	15.7	17.8	195.0	-0.778
p-Me	13.6 (12)	198.2	208.7	2.6	2.9	8.5	8.4	182.4	-0.311
p-Et	8.8 (7.2)	192.8	203.3	3.2	3.6	9.7	9.4	183.0	-0.295
p-*i*-Pr	8.2	191.7	202.2	3.7	4.1	10.8	-	183.5	-0.280
p-*t*-Bu	15.6	198.4	208.8	4.3	4.8	11.6	-	184.2	-0.256
p-F	-25.2 (-27.8)	164.6	175.4	-2.7	-2.6	3.7	1.3	177.2	-0.073
m-Me	13.6	200.1	210.9	0.6	0.7	2.0	-	180.5	-0.066
m-Et	8.8	195.0	205.7	1.0	1.1	2.4	-	180.8	-0.064
m-*i*-Pr	8.2	194.0	204.8	1.4	1.5	-	-	181.2	-0.06
m-*t*-Bu	15.6	201.0	211.8	1.7	1.8	3.8	-	181.5	-0.059
H	21.3 (19.8)	208.5	219.4	0	0	0	0	179.8	0
m-OMe	-17.6	172.0	183.1	-2.5	-2.6	-	-	177.4	0.047
m-OH	-26.6	164.9	176.0	-4.4	-4.6	-5.3	-	175.5	0.04[g]
p-Cl	13.5 (12.2)	206.1	217.0	-5.5	-5.5	-	1.1	174.4	0.114
p-Br	23.9	215.7	226.5	-4.7	-4.5	-	-	175.2	0.15
m-F	-25.2	172.1	183.4	-10.2	-10.6	-7.5	-	169.7	0.352
m-Cl	13.5	207.7	218.8	-7.0	-7.3	-	-	172.8	0.399
m-CF$_3$	-127.6	73.0	84.5	-13.4	-14.1	-	-	166.4	0.52
m-CN	52.2	248.4	259.6	-9.0	-9.3	-14.0	-	170.8	0.58
p-CN	52.2 (58.5)	249.1	260.4	-9.7	-10.1	-13.8	13.5	170.1	0.66

[a] Experimental values (in parentheses) from Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. [b] Calculated from $\Delta H_r = \Delta H_f°(R^+) - \Delta H_f°(R - H) - \Delta H_f°(X - R^+) + \Delta H_f°(X - RH)$. [c] Ab initio calculated data of process 1a from ref 24. [d] Experimental data of process 1a from ref 25. [e] Calculated from $PA = \Delta H_f°(H^+) + \Delta H_f°(R - H) - \Delta H_f°(R^+)$. $\Delta H_f°(H^+) = 367.7$ [f] Data from ref. 23. [g] Taken from Taft, R. W., Jr. *J. Phys. Chem.* **1960**, *64*, 1805.

Scheme I



Process 1a; Y = H
Process 1b; Y = Br

In the cases of meta and para methoxyarenes and their related carbocations, two types of conformations were also considered: the one where the methoxy group is coplanar to the phenyl ring and the other where it is perpendicular. In all the cases, it was found that the perpendicular conformation is about 0.4–0.6 kcal/mol more stable than the planar conformation. In the calculations of para carbomethoxyarenes and their associated carbocations the two conformations considered in particular were the one where the carbonyl group is perpendicular to the phenyl ring and the other where it is coplanar. For all the conformations considered, the one with the lowest energy was selected for the correlation analysis, except for para and meta methoxyarenes and arenes containing a carbonyl group. In these cases, the energies for the planar conformations were chosen.

Electrophilic Aromatic Substitution Processes. Table II shows the calculated properties of 23 substituted benzenes and their corresponding protonated and brominated analogs. The selection of these compounds was made on the basis of the diverse physicochemical properties of the substituent groups. The values given in Table II include the heats of formation of the benzene derivatives, $\Delta H_f°(XC_6H_5)$, protonated and brominated benzene derivatives, $\Delta H_f°(XC_6H_5H^+)$ and $\Delta H_f°(XC_6H_5Br^+)$, respectively, as well as the energies for the isodemic processes 1a, $(\Delta H_r)_{1a}$, 1b, $(\Delta H_r)_{1b}$ (Scheme I), and the proton affinity, PA of the substituted benzenes.

Table III. Correlation of Reaction Constants Calculated from the Equation

$$\Delta H_r = \rho_{calc}\sigma^+ + C$$

process	ρ_{calc}	C^a	n^b	r^c
1a	-17.2 ± 0.7	-1.3 ± 2.0	23	0.981
1b	-18.2 ± 0.8	-1.3 ± 2.1	23	0.982
2a	-14.1 ± 0.8	-2.4 ± 2.2	16	0.977
2b	-14.1 ± 1.0	-3.3 ± 2.8	16	0.964
3a	-7.9 ± 0.5	-1.5 ± 1.2	15	0.978
3b	-7.7 ± 0.5	-0.9 ± 1.4	15	0.970
4a	-6.6 ± 0.6	-2.1 ± 1.4	10	0.968
4b	-6.5 ± 0.6	-2.7 ± 1.4	10	0.961
4c	-5.3 ± 0.8	-2.8 ± 1.9	10	0.920

[a] Value of intercept. [b] Number of substituents correlated. [c] Value of correlation coefficient.

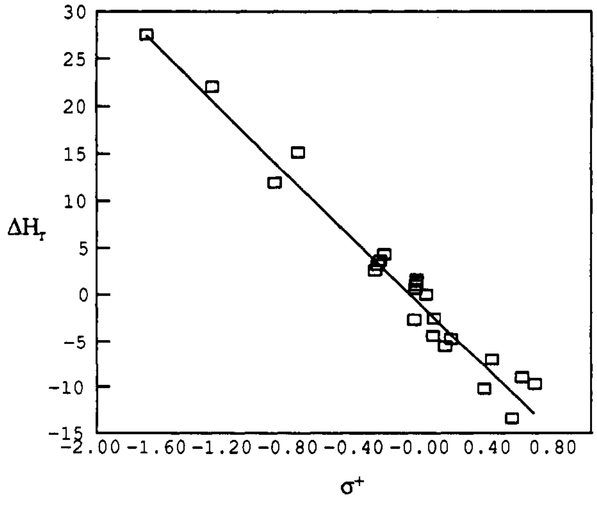


Figure 1. Calculated ΔH_r values (kcal/mol) vs σ^+ for the isodesmic process 1a.

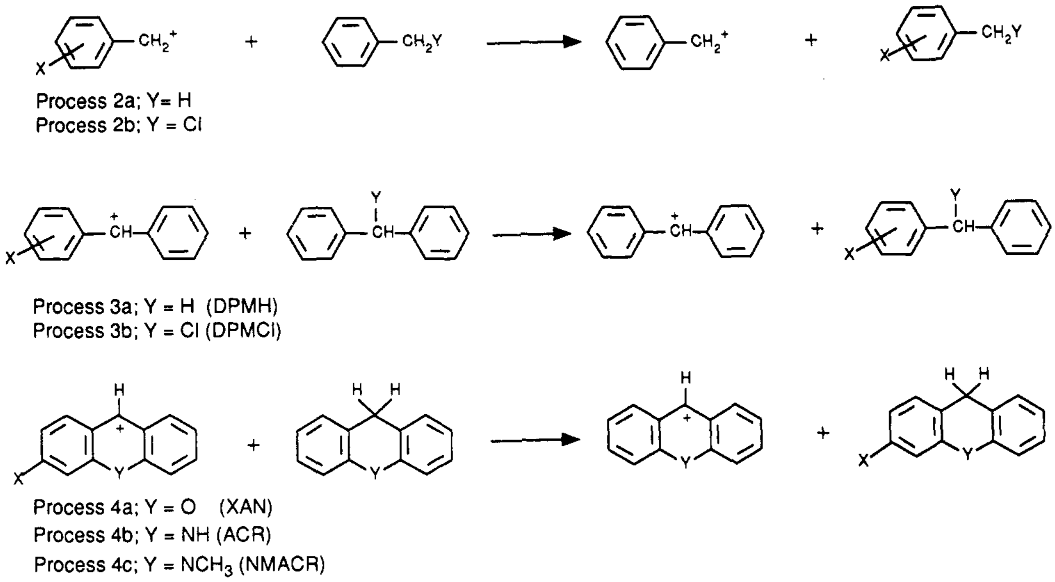
The data summarized in Table II were examined for linear relationships with both σ and σ^+ values.[23] They were found to follow reasonably well the simple expression shown in eq 1, where C is a constant (intercept) and ρ_{calc} is the slope.

$$\Delta H_r = \rho_{calc}\sigma^+ + C \quad (1)$$

---

(23) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

Scheme II



Process 2a; Y = H
Process 2b; Y = Cl

Process 3a; Y = H (DPMH)
Process 3b; Y = Cl (DPMCl)

Process 4a; Y = O (XAN)
Process 4b; Y = NH (ACR)
Process 4c; Y = NCH$_3$ (NMACR)

The results for the isodesmic processes 1a and 1b are shown in the first two entries of Table III. The correlation for process 1a is shown graphically in Figure 1. Not unexpectedly, correlations using standard Hammett σ substituents were found to be less satisfactory than those obtained using Brown σ^+ constants (e.g., correlation coefficients of 0.951 vs 0.981, respectively, for process 1a) for these processes. As would be expected, those substituents that act as strong π-electron-donating groups such as p-N(CH$_3$)$_2$, p-NH$_2$, and p-OCH$_3$ (whose σ^+ and σ constants differ greatly) showed the greatest deviation from a linear relationship when σ values were used in the attempted correlation. This reinforces *kinetic* arguments made on experimental grounds that there are important π-electron resonance interactions between the strongly π-electron-donating groups and the incipient carbocation centers in activated complexes at the transition states of species undergoing electrophilic aromatic substitution reactions.[23] Although these results are unremarkable, it is reassuring that the MNDO method provides such intuitively satisfying predictions when applied to this task.

Examination of Table II indicates a good correlation between the calculated MNDO energy differences and the experimentally derived σ^+ values. The few systematic deviations become pronounced, and their significance may be understood. For example, the ordering of alkyl substituent effects shows that the smaller alkyl groups are not as capable of stabilizing positive charge as is the bulky *tert*-butyl group. These results are in agreement with the conclusion that the Baker–Nathan ordering of alkyl substituent effects in solution is caused by the solvent.[24-27] The most interesting feature is the distinction between p-OH and p-OCH$_3$ groups in their abilities to stabilize positive charge. Whereas a linear correlation between σ^+ and the calculated perturbational effect of the methoxy group is reasonable, the hydroxyl group seems not to be as effective in stabilizing positive charge as its σ^+ value would seem to indicate. This discrepancy may be attributed to the tendency of the hydroxyl group to engage in hydrogen bonding in condensed media. As pointed out by others, such an interaction might result in an exaggeration of the hydroxyl group's intrinsic electron-donating capability.[24] Also of considerable interest is the observation that the energies of para groups (F, OH, OCH$_3$) compared to those of the corresponding meta groups reflect well the relative electron-donating and -attracting effects of each of the groups.

Comparison between the correlation analyses for processes 1a and 1b (Scheme I) indicates that the intrinsic substituent effect in process 1b ($\rho_{\text{calc}} = -18.2$) is slightly stronger than that in process 1a ($\rho_{\text{calc}} = -17.2$). This may be attributed to the likelihood that positive charges on brominated benzenonium ions are slightly less stabilized than in the cases of protonated benzenonium ions due to the electron-withdrawing inductive effect of bromine compared to hydrogen. There will thus be more demand for stabilization through release of electron density by the substituents and the ρ value will be more negative for the brominated benzenonium ions than for the protonated benzenonium ions. However, the close similarity between the ρ values for both processes suggests that a model using the protonation of benzene rings represents a suitable archetype for electrophilic attack on arene rings.

In order to establish further credence to the reliability of this computational approach, the calculated differential energies for process 1a were compared with gas-phase experimental values[25] and ab initio STO-3G based calculated values[24] determined previously. These results show a good agreement among the three different methods (eq 2).[28]

$$(\Delta H_r)_{1a} = (1.20 \pm 0.10)\Delta E_1 + (2.14 \pm 3.51) \qquad (2)$$

The values of ΔE_1 are the energy differences calculated by the ab initio method using the STO-3G basis set.[24] The number of substituents examined was 16 and the correlation coefficient was 0.952. As ΔE_1 was earlier shown to correlate directly with gas-phase experimental values,[28] the correlation in eq 2 serves to establish the relationship of all three data sets. It is worth pointing out that the differences between the calculated ρ values for *thermodynamic* processes 1a and 1b (−17.2 and −18.2, respectively)

---

[24] McKelvey, J. M.; Alexandratos, S.; Streitwieser, A., Jr.; Abboud, J.-L. M.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 244.

[25] Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452.

[26] Hehre, W. J.; McIver, R. T., Jr.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7162.

[27] Arnett, E. M.; Abboud, J.-L. M. *J. Am. Chem. Soc.* **1975**, *97*, 3865.

[28] A straight line with a slope of unity was obtained from the correlation of the experimental ΔE_2 and STO-3G ΔE_1 values. See ref 25.

Table IV. MNDO-Calculated Energies (kcal/mol) for Process 2

substituent X	$\Delta H_f°(XC_6H_4CH_3)$	$\Delta H_f°(XC_6H_4CH_2^+)$[a]	$\Delta H_f°(XC_6H_4CH_2Cl)$	$(\Delta H_r)_{2a}$[b]	$(\Delta H_r)_{2b}$[b]	$HIA(XC_6H_4CH_2^+)$[c]
p-N(Me)$_2$	25.8	209.3	18.5	21.0	20.4	216.7
p-NH$_2$	14.1	202.5	7.2	16.1	16.0	221.6
p-OH	−34.5	161.6	−44.0	8.4	5.6	229.3
p-OMe	−25.2	168.1 (160)	−35.0	11.1	10.1	226.6
p-Me	5.8	208.6 (202)	−1.0	1.7	1.7	236.0
m-NH$_2$	14.5	219.3	7.6	−0.3	−0.5	238.0
H	13.6	218.0 (216)	6.9	0	0	237.7
m-Me	5.9	209.9	−0.7	0.5	0.6	237.2
p-F	−33.0	174.7	−41.9	−3.2	−5.3	240.9
m-OH	−34.2	173.0	−43.1	−2.6	−4.8	240.3
p-Cl	5.8	215.5 (213)	−0.5	−5.3	−4.8	243.0
m-Cl	5.8	216.4	−2.8	−6.1	−8.0	243.8
p-COOMe	−65.6	146.4	−74.2	−7.6	−9.5	245.2
m-CF$_3$	−135.2	81.0	−143.4	−11.8	−13.3	249.5
p-CF$_3$	−135.4	84.9	−143.3	−15.8	−17.1	253.5
p-CN	44.3	257.7 (262)	38.4	−8.9	−8.2	246.6

[a] Experimental values (in parentheses) from Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 7439 and references cited therein. [b] See Table II, note *b*. [c] Calculated from $HIA(R^+) = \Delta H_f°(R^+) + \Delta H_f°(H^-) - \Delta H_f°(R - H)$, $\Delta H_f°(H^-) = 33.2$.[7]

Table V. MNDO-Calculated Energies (kcal/mol) for Process 3

substituent X	$\Delta H_f°(DPMH)$	$\Delta H_f°(DPM^+)$	$\Delta H_f°(DPMCl)$	$(\Delta H_r)_{3a}$[a]	$(\Delta H_r)_{3b}$[a]	$HIA(DPM^+)$[b]
p-NMe$_2$	51.0	229.3	47.7	10.7	12.1	211.5
p-NH$_2$	43.3	222.1	39.0	9.7	10.5	212.6
p-OH	−5.1	179.3	−10.0	4.7	4.4	217.6
p-OMe	4.0	186.7	−0.9	6.3	6.1	216.0
p-Me	35.2	223.5	30.7	0.8	1.0	221.5
m-NH$_2$	44.7	233.3	40.8	0.5	1.2	221.8
m-Me	35.6	224.4	30.8	0.2	0.1	222.0
p-F	−2.7	188.7	−7.2	−2.4	−2.3	224.6
H	43.1	232.1	38.4	0	0	222.3
m-OH	−4.6	185.6	−8.3	−1.1	−0.2	223.4
p-Cl	35.4	228.6	31.3	−4.2	−3.7	226.4
m-Cl	35.4	228.7	32.5	−4.3	−2.5	226.6
p-COOMe	−35.4	158.3	−38.9	−4.7	−3.5	226.9
m-CF$_3$	−104.7	91.4	−109.2	−7.0	−7.0	229.3
p-CN	73.8	269.5	70.6	−6.7	−5.3	228.9

[a] See Table II, note *b*. [b] See Table IV, note *c*.

Table VI. MNDO-Calculated Energies (kcal/mol) for Process 4

substituent X	$\Delta H_f°(XAN)$	$\Delta H_f°(XAN^+)$	$\Delta H_f°(ACR)$	$\Delta H_f°(ACR^+)$	$\Delta H_f°(N\text{-}MACR)$	$\Delta H_f°(N\text{-}MACR^+)$	$(\Delta H_r)_{4a}$[a]	$(\Delta H_r)_{4b}$[a]	$(\Delta H_r)_{4c}$[a]
NMe$_2$	13.9	182.6	57.8	215.1	62.0	226.8	−8.3	−8.7	−3.8
NH$_2$	5.1	174.9	46.0	207.2	54.5	218.3	−7.2	−5.0	−4.8
OH	43.6	130.3	−2.5	161.3	5.9	172.1	−3.1	−2.3	−2.3
OMe	−34.4	138.3	6.2	169.3	14.9	180.2	−4.3	−3.0	−3.3
Me	−3.1	173.1	37.6	203.4	46.0	214.5	−0.8	−0.2	−0.1
H	4.5	181.5	45.8	211.9	54.1	222.6	0	0	0
F	−41.7	139.0	−1.4	168.9	7.3	179.7	3.8	4.2	3.9
Cl	−2.8	178.6	38.1	208.7	46.3	219.3	4.3	4.5	4.6
COOMe	−73.8	108.3	−33.4	138.8	−24.7	151.2	5.1	6.1	7.5
CF$_3$	143.3	44.4	102.9	73.9	−93.9	84.5	10.7	10.7	9.8
CN	36.5	220.0	76.8	250.0	85.7	260.6	6.5	7.1	6.3

[a] See Table II, note *b*.

and the experimental solution *kinetic* values for electrophilic aromatic substitution ($\rho = -4.4$ to -12.2)[23] are likely the result of both solvent participation and the only partial development of the substituent effects in activated complexes at the rate-determining transition states of arenes undergoing electrophilic substitutions.[24]

Solvolysis (Dissociation) Reactions and Hydride Affinities of Benzyl, Benzhydryl, and Aromatic Fused Three-Ring Systems. Tables IV–VI list the properties calculated for the isodesmic processes 2, 3, and 4, respectively (Scheme II). The value of ΔH_r for each isodesmic process was calculated from the heat of formation ($\Delta H_r°$) of substituted and unsubstituted hydrocarbons or benzyl-like halides and their carbocations. It corresponds to the enthalpy change for each process.

The values of ΔH_r for each process were examined for linear relationships with σ^+. The results which were obtained are shown as entries 3–9 in Table III. Examination of these results again indicates reasonably good correlations between σ^+ values and the energy differences ΔH_r, except for process 4c which shows a relatively poor correlation.

In processes 4a–c the CF$_3$ derivatives were excluded from the analysis because of the poorly predicted values of their energies. However, the overall correlation results are satisfactory. The extent of the systematic deviations in the behavior of the substrates with substituents in the para and the corresponding meta positions (see Tables IV and V) is again pronounced, similar to the behavior observed for the electrophilic aromatic substitutions.

Examination of Table III indicates that the ρ values calculated for the hydride affinity processes 2a and 3a and those of the solvolysis processes 2b and 3b are almost identical. This is not surprising as it simply indicates that there is little differential substituent perturbation on the

Table VII. MNDO-Calculated Ionization Potentials (eV) for Substituted Benzenes, Toluenes, Diphenylmethanes, Tolyl Chlorides, and Benzhydryl Chlorides and the Energies (kcal/mol) for Process 5

substituent X	IP (XC_6H_5)[a]	IP ($XC_6H_4CH_3$)	IP ($XC_6H_4CH_2Cl$)	IP (DPMH)	IP (DPMCl)	$\Delta H_f°$ ($XC_6H_4CH_3^{\cdot +}$)	($\Delta H_f°$) ($XC_6H_4CH_3^{\cdot +}$)	$(\Delta H_r)_5$[b]	$\Delta H_r)_5$[b,c]
p-N(Me)$_2$	8.27	8.22	8.48	9.18	9.43	202.2	193.4	27.1	31.9
p-NH$_2$	8.75 (7.70)	8.69	8.97	8.69	8.92	196.5	188.7	21.2	24.9
p-OH	8.88	8.82	9.15	8.82	9.07	157.4	152.2	11.7	12.7
p-OMe	8.84 (8.40)	8.77	9.10	8.78	9.01	163.3	157.6	15.0	16.6
p-Me	9.28 (8.82)	9.18	9.50	9.10	9.42	206.3	202.2	3.1	3.1
p-Et	9.27 (8.80)	–	–	–	–	–	–	–	–
p-*t*-Bu	9.28 (9.25)	–	–	–	–	–	–	–	–
p-*i*-Pr	9.29	–	–	–	–	–	–	–	–
m-NH$_2$	–	8.75	8.99	8.74	8.92	197.7	189.6	20.4	24.4
p-F	9.47 (9.19)	9.37	9.71	9.34	9.61	172.6	168.6	−2.0	−2.2
m-CH$_3$	–	9.24	9.52	9.21	9.52	208.2	203.2	1.3	−2.1
H	9.40 (9.25)	9.28 (8.82)	9.62	9.23	9.49	217.2	213.1	0	0
m-OH	–	8.88	9.14	8.88	9.06	159.1	153.4	9.1	11.9
p-Cl	9.62	9.51	9.82	9.38	9.64	213.7	209.7	−4.4	−4.4
p-Br	9.55	–	–	–	–	–	–	–	–
m-Cl	–	9.58	9.85	9.38	9.65	215.8	210.8	−6.4	−5.6
p-COOMe	–	9.88	10.15	9.54	9.77	150.9	146.1	−11.3	−12.3
m-CF$_3$	–	9.94	10.28	9.49	9.75	82.4	77.8	−14.0	−13.6
p-CF$_3$	10.07 (9.68)	10.06	10.29	9.56	9.80	84.7	80.6	−16.5	−16.6
p-CN	9.82 (9.70)	9.69	10.00	9.47	9.71	256.8	252.0	−8.9	−8.3

[a] Experimental data (in parentheses) from ref 36. [b] See Table II, note *b*. [c] Calculated by UHF method.

species caused by replacement of a hydrogen by a chlorine atom in the uncharged species. This observation indicates that the use of the simple hydride affinity process is a good model with which to study Hammett-type linear-free-energy relationships for solvolysis reactions.

It is known that in solution the Hammett free-energy relationship can be useful in obtaining information about the position of the activated complex at the transition state when the substituent effect is transmitted by resonance in π-systems. It is also true in kinetic phenomena one expects that the less stabilized the incipient ion the later the transition state will occur along the reaction coordinate. The carbocationic transition-state position in the solvolysis reaction of an alkyl halide frequently depends on the importance of ion pairs in the reaction. When a carbocationic activated complex at the transition state develops in a way that resembles contact ion pairs, it will have less charge separation than if developed in the way of solvent-separated ion pairs. That produces a relatively lower ρ value. Similarly, solvolysis reactions of two different alkyl halides could lead to different carbocationic transition states with different charge separation and different ρ values in a way that reflects both the relative intrinsic internal abilities of the two systems to bear positive charges and to external effects caused by varying degrees of solvent particiption.

In the gas phase the comparison between contact ion pair and solvent-separated ion pair is not germane, whereas the comparison between reactions of different substrates is of considerable interest since it reflects the charge separation, the internal electron demands of the system without the interference of solvent, and, in the case of kinetic studies, the relative positions of the carbocationic transition states along a reaction coordinate.

The ρ_{calc} values of processes 2, 3, and 4 follow the sequence 4 > 3 > 2 (Table III). These results can be understood by consideration of the relative natures of the carbocationic species. In process 2 the benzyl carbocation is less stabilized than that of the benzhydryl (process 3), and the latter is even less than that of the fused three-ring system (process 4) because of the ability of the additional rings and heteroatom ring substituents to stabilize the carbocations by charge disposal. One way of regarding this is to consider that a more concentrated positive charge at the substitution center causes larger demand for electron density from the substituents. This is manifested by the production of a more negative ρ_{calc} value.[29] The reverse effect, namely a smaller response to perturbations caused by substituents, is expected in systems supporting generally more delocalized positive charges. A similar attenuation or "leveling" of substituent effects would be expected from external perturbations which lead to charge dispersal such as favorable solvent interactions. All such effects should lead to diminution of the substituent effects estimated from the MNDO calculations presented here which represent theoretical gas phase phenomena.

Similarly, the *N*-methyldihydroacridine ion (process 4c) is more stabilized than that of the dihydroacridine (process 4b) because of the electron-donating effect of the methyl group. Hence, the ρ_{calc} value is less negative. Not surprisingly, the resemblance between the ρ_{calc} values of processes 4a and 4b indicates that nitrogen and oxygen ring atoms have similar abilities to stabilize the ions.

It should be added that the experimental ρ values obtained from studies of kinetics for solvolysis reactions range from −1.3 to −5.64.[23,30] The differences between these experimental kinetic values and the (thermodynamic) ρ_{calc} values found here (−5.3 to −18.2) no doubt stem from the role played by solvent and the only inchoate development of the substituent effects in the activated complexes at the rate-determining transition states of the solvolysis reactions.[24]

Correlation Analysis of σ^+ with the Ionization Potentials of Substituted Benzenes and Toluenes and Their Applicability to Understanding the Stability of the Derived Radical Cation Species. Radical cations have come under intense study due to a growing realization that they are intermediates in a wide variety of organic reactions,[31] especially in the oxidations of aromatic substrates by peroxy disulfate.[32-34] Although general struc-

---

(29) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987.

(30) Okamoto, Y.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 485. Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Rao, C. G.; Rho, M. M. *J. Am. Chem. Soc.* **1977**, *99*, 5373. Tanida, H.; Tsushima, T. *J. Am. Chem. Soc.* **1970**, *92*, 3397. Tanida, H.; Matsumura, H. *J. Am. Chem. Soc.* **1973**, *95*, 1586.

(31) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–189.

(32) Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860.

(33) Walling, C.; Camaioni, D. M.; Kim, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 4814. Walling, C.; Camaioni, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1603.

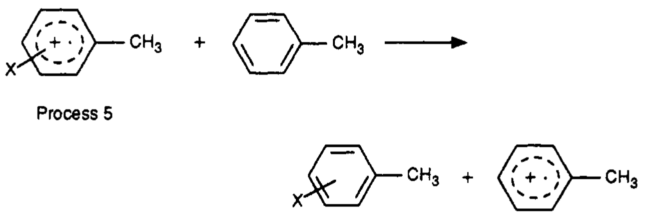
Table VIII. Correlation of MNDO-Calculated Ionization Potentials (eV) with σ^+ Constants from the Equation

$$\mathrm{IP} = B\sigma^+ + C$$

substrate	B^a	C^b	n^c	r^d	$\rho_{\mathrm{calc}}{}^e$
$XC_6H_4CH_3$	0.69 ± 0.05	9.42 ± 0.14	14	0.970	−15.92
$XC_6H_4CH_2Cl$	0.69 ± 0.05	9.72 ± 0.13	14	0.973	−15.95
XDPMH	0.46 ± 0.03	9.25 ± 0.07	13	0.976	−10.66
XDPMCl	0.47 ± 0.03	9.51 ± 0.08	13	0.971	−10.77
XC_6H_5	0.69 ± 0.04	9.49 ± 0.09	14	0.983	−15.93

[a] Value of slope. [b] Value of intercept. [c] Number of substituents correlated. [d] Value of correlation coefficient. [e] Calculated from slope following conversion to units of kilocalories/mole.

Scheme III



ture–reactivity relationships and complex solvent dependencies are emerging from these studies,[35] quantitative structure–reactivity relationships are still undeveloped.

The gas-phase ionization potentials of many organic species and the energies and the relative stabilities of a variety of radical cation species are well documented.[7,36] However, to our knowledge, there has been no systematic work on the quantitative structure–reactivity relationships of these measured parameters with Hammett-type constants.

Table VII shows the calculated ionization potentials, IP in eV, for substituted toluenes, benzyl chlorides, diphenylmethanes, benzhydryl chlorides, and benzenes along with the energy differences $(\Delta H_r)_5$ for the isodesmic process 5 (Scheme III). The correlation analyses of these results with σ^+ are shown in Table VIII. The ρ values were calculated for the isodesmic process and the ionizations by converting the IP values to kcal units.[37] For all entries except the last, the IP and ΔH_r values of the substituted m-NH_2 and m-OH derivatives were excluded from the correlation analysis because of their poorly predicted values.[38] The $N(CH_3)_2$-substituted derivatives gave poorly predicted IP values for the ionizations of the diphenylmethane and benzhydryl chloride systems. These IP values were also excluded from the correlation analysis.

Isodesmic process 5, involving substituted toluenes (Scheme III), was found to follow the linear correlations shown in eq 3 (RHF method) and eq 4 (UHF method), with 14 substituents included and correlation coefficients of 0.982 (RHF) and 0.981 (UHF). As mentioned above,

$$\Delta H_r = (-17.44 \pm 0.96)\sigma^+ - (1.80 \pm 2.57) \quad (3)$$

$$\Delta H_r = (-19.16 \pm 1.08)\sigma^+ - (1.18 \pm 2.97) \quad (4)$$

the m-NH_2 and m-OH substituted derivatives were excluded in the correlation analysis of process 5 due to poorly predicted values, similar to what was observed with the IP values of the corresponding neutral molecules.[38] Energy calculations obtained with careful driving of the dihedral angle ϕ and appropriate optimization provided assurance that the energy minima reported were of global and not local nature. Removal of the values of these two substituents from the correlation analyses for the other processes produced no change in the correlation coefficients. The basis for the anomalous behavior for the substituted m-NH_2 and m-OH toluene derivatives in process 5 appears to be a failure of the semiempirical method to distinguish between meta and para substituents for both NH_2 and OH groups in the radical cations. The calculated atomic charges (on N or O) and the bond lengths of the heteroatom-ring carbon bonds were found to be virtually the same for each of the respective substituents in both the meta and para positions. We do not presently know the cause of this effect.

Examination of the ρ_{calc} values found for the scope of ionization potentials investigated indicates that in systems with one aromatic ring (benzene and toluene) the electronic demand on substituents is higher than in those with two aromatic rings ($\rho \sim -16$ vs -11). Again, the explanation of this difference is found in the reduced stabilization of the ion in benzene or toluene systems relative to that of the diphenylmethane system, in analogy to that observed from kinetic studies of incipient cations in solvolysis reactions. The resemblance between the σ_{calc} values of the hydrocarbon systems (toluene and DPMH) and their corresponding chloride indicates the minor effect of the presence of chlorine in place of hydrogen in the stabilization of radical cation species.

Isodesmic process 5 is a thermodynamic one, whereas the MNDO-calculated ionization potential conceptually involves a Franck–Condon vertical transition that likely leads to radical cation products of different geometry than those in process 5. It is probable that part of the difference between the ρ_{calc} values determined for process 5 (−17.4 or −19.2) and that for the ionization potentials of substituted toluenes (−15.9) stems both from underestimation of the calculated heats of formation for radical cation species[13] and overestimation of the calculated ionization potentials for neutral compounds.[12] The magnitudes of the deviations may not be the same in both cases.

The overall results indicate that the use of ionization potentials of neutral species is a good model to estimate heats of formation of the corresponding radical cation species and, in particular, to compare the intrinsic substituent effects in two different processes that involve radical cation species as intermediates, such as oxidation of aromatic systems (toluene etc.)

Conclusions

The results presented in this study show that, on balance, the semiempirical MNDO method compares favorably with the ab initio method (at the STO-3G level) for accomodating quantitatively the substituent effects in a

---

(34) Eberhardt, M. *J. Org. Chem.* **1977**, *42*, 832.

(35) Walling, C.; El-Taliawi, G. M.; Amaranth, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 7573 and references cited therein.

(36) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, B. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser.*; Natl. Bur. Stand., No. 26, 1969. Levin, R. G.; Lias, S. G. *Natl. Stand. Ref. Data Ser.*; Natl. Bur. Stand., No. 71, 1982.

(37) For example, the ρ value for the isodesmic process of substituted toluenes was calculated from the correlation analysis of $-\Delta$IP in kilocalories with σ^+ where $\Delta\mathrm{IP} = \mathrm{IP}_{C_6H_5CH_3\cdot+} - \mathrm{IP}_{XC_6H_5CH_3\cdot}$. The factor used for the conversion of eV units to kcal units is 1 eV = 23.0609 kcal/mol.

(38) Essentially the same results were also obtained using the AM1 or PM3 semiempirical molecular orbital methods.

J. Org. Chem. 1991, 56, 195–203

variety of reactions that involve carbocations and radical cations as intermediates. Comparisons can be made with condensed phase and kinetic experiments for distinguishing such phenomena as solvation effects from internal electronic effects and the degree of structural development of activated complexes at the transition state in reactions in which charge is developed. We conclude that the MNDO method can be used to estimate the electronic effects of a wide variety of aromatic systems that are more expensive to deal with by the ab initio model. The MNDO method should be useful in making predictions and quantitative analysis of chemical phenomena as well as of biological processes.

Acknowledgment. We thank the Ohio Supercomputer Center for a grant of time on the CRAY X-MP/28 computer.

Registry No. H, 12408-02-5.

Supplementary Material Available: AMPAC/MOPAC output files for each of the energy-minimized structures (246 pages). Ordering information is given on any current masthead page.

Generation and Oligomerization of Bicyclo[2.2.2]octyne and Properties of Tris(bicyclo[2.2.2]octeno)benzene Obtained from the Linear Trimer

Koichi Komatsu,* Shuji Aonuma, Yasuhisa Jinbu, Ryotaro Tsuji, Chitaru Hirosawa, and Ken'ichi Takeuchi

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received July 3, 1990

Reaction of 2,3-dibromobicyclo[2.2.2]oct-2-ene (**10**) with *n*-butyllithium in THF at −78 °C affords a series of oligomeric dibromides **11** (n = 2–5), which are composed of linearly bonded bicyclo[2.2.2]oct-2-ene units. A trapping experiment indicated that the reaction proceeds via formation of a highly strained acetylene, bicyclo[2.2.2]octyne (**18**), as a reactive intermediate. Upon treatment with sodium naphthalenide, the trimer **11** (n = 3) reductively cyclizes to tris(bicyclo[2.2.2]octeno)benzene (**12**) in high yield. The benzene **12** exhibits a reversible oxidation wave at +1.25 V vs $Ag/AgNO_3$ on cyclic voltammetry and gives a stable cation radical $\mathbf{12}^{\bullet+}$ electrolytically or by oxidation with H_2SO_4 in air. In FSO_3H, **12** is 100% protonated to give the arenium ion **22**. The results of variable-temperature ^{13}C NMR study indicate that the activation energy for the intermolecular proton transfer of **22** is lower than that for the hexamethylbenzenium ion (**23**). The rate of intramolecular hydrogen migration is also much faster in **22**. These results are in agreement with the relative instability of **22** (pK_{AH^+} −10.2) as compared with **23** (pK_{AH^+} −9.01).

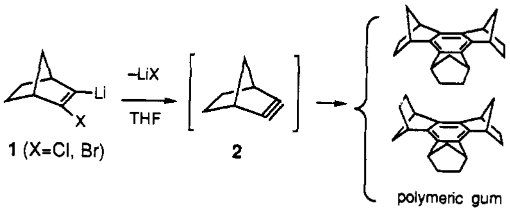
The cyclotrimerization of alkyne is one of the most simple and practical means for the synthesis of benzene derivatives,[1] and a variety of transition-metal catalysts have successfully been employed in this process.[2] Conversely, the formation of benzene derivatives has been taken as evidence for generation of alkynes, especially when the alkyne is structurally too unstable to be isolated;[3] however, the mechanism for such cyclotrimerization has rarely been discussed in detail.

For example, Gassman and Gennick reported generation of bicyclo[2.2.1]heptyne (norbornyne, **2**) and its conversion to the corresponding benzene derivatives **3** and **4** (Scheme I).[4] Although trapping of the alkyne **2** with dienes was not successful,[5] the notable effectiveness of transition-metal catalysts for cyclotrimerization supports the intermediate formation of this most strained bicyclic acetylene.

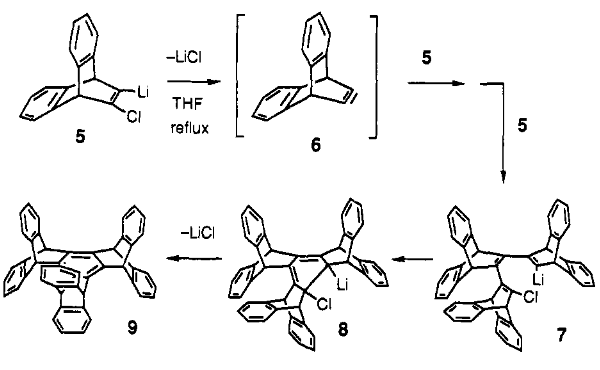
Quite recently, Shahlai and Hart elegantly demonstrated that the bicyclo[2.2.2]octyne derivative **6** generated from the 2-chloro-3-lithiobicycloalkene **5** undergoes stepwise reaction with **5**, which is terminated by electrocyclization followed by LiCl elimination to give the benzene derivative **9** (Scheme II).[6]

In an independent study, we found that lithiation of 2,3-dibromobicyclo[2.2.2]oct-2-ene (**10**) with *n*-BuLi gave both the trimeric dibromide **11** (n = 3) and the benzene derivative **12** in moderate yields (Scheme III).[7] The

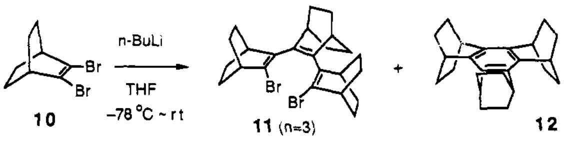
Scheme I



Scheme II



Scheme III



---

(1) Heaney, H. In *Comprehensive Organic Chemistry*; Stoddart, J. F., Ed.; Pergamon; Oxford, 1979; Vol. I, p 250.

(2) For example, see: Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

(3) Pericàs, M. A.; Riera, A.; Rossell, O.; Serratosa, F.; Seco, M. *J. Chem. Soc., Chem. Commun.* **1988**, 942 and references cited therein.

(4) Gassman, P. G.; Gennick, I. *J. Am. Chem. Soc.* **1980**, *102*, 6864.

(5) See: Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427, footnote 27.

(6) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 7136.

0022-3263/91/1956-0195$02.50/0 © 1991 American Chemical Society