

Ab initio MO study of benzylic cations. Part 3. Protonated benzoyl derivatives†

Kazuhide Nakata,^{1‡} Mizue Fujio,^{1*} Masaaki Mishima,¹ Yuho Tsuno¹ and Kichisuke Nishimoto²

¹Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812-8581, Japan

²Institute for Fundamental Chemistry, Kyoto 606-8103, Japan

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ABSTRACT: Structures of α -hydroxybenzylic cations and their conjugate bases, which cover a wide variation of stability, were optimized by means of *ab initio* molecular orbital method at the RHF/6–31G* level. Total energies were calculated at the MP2/6–31G*//RHF/6–31G* + ZPE (scaled 0.9) level. Calculated relative proton affinities of the respective neutral molecules (benzoyl compounds; conjugate bases of α -hydroxybenzylic cations) agreed well with the corresponding basicities in the gas phase. The geometries of α -amino- α -hydroxybenzyl and α -hydroxy- α -dimethylaminobenzyl cations were also optimized at the fixed dihedral angles between the cationic $2p\pi$ orbital and the benzene π orbital (ϕ), and between the cationic $2p\pi$ orbital and lone pair electron orbital of the α -substituent (θ). The changes in Wiberg bond orders and the rotational potentials about ϕ and θ showed that the degree of resonance interaction between the cationic center and phenyl ring is balanced by the electronic effects of α -substituents in benzylic cations. The obtained theoretical indices of all parent cations such as Mulliken population, Wiberg bond order and bond lengths were correlated linearly with the resonance demand parameter (r value) which were given by the Yukawa–Tsuno substituent effect analysis in the gas phase and in aqueous solution. These relationships are consistent with those for other benzylic cations such as destabilized carbocations and sterically hindered cations studied previously. This confirms that the empirical r value has a definitive physical meaning, i.e. a measure of the resonance interaction between the cationic center and the aryl moiety. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: Yukawa–Tsuno equation; substituent effect; α -hydroxybenzylic cation; benzoyl compound; *ab initio* calculation; basicity; proton affinity

INTRODUCTION

The linear free energy relationship has been used as an extremely useful tool in the exploration of reaction mechanisms.² In particular, the Yukawa–Tsuno (Y–T) equation:^{3,4}

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

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 is one of the most useful tools for predicting characteristics of transition states and intermediates whose ionic centers are affected by the benzene π -system, and has been widely applied with success to

various systems not only in solution⁵ but also in the gas phase.^{6,7}

This equation is characterized by the empirically obtained resonance demand parameter r , which has been used as a parameter describing the degree of resonance interaction between the reaction center and the benzene π -system.

While a series of tertiary α,α -dialkylbenzyl solvolyses showed linear Brown $\rho^+\sigma^+$ correlations intrinsically ($r=1.00$),⁸ the solvolyses of secondary benzylic precursors such as α -phenylethyl chlorides^{5d} and α -*tert*-butylbenzyl tosylates^{5e} gave linear correlations in terms of Eqn (1) with slightly enhanced r value of 1.1–1.2. The solvolyses of extremely destabilized carbocationic systems such as 1-ary1-1-(trifluoromethyl)ethyl tosylates^{5a} and 1-ary1-2,2,2-trifluoroethyl tosylates^{5b} gave linear Y–T plots with extremely high r values of 1.39 and 1.51, respectively. On the other hand, the resonance demand of a carbenium ion was reduced significantly by decreased coplanarity between the reaction center and the phenyl ring. The solvolyses of α -*tert*-butyl- α -methylbenzyl chlorides,⁵ⁱ α -*tert*-butyl- α -neopentylbenzyl *p*-nitrobenzoates,^{5j} and α -*tert*-butyl- α -isopropylbenzyl *p*-nitrobenzoates^{5j} afford excellent linear Y–T correlations with

*Correspondence to: M. Fujio, Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

Email: fujio@ms.ifoc.kyushu-u.ac.jp

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Table 1. Summary of ρ and r values in solution and gas phase

R_1, R_2^a	r_{sol}^b	r_{gas}^c	ρ_{gas}^c
<i>α-Hydroxy systems:</i>			
CF ₃ , OH (6)		1.20 ^d	-11.5 ^d
H, OH (1)	1.06 ^e	1.04 ^f	-12.1 ^f
Me, OH (2)	0.71 ^g	0.78 ^h	-12.3 ^h
MeO, OH (3)	0.50 ⁱ	0.45 ^j	-11.9 ^j
NH ₂ , OH (4)	0.35 ^k		
NMe ₂ , OH (5)		0.23 ^l	-11.8 ^l
<i>Other systems:^m</i>			
CF ₃ , H (13)	1.51	1.53	-14.6
CF ₃ , Me (14)	1.39	1.40	-14.0
H, H (15)	1.28	1.29	-14.0
Me, H (16)	1.15	1.14	-13.6
<i>t</i> -Bu, H (17)	1.09		
Me, Me (18)	1.00	1.00	-13.0
Et, Me (19)	1.04	1.01	-12.6
Et, Et (20)	1.02	0.98	-13.1
<i>i</i> -Pr, <i>i</i> -Pr (21)	1.01		
<i>t</i> -Bu, Me (22)	0.91	0.86	-12.5
<i>t</i> -Bu, <i>neo</i> -Pen (23)	0.78 ⁿ	0.82	-9.2
<i>t</i> -Bu, <i>i</i> -Pr (24)	0.66 ⁿ		
<i>t</i> -Bu, <i>t</i> -Bu (25)	0.28		
Benzobicyclo (26) ^o	0.00		

^a R₁ and R₂ are substituents at the α -position.

^b The r values given in Y-T analysis of the solvolyses.

^c The r and ρ values given in Y-T analysis of the gas-phase stabilities.

The ρ s are in units of kcal mol⁻¹.

^d Ref. 7a.

^e Ref. 10a.

^f Refs 7b and 7f.

^g Ref. 10b.

^h Refs 7c and 7f.

ⁱ Ref. 10c.

^j Refs 7d and 7f.

^k Ref. 10d.

^l Ref. 7e.

^m Ref. 1 and references cited therein.

ⁿ Ref. 5j.

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

$r = 0.91, 0.78$ and 0.66 , respectively. In the case of the solvolysis of α, α -di-*tert*-butylbenzyl *p*-nitrobenzoates,^{5k} $r = 0.28$, which is comparable to the r value for the Hammett σ scale.⁹ In the solvolysis of 4-methylbenzobicyclo[2.2.2]octen-1-yl triflates,^{5l} where the carbocation $2p\pi$ AO located at the bridgehead of the bicyclic skeleton is set orthogonal to the benzo- π -orbital, the r value was found to be 0.0.

The r values for the gas-phase stabilities of the cations have the same values as those of the corresponding benzylic S_N1 solvolyses (Table 1). From this identity, the varying resonance demand r in solvolysis should be an essential feature of the incipient carbocation intermediate and of the solvolysis transition state. The structures of the transition states of S_N1 solvolysis can be approximated reasonably by those of cations.

Moreover, the r value is directly related to the intrinsic stability of the parent cation.^{6e,7a} Hence, *ab initio* calculations, which are useful for determining the

structures and energies of cations in the gas phase, can be used to find the underlying relationship between quantum chemical quantities and experimental r values.

In previous papers,^{1,11} the structures of some benzylic cations were optimized, and we found the relationship between theoretical indices obtained and the r value. In those papers, we selected sterically resonance-hindered benzylic cations for small r values, which have bulky substituents at the α -positions. Benzylic cations which have an electron-releasing group at the α -position should also give small r values, because of the decrease in the resonance requirement of the cationic center to the phenyl ring. In order to clarify the theoretical meaning of the r value, it is desirable to extend theoretical research to these stable benzylic cations.

Substituent effects on basicities for some benzoyl compounds have been investigated experimentally both in solution¹⁰ and the gas phase.⁷ Basicities in the gas phase were measured by means of proton transfer equilibria in two differently substituted substrates. The resulting parameter should reflect the intrinsic stabilities of conjugate cations, i.e. α -hydroxybenzylic cations. In solution, substituent effect analysis of the basicities of benzaldehydes,^{10a} acetophenones^{10b} and methyl benzoates^{10c} gave r values of 1.06, 0.71 and 0.50, respectively. The r value decreases monotonically when the substituent attached to the benzoyl group changes from hydrogen via a methyl to a methoxy group. Substituent effects in the gas phase of these compounds give the same r values as those in the solution phase, as shown in Table 1. In addition, the r value of the benzamide system^{10d} in solution ($r = 0.35$) is lower than those of the above systems, and agrees with that of *N,N*-dimethylbenzamide^{7e} in the gas phase ($r = 0.23$). In the case of α, α, α -trifluoroacetophenone,^{7a} which has an electron-attracting CF₃ group at the conjugate cationic center, the r value is 1.2, which is larger than that of the benzaldehyde system. The change in the r value can be interpreted as a change in the degree of resonance requirement of conjugate cations to the phenyl ring, which is affected by the electron-releasing ability of substituents connected to the benzoyl group.

In this work, we extended *ab initio* calculation to these α -hydroxybenzylic cations, and the relationships between the calculated indices and the experimental r values were investigated.

METHOD

The *ab initio* LCAO-MO calculations¹² were carried out for the α -hydroxybenzylic cations and their conjugate bases, i.e. benzoyl derivatives, as shown in Fig. 1. The numbering of atoms and dihedral angles ϕ and θ are also given in Fig. 1.

All calculations were performed on an IBM RS/6000 computer with the Gaussian-94 suite of programs.¹³

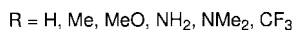
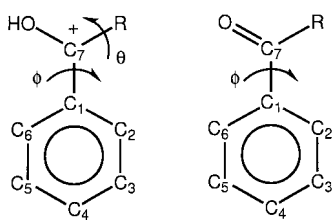


Figure 1. α -Hydroxybenzyl cations and their conjugate bases (benzoyl compounds) studied

Geometries were optimized completely by the gradient procedure at C_1 symmetry. The closed-shell restricted Hartree–Fock calculation with 3–21G and 6–31G* basis sets was applied to find stationary points on the potential energy surface (PES). At the RHF/6–31G* level all optimized structures were checked by the analysis of harmonic vibrational frequencies obtained from diagonalization of force constant matrices. Electron-correlation contributions were estimated by Møller–Plesset perturbation theory¹⁴ to improve the

calculated energies; single-point MP2 calculations were carried out at the 6–31G* basis set using the frozen-core approximation. The final energies were corrected for RHF/6–31G* zero-point energy (ZPE) differences scaled by a factor of 0.9.¹⁵ Mulliken population analysis (MPA)¹⁶ was carried out for benzyl cations at the RHF/6–31G* level, to discuss quantitatively the relationship between the r value in the Y–T equation and populations of electrons at atomic centers. Wiberg bond orders in natural bonding orbital (NBO)^{17,18} analysis were also calculated to discuss the origin of the r value. In order to study how the total energy is affected by the conformation of the α -methyl group, the rotational potential about C₇–C₈ bond of the α -hydroxy- α -methylbenzyl cation (**2**) was calculated by geometry optimization techniques, changing the dihedral angle \angle H₈C₈C₇C₁ (θ) from 0 to 60°. For the purpose of examination of the importance of the coplanarity between the phenyl ring and the R group (shown in Fig. 1) to the cationic 2p π orbital in α -amino- α -hydroxybenzyl (**4**) and α -dimethylamino- α -hydroxybenzyl (**5**) cations, the rotational potentials about the C₁–C₇ and C₇–N₁ bonds for these cations were also calculated by geometry optimiza-

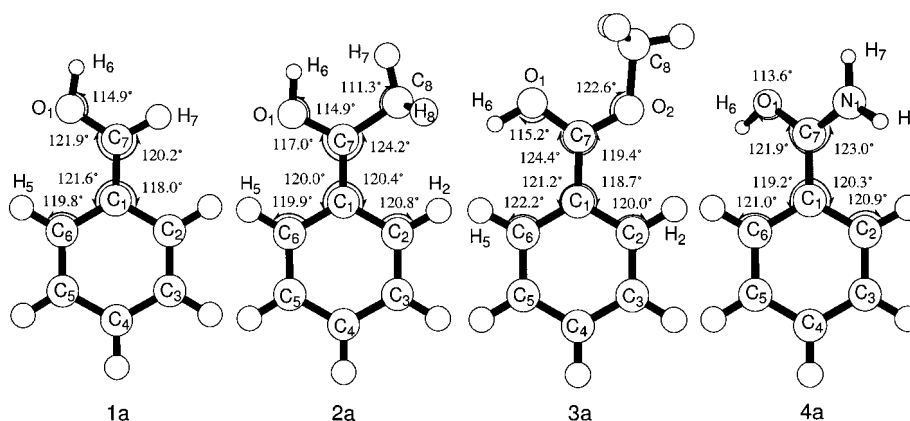


Figure 2. RHF/6–31G* optimized structures of **1a–4a**

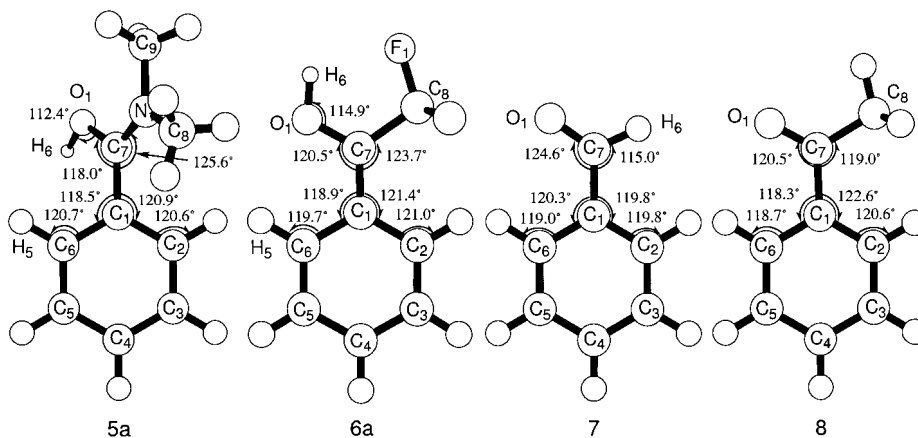


Figure 3. RHF/6–31G* optimized structures of **5a–8**

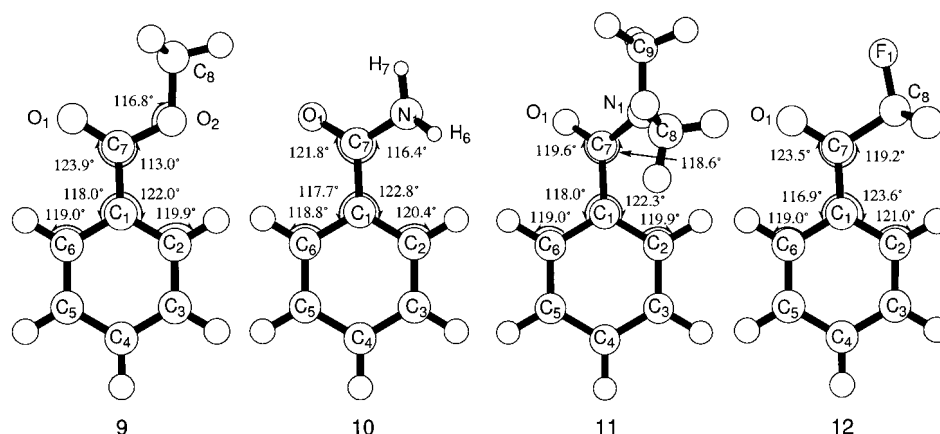


Figure 4. RHF/6-31G* optimized structures of 9-12

tion techniques, changing the dihedral angles ϕ and θ from 0 to 90°.

RESULTS AND DISCUSSION

Energies and geometries

The optimized structures (global minima) of α -hydroxybenzyl cations and benzoyl derivatives at the RHF/6-31G* level are shown in Fig. 2, Fig. 3 and Fig. 4 and selected geometric parameters are summarized in Tables 2 and 3. The angle ϕ denotes the dihedral angles of the O—C₇—R plane with respect to the aromatic plane as shown in Fig. 1. Total energies are listed in Table 4. The calculated dihedral angles \angle OC₇C₁R, \angle C₂C₁C₇C₆, \angle C₁C₂C₃C₄, \angle C₂C₃C₄C₅, \angle C₃C₄C₅C₆, \angle C₄C₅C₆C₁, \angle C₅C₆C₁C₂ and \angle C₆C₁C₂C₃ were found to be less than

1.0° in all cations (1-6), indicating that phenyl rings and the O—C₇—C₁—R planes actually have coplanar frameworks. Hence the effects of OH and R α -substituents on the electronic structure of the cation and on the change in the dihedral angles ϕ and θ can be considered to be real factors in determining the degree of resonance interaction, which are reflected by the changes in atomic charges and bond orders in the aromatic moiety. Optimized geometries of the respective benzylic cation are discussed below.

α -Hydroxybenzyl cation (1). Two minima **1a** and **1b** were obtained, which are the rotamers with respect to the C _{α} —O (C₇—O₁) bond. Both **1a** and **1b** are configured to gain the maximum conjugative stabilization between the α -hydroxyl group and the cationic center C₇; \angle H₆O₁C₇C₁ are 180° in **1a** and 0° in **1b**. In all other calculated cations (1-6), two minima concerning conformations of the α -

Table 2. Selected geometric parameters^a of 1a-6a optimized at the RHF/6-31G* level

Parameter	Cation ^b					
	R=H (1a)	R=Me (2a)	R=MeO (3a)	R=NH ₂ (4a)	R=NMe ₂ (5a)	R=CF ₃ (6a)
C ₁ —C ₂	1.413	1.410	1.400	1.396	1.393	1.420
C ₂ —C ₃	1.372	1.373	1.379	1.380	1.382	1.370
C ₃ —C ₄	1.393	1.393	1.388	1.389	1.388	1.395
C ₄ —C ₅	1.400	1.392	1.392	1.388	1.387	1.397
C ₅ —C ₆	1.369	1.374	1.375	1.380	1.382	1.368
C ₆ —C ₁	1.416	1.411	1.402	1.397	1.394	1.421
C ₁ —C ₇	1.394	1.420	1.447	1.461	1.477	1.397
C ₇ —R	1.078	1.496	1.258	1.295	1.288	1.544
C ₇ —O	1.276	1.280	1.283	1.290	1.302	1.274
C ₇ —C ₁ —C ₂	118.0	120.4	118.7	120.3	120.9	121.4
C ₇ —C ₁ —C ₆	121.6	120.0	121.2	119.2	118.5	118.9
C ₁ —C ₇ —R	120.2	124.2	119.4	123.0	125.6	123.7
C ₁ —C ₇ —O	121.9	117.0	124.4	121.9	118.0	120.5
C ₆ —O ₁ —C ₇ —C ₁	180.0	180.0	-2.4	-10.6	-9.4	174.8
ϕ	0.0	0.0	5.6	33.8	50.7	0.0

^a Distance in Å, angles in degrees.

^b Rs are α -substituents shown in Fig. 1.

Table 3. Selected geometric parameters^a of **7–12** optimized at the RHF/6–31G* level

Parameter	Benzoyl derivative ^b					
	R=H (7)	R=Me (8)	R=MeO (9)	R=NH ₂ (10)	R=NMe ₂ (11)	R=CF ₃ (12)
C ₁ —C ₂	1.388	1.390	1.390	1.390	1.390	1.392
C ₂ —C ₃	1.386	1.386	1.384	1.385	1.385	1.384
C ₃ —C ₄	1.385	1.384	1.386	1.385	1.385	1.385
C ₄ —C ₅	1.390	1.388	1.387	1.387	1.386	1.388
C ₅ —C ₆	1.381	1.382	1.383	1.383	1.384	1.380
C ₆ —C ₁	1.392	1.393	1.390	1.390	1.389	1.394
C ₁ —C ₇	1.483	1.500	1.490	1.500	1.504	1.489
C ₇ —R	1.095	1.514	1.325	1.364	1.366	1.540
C ₇ —O	1.191	1.195	1.191	1.200	1.202	1.187
C ₇ —C ₁ —C ₂	119.8	122.6	122.0	122.8	122.3	123.6
C ₇ —C ₁ —C ₆	120.3	118.3	118.0	117.7	118.0	116.9
C ₁ —C ₇ —R	115.0	119.0	113.0	116.4	118.6	119.2
C ₁ —C ₇ —O	124.6	120.5	123.9	121.8	119.6	123.5
ϕ	0	0	0	22.0	40.6	0

^a Distance in Å, angles in degrees.^b Rs are α -substituents shown in Fig. 1.**Table 4.** Total energies (-au) of calculated cations and benzoyl compounds

Species ^a	Theoretical level			
	RHF/3–21G	RHF/6–31G*	MP2/6–31G*//RHF/6–31G*	ZPE ^b
1a	341.848931	343.770350	344.807245	-0.132281(0)
1b	341.844276	343.766345	344.803654	-0.132283(0)
2a	380.685712	382.820665	383.990532	-0.161696(0)
2b	380.681328	382.817432	383.987927	-0.161635(0)
3a	455.144052	457.689987	459.033099	-0.167722(0)
3b	455.140832	457.686107	459.028428	-0.167644(0)
3c	455.139322	457.683106	459.027346	-0.168239(0)
3d	455.128776	457.676596	459.022503	-0.168141(0)
27	455.115969	457.645967	459.001553	-0.165867(0)
4a	396.629414	398.846364	400.050414	-0.151626(0)
4b	396.625573	398.842088	400.044292	-0.151115(0)
5a	474.264531	476.910822	478.382806	-0.212006(0)
5b	474.255848	476.903268	478.374436	-0.212045(0)
28a	474.248970	476.894139	478.370434	-0.212738(0)
28b	474.240468	476.887489	478.364423	-0.212763(0)
6a	675.631156	679.366810	681.039863	-0.138160(0)
6b	675.621306	679.358635	681.031384	-0.137912(0)
7	341.511421	343.433510	344.482842	-0.118256(0)
8	380.340537	382.476375	383.658101	-0.148266(0)
9	454.803353	457.351392	458.705388	-0.154767(0)
10	396.266909	398.488954	399.701890	-0.137467(0)
11	473.885749	476.539208	478.018902	-0.197701(0)
12	675.316421	679.047376	680.728879	-0.124728(0)

^a Numbers as in the text.^b Zero-point energies (uncorrected) at the RHF/6–31G* level. Values in parentheses are the number of imaginary frequencies in the frequency calculation.

hydroxyl group are also seen. For the phenyl ring, the C₂—C₃ and C₅—C₆ bond lengths are shorter than that of benzene (1.39 Å). On the other hand, other bonds (C₁—C₂, C₃—C₄, C₄—C₅ and C₆—C₁) are longer. Quinoid structures in the phenyl ring are seen not only in other α -hydroxy cations (**1–6**) but also all other delocalized benzylic cations reported in previous papers.^{1,11} The changes in bond lengths in the phenyl ring of benzylic

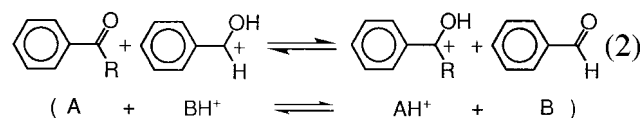
cations are discussed later. All atoms in **1a** and **1b** lie on the same plane ($\phi = 0^\circ$) to form C_s symmetry. Contributions of the α -hydroxyl group and the phenyl ring to the cationic center C₇ are both important factors in stabilizing the cation **1**. The cation **1a** is more stable than **1b** by 2.3 kcal mol⁻¹ at our final level [MP2/6-31G*//RHF/6-31G* + ZPE (scaled 0.9)]. This is attributed to the larger steric repulsion between H₅ and H₆ in **1b**. Since the

angles $\angle H_6O_1C_7$, $\angle O_1C_7C_1$, $\angle C_7C_1C_6$ and $\angle C_1C_6H_5$ in **1b** are larger than the corresponding angles in **1a**, these angles expand so as to release the steric repulsion between H_5 and H_6 in **1b**.

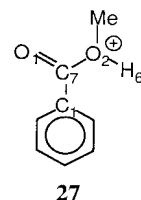
α -Hydroxy- α -methylbenzyl cation (2). Two minima, which are the rotamers around the C_α —O bond, were obtained. The cation **2a** is more stable than **2b** by $1.6 \text{ kcal mol}^{-1}$. This is attributed to the larger steric repulsion between H_5 and H_6 in **2b** than that in **2a**, similarly to the cation **1**. The angles $\angle H_6O_1C_7$, $\angle O_1C_7C_1$, $\angle C_7C_1C_6$ and $\angle C_1C_6H_5$ in **2b** are larger than those in **2a**. The increments in these angles for **2** are of the same order as those for cation **1**. Further, $\phi = 0^\circ$ in **2a** (C_s symmetry) and $\phi = 5.4^\circ$ in **2b**, which also supports the cause of the instability in **2b**. The angle $\angle H_7C_8C_7$ in **2a** is slightly larger than the normal tetrahedral angle in **2b**. This can be explained by the steric repulsion between α -hydroxyl and α -methyl groups in **2a**, although the factor is not important in determining the stability of **2a** and **2b**. In cation **2b**, the α -hydroxyl group is configured to conjugate fully with the cationic center C_7 ($\angle H_6O_1C_7C_1 = 1.9^\circ$), while the phenyl group deviates from the coplanar conformation ($\phi = 5.4^\circ$). The α -hydroxyl group may play a more important role in stabilizing the cation **2** than the phenyl ring, because a hydroxyl group is better electron donor than a phenyl group. With respect to the conformation of the α -methyl group, a hydrogen of the methyl group is on the opposite side of the phenyl ring; $\angle H_7C_8C_7C_1 = 180^\circ$ in **2a** and 173.3° in **2b**. In simple alkyl cations, a C—H bond of the methyl group is aligned with the adjacent cationic $2p\pi$ orbital so as to participate by hyperconjugation.¹⁹ In order to examine the effect of the α -methyl group of cation **2**, the structures of cations **2a** and **2b** were optimized at the RHF/6-31G* level with a fixed dihedral angle $\angle H_8C_8C_7C_1$ (θ), changing in 10° intervals from 0° to 60° . In this calculation, the phenyl ring and C_7 , C_8 , O_1 and H_6 lie on the same plane. The potential energies in both **2a** and **2b** take minimum values at $\theta = 60^\circ$ and increase monotonically with decrease in θ . This means that the steric repulsion between H_2 and H_8 (i.e. α -methyl and phenyl groups) becomes important around $\theta = 0^\circ$. The rotational barriers of **2a** and **2b** are 0.2 and $0.7 \text{ kcal mol}^{-1}$, respectively; some steric repulsion between H_6 and H_7 (i.e. α -hydroxyl and α -methyl groups) exists in **2a**. The conformations with $\angle H_7C_8C_7C_1 = 90^\circ$ ($\theta = -30^\circ$) were not found as energy minima in either **2a** or **2b**. The hyperconjugative stabilization is not important in this cation, similarly to the α -methylbenzyl cation.¹¹ The large degree of charge delocalization to the aromatic moiety ($+0.371$ by MPA in **2a**) may weaken the necessity for hyperconjugation from α -methyl group.

α -Hydroxy- α -methoxybenzyl cation (3). Four minima, which correspond to the rotamers of α -hydroxyl and α -methoxy groups, were obtained. The cation **3a** is more stable by $2.9 \text{ kcal mol}^{-1}$ than **3b**, by $3.9 \text{ kcal mol}^{-1}$ than

3c and by $6.9 \text{ kcal mol}^{-1}$ than **3d**. The angles $\angle C_8O_2C_7$, $\angle O_2C_7C_1$, $\angle C_7C_1C_2$ and $\angle C_1C_2H_2$ in **3c** and **3d** are larger than those in **3a** and **3b**. The dihedral angles $\angle C_8O_2C_7C_1$ are 17° and -15° in **3c** and **3d**, whereas they are -179° and 180° in **3a** and **3b**, respectively. The size of the dihedral angle is attributed to the steric repulsion between α -methoxy and phenyl groups, which makes **3c** and **3d** unstable. Steric repulsion between H_5 and H_6 makes **3d** unstable compared with **3c**, $\angle H_6O_1C_7C_1 = -177^\circ$ in **3c** and -9° in **3d**, and $\phi = 28^\circ$ in **3c** and 42° in **3d**. The conformation of the functional groups in **3c** and **3d** shows that the resonance stabilization of the cationic center C_7 from the α -hydroxyl and α -methoxy groups is more important than that from the phenyl ring. In the cations **3a** and **3b**, α -hydroxyl, α -methoxy and phenyl groups take configurations which make possible almost full resonance stabilization; $\angle H_6O_1C_7C_1 = -2.4^\circ$ in **3a** and 180.0° in **3b**, $\angle C_8O_2C_7C_1 = -179.2^\circ$ in **3a** and 180.0° in **3b** and $\phi = 5.6^\circ$ in **3a** and 0.0° in **3b**. The cation **3a** is more stable than **3b**. The steric repulsion between α -hydroxyl and α -methoxy groups is larger than that between α -hydroxyl and phenyl groups. In the gas-phase experiment, the intrinsic stability of the cation **3** was determined by means of the ICR method, measuring the equilibrium constant of the proton transfer equilibrium expressed by the following equation (R = MeO):



There are two basic sites in the precursor **9**; protonation on the carbonyl oxygen (O_1) generates **3**, and that on the methoxy oxygen (O_2) generates **27**. In order to establish which site is protonated, the geometry of the O_2 -protonated cation **27** was also optimized at the RHF/6-31G* level, and its stability was compared with that of **3**. One energy minimum was found for **27** with $\angle \text{MeO}_2C_7C_1 = -178.3^\circ$ and $\angle H_6O_2C_7\text{Me} = 144.3^\circ$. The cation **3a** is more stable than **27** by $18.7 \text{ kcal mol}^{-1}$ at our final level [MP2/6-31G**//RHF/6-31G*+ZPE (scaled 0.9)]. No other local minima of **27** were found. The cation **3** was really generated in the ICR (mass) spectrometer, and the r_{gas} value of 0.45 reflects the character of the cation **3**.

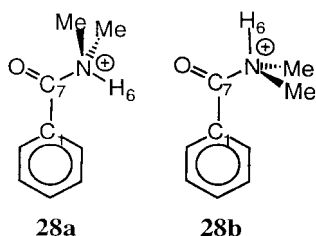


α -Amino- α -hydroxybenzyl cation (4). Two minima **4a** and **4b** were obtained, which are the rotamers of the C_α —O bond. The cation **4a** is more stable than **4b** by $3.6 \text{ kcal mol}^{-1}$. The dihedral angle $\phi = 34^\circ$ in **4a** and $\phi = 17^\circ$ in **4b**. In both cations, lone pairs of hydroxyl and

amino groups are configured to maintain the maximum conjugative stabilization with the vacant $2p\pi$ orbital; the dihedral angle $\angle H_6O_1C_7C_1 = -10.6^\circ$ and 174.8° , $\angle H_7N_1C_7C_1 = 176.9^\circ$ and 175.9° and $\angle H_8N_1C_7C_1 = -7.7^\circ$ and -5.2° in **4a** and **4b**, respectively. In addition, the geometry of N_1 takes a planar trigonal structure; $\angle H_7N_1C_7H_8 = -175.6^\circ$ and -179.0° in **4a** and **4b**, respectively. The contribution of the resonance stabilization from the phenyl ring is not important. The difference in stability between **4a** and **4b** should be ascribed to the steric repulsion of H_6 and the amino group; $\angle H_6O_1C_7 = 113.6^\circ$ and 116.2° and $\angle O_1C_7N_1 = 114.1^\circ$ and 120.1° in **4a** and **4b**, respectively.

α -Dimethylamino- α -hydroxybenzyl cation (5). Two minima **5a** and **5b** were obtained, which are the rotamers of the $C_\alpha-O$ bond. The cation **5a** is more stable than **5b** by $5.3 \text{ kcal mol}^{-1}$. The steric repulsion between α -hydroxyl and α -dimethylamino groups is larger than that between α -hydroxyl and phenyl groups. In both cations, α -hydroxyl and α -dimethylamino groups take conformations so as to conjugate fully with the cationic center C_7 ; the deviations from coplanarity of the dimethylamino group are 9° in **5a** and 12° in **5b** and of the hydroxyl group are 8° in **5a** and 10° in **5b**. In contrast, $\phi = 51^\circ$ in **5a** and $\phi = 40^\circ$ in **5b**, suggesting the conjugative stabilization from the phenyl ring is less important in these cations, the same as in the cations **4**.

As a similar case to the cation **3**, there are two basic sites in the precursor **11** due to protonation, the carbonyl oxygen and dimethylamino nitrogen. The optimized geometry of the N -protonated cation **28** is located to two energy minima as **28a** and **28b**, which are rotamers of the protonated dimethylamino group; $\angle H_6NC_7C_1 = 17.4^\circ$ in **28a** and 180.0° in **28b**. The cation **28a** is more stable than **28b** by $3.8 \text{ kcal mol}^{-1}$. The cation **5a** is more stable than **28a** by $8.2 \text{ kcal mol}^{-1}$ at our final level. No other local minima were found. The protonation should occur at O_1 in **11**, the carbocation **5** was actually generated in the ICR and the r_{gas} value of 0.23 reflects the stability of the cation **5**.



α -Hydroxy- α -trifluoromethylbenzyl cation (6). Two minima **6a** and **6b** were found. The cation **6a** is more stable than **6b** by $5.2 \text{ kcal mol}^{-1}$. The instability of **6b** is attributed to the steric repulsion between H_5 and H_6 , which is similar to that in cation **2**; the angles $\angle H_6O_1C_7$, $\angle O_1C_7C_1$, $\angle C_7C_1C_6$, $\angle C_1C_6H_5$, in **6b** are larger than those in **6a**. Both cations **6a** and **6b** have $\phi = 0^\circ$ (C_s symmetry),

which is contrast to $\phi = 5^\circ$ in the cation **2b**. This coplanarity may be explained by the increased resonance demand on the phenyl ring due to the destabilization of the cationic center C_7 by the electron-attracting trifluoromethyl group.

Neutral benzoyl compounds (7–12). Optimized structures of **7–12**, which are the conjugative bases of **1–6**, respectively, are shown in Fig. 3 and Fig. 4. In species **7–12**, the bond lengths of C_1-C_7 and the phenyl ring are almost constant, which is contrast to the conjugate acid ions, α -hydroxybenzyl cations. In detail, these benzoyl compounds are C_s symmetry except for **10** and **11**; there is a weak resonance interaction between the phenyl ring and carbonyl group. In benzamide (**10**) and N,N -dimethylbenzamide (**11**), $\phi = 22^\circ$ and 41° , respectively, due to the steric effect in R (amino and dimethylamino) groups. The dihedral angle $\angle C_8N_1C_7C_9 = 153.2^\circ$ in **11**, which is larger than $\angle C_1N_1C_2C_3 = 126.6^\circ$ in trimethylamine. Also, the dihedral angle $\angle H_6N_1C_7H_7 = 145.4^\circ$ in **10**, which is larger than the corresponding dihedral angle (120.6°) in methylamine. These larger dihedral angles in **10** and **11** may be attributed to the conjugative interaction between N_1 and the neighboring π -system.

Inspection of *ab initio* energy. Gas-phase basicities for a variety of compounds have been determined based on the equilibrium constant for the gas phase proton transfer reaction between two bases.²⁰ The free energy change (ΔG°) of proton transfer equilibria (2) in the gas phase for benzoyl compounds was determined by means of the ion cyclotron resonance (ICR) method:⁷

$$\delta\Delta G^\circ = \Delta G^\circ(\text{AH}^+) + \Delta G^\circ(\text{B}) - \Delta G^\circ(\text{A}) - \Delta G^\circ(\text{BH}^+) \quad (3)$$

The energy difference in the isodesmic reaction (2) can also be estimated by the *ab initio* MO method. Comparison of these calculated and experimental energies makes it possible to examine the validity of the present calculation level. The absolute gas-phase basicity (GB) is expressed as

$$GB = -[\Delta G^\circ(\text{AH}^+) - \Delta G^\circ(\text{A})] \quad (4)$$

and the proton affinity (PA) is expressed as

$$PA = -[\Delta E^\circ(\text{AH}^+) - \Delta E^\circ(\text{A})] \quad (5)$$

Relative free energy changes obtained experimentally by the ICR method and the calculated energy change at the MP2/6-31G**/RHF/6-31G* + ZPE (scaled 0.9) level, which are both determined by means of Eqn (2), are summarized in Table 5 together with their calculated PA and experimental GB values. At the RHF/3-21G level, marked deviations for the most stable isomers are 5 kcal mol^{-1} in **5a** and **6a**. At the RHF/6-31G* level, it is *ca* 4 kcal mol^{-1} in **6a**. The relative stabilities for cations **1a–3a** and **5a–6a** with respect to **1a** calculated at

Table 5. Experimental and calculated energies (kcal mol⁻¹).

R		Absolute <i>GB</i> value ^a	- ΔGB^b	Calculated <i>PA</i> value ^c	- ΔPA^d	
H	(expt)	192.1 ^e	0.0			
	(1a) (1b)			195.6 193.4	0 2.2	
Me	(expt)	197.3 ^f	-5.2			
	(2a) (2b)			201.0 199.4	-5.4 -3.8	
MeO	(expt)	195.7 ^g	-3.6			
	(3a) (3b) (3c) (3d)			198.3 195.4 194.4 191.4	-2.7 0.2 1.2 4.2	
	NH ₂	(4a) (4b)			210.7 207.2	-15.1 -11.6
		(expt)	213.8 ^h	-21.7		
NMe ₂	(5a) (5b)			220.3 215.0	-24.7 -19.4	
	(expt)	184.4 ⁱ	7.7			
CF ₃	(6a) (6b)			187.6 182.4	8.0 13.2	

^a See Eqn (4).^b See Eqns (2) and (3). Relative to R=H derivative.^c See Eqn (5).^d $-\Delta PA = \Delta E^\circ(AH^+) + \Delta E^\circ(7) - \Delta E^\circ(A) - \Delta E^\circ(1a)$; relative to R=H (**1a**) derivative.^e Refs 7b and 7f.^f Refs 7c and 7f.^g Refs 7d and 7f.^h Ref. 7e.ⁱ Ref. 7a.

the MP2/6-31G**/RHF/6-31G* + ZPE (scaled 0.9) level were plotted against those determined in the gas phase, as shown in Fig. 5. An approximately linear relationship with a slope of unity exists over a wide range of *ca* 30 kcal mol⁻¹ for these most stable isomers (**1a**, **2a**, **3a**, **5a** and **6a**). The maximum deviation from the 1:1 line for

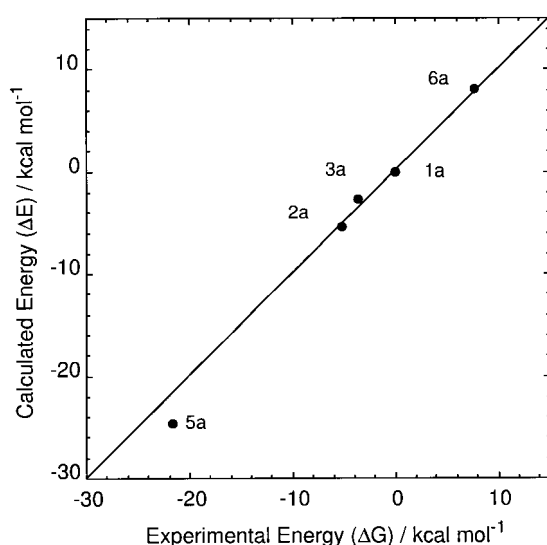


Figure 5. Calculated [MP2/6-31G**/RHF/6-31G* + ZPE (scaled 0.9) level] vs experimental energy with respect to the isodesmic reactions (2)

the most stable isomers is *ca* 3 kcal mol⁻¹ for cation **5a**. Plots for other isomers deviate upward from the correlation line, reflecting the steric repulsion of α -substituents and the phenyl ring. Although thermodynamic quantities for cations should be given as averages of statistical contributions of isomers, the calculated energy for the most stable isomers reproduced the experimental values well. That is, other conformations are not important in determining the features of cations **1-6**. It has been reported that single-point MP2 correlations on 6-31 + G* structures for acids and their conjugate bases give gas-phase acidities that agree with the experimental values within experimental uncertainty.²¹ Further correction to 298 K for the contributions of the translational, rotational and vibrational partition functions to ΔE makes only a slight difference in most of acidities.²¹ The present level of calculation seems to be sufficient to reproduce the experimental values for these benzylic derivatives.

Rotational potentials with respect to the dihedral angles ϕ and θ in **4a** and **5a**

In order to examine the importance of the resonance contribution of the phenyl ring, structures of **4a** were calculated at the RHF/6-31G* and MP2/6-31G**/RHF/6-31G* levels with a fixed dihedral angle ϕ , changing in

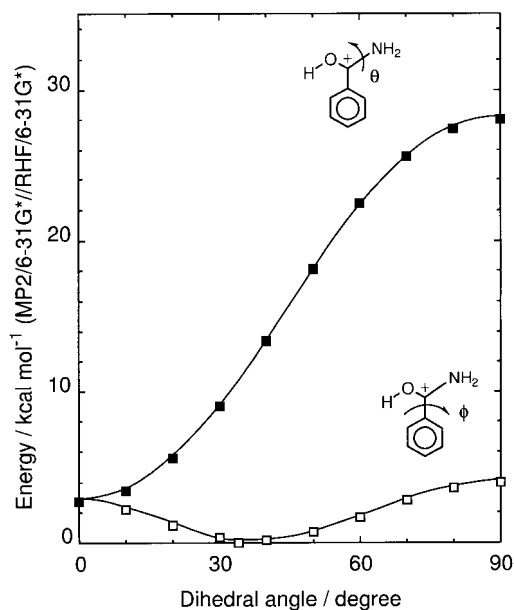


Figure 6. Potential energy surface of α -amino- α -hydroxybenzyl cation (**4a**) at the MP2/6-31G*//RHF/6-31G* level

10° intervals from 0° to 90° . In the calculations, the phenyl ring is fixed in the plane. Potential energies at the MP2/6-31G*//RHF/6-31G* level were plotted against ϕ , shown as open squares in Fig. 6. For the cation **4a**, the potential energy curve was increased by *ca* 3 kcal mol^{-1} from the equilibrium structure ($\phi = 34^\circ$) to the coplanar structure ($\phi = 0^\circ$). This rotational barrier may be attributed mainly to the steric repulsion between α -substituents and the phenyl ring. On the other hand, the barrier from the equilibrium structure ($\phi = 34^\circ$) to the orthogonal structure ($\phi = 90^\circ$) is *ca* 4 kcal mol^{-1} , which may be attributed mainly to the loss of resonance stabilization. The corresponding potential curve of the tertiary α,α -dimethylbenzyl cation shows a monotonic increase from $\phi = 0^\circ$ to 90° , and the rotational barrier is *ca* 21 kcal mol^{-1} at the same (MP2/6-31G*//RHF/6-31G*) level.¹ The small rotational barrier of **4a** relative to the α,α -dimethylbenzyl cation shows that the cation **4** is stabilized significantly by α -substituents, and the resonance requirement of the cation center C_7 to the phenyl ring is small. This is consistent with $\angle H_7N_1C_7H_8 = -175.6^\circ$ in **4a**; the N_1 atom has a planar structure so as to conjugate fully with the cationic center.

The electron-donating ability of planar amino groups should be the important factor in stabilizing the cation **4**. When the amino group is rotated around the C_7-N_1 bond, the electronic effect with respect to the cationic center should be changed drastically. This change should also influence the resonance interaction between the cationic center C_7 and the phenyl ring, the resonance demand *r* value. In this respect, the geometries of **4a** were optimized with a fixed dihedral angle θ changing in 10° intervals from 0° to 90° . The angle θ is the dihedral angle

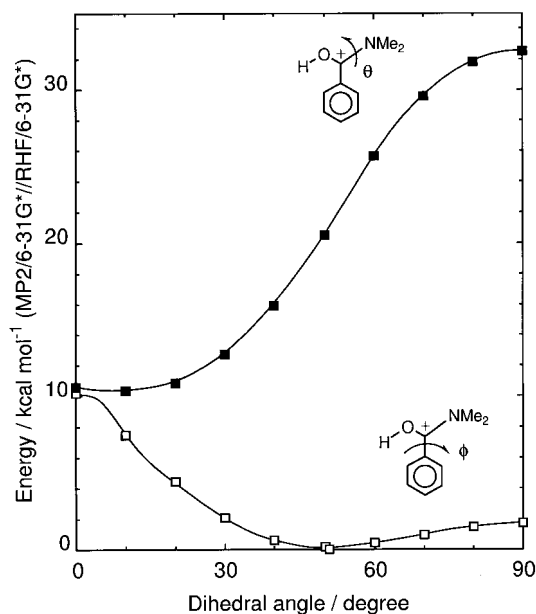


Figure 7. Potential energy surface of α -dimethylamino- α -hydroxybenzyl cation (**5a**) at the MP2/6-31G*//RHF/6-31G* level

between the cationic $2p\pi$ orbital on C_7 and the lone pair on N_1 . The lone pair has the direction of N_1-X_1 which is a dummy atom defined by $\angle X_1N_1C_7H_7 = -\angle X_1N_1C_7H_8$. The phenyl ring, C_7 , hydroxyl group and N atom were fixed to be planar. The angular profile of the potential energies at the MP2/6-31G*//RHF/6-31G* level were plotted against θ , shown as closed squares in Fig. 6. The energy increases monotonically with increase in θ and reaches 25 kcal mol^{-1} in **4a** ($\theta = 90^\circ$). The energy increment should be related to the loss of resonance interaction between the amino group and the cationic center, accompanying the decrease in coplanarity. Steric hindrance (*ca* 3 kcal mol^{-1}) exists between the phenyl group and α -substituents at $\theta = 0^\circ$. This steric effect should decrease as θ increases. Thus, in the equilibrium structure of **4a**, the amino group contributes significantly (*ca* 28 kcal mol^{-1}) to stabilization by the resonance effect. The dihedral angle $\angle H_7N_1C_7H_8 = 180^\circ$ in **4a** ($\theta = 0^\circ$); the nitrogen atom takes a planar structure, and there is maximum conjugation between the lone pair and cationic $2p\pi$ orbital. As θ increases, $\angle H_7N_1C_7H_8$ decreases monotonically, and the structure of the nitrogen atom approaches tetrahedral. In **4a** ($\theta = 90^\circ$), $\angle H_7N_1C_7H_8 = 120.3^\circ$ which is of the same order as the corresponding dihedral angle of ammonia (114.8°);²² the lone pair on N_1 is not involved in the conjugation with the cationic $2p\pi$ orbital on C_7 . Geometries on the nitrogen atom also reflect a change in resonance interaction through the dihedral angle θ .

Rotational potentials around ϕ and θ for **5a** were also calculated in the same manner as for **4a**. Potential energies are plotted against ϕ as open squares in Fig. 7. In

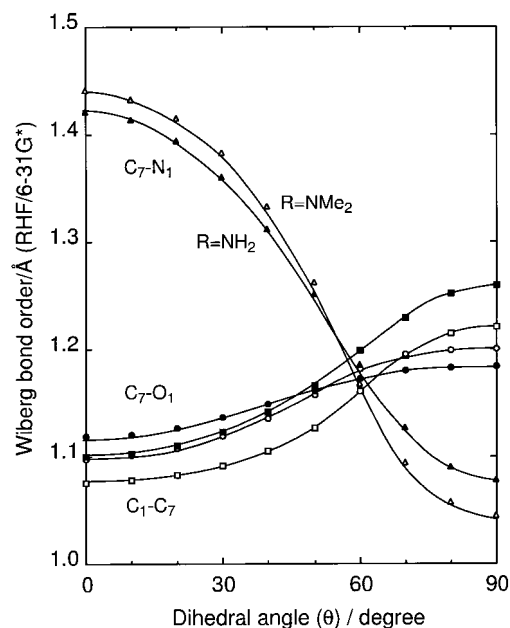


Figure 8. Wiberg bond order of C_7-N_1 , C_7-O_1 and C_1-C_7 bonds in **4a** (closed symbols) and **5a** (open symbols) vs θ , which is the angle between the empty $2p\pi$ orbital on C_7 and the lone pair on N_1 . Triangles, C_7-N_1 ; circles, C_7-O_1 ; squares, C_1-C_7

the cation **5a**, the rotational barriers are *ca* 10 kcal mol⁻¹ to the coplanar and only *ca* 2 kcal mol⁻¹ to the orthogonal structure from the equilibrium structure. The rotational barrier to the coplanar structure in **5a** is three times larger than that in **4a** owing mainly to the bulkiness of the dimethylamino group. On the other hand, the barrier to the orthogonal structure is lower than that in **4a**. The cation **5** should be stabilized significantly by α -substituents, and thus the resonance requirement of the cation center C_7 to the phenyl ring becomes small. The dihedral angle $\angle C_8N_1C_7C_9 = -175.0^\circ$ in **5a**; the N_1 atom has a planar structure so as to exert full conjugation between the cationic center and the lone pair on the nitrogen atom.

The potential energies of **5a** are plotted against θ as closed squares in Fig. 7. The method of calculation and the definition of θ are the same as those for **4a**. The cation **5a** has almost a constant energy (within 0.3 kcal mol⁻¹) from $\theta = 0^\circ$ to 20° . With increase in θ , the energy increases monotonically and reaches to 22 kcal mol⁻¹ in **5a** ($\theta = 90^\circ$) from **5a** ($\theta = 20^\circ$). This should be caused by the loss of resonance interaction between the dimethylamino group and the cationic center, due to the decrease in coplanarity. Steric hindrance more than 10 kcal mol⁻¹ exists between the phenyl group and α -substituents even in **5a** ($\theta = 0^\circ$). This steric effect should decrease as θ increases. Thus, in the equilibrium structure of **5a** the dimethylamino group contributes significantly (*ca* 30 kcal mol⁻¹) to stabilization of the cation by the resonance effect. The dihedral angle of

$\angle C_9N_1C_7C_8 = 180^\circ$ in **5a** ($\theta = 0^\circ$); there is maximum conjugation between the lone pair on the nitrogen atom and the cationic $2p\pi$ orbital, similarly to **4a**. As θ increases, $\angle C_9N_1C_7C_8$ decreases monotonically, and the structure of the nitrogen atom becomes tetrahedral. In **5a** ($\theta = 90^\circ$), $\angle C_9N_1C_7C_8 = 129.5^\circ$, which is close to the corresponding dihedral angle of dimethylamine (125.4°);²² the lone pair on N_1 is not associated with the conjugation with the cationic $2p\pi$ orbital on C_7 . Similarly to the cation **4a**, the geometries on the nitrogen atom also reflect a change of resonance interaction by the dihedral angle θ . As we have seen here, resonance effects from the amino and dimethylamino groups contribute more in **4a** and **5a** than those from phenyl rings. In other words, steric and resonance effects of the phenyl rings with respect to stability of the cations **4a** and **5a** are not so important.

Wiberg bond orders of C_7-N_1 (closed triangles), C_1-C_7 (closed squares) and C_7-O_1 (closed circles) in **4a** are plotted against θ in Fig. 8. Plots for **5a** are included in Fig. 8 with corresponding open symbols. The bond order of C_7-N_1 is 1.4 in **4a** and **5a** ($\theta = 0^\circ$), and decreases monotonically as θ increases, reaching 1.0–1.1 at $\theta = 90^\circ$. The π interactions of C_7 with amino and dimethylamino groups decrease with their decreased coplanarity. The decrease in the C_7-N_1 bond order by loss of coplanarity (from $\theta = 0^\circ$ to 90°) is larger in **5a** than **4a**. This should be attributed to the larger resonance ability of the dimethylamino group ($\Delta\bar{\sigma}_R^+ = -1.3$) than that of the amino group ($\Delta\bar{\sigma}_R^+ = 1.1$), resulting in a smaller r value for **5a** (0.23) than **4a** (0.35). The bond orders of C_1-C_7 and C_7-O_1 increase from 1.1 to 1.2 as θ increases in both cations; the double bond character is strengthened slightly in these bonds. This can be explained by the enhanced resonance requirement of the cationic center C_7 to hydroxyl and phenyl groups as a result of the decrease in the π contribution from amino and dimethylamino groups. It is readily seen from these plots in Fig. 8 that the degree of resonance effect between C_7 and the phenyl ring, i.e. the r value, depends on the balance of the electronic effects of the phenyl group and α -substituents in benzylic cations. The trends of other indices such as bond lengths and charge distributions also support this conclusion.

Charge vs r value

In electronic theory, the charge density at a given atom is a useful tool for predicting characteristics or reactivities of molecules qualitatively. The r value has been explained as the degree of π -charge delocalization to the benzene ring from the reaction center at the transition state. In order to discuss this concept from the viewpoint of theoretical chemistry, the relationships between atomic charges on some positions and the r value were examined. Atomic charges on the respective carbons of α -hydroxybenzylic cations were calculated by Mulliken

Table 6. Atomic charges given by Mulliken population analysis for benzylic cations

Cation ^a	Charge ^b (RHF/6-31G*)						
	C ₁	<i>Ortho</i> ^c	<i>Meta</i> ^d	<i>Para</i> ^e	C ₇	OH	R
1a	-0.133	0.157	0.047	0.166	0.617	-0.058	0.000
2a	-0.141	0.139	0.044	0.146	0.546	-0.095	0.178
3a	-0.149	0.097	0.050	0.126	0.893	-0.118	-0.046
4a	-0.111	0.061	0.062	0.111	0.783	-0.119	0.090
5a	-0.137	0.059	0.058	0.093	0.791	-0.145	0.164
6a	-0.138	0.181	0.047	0.179	0.391	-0.086	0.198

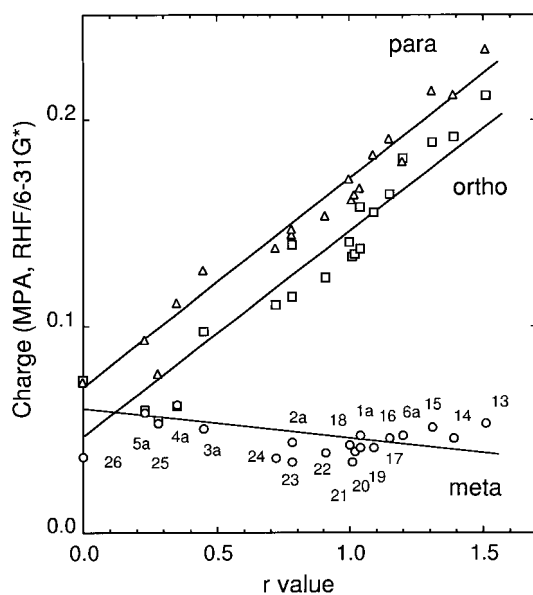
^a Numbers as in the text.^b Atomic charges on each position with hydrogens summed into atoms.^c Average atomic charge of C₂ and C₆.^d Average atomic charge of C₃ and C₅.^e Atomic charge of C₄.

population analysis (MPA) and are summarized in Table 6. Averaged values are used for atomic charges on *ortho* [(C₂+C₆)/2] and *meta* [(C₃+C₅)/2] positions. The charge on a hydrogen is summed up into that on the carbon atom. Atomic charges on *ortho*, *meta* and *para* positions of α -hydroxybenzylic cations, and also other benzylic cations, are plotted against the *r* values in Fig. 9. The *r* values used in Figs 9–12 are those obtained in the gas phase for **1–3**, **5** and **6** and in solution for **4**. The same *r* values were obtained in solution and in the gas phase for all benzylic cations examined (Table 1), so that the *r* value of **4** in the gas phase can be substituted by that in the solution phase. In Fig. 9 the plots are for most stable isomers, because only they reproduce the experimental energies, as discussed earlier. Indeed, the best correlation is given in the plots for the most stable isomers. Atomic charges of other unstable isomers deviate from the

correlation line mainly owing to the steric effect between α -hydroxyl and phenyl groups. As seen in Fig. 9 for **1a–6a**, charges on the *para* and *ortho* positions increase linearly with the same slope as the *r* value increases. The atomic charge on the *para* position is larger than that on the *ortho* position except for the cation **6a**. The *meta* charge is almost constant for all cations. These correlation lines for **1a–6a** satisfy the identical correlation of other benzylic cations.¹¹

Benzylic cations may be classified into three groups. (1) For cations in which an electron-withdrawing group (such as CF₃) is introduced at the α -position, unstable cationic centers increase the resonance demand compared with the standard α -cumyl system (*r* = 1). (2) In contrast, for cations which have an electron-releasing group (such as OCH₃) at the α -position, the resonance demand decreases. (3) For cations in which a bulky substituent (such as *t*-Bu) is introduced at the α -position, the *r* value decreases accompanied by decreased overlapping of the benzylic 2p π orbital and benzene π -system. The cations **4** and **5** may belong to both groups (2) and (3). For all cations which belong to these three groups, the atomic charges the *ortho*, *meta* and *para* positions are linearly correlated with the *r* value over a wide range from 0 to 1.5, as shown in Fig. 9. These relationships are consistent with the prediction of the electronic theory. Hence the *r* value is a real parameter indicating the degree of resonance interaction between the benzylic 2p π orbital and benzene π -system.

The total net charges on the phenyl ring and α -hydroxyl group (hereafter group charge) for **1a–6a** were plotted against the *r* value as shown in Fig. 10. Plots of net charges on the phenyl ring and α -methyl and α -*t*-Bu groups for other benzylic cations are also included in Fig. 10. A linear correlation was obtained for group charges in **1a–6a**. Also in this plot, the best relationships were obtained for the most stable isomers. Plots of other isomers for **1–6** deviated from this correlation line. For **1a–6a**, charges on both the phenyl ring and hydroxyl group increase as the *r* value increases. Charge dispersion to the phenyl ring and hydroxyl group from the cationic

**Figure 9.** Atomic charge on *o*-, *m*- and *p*-positions of phenyl ring (RHF/6-31G*) vs *r* values for benzylic cations. Numbers as in Table 1

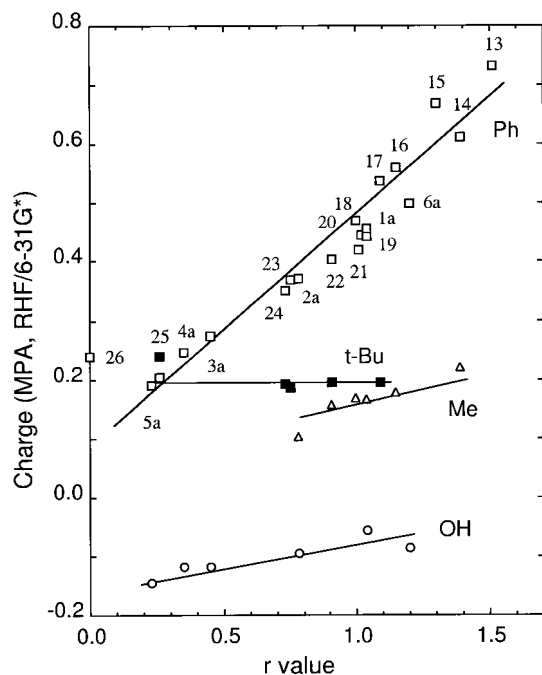


Figure 10. Atomic charge on the phenyl ring and α -substituents (RHF/6-31G*) vs r values for benzylic cations. Numbers as in Table 1

center changes accompanied by the change in the contribution from another α -substituent. That is, in **6a**, the electron-attracting α -trifluoromethyl group destabilizes the cationic center (C_7), which requires resonance stabilization significantly to the other substituents. Thus a larger amount of charge was delocalized in the neighboring phenyl and hydroxyl groups in **6a**. In contrast, the stabilization requirement to phenyl and hydroxyl groups is small in cations **4a** and **5a** owing to the electron-releasing α -amino and α -dimethylamino groups, respectively. Hence the charge delocalization to phenyl and hydroxyl moieties is small in cations **4a** and **5a**. The charge delocalization for these cations suggests a competitive contribution to the cationic center from α -substituents and the phenyl ring. The behavior of the charge distribution on the phenyl ring for cations **1a–6a** satisfies the same relationship as those for other benzylic cations. Group charges on the phenyl ring increase linearly from +0.2 to +0.7 when the r value changes from 0 to 1.5. Simultaneously, linear relationships against the r value were observed for charge on the α -methyl group in cations **2**, **14**, **16**, **18**, **19** and **22** and on the α -*t*-Bu group in cations **17**, **22**, **23**, **24** and **25**. These facts also support a competitive contribution from α -substituents at the cationic center. The degree of contribution from the phenyl ring is directly related to the r value. Charge delocalizations to both α -methyl and α -hydroxyl groups are less sensitive to the r value than that of the phenyl group, and more sensitive than that of α -*t*-Bu group. The

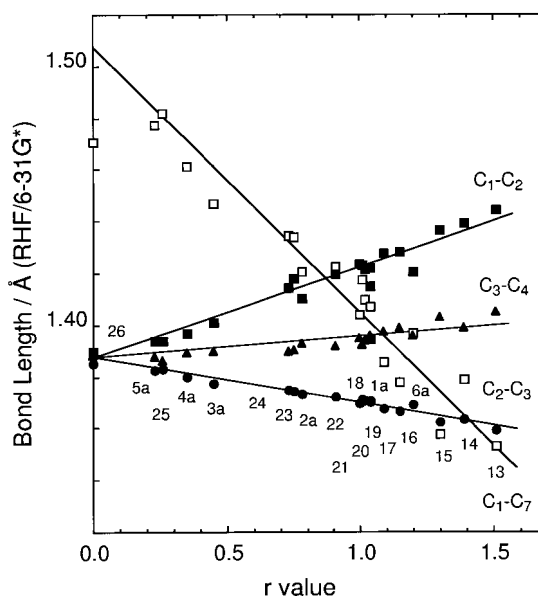
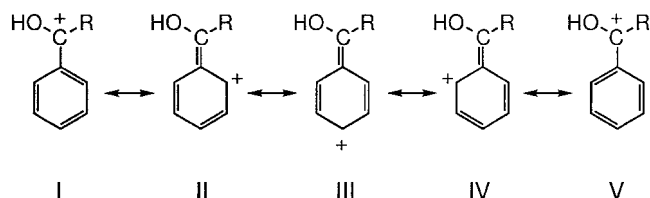


Figure 11. Bond length vs r value for benzylic cations. Numbers as in Table 1

high sensitivity of the phenyl ring may be accounted for by the larger capacity (or orbitals) which accepts charges.

Bond length vs r value

Bond lengths of cations, summarized in Table 2, should change reflecting the degree of resonance contribution from α -substituents to the cationic center. The C_1 — C_2 , C_2 — C_3 , C_3 — C_4 and C_1 — C_7 bond lengths for the most stable isomers (**1a–6a**) are plotted against the r value in Fig. 11 together with those for other benzylic cations. For **1a–6a**, the C_1 — C_7 bond length decreases linearly as the r value increases. The double bond character of C_1 — C_7 increases, as the degree of contribution from the phenyl ring increases. Bond alternations in the benzene framework were observed; the C_1 — C_2 and C_3 — C_4 bond lengths are lengthened but C_2 — C_3 is shortened as the r value increases. This is interpreted as the degree of contribution of canonical structures (II–IV).



For all α -hydroxybenzylic cations (**1–6**), the plots for the most stable isomers give excellent correlations. Changes in the bond lengths of C_1 — C_2 , C_2 — C_3 , C_3 — C_4 and C_1 — C_7 make it possible to detect the degree of resonance requirement of the cationic center C_7 to the

phenyl ring. The length of the C_α —O bond (Table 2) decreases linearly as the r value increases. This fact also supports a competitive contribution from substituents to the cationic center.

Wiberg bond order vs r value

Wiberg bond orders of C_1 — C_2 , C_2 — C_3 , C_3 — C_4 and C_1 — C_7 for cations **1a**–**6a** are summarized in Table 7, and are plotted against the r values together with data for other benzylic cations in Fig. 12. Good linear correlations were obtained for every bond. Strictly, some patterns exist according to the type of benzylic cations. For example, the plots for α -hydroxy cations (**1a**–**6a**) for C_1 — C_7 show an excellent linear correlation with a smaller slope than that of correlation line for α -alkylbenzylic cations. The same tendency as for the C_1 — C_7 bond is observed for the C_1 — C_2 , C_2 — C_3 and C_3 — C_4 bonds. Changes in Wiberg bond order may not only depend on the contribution of the phenyl ring to the cationic center. Some additional effect caused by the type of α -substituents can also be seen in α -CF₃-substituted benzylic cations; the plots for **13**, **14** and **6a** show a linear correlation with a large slope compared with that for α -alkylbenzylic cations. However, the Wiberg bond orders are approximately linearly related to the r value. The correlation pattern can be well explained by the electronic theory. Although a family dependence of this type can be seen in the plots of bond lengths and charge distributions, this complex result does not seriously affect the discussion of the relationship between these indices and the r values.

The empirical r values in the Y–T substituent effect analysis for benzylic solvolyses, equilibria and thermodynamic stabilities of benzylic cations are well correlated with all calculated indices (charge distribution, bond length and bond order) of the corresponding benzylic cations including α -hydroxybenzylic cations. These benzylic cations have electronically and sterically various α -substituents which affect their r values. That

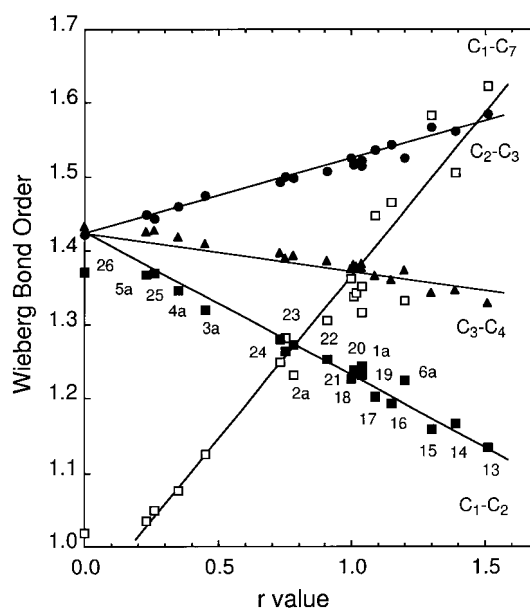


Figure 12. Wiberg bond orders from NBO analysis (RHF/6-31G*) vs r values for benzylic cations. Numbers as in Table 1

is, these relationships apply not only to the unstable cations¹¹ and the sterically hindered¹ cations reported previously, but also to the present stable α -hydroxybenzylic cations. The relationship between each theoretical index and the r value agreed completely with the prediction by the electronic theory.

Although the ρ_{gas} values seem to change with the r_{gas} values in other benzylic systems (**13**–**23**), it has become apparent that the r values are independent of the ρ values (Table 1). The ρ_{gas} values for stable α -hydroxybenzylic systems (**1**–**6** in Table 1) are constant, whereas the corresponding ρ_{gas} values for other α -substituents change drastically with changes in electronic and steric effects.

These results suggest that the r value is real parameter indicating the degree of resonance interaction between the benzylic $p\pi$ -orbital and the benzene π -system.

Table 7. Wiberg bond orders from NBO analysis for benzylic cations

Cation ^a	Wiberg bond order					
	C_1 — C_7	C_1 — C_o ^b	C_o — C_m ^c	C_m — C_p ^d	C_7 —O	C_7 —R
1a	1.3149	1.2439	1.5141	1.3823	1.2251	0.9209
2a	1.2310	1.2731	1.4979	1.3938	1.2208	1.0474
3a	1.1240	1.3186	1.4752	1.4090	1.1552	1.2218
4a	1.0749	1.3468	1.4596	1.4185	1.1444	1.4281
5a	1.0344	1.3688	1.4488	1.4257	1.1108	1.4720
6a	1.3320	1.2244	1.5245	1.3740	1.2314	0.9303

^a Numbers as in the text.

^b Average of bonds C_1 — C_2 and C_6 — C_1 .

^c Average of bonds C_2 — C_3 and C_5 — C_6 .

^d Average of bonds C_3 — C_4 and C_4 — C_5 .

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