Acetolysis Reactivities of Substituted Benzyl and Polycyclic Arylmethyl *p*-Toluenesulfonates. Correlations with SCF–π and CNDO MO Methods[1]

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Abstract: Acetolysis kinetics were determined for several substituted benzyl tosylates. Relative rates at 40° are *p*-CH_3, 56.3; *m*-CH_3, 2.66; *p*-F, 2.45; H, 1.00; *p*-Cl, 0.504; *m*-Cl, 0.0510; *m*-CF_3, 0.0261; *p*-CF_3, 0.0162. Comparison with Brown and Okamoto's σ^+ values gives a division into two lines, one for activating substituents giving $\rho = -5.71 \pm 0.09$, and one for deactivating substituents having $\rho = -2.33 \pm 0.04$. Similar kinetic studies are described for acetolysis of polycyclic arylmethyl tosylates. Using the $\rho\sigma^+$ correlation derived above for activating substituents the relative rates are converted to σ^+ values for comparison with other values and with MO theories. Relative rates at 40° and corresponding σ^+ values are, respectively, phenyl, 1.00, 0.00; 1-naphthyl, 94, −0.345; 2-naphthyl, 12.7, −0.193; 2-anthracyl, 167, −0.389; 2-phenanthryl, 15.0, −0.207; 3-phenanthryl, 50, −0.298; 9-phenanthryl, 107, −0.356; 2-pyrenyl, 5.3, 0.128; 4-pyrenyl, 90, −0.342; 3-fluoranthyl, 580, −0.483; 8-fluoranthyl, 400, −0.455; 2-biphenylenyl, 5.6, −0.130. These σ^+ values are compared with several MO theories. SCF–π methods give only fair correlations, but CNDO/2 gives a good correlation. The CNDO/2 method also gives a good linear correlation for the substituted benzyl cations, but the slopes are not the same. The CNDO/2 method does not scale charge delocalization on the same basis as charge–dipole interactions.

For some years we have been interested in applying various levels of molecular orbital theory to carbonium ion reactions. For this purpose, solvolysis reactions, especially of the limiting type, of polycyclic arylcarbinyl compounds are especially valuable for studying the properties of π-electron systems. The acetolyses of arylmethyl tosylates have a relatively high degree of carbonium ion character. Only the studies of Dewar and Sampson of arylmethyl chlorides in formic acid have greater carbonium ion character.[3] Our studies in this area are now substantially complete, and it is appropriate to report the results at this time. Our logical development starts with the acetolyses of substituted benzyl tosylates and the establishment of a linear $\rho\sigma^+$ correlation for activating substituents. The value of ρ thus developed is applied to the relative reactivities of polycyclic arylmethyl tosylates to derive the corresponding σ^+ values for these systems. These values are compared with other derivations from the literature and are used as experimental quantities for comparison with various molecular orbital calculations.

Preparation of Tosylates. *p*-Toluenesulfonate esters are often prepared by the Tipson[4] procedure of reaction of an alcohol with tosyl chloride in pyridine; this procedure works for the preparation of benzyl tosylate itself but only in poor yield. It and reactive benzylic tosylates undergo reaction with the tertiary amine after they are formed. Kochi and Hammond[5] prepared a variety of substituted benzyl tosylates by reaction of a suspension of sodium benzylate in ether with tosyl chloride. In our hands this method was satisfactory for a few benzyl alcohols, but for some of the other carbinols the amount of handling necessary to secure a clear solution of the tosylate in ether often led to polymerization. The use of potassium *t*-butoxide in *t*-butyl alcohol was found to give generally better results. Several of the tosylates could be prepared by a simple Schotten–Bauman procedure using aqueous sodium hydroxide in dioxane. However, the best general preparation was found to be that of Emmons and Ferris,[6] which involves the metathesis of silver *p*-toluenesulfonate with the benzyl chloride in acetonitrile. This method was especially valuable with the conductivity kinetics (*vide infra*).

Although several of the tosylates were obtained crystalline and had satisfactory analyses, the melting points are difficult to reproduce and are not a good criterion of purity. Purity was monitored instead by ir or nmr spectra and by infinity titers in the kinetics. The benzylic tosylates have a strong ir band at 9.2 μ (9.3 μ in tosyl chloride) and a benzylic hydrogen resonance in the nmr occurs at δ 5.0–5.1 ppm.

Kinetic Methods. Several kinetic procedures were explored for the acetolysis studies. The traditional sealed tube (ST) technique is entirely suitable for the less reactive systems. The titrations of the *p*-toluenesulfonic acid liberated were carried out potentiometrically. For faster compounds an intermittant titration (IT) method[7,8] was found to be convenient. In this method the reaction was carried out in a specially designed cell containing an air stirrer and two electrodes. An aliquot of sodium acetate was added, and, as solvolysis developed, the liberated *p*-toluenesulfonic acid gradually carried out its own potentiometric titration. When

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[2] (a) National Institutes of Health Predoctoral Fellow, 1964–1967. (b) National Institutes of Health Postdoctoral Fellow, 1968–1969.

[3] M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2946 (1957).

[4] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[5] J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, **75**, 3443 (1953).

[6] W. D. Emmons and A. F. Ferris, *ibid.*, **75**, 2257 (1953).

[7] P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949).

[8] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

Table I. Acetolysis Rates of Substituted Benzyl Tosylates

Substituent	Temp, °C	10^2[ROTs], mol/l.	Method[a]	10^6k, sec^{-1}
H	25.0 ± 0.05	4–9	ST	0.279 ± 0.006, 0.275[b]
	40.0 ± 0.05	4–10	ST	1.70 ± 0.01, 1.68 ± 0.03, 1.68 ± 0.01, 1.70 ± 0.04, 1.67 ± 0.04, 1.69 ± 0.03
		8	IT	1.72 ± 0.003
		3	ST	2.34[c]
		6	ST	0.160[d]
	50.0 ± 0.05	4	ST	5.28 ± 0.03
p-Me	40.0 ± 0.05	2–8	IT	85.2 ± 0.8, 93.1 ± 0.5, 98.0 ± 1.2, 95.6 ± 0.6, 97.3
		9	IT	111[e]
		7	IT	306[f]
		0.04–6	C	95.9 ± 0.7, 99 ± 1, 100 ± 0.3, 85.8 ± 1.8
	50.0 ± 0.10	6	SF	267 ± 18
		0.8	C	240 ± 3, 267 ± 3
	50.2 ± 0.10	6	SF	272 ± 11
	60.0 ± 0.20	0.04–0.8	C	700 ± 16, 709 ± 10, 712 ± 7, 731 ± 8, 740 ± 10
m-Me	40.0 ± 0.05	4–5	IT	4.58 ± 0.14, 4.50
m-Cl	25.0 ± 0.03	4	ST	0.0136 ± 0.0003
	39.9 ± 0.02	4	ST	0.088 ± 0.001
	40.0 ± 0.05	6	ST	0.085 ± 0.002
	50.1 ± 0.10	4	ST	0.272 ± 0.003
	58.8 ± 0.15	4	ST	0.726 ± 0.02, 0.668 ± 0.05
p-Cl	25.0 ± 0.05	4	ST	0.135 ± 0.003
	39.9	0.02	C	0.86 ± 0.08
	40.0 ± 0.05	2–4	ST	0.82 ± 0.03, 0.83, ± 0.02, 0.87 ± 0.01, 0.94 ± 0.05
	50.0 ± 0.08	2–4	ST	2.51 + 0.16, 2.65 ± 0.08
	60.0 ± 0.10	2	ST	7.64 ± 0.17, 7.41 ± 0.14
	60.0	0.02–0.04	C	6.41 ± 0.14, 7.55 ± 0.08, 7.67 ± 0.08
p-F	25.0 ± 0.02	3	ST	0.712 ± 0.008
	25.0	8	C	0.75 ± 0.06
	40.0 ± 0.02	3	ST	4.19 ± 0.07
	50.1 ± 0.10	0.04–5	C	12.2 ± 0.4, 12.3 ± 0.3
	59.9 ± 0.02	3	ST	36.5 ± 0.9
	60.0	0.02–20	C	41.6 ± 1.3, 44.2 ± 0.4, 37.6 ± 2.3, 34.7 ± 1.0, 43.8 ± 1.1, 36.1 ± 0.6, 42.5 ± 0.9, 36.5 ± 1.5, 32.8 ± 0.7, 36.9 ± 0.6, 42.9 ± 0.2, 37.8 ± 0.5
m-CF_3	58.8 ± 0.15	4	ST	0.371 ± 0.01, 0.352 ± 0.02
	79.9 ± 0.01	2	ST	2.91 ± 0.18
p-CF_3	58.8 ± 0.15	2	ST	0.221 ± 0.04, 0.204 ± 0.03
	79.9 ± 0.02	2	ST	1.62 ± 0.13

[a] ST = sealed tube, IT = intermittant titration, SF = stoppered flask, C = conductivity. [b] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele [*J. Amer. Chem. Soc.*, **89**, 370 (1967)] report 0.261 ± 0.003. [c] Contained 0.080 *M* NaOAc. [d] In propionic acid. [e] $LiClO_4$ present varied from 0.0091 to 0.0076 *M* from beginning to end of run. [f] $LiClO_4$ present varied from 0.077 to 0.071 *M* from beginning to end of run.

the liberated acid passed the equivalence point for the sodium acetate added, a new aliquot was added. The results were recorded continuously and the inflection points (equivalence points) were converted to rate constants in the usual way. This method could be used for half-lives of several minutes to several hours. Nevertheless, care is required to avoid systematic errors. In the IT method, a normal first-order kinetic treatment of the data for large polycyclic systems sometimes gave curves instead of straight lines. Sometimes this behavior appeared to result from a low rate of solution of material; at other times such erratic behavior resulted from poor infinity measurements. Such runs generally had to be discarded. All of the original data was examined recently with the nonlinear least squares LSKIN1 program of DeTar and DeTar.[9] Care must be used in the use of such a program, especially if the variable infinity option is used with data that do not span at least two half-lives or so of reaction. An alternative method (SF) for moderately reactive compounds utilized a single batch of kinetic solution in a flask stoppered with a serum cap. Aliquots were removed by an automatic pipet equipped with a syringe needle and drained into cold propionic acid. The solution was titrated potentiometrically in the cold.

All of these procedures required rather high concentrations (~0.05 *M*) of the benzyl tosylate. These concentrations were difficult to reach with the polycyclic compounds; hence, a study was made of conductivity techniques. Such conductivity studies in acetic acid are not straightforward. Because of the low dielectric constant of acetic acid, the conductance of solutions is sensitive to small amounts of water and it is difficult to make standard anhydrous solutions of toluenesulfonic acid which could be used to evaluate the parameters required in the Fuoss–Onsager conductance equation. However, Gramstad[10] found that a plot of

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(9) D. DeTar and C. E. DeTar, "Computer Programs for Chemistry," Vol. 1, W. A. Benjamin, Inc., New York, N. Y., 1968. We are indebted to Professor DeTar for a copy of this program before publication.

(10) T. Gramstad, *Tidsskr. Kjemi. Bergv. Met.*, **19**, 62 (1959).

Table II. Activation Parameters for the Acetolysis of Arylmethyl Tosylates

RCH_2OTs, R	ΔH^*, kcal/mol	ΔS^*, eu	10^6k, sec^{-1} [a] (40°)
p-Tolyl	20.3 ± 0.2	−7.7 ± 0.6	96.3
m-Tolyl			4.54
p-Fluorophenyl	21.55 ± 0.11	−9.8 ± 0.4	4.19
Phenyl[b,c]	22.0 ± 0.2	−10.3 ± 0.6	1.71
p-Chlorophenyl	21.7 ± 0.3	−12.4 ± 1.0	0.862
m-Chlorophenyl[d]	22.2 ± 0.3	−15.4 ± 1.1	0.0871
m-Trifluoromethylphenyl	22.4 ± 0.7	−16.3 ± 1.9	0.0446
p-Trifluoromethylphenyl	21.8 ± 0.7	−19.2 ± 2.0	0.0277
3-Phenanthryl	20.0 ± 0.8	−8.9 ± 2.5	85.5
2-Biphenylenyl	21.2 ± 0.5	−9.4 ± 1.5	9.57

[a] Calculated from the activation parameters. [b] Brown, *et al.*, report $\Delta H^* = 21.2$, $\Delta S^* = -12.7$. [c] See Table I, footnote *b*. [d] Brown, *et al.*, report $\Delta H^* = 21.5$, $\Delta S^* = -17.4$.

specific conductance *vs.* concentration was linear over wide ranges for several sulfonic acids in acetic acid. We confirmed this result for *p*-toluenesulfonic acid in acetic acid at 40° and showed that kinetic studies with several benzyl tosylates, assuming linear dependence of conductance on concentration during the course of a run, gave rates that agreed with the titrimetric studies.[11] These conductivity studies generally used tosylates prepared by the Emmons and Ferris[6] procedure (*vide supra*).

Results and Discussion

Substituted Benzyl Tosylates. In addition to benzyl tosylate itself, kinetic studies were carried out with *m*- and *p*-methyl, *m*- and *p*-chloro, *m*- and *p*-trifluoromethyl, and *p*-fluoro substituents. The results are summarized in Table I, in which the rate constants were evaluated generally by DeTar's LSKIN1 least-squares first-order kinetics computer program.[6] The errors assigned are the standard deviations.

Table I shows that the intermittant titration (IT) and sealed tube (ST) methods generally agree rather well. The conductivity studies show larger individual variations but the average of replicate runs agrees well with the titrimetric determinations.[11]

All of the titrimetric results were used with DeTar's ACTENG program[12] to calculate the activation parameters. These activation parameters are summarized in Table II.

Our acetolysis rate for benzyl tosylate at 25° agrees reasonably well with that reported by Winstein, Grunwald, and Jones.[13] Activation parameters for benzyl tosylate and *m*-chlorobenzyl tosylate have also been reported by Brown, *et al.*[14] Their values, based on fewer measurements, differ slightly but significantly from ours. For the substituents H, *m*-Me, *p*-Me, and *p*-MeO, these authors found a linear correlation with σ^+.

When all of our substituents are plotted on a σ^+ scale, we find that a single linear correlation does not obtain over the whole range (Figure 1). Such curvature was also found by Hammond, *et al.*,[15] for solvolyses of substituted benzyl tosylates in aqueous acetone. The Hammond group found that their data were best represented by a smooth curve for substituents ranging from *p*-methoxy to *p*-nitro. The data could be treated, albeit less satisfactorily, by two lines intersecting near hydrogen with slopes of $\rho = -5.6$ for activating substituents and $\rho = -1.9$ for deactivating substituents in 55.6% aqueous acetone. This solvent has greater ionizing power and greater nucleophilicity than acetic acid—in the aqueous solvent, benzyl tosylate is 39 times as reactive as in acetic acid at 25°—and Hammond, *et al.*, provide a strong case for a gradual change in solvolysis mechanism from more displacement character at the *p*-nitro end to more carbonium ion character at the *p*-methoxy end. However, the acetic acid results do not show such a smooth and gradual transition of mechanism. Instead, H, *p*-F, *m*-Me, and *p*-Me are excellently represented by one least-squares line with $\rho = -5.71 \pm 0.09$ (at 40°) and a correlation coefficient of 0.9997. For these compounds, a single mechanism with a high degree of carbonium ion character is indicated. *m*-Cl, *m*-CF_3, and *p*-CF_3 form a second line with $\rho = -2.33 \pm 0.04$ and a correlation coefficient of 0.9998. For these strongly electron-withdrawing sub-

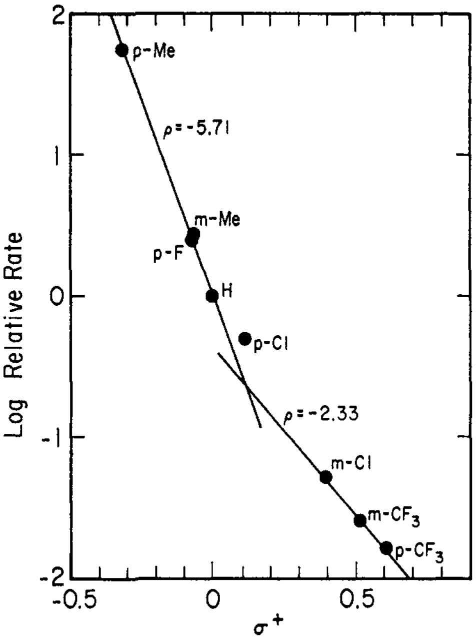

Figure 1. $\rho\sigma^+$ correlation for acetolysis of substituted benzyl tosylates at 40° showing division into two lines.

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(11) H. A. Hammond and A. Streitwieser, Jr., *Anal. Chem.*, **41**, 2032 (1969).

(12) D. F. DeTar, "Computer Programs for Chemistry," Vol. 3, W. A. Benjamin, Inc., New York, N. Y., 1969. We are indebted to Professor DeTar for a copy of his program in advance of publication.

(13) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951).

(14) See Table I, footnote *b*.

(15) G. S. Hammond, C. E. Reeder, F. T. Fang, and J. K. Kochi, *J. Amer. Chem. Soc.*, **80**, 568 (1958).

Table III. Acetolysis of Arylmethyl Tosylates at 40.0°

Ar	N($CHCl_3$)	10^5k, sec^{-1} [a]	10^5k, sec^{-1},[b] in AcOH
1-Naphthyl		158 ± 2, 153 ± 1, 173 ± 2	161
	0.041	127 ± 7, 128 ± 1, 126 ± 1, 133 ± 2	
	0.078	108 ± 1, 118 ± 0.3, 112 ± 0.7	
	0.112	91.7 ± 0.5, 91.7 ± 7	
2-Naphthyl		22 ± 1,[c] 21.1 ± 0.2, 20.3 ± 0.3, 22.0 ± 0.3, 21.3 ± 0.1, 23.3 ± 0.2	
	0.041	16.7 ± 0.1	20.4
2-Anthracyl		280 ± 16,[d] 290 ± 23[d]	
	0.112	165 ± 2	283
2-Phenanthryl		25.7 ± 0.9, 25.7 ± 0.1	
3-Phenanthryl		79.3 ± 0.6, 93.8 ± 0.8, 86 ± 5,[d,e] 650 ± 17,[d,f] 567 ± 4,[d,f] 750 ± 12,[d,f] 683 ± 17,[d,f] 617 ± 5[d,f]	
9-Phenanthryl		180 ± 2, 190 ± 1, 178 ± 2	
2-Pyrenyl		8.7 ± 0.3,[g] 10.2 ± 0.07,[g] 8.5 ± 0.08,[g] 9.0 ± 0.08[g]	
	~0.02	8.3 ± 0.8	9.1
	0.049	7.8 ± 0.3	9.9
4-Pyrenyl		123 ± 1, 153 ± 3, 153 ± 5, 132 ± 1, 200 ± 2	
	0.112	143 ± 0.3, 142 ± 0.7	245
3-Fluoranthyl	0.078	673 ± 7	982
	0.112	585 ± 5, 583 ± 5	1000
8-Fluoranthyl	0.041	567 ± 33, 583 ± 33	700
	0.078	450 ± 10	656
	0.112	400 ± 13	687
2-Biphenylenyl		9.7 ± 0.3,[d] 9.2 ± 0.1,[d] 1.72 ± 0.03,[d,h] 55 ± 1,[d,i] 80 ± 2[d,i]	

[a] Except where indicated rates were obtained by the intermittant titration method with substrate concentrations of 0.01–0.05 M. [b] Extrapolated to pure AcOH with eq 2, $a = -2.1$. [c] Titration of aliquots. [d] Conductivity method with substrate concentrations of 4×10^{-5} to 6×10^{-4} M; ref 11. [e] 39.8°. [f] 59.7°. [g] A solution of the tosylate in chloroform was added to acetic acid and part of the solution was pumped off before the intermittent titration was begun in order to remove the chloroform. Chlorine analyses of the kinetic solution showed less than 0.3 mol % $CHCl_3$ remained. [h] 25.0°. [i] 60.0°.

stituents a mechanism with greater displacement by solvent and less carbonium ion character is required. Note that *p*-chlorobenzyl tosylate, whose σ^+ value is close to the point of intersection of both lines, reacts faster than either line would predict. Presumably this compound solvolyzes in acetic acid by a combination of both mechanisms. It should be mentioned also that the acetolysis data as a whole give no correlation with Swain and Lupton's $\mathcal{F}\mathcal{R}$ treatment.[16]

It should be mentioned that the points in Figure 1 can be fitted to a single line with $\rho = -3.64$ with a superficially satisfactory correlation coefficient of 0.986; however, the deviations of the points from such a single line are clearly not random and such a treatment of the data would be most improper. Figure 1 shows that the reactants clearly fall into two distinct groups.

A difference in behavior of the two groups of reactants is also apparent in the activation parameters. The enthalpy of activation varies but little for all substituents: ΔH^* is lowest for the *p*-Me compound, 20.3 ± 0.2 kcal/mol; all of the other compounds have $\Delta H^* = 22 \pm 0.5$ kcal/mol. A monotonic decrease in ΔH^* with increasing reactivity occurs only for the "carbonium ion" group. The entropy of activation, however, changes in a monotonic fashion over the entire sequence but divides into two groups. The "carbonium ion" group has $\Delta S^* \cong -8$ to -10 eu whereas for the "displacement group," $\Delta S^* \cong -15$ to -19 eu. A more negative ΔS^* for the latter group is consistent with a greater localization of a nucleophilic solvent molecule. The *p*-Cl compound has an intermediate ΔS^* value.

Several lines of evidence indicate that the acetolysis of benzyl tosylate is about as limiting a solvolysis as is the acetolysis of secondary alkyl sulfonates. The α-deuterium isotope effect for benzyl-α-d_2 tosylate, $k_H/k_D = 1.12$ per deuterium,[17] is comparable to that for secondary alkyl sulfonates and indicates a comparable degree of freedom of the carbonium ion at the transition state.[18] From the rate of formolysis of benzyl tosylate, the apparent m(RCOOH) value is found to be 0.85, comparable to the values of 0.66–0.83 found for secondary alkyl sulfonates.[18]

Applying Fainberg and Winstein's[19] salt effect equation, eq 1, to the effect of sodium acetate on the acetolysis of benzyl tosylate we find $b = 4.8$. This

$$k = k^0(1 + b[\text{salt}]) \qquad (1)$$

may be compared to the values reported for sodium acetate with *n*-hexyl *p*-nitrobenzenesulfonate, 13.8, compared to cyclohexyl *p*-nitrobenzenesulfonate, 1.6,[20] and 1-octyl tosylate, 19, compared to 2-octyl tosylate, 2.5.[21]

Finally, it has been shown that benzyl *p*-nitrobenzenesulfonate can undergo an ion-pair reaction with lithium tosylate in acetic acid.[22] Free carbonium ions are certainly not involved in the acetolysis of benzyl

(16) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(17) K. Mislow, S. Borcic, and V. Prelog, *Helv. Chim. Acta*, **40**, 2477 (1957).

(18) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(19) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2767 (1956).

(20) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965).

(21) Calculated by G. A. Dafforn from the data of W. Pritzkow and K. H. Schoeppler, *Chem. Ber.*, **95**, 834 (1962).

(22) A. Streitwieser, Jr., and T. D. Walsh, *J. Amer. Chem. Soc.*, **87**, 3686 (1965).

tosylate since reaction involves a high degree of inversion of configuration rather than racemization,[23] but all of the evidence suggests that an electron-deficient intermediate is involved in which substantial positive charge is delocalized to the aromatic ring. This conclusion must also extend to benzyl tosylates containing activating substituents.

We conclude with a further observation concerning the rate effect of the CF_3 substituents. Sheppard has suggested[24] that some fluorine p orbitals of a *m*-CF_3 group are so located that they can overlap with the *para* position of a benzene ring and provide an electron-donating effect. The operation of such an effect to a significant extent would mean that σ^+ for a *m*-CF_3 group should be *more negative* than the normal σ. Both in the present study and in the earlier work of Brown and Okamoto,[25] σ^+ for *m*-CF_3, 0.52, is *more positive* than σ, 0.42. A more positive value is expected for the operation of an electron-withdrawing field effect on electron deficiency in the benzene ring compared to the effect on a side chain. The actual values of these various σ constants indicate that Sheppard's effect does not operate to any significant extent.

Polycyclic Arylmethyl Tosylates. Most of the results were obtained with the IT method and are summarized in Table III. In several cases it was necessary because of low rates of solution to add the substrate as a solution in an inert solvent. Chloroform was found to be suitable for this purpose. In order to extrapolate to a rate in pure acetic acid, we also studied the effect of chloroform on the rate of acetolysis of α-naphthylmethyl tosylate. Fainberg and Winstein[26] have shown that the effect of such diluants in small concentration is of the form

$$\log k/k^0 = aN \qquad (2)$$

in which N is the mole fraction of diluant. Figure 2 shows that this equation holds for α-naphthylmethyl tosylate acetolysis with $a = -2.1$ for chloroform. The data given for 8-fluoranthylmethyl tosylate in Table III show good agreement for the same slope. Accordingly, this value was used for all of the arylmethyl tosylates for which such extrapolation was necessary.

The results are averaged and given as rates relative to benzyl tosylate in Table IV. Because of additional data and the nonlinear least squares treatment of the data, these results differ somewhat from those reported previously in a preliminary form.[18,27] However, only for the 3-fluoranthylmethyl system is the deviation significant.

These relative rates are converted to σ^+ values with two important assumptions: (1) we assume the application of a *linear* Hammett relation to the experimental solvolysis rates; (2) the applicable ρ value is -5.71 ± 0.09 as derived from the previous correlation of acetolysis rates of substituted benzyl tosylates with activating substituents (*vide supra*). These assumptions imply that any internal return effects are essentially constant over the series of compounds (that is, the *experimental* solvolysis rate constant is a reasonable measure of relative *ionization* rate) and that the degree of charge separation at the transition state is essentially constant for this series. These assumptions are justified by the following results.

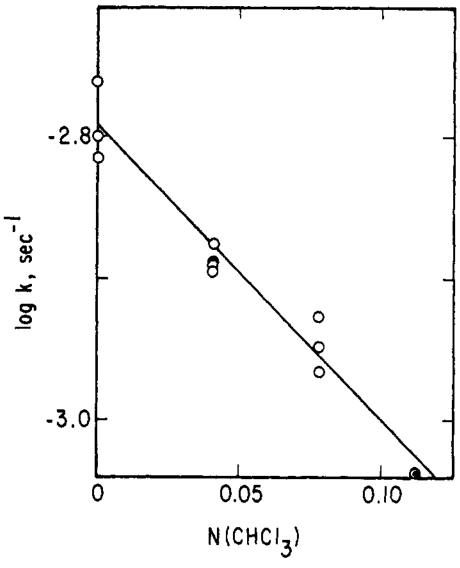

Figure 2. Effect of $CHCl_3$ concentration on rate of acetolysis of 1-naphthylmethyl tosylate.

Table IV. Summary of Acetolysis Reactivities of Arylmethyl Tosylates

$ArCH_2OTs$, Ar	Relative rate, 40°	σ^+	$\sigma^{+\,a}$
Phenyl	1.00	0	
1-Naphthyl	94.0	−0.345	−0.35
2-Naphthyl	12.7	−0.193	−0.20
2-Anthracyl	167	−0.389	
2-Phenanthryl	15	−0.207	−0.20
3-Phenanthryl	50	−0.298	−0.31
9-Phenanthryl	107	−0.356	−0.36
2-Pyrenyl	5.3	−0.128	
4-Pyrenyl	90	−0.342	
3-Fluoranthyl	580	−0.483	
8-Fluoranthyl	400	−0.455	
2-Biphenylenyl[b]	5.6	−0.130	
1-Anthracyl			−0.56

[a] B. G. Van Leuwen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **90**, 7056 (1968). [b] See ref 11.

Note that the activation parameters for 3-phenanthryl and 2-biphenylenyl correspond to those of activating groups in substituted benzyl tosylate acetolysis (Table II). The ΔS^* are especially revealing. The values for these polycyclics of about −9 eu (Table II) are close to those for *p*-CH_3 (−8 eu) and *p*-F (−10 eu) and are far more positive than those for the deactivating substituents, *m*-CF_3 (−16 eu) and *p*-CF_3 (−19 eu), which apparently solvolyze *via* a more displacement type of transition state.

The derived σ^+ values for polycyclic arylmethyl cations are summarized in Table IV. Despite the many solvolysis studies of benzylic and arylmethyl systems dispersed through the literature, there are surprisingly few data under comparable conditions for which a $\rho\sigma^+$ correlation established for substituted benzyl compounds can be used to derive σ^+ values for

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(23) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Amer. Chem. Soc.*, 87, 3682 (1965).

(24) W. A. Sheppard, *ibid.*, 87, 2410 (1965).

(25) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(26) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(27) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 12.

Table V. Correlation of Other Solvolysis Systems with σ^+

Solvolysis system[a]	ρ	Log k_0	No. of points	Cor coeff	Std dev of fit
$ArCH_2Cl$, 80% aqueous EtOH	−1.735	5.693	6	0.978	0.055
$ArCH_2Cl$, 79.5% aqueous dioxane	−0.99	8.19	4	0.86	0.12
$ArCH_2Cl$, 50.7% aqueous dioxane	−1.45	6.64	6	0.89	0.13
$ArCH_2Cl$, HCOOH, 0.38 M H_2O	−7.453	6.994	6	0.998	0.069
$ArCH_2Cl$, H_2O–HCOOH–dioxane	−5.288	7.985	10	0.965	0.23
$ArCHClCH_3$, 80% aqueous acetone	−3.62	6.16	7	0.925	0.22
$ArCCl(CH_3)_2$, EtOH	−2.29	4.59	6	0.730	0.32
$ArCH_2Cl$, KI, acetone	−1.668	3.224	8	0.933	0.11

[a] These solvolysis systems are those listed in Table 12.4 of ref 27. The data used and references cited are listed there.

polycyclic arylmethyl systems.[28] The most complete such study is that reported recently by van Leuwen and Ouellette,[29] in acetolysis of arylmethylmercuric perchlorates. Their σ^+ values as listed in Table IV are in excellent agreement with ours. This agreement justifies our use of a ρ value derived from activating substituents in a two-line treatment of acetolysis of substituted benzyl tosylates. If the latter data actually corresponded to a curve or to a single line for all substituents, we would not expect such agreement between the two reaction series. It is also noteworthy that the ρ value for the arylmethylmercuric solvolysis of −7.0 represents somewhat greater electronic demand than our solvolysis system. Nevertheless, as summarized by van Leuwen and Ouellette,[29] other derivations of σ^+ for polycyclic aryl systems, particularly those using electrophilic aromatic substitution reactions, do not agree with the values in Table IV. Clearly, the same σ^+ values do not necessarily apply to the process for extending a π system ($ArH \rightarrow ArCH_2^+$) as for contracting it ($ArH \rightarrow ArH_2^+$).

It has been pointed out previously that various solvolysis reactivities of polycyclic arylmethyl systems correlate with each other.[18,27] Such correlations are equivalent to correlations of each of these solvolytic systems with σ^+. Thus the present σ^+ values supplant the so-called "σ" values[27] for arylmethyl groups and "σ" should be discarded. The least squares correlation results from several previous studies are summarized in Table V. Note that many of these correlations, particularly those in aqueous solvents, are of rather poor quality. The results of Dewar and Sampson,[3] however, for formolysis of arylmethyl chlorides do correlate excellently with the present σ^+ values and permit the derivation of σ^+ values for additional aromatic systems. A final summary of the present σ^+ values rounded to two figures is given in Table VI.

The linear correlation of the arylmethyl chloride formolysis reactivities with experimental rates for arylmethyl tosylate acetolysis provides an important argument against significantly varying internal return in either reaction. These reaction systems are sufficiently different that an accidental coincidence of an internal return effect that changed significantly with structure would be most remarkable. A final justification for our derivation of these σ^+ values comes from several SCF molecular orbital correlations (*vide infra*). Over the series of systems studied linear correlations are found in which the deviations are random and show no suggestion of the curvature expected if our fundamental assumptions are seriously invalid.

Table VI. Summary of σ^+ Values for $ArCH_2$ Groups

Symbol in figures	Ar	σ^+
P	Phenyl	0
1N	1-Naphthyl	−0.35
2N	2-Naphthyl	−0.20
1A	1-Anthracyl	−0.56
2A	2-Anthracyl	−0.39
1Ph	1-Phenanthryl	−0.33[a]
2Ph	2-Phenanthryl	−0.20
3Ph	3-Phenanthryl	−0.30
9Ph	9-Phenanthryl	−0.36
1Py	1-Pyrenyl	−1.0[b]
2Py	2-Pyrenyl	−0.13
4Py	4-Pyrenyl	−0.34
2T	2-Triphenylenyl	−0.21[a]
6C	6-Chrysenyl	−0.55[a]
3F	3-Fluoranthyl	−0.48
8F	8-Fluoranthyl	−0.455
2B	2-Biphenylenyl	−0.13

[a] Derived from HCOOH–0.38 M H_2O results, Table V. [b] Derived from H_2O–HCOOH–dioxane and 80% aqueous acetone results, Table V.

Molecular Orbital Calculations, HMO. The original objective in studying the polycyclic systems was to compare the experimental results with π–MO calculations. In the π approximation, the energy differences from one polycyclic system to another are ascribed completely to the π electrons, the σ-electronic changes being assumed to be constant for the series. In eq 3, $ArCH_2X$ is taken to be represented by the π system of Ar alone, and the corresponding HMO π-electronic energies are calculated in standard ways.[27] Our

$$E(ArCH_2^+) - E(ArCH_2X) = \Delta E_\pi \qquad (3)$$

general approach with the HMO method, begun many years ago, was to try to establish a reasonable MO correlation first for simple benzenoid systems, then to extend it to nonalternant (fluoranthene) and strained (biphenylene) systems, and finally to introduce heteroatoms. As is now well known, even the simple benzenoid compounds fail to give a good correlation with the simple HMO method. This failure is demonstrated in Figure 3 in which the σ^+ values are plotted against the corresponding ΔE_π of eq 3 (in units of β, Table VII).[30] The main features of such a diagram have been discussed several times in the past[3,27] and will not be treated at length here. Dispersion into "benzylic"

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(28) See ref 29 for a more extended discussion.

(29) See Table IV, footnote *a*.

(30) The HMO quantities are given in ref 27 and may be derived from C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, London, 1965, and A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, London, 1965.

Table VII. Molecular Orbital Energy Changes for Arylmethyl Cations

Ar in $ArCH_2^+$	HMO, $\Delta E\pi, \beta$	NM SCF-π, $\Delta\Delta E\pi$, eV	CNDO/2 ΔE, eV	$q(CH_2)$
Phenyl	0.721	0	34.237	+0.410
1-Naphthyl	0.812	0.511	33.416	0.310
2-Naphthyl	0.744	0.264	33.743	0.356
1-Anthracyl	0.848	0.751		
2-Anthracyl	0.769	0.445	33.357	0.300
1-Phenanthryl	0.803	0.581		
2-Phenanthryl	0.736	0.316	33.621	0.350
3-Phenanthryl	0.754	0.417	33.481	0.327
9-Phenanthryl	0.813	0.594	33.215	0.292
1-Pyrenyl	0.868	0.973		
2-Pyrenyl	0.717	0.360	33.737	0.368
4-Pyrenyl	0.828	0.706	33.082	0.264
2-Triphenylenyl	0.745	0.406		
6-Chrysenyl	0.838	0.805		
3-Fluoranthyl	0.780	0.610	33.112	0.275
8-Fluoranthyl	0.764	0.544	33.182	0.318
2-Biphenylenyl	0.801	0.463	33.401	0.307

and "α-naphthylmethyl" groups occurs as discussed previously, but even within one type of position significant deviations occur. The nonalternant fluoranthylmethyl systems do not fit the other compounds. 1-Pyrenylmethyl appears to be more reactive than predicted from other "α-naphthyl" groups but its σ^+ value is subject to substantial error. The exceptionally low reactivity of the 2-biphenylenemethyl system undoubtedly reflects at least in part the exaggeration of conjugation produced by the HMO method in which the same value of β is used for the long bonds joining the rings as for the intraring bonds. Note also that for this compound, our σ^+ value differs greatly from the value, −0.625, derived from the pyrolysis method of Blatchly and Taylor.[31] We cannot account for this large difference in results. The unusual character of the biphenylene system would certainly justify further reactivity studies of both the 1 and 2 positions.

SCF–π Calculations. Dewar and Thompson[32] have studied several parameter sets and models within a Pople-type SCF–π framework for the π-system change: $Ar \rightarrow ArCH_2^+$. They obtained fairly good correlations when their calculations were applied only to arylmethyl chloride formolysis reactivities and they made some significant findings; for example, the dispersion into α- and β-naphthylmethyl types prevalent in HMO treatments disappeared when electron-repulsion terms were included. Clearly, the more extended β-naphthylmethyl structures involve less electron repulsion than the α isomers and have systematically distorted reactivities in HMO calculations.

However, when the Dewar and Thompson calculations are applied to the present more extensive set of equivalent σ^+ values, the correlations are not nearly so good. For example, their SPO with fixed β applied only to the phenyl (P), naphthyl (1N, 2N), phenanthryl (1Ph, 2Ph, 3Ph, 9Ph), triphenylyl (2T), and chrysyl (6C) systems gives a correlation coefficient of 0.966, whereas, when the types of structures are extended to anthracyl (2A), pyrenyl (2Py, 4Py), and fluoranthyl (3F, 8F), the correlation coefficient drops to 0.880. The results of all four of their SCF–π methods, PPP and SPO with "fixed" and with "self-consistent" β, are summarized in Table VIII. All methods show a great deal of scatter. We note that these applications of the Dewar–Thompson calculations are more extensive than the recent treatment of van Leuwen and Ouellette[33] using their data on acetolysis of arylmethyl-

Table VIII. SCF Correlations with σ^+

Method	Slope	Std dev of fit	Cor coeff
NM	−0.678	0.071	0.900
PPP-β_0	−0.548	0.076	0.869
SPO-β_0	−0.540	0.073	0.880
PPP-SCβ	−0.717	0.070	0.890
SPO-SCβ	−0.685	0.093	0.794
CNDO/2	0.392	0.053	0.937

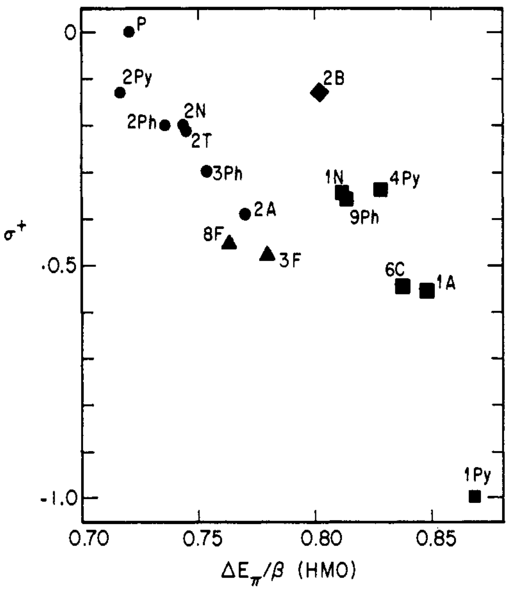

Figure 3. Correlation of σ^+ values for $ArCH_2^+$ groups as a function of HMO $\Delta E\pi$. Symbols are defined in Table VI. Types of position are as follows: ○, benzylic; □, α-naphthylmethyl; △, fluoranthylmethyl; ◊, biphenylenylmethyl.

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(31) J. Blatchly and R. Taylor, *J. Chem. Soc. B*, 1402 (1968).

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

(33) B. G. van Leuwen and R. J. Ouellette, *ibid.*, 90, 7056 (1968).

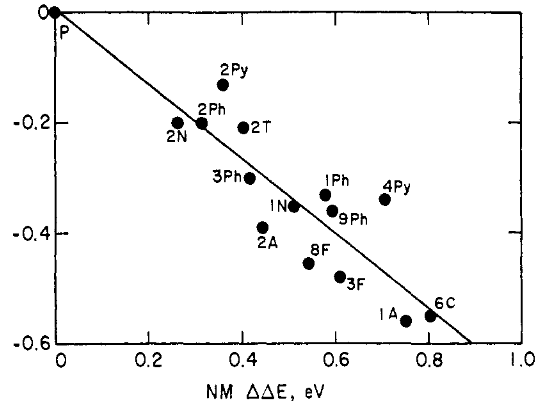

Figure 4. Correlation of σ^+ values for $ArCH_2^+$ groups as a function of SCF–π ΔE relative to benzyl using Nishimoto–Mataga integrals.

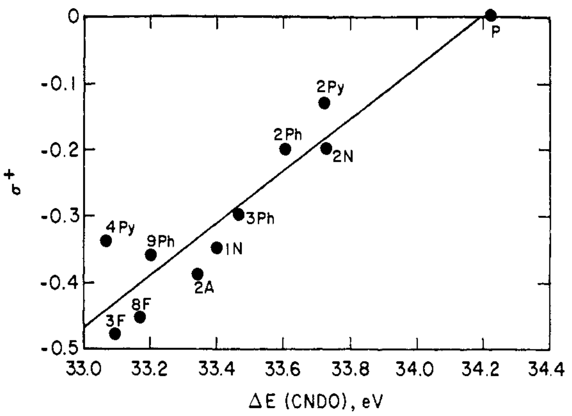

Figure 5. Correlation of σ^+ values for polycyclic $ArCH_2^+$ groups as a function of CNDO/2 ΔE for the reaction $ArCH_3 \rightarrow ArCH_2^+$.

mercuric perchlorates, but the general results are comparable.

In our own calculations we adopted the "standard structure" technique in which the benzenoid systems were treated as having regular hexagons with all C–C bonds set at 1.40 Å; the Dewar and Thompson results showed little advantage in the SCβ method in which the structures are varied to give β's consistent with bond orders. Furthermore, Gleicher[34] has shown recently that explicit consideration of distortion energies does not improve correlations between theory and experiment for arylmethyl cations. For electron repulsion integrals, γ, we used the Nishimoto–Mataga (NM)[35] approximation, in which the repulsion integrals tend to be somewhat lower than other formulations; γ_{11} was taken as 11.08 eV. For β, we used the Dewar procedure,

$$\beta = -{}^1/_4(\gamma_{11} - \gamma_{12}) - {}^1/_2 f(\beta) \qquad (4)$$

with the above values for γ and with $f(\beta) = 1.589$.[36] This method gives $\beta(1.40\ \text{Å}) = -2.231$ eV and actually is very close to the value, -2.26 eV, derived from the application of NM repulsion integrals to the spectrum of benzene.[37] The results for the energy differences between Ar and $ArCH_2^+$ relative to the benzene–benzyl cation value are given in Table VII. A plot of the results in Figure 4 shows a pattern not much different from those of Dewar and Thompson.[32] There is substantial scatter and the correlation coefficient (Table VIII) of 0.90 represents only a fair correlation. The comparisons in Table VIII show that the pattern of results is largely independent of the structural model or parameter set used. Note that the nonalternant fluoranthene systems fare about as well as the other compounds. Because of the approximate nature of the experimental value of σ^+ for the 1-pyrenylmethyl system, it was not included in the correlations; our calculated value from Figure 4 of -0.65 does not agree at all with the experimental value of *ca.* -1.0 (Table VI). Indeed, all of the pyrene positions are poorly represented. Finally, the value of σ^+ calculated for 2-biphenylenylmethyl cation (with long bonds taken as 1.51 Å), -0.34, is much higher than the experimental value, -0.13.

CNDO Calculations. Of the several all-valence-electron semiempirical SCF methods now available,[38] the CNDO/2 method of Pople, Santry, and Segal[39] has been especially popular because of its general availability as program 100 of the Quantum Chemistry Program Exchange. In applying this method to an attempted correlation with σ^+ values, we used a modified version of this program to calculate the energy change: $ArCH_3 \rightarrow ArCH_2^+$. The "standard structure" method was again used with all C–C bonds set at 1.39 Å, except for C–CH_3 (1.54 Å), and all C–H bonds set at 1.09 Å. Although various parameter sets have been suggested,[40] we used the original values of Pople, *et al.*;[39] our aim at this point was not to optimize parameters for a best correlation but to determine whether such all-valence-electron methods can accommodate the general *pattern* of the results. The ΔE values calculated are summarized in Table VII. The computer time available limited the number of large systems we could calculate.

The correlation of these ΔE values with σ^+ is shown in Figure 5. The resulting correlation with a correlation coefficient of 0.937 is the best result with any SCF method. Some important features of the results are the clear absence of any division into α- and β-naphthylmethyl types and the accommodation of the nonalternant fluoranthyl systems on a par with the others. The "normal" system farthest from the regression line is that of 4-pyrenylmethyl cation. This system was also poorly represented in the SCF–π methods and a reinvestigation of its σ^+ value is suggested;[41] the present experimental value is based primarily on some rather old kinetic measurements and there is some uncertainty in the results (Table III).

We have shown elsewhere[42] that the CNDO ΔE values correlate excellently with corresponding ΔE_π values from SCF–π calculations and that the change in ΔE with structure is determined principally by charge

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(34) G. J. Gleicher, *J. Amer. Chem. Soc.*, **90**, 3397 (1968).

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

(36) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965).

(37) G. Hafelinger, A. Streitwieser, Jr., and J. S. Wright, *Ber. Bunsenges. Phys. Chem*, **73**, 456 (1969).

(38) Some examples are T. Yonezawa, K. Yamaguchi, and H. Kato *Bull. Chem. Soc. Jap.*, **40**, 536 (1967); T. Yonezawa, H. Kato, and H. Konishi, *ibid.*, **40**, 1071 (1967); and M. J. S. Dewar and G. Klopman, *J. Amer. Chem. Soc.*, **89**, 3089 (1967).

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

(40) For example, K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968); J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta*, **7**, 32 (1967).

(41) Such a study is in progress.

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

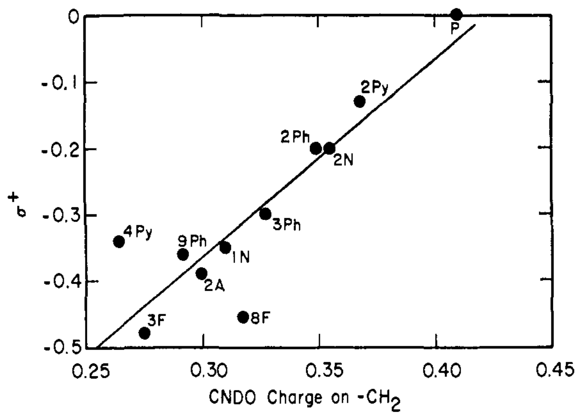

Figure 6. Correlation of σ^+ values for polycyclic $ArCH_2^+$ groups as a function of the total charge on the exocyclic CH_2 group by the CNDO/2 method. The slope is 2.977, standard deviation of the fit is 0.070, and the correlation coefficient is 0.89.

delocalization. A glance at the total charge of the exocyclic CH_2 group in the arylmethyl cations summarized in Table VII shows the wide variation from +0.41 for benzyl cation to +0.26 for 4-pyrenylmethyl cation. In fact, a simple correlation of σ^+ against the $-CH_2$ charge gives a fair correlation (Figure 6).

The comparative success of the present calculations suggests also that other parameter sets might do even better; however, it should be noted that the biphenylene system is poorly represented by the present calculations in which the "long" bonds in the four-membered ring were taken as 1.50 Å. The calculated reactivity ($\sigma^+ = -0.31$) is still greater than the experimental value (-0.13). Additional calculations with varying geometries did not change this result and may well demonstrate an inadequacy of CNDO-type methods in handling strained systems.

One virtue of all-valence-electron methods is that they are not limited to polycyclic π systems. We studied several substituted benzyl cations with substituents comprised of first row atoms: CH_3, F, CF_3, OCH_3, NO_2. The calculated ΔE values (Table IX) are compared with the known σ^+ values in Figure 7. The results give an excellent correlation with a slope of 1.112, a standard deviation of the fit of 0.13, and a correlation coefficient of 0.967; however, this slope is substantially different from that of the polycyclic systems (dotted line in Figure 7). We interpret this discrepancy in terms of a difference in interaction mechanisms. We note that the charge distribution of most of the substituted benzyl cations is little different from that of benzyl cation itself; the results summarized in Table IX show that the net charge of the benzyl CH_2 group is essentially constant (0.39–0.41) for all but strongly electron-donating conjugating substituents (*e.g.*, $p\text{-}CH_3O$). For such systems, the principal interaction mechanism of the substituent is a charge–dipole electrostatic effect rather than charge delocalization. The CNDO procedure clearly does not handle these two effects on the same basis and caution is clearly called for in interpreting results in systems where both interactions are mixed. It is possible that this limitation can be reduced with a suitable choice of parameter values; if so, the present sets of experimental data should help to define such parameters.

Table IX. CNDO/2 Calculations on Substituted Benzyl Cations

Substituent	ΔE, eV	$q(-CH_2)$
H	34.237	+0.4101
$m\text{-}CH_3$	34.184	0.4051
$p\text{-}CH_3$	33.847	0.3801
m-F	34.601	0.4147
p-F	34.121	0.3892
$m\text{-}OCH_3$	34.331	0.4060
$p\text{-}OCH_3$	33.795	0.3701
$m\text{-}CF_3$	34.672	0.4124
$p\text{-}CF_3$	34.728	0.4091
$p\text{-}NO_2$	35.086	0.4114

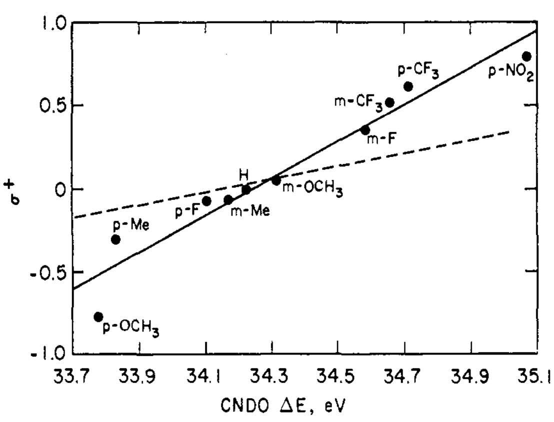

Figure 7. Correlation of σ^+ values for substituted benzyl cations as a function of CNDO/2 ΔE. The dotted line is the correlation for polycyclic systems from Figure 5.

Conclusion

All of the molecular orbital methods tested have restricted application to the chemistry of arylmethyl cations. The HMO method can be applied to only very limited structural changes. SCF-π and CNDO/2 methods can be applied to arylmethyl cations derived from "normal" benzenoid systems but cannot be applied on the same basis to systems involving strained rings. The CNDO/2 method can be applied to a given π system with varying substituents but cannot be used when both the π system and the substituent are changed.

Experimental Section

Materials. The substituted benzyl alcohols and polycyclic arylcarbinols used were commercial materials or were prepared from the corresponding aldehyde, acid, or ester by reduction with lithium aluminum hydride. The alcohols were fractionated or recrystallized before use. The benzyl chlorides were generally commercially available and were redistilled before use. The polycyclic arylcarbinols are well-known compounds and gave properties corresponding to the literature; some are now commercial items. The pyrenyl-, fluoranthyl-, and anthracenylcarbinols and the preparation of the chlorides have been reported previously.[43]

Anhydrous acetic acid was prepared by refluxing reagent grade glacial acetic acid with acetic anhydride and a small amount of sulfuric acid or p-toluenesulfonic acid and fractionating. The distillate, bp 117–117.5°, was stored under nitrogen and decanted with nitrogen pressure as needed.

2-Chloromethylbiphenylene. 2-Carbomethoxybiphenylene[44] was reduced with lithium aluminum hydride to the carbinol.

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(43) A. Streitwieser, Jr., and W. C. Langworthy, *J. Amer. Chem. Soc.*, **85**, 1757 (1963).

(44) W. Baker, A. J. Boulton, C. R. Harrison, and J. F. W. McOmie, *Proc. Chem. Soc.*, 414 (1964).

About 5 ml of thionyl chloride was added to 300 mg of the carbinol and, after solution was complete, the thionyl chloride was removed on a rotary evaporator and the residual solid was crystallized from petroleum ether to yield 106 mg of yellow solid, mp 94–96°.

Anal.[45] Calcd for $C_{13}H_9Cl$: C, 77.8; H, 4.5; Cl, 17.7. Found: C, 77.6; H, 4.6; Cl, 17.5.

p-**Toluenesulfonates.** Several methods were explored. In the older work most of the tosylates were prepared by a Schotten-Baumann procedure using dioxane. The recent preparations used the benzyl chloride–silver tosylate method.[6] Examples of both methods follow:

(a) *p*-**Chlorobenzyl** *p*-**Toluenesulfonate.** To 3.4 g (0.024 mol) of *p*-chlorobenzyl alcohol, bp 130–131° (18 mm), in 25 ml of dioxane was added 6.8 g (0.034 mol) of *p*-toluenesulfonyl chloride and 11 ml of 40% NaOH. After stirring at 15° for 18 hr the mixture was poured into ice–water and filtered. The solid was dissolved in ether and dried with sodium carbonate, the ether was evaporated, and the product was recrystallized from 300 ml of hexane yielding 5.47 g (77%) of tosylate, mp 51.6–53.0° (lit.[46] mp 53.0–3.5°).

A similar procedure was used to prepare each of the following benzyl tosylates: *p*-methyl, *m*-methyl, *m*-chloro (mp 81–83° dec; lit.[46] mp 81.5–2.0°).

(b) *m*-**Trifluoromethylbenzyl** *p*-**Toluenesulfonate.** Silver tosylate was prepared by treating 11.65 g of commercial silver oxide with 19.06 g of *p*-toluenesulfonic acid monohydrate in 250 ml of acetonitrile. After stirring for 2 hr a small amount of unreacted silver oxide was filtered off. Acetonitrile was removed from the filtrate on a rotary evaporator. A mixture of 6.10 g (0.0218 mol) of this silver tosylate and 4.22 g (0.0217 mol) of *m*-trifluoromethylbenzyl chloride in 250 ml of acetonitrile was refluxed overnight. After filtering, the solvent was removed on a rotary evaporator. Anhydrous ether (200 ml) was added to the residue. After standing overnight, the mixture was filtered through sintered glass and the ether was removed at reduced pressure. Addition of 5 ml of petroleum ether (bp 30–60°) gave white crystals, yield 2.60 g (36%), mp 61–63°.

Anal.[45] Calcd for $C_{15}H_{13}O_3SF_3$: C, 54.6; H, 4.0; S, 9.7. Found: C, 54.4; H, 4.2; S, 9.6.

(c) *p*-**Trifluoromethylbenzyl** *p*-**Toluenesulfonate.** *p*-Trifluoromethylbenzoyl chloride was reduced with lithium aluminum hydride to give the alcohol, bp 98.5–99.9° (16 mm), mp 22–23°. The chloride was prepared with thionyl chloride and treated with silver tosylate as above to give product, mp 51–53°.

Anal.[45] Calcd for $C_{15}H_{13}O_3SF_3$: C, 54.6; H, 4.0; S, 9.7. Found: C, 54.8; H, 4.2; S, 9.5.

Similar preparations were applied to benzyl tosylate, mp 54–56° (lit.[5] mp 57–58°); *m*-chloro, mp 80–81° (lit.[8] mp 81.5–82.0°); *p*-chloro, mp 52.3° (lit.[46] mp 53–53.5°); *p*-fluoro, mp 48.5–52.5°; and *p*-methyl.

(d) 1-Naphthylcarbinyl *p*-**Toluenesulfonate.** To 1.26 g (8 mmol) of carbinol maintained at 15° in 15 ml of dioxane was added 2.2 g (11 mmol) of *p*-toluenesulfonyl chloride and 4 ml of 40% aqueous sodium hydroxide. After stirring for 10 hr at 15° the mixture was poured into ice water and the precipitated crystals were filtered and recrystallized three times from ether; yield, 1.56 g (63%) of tosylate, pure by ir. Other recrystallizing solvents used were chloroform–hexane, benzene–hexane, and tetrahydrofuran–hexane. In the reaction of 2-pyrenylcarbinol, tetrahydrofuran was used in place of dioxane because of solubility.

For the conductivity runs, the tosylates were prepared by reaction of the chloromethylarenes with silver tosylate in acetonitrile.[6] After reaction, solvent was removed *in vacuo*, ether was added, and the filtered solutions were used directly for the kinetic experiments.

Kinetics. (a) Sealed Tube Method. Aliquots of a solution of the tosylate in acetic acid were sealed in tubes, placed in a thermostat, and removed periodically. The titrations of the aliquots with standard solutions of sodium acetate in acetic acid were carried out potentiometrically using calomel and glass electrodes. In the early work a Beckman Model G pH meter was modified by imposing a variable external counter-emf[47] and a silver–silver chloride electrode was occasionally used. Later work made use of a Potentiograph E 336 (Metrohm Ltd., Herisan, Switzerland).

(b) Stoppered Flask Method. The entire kinetic solution was contained in a 100-ml flask sealed with a rubber serum cap. After temperature equilibration in the thermostat, aliquots were withdrawn using an automatic pipet equipped with a syringe needle and were drained into an equal volume of propionic acid at −20° to quench the reaction. The samples were then titrated at 0°. This method was used only for the relatively fast rate of *p*-methylbenzyl tosylate at 50°. It was tried with less reactive compounds but gave erratic results presumably by reaction of the serum cap with warm acetic acid vapor and because the seal is insufficient over long periods.

(c) Intermittent Titration Method. This method was based on previous procedures.[7,8]

Production of acidity was followed with glass and calomel electrodes and the titrating solution of tetramethylammonium or sodium acetate in acetic acid was added from a Gilmont microburet or by radiological micropipet, the concentration being sufficiently high that dilution at the completion of solvolysis was only 5–10%. An air-driven stirrer entered a Teflon bearing and a slow stream of acetic acid saturated nitrogen was passed through or over the solution. The potential corresponding to the equivalence point was determined at the beginning and end of each run and during a run corresponds to the point of maximum change of emf with time for each aliquot. The cell was charged with the kinetic solution and aliquots of the acetate solution were added, each aliquot being added when the acid produced by solvolysis had completely neutralized the preceding aliquot. The time for reaching the end point was recorded for each aliquot.[48] In later work a recorder was attached to give as chart output a series of "titration curves" for each aliquot. The results were then obtained by normal first-order treatments;[8] all of the older data were completely recalculated using the LSKIN1 program.[9]

In the case of 4-pyrenylmethyl tosylate the product from several kinetic runs was combined and diluted with water to recover the crude acetate; treatment with lithium aluminum hydride produced the original carbinol.

(d) Conductivity Method. This method has been described in detail elsewhere.[11]

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(45) Analysis by Chemical Analysis Services Laboratory, College of Chemistry, University of California, Berkeley, Calif.

(46) F. T. Fang, J. K. Kochi, and G. S. Hammond, *J. Amer. Chem. Soc.*, 80, 563 (1958).

(47) S. Winstein and H. Marshall, *ibid.*, 74, 1120 (1952).

(48) For complete details, see R. H. Jagow, Dissertation, University of California, Berkeley, Calif., 1964.