

Theoretical studies on empirical structure–reactivity relationship: the Yukawa–Tsuno equation

Kazuhide Nakata,¹ Mizue Fujio,^{2*} Kichisuke Nishimoto³ and Yuho Tsuno²

¹Science Research Center, Hosei University, Fujimi, Chiyoda-ku, Tokyo 102-8160, Japan

²Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

³Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho Okayama 700-0005, Japan

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ABSTRACT: The substituent-dependent stabilization energies ($\delta_X\Delta E$) of a series of α,α -R₁R₂ benzyl cations were determined by means of *ab initio* calculation at the MP2/6–31G*//RHF/6–31G* + ZPE (scaled 0.8929) level, based on the isodesmic hydride transfer reactions between ring X-substituted and unsubstituted R₁R₂ benzyl cations. Substituent stabilities ($\delta_X\Delta E$) of α,α -dimethylbenzyl cations were determined in the same way, to define a reference set of the *ab initio* σ^+ values. The ($\delta_X\Delta E$) of α,α -dimethylbenzyl cations of which the cation center is set orthogonal to the benzene π -system were correlated linearly with σ^0 (solution). Based on this correlation, a set of *ab initio* σ^0 constants [$(\sigma^0)_{ab}$] was determined. The *ab initio* resonance substituent constants ($\Delta\bar{\sigma}_R^+$)_{ab} were defined as $(\sigma^+)_{ab} - (\sigma^0)_{ab}$. Employing the present *ab initio* set of $(\sigma^0)_{ab}$ and ($\Delta\bar{\sigma}_R^+$)_{ab} constants, the *ab initio* Yukawa–Tsuno (Y–T) equation was applied to 18 sets of cation stabilities $\delta_X\Delta E$ associated with hydride transfer reaction systems. Successful applications of the *ab initio* Y–T equation confirm the theoretical validity of the empirical Y–T relationship; in practice, the Y–T equation makes it possible to divide the electronic substituent effect into the non-resonance and resonance contributions. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: Yukawa–Tsuno equation; substituent effects; *ab initio* calculation; benzyl cations; hydride transfer reaction

INTRODUCTION

The linear free energy relationship (LFER)¹ is an extremely useful tool in the exploration of reaction mechanisms in a wide variety of situations. In particular, the Yukawa–Tsuno (Y–T) equation [Eqn. (1)]^{2–5} is one of the most useful tool to predict the characteristics of a transition state whose reaction center is affected by an aromatic system.

$$\log(k/k_0) \text{ or } \log(K/K_0) = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+) \quad (1)$$

where k (or K) is the rate (or equilibrium) constant for a given reaction of a ring-substituted derivative and k_0 (or K_0) is the corresponding value for the unsubstituted compound. σ^0 is the normal substituent constant⁴ which is thought to be free from any additional π -electronic interaction between the substituent and the reaction center. $\Delta\bar{\sigma}_R^+$ ($\equiv \sigma^+ - \sigma^0$) is the resonance substituent constant to measure the capability for π -delocalization of π -electron donor p -substituents.

The empirical Y–T equation [Eqn. (1)] has been

applied to a wide variety of reactions and equilibria,^{3–5} all showing excellent linear correlations. In the present analysis, for simplicity, we will deal with closely limited reaction systems, the equilibria of benzyl cation formation. The structures of the cations studied here and their abbreviations are summarized in Table 1. The corresponding solvolyses (except artificial cations of **2**, **16** and **17**) were confirmed to show excellent linearity in analyses with Eqn. (1), giving significant reaction constants (ρ and r values). The resultant ρ and r values are used to estimate transition state structures or to characterize the intermediate cation species. Hence it is necessary to make clear the physical meanings of these reaction constants in order to employ Eqn. (1) effectively. The r value, called the resonance demand, is discussed as a measure of the degree of resonance interaction between the carbocation center and benzene π -system.⁶ The change in ρ value for a given reaction may provide important information regarding the position of the transition state along the reaction coordinate. The behavior of the ρ value becomes more complex with the inclusion of the effects of solvent, temperature and leaving group. In order to make clear the physical meaning of the susceptibility parameters ρ and r , it is necessary to obtain these values on the stabilities of corresponding cations in the gas phase where the aforementioned interfering effects are completely ex-

*Correspondence to: M. Fujio, Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan.

E-mail: fujio@ms.ifoc.kyushu-u.ac.jp

Table 1. Numbering of reaction systems and corresponding α -substituents

[n] ^a	R ₁ ^a	R ₂ ^a
1	CH ₃	CH ₃
2	CH ₃	CH ₃ (90°) ^b
3	CF ₃	CF ₃
4	CF ₃	CN
5	CF ₃	H
6	CF ₃	CH ₃
7	H	H
8	CH ₃	H
9	CF ₃	OH
10	COOH	OH
11	H	OH
12	CH ₃	OH
13	CH ₃ O	OH
14	NH ₂	OH
15	N(CH ₃) ₂	OH
16	H	H (90°) ^b
17	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉ (90°) ^b
18	Benzobicyclo ^c	

^a Refer to Eqn. (2).

^b The R₁—C₇—R₂ plane is fixed orthogonal to the benzene (C₁—C₆) plane ($\phi = 90^\circ$). Refer to Chart 1 for numbering of atoms.

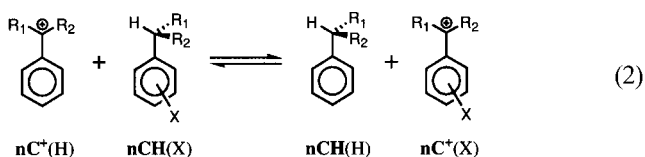
^c 4-Methylbenzobicyclo[2.2.2]octen-1-yl system.

cluded. Such an approach will also confirm the correctness of Eqn. (1).

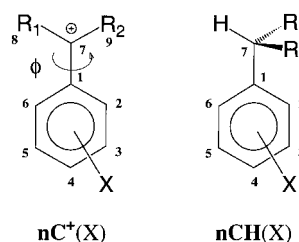
Although the experimental data on the thermodynamic stabilities of benzyl cations in the gas phase are widely available from our ion cyclotron resonance determinations,⁷ the substituents involved are limited because of experimental difficulties in the ICR ion formation and also in the preparation of appropriate compounds. In recent years, *ab initio* calculations have provided reasonable results on the optimized geometries and the relative energies of organic compounds.^{6,8,9} Thus, using advanced MO calculations, we have obtained a wide set of substituent stabilization energies $\delta_X \Delta E$ for various benzyl cations (\mathbf{nC}^+). The two sets of substituent parameters essential to the Y–T correlation are also derived from theoretical, substituent-induced stabilization energies based on the *ab initio* calculation. Substituent effect analyses for systems having different degree of resonance were carried out in order to inspect the validity of the Y–T equation.

METHOD

All reaction systems examined in this study are hydride transfer equilibria as shown in Eqn. (2):



The [n] represents respective reaction systems examined where R₁ and R₂ are their 18 sets of paired α -substituents as summarized in Table 1. Numberings of atoms for benzyl cations and corresponding neutral species are shown in Chart 1. The letters in parentheses (X) denote

**Chart 1**

18 different ring substituents that are selected in a wide variety of electronic features from *p*-Me₂N to *p*-NO₂. \mathbf{nC}^+ represents a benzyl cation where the benzyl hydrogen atom is removed as a hydride ion from the corresponding neutral species \mathbf{nCH} . Equation (2) comprises hydride transfer equilibria between *para*- or *meta*-substituted α -R₁, α -R₂-benzyl cations [$\mathbf{nC}^+(\text{X})$] and the unsubstituted form [$\mathbf{nC}^+(\text{H})$]. The relative stability $\delta_X \Delta E_{\mathbf{nC}^+(\text{X})}$ of a cationic derivative [$\mathbf{nC}^+(\text{X})$] in a reaction system **n** is determined as

$$\begin{aligned}
 \delta_X \Delta E_{\mathbf{nC}^+(\text{X})} &= E_{\mathbf{nC}^+(\text{X})} + E_{\mathbf{nCH}(\text{H})} - E_{\mathbf{nC}^+(\text{H})} \\
 &\quad - E_{\mathbf{nCH}(\text{X})} \quad (3)
 \end{aligned}$$

where all the *E* values are the electronic energies of respective species calculated by means of the *ab initio* method. The substituent stabilization energies $\delta_X \Delta E_{\mathbf{nC}^+(\text{X})}$ of respective benzyl cations \mathbf{nC}^+ systems are subjected to substituent effect analysis and also to the determination of *ab initio* substituent constants.

All calculations were performed on a Digital UNIX workstation with the Gaussian 98 suite of programs.¹⁰ The geometries of all species were optimized at the RHF/3–21G and RHF/6–31G* levels. Using the RHF/6–31G* optimized structure, frequency calculations were performed at the same level in order to confirm the structures being minima and to obtain zero point energies (ZPEs). To improve the calculated energies, electron-correlation contributions were estimated by means of a perturbation theory and a hybrid density-functional theory; single-point calculations of the Møller–Plesset correlation energy correction truncated at the second order (MP2)¹¹ and Becke's three-parameter hybrid method using the LYP correlation functional (B3LYP)¹² were carried out at the 6–31G* basis set. The respective energies were corrected for RHF/6–31G* ZPE differences scaled by a factor of 0.8929.^{13,14}

For comparison, geometries were further optimized at the B3LYP/6–31G* level for α,α -dimethylbenzyl system [1]. ZPE corrections and thermal corrections to Gibbs

free energies were applied to obtained energies with an appropriate scaling factor of 0.9804^{13,14} performing the frequency calculations at the same level.

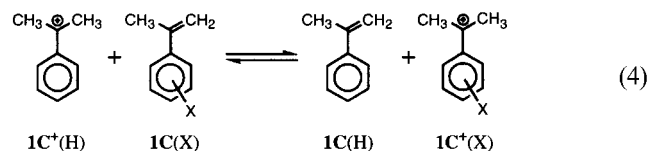
RESULTS AND DISCUSSION

Optimization

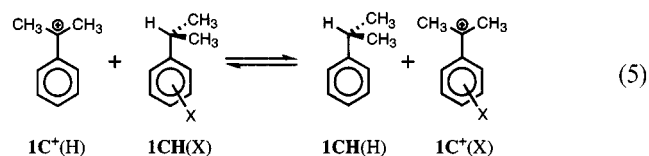
All possible conformations of the geometrical variety of the ring substituents and side chains were optimized for all species. The energies of the most stable conformers (global minima) were used in this study. For all benzyl species (**1**–**18**), serious differences in geometries are not observed in a variety of calculation levels. For all species except for 90°-fixed cations (**2C**⁺, **16C**⁺ and **17C**⁺), no imaginary frequencies are observed in frequency calculations at both the RHF/6–31G* and B3LYP/6–31G* levels, confirming minimum energy structures of these species. For 90°-fixed benzyl cations, atoms forming the benzene ring and C₇ are set in a plane that is fixed orthogonal to the R₁–C₇–R₂ plane. The TS optimization calculation on the rotation of the C₁–C₇ bond for the unsubstituted α,α -dimethylbenzyl cation gave the same energy and geometry as that in **2C**⁺(H). The same procedure for all derivatives should result in 90°-fixed benzylic cations. As a result, one imaginary frequency was observed with the Hartree–Fock (HF) theory for almost all derivatives. The vibrational modes concerned are those of the rotation of R₁–C₇–R₂ planes around the C₁–C₇ bonds. These structures should correspond to the transition states in the rotation of α -substituents of the benzyl cations. These 90°-fixed cation systems look appropriate as the least stable rotational isomer with no resonance interaction between cationic center C₇ and aromatic ring. For some ring-substituted derivatives of these systems, two imaginary frequencies whose modes are the rotation of R₁–C₇–R₂ planes and substituents were observed at the RHF/6–31G* level. It may be due to the symmetry element. For another few derivatives in **17C**⁺, no imaginary frequencies were observed. This may be due to steric factors. In **2C**⁺, the structures were the same as those obtained at the B3LYP/6–31G* level, and the frequency calculations at the same level gave one imaginary frequency for all derivatives. As described later, relative energies ($\delta_X\Delta E$) calculated at the satisfactory levels agree with one another regardless of the theory (HF and DFT). Thus, the obtained energies and also structures for these derivatives should be identical with those of the corresponding cation transition states (unpublished results), where any type of resonance effects are absent. Accordingly, we can use these 90°-fixed cations as theoretically acceptable model compounds that have no resonance stabilization at any calculation level.

In order to check the validity of the calculation level adopted, stabilization energies of **1C**⁺(X) were also

determined by the isodesmic proton transfer reaction [Eqn. (4)] that can be directly compared with the experimental data. Relative stabilization energies were determined in the same manner with Eqn. (3).



The results are listed in Table 2, together with those from the gas-phase (ICR) experiment.^{7f,15} Data for *p*-OH and *p*-NO₂ derivatives are not available owing to experimental difficulties.^{7f} In order to examine the applicability of the calculation levels for reproducing the experimental data, calculated stabilization energies at the respective calculation levels were compared with the experimental values.^{7f} These values appear to be in good agreement with the experimental values for a whole range at any calculation level. The results of linear regression analyses for these data are summarized in Table 3. In all these analyses, the stability of the *p*-NH₂ derivative was calculated to be slightly higher than the observed value, owing to some experimental difficulties. A good linear relationship was obtained without the *p*-NH₂ derivative. The correlation for the data calculated at the RHF/3–21G level is the worst in these analyses with respect to both correlation coefficient (*R*) and standard deviation (SD). For *m*-CH₃O derivative, MP2 and B3LYP calculation including the electron correlation effect improves the reproducibility of the experimental data significantly. A similar improvement was also observed for *p*-Cl and less stable derivatives. All calculation methods considering the electron correlation provide excellent statistical results^{7h} with *R* > 0.995. In these calculations, the MP2/6–31G*//RHF/6–31G* + ZPE level is the most time-saving method which can be considered appropriate to use in the present work. The $\delta_X\Delta E_{\text{nC}^+}$ values are calculated at the same level for the isodesmic reaction of cumyl cations [**1**] comprising hydride transfer equilibria in Eqn. (5).



The $\delta_X\Delta E_{\text{nC}^+}$ results (in Table 4) are essentially identical with the values calculated for the proton transfer equilibria in Eqn. (4).

The plot of data calculated with Eqn. (4) at this level against the corresponding ICR data is shown in Fig. 1. The slope of the plot is larger than unity (1.15), which does not depend on the calculation level of both theory and basis sets. This may be derived from experimental

Table 2. Energy change of isodesmic reaction [Eqn. (4)] of [1] in kcal mol⁻¹

Substituent (X)	$\delta_X \Delta E$					$\delta_X \Delta G^0$	Exptl ^d
	RHF/3-21G		MP2/6-31G*// RHF/6-31G* ^a	B3LYP/6-31G*// RHF/6-31G* ^a	B3LYP/6-31G* ^b		
	RHF/6-31G* ^a			B3LYP/6-31G* ^c			
<i>p</i> -NMe ₂	26.12	23.74	24.97	24.30	24.59	24.55	23.0
<i>p</i> -NH ₂	22.43	19.60	19.22	19.77	20.08	19.36	15.1
<i>p</i> -MeO	11.64	11.67	11.48	12.11	12.24	12.20	10.5
<i>p</i> -OH	8.16	8.74	8.24	9.26	9.31	9.09	
<i>p,m</i> -Me ₂	6.18	5.86	6.48	6.76	6.97	7.05	5.1
<i>p</i> -OMe, <i>m</i> -Cl	4.39	5.72	6.45	7.31	7.48	7.43	6.7
<i>p</i> -Me	5.05	4.86	4.44	5.01	5.10	4.96	4.1
<i>m</i> -MeO	-0.59	-0.63	2.56	2.44	2.33	2.69	2.1
<i>m</i> -Me	1.57	1.35	2.30	2.23	2.24	1.60	1.8
H	0.00	0.00	0.00	0.00	0.00	0.00	0.0
<i>p</i> -F	-3.12	-0.86	-1.01	0.03	0.02	-0.44	-0.1
<i>p</i> -Cl	-6.91	-3.87	-1.98	-1.57	-1.76	-2.22	-0.4
<i>m</i> -F	-7.94	-6.85	-4.93	-4.60	-4.79	-4.91	-5.1
<i>m</i> -Cl	-8.35	-6.73	-5.80	-5.53	-5.63	-5.65	-4.7
<i>m</i> -CF ₃	-9.79	-7.59	-8.18	-7.08	-7.07	-6.94	-6.3
<i>p</i> -CF ₃	-12.96	-9.77	-8.64	-8.00	-8.04	-7.81	-7.2
<i>p</i> -CN	-12.70	-13.53	-11.18	-11.21	-11.02	-11.25	-9.5
<i>p</i> -NO ₂	-18.99	-17.67	-13.18	-14.71	-14.47	-14.29	(-8.4) ^e

^{a,b} Included zero point energy correction. ZPEs are calculated at the RHF/6-31G* level for (a) and the B3LYP/6-31G* level for (b) which are scaled 0.8929 and 0.9804, respectively.

^c Thermal correction to Gibbs free energy was applied.

^d Ref. 7f and 15 and references cited therein.

^e Protonation occurred on the substituent nitro group.

data, or the calculations at the present levels overestimate the interaction between the substituent and the C⁺ center. In any case, a comparison of the calculated stabilities between some cation series is beneficial, because the common factors involved in these calculations should cancel out.

The cation stabilization energies $\Delta E_{n\text{C}^+}$ for various benzyl systems (**1**–**18**) were calculated at the MP2/6-31G*//RHF/6-31G* + ZPE level. The substituent stabilization energies $\delta_X \Delta E_{n\text{C}^+}$, or in short $\delta_X \Delta E$, were calculated by means of Eqn. (3), and are listed in Tables 4 and 5. For these energy values, $\delta_X \Delta E$, a positive value

indicates increasing stabilization and a negative value decreasing stabilization.

Substituent stabilization energies, $\delta_X \Delta E$

A simple linear substituent effect correlation [Eqn. (6)] was examined for application to sets of $\delta_X \Delta E$ for the respective cations **n** = [**2**]–[**18**] with reference to $\delta_X \Delta E$ for the cumyl cation **1C**⁺, on which the definition of the Brown σ^+ (solution) constants was based.

$$\delta_X \Delta E_{n\text{C}^+} = \lambda(\delta_X \Delta E_{1\text{C}^+}) + c \quad (6),$$

where λ is the susceptibility parameter referred to the relative ratio of ρ^+ for cation **nC**⁺ to **1C**⁺. The correlation results are shown in Table 6.

The λ value changes significantly from cation to cation, but the correlations [Eqn. (6)] for all the X substituents are mostly unsatisfactory. Nevertheless, Eqn. (6) holds precisely for the so-called *non-resonance substituents*, i.e. all *meta*-substituents and *p*- π -acceptors, with a parameter λ_{nr} based on *non resonance* substituents in all the cation sets.

As a result, it is confirmed that substituent effects ($\delta_X \Delta E$) for various benzyl cation systems cannot be described by any single set of substituent constants, such as σ^+ or σ^0 .

In Fig. 2, $(\delta_X \Delta E_{n\text{C}^+})/\lambda_{nr}$ values for the respective

Table 3. Results of linear regression analysis for $\delta_X \Delta E_{\text{calcd}}$ or $\delta_X \Delta G^0_{\text{calcd}}$ against $\delta_X \Delta G^0_{\text{exptl}}$ ^a

Theory level	<i>a</i>	<i>b</i>	<i>R</i>	SD
RHF/3-21G	1.32	-1.95	0.982	2.24
RHF/6-31G* + ZPE	1.18	-1.16	0.990	1.47
MP2/6-31G*//RHF/6-31G* + ZPE	1.15	-0.26	0.996	0.93
B3LYP/6-31G*//RHF/6-31G* + ZPE	1.13	0.14	0.995	1.00
B3LYP/6-31G* + ZPE	1.15	0.16	0.995	1.03
B3LYP/6-31G* + TC ^b	1.14	0.04	0.995	1.00

^a For Eqn. (4). Least-squares method was applied for $\delta_X \Delta E_{\text{calcd}}$ or $\delta_X \Delta G^0_{\text{calcd}} = a(\delta_X \Delta G^0_{\text{exptl}}) + b$. *R* and SD are correlation coefficient and standard deviation, respectively.

^b ZPE correlations and thermal corrections to Gibbs free energy were applied (see text).

Table 4. $\delta_X\Delta E$ for various benzyl cation systems (1–9)^a

Substituent (X)	$\delta_X\Delta E^b$ (kcal mol ⁻¹)								
	1	2	3	4	5	6	7	8	9
<i>p</i> -NMe ₂	25.35	7.25	39.23	38.66	36.27	31.70	33.02	28.42	25.41
<i>p</i> -NH ₂	19.53	4.91	30.55	29.82	28.42	24.52	25.96	22.12	19.22
<i>p</i> -MeO	11.66	2.51	19.52	19.00	17.96	15.31	16.28	13.61	11.47
<i>p</i> -OH	8.40	0.90	14.48	13.91	13.32	11.22	12.07	9.88	8.00
<i>p,m</i> -Me ₂	6.61	3.23	9.73	9.75	9.36	8.09	8.70	7.46	6.68
<i>p</i> -OMe, <i>m</i> -Cl	6.42	-1.36	14.26	14.06	12.40	10.11	10.26	8.11	6.67
<i>p</i> -Me	4.59	1.76	7.20	6.99	6.68	5.74	6.21	5.17	4.50
<i>m</i> -MeO	2.67	2.45	4.01	4.54	4.64	3.52	3.80	3.43	2.84
<i>m</i> -Me	2.42	1.66	3.15	3.33	3.24	2.82	3.16	2.70	2.48
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>p</i> -F	-1.04	-3.50	1.09	0.86	0.45	-0.12	-0.13	-0.68	-1.22
<i>p</i> -Cl	-2.04	-4.26	0.94	1.06	-0.11	-0.74	-1.19	-1.73	-1.86
<i>m</i> -F	-5.09	-4.14	-6.00	-5.58	-6.05	-5.42	-6.35	-5.40	-4.94
<i>m</i> -Cl	-6.02	-4.67	-6.31	-5.86	-6.55	-6.07	-7.12	-6.38	-5.57
<i>m</i> -CF ₃	-8.44	-6.70	-8.95	-8.71	-9.40	-8.56	-9.83	-8.99	-8.02
<i>p</i> -CF ₃	-8.82	-6.80	-9.46	-9.05	-9.86	-9.07	-10.29	-9.48	-8.34
<i>p</i> -CN	-11.41	-9.74	-11.21	-10.61	-11.99	-11.29	-12.86	-12.04	-10.81
<i>p</i> -NO ₂	-13.42	-10.54	-14.33	-13.63	-14.99	-13.76	-15.69	-14.32	-12.76

^a Energy changes in hydride transfer equilibria of Eqn. (2). See Table 1 for reaction number (n).

^b Calculated at the MP2/6-31G**//RHF/6-31G* + ZPE (scaled 0.8929) level.

benzyl cation systems [1]–[18] are plotted against $\delta_X\Delta E_{1C^+}$ values for cumyl cations $1C^+$. Plots of *non-resonance* (*meta* and *p*- π -acceptors) substituents fall on a single correlation line with a slope of unity for all cation systems. Plots of *p*- π -donor substituents display significant deviations from the unit-slope correlation line.

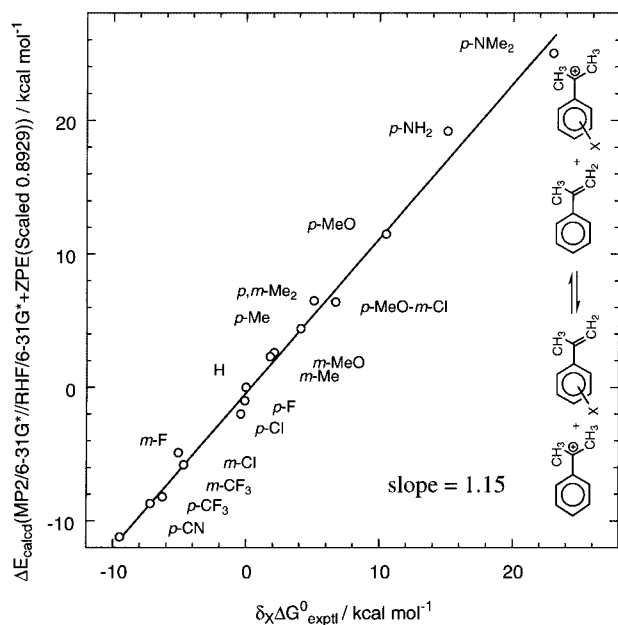


Figure 1. Calculated $\delta_X\Delta E$ vs experimental $\delta_X\Delta G^0$ for the reaction Eqn. (4) of [1], giving $\delta_X\Delta E_{\text{calcd}} = 1.15(\delta_X\Delta G^0_{\text{exptl}}) - 0.26$, with correlation coefficient $R = 0.996$

The *ab initio* σ^0 constant

Earlier, we pointed out¹⁶ that solvolysis rates of benzo-bicyclo[2.2.2]octen-1-yl triflates (**18OTf**) are excellently correlated with σ^0 . The transition state or the intermediate of this solvolysis should be simulated by the benzo-bicyclo[2.2.2]octen-1-yl cation (**18C⁺**) in which the cationic $2p\pi$ -orbital is fixed orthogonal to neighboring benzene ring. Thus, the relative reactivities or the relative cation stabilities of the [18] set can be an appropriate reference set of σ^0 . The 90° -fixed cations (**2C⁺**, **16C⁺** and **17C⁺**) are theoretical models of **18C⁺**, which can also be reference systems for σ^0 . Relative substituent stabilities ($\delta_X\Delta E$) of **2C⁺**, **16C⁺** and **17C⁺** are plotted against $\delta_X\Delta E$ of **18C⁺** in Fig. 3 for comparison.

For the 90° -fixed α,α -dimethylbenzyl system [2], plots (closed circles) of $\delta_X\Delta E$ for *non-resonance* groups against those for [18] are correlated linearly with a slope of 1.05. It is most important that plots of *para* electron-donating groups (open circles) are also involved in the same correlation. This shows that the substituent effect on $\delta_X\Delta E$ for reaction [2] is the same as that in [18]. The orthogonal cationic center is positioned neighboring the aryl moiety so that the aryl polar effects of substituents remain essentially the same while any resonance stabilization is absent. For relative substituent stabilities ($\delta_X\Delta E$) of other 90° -fixed systems [16] and [17], the same substituent effects were observed. All these systems are appropriate reference systems to define σ^0 .

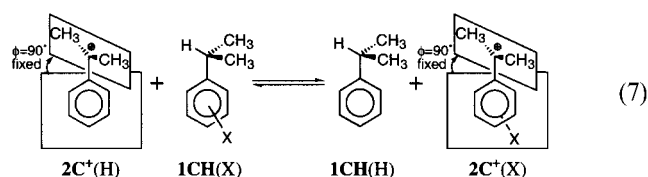
In this study, the isodesmic reaction [Eqn. (7)] of [2] is taken here as the reference system for σ^0 , since the corresponding coplanar cation system was taken as the

Table 5. $\delta_X\Delta E$ for various benzyl cation systems (10–18)^a

Substituent (X)	$\delta_X\Delta E^b$ (kcal mol ⁻¹)								
	10	11	12	13	14	15	16	17	18
<i>p</i> -NMe ₂	24.64	22.85	20.18	14.84	12.55	9.58	9.33	6.01	6.27
<i>p</i> -NH ₂	18.75	17.39	15.18	10.75	8.84	6.74	6.49	4.00	4.13
<i>p</i> -MeO	11.02	10.34	8.78	6.10	4.89	3.61	3.35	2.02	2.34
<i>p</i> -OH	7.81	7.18	6.01	3.75	2.70	1.85	1.27	0.66	0.87
<i>p,m</i> -Me ₂	6.43	6.23	5.46	4.56	4.25	3.40	4.41	2.64	2.85
<i>p</i> -OMe, <i>m</i> -Cl	6.17	5.34	4.03	1.77	0.75	-0.06	-1.35	-1.31	-2.00
<i>p</i> -Me	4.29	4.16	3.62	2.77	2.51	1.97	2.41	1.46	1.50
<i>m</i> -MeO	2.85	2.82	2.14	2.27	2.77	2.05	2.96	2.05	2.09
<i>m</i> -Me	2.41	2.46	2.11	2.02	1.98	1.60	2.36	1.32	1.54
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>p</i> -F	-1.07	-1.45	-1.64	-2.67	-3.03	-2.94	-4.24	-3.07	-3.49
<i>p</i> -Cl	-1.85	-2.37	-2.55	-3.40	-3.79	-3.72	-4.90	-3.79	-4.28
<i>m</i> -F	-4.73	-4.96	-4.57	-4.24	-4.23	-3.80	-5.13	-3.52	-3.79
<i>m</i> -Cl	-5.50	-5.78	-5.41	-5.02	-4.92	-4.39	-5.59	-4.04	-4.59
<i>m</i> -CF ₃	-8.06	-8.22	-7.44	-7.29	-7.12	-6.33	-7.86	-5.84	-6.57
<i>p</i> -CF ₃	-7.65	-8.45	-7.78	-7.38	-7.24	-6.55	-7.91	-6.03	-6.47
<i>p</i> -CN	-10.63	-11.03	-10.39	-10.09	-10.27	-9.32	-11.38	-8.63	-9.42
<i>p</i> -NO ₂	-12.44	-12.82	-11.90	-11.18	-11.28	-10.12	-12.38	-9.30	-10.11

^{a,b} See footnotes a and b in Table 4.

reference system to define σ^+ experimentally in the gas phase.



In Fig. 4, $\delta_X\Delta E$ for reaction [2] are plotted against *expl* (σ^0)_{soln} constants.⁴ A fairly good correlation for the whole substituents exists ($R = 0.980$ and $SD = \pm 1.03$). In detail, plots of the non-resonance substituents, *m*-CH₃, H, *m*-F, *m*-Cl, *m*-CF₃, *p*-CF₃ and *p*-NO₂, fall on a linear correlation with a slope (ρ_m) of -13.7 , $R = 0.997$ and $SD = \pm 0.38$. *Para* electron-donating substituents are also on the ρ_m line, giving comparable apparent σ^0 values with solution-phase *expl* (σ^0)_{soln} constants. The plot for the *p*-OH derivative shows a marked downward deviation, which may be caused by the strong hydrogen bonding of solvent molecules with substituents.^{7f} The considerable upward deviation for the *m*-CH₃O derivative may be due to the polarizability effect, which is not significant in solution.^{7f} Using the correlation result, the apparent substituent constants of this reaction were calculated. The obtained *ab initio* σ^0 values, (σ^0)_{ab}, are listed in Table 7. The resulting constants are generally identical with the experimental (σ^0)_{soln} values^{4,17} for common substituents.

The *ab initio* resonance substituent constant ($\Delta\sigma_R^+$)_{ab}

In Fig. 5, calculated values of $\delta_X\Delta E$ for Eqn. (5) are plotted against the Brown σ^+ (solution value).¹⁸ The plots for a few substituents seem to deviate irregularly from the correlation line. The deviations for the *p*-OH and *m*-CH₃O derivatives may be attributed to the specific solvation of the substituents. There is a good correlation for the other substituents over a wide range of ca 40 kcal mol⁻¹ (1 kcal = 4.184 kJ); the degree of resonance between the cationic center and the benzene π -system in this equilibrium is comparable to the experimental reference system for σ^+ , the solvolysis of α,α -dimethylbenzyl chlorides.¹⁸ Despite significant deviations of several particular substituents in the plot against solution (σ^+)_{soln}, in the *ab initio* $\delta_X\Delta E_{nC^+}$ vs $\delta_X\Delta E_{1C^+}$ correlation, all the non-resonance substituents show a precise linear dependence. Thus, the *ab initio* (σ^0)_{ab} was defined as above, and the *non-resonance* correlation $\rho_m = -16.9$ for $1C^+$ was determined based thereon. Using this ρ_m value, a set of *ab initio* σ^+ values, (σ^+)_{ab}, was estimated from the $\delta_X\Delta E$, and then a set of theoretical resonance substituent parameters ($\Delta\sigma_R^+$)_{ab} were defined as (σ^+)_{ab} - (σ^0)_{ab} (Table 7).

Optimized geometries and charge distributions

In the present study, the cumyl cations $1C^+$ and their orthogonal (90°-fixed) cations system were taken as the reference cation systems to define $r = 0$ and 1.00.

Table 6. Results of linear regression analysis for $\delta_X\Delta E$ for various benzyl cation systems against that for α,α -dimethylbenzyl cations^a

Reaction [n]		λ	c	R^c
1	whole	1	0	1
	non-resonance ^b	1	0	1
2	whole	0.453	-2.29	0.9287
	non-resonance ^b	0.805	0.03	0.9981
3	whole	1.394	2.45	0.9932
	non-resonance ^b	1.095	0.40	0.9968
4	whole	1.357	2.55	0.9931
	non-resonance ^b	1.073	0.64	0.9950
5	whole	1.336	1.77	0.9969
	non-resonance ^b	1.163	0.52	0.9969
6	whole	1.178	1.17	0.9980
	non-resonance ^b	1.047	0.24	0.9991
7	whole	1.272	0.90	0.9989
	non-resonance ^b	1.187	0.21	0.9990
8	whole	1.110	0.39	0.9998
	non-resonance ^b	1.085	0.19	0.9997
9	whole	0.979	0.17	0.9998
	non-resonance ^b	0.963	0.13	0.9999
10	whole	0.949	0.15	0.9997
	non-resonance ^b	0.939	0.16	0.9992
11	whole	0.919	-0.29	0.9995
	non-resonance ^b	0.972	0.09	0.9999
12	whole	0.821	-0.55	0.9989
	non-resonance ^b	0.884	-0.08	0.9998
13	whole	0.665	-1.30	0.9890
	non-resonance ^b	0.851	0.00	0.9994
14	whole	0.604	-1.64	0.9753
	non-resonance ^b	0.867	0.16	0.9986
15	whole	0.500	-1.78	0.9649
	non-resonance ^b	0.763	-0.02	0.9983
16	whole	0.556	-2.53	0.9343
	non-resonance ^b	0.957	0.12	0.9983
17	whole	0.388	-2.09	0.9239
	non-resonance ^b	0.703	-0.02	0.9977
18	whole	0.418	-2.35	0.9179
	non-resonance ^b	0.766	-0.05	0.9979

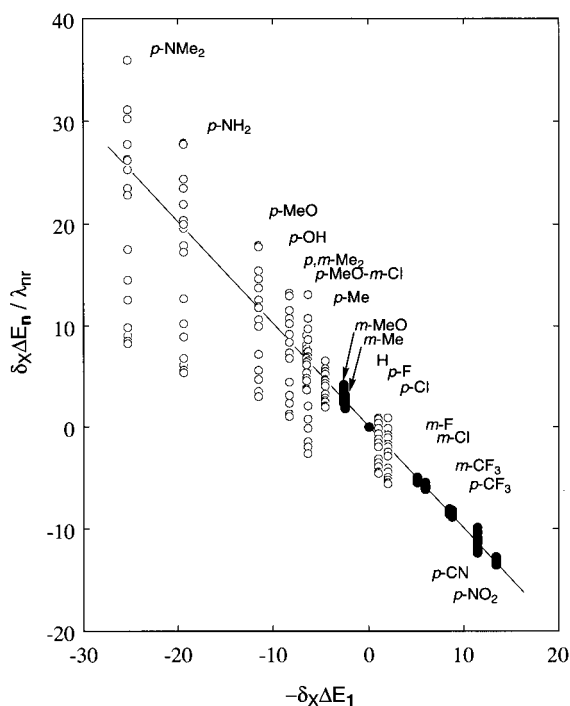
^a Least-squares method was applied for $\delta_X\Delta E_n = \lambda(\delta_X\Delta E_1) + c$ for all ring substituents.

^b *m*-Substituents and *p*- π -acceptors.

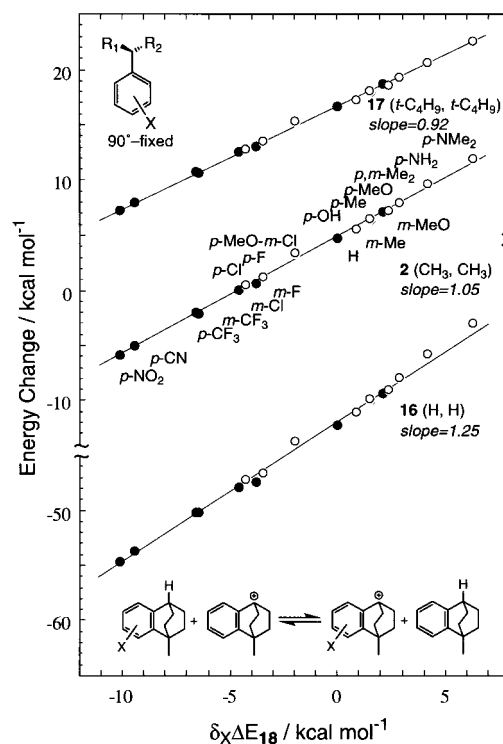
^c *R* is correlation coefficient.

Therefore, we now examine briefly the deviation from coplanarity of optimized cumyl cations.

The cation **1C**⁺(H) takes essentially a coplanar structure, implying substantial resonance interaction. In detail, the dihedral angle ϕ is calculated as 5.0° ($\phi = 8^\circ$ was reported by Laube *et al.*¹⁹). Steric repulsion between α -substituents and *peri*-hydrogen at the *ortho* carbon may sometimes be effective. The dihedral angles (ϕ) decreased for electron-donating substituents ($\phi = 2.2^\circ$ in the *p*-NMe₂ derivative) and increased for electron-withdrawing substituents ($\phi = 7.1^\circ$ in the *p*-NO₂ derivative). While ϕ seems to change with the stabilization ability of substituents due to resonance interaction, the differences between energy minima and coplanar structure ($\phi = 0^\circ$) are calculated to be less than 0.15 kcal

**Figure 2.** Plots of $\delta_X\Delta E/\lambda_{nr}$ for [1]–[18] vs $\delta_X\Delta E$ for [1]

mol^{-1} for all derivatives (unpublished results). Thus, the secondary influence on the calculated energy caused by the change in ϕ is generally negligible for *tert*-benzyl cations having non-bulky α -R groups in the substituent

**Figure 3.** Energy changes for orthogonal (90° -fixed) benzyl cations vs $\delta_X\Delta E$ for 4-methylbenzobicyclo[2.2.2]octen-1-yl cations

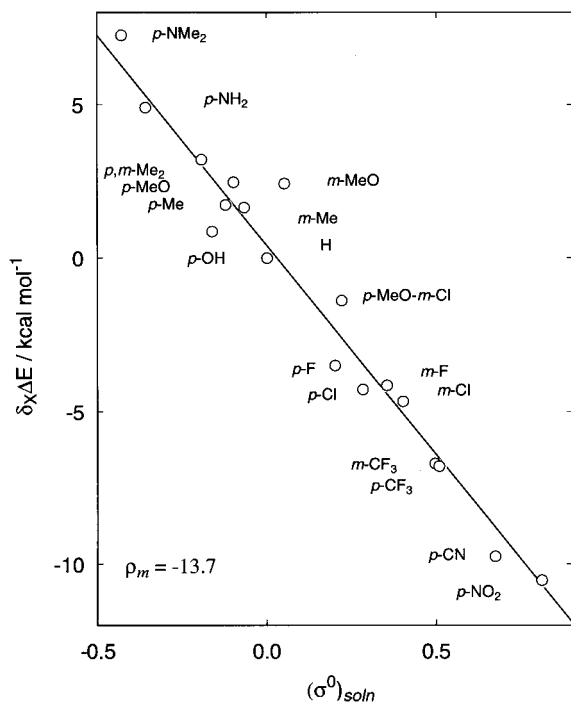


Figure 4. Correlation of $\delta_X \Delta E$ in Eqn. (7) with $(\sigma^0)_{\text{soln}}$

effect analysis. The α,α -dimethylbenzyl cation system ($\mathbf{1C}^+$) is considered as good a reference system for σ^+ .

Substituent changes in the cation stability used to be related to the change in some specified structural properties of the molecule. In Table 8, relevant geometric parameters and charge densities calculated at the RHF/6-31G* level are summarized for $\mathbf{1C}^+$, $\mathbf{2C}^+$ and $\mathbf{1CH}$.

The C_1 — C_7 bond length in unsubstituted 2-phenyl-

Table 7. *Ab initio* σ values

Substituent (X)	$\sigma^+{}^a$	σ^{0b}	$\Delta\sigma_R^+{}^c$
<i>p</i> -NMe ₂	-1.475	-0.499	-0.976
<i>p</i> -NH ₂	-1.131	-0.328	-0.803
<i>p</i> -MeO	-0.665	-0.153	-0.512
<i>p</i> -OH	-0.472	-0.035	-0.437
<i>p,m</i> -Me ₂	-0.366	-0.206	-0.160
<i>p</i> -OMe, <i>m</i> -Cl	-0.355	0.130	-0.485
<i>p</i> -Me	-0.247	-0.098	-0.149
<i>m</i> -MeO	-0.149	-0.149	0.000
<i>m</i> -Me	-0.091	-0.091	0.000
H	0.000	0.000	0.000
<i>p</i> -F	0.086	0.286	-0.200
<i>p</i> -Cl	0.145	0.342	-0.197
<i>m</i> -F	0.333	0.333	0.000
<i>m</i> -Cl	0.372	0.372	0.000
<i>m</i> -CF ₃	0.520	0.520	0.000
<i>p</i> -CF ₃	0.527	0.527	0.000
<i>p</i> -CN	0.742	0.742	0.000
<i>p</i> -NO ₂	0.800	0.800	0.000

^a Obtained from the σ^+ plot of $\delta_X \Delta E$ of [1], on the basis of $\rho_m = -16.9$.

^b Obtained from the σ^0 plot of $\delta_X \Delta E$ of [2], on the basis of $\rho_m = -13.7$.

^c $\sigma^+ - \sigma^0$.

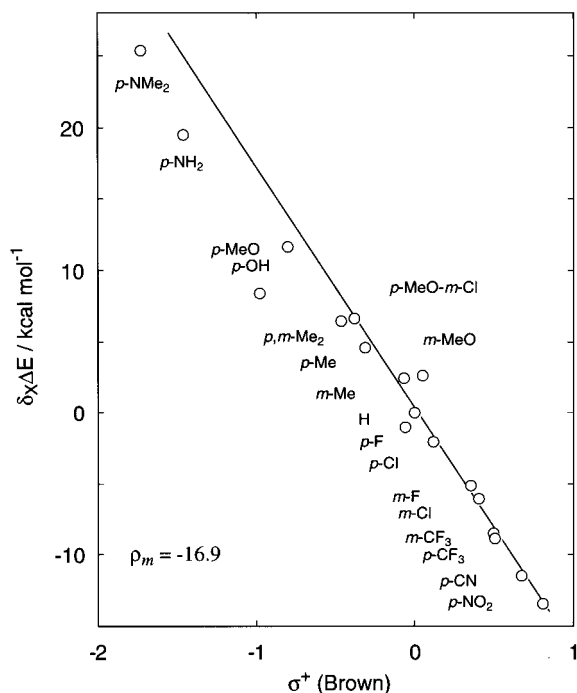


Figure 5. Plot of $\delta_X \Delta E$ in Eqn. (5) for cumyl cation $\mathbf{1C}^+$ vs the Brown σ^+ (soln)

propane [$\mathbf{1C(H)}$] is 1.52 Å, which is close to the typical carbon–carbon single bond length. All the carbon–carbon bond lengths in the phenyl ring (1.39 Å) are identical with the carbon–carbon bond length in benzene (1.386 Å) (calculated at the RHF/6-31G* level). Not only for all ring-substituted derivatives of $\mathbf{1CH}$ but also for all neutral species \mathbf{nCH} calculated, no change is found with respect to these bond lengths.

In the unsubstituted α,α -dimethylbenzyl cation [$\mathbf{1C}^+(\text{H})$], the C_1 — C_7 bond length is 1.404 Å, which is shorter than the length of typical carbon–carbon single bond. The C_2 — C_3 bond was shortened and C_1 — C_2 and C_3 — C_4 were elongated from the bond length of benzene. This is referred to as the change in π bond order caused by resonance interaction with the cation center. The tendency to approach a quinoidal structure is strengthened for the electron-donating X and weakened for the electron-withdrawing substituents; such a change in bond length is in line with the qualitative prediction of organic electronic theory.

In all the benzyl cation systems, bond lengths C_1 — C_7 and C_2 — C_3 were shortened whereas C_1 — C_2 and C_3 — C_4 were elongated from the lengths of the corresponding neutral species, that is, the same tendency as with $\mathbf{1C}^+$ but different in magnitude. The 90°-fixed cations $\mathbf{2C}^+$, $\mathbf{16C}^+$ and $\mathbf{17C}^+$ show an almost negligible tendency for changes in bond length. The skeletal structure of $\mathbf{2C}^+(\text{H})$ is close to that of neutral $\mathbf{1CH(H)}$.

Charges in Table 8 were estimated by means of Mulliken population analysis.²⁰ The sum of atomic charges in the aromatic moiety including the ring sub-

Table 8. Selected geometric parameters and charges at the RHF/6–31G* level

Substituent (X)	C ₁ –C ₇ ^a			Σq ^{±b}		
	1C ⁺ (X)	2C ⁺ (X)	1CH(X)	1C ⁺ (X)	2C ⁺ (X)	1CH(X)
<i>p</i> -NMe ₂	1.3681	1.4727	1.5213	0.644	0.247	–0.002
<i>p</i> -NH ₂	1.3715	1.4744	1.5220	0.617	0.241	–0.003
<i>p</i> -MeO	1.3808	1.4759	1.5218	0.566	0.232	–0.008
<i>p</i> -OH	1.3840	1.4767	1.5223	0.546	0.228	–0.009
<i>p,m</i> -Me ₂	1.3952	1.4754	1.5222	0.511	0.231	–0.008
<i>p</i> -OMe, <i>m</i> -Cl	1.3838	1.4775	1.5219	0.545	0.220	–0.023
<i>p</i> -Me	1.3951	1.4762	1.5220	0.505	0.227	–0.011
<i>m</i> -MeO	1.4108	1.4769	1.5227	0.452	0.220	–0.012
<i>m</i> -Me	1.4033	1.4767	1.5226	0.477	0.226	–0.011
H	1.4040	1.4773	1.5225	0.468	0.222	–0.013
<i>p</i> -F	1.3969	1.4788	1.5227	0.484	0.215	–0.020
<i>p</i> -Cl	1.4008	1.4784	1.5221	0.473	0.212	–0.026
<i>m</i> -F	1.4112	1.4790	1.5221	0.436	0.206	–0.028
<i>m</i> -Cl	1.4091	1.4792	1.5226	0.441	0.209	–0.030
<i>m</i> -CF ₃	1.4080	1.4800	1.5224	0.441	0.205	–0.032
<i>p</i> -CF ₃	1.4118	1.4792	1.5217	0.431	0.205	–0.031
<i>p</i> -CN	1.4134	1.4800	1.5217	0.424	0.199	–0.039
<i>p</i> -NO ₂	1.4207	1.4805	1.5213	0.395	0.192	–0.045

^a In units of Å. Refer to Chart 1 for numbering of atoms.

^b Sum of atomic charge on aromatic moiety including that on ring substituents. Estimated by Mulliken population analysis.

stituents (ΣΔq[±]) may be a good measure of delocalization of charges on the cationic center C₇ to the benzene ring.⁶ For the neutral systems, there is no significant substituent change in ΣΔq[±]. For cations 1C⁺ and 2C⁺, extensive charge delocalization to the aromatic moiety can be seen. For X = H, the delocalization ΣΔq[±] = 0.468 in the coplanar 1C⁺(H) is twice as large as ΣΔq[±] = 0.222 in the 90°-fixed 2C⁺(H). This indicates the importance of π-charge delocalization through the π-bond (C₁–C₇) in 1C⁺(H); such delocalization is not allowed geometrically in 2C⁺(H). Most important, the δ_XΣΔq[±] value for 1C⁺ changes significantly with substituent change. Electron donating substituents makes ΣΔq[±] larger and electron-withdrawing substituents make it smaller. Although ΣΔq[±] for 2C⁺ changes in the same way as that for 1C⁺, its magnitude is not so pronounced. The trend of the change in delocalization with substituents in both systems is consistent with that of the change in bond lengths discussed above.

Application of *ab initio* Y–T equation

In order to examine the general applicability, the *ab initio* Y–T Eqn. (8) using the *ab initio* substituent parameters in Table 7 was applied to δ_XΔE for hydride transfer reactions of various benzyl cation systems (1–18):

$$\delta_X \Delta E = \rho \{ (\sigma^0)_{ab} + r(\Delta\bar{\sigma}_R^+)_{ab} \} \quad (8)$$

The results of the *ab initio* Y–T analysis are summarized in Table 9.

The reaction [10] comprises hydride transfer equilibria of ring-substituted α-carboxy-α-hydroxybenzyl cations [10C⁺(X)] and unsubstituted cation [10C⁺(H)]. Corresponding neutral species are mandelic acids [10CH(X)]. In Fig. 6, substituent energy changes δ_XΔE of this reaction [10] are plotted against those of the reaction [1]. A regression analysis indicates an excellent linear correlation for all 18 substituents from *p*-NMe₂ to *p*-

Table 9. Results of Yukawa–Tsunno Analyses

Systems	ρ	r	δ _n ΔE(H) ^a	R ^b	SD ^c	n ^d
1	–16.9	1.00	0.00	1		18
2	–13.7	0.00	–19.24	1		18
3	–18.3	1.66	–46.95	0.9990	±0.71	18
4	–17.9	1.64	–38.61	0.9986	±0.79	18
5	–19.3	1.39	–33.14	0.9990	±0.66	18
6	–17.5	1.31	–23.55	0.9994	±0.46	18
7	–19.8	1.19	–18.75	0.9992	±0.55	18
8	–18.1	1.08	–6.88	0.9995	±0.37	18
9	–16.2	1.04	–5.84	0.9995	±0.34	18
10	–15.8	1.03	3.66	0.9995	±0.32	18
11	–16.4	0.89	9.47	0.9996	±0.28	18
12	–15.0	0.83	15.73	0.9996	±0.26	18
13	–14.4	0.50	26.64	0.9995	±0.23	18
14	–14.6	0.31	38.52	0.9996	±0.20	18
15	–12.9	0.22	46.04	0.9997	±0.13	18
16	–16.3	0.04	–66.26	0.9994	±0.23	18
17	–11.8	–0.01	–7.35	0.9998	±0.10	18
18	–13.0	–0.03	–23.99	0.9993	±0.19	18

^a Stabilities of nC⁺(H) to 1C⁺(H) determined by hydride transfer equilibria.

^b Correlation coefficient.

^c Standard deviation of calculated points from the regression line.

^d The number of points involved in the calculation.

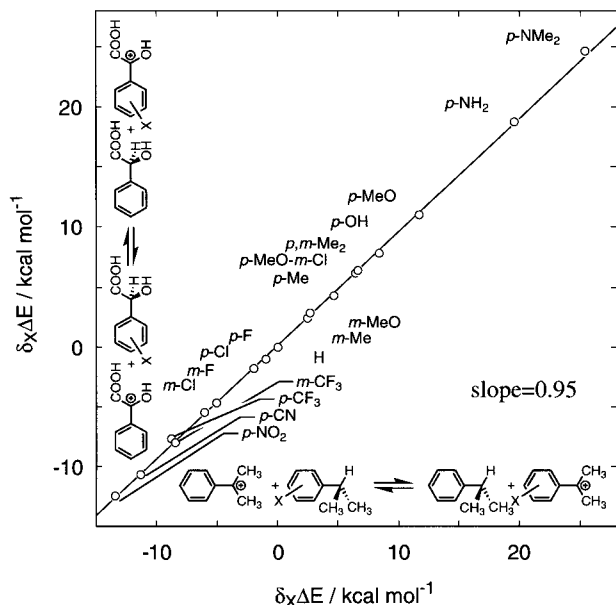


Figure 6. Plot of $\delta_X \Delta E$ for [10] vs $\delta_X \Delta E$ for [1]

NO_2 over a wide range of energy change, 35 kcal mol^{-1} :

$$\delta_X \Delta E_{10} = 0.95(\delta_X \Delta E_1) + 0.15 \quad (9)$$

with $R = 0.9997$ and $\text{SD} = \pm 0.24$. This result suggests that the resonance demand in the substituent effect on $\delta_X \Delta E$ of reaction [10] is equivalent to that in reaction [1]. The essentially identical r value for both systems is caused from the fact that the sums of participations from the α -substituents are equivalent in both benzyl cations. A direct analysis of [10] by means of the *ab initio* Y–T equation gave $\rho = -15.8$ and $r = 1.03$ with good accuracy.

The substituent effect on $\delta_X \Delta E$ of reaction [3], comprised of hydride transfer reactions between ring-substituted α, α -di(trifluoromethyl)benzyl cations $3\text{C}^+(\text{X})$ and their unsubstituted hydride $3\text{CH}(\text{H})$, was analyzed by the *ab initio* Y–T Eqn. (8), affording $\rho = -18.3$ and $r = 1.66$ ($R = 0.999$ and $\text{SD} = \pm 0.71$). In the Y–T plot (Fig. 7) for [3], no simple linearity against *ab initio* $(\sigma^+)_{ab}$ is recognized in the correlation for the whole range of substituents (open circles), suggesting the limitation of the linear substituent effect correlation analysis in terms of a single set of substituent constants. There is an excellent linear correlation for the *non-resonance* substituents, i.e. *meta* and *para* electron-withdrawing groups. For *para* π -donor substituents, on the other hand, the plots deviate upwards from the reference *non-resonance* correlation (ρ_m) line; the deviations seem to be precisely proportional to the resonance capabilities of substituents. In this plot, the line segments between $(\sigma^+)_{ab}$ and $(\sigma^0)_{ab}$ values for *para* π -donor substituents represent the resonance capabilities of these substituents, i.e. their $\Delta\bar{\sigma}_R^+$ values. The ρ_m correlation line divides all

the *resonance line-segments* at a constant external ratio of 1.66, which corresponds to the r -value of this system.

The enhanced r value of 1.66 should be attributed to the thermal instability of α, α -di(trifluoromethyl)benzyl cation; $3\text{C}^+(\text{H})$ is significantly less stable than the α, α -dimethylbenzyl cation [$1\text{C}^+(\text{H})$] by 47 kcal mol^{-1} . In other words, the change of α -substituents from methyl groups in the σ^+ reference reaction [1] to electron-withdrawing α -trifluoromethyl groups in reaction [3] causes an enhanced demand of resonance stabilization (or charge delocalization) from the aromatic moiety. The more electron-withdrawing the α -substituents, the larger is the r value.

Reaction [13] comprises hydride transfer equilibria of ring-substituted α -methoxy- α -hydroxybenzyl cations [$13\text{C}^+(\text{X})$] and the corresponding α -methoxybenzyl alcohols [$13\text{CH}(\text{X})$]. The behavior of substituents in $\delta_X \Delta E$ of this equilibrium is illustrated by the Y–T plot in Fig. 8. Again, while the substituent effects are not correlated linearly for all the substituents, the *non-resonance* (*meta* and *p*- π -acceptors) substituents are correlated linearly with $(\sigma^0)_{ab}$. The Y–T correlation (ρ) line, i.e. ρ_m line, can be defined as a unique line dividing all the resonance line segments for *para* π -donors at a constant internal ratio of 0.50, which represents the r value of this system. The application of Eqn. (8) to this system gives an excellent correlation with $\rho = -14.4$ and $r = 0.50$ ($R = 0.9995$ and $\text{SD} = \pm 0.23$). In reaction [13], both methoxy and hydroxy groups at the α -position are strong electron donors. A large amount of charge is delocalized to these α substituents to stabilize the cation,

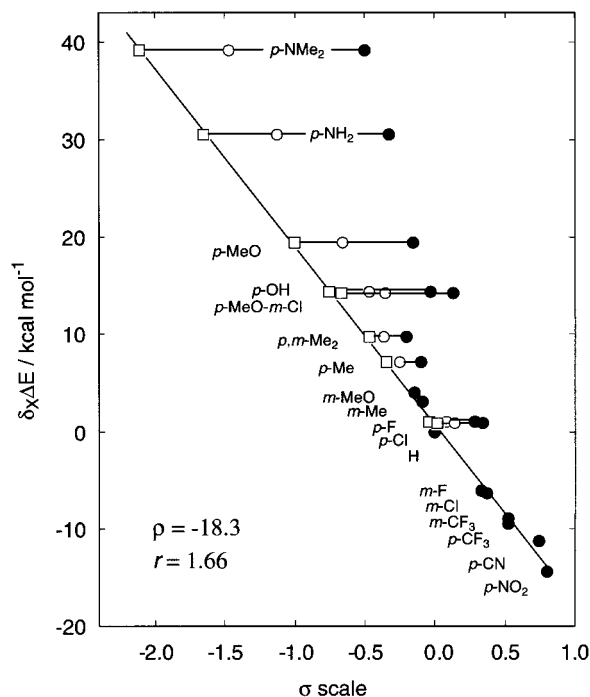


Figure 7. The *ab initio* Y–T plot $(\bar{\sigma})_{ab}$ of the substituent effect on $\delta_X \Delta E$ for [3]: \circ , $(\sigma^+)_{ab}$; \bullet , $(\sigma^0)_{ab}$; \square , $(\bar{\sigma})_{ab}$ for $r = 1.66$

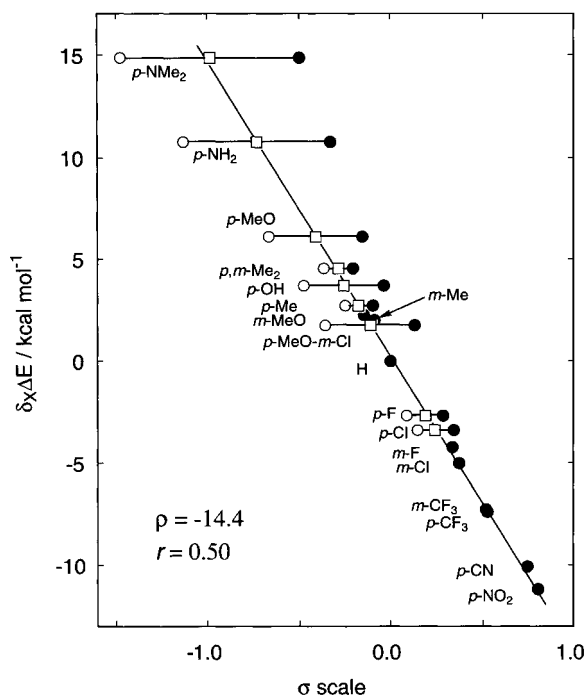


Figure 8. The *ab initio* Y–T plot $(\bar{\sigma})_{ab}$ of the substituent effect on $\delta_X \Delta E$ for [13]: \circ , $(\sigma^+)_{ab}$; \bullet , $(\sigma^0)_{ab}$; \square , $(\bar{\sigma})_{ab}$ for $r = 0.50$

which decreases the necessity for resonance participation. This is the reason why the r value of this system is small compared with the reference reaction [1].

As shown in Table 9, the *ab initio* Y–T Eqn. (8) with *ab initio* substituent parameters was found to be very precisely applicable to various reactions. The high precision of the resulting correlations confirms the validity of the Y–T relationship and the high quality of the accurate parameter values. It should be noted again that the substituent energy quantities $\delta_X \Delta E$ are all primary values computed based on *ab initio* MO theory. Furthermore, we emphasize that the parameters involved, $(\sigma^0)_{ab}$ and $(\Delta\bar{\sigma}_R^+)_{ab}$, are also the primary theoretical quantities derived directly by *ab initio* calculation. This lends strong support to the theoretical validity of our empirical Y–T relationship Eqn. (1) in the solution-phase chemistry, and provides proper physical meanings for the parameters and variables involved therein.

It is worthy of note, however, that the magnitude of the $(\Delta\bar{\sigma}_R^+)_{ab}$ parameters is appreciably reduced compared with the solution values. Nevertheless, as shown in Fig. 9, it is remarkable that there exists a precise linearity between the theoretical $(\Delta\bar{\sigma}_R^+)_{ab}$ and the original solution values of $\Delta\bar{\sigma}_R^+$ for all substituents:

$$(\Delta\bar{\sigma}_R^+)_{ab} = 0.72(\Delta\bar{\sigma}_R^+)_{\text{soln}} \quad (10)$$

where $R = 0.9969$, except for *p*-OH. The only serious deviation, *p*-OH, may be due to solvent modification of the substituent, and in fact its $\Delta\bar{\sigma}_R^+$ value in gas-phase chemistry^{5,7} just falls on the correlation line. While we are not prepared at the moment to provide any decisive

speculation concerning the cause of the reduced proportionality of the theoretical $(\Delta\bar{\sigma}_R^+)_{ab}$ parameter scale, it is reasonable to refer to the solvation effect. Whatever the cause of the constant proportionality is, $(\Delta\bar{\sigma}_R^+)_{ab}$ should be a precise general measure of the relative intrinsic capabilities of π -delocalization of substituents.

It should be noted that the substituent effects on the gas-phase ionization equilibria of various benzyl cations were treated successfully with the Y–T Eqn. (1), using slightly modified gas-phase substituent parameters.^{5,7} Whereas the gas-phase $(\sigma^+)_{\text{gas}}$ constants were determined from $\delta_X \Delta G_{\text{gas}}^0$ for cumyl cations by the ICR experiments, the appropriate $\delta_X \Delta G_{\text{gas}}^0$ set of the *unenhanced-resonance* ($r = 0$) σ^0 -benzyl cation system was hardly available. Thus, by using the ordinary $(\Delta\bar{\sigma}_R^+)_{\text{soln}}$ parameters instead of the gas-phase parameters $(\Delta\bar{\sigma}_R^+)_{\text{gas}}$, the Y–T treatment was practically applied in the form Eqn. (11):

$$\delta_X \Delta G_{\text{gas}}^0 = \rho[(\sigma^+)_{\text{gas}} + (r - 1)(\Delta\bar{\sigma}_R^+)_{\text{soln}}] \quad (11)$$

This gas-phase Y–T equation was widely applied with excellent precision ($R > 0.996$) for 30 different carbocation sets.^{5,7} Based on these correlational results, appropriate corrections for the best-fit values were applied for the $(\Delta\bar{\sigma}_R^+)_{\text{gas}}$ parameters but were not important for most substituents except *p*-OH (Fig. 9). The defined set of experimental $(\Delta\bar{\sigma}_R^+)_{\text{gas}}$ parameters satisfies the same relation [Eqn. (10)] with $(\Delta\bar{\sigma}_R^+)_{ab}$. In general, substituent effects on gas-phase $\delta_X \Delta G_{\text{gas}}^0$ values should be comparable to the effects on theoretical $\delta_X \Delta E_{ab}$ values. As the experimental $(\sigma^+)_{\text{gas}}$ has been found to be identical to the corresponding *ab initio* value $(\sigma^+)_{ab}$, it is evident that the assumed reference $(\sigma^0)_{\text{gas}}$ scale for $r = 0$ in Eqn. (11)

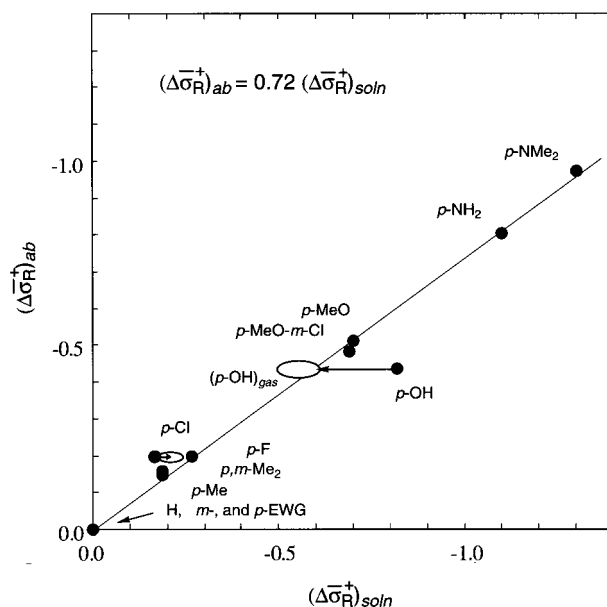


Figure 9. Linear relationship between $(\Delta\bar{\sigma}_R^+)_{\text{soln}}$ in solution and *ab initio* $(\Delta\bar{\sigma}_R^+)_{ab}$; \circ , $(\Delta\bar{\sigma}_R^+)_{\text{gas}}$

must involve too low a resonance ($\Delta\bar{\sigma}_R^+$) contribution. In order to discuss the significance of r values in gas-phase and *ab initio* Y–T correlations on the same scale, Eqn. (11) should be deduced to the *ab initio* Y–T Eqn. (8) by combination with Eqn. (10).

We emphasize here that the unempirical *ab initio* Y–T relationship generally holds very precisely for experimental gas-phase substituent effects $\delta_X\Delta G_{\text{gas}}^0$ for various benzyl cation equilibria. As a result, the empirical Y–T relationship [Eqn. (1)] and the substituent parameters involved therein can be reproduced theoretically, substantiating the validity of the concept of varying resonance demand deduced from the empirical Y–T relationship.

Reaction constants

In general, the reaction constants ρ and r are referred to as the susceptibility parameters of a reaction to the non-resonance and resonance effects of substituents, respectively. Both parameters vary widely from reaction to reaction; in the present study, they vary with different carbocation systems, free from reaction conditions. The reaction constant ρ , a susceptibility parameter of change in $\delta_X\Delta E_{\text{nC}^+}$ to unit change in $(\sigma^0)_{\text{ab}}$ scale, is a highly important parameter since it is considered to be inherent in the cation nC^+ . The resonance reaction constant r , which used to be called the ‘resonance demand’ parameter, is a measure of the degree of resonance interaction between the carbocation center and benzene π -system.⁶ On the basis of the linear correlations of r values against relevant theoretical parameters, such as bond lengths and bond orders of the C₁–C₇ bonds, central cation charges, and aryl charge delocalization $\Sigma\Delta q^+$, the parameter r has been approved as a measure of resonance demand.

Physical organic chemists used to have particular interest in the selectivity–stability relationship, which is intimately related to the empirical reactivity–selectivity principle; here, ρ and r are independent selectivity parameters. Both selectivity parameters ρ and r tend to decrease with increasing stability. For ρ parameters, the inverse proportionality relation against $-\delta_{\text{n}}\Delta E_{\text{nC}^+}$ (X = H) is only fair or no more than qualitative; the linearity is insignificant ($R < 0.880$). In contrast, the selectivity–stability relationship, r_{ab} vs $-\delta_{\text{n}}\Delta E_{\text{nC}^+}$ (X = H), is observed to be satisfactorily linear ($R = 0.988$) as shown in Fig. 10:

$$r = 0.97 - 0.0159[\delta_{\text{n}}\Delta E_{\text{nC}^+}(\text{X} = \text{H})] \quad (12)$$

Equation (12) is a quantitative expression of the empirical stability–selectivity principle that the more stable the intermediate cation, the weaker is the demand for π -electron delocalization. Equation (12) provides reasonable physical characterization for the r parameter.

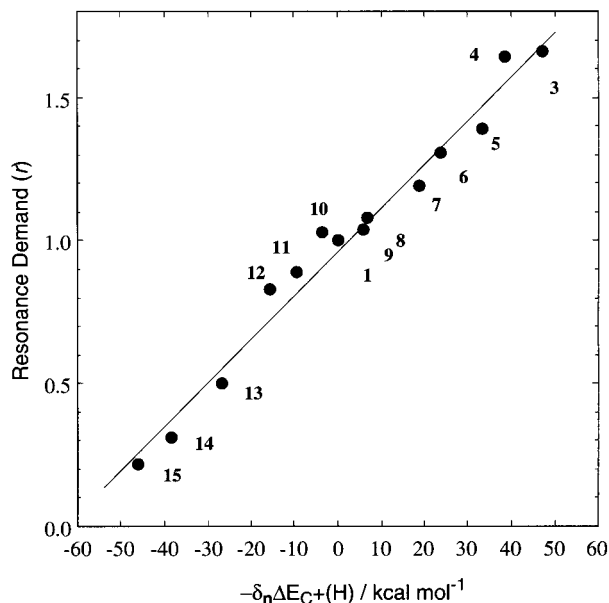


Figure 10. r Value vs $-\delta_{\text{n}}\Delta E_{\text{C}^+}(\text{H})$ for benzyl cation systems

It is instructive to deal with the r value by a physical organic tool, correlation analysis. The r value for all systems can be correlated in terms of the following equation with the *ab initio* substituent constants $(\sigma^0)_{\text{ab}}$ and $(\Delta\bar{\sigma}_R^+)_{\text{ab}}$ of substituents R₁ and R₂ as shown in Fig. 11:

$$r = 0.35 \Sigma(\sigma^0)_{\text{ab}} + 0.61 \Sigma(\Delta\bar{\sigma}_R^+)_{\text{ab}} + 1.21 \quad (13)$$

where $\Sigma \sigma^0 = \sigma^0(\text{R}_1) + \sigma^0(\text{R}_2)$ and $\Sigma \Delta\bar{\sigma}_R^+ = \Delta\bar{\sigma}_R^+(\text{R}_1) + \Delta\bar{\sigma}_R^+(\text{R}_2)$. Clearly, the system possessing electron-

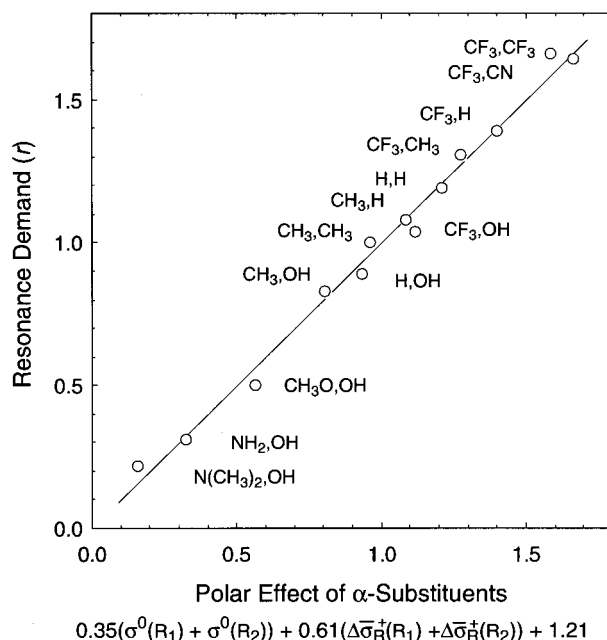


Figure 11. r Value vs polar effects of α -substituents (R₁, R₂)

donating α -R groups has a reduced r value, and the change in r can quantitatively be related to electronic effects of α -R groups. The positive charge formed at the benzyl position is stabilized complementarily by π -delocalization into the aryl π -system and into α -substituents. This suggests simply that the r value should be inherent in the electronic structure of the cation itself.

The present ρ_{ab} values just reflect the thermodynamic character of the parent cations and are of course free from any external effect such as solvents and temperature. The ρ parameter also should be inherent in the cation, or is even more rigidly than the r parameter stuck with the core structure of the cation. Hence the ρ_{ab} values are not related to the stabilities of cations, in contrast to r values. Nevertheless, we emphasize that in solution chemistry, ρ is often involved in the selectivity–reactivity relationship. The extended Brønsted relationship or the Leffler–Hammond rate–equilibrium relationship is much more concerned with the ρ value.²¹ Thus, the ρ_{ab} parameter is expected to play an important role in understanding solution chemistry.

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