

Theoretical Studies of Substituted Naphthylcarbinyl Cations and Associated Correlation Analysis

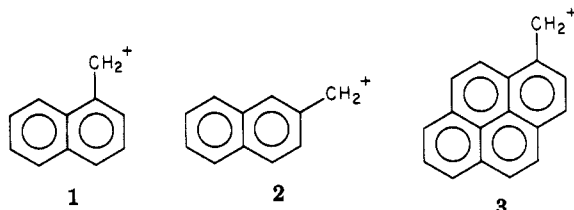
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Received January 18, 1982

Minimal basis set *ab initio* calculations are performed on naphthalenes and naphthalenecarbinyl cations substituted by CH₃, F, CF₃, CN, CH₃O, NH₂, and NO₂. Suitable substitution reverses the inherent stability of a 1-naphthylcarbinyl cation over a 2-naphthylcarbinyl cation. Homodesmotic stabilization energies are correlated according to a modified Dewar-Grisdale equation as well as Taft's dual substituent parameter (DSP) equation, and the results are compared with published experimental data and corresponding treatments for benzyl cations.

Naphthylcarbinyl cations 1 and 2 are intriguing subjects



for study since they offer ten sterically unencumbered substitution sites instead of only two as in benzyl cation. Furthermore, they furnish a link between the much-studied benzyl cations and higher polycyclic aromatic carbinyl cations such as 1-pyrenylcarbinyl cation (3) for which there are considerably fewer data.¹⁻⁴ One reason for interest in species such as 3 is their relevance to the bay-region theory for carcinogenicity of polycyclic aromatic hydrocarbons (PAHs).^{5,6} In fact, 1-naphthylcarbinyl cation (1) can be regarded as the simplest bay-region carbonium ion. Although the actual intermediacy of carbonium ions in PAH metabolism is not established and subtle stereochemical details are beginning to emerge,⁶ the theory rests in part upon relative carbonium ion stabilization energies.

Simple Hückel molecular orbital theory has long furnished understanding of benzylic reactivity and forms part of the framework for the bay-region theory. However, in order to quantitatively analyze the effects of diverse substituents on reactivity, more complex theoretical procedures are required. Minimal basis set *ab initio* molecular orbital calculations have been employed to obtain gas-phase proton affinities of substituted benzenes,⁷ benzaldehydes,⁸ and α -methylstyrenes,⁸ to calculate the stabilities of benzyl cations and the energetics of various proton-transfer reactions,⁹ and to understand interactions between two or more substituents on a benzene ring.¹⁰ Such theoretical studies allow separation of solvent effects and dissection of substituent interactions into components and disclose other features. Examples include the prediction that a *p*-nitro substituent on a benzyl cation is perpendicular to the ring while a *m*-nitro substituent is coplanar and that a *p*-amino group on the benzyl cation is planar while a *m*-amino substituent as well as amino substituents on aniline are pyramidal.^{8,11} Indeed, correlation of calculated and experimental gas-phase proton affinities permitted the assignment of protonation sites (ring vs. substituent) in a series of substituted benzenes.¹²

Correlation of substituent effects is based upon the pioneering research of Hammett and others.¹³ Brown and Okamoto recognized that certain substituents exhibited enhanced interactions on benzylic cations due to direct resonance interactions with the reaction center. Thus, a new set of substituent constants, σ^+ , was developed.¹⁴ The correlation treatment of systems such as naphthylcarbinyl is considerably more complex than benzyl. Two general approaches are employed. One method, proposed by Dewar and Grisdale² and subsequently modified,¹⁵ obtains a different substituent constant for each ring position (σ_{ij} or σ_{ij}^+), and the slope, ρ , is assumed to be constant for a given reaction type. An advantage of this approach is that it allows one to neatly dissect the substituent effect into electrostatic and resonance effects predictable from parameters derived from the parent ion. A disadvantage is the large number of parameters so obtained. Forsyth has introduced a simple modification to the basic Dewar-Grisdale approach as well as two slightly more complex modifications termed SUMCHIN1 and SUMCHIN2.¹⁶ An alternative approach involves multiparameter extensions of the Hammett equation¹⁷ such as Taft's dual substituent parameter (DSP) equation¹⁸ which assumes a universal set

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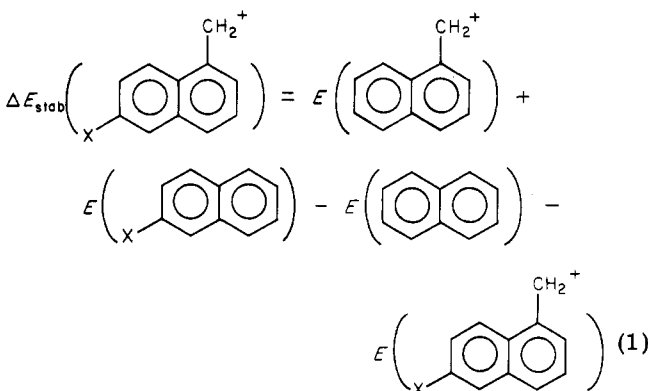
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of substituent parameters (σ_I , σ_R ; σ_I , σ_R^+ , etc.) and obtains reaction sensitivities (ρ_I , ρ_R^+ , etc.) which depend upon substitution site.

In the present study, minimal basis set ab initio calculations have been carried out on derivatives of 1 and 2 at their ten sterically unencumbered positions. A uniform treatment of substituents including H, CH₃, F, CF₃, CN, CH₃O, NH₂, and NO₂ has been employed to obtain stabilization energies. These stabilization energies are correlated by using Forsyth's modified Dewar-Grisdale treatment¹⁶ as well as the Taft DSP equation.¹⁸ (It is not the purpose of the present study to attempt to identify the best correlation method. Rather, a simple illustration of each of the two general correlation procedures has been chosen.) The results are compared with analogous treatments of published experimental data and also compared with correlations for benzyl derivatives.

Method

The GAUSSIAN 70 program¹⁹ and the STO-3G basis set²⁰ have been employed throughout the present investigation. A standard idealized geometry has been maintained throughout for naphthalenes and naphthylcarbiny cations,²¹ and a standard set of substituent geometries²² has also been utilized. Homodesmotic²³ stabilization energies are calculated according to equations such as eq 1 (1-



naphthylcarbiny or 2-naphthylcarbiny cation as well as 1-substituted or 2-substituted naphthalene is employed as appropriate for the substituted ion examined). This approach tends to cancel errors due to basis set deficiencies and lack of electron correlation and also tends to cancel differential steric effects, thus allowing derivatives of 1-naphthylcarbiny and 2-naphthylcarbiny cations to be compared directly. A positive value for ΔE_{stab} corresponds

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(21) For naphthalene, naphthalenecarbiny cations, and their derivatives: all ring C-C bonds, 1.395 Å; all C-H, 1.08 Å; all angles 120°; C₁(or C₂)-C₁₁, 1.368 Å.

(22) Derivative substituents replace the appropriate hydrogen. Geometries: C-F, 1.35 Å; CH₃, C-C, 1.51 Å, C-H, 1.10 Å, tetrahedral; CF₃, C-C, 1.51 Å, C-F, 1.37 Å, tetrahedral; NO₂ (planar or perpendicular), C-N, 1.48 Å, N-O, 1.21 Å, angles 120°; NH₂ (planar conjugate or planar perpendicular), C-N, 1.402 Å, N-H, 1.001 Å, angles 120°; NH₂ (pyramidal), C-N, 1.402 Å, N-H, 1.001 Å, HNH angle 113.1°, angle between HNH plane and ring plane, 37.5°; CN, C-C, 1.419 Å, C-N, 1.158 Å, linear; CH₃O, C-O, 1.36 Å, O-C, 1.43 Å, C-H, 1.09 Å, COC angle 121°, tetrahedral.

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Table I. Total STO-3G Energies (Negative Values of Calculated Energies in Hartrees) of Substituted Naphthalenes (1-N and 2-N), 1-Naphthylcarbiny (3 α , 4 α , etc.), and 2-Naphthylcarbiny (4 β , 5 β , etc.) Cations^a

	H	CH ₃	F	CF ₃	CN	CH ₃ O	NH ₂ (pyr con)	NH ₂ (plan con)	NH ₂ (plan perp)	NO ₂ (plan con)	NO ₂ (plan perp)
1-N	378.674 50	417.251 31	476.134 67	709.625 17	469.226 22	491.089 02	432.984 35	432.984 35	432.971 51	579.348 57	579.354 45
2-N	378.674 50	417.257 54	476.134 55	709.639 34	469.226 68	491.087 68	432.989 12	432.989 12	432.971 62	579.364 14	579.365 88
3 α	416.446 60	455.031 38	513.896 61	747.401 54	506.981 44	528.857 20	470.763 53	470.761 37	470.747 29	617.113 57	617.103 91
4 α	416.446 60	455.032 75	513.910 59	747.386 37	506.979 20	528.855 45	470.789 79	470.791 83	470.749 63	617.093 00	617.099 12
5 α	416.446 60	455.026 81	513.904 76	747.392 95	506.984 17	528.871 26	470.769 40	470.768 41	470.747 96	617.108 53	617.106 92
6 α	416.446 60	455.031 72	513.901 05	747.403 55	506.984 92	528.860 85	470.767 69	470.765 79	470.746 32	617.117 96	617.109 39
7 α	416.446 60	455.034 22	513.905 61	747.402 93	506.980 36	528.870 62	470.778 18	470.778 01	470.747 14	617.116 53	617.108 41
4 β	416.443 31	455.022 56	513.897 67	747.386 97	506.980 07	528.859 92	470.760 15	470.757 89	470.743 58	617.099 66	617.103 12
5 β	416.443 31	455.021 81	513.897 42	747.388 64	506.981 93	528.858 60	470.757 89	470.755 26	470.743 64	617.103 72	617.105 21
6 β	416.443 31	455.031 76	513.903 13	747.399 16	506.980 74	528.868 69	470.777 81	470.778 09	470.744 02	617.111 82	617.104 42
7 β	416.443 31	455.028 48	513.897 74	747.400 27	506.981 70	528.857 66	470.764 49	470.762 61	470.743 14	617.114 74	617.106 02
8 β	416.443 31	455.023 57	513.902 09	747.390 60	506.982 06	528.869 67	470.766 72	470.765 83	470.744 85	617.108 05	617.104 66

^a See ref 21 and 22 for details of molecular geometries.

Table II. Homodesmotic Stabilization Energies (kcal/mol) Obtained from Data in Table I through Use of Equations such as 1 Where Appropriate Changes Are Made for α - or β -Naphthylcarbinyl Cations and Positions of Substitution^a

posi- tion	cation						
	CH ₃	F	CF ₃	CN	CH ₃ O	NH ₂	NO ₂
3 α	1.09	-6.29	-6.21	-10.86	-1.61	-0.80	-14.21
4 α	5.86	2.40	-6.83	-11.99	15.26	19.73	-17.20
5 α	2.14	-1.25	-2.70	-6.82	6.36	5.66	-11.29
6 α	1.31	-3.51	-4.94	-8.68	0.67	1.81	-11.46
7 α	2.87	-0.65	-5.33	-9.04	6.80	8.39	-12.35
4 β	1.52	-3.65	-4.41	-9.39	1.30	1.91	-12.65
5 β	1.05	-3.81	-3.36	-8.23	0.47	0.49	-11.34
6 β	3.38	-0.15	-5.65	-9.26	7.64	10.38	-13.26
7 β	1.33	-3.54	-4.95	-8.66	0.72	1.85	-11.43
8 β	2.15	-0.88	-2.13	-8.14	7.41	6.03	-9.55

^a A positive value corresponds to stabilization; a negative value connotes destabilization. For NH₂ and NO₂, comparisons are made by using only the most stable substituent geometries for the neutral molecule and the cation.

to stabilization while a negative value indicates destabilization. Although the results calculated are of the $\Delta\Delta E$ type (roughly equivalent to $\Delta\Delta H$ results), they are relevant to Hammett-type relationships which are linear free-energy relationships ($\Delta\Delta G$). One would anticipate that, for a given reaction series, gas-phase entropy changes should remain essentially constant and that $\Delta\Delta S$ will be about zero. In fact, in a study of gas-phase basicities of substituted benzenes, Lau and Kebarle¹² showed that ΔS for protonation of both fluorobenzene and chlorobenzene was -3.5 ± 0.1 eu, in excellent agreement with the entropy change expected solely from the change in rotational symmetry number ($\Delta S_{\text{rot}} = -3.56$ eu), and this assumption was employed in the analyses of the protonations of other substituted benzenes.

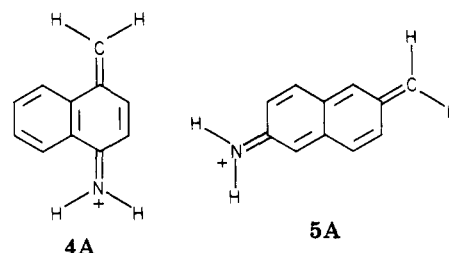
Results

Table I lists the total energies of neutral naphthalene derivatives (1-N and 2-N) as well as naphthylcarbinyl cations (3 α , 4 β , etc. where α refers to the 1-naphthylcarbinyl series, β refers to the 2-naphthylcarbinyl series, and the numbers refer to substituent positions). Table II lists homodesmotic stabilization energies for the substituted cations calculated according to equations such as eq 1; for the NH₂ and NO₂ groups, the most stable substituent structure (pyramidal conjugated, planar conjugated, or planar perpendicular for NH₂; planar conjugated or planar perpendicular for NO₂) was chosen for the neutral molecule and the cation, and the results were employed homodesmotically.

In accord with expectation, 1-naphthylcarbinyl cation (1), a "bay-region" cation, is calculated to be 2.05 kcal/mol more stable than 2-naphthylcarbinyl cation (2) despite the presence of peri interactions in the former that have not been relaxed computationally. An optimization study could be expected to increase this energy difference. Mass spectrometric studies of the ionization energies of 1-naphthylcarbinyl and 2-naphthylcarbinyl radicals appear to indicate a 4.8 ± 0.3 kcal/mol enthalpy difference favoring 1 over 2.²⁴ However, the possibility remains that

other species such as benzotropylium are generated under these conditions.²⁵ Under solvolytic conditions which favor development of a high degree of carbonium ion character,³ the free energy of activation for acetolysis (40 °C, $\rho = -5.71$) of 1-naphthylcarbinyl tosylate is 1.25 kcal/mol lower than that for the 2-naphthyl isomer,³ and hydrolysis (45 °C, 80% aqueous acetone) of 1-(1-naphthyl)ethyl chloride has a free energy of activation difference of 0.59 kcal/mol favoring its solvolysis over that of 1-(2-naphthyl)ethyl chloride.²⁶⁻²⁸ Although smaller energy differences, compared to calculated values, are consistent with (a) reactions in solution as opposed to gas phase and (b) partial charge development in the transition state, it is not readily apparent how to assess solution entropy contributions.

It is fairly obvious, yet worth remarking, that substituents can cause bay-region carbonium ions to be less stable than their non-bay-region isomers. For example, in the fluoro series, both the 6 β and 8 β isomers are calculated to be more stable than the 3 α and 6 α isomers. The 4 α -trifluoromethyl derivative is calculated to be the least stable of ten isomers. Other patterns also emerge. The quinoid structures for 4-amino-1-naphthylcarbinyl cation (4A) and



6-amino-2-naphthylcarbinyl cation (5A) cause these two species to have planar amino groups in contrast to all of the remaining ions and neutrals, calculated here, which are predicted to have pyramidal amino groups.

Discussion

One means for analyzing the results reported here is through application of the Dewar-Grisdale method² whereby a different substituent constant is specified for each position. For this purpose, Forsyth's modified Dewar approach¹⁶ has been employed where Δq corresponds to the regional charge (carbon plus attached hydrogen)²⁹ difference upon changing from Ar to ArCH₂⁺. Results have been calculated by using STO-3G data rather than CNDO/2 data as in the original work. Furthermore, the appropriate substituent constants have been chosen from a recent critical compilation.³⁰ In the present study and in previous work⁸ we have found better correlations of these calculations with this recent compilation of substituent constants than with those of Brown and Okamoto,¹⁴ particularly for CN and CF₃ substituents. In Table III are found the σ^+ values employed in this study and corresponding values for M^+ and F^+ . In Table IV are listed reciprocals of the distance, in units of benzene bond length,

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(24) (a) Harrison, A. G.; Lossing, F. P. *J. Am. Chem. Soc.* 1960, 82, 1052-1055. (b) Comparison of "methyl cation stabilization" energies according to $\text{ArCH}_2^+ + \text{CH}_4 \rightarrow \text{ArCH}_3 + \text{CH}_3^+$ indicates 74 kcal/mol of stabilization for benzyl cation, 83 kcal/mol of stabilization for 2-naphthylcarbinyl cation, and 89 kcal/mol of stabilization for the 1-naphthylcarbinyl cation.

Table III. Values of Substituent Constants³⁰ and Associated Values of Parameters for the Dewar-Gridale Equation^a

	σ_m^+	σ_p^+	M^+	F^+
CH ₃ O	0.10	-0.78	-6.41	0.882
NH ₂	-0.09	-1.3	-9.04	0.844
F	0.34	-0.07	-2.70	0.889
CH ₃	-0.06	-0.31	-1.91	0.108
CF ₃	0.46	0.53	-0.97	0.690
CN	0.62	0.70	1.20	0.943
NO ₂	0.71	0.81	1.44	1.071
Cl	0.37	0.11	-1.56	0.814
Br	0.37	0.15	-1.26	0.781
C ₂ H ₅	-0.08	-0.30	-1.71	0.050
CH ₃ S	0.14	-0.60	-5.34	0.833

^a $\sigma_{ij}^+ = F^+/r_{ij} + \Delta q_{ij}M^+$, where Δq_{ij} is that defined in ref 16.

Table IV. Reciprocals of Distances between the Reaction Center and Substituent Site, Calculated Changes in Regional Charge, and Experimental ¹³C Chemical Shift Response Slopes

	$1/r_{ij}^a$	Δq_{ij}^b	rel ¹³ C chem shift response slope ^c
meta	0.577	0.0638	0.197
para	0.500	0.1905	1.000
3 α	0.577	0.0425	0.112
4 α	0.500	0.1998	1.052
5 α	0.378	0.0859	0.152
6 α	0.333	0.0558	0.081
7 α	0.378	0.1066	0.301
4 β	0.577	0.0721	0.144
5 β	0.333	0.0436	0.075
6 β	0.277	0.1156	0.605
7 β	0.289	0.0577	0.150
8 β	0.378	0.0827	0.339

^a Values are reciprocals of units of benzene bond length lengths. ^b Changes in regional charge in change from Ar to ArCH₂⁺. ^c Values taken from Table IV in ref 31.

between the reaction center and substituent site, Δq , and the relative response slopes of ¹³C chemical shifts for the relevant positions in benzyl and naphthylcarbiny cations (selected from Table IV of ref 31). For the 12 substitution sites, the chemical shift response slopes plotted vs. CNDO/2-calculated changes in regional charge³¹ has a slope (m) of 4.86, an intercept (b) of -0.071, and a correlation coefficient (r) of 0.9490, while a 12-point plot vs. STO-3G-calculated changes in regional charge (Table IV) indicates a slope of 6.40, an intercept of -0.25, and a correlation coefficient of 0.9715.

The 72 tabulated stabilization energies [see Table II; there are only two values for H-substituted (parent) cations 1 and 2] have been correlated with σ_{ij}^+ from the data in Table III and plotted in Figure 1. The slope is calculated to be -16.78, the intercept to be -0.46, and the correlation coefficient to be -0.9599. It is clear that the nitro-substituted species almost all differ from the expected value by 2-5 kcal/mol. The slope corresponds to a ρ value of -12.3. The naphthylcarbiny correlation can be compared to that of benzyl cation by using published⁹ STO-3G stabilization energies for the latter along with the same σ_{ij}^+ values employed in this study (see data in Table III). The resulting values are as follows: slope, -19.72; intercept, 0.56; correlation coefficient, -0.9826 ($n = 17$). This corresponds to a ρ value of -14.5. In principle, the two values for ρ should be the same. The discrepancy results from

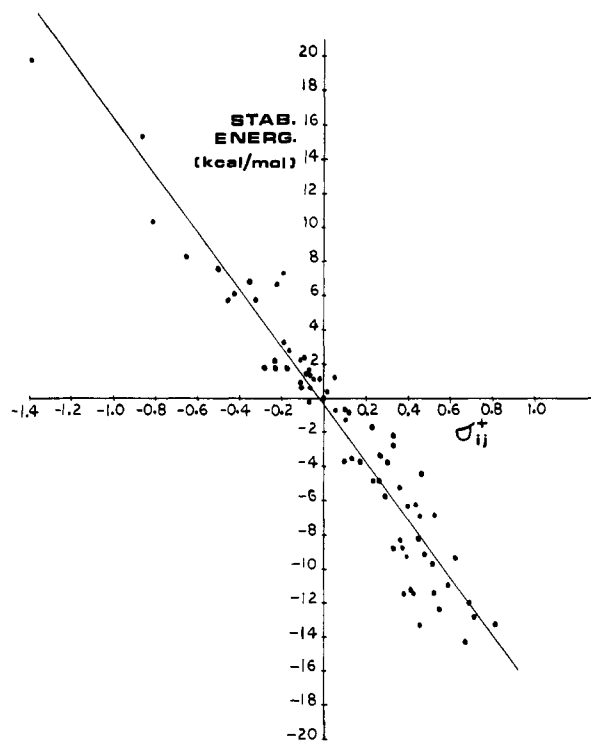


Figure 1. Calculated stabilization energies of naphthylcarbiny cations (Table II) vs. σ_{ij}^+ . Correlation analysis: $n = 72$, $m = -16.78$, $b = -0.46$, $r = -0.9599$.

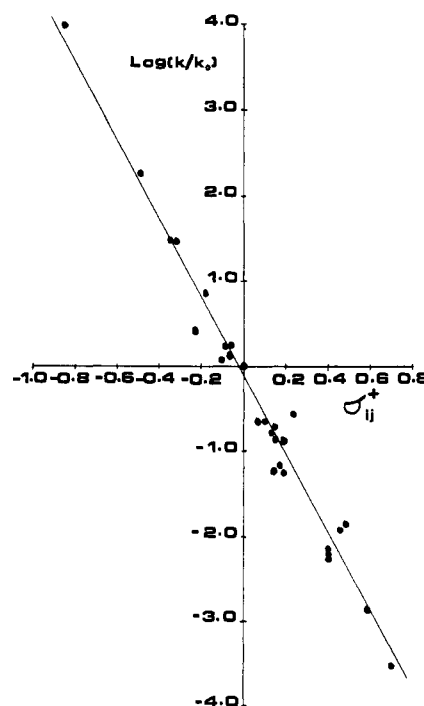


Figure 2. Plot of $\log(k/k_0)$ (solvolysis) for substituted naphthylcarbiny chlorides²⁶⁻²⁸ vs. σ_{ij}^+ . Correlation analysis: $n = 24$, $m = -4.53$, $b = -0.14$, $r = -0.9879$.

differences in molecular structure assumptions, choice of substituent sets, and inadequacies in calculational and correlational methods. If one uses the same set of σ_{ij}^+ (as well as data for Cl, Br, C₂H₅, and CH₃S, based on the same assumptions; see Table III) and uses it to correlate experimental values of $\log(k/k_0)$ (solvolysis) for the naphthylcarbiny series [$n = 24$, actually 1-(1-naphthyl)ethyl chlorides and 1-(2-naphthyl)ethyl chlorides], the results are as follows: slope (identical with ρ), -4.53; intercept, -0.14; correlation coefficient, -0.9879. These data are

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Table V. Correlations of Calculated Stabilization Energies^a of Benzyl Cations vs. σ^+ ,³⁰ Calculated Stabilization Energies of Naphthylcarbinyl Cations (Table II), and Experimental $\log k/k_0$ ²⁶⁻²⁸ vs. σ_{ij}^+ ^a

	<i>n</i>	<i>m</i>	<i>b</i>	<i>r</i>	ρ
benzyl calcd	17	-19.72	0.56	-0.9826	-14.5
naphthyl-carbinyl calcd	72	-16.78	-0.46	-0.9599	-12.3
naphthyl-carbinyl expt	24	-4.53	-0.14	-0.9879	-4.53

^a See Table III.

plotted in Figure 2. The summary of these three data sets is in Table V. Direct comparison of experimental $\log(k/k_0)$ (solvolysis) and calculated stabilization energies affords comparable correlations (Figure 3).

The second general means for examining correlations in the naphthalene series is through dual-parameter treatments.¹⁷ As an example of this approach, the Taft dual substituent parameter (DSP) equation¹⁸ (eq 2) has

$$\log k/k_0 = \sigma_I \rho_I + \sigma_R^+ \rho_R^+ + \gamma \quad (2)$$

been investigated for correlations of experimental and calculated data. One instructive aspect of this equation is its apparent ability to separate inductive and resonance effects. The factor $\lambda (= \rho_R^+ / \rho_I)$ is a measure of the relative importance of these effects at each position.¹⁸ The dual-parameter equation for changes in stabilization energies is given by eq 3. Assumption of negligible differ-

$$\Delta\Delta E = \sigma_I m_I + \sigma_R^+ m_R^+ + \delta \quad (3)$$

ential entropy effects allows one to determine approximate values for ρ_I and ρ_R^+ by dividing m_I and m_R^+ , respectively, by the factor $2.303RT$.

Theoretically calculated values of ρ_I and ρ_R^+ as well as $\lambda (= \rho_R^+ / \rho_I)$ and relative ρ_R^+ [ρ_R^+ (*p*-benzyl) = 1.000 (as-

Table VI. Theoretically Derived DSP Parameters (See Eq 2 and 3) Based on Values of ρ_I and ρ_R^+ from Table V of Ref 18, Stabilization Energies for Naphthylcarbinyl Cations from Table II and Stabilization Energies for Benzyl Cations from Ref 9^a

position	m_I	m_R^+	γ	<i>R</i>	ρ_I	ρ_R^+	λ	rel ρ_R^+	rel ρ_I
meta of benzyl	-21.15	-2.84	0.36	0.9645	-15.51	-2.08	0.134	0.155	1.018
para of benzyl	-20.78	-18.34	0.84	0.9875	-15.24	-13.45	0.883	1.000	1.000
3 α	-18.12	-1.74	0.15	0.9604	-13.29	-1.28	0.096	0.095	0.872
4 α	-18.71	-15.31	0.86	0.9780	-13.72	-11.23	0.818	0.836	0.900
5 α	-11.78	-5.63	0.53	0.9268	-8.64	-4.13	0.478	0.307	0.567
6 α	-13.98	-3.03	0.12	0.9610	-10.25	-2.22	0.217	0.165	0.673
7 α	-14.06	-7.58	0.32	0.9687	-10.31	-5.56	0.539	0.413	0.677
4 β	-15.09	-3.29	0.29	0.9438	-11.07	-2.41	0.218	0.179	0.726
5 β	-13.40	-2.14	0.29	0.9253	-9.83	-1.57	0.160	0.117	0.645
6 β	-14.89	-8.76	0.42	0.9742	-10.92	-6.42	0.588	0.478	0.717
7 β	-13.99	-3.05	0.13	0.9618	-10.26	-2.24	0.218	0.166	0.673
8 β	-10.88	-6.00	0.46	0.9235	-7.98	-4.40	0.551	0.327	0.524

^a Selected same substituents as for naphthylcarbinyl species; eight data points for each correlation.

Table VII. DSP Parameters Derived from Experimental Data^a

position	<i>n</i>	ρ_I	ρ_R^+	δ	<i>R</i>	λ	ρ_I	ρ_R^+
meta of benzyl	4	-5.06	-1.12	0.00	0.9991	0.221	0.894	0.180
para of benzyl	5	-5.66	-6.21	-0.07	0.9996	1.097	1.000	1.000
3 α	5	-5.20	-0.72	0.00	0.9969	0.138	0.919	0.116
4 α	6	-5.21	-5.22	0.02	0.9994	1.002	0.920	0.841
5 α	5	-3.37	-1.21	0.00	0.9946	0.359	0.595	0.195
6 α	4	-2.48	-0.79	-0.03	0.9986	0.320	0.438	0.128
7 α	5	-3.06	-2.16	0.00	0.9948	0.706	0.541	0.348
6 β	5	-3.25	-3.03	-0.02	0.9995	0.932	0.574	0.488
7 β	4	-3.27	-0.97	-0.07	0.9964	0.296	0.578	0.156

^a See ref 26-28; "meta of benzyl" and "para of benzyl" actually correspond to meta and para derivatives of 1-phenylethyl chlorides. Likewise, "naphthylcarbinyl" derivatives are actually substituted 1-(1-naphthyl)ethyl chlorides (e.g., 3 α , 4 α , etc.) or substituted 1-(2-naphthyl)ethyl chlorides (e.g., 4 β , 5 β , etc.). Only substituents whose σ_I and σ_R^+ values are found in Table V of ref 18 are included in these correlations (thus accounting for slight discrepancies with correlations in Table I of ref 32).

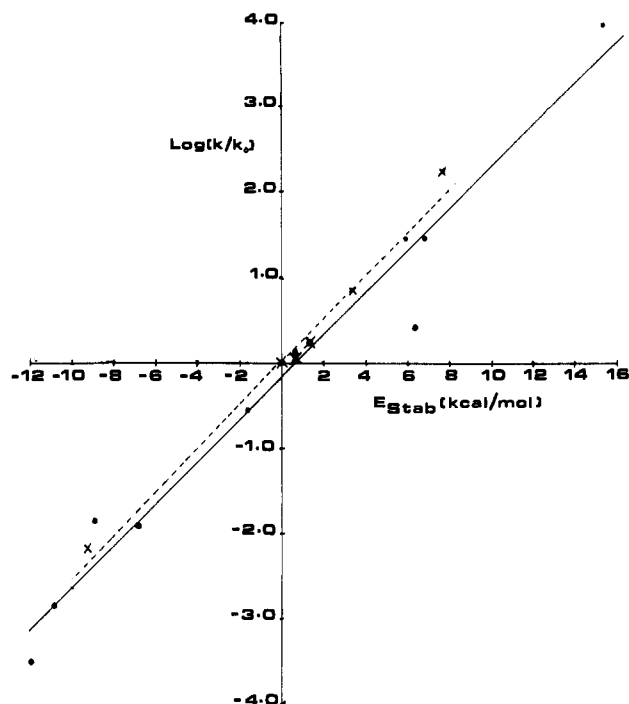


Figure 3. Plots of experimental values of $\log(k/k_0)$ for solvolysis of 1-(1-naphthyl)ethyl chlorides (denoted by \bullet) and 1-(2-naphthyl)ethyl chlorides (denoted by \times), taken from Table V of ref 27, vs. calculated isodesmic stabilization energies of substituted 1- and 2-naphthylcarbinyl cations. The correlation with 1-naphthylcarbinyl cations ($n = 12$, $m = 0.248$, $b = -0.16$, $r = 0.982$) is comparable to that involving 2-naphthylcarbinyl cations ($n = 6$, $m = 0.255$, $b = 0.03$, $r = 0.994$). Taking the two data sets together, one obtains $n = 17$, $m = 0.250$, $b = -0.10$, and $r = 0.983$.

sumed)] values are listed in Table VI. Corresponding experimental values are listed in Table VII. (Similar correlations were made by Forsyth and Sandel;³² see note

Table VIII. Linear Correlations between Theoretical and Experimental ρ_R^+ Values and Two Predictors of Resonance Effects, Δq_{ij} (Ar to ArCH_2^+ , Regional, STO-3G) and ^{13}C Chemical Shift Response Slope a

correlation	<i>n</i>	<i>m</i>	<i>b</i>	<i>r</i>
theor ρ_R^+ vs. Δq_{ij}	12	-72.99	2.04	-0.9831
theor ρ_R^+ vs. ^{13}C response slope	12	-10.87	-0.94	-0.9653
exptl ρ_R^+ vs. Δq_{ij}	9	-34.36	1.12	-0.9756
exptl ρ_R^+ vs. ^{13}C response slope	9	-5.22	-0.27	-0.9825
^{13}C response slope vs. Δq_{ij}	12	6.40	-0.25	0.9715
theor ρ_I vs. Δq_{ij}	12	-19.67	-9.59	-0.4223
theor ρ_I vs. ^{13}C response slope	12	-3.45	-10.21	-0.4884
exptl ρ_I vs. Δq_{ij}	9	-9.33	-3.11	-0.4530
exptl ρ_I vs. ^{13}C response slope	9	-1.67	-3.38	-0.5836

^a The relationship between these two predictors is also examined (see also Figure 3). For comparison, the same four correlations are made with the inductive parameter ρ_I ; it is clear that the resulting correlations are very poor.

in Table VII). A plot of theoretically derived ρ_R^+ values vs. the corresponding experimental values ($n = 9$) gives the following: slope, 2.10; intercept, -0.41; correlation coefficient, 0.9904. Even more to the point, the slope of the theoretically derived relative ρ_R^+ vs. the corresponding experimental value is 0.968 with an intercept of 0.03. Thus, there is good correspondence between resonance effects in the two data sets. However, the correspondence between theoretical and experimental inductive effects is not as good. A plot of theoretical vs. experimental ρ_I has a slope of 1.851, an intercept of -4.50, and a correlation coefficient of 0.8956. A plot of theoretical vs. experimental relative ρ_I has a slope of 0.689 and an intercept of 0.296. A plot of the theoretical vs. the experimental λ value exhibits a slope of 0.750, an intercept of 0.02, and a correlation coefficient of 0.9531. It is clear that the theoretical treatment is only about 75% as sensitive to inductive effects as it is to resonance effects, the latter being adequately calculated. Finally, one should note that double-linear correlation coefficients for experimental and theoretical data cited in this work cannot be strictly compared. The reason is that the number of experimental data points ($n = 4-6$) is much closer to the smallest number ($n = 4$) employable for a meaningful correlation coefficient than is the number of theoretical data points ($n = 8$). Furthermore, measures of goodness of fit such as SD/rms exaggerate these differences.

Correlations of ρ_R^+ with experimental and theoretical parameters have been investigated by Forsyth and Sandel.³² They find their best correlation between ρ_R^+ and the ^{13}C response slope, both experimentally derived data sets. In Table VIII are summarized similar correlations arising from the present study. In this limited study the best correlations are between a pair of theoretically derived parameters, ρ_R^+ (theor) and Δq_{ij} (Ar to ArCH_2^+ , regional, STO-3G), and a pair of experimentally derived parameters, ρ_R^+ (exptl) vs. ^{13}C response slope. Values of theoretical and experimental ρ_R^+ as well as ^{13}C response slopes vs. Δq_{ij} are plotted in Figure 4.

Conclusions

STO-3G calculations treat resonance effects in naphthylcarbonyl cations quite well but appear to underes-

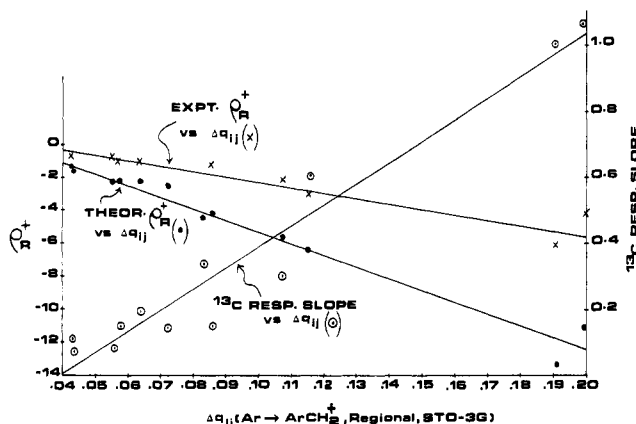


Figure 4. Plots of theoretical and experimental ρ_R^+ and ^{13}C chemical shift response slopes vs. Δq_{ij} (Ar to ArCH_2^+ , regional, STO-3G). The correlation values for the theoretical ρ_R^+ vs. Δq_{ij} are $n = 12$, $m = -72.99$, $b = 2.04$, and $r = -0.9831$. The correlation values for the experimental ρ_R^+ vs. Δq_{ij} are $n = 9$, $m = -34.36$, $b = 1.12$, and $r = -0.9756$. The correlation values for the ^{13}C response slope vs. Δq_{ij} are $n = 12$, $m = 6.40$, $b = -0.25$, and $r = 0.9715$.

timate differential inductive effects. The calculations predict significant substituent effects in altering relative cation stabilities even when these substituents are fairly remote from the reaction center. This calculational approach may aid in the understanding of bioreactivities of polycyclic aromatic hydrocarbons (PAHs). Additional calculations can be performed on higher homologues such as anthracylcarbonyl and phenanthrylcarbonyl cations. Combining these data with calculational data on benzyl and naphthylcarbonyl cations should allow one to generate a gas-phase ρ value corresponding to Streitwieser's σ^+ scale³ for various substituted PAHs (e.g., 3-phenanthryl, 4-pyrenyl, etc.). This will allow the placement of substituted PAHs on the same scale.

Acknowledgment. We thank Professor Joel F. Liebman for useful discussions and Mr. Mathew Friedman for some calculational work.

Registry No. 1, 25414-97-5; 1 3- CH_3 , 81970-37-8; 1 4- CH_3 , 81970-38-9; 1 5- CH_3 , 81970-39-0; 1 6- CH_3 , 81970-40-3; 1 7- CH_3 , 81970-41-4; 1 3-F, 81970-42-5; 1 4-F, 81970-43-6; 1 5-F, 81970-44-7; 1 6-F, 81970-45-8; 1 7-F, 81987-36-2; 1 3- CF_3 , 81970-46-9; 1 4- CF_3 , 81970-47-0; 1 5- CF_3 , 81970-48-1; 1 6- CF_3 , 81970-49-2; 1 7- CF_3 , 81970-50-5; 1 3-CN, 81970-51-6; 4-CN, 81970-52-7; 1 5-CN, 81970-53-8; 1 6-CN, 81970-54-9; 1 7-CN, 81970-55-0; 1 3- CH_3O , 81970-56-1; 1 4- CH_3O , 81970-57-2; 1 5- CH_3O , 81970-58-3; 1 6- CH_3O , 81970-59-4; 1 7- CH_3O , 81970-60-7; 1 3- NH_2 , 81970-61-8; 1 4- NH_2 , 81970-62-9; 1 5- NH_2 , 81970-63-0; 1 6- NH_2 , 81970-64-1; 1 7- NH_2 , 81970-65-2; 1 3 NO_2 , 81970-66-3; 1 4- NO_2 , 81970-67-4; 1 5- NO_2 , 81970-68-5; 1 6- NO_2 , 81970-69-6; 1 7- NO_2 , 81970-70-9; 2, 25415-01-4; 2 4- CH_3 , 81970-71-0; 2 5- CH_3 , 81970-72-1; 2 6- CH_3 , 81970-73-2; 2 7- CH_3 , 81970-74-3; 2 8- CH_3 , 81970-75-4; 2 4-F, 81970-76-5; 2 5-F, 81970-77-6; 2 6-F, 81970-78-7; 2 7-F, 81970-79-8; 2 8-F, 81970-80-1; 2 4- CF_3 , 81970-81-2; 2 5- CF_3 , 81970-82-3; 2 6- CF_3 , 81970-83-4; 2 7- CF_3 , 81970-84-5; 2 8- CF_3 , 81970-85-6; 2 4-CN, 81970-86-7; 2 5-CN, 81970-87-8; 2 6-CN, 81970-88-9; 2 7-CN, 81987-37-3; 2 8-CN, 81970-89-0; 2 4- CH_3O , 81970-90-3; 2 5- CH_3O , 81970-91-4; 2 6- CH_3O , 81970-92-5; 2 7- CH_3O , 81970-93-6; 2 8- CH_3O , 81970-94-7; 2 4- NH_2 , 81970-95-8; 2 5- NH_2 , 81970-96-9; 2 6- NH_2 , 81970-97-0; 2 7- NH_2 , 81970-98-1; 2 8- NH_2 , 81970-99-2; 2 4- NO_2 , 81971-00-8; 2 5- NO_2 , 81971-01-9; 2 6- NO_2 , 81971-02-0; 2 7- NO_2 , 81971-03-1; 2 8- NO_2 , 81971-04-2; naphthalene, 91-20-3; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; 1-fluoronaphthalene, 321-38-0; 2-fluoronaphthalene, 323-09-1; 1-(trifluoromethyl)naphthalene, 26458-04-8; 2-(trifluoromethyl)naphthalene, 581-90-8; 1-naphthalenecarbonitrile, 86-53-3; 2-naphthalenecarbonitrile, 613-46-7; 1-methoxynaphthalene, 2216-69-5; 2-methoxynaphthalene, 93-04-9; 1-naphthalenamine, 134-32-7; 2-naphthalenamine, 91-59-8; 1-nitronaphthalene, 86-57-7; 2-nitronaphthalene, 581-89-5.