JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 21–28
DOI:10.1002/poc.439

Extended charge delocalization to 4-phenoxy substituent in benzhydryl solvolysis: possible contribution of non-canonical resonance structure in the cationic transition state

Kwang-Ting Liu,* Chih-Shiow Chuang and Bih-yaw Jin*

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, ROC

Received 23 April 2001; revised 14 June 2001; accepted 6 July 2001

ABSTRACT: Solvolytic reactivities of 4-nitrobenzhydryl bromides (**2b**–**5b**) and chlorides (**2c**–**5c**) were studied using single- and dual-parameter Grunwald–Winstein-type correlation analyses with Y_{BnX} and $Y_{x\mathrm{BnX}}$ scales, respectively. Extended charge delocalization over two aryl rings at cationic transition states were found for **3** and **5**, but not for **2** or **4**. Calculations of the charge distributions in **3c** and in the corresponding cation **3a** were performed using a Hartree–Fock approximation (RHF/6-31G* basis set) and density functional models (pBP/DN** and other basis sets), respectively, on Mulliken population analysis and on electrostatic potential analysis. The possible contribution of non-canonical resonance structure is discussed.

KEYWORDS: benzhydryl halides; *ab initio* calculations; correlation analysis; kinetics; non-canonical resonance

INTRODUCTION

The solvolysis of the benzhydryl system is generally considered to proceed *via* a unimolecular ionization mechanism.[1] Theoretical studies using AM1 calculations indicated that the transition state was at about a little earlier than the half-way point along the reaction coordinate for the formation of the cationic intermediate.[2] Intramolecular nucleophilic participation was realized in the solvolysis of several *ortho* substituted benzhydryl halides, such as *o*-nitro- and *o*-carbophenoxybenzhydryl bromides[3,4] and chlorides,[3] especially in solvents of low nucleophilicity.[5]

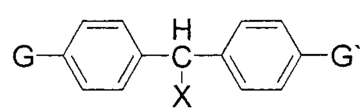
In the study of the solvolytic mechanism, correlation of rates of solvolysis using single- or dual-parameter Grunwald–Winstein equations [Eqns (1)[6] or (2)[7]] with appropriate scales of solvent ionizing power Y and solvent nucleophilicity N has generally been employed as an effective tool for detecting the involvement of solvent participation. Some recent examples are shown in Ref. 8.

$$\log k = mY \qquad (1)$$

$$\log k = mY + lN \qquad (2)$$

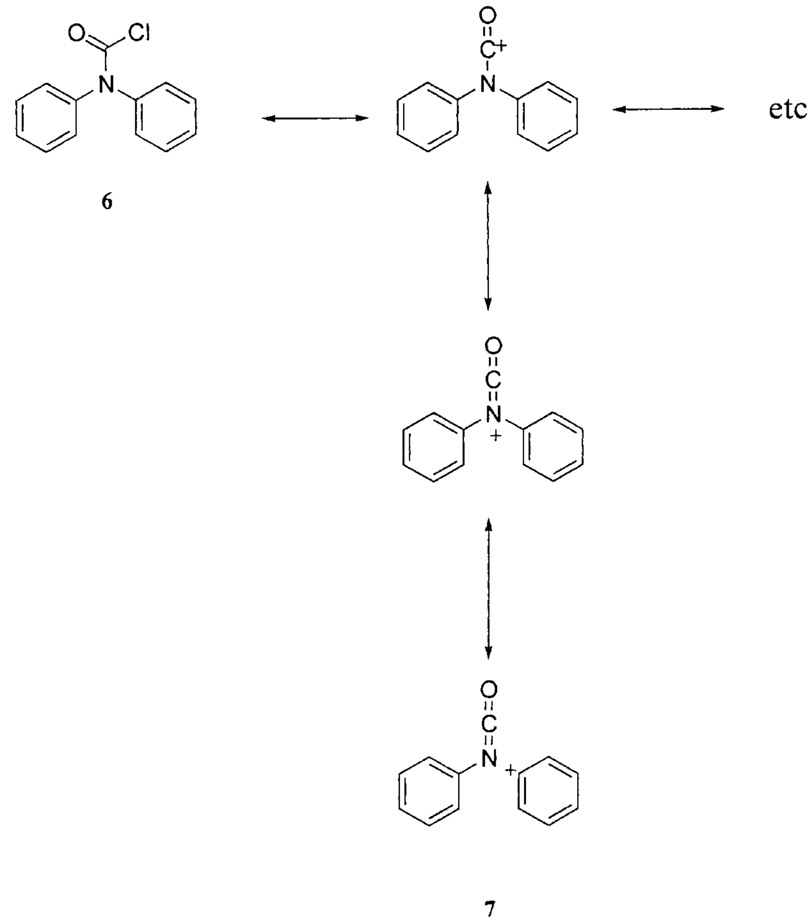
*Correspondence to: K.-T. Liu or B. Jin, Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, ROC.
Contract/grant sponsor: The National Science Council, Republic of China.

In our previous studies we employed Y_{BnX} and $Y_{x\mathrm{BnX}}$ scales of solvent ionizing power[9] to demonstrate the variation of extent of charge delocalization in the cationic transition state for the solvolysis of benzhydryl bromides[10] or chlorides[11] containing different substituents. Moreover, for 4-nitrobenzhydryl bromide (**2b**)[10] and chloride (**2c**),[11] linear correlation using the dual-parameter equation in Eqn. (2) with Y_{BnX} and N (N_{OTs} or N_{T}) indicated nucleophilic solvent participation in solvolysis and the positive charge delocalized mainly over the unsubstituted phenyl ring. To extend our investigation on the solvolysis of disubstituted benzhydryl systems, a series of 4′-substituted 4-nitrobenzhydryl bromides (**3b**–**5b**) and chlorides (**3c**–**5c**) were studied.



G = G\` = H	X = Br (**1b**)	X = Cl (**1c**)
G = H , G\` = 4-NO_2	X = Br (**2b**)	X = Cl (**2c**)
G = 4-C_6H_4O , G\` = 4-NO_2	X = Br (**3b**)	X = Cl (**3c**)
G = 4-CH_3 , G\` = 4-NO_2	X = Br (**4b**)	X = Cl (**4c**)
G = 4-C_6H_5 , G\` = 4-NO_2	X = Br (**5b**)	X = Cl (**5c**)

On the other hand, recent work on the solvolysis of *N,N*-diphenylcarbamoyl chloride (**6**) suggested a possible contribution of non-canonical resonance structure in the



Scheme 1

cationic transition state (**7**) (Scheme 1).[12] Thus, it is desirable to examine other systems to find out if a similar phenomenon could also be observed. Indeed, an excellent linear relationship for the single-parameter equation in Eqn. (1) with $Y_{x\mathrm{BnX}}$ scales in the case of 4′-phenoxy derivatives (**3b** and **3c**) was observed. *Ab initio* calculations were to confirm positive charge distribution to the phenoxy ring in the 4-nitrophenyl-4-phenoxyphenylmethyl cation (**3a**), and to suggest a possible contribution of non-canonical resonance structure.

RESULTS AND DISCUSSION

4′-Substituted 4-nitrobenzhydryl halides **3b–5b** and **3c–5c** were prepared from the corresponding alcohols by using conventional methods. Solvolyses were carried out in a variety of solvents, and kinetic measurements were performed by the conductimetric method. Pertinent rate constants at 25 °C are listed in Table 1. The preference of using N_{OTs}, rather than N_{T}, has already been demonstrated.[11] Thus, regression analyses of log k values against Y_{BnBr},[13] Y_{BnCl},[14] $Y_{x\mathrm{BnBr}}$[10b] or $Y_{x\mathrm{BnCl}}$[11] using the single-parameter equation in Eqn. (1) and against the combination of N_{OTs}[15] and Y_{BnX} or $Y_{x\mathrm{BnX}}$ using the dual-parameter equation in Eqn. (2) were performed. The results of best correlation for **1b–5b** and for **1c–5c** are shown in Table 2.

From Table 2 it is obvious that the effect of an activating *para*-methyl or *para*-phenyl substituent in the aryl moiety is not enough to overshadow the influence by the strongly deactivating *para*-nitro group in the other ring. Non-limiting mechanisms for the solvolysis, similar to the behavior of 4-nitrobenzhydry bromide (**2b**)[10b] and chloride (**2c**),[11] were again the result. The decreasing order of l values in Eqn. (2) for **2b** and **4b**, and also for **2c** and **4c**, suggests a lesser extent of solvent participation due to the presence of the electron-donating methyl group. The linear relationship with N_{OTs} and Y_{BnX} in Eqn. (2) for **4b** and **4c** could be considered as an indication of the positive charge delocalization mainly over the 4-methylphenyl ring. For the cation (**5a**) derived from **5b** or **5c**, the extended charge delocalization over the biphenyl rings due to resonance stabilization (Scheme 2) could be realized from the observed linear correlation with N_{OTs} and $Y_{x\mathrm{BnX}}$.

Substrates containing the more strongly activating *para*-phenoxy group (**3b** and **3c**) were more reactive than

Table 1. Solvolysis rate constants of disubstituted benzhydryl halides at 25 °C

	Rate constant (s^{-1})					
Solvent[a]	**3b**	**4b**	**5b**	**3c**	**4c**	**5c**
100E	3.551×10^{-3}	1.003×10^{-4}	4.125×10^{-5}	2.672×10^{-4}	5.004×10^{-6}	
90E	1.524×10^{-2}	4.685×10^{-4}	1.954×10^{-4}	1.204×10^{-3}	2.340×10^{-5}	
80E	4.723×10^{-2}	1.247×10^{-3}	5.120×10^{-4}	4.256×10^{-3}	7.331×10^{-5}	
70E	1.463×10^{-1}	3.235×10^{-3}	1.270×10^{-3}	1.035×10^{-2}	2.280×10^{-4}	7.845×10^{-5}
60E		7.900×10^{-3}	3.449×10^{-3}	2.892×10^{-2}	5.737×10^{-4}	2.142×10^{-4}
50E		2.312×10^{-2}	8.624×10^{-3}	8.123×10^{-2}	2.026×10^{-3}	8.123×10^{-4}
90A		7.448×10^{-5}			3.004×10^{-6}	
80A	5.186×10^{-3}	3.213×10^{-4}	4.012×10^{-5}	2.052×10^{-4}	1.561×10^{-5}	
70A	2.721×10^{-2}	9.884×10^{-4}	1.710×10^{-4}	1.286×10^{-3}	5.780×10^{-5}	8.443×10^{-6}
60A	1.123×10^{-1}	3.035×10^{-3}	6.983×10^{-4}	5.769×10^{-3}	1.854×10^{-4}	4.123×10^{-5}
50A		9.799×10^{-3}	2.861×10^{-3}	2.488×10^{-2}	6.294×10^{-4}	2.014×10^{-4}
100M	4.742×10^{-2}	8.432×10^{-4}	4.437×10^{-4}	2.181×10^{-3}	5.161×10^{-5}	
90M	1.691×10^{-1}	2.548×10^{-3}	1.336×10^{-3}	8.561×10^{-3}	1.600×10^{-4}	8.113×10^{-5}
80M	5.408×10^{-1}[b]	8.261×10^{-3}	3.906×10^{-3}	2.954×10^{-2}	5.420×10^{-4}	2.515×10^{-4}
70M		2.518×10^{-2}	1.122×10^{-2}	7.318×10^{-2}	1.750×10^{-3}	7.398×10^{-4}
60M		6.119×10^{-2}	3.062×10^{-2}		4.873×10^{-3}	2.312×10^{-3}
100T		5.738×10^{-2}	3.472×10^{-2}	6.342×10^{-1}[b]	1.048×10^{-2}	6.935×10^{-3}
80T20E	1.070×10^{0}[b]	1.052×10^{-2}	6.807×10^{-3}	1.248×10^{-1}	1.504×10^{-3}	1.256×10^{-3}
60T40E	2.148×10^{-1}[b]	2.304×10^{-3}	1.284×10^{-3}	2.490×10^{-2}	2.432×10^{-4}	2.207×10^{-4}
40T60E	4.476×10^{-2}	7.449×10^{-4}	2.273×10^{-4}	4.371×10^{-3}	4.221×10^{-5}	

[a] Solvents abbreviations: A = acetone, E = ethanol, M = methanol, T = 2,2,2-trifluoroethanol. The numbers denote volume percent of the specific solvent in the mixture.
[b] From extrapolation of rate constants obtained at other temperatures by using an Arrhenius plot.

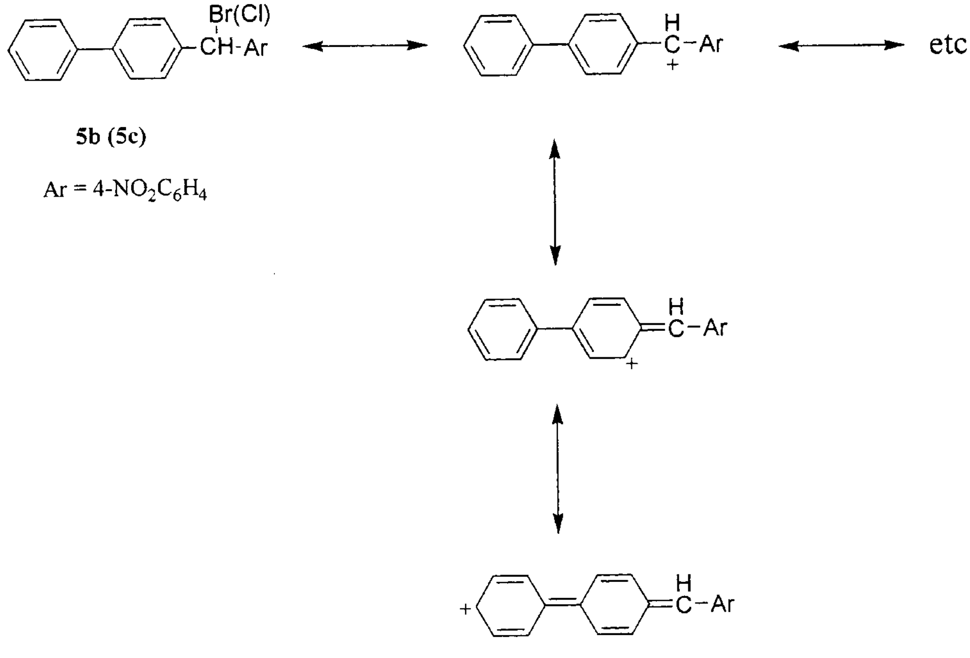
those containing *para*-methyl or *para*-phenyl (Table 1). Both **3b** and **3c** were found to solvolyze *via* a limiting S_N1 mechanism, since excellent linear correlation with the single-parameter equation in Eqn. (1) was observed (Table 2). This is likely due to the swamping of the influence of the electron-withdrawing *para*-nitro group by the electron-donating *para*-phenoxy group. In fact, **3b** is more reactive than the non-substituted benzhydryl bromide **1b**,[10b] and **3c** is also more reactive than **1c**.[11] More remarkably, the excellent linear log k–$Y_{x\mathrm{BnX}}$ plots [Eqn. (1)] suggest a limiting S_N1 mechanism with extended positive charge delocalization over two aryl rings. Since previous studies suggested that the charge delocalization over the deactivating 4-nitrophenyl ring was relatively insignificant in the solvolytic transition state for 4-nitrobenzhydryl halides **2b**[10] and **2c**,[11] a spread of positive charge to both rings in the 4-phenoxyphenyl moiety for the solvolysis of **3b** and **3c** might be considered as a consequence.

Accordingly, *ab initio* calculations on the charge distribution in **3c** and the corresponding 4-nitrophenyl-4-phenoxyphenylmethyl cation **3a** were carried out in order to judge whether or not the chemical evidence for such a spread of charge is conceivable. From our previous experience,[12] the difference of charge between the partial charge at certain position of the neutral molecule and the cation (Δcharge) showed only very small variation if Mulliken population analysis[16] or natural population analysis[17] were applied. In addition, calculations of charge distributions using density functional theory

Table 2. Correlation analyses using Grunwald–Winstein equations

Substrate	Parameters	n	R	m	S.d.	l	S.d.
1b[10b]	$Y_{x\mathrm{BnBr}}$	13	0.999	0.993	0.015		
2b[a]	Y_{BnBr}, N_{OTs}	14	0.987	0.801	0.037	0.521	0.056
3b	$Y_{x\mathrm{BnBr}}$	12	0.994	0.881	0.029		
4b	Y_{BnBr}, N_{OTs}	17	0.993	0.764	0.025	0.164	0.035
5b	$Y_{x\mathrm{BnBr}}$, N_{OTs}	17	0.996	0.909	0.022	0.215	0.03
1c[11]	$Y_{x\mathrm{BnCl}}$	13	0.994	1.02	0.034		
2c[11]	Y_{BnCl}, N_{OTs}	13	0.993	0.843	0.037	0.473	0.059
3c	$Y_{x\mathrm{BnCl}}$	18	0.995	0.767	0.018		
4c	Y_{BnCl}, N_{OTs}	17	0.991	0.742	0.031	0.219	0.053
5c	$Y_{x\mathrm{BnCl}}$, N_{OTs}	11	0.997	0.872	0.025	0.134	0.028

[a] The data in Ref. 10b were used.



5b (5c)

Ar = 4-$NO_2C_6H_4$

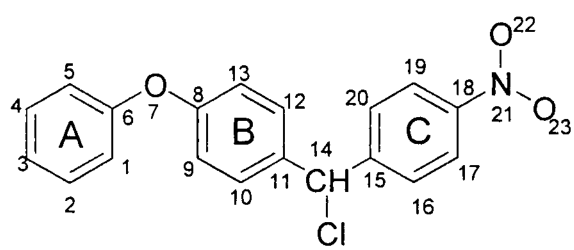
5a

Scheme 2

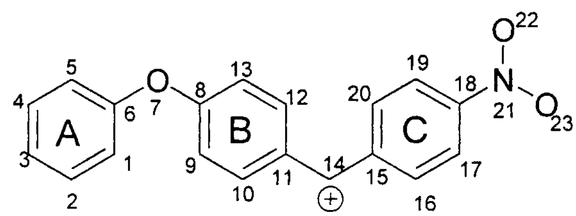
(DFT) with several different functionals, such as SVWN, BP and pBP, were found to give similar results in the case of **6** and its acylium ion **7**.[12] Mulliken population analysis and electrostatic potential analysis[18] of charge distributions in **3c** and the corresponding carbenium ion (**3a**) (Scheme 3) were then carried out. The results from restricted Hartree–Fock (RHF) approximations are given in Table 3. Since we also found in the present study that the differences were small among the above-mentioned DFT methods, only the outcomes from pBP/DN** are reported in Table 4. The change of partial charge distribution is designated as 'Δcharge' in those tables.

Since both RHF and DFT methods using different basis sets gave comparable results, the estimation could be considered reliable. All four sets of data in Tables 3 and 4 show Δcharge of greater than 0.1 for ring A; this implies that a considerable amount of positive charge is developed at the phenyl ring of the phenoxy group in cation **3a** compared with the precursor **3c**. Moreover, much more positive charge was developed in the 4-phenoxyphenyl moiety (0.466 to 0.546) than in the 4-nitrophenyl moiety (0.104 to 0.253). Obviously, calculated charge distributions are in line with the conclusion deduced from the regression analyses of solvolytic data (Table 2), similar to those observed before.[11,12]

The enhanced positive charge (0.104 to 0.175) on the phenyl ring A in **3c** is unlikely to be due to a delocalization to the phenoxy group from the canonical resonance theory,[19] since no tetravalent oxygen is possible in any contributing structure based on the conditions of resonance (Scheme 4). Concerning the inductive effect, a comparison of the substituent constants[20,21] (Table 5) indicates that for inductive effect the 4-methoxy is an electron-donating group (σ and σ^o are moderately negative) and the 4-phenoxy (σ and σ^o are nearly zero) is not. Thus, the partial positive charge on



3c



3a

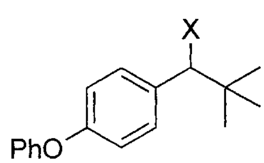
Scheme 3

Table 3. Calculated atomic charges by Hartree-Fock approximations at the 6-31G* level

	3c		3a		Δcharge	
Atom[a]	M[b]	E[c]	M	E	M	E
C-1	−0.015	−0.125	0.016	−0.170	0.031	−0.045
C-2	0.019	0.042	0.043	0.126	0.024	0.084
C-3	−0.001	−0.045	0.049	−0.043	0.050	0.002
C-4	0.016	0.062	0.044	0.115	0.028	0.053
C-5	−0.009	−0.134	0.017	−0.156	0.026	−0.022
C-6	0.385	0.470	0.330	0.543	−0.055	0.073
O-7	−0.745	−0.480	−0.651	−0.464	0.094	0.016
C-8	0.416	0.484	0.519	0.818	0.103	0.334
C-9	−0.020	−0.140	−0.005	−0.322	0.015	−0.182
C-10	0.047	0.017	0.160	0.307	0.113	0.290
C-11	0.053	0.096	−0.045	−0.137	−0.098	−0.233
C-12	0.009	−0.008	0.153	0.252	0.144	0.260
C-13	−0.010	−0.133	0.014	−0.254	0.024	−0.121
C-14	−0.080	0.089	0.182	0.164	0.262	0.055
C-15	0.106	0.230	−0.013	0.114	−0.119	−0.116
C-16	0.032	−0.044	0.038	0.038	0.006	0.082
C-17	0.117	0.033	0.133	0.033	0.016	0.000
C-18	0.172	0.073	0.177	0.033	0.005	−0.040
C-19	0.124	0.054	0.140	0.078	0.016	0.024
C-20	−0.010	−0.088	0.055	−0.003	0.065	0.085
N-21	0.413	0.636	0.530	0.823	0.117	0.187
O-22	−0.441	−0.426	−0.441	−0.446	0.000	−0.020
O-23	−0.441	−0.425	−0.445	−0.450	−0.004	−0.025
Cl	−0.136	−0.238				
Sum						
Ring-A	0.395	0.270	0.499	0.415	0.104	0.145
4-Phenoxy	−0.350	−0.210	−0.152	−0.049	0.198	0.161
Ring-B	0.495	0.316	0.796	0.664	0.301	0.348
Ring-C	0.540	0.531	0.258	0.293	−0.009	0.035
4-$NO_2C_6H_4$	0.071	0.043	0.175	0.180	0.104	0.177

[a] Referred to structural formula **3c** and **3a**; charges on hydrogen atoms were summed into the attached carbon atoms.
[b] Mulliken population analyses.
[c] Electrostatic potential analyses.

the phenyl ring A in the 4-phenoxy group cannot be attributed to the +I effect.



X = Br (**8b**)
X = Cl (**8c**)

Moreover, solvolysis of α-*tert*-butyl-(4-phenoxy)phenylmethyl bromide (**8b**) and chloride (**8c**) were also found to exhibit excellent linear log$k$–$Y_{x\mathrm{BnX}}$ plots.[22] The correlation coefficient R was 0.995 for **8b** and 0.994 for **8c**. The detailed data will be reported elsewhere. Again, extended positive charge delocalization over the two rings of the 4-phenoxyphenyl moiety could be concluded to exist in the cationic transition state in these cases. In addition to the acylium ion (**5**) from *N,N*-diphenylcarbamoyl chloride (**4**) found in our previous work,[12] the significance of certain kinds of non-canonical resonance structure was also suggested in many other systems, such as methylated malonaldehyde,[23] xylylene radical anions,[24] spiro[2.5]octa-1,47-trien-6-ones[25] and compounds with a thiazoline ring.[26] Consequently, the contribution of a non-canonical resonance structure for the aryl-(4-phenoxy)phenylmethyl cation, such as **9** (Scheme 5), is likely to be an explanation for the present observations.

CONCLUSION

Our previous studies provided evidence of agreements between the results of calculated charge distributions and the conclusion deduced from the regression analyses of solvolytic data in several cases.[10–12] The present work on the solvolytic reactivity of substituted 4-nitrobenzhydryl bromides (**3b–5b**) and chlorides (**3c–5c**) indicated extended charge delocalization over two aryl rings at cationic transition states were found

Table 4. Calculated atomic charges by DFT methods (pBP/DN**)

	3c		3a		Δcharge	
Atom[a]	M[b]	E[c]	M	E	M	E
C-1	−0.001	−0.112	0.039	−0.124	0.040	−0.012
C-2	0.013	0.039	0.084	0.095	0.071	0.056
C-3	0.001	−0.047	0.049	−0.003	0.048	0.044
C-4	0.007	0.045	0.044	0.084	0.037	0.039
C-5	0.014	−0.113	0.049	−0.110	0.035	0.003
C-6	0.190	0.431	0.126	0.476	−0.064	0.045
O-7	−0.359	−0.418	−0.314	−0.373	0.045	0.045
C-8	0.218	0.434	0.254	0.566	0.036	0.132
C-9	0.001	−0.114	0.087	−0.179	0.086	−0.065
C-10	0.029	−0.058	0.073	0.128	0.042	0.186
C-11	0.087	0.247	0.049	0.150	−0.038	−0.097
C-12	0.001	−0.091	0.007	0.053	0.006	0.144
C-13	0.012	−0.086	0.033	−0.060	0.021	0.026
C-14	−0.201	−0.098	0.108	−0.035	0.309	0.053
C-15	0.105	0.262	0.027	0.153	−0.078	−0.109
C-16	0.034	−0.020	0.058	0.054	0.024	0.074
C-17	0.091	−0.020	0.134	−0.001	0.043	0.019
C-18	0.002	0.084	0.026	0.167	0.024	0.083
C-19	0.090	0.011	0.139	−0.030	0.049	0.041
C-20	0.011	−0.073	0.022	0.079	0.011	0.152
N-21	0.345	0.619	0.356	0.587	0.011	−0.032
O-22	−0.294	−0.388	−0.255	−0.336	0.039	0.052
O-23	−0.294	−0.393	−0.258	−0.338	0.036	0.055
Cl	−0.066	−0.138				
Sum						
Ring-A	0.224	0.243	0.391	0.418	0.167	0.175
4-Phenoxy	−0.171	−0.175	0.077	0.045	0.248	0.220
Ring-B	0.348	0.332	0.566	0.658	0.218	0.326
Ring-C	0.333	0.244	0.406	0.422	0.073	0.178
4-$NO_2C_6H_4$	0.090	0.082	0.249	0.335	0.159	0.253

[a] Referred to structural formula **3c** and **3a**; charges on hydrogen atoms were summed into the attached carbon atoms.
[b] Mulliken population analyses.
[c] Electrostatic potential analyses.

for **3** and **5**, but not for **4**, from single- and dual-parameter Grunwald–Winstein-type correlation analyses [Eqns (1) and (2)] with $Y_{\rm BnX}$ and $Y_{x\rm BnX}$ scales. *Ab initio* calculations of the charge distributions were performed using an RHF approximation with the 6–31G* basis set, and DFT models with pBP/DN** and other basis sets, respectively, on Mulliken population analysis and on electrostatic potential analysis. Positive charge delocalization to the phenoxy ring (ring A) in 4-nitrophenyl-4-phenoxyphenylmethyl cation (**3a**) was confirmed. Such an outcome cannot be attributed to a canonical resonance or inductive effect. The contribution of a non-canonical resonance structure **9** is, therefore, likely a possible explanation. The observation of linear log$k$–$Y_{x\rm BnX}$ plots suggested a limiting S_N1 mechanism for the solvolysis of the parent benzhydryl bromide (**1b**)[4] and chloride (**1c**),[5] and the delocalization of positive charge over both phenyl rings in the transition state.

The agreements between charge distributions from quantum chemical computation and of the correlation analysis of solvolytic reactivities observed in this and previous studies seem to suggest a promising combination for a better understanding of solvolysis mechanisms. In addition, a significant contribution of non-canonical resonance in the cationic transition state could be deduced. Further work to extend the scope of its applicability is in progress.

Table 5. Comparison of substituent constants

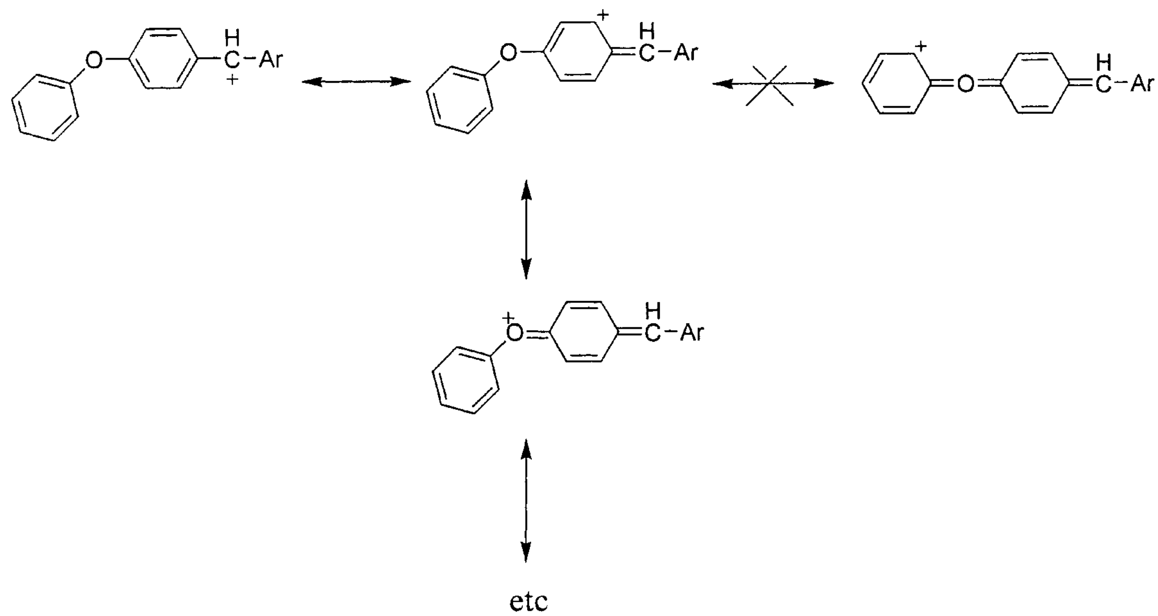
	σ_p^{+}[a]	σ_p[a]	σ_p^{o}[b]
4-OCH_3	−0.78	−0.27	−0.10
4-OC_6H_5	−0.50	−0.03	0.063

[a] Ref. 20.
[b] Ref. 21.

EXPERIMENTAL

Materials

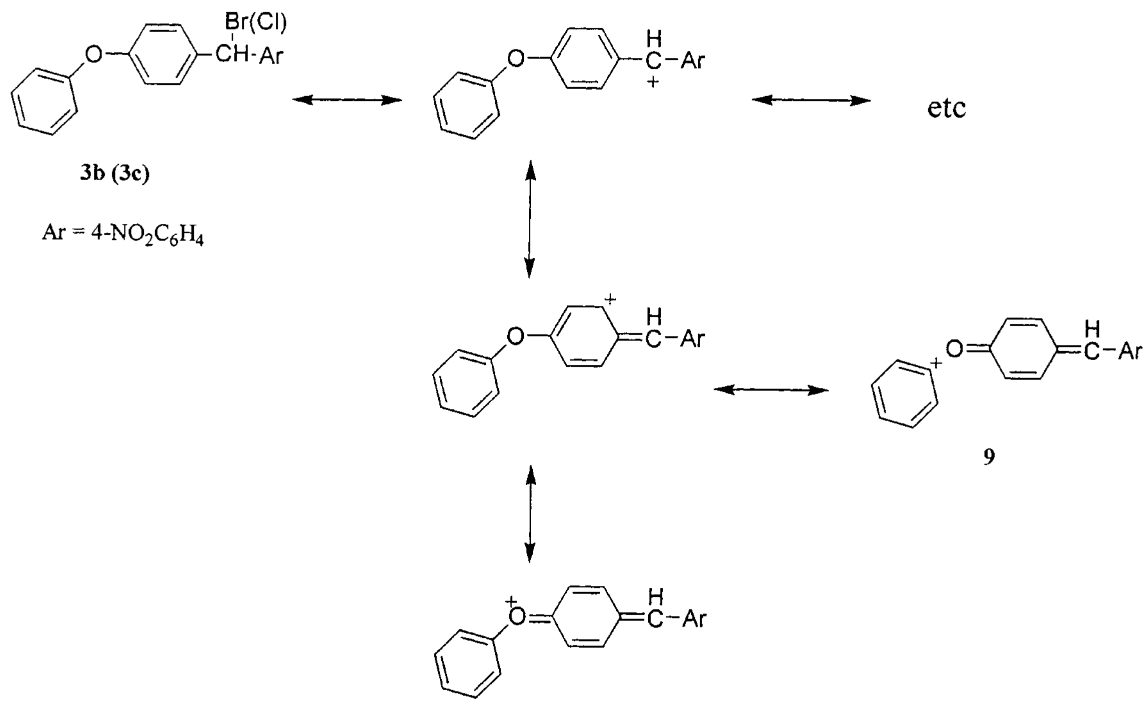
4-Substituted-4-nitrobenzhydryl halides **3b–5b** and **3c–**



3a

Ar = 4-$NO_2C_6H_4$

Scheme 4



3a

Scheme 5

5c were prepared by conventional halogenation[10b,11] of the corresponding alcohols, which had been synthesized from Friedel–Crafts acylation of appropriate arenes with 4-nitrobenzoyl chloride and followed by reduction of the resulting ketones with sodium borohydride. All products exhibited infrared, ^1H and ^{13}C NMR spectra in agreement with the assigned structures. Correct elemental analyses were obtained for new compounds.

4-Nitro-4′-phenoxybenzhydryl bromide (**3b**), m.p. 72–73 °C. Found: C, 59.27; H, 3.61. $C_{19}H_{14}BrNO_3$ requires C, 59.39; H, 3.67%.
4-Nitro-4′-phenylbenzhydryl bromide (**5b**), m.p. 93–94 °C. Found: C, 62.19; H, 3.95. $C_{19}H_{14}BrNO_2$ requires C, 62.97; H, 3.83%.
4-Nitro-4′-phenoxybenzhydryl chloride (**3c**), m.p. 62–63 °C. Found: C, 67.12; H, 4.09. $C_{19}H_{14}ClNO_3$ requires C, 67.16; H, 4.15%.
4-Nitro-4′-phenylbenzhydryl chloride (**5c**), m.p. 88–89 °C. Found: C, 70.57; H, 4.53. $C_{19}H_{14}ClNO_2$ requires C, 70.48; H, 4.36%.

Solvents for kinetic studies were purified according to standard methods,[27] and were freshly distilled under nitrogen. Doubly de-ionized water was degassed prior to the preparation of aqueous solvent systems for solvolysis.

Kinetic measurements

Conductimetric rate constants were measured at least in duplicate as described.[28] The conductivity cells containing solution of 1×10^{-4} to 1×10^{-5} M were placed in a thermostatic bath with a temperature variation of ±0.02 °C. Rate constants greater than 0.17 s^{-1}, or with a half-life shorter than 4 s, were monitored at lower temperatures and were extrapolated to those at 25 °C by using an Arrhenius plot. The experimental error was generally smaller than 1%, even for a fairly fast reaction [for instance, $k = (1.691 \pm 0.007) \times 10^{-1}$ s^{-1} for **3b** in 90M].

Calculations

All calculations were carried out using the Spartan program package.[29] The initial equilibrium geometries of **3a** and **3c** were first optimized using the AM1 semi-empirical method. Then the complete structure optimizations were performed by four different models: the Hartree-Fock self-consistent field method, and DFT with SVWN, BP and pBP functionals. The default option for the geometry optimization is adopted in this study. The convergence criterion for the geometry optimization is also chosen from the default option. The results from RHF/6-31G* are given in Table 3. For DFT methods, the three basis sets DN, DN* and DN** were used to check their effects on the charge distribution. Only the data from pBP/DN** are shown in Table 4.

Acknowledgements

We are indebted to the National Science Council, Republic of China, for financial support of this research, and to National Center for High-Performance Computing for providing the Spartan program packages for the *ab initio* calculations.

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