行政院國家科學委員會補助專題研究計畫成果報告

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※　取代基效應對一些液晶性質及苯甲　※

※　反應物溶離活性之研究　※

※　Substituent effects on the properties of some liquid　※

※　crystals and on the solvolytic reactivity of benzylic　※

※　substrates.　※

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計畫類別：☑個別型計畫　□整合型計畫

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計畫主持人：劉廣定

共同主持人：

本成果報告包括以下應繳交之附件：

□赴國外出差或研習心得報告一份

□赴大陸地區出差或研習心得報告一份

□出席國際學術會議心得報告及發表之論文各一份

□國際合作研究計畫國外研究報告書一份

執行單位：臺灣大學化學系

摘　要

本年度完成之工作包括：

（一）補充修訂上年度萘甲醯氯之溶離反應研究結果，將於近日正式刊出(附件一)。
（二）補充修訂以往對 4-苯氧基取代之苯甲反應物之溶離反應，已正式發表（附件二、三）。
（三）合成七種含嘧啶類衍生物並研究其液晶性質，已正式發表（附件四）。
（四）合成五種苯環含不同取代基之雙胺席夫鹽及五種含不同取代基之羥胺，並製出五種雙胺席夫鹽之鈀錯鹽並研究其液晶性質。
（三）其他研究仍在繼續進行中。

關鍵詞

溶離反應，萘甲醯氯，4-苯氧取代苯甲反應物，嘧啶衍生物，席夫鹽，液晶

Abstract

The work done in this year is presented as follows:

(1) Additional work and revision were done on the solvolysis of naphthoyl chlorides reported last year. It will be published soon in *Journal of Physical Organic Chemistry* (Appendix 1)

(2) Additional work and revision were done on the sdolvolysis studies of 4-phenoxy substituted benzylic systems reported last year. It was published in *Journal of the Chinese Chemistry Society* **2001**, *48*, 1047-1052 (Appendix 2) and in *Journal of Physical Organic Chemistry* **2002**, *15*, 21-28. (Appendix 3)

(3) Preparation of seven liquid crystals which are pyrimidine devivatives. (Appendix 4)

(4) Five substituted aromatic diamine Schiff's bases and five substituted hydroxylamine Schiff's bases were synthesized. Copper(II) complexes of those diamine Schiff's bases were studies.

(5) Other work is in progress

Keywords

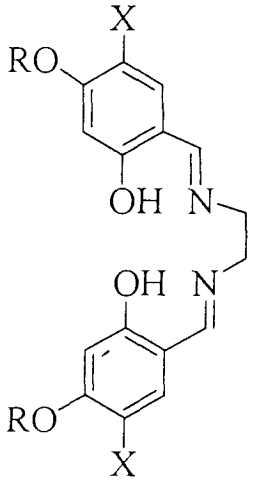
Solvolysis, naphthoyl chlorides,4-phenoxy benzylic substratesd, pyrimidine derivatives, Schiff's bases, liquid crystals

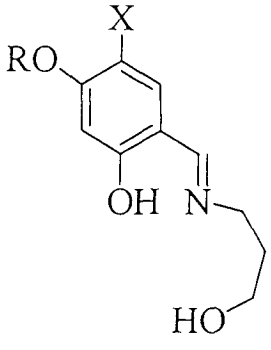
ANNUAL REPORT (2001-2002)

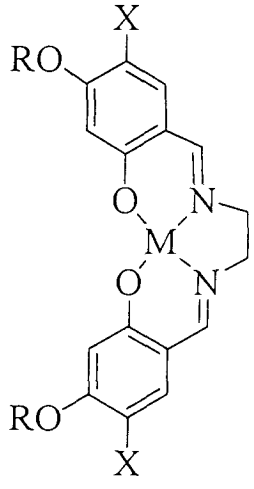
The following results were published :

1. Splvolyses of naphthoyl chlorides. Sovent effect and Grunwald-Winstein correlation ananlyses with Y_{xBnCl} scales, will be published in *Journal of Physical Organic Chemistry* **2002** (Appendix 1).
2. Solvolysis of 1-*tert*-Butyl-1-(4-phenoxyphenyl)methyl Bromide and Chloride. Further example for Possible Contribution of Non-canonical Resonance Structure in the Transition State, was published in *Journal of the Chinese Chemistry Society* **2001**, *48*, 1047-1052 (Appendix 2).
3. Extended charge delocalization to 4-phenoxy substitutent in benzhydryl solvolysis: possible contribution of non-canonical resonance structure in the cationic transition state, was published in *Journal of Physical Organic Chemistry* **2002**, *15*, 21-28. (Appendix 3)
4. Formation of hexagonal columnar phases by heterocyclic pyrimidine derivatives, was published in *Liquid Crystals* **2002**, *29*, 237-242.

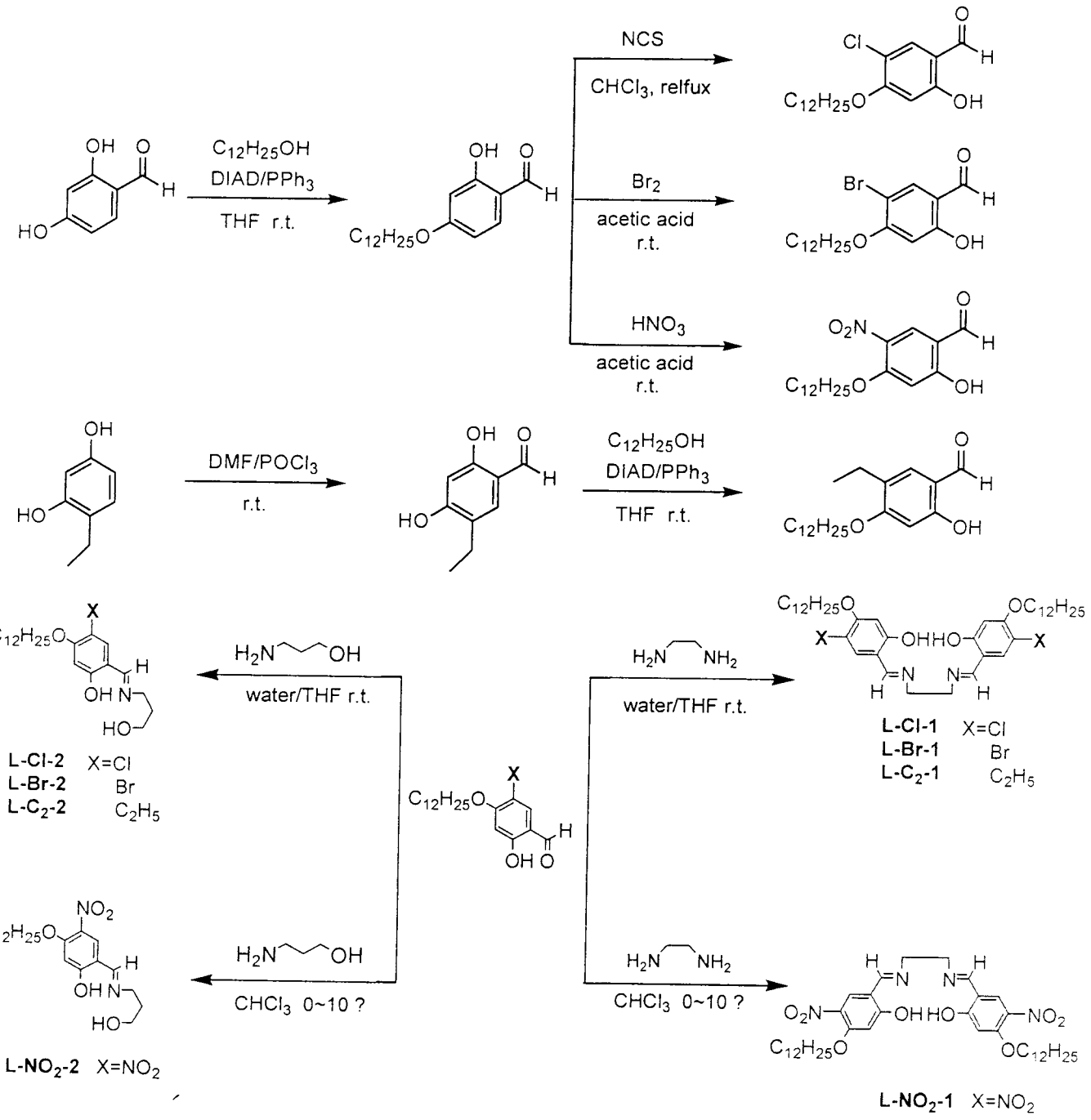
The following Schiff's bases were prepared according to the schemes described.

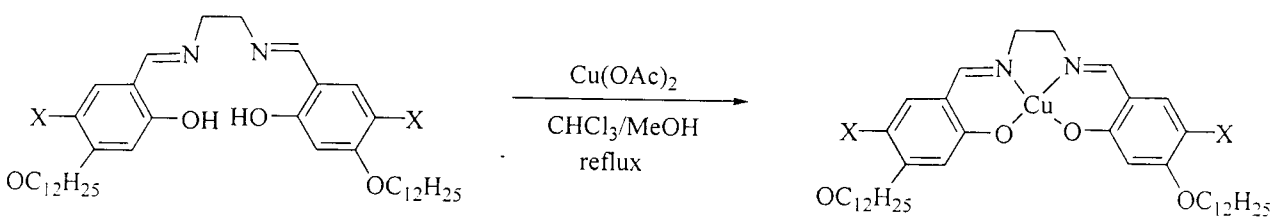






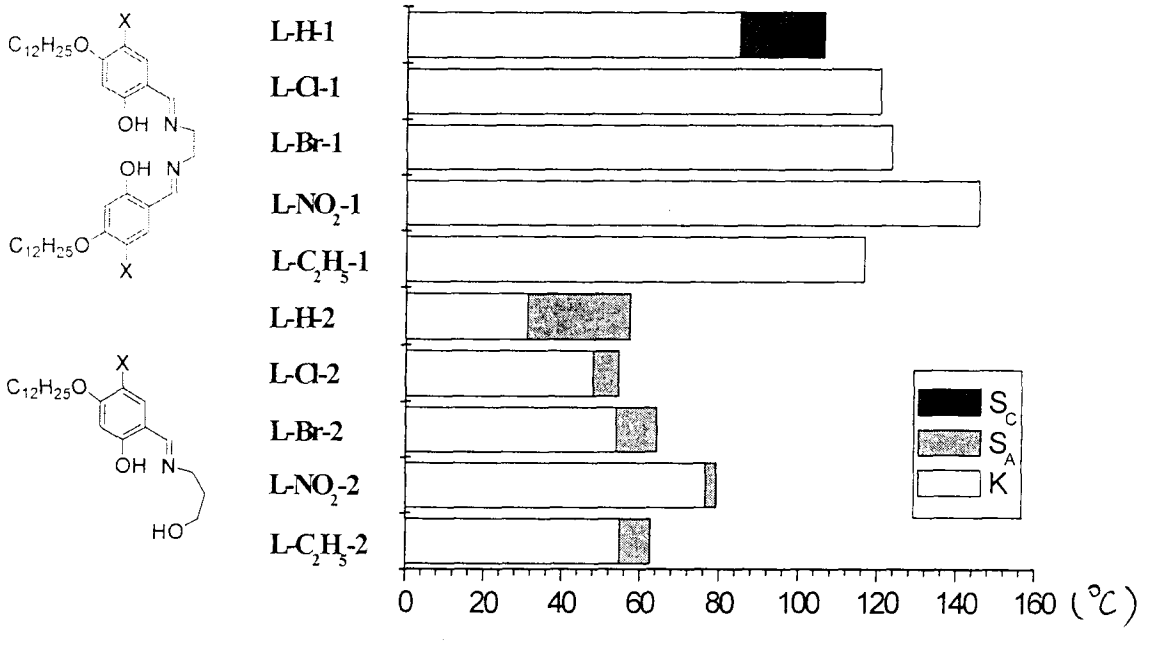
sb-C-H-1 X=H
sb-C-cl-1 Cl
sb-C-br-1 Br
sb-C-no2-1 NO_2
sb-C-c2-1 C_2H_5
M = Cu





sb-C-H-1 X=H
sb-C-cl-1 Cl
sb-C-br-1 Br
sb-C-no2-1 NO_2
sb-C-c2-1 C_2H_5

Thermal properties of Schiff's bases are shown in the following diagram:



Unfortunately, none of the copper(II) complex of the diamines was found to be a liquid crystal.

Other work is in progress

Journal of the Chinese Chemical Society, **2001**, *48*, 1047-1052

Solvolysis of 1-*tert*-Butyl-1-(4-phenoxyphenyl) Methyl Bromide and Chloride. Further Example for Possible Contribution of Non-canonical Resonance Structure in the Transition State

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The solvolysis of 1-*tert*-butyl-1-(4-phenoxy)methyl bromide (**5b**) and chloride (**5c**) in a variety of solvents were carried out. Limiting S_N1 mechanisms were suggested from the observation of linear relationships using single-parameter Winstein-Grunwald type correlation between logarithm of rate constants with Y_{xBnBr} and Y_{xBnCl} scales, respectively. This result indicated positive charge delocalization over both aryl rings and provided further evidence for possible contribution of non-canonical resonance structure in the cationic transition state.

INTRODUCTION

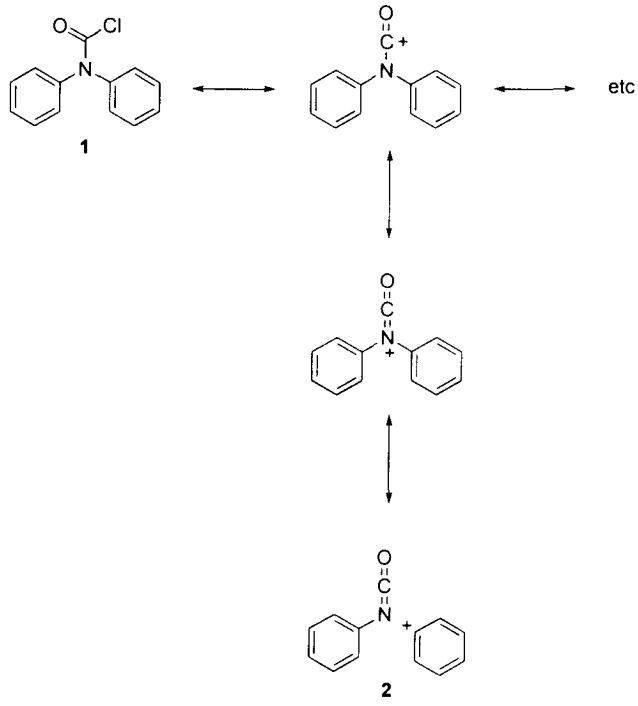
Grunwald-Winstein type correlation analyses (Eqs 1 and 2),[1,2] in which Y is the solvent ionizing power and N is the nucleophilicity, have long been a useful tool in the study of solvolytic mechanisms for organic reactions.[3] Different Y_X scales have been developed for aliphatic and alicyclic substrates (RX) containing a different leaving group X.[4] In our previous studies, new Y_{BnX}[5] and Y_{xBnX}[6] scales were suggested for dealing with the solvolysis of benzylic substrates with positive charge delocalization over one and two aryl rings, respectively. These new scales could also be applied to the solvolysis of certain aromatic acyl halides, such as, Y_{BnCl} to benzoyl chlorides[7] and Y_{BnBr} to benzoyl bromides.[8]

$$\log(k/k_o) = mY \quad (1)$$

$$\log(k/k_o) = mY + lN \quad (2)$$

More interestingly, extended charge delocalization over both phenyl rings in the cationic transition state of the solvolysis of *N,N*-diphenylcarbamoyl chloride (**1**) was realized based on the observation of linear correlations with Y_{xBnCl} scale, and *ab initio* calculations.[9] Possible contribution of non-canonical resonance structure (**2**) was thus proposed (Scheme I).[9] Similarly, in the solvolysis of 4-nitro-4′-phenoxybenzhydryl bromide (**3b**) and chloride (**3c**) a non-canonical resonance structure (**4**) (Scheme II) was also considered to be involved in the transition state.[10] More evidence is needed to confirm the generalization of the significance of non-canonical resonance in the cationic transition state of solvolysis.

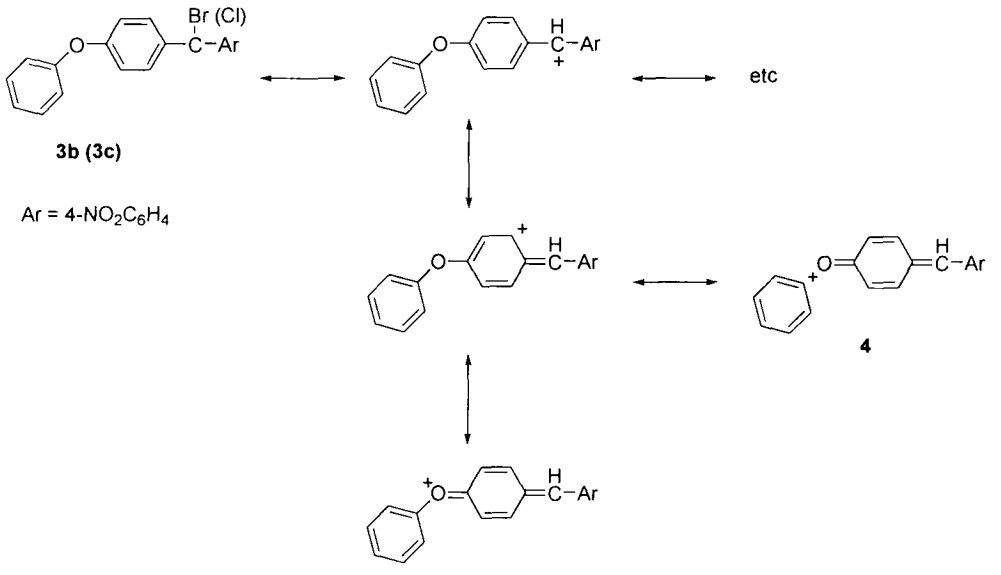
Scheme I



Since the solvolysis of 1-aryl-1-*tert*-butylmethyl derivatives was generally considered to proceed via limiting S_N1 mechanism,[5a,11-13] we undertook to examine the solvent effects on the solvolytic reactivity of 1-*tert*-butyl-1-(4-phen-

Dedicated to Professor Sheng-lieh Liu on the occasion of his ninetieth birthday.

Scheme II



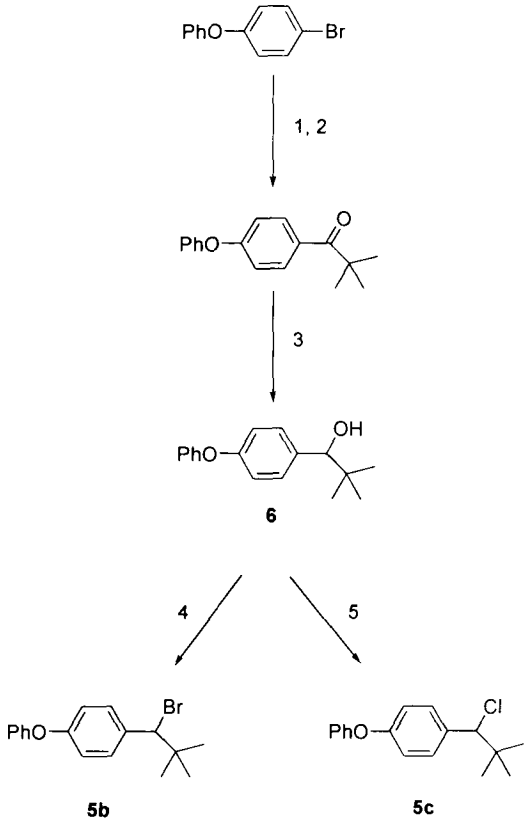
oxy)methyl bromide (**5b**) and chloride (**5c**) in order to explore the possibility of contribution of non-canonical resonance structure in the transition state. The results are reported herein.

RESULTS AND DISCUSSION

The preparation of 1-*tert*-butyl-1-(4-phenoxy)methyl bromide (**5b**) and of 1-*tert*-butyl-1-(4-phenoxy)methyl chloride (**5c**) were carried out by using the conventional method from bromination[5a] and chlorination,[5b] respectively, of the corresponding alcohols (**6**), which had been synthesized according to Scheme III. Solvolytic rate constants in various solvents were measured conductimetrically. Reproducible rate constants (± 2%) at 25 °C were obtained from direct measurement of duplicate runs, or from Arrhenius plots of data measured at other temperatures. Pertinent data at 25 °C are listed in Table 1.

The results of correlation analyses of log *k* in Table 1 against corresponding Y_{BnX} (Y_{BnBr} and Y_{BnCl}) and Y_{xBnX} (Y_{xBnBr} and Y_{xBnCl}) scales, respectively, by using single-parameter Grunwald-Winstein equation (1) are given in Table 2. The observed excellent linear relationship and the slope (*m* value) closed to unity for **5b** (correlation coefficient $R = 0.995$ and $m = 0.936$) and **5c** ($R = 0.994$ and $m = 0.996$) clearly indicate both substrates are solvolyzed via limiting S_N1 mechanisms, as was deduced from the original Grunwald-Winstein equa-

Scheme III



1, Mg, THF; 2, $(CH_3)_3COCl$; 3, $NaBH_4$, MeOH
4, PBr_3, CH_2Cl_2; 5, $SOCl_2$, CH_2Cl_2

Table 1. Solvolysis Rate Constants (s^{-1}) of α-*tert*-Butyl-(4-phenoxy)phenylmethyl Halides (**5b** and **5c**) at 25 °C

Solvent[a]	5b	5c
100E	1.13×10^{-4}	
90E	4.65×10^{-4}	
80E	1.75×10^{-3}	8.13×10^{-5}
70E	4.87×10^{-3}	2.32×10^{-4}
60E	1.18×10^{-2}	6.83×10^{-4}
50E		2.13×10^{-4}
90A	2.78×10^{-5}	
80A	2.01×10^{-4}	
70A	9.53×10^{-4}	1.19×10^{-5}
60A	4.22×10^{-3}	8.35×10^{-5}
50A	1.68×10^{-2}	5.52×10^{-4}
100M	1.58×10^{-3}	
90M	5.84×10^{-3}	
80M	1.94×10^{-2}	6.67×10^{-4}
70M		1.61×10^{-3}
60M		4.75×10^{-3}
80T20E	9.61×10^{-2}	1.05×10^{-2}
60T40E	1.21×10^{-2}	6.48×10^{-4}

[a] For abbreviation of solvents: A = acetone, E = ethanol, M = methanol, T = 2,2,2-trifluoroethanol. The numbers denote volume percent of the specific solvent in the mixture.

Table 2. Correlation Analyses Using Single Parameter Equation (1)

Substrate	Parameters	n^a	R	M (s.d.)[b]
5b	Y_{BnBr}	15	0.987	0.909 (0.038)
	Y_{xBnBr}	15	0.995	0.935 (0.023)
5c	Y_{BnCl}	13	0.984	0.939 (0.050)
	Y_{xBnCl}	13	0.994	0.996 (0.032)

[a] Numbers of data points. [b] Standard deviation.

tion[1-3] and similar to other analogous systems previously observed.[11-13] Moreover, an extended positive charge delocalization over both phenyl rings is likely to be involved in the transition state, since the parameters Y_{xBnBr} and Y_{xBnCl} have been derived from the system with extended charge delocalization in the cationic transition state.[6]

However, the spreading of positive charge to the phenyl ring in the phenoxy group seems to be unlikely due to a delocalization to the phenoxy group from the canonical resonance theory,[14] since no tetravalent oxygen is possible in any contributing structure based on the conditions of resonance (Scheme IV). Although the group electronegativity for methoxy and for phenoxy group is nearly the same,[15] the substituent constants σ and σ° are significantly negative for methoxy but are close to zero for 4-phenoxy group.[16,17] Therefore, a +I inductive effect is improbable the origin of such kind of charge delocalization. On the other hand, linear Hammett plots with σ^+ constants (eqn 3)[18] were realized from the rate constants for 1-aryl-1-*tert*-butylmethyl bromides (**9**) and 1-aryl-1-*tert*-butylmethyl chloride (**10**) obtained in this and previous[5a,11b] studies by using -0.54[12a] as the σ^+ constant for 4-phenoxy substituent. Some representative data are given in Table 3. Therefore, a proper account of the charge delocalization over both aryl rings in the solvolytic transition state for **5b** and **5c** would be desirable.

$$\log(k/k_o) = \rho\sigma^+ \quad (3)$$

In our previous studies evidence of agreements between the results of calculated charge distributions and the conclusion deduced from the regression analyses of solvolytic data in benzhydryl,[6a,6b,10,19] 9-aryl-9-fluorenyl[20] and *N,N*-diphenylcarbamoyl[9] systems were demonstrated. From Grunwald-Winstein type correlation analyses on the solvolytic reactivity of substituted 4-nitro-4′-phenoxy benzhydryl bromide (**3b**) and chloride (**3c**), and *ab initio* calculations of the charge

Scheme IV

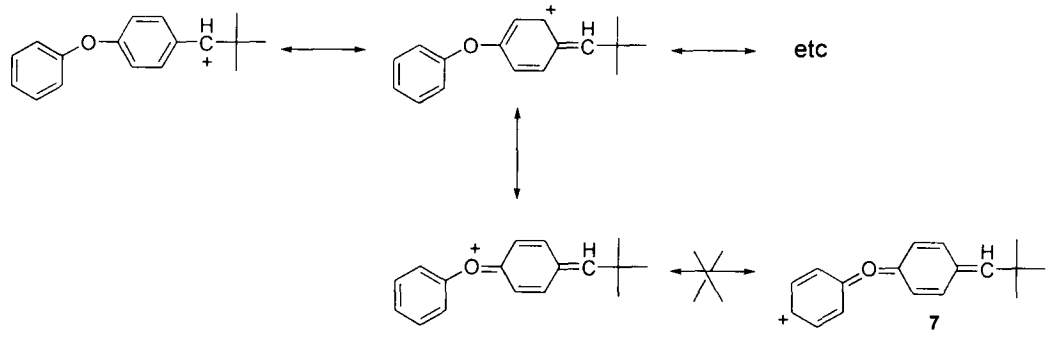


Table 3. Hammett Plots of Selective log k Values Against σ^+ Constants

Substrate	Solvent	n^a	ρ	R	$s.d.^b$
9	80E	7	-6.78	0.998	0.232
	60A	7	-6.76	0.997	0.264
	80M	7	-6.79	0.997	0.264
	60T40E	7	-6.89	0.997	0.266
10	80E	7	-6.84	0.998	0.238
	50A	7	-6.71	0.998	0.211
	80M	7	-6.77	0.998	0.239
	60T40E	7	-6.83	0.997	0.253

[a] Number of substrates bearing 4-OCH_3, 4-SCH_3, 4-OPh, 3,5-$(CH_3)_2$, 4-CH_3, H and 3-Cl substituents, respectively. Rate data from Refs. 5a and 13b, and this work. [b] Standard deviation.

distributions in the corresponding 4-nitrophenyl-4′-phenoxyphenylmethyl cation, positive charge delocalization to the phenoxy ring was concluded and a possible contribution of non-canonical resonance structure (**4**) in the transition state was suggested (Scheme II).[10] Since both 4-nitro-4′-phenoxybenzhydryl halides (**3b** and **3c**) and 1-*tert*-butyl-1-(4-phenoxy)methyl halides (**5b** and **5c**) bear the same 4-phenoxy substituent, solvolyzing with limiting S_N1 process and showing linear correlation with Y_{xBnX} parameters, a similar transition state structure is likely to be involved. Therefore, the contribution of non-canonical resonance structure (**8**) would be plausibly accounted for the spread of positive charge to both rings of the 4-phenoxyphenyl moiety in the solvolytic transition state for the solvolysis of **5b** and **5c** (Scheme V). Computation of charge distribution in this and a series of other 1-aryl-1-*tert*-butylmethyl cations is currently being undertaken. Preliminary data suggested an agreement with kinetic results. The details will be reported after the completion of the study.

Recently, many reports have been made to show the significance of certain kinds of non-canonical resonance structure in a variety of systems after the work on natural resonance theory by Weinhold and coworkers.[21] In addition to our previous study on the acylium ion **2** from **1** (Scheme I), there are other examples such as compounds containing a thiazoline ring[22] or 4-(dimethylamino)-2′-hydroxy-chalcone,[23] and the origin of anomeric effect.[24,25] Non-canonical resonance is thus likely more common in organic chemistry than generally considered in terms of hyperconjugation.[26]

EXPERIMENTAL SECTION

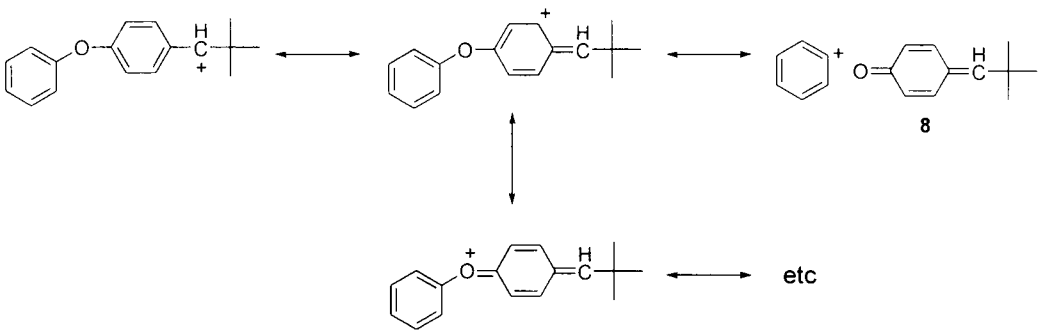
General Remarks

Proton and carbon-13 NMR spectra were recorded on a Bruker Model AM-300 or AC-200 instrument. Infrared spectra were measured on a Nicolet Magna II 550 spectrometer. Elemental analyses were performed in the Microanalytical Laboratory at the Department of Chemistry, National Taiwan University.

Materials

Commercially available spectral-grade or reagent-grade solvents were used directly for preparative purposes. The solvent was purified following conventional methods[26] for kinetic studies. Doubly de-ionized water was used to prepare aqueous solvent mixtures for solvolysis. From 1-bromo-4-phenoxylbnzene (Aldrich) 1-*tert*-butyl-1-(4-phenoxyphenyl)methyl bromide (**5b**) and chloride (**5c**) were prepared by using the conventional methods in Scheme III as previously described.[5a,13b] The overall yield for **5b** (mp 41-42 °C) and **5c** (mp 36-37 °C) was about 50% from 20-mmole reactions. Their spectral and analytical data were found to be in harmony with the assigned structures.

Scheme V



Kinetic Measurements

Rate constants were measured by the use of conductimetric method at least in duplicate. The conductivity cells containing a solution of 1×10^{-4} to 1×10^{-5} M were placed in a thermostat with a temperature variation of ± 0.02 °C. A small amount (ca. 0.1%) of 2,6-dimethylpyridine was added to the solution in some cases to prevent curvature of the rate constant plot. The maximum error of k is around ± 2%. The results are shown in Table 1.

ACKNOWLEDGEMENTS

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Key Words

Solvolysis; Correlation analysis; $Y_{x\text{BnBr}}$ and $Y_{x\text{BnCl}}$ scales; Non-canonical resonance; Transition state.

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

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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_{xBnX} 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. Copyright © 2001 John Wiley & Sons, Ltd.

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.

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

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

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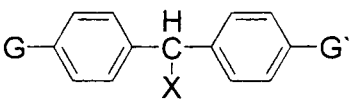
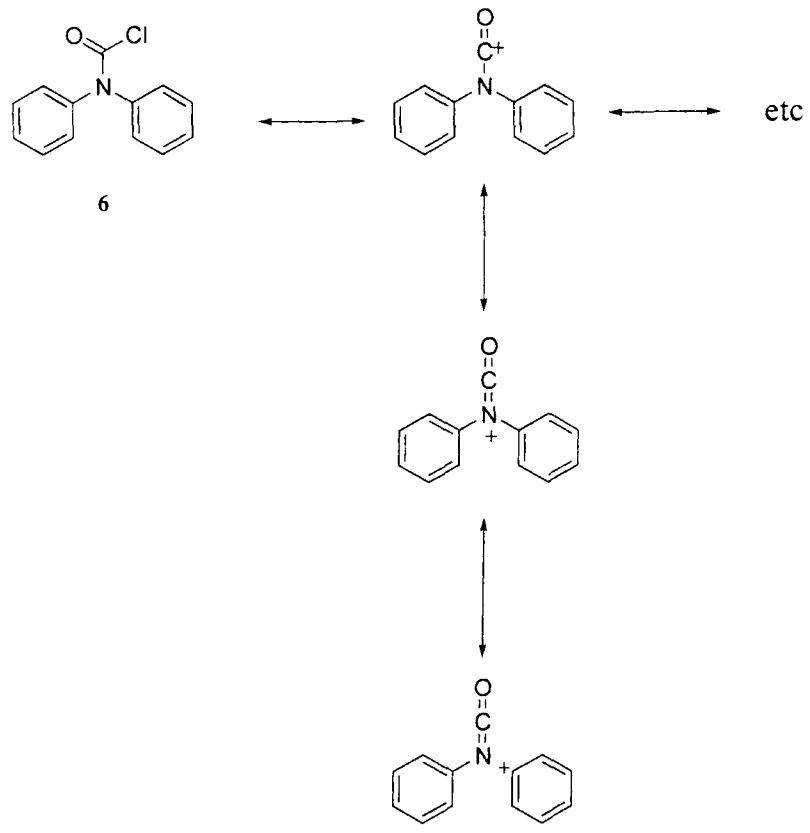
In our previous studies we employed Y_{BnX} and Y_{xBnX} scales of solvent ionizing power[9] to demonstrate the variation of extent of charge delocalization in the cationic transition state for the solvolysis of benzhydryl bromides[10] or chlorides[11] containing different substituents. Moreover, for 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



6 7

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

Solvent[a]	Rate constant (s^{-1})					
	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.

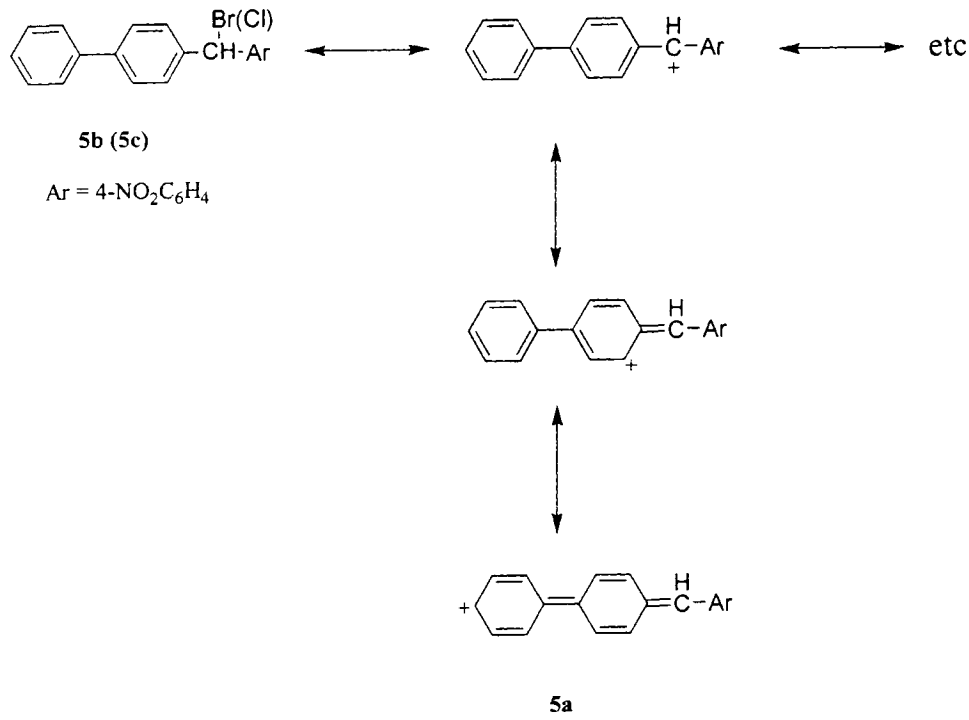
those containing *para*-methyl or *para*-phenyl (Table 1). Both **3b** and **3c** were found to solvolyze *via* a limiting S_N1 mechanism, since excellent linear correlation with the single-parameter equation in Eqn. (1) was observed (Table 2). This is likely due to the swamping of the influence of the 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.

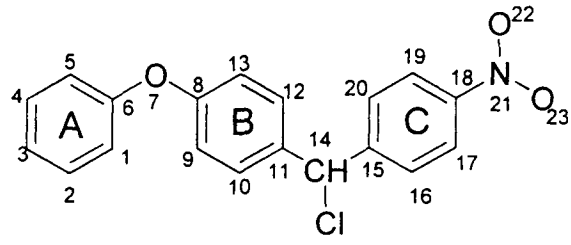


Scheme 2

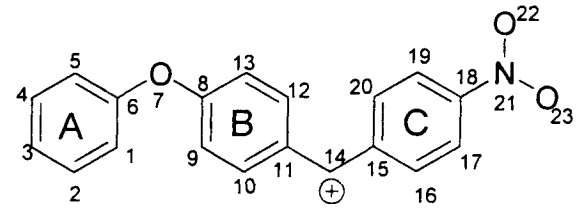
(DFT) with several different functionals, such as SVWN, BP and pBP, were found to give similar results in the case of **6** and its acylium ion **7**.[12] Mulliken population analysis and electrostatic potential analysis[18] of charge distributions in **3c** and the corresponding carbenium ion (**3a**) (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

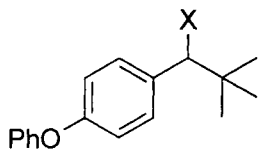
Scheme 3

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_{BnX} and Y_{xBnX} 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_{xBnX} 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.

Table 5. Comparison of substituent constants

	σ_p^{+a}	σ_p^{a}	σ_p^{ob}
4-OCH_3	−0.78	−0.27	−0.10
4-OC_6H_5	−0.50	−0.03	0.063

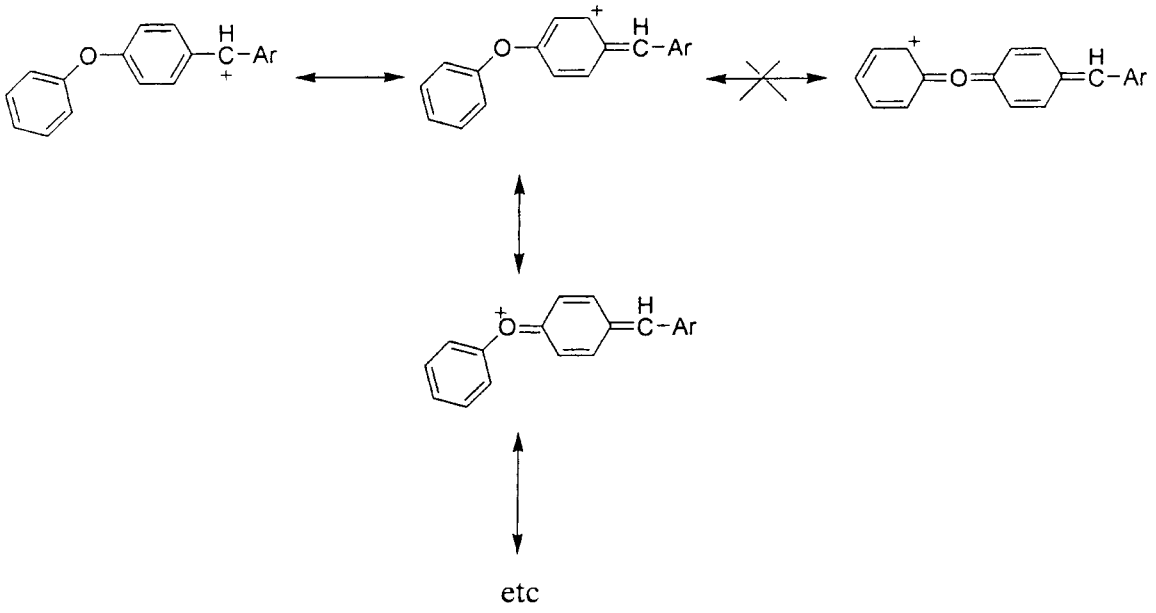
[a] Ref. 20.
[b] Ref. 21.

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.

EXPERIMENTAL

Materials

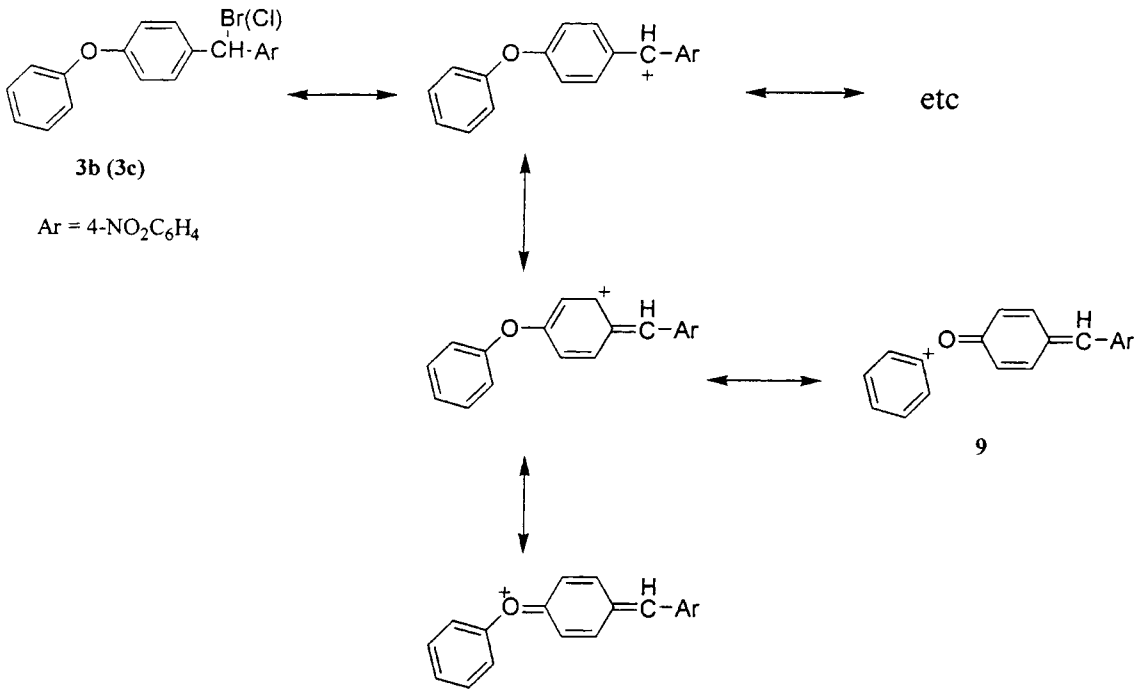
4-Substituted-4-nitrobenzhydryl halides **3b–5b** and **3c–**



3a

Ar = 4-$NO_2C_6H_4$

Scheme 4



3b (3c)

Ar = 4-$NO_2C_6H_4$

9

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

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Formation of hexagonal columnar phases by heterocyclic pyrimidine derivatives

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The synthesis, characterization, and mesomorphic properties of a new type of heteronuclear compounds derived from pyrimidine as core group are reported. These compounds were prepared by condensation reactions of appropriate acetophenones and benzonitriles in the presence of trifluoromethanesulphonic anhydride. They were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis, and their phase transitions characterized and studied by thermal analysis and polarizating microscopy. These compounds exhibit hexagonal columnar (Col_h) phases, as expected for disk-like molecules; the formation of columnar phases was found to be dependent on the numbers of alkoxy side chains attached. For those compounds having the same numbers of flexible side chains attached, the one with a preferred unsymmetric structure exhibited better mesomorphic properties. The observed improved mesomorphic behaviour of these compounds over other similar all-carbon heterocyclic compounds is attributed to the greater polarization of nitrogen atoms in the core ring.

1. Introduction

Numerous new mesogenic compounds exhibiting columnar phases have been prepared and studied since the discovery of the first thermotropic discotic liquid crystals by Chandrasekhar *et al.* [1] in 1977. A better understanding of the relationship between molecular structure and mesomorphic properties will assist in the development of materials for advanced applications. In general, molecular structures with an overall circular geometric shape are crucially required for formation of columnar phases. However, rod-like molecules are also known to generate such columnar phases in an anti-parallel arrangement [2]. The formation of columnar phases is also found to be dependent on side chain density around the central core group. On the other hand, adding more side chains and/or extending longer carbon chains are essential for disc-shaped molecules with a larger or more rigid core group. Typical phases observed in these discotic materials are hexagonal columnar (Col_h), rectangular columnar (Col_r) and nematic discotic phases (N_D).

Numerous examples of hydrocarbon structures [3] used as core groups exhibiting columnar phases have been reported. However, examples of heterocyclic structures [4, 5] used as core groups are relatively fewer. The presence of nitrogen, sulfur or oxygen atoms in these heterocyclic rings [4, 5], which probably introduce a transverse dipole moment, often result in a change in dielectric anisotropy. The formation of liquid crystallinity in such heterocyclic compounds might be facilitated by weak π–π interaction between these aromatic or heterocyclic rings.

In this work, a new type of disc-like compounds **1–7** in which an unsaturated pyrimidine ring is utilized as the rigid core group, were prepared and their mesomorphic properties studied (see the figure). Compounds **3–7** exhibited columnar phases; compounds **1.2** were non-mesogenic.

2. Results and discussion

2.1. *Synthesis and characterization*

Typical synthetic pathways to the pyrimidine derivatives (compounds **1,2** or **5–7**) are summarized in schemes 1 and 2. Original attempts to prepare these compounds by condensation [6] or β-diketones and benzaldehydes in the presence of sodium hydride and ammonium acetate with bubbling oxygen were unsuccessful. Instead, these compounds were obtained by the condensation of appropriate substituted acetophenones with two equivalents of benzonitriles and trifluoromethanesulphonic anhydride in dried nitroethane [7]. The reaction products isolated varied with the numbers of alkoxy side chains in the

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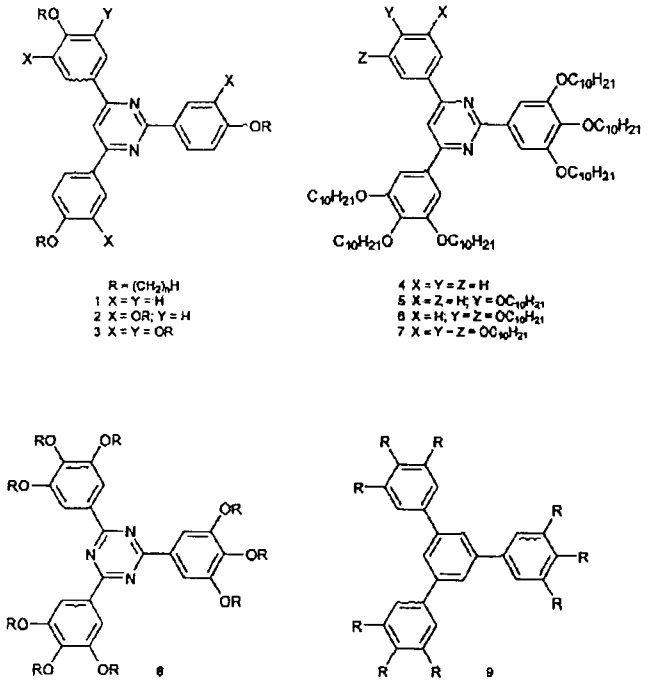
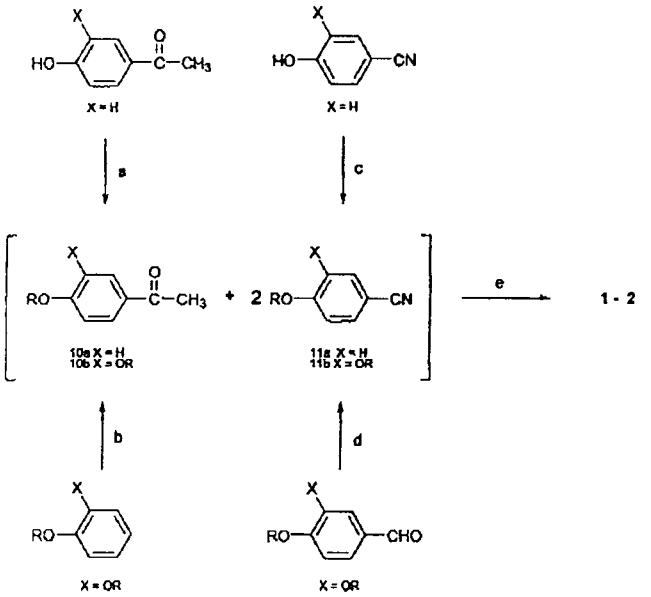
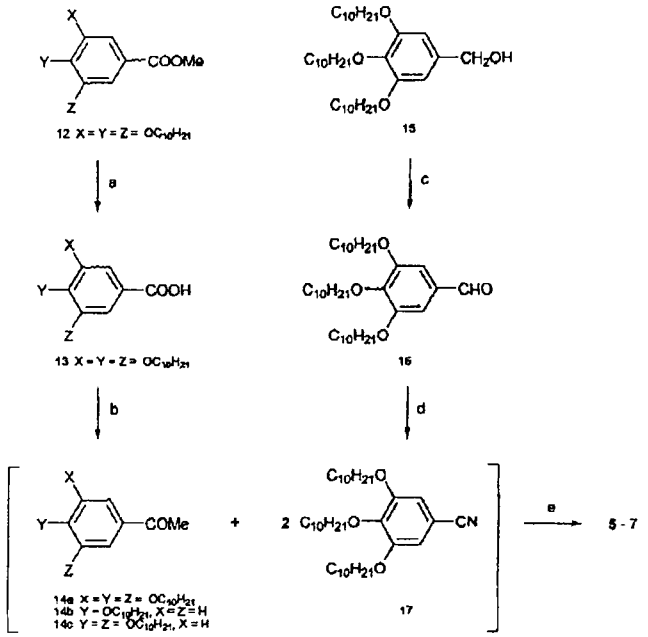


Figure. Structures of the compounds studied.



Scheme 1. Conditions and reagents: (a) *n*-alkyl bromide (1.0 eq), K_2CO_3 (2.0 eq), reflux in CH_3COCH_3, 24 h, 71–92%; (b) CH_3COCl (1.1 eq), stirred at rt, then reflux in CH_2Cl_2, 12 h, 71–83%; (c) *n*-alkyl bromide (1.0 eq), K_2CO_3 (2.0 eq), reflux in DMF, 24 h, 69–78%; (d) pyridine hydrochloride (1.5 eq), reflux in nitroethane, 12 h, 79–87%; (e) trifluoromethane sulphonic anhydride (1.0 eq), stirred at rt, in CH_2Cl_2, 48 h.

reactants used. Reactions of 4-alkoxyacetophene **10a** or 3,4-dialkoxyacetophenone **10b** and 4-alkoxybenzonitrile **11a** or 3,4-dialkoxybenzonitrile **11b** as reactants



Scheme 2. Conditions and reagents: (a) KOH (3.0 eq), reflux in THF/H_2O (9/1), 24 h, 82–96%; (b) methyl lithium (2.0 eq), stirred at rt, then reflux in dried THF, 12 h, 72–84%; (c) pyridinium chlorochromate (2.0 eq), stirred at rt in CH_2Cl_2, 3 h, 75–85%; (d) pyridine hydrochloride (1.5 eq), reflux in nitroethane, 12 h, 81–89%; (e) trifluoromethane sulphonic anhydride (1.1 eq), stirred in CH_2Cl_2, at rt, 48 h.

gave only the single products 2,4,6-tri(4′-alkoxyphenyl)-pyrimidine **1** or 2,4,6-tri(3′,4′-dialkoxyphenyl)pyrimidine **2**. However, when a tri-substituted reactant: 3,4,5-trialkoxyacetophene **14a–c** and/or 3,4,5-trialkoxybenzonitrile **17** were used, this reaction gave a mixture of two products: 2,4,6-tri(3′,4′,5′-trialkoxyphenyl)pyrimidine **3–7** and 2,4,6-tri(3′,4′5′-trialkoxyphenyl)-1,3,5-triazine **8**. These products were separated and purified by flash chromatography; the yields of compounds **3–7** and **8** were in the range 19–32% and 39–53%, respectively. All these reported compounds were characterized by ^1H and ^{13}C NMR, mass spectroscopy and elemental analysis. Toward the close of our work, a series of 2,4,6-tri(3,4,5-trialkoxyphenyl)triazines was reported [8]; these compounds were prepared by the reaction of 3,4,5-trialkoxybenzonitriles in trifluoromethanesulphonic anhydride. Therefore this series of triazine derivatives, although found to exhibit hexagonal columnar phases, is excluded from this paper.

2.2. *Mesomorphic properties*

A few disc-like all-carbon compounds [9] based on hexa- and nona-substituted 1,3,5-triphenylbenzenes **9** were previously prepared by Scherowsky. These all-carbon benzene-based derivatives with chiral or non-chiral ester substituents were found to be non-mesogenic.

The lack of mesomorphic properties observed in this type of disc-like molecule was attributed to the absence of delocalization of π-electrons over all four rings due to non-planar conformations. However, some derivatives used as dopants did induce cholesteric phases in nematic discotics. In this work a series of structurally similar compounds in which two of the carbon atoms on the central benzene core group are replaced by two N atoms were prepared, and their mesomorphic properties studied. The presence of two nitrogen atoms in this heterocyclic ring might produce a change in dielectric anisotropy, and possibly induce mesomorphic behaviour.

The liquid crystalline behaviour of compounds **1–7** was studied by thermal analysis (DSC) and polarizing optical microscopy. The phase transitions and thermodynamic data are summarized in the table. The formation of columnar mesophases was found to be dependent on the number of flexible side chains attached to the core group. All compounds of type **1,2** formed crystalline phases regardless of the carbon length of the alkoxy side chains. The lack of liquid crystallinity in compounds **1** and **2** with three or six side chains, respectively, was supposed due to an insufficiency of side chain density for formation of a stable columnar phase. The formation of columnar phases was generally found to depend crucially on the side chain density, and most columnar mesogens have at least six side chains. In fact a few examples of metallomesogenic structures with three side chains which exhibit columnar phases have been reported [10]. The molecules in this type of correlated columnar phase are generally organized with an antiparallel arrangement within the columns.

Table. Phase behaviour of compounds **1–7**: *n* represents the number of carbons in the alkoxy chain. Cr = crystal; Col_{hd} = disordered hexagonal columnar; I = isotropic. The transition temperature (°C) and enthalpies (in parentheses, kJ mol^{-1}) determined by DSC at a scan rate of 10.0 C min^{-1}.

Compound	*n*	Transitions
1	8	Cr $\underset{31.5\ (28.7)}{\overset{74.8\ (32.6)}{\rightleftharpoons}}$ I
	12	Cr $\underset{33.8\ (57.8)}{\overset{64.5\ (48.7)}{\rightleftharpoons}}$ I
2	8	Cr $\underset{80.0\ (50.9)}{\overset{101.3\ (47.5)}{\rightleftharpoons}}$ I
	12	Cr $\underset{83.5\ (89.6)}{\overset{106.7\ (83.1)}{\rightleftharpoons}}$ I
3	10	Cr $\underset{34.6\ (34.9)}{\overset{59.7\ (32.5)}{\rightleftharpoons}}$ Col_{hd} $\underset{97.7\ (3.85)}{\overset{105.0\ (4.96)}{\rightleftharpoons}}$ I
4	10	Cr $\underset{37.9\ (34.2)}{\overset{45.7\ (36.0)}{\rightleftharpoons}}$ Col_{hd} $\underset{73.6\ (2.57)}{\overset{82.9\ (2.70)}{\rightleftharpoons}}$ I
5	10	Cr $\underset{41.5\ (48.5)}{\overset{56.5\ (49.0)}{\rightleftharpoons}}$ Col_{hd} $\underset{104.0\ (3.20)}{\overset{114.0\ (3.70)}{\rightleftharpoons}}$ I
6	10	Cr $\underset{5.92\ (27.0)}{\overset{36.2\ (26.6)}{\rightleftharpoons}}$ Col_{hd} $\underset{124.3\ (5.35)}{\overset{131.4\ (5.03)}{\rightleftharpoons}}$ I
7	10	Cr $\underset{34.0\ (15.0)}{\overset{62.1\ (15.6)}{\rightleftharpoons}}$ Col_{hd} $\underset{134.4\ (6.23)}{\overset{140.5\ (6.52)}{\rightleftharpoons}}$ I

However, all the compounds **3–7** with enhanced side chains exhibited columnar phases. Interestingly, compound **4**, which has six side chains, the same as compound **2**, formed a columnar phase. The better mesomorphic properties for compound **4** over **2** is attributed to an unsymmetric structure, which results in a less regular packing in the solid states. Continuing to increase the numbers of side chains from seven (**5**), eight (**6**) to nine (**7**) resulted in improved mesomorphic behaviour. Thermal results showed that compounds **3–7** exhibit enantiotropic behaviour. In DSC all the compounds melt to give crystal-to-columnar and columnar-to-isotropic transitions (Cr → Col → I), typical for discotic molecules. Mesophase-to-isotropic transitions for the compounds were observed in the lower temperature range at 36.2–140.5°C on heating, and the temperature range of the columnar phase was 36–119°C. This temperature range increased with the numbers of side chains, with compounds **6** and **7** having a wider temperature range than other compounds. The mesophase was characteristically identified as hexagonal columnar (Col_h) based on optical texture observations. A typically pseudo focal-conic texture with linear birefringent defects was clearly observed on slow cooling from the isotropic liquid, as often obtained for discotic molecules. In addition, a relatively smaller enthalpy for the columnar-to-isotropic transition was observed indicating that the mesophases were highly disordered.

3. Summary

A new class of disc-like heterocyclic molecules based on pyrimidine derivatives as core group has been prepared, and these compounds have been demonstrated to exhibit columnar phases. The presence of nitrogen atoms, which are more polarized, in the heterocyclic ring believed to be responsible for the enhanced mesomorphic properties over other analogous all-carbons rings. In addition molecules with a lower symmetry or unsymmetrical structure are readily amenable to the formation of columnar phases.

4. Experimental

All chemicals and solvents were reagent grades from Aldrich Chemical Co. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200 instrument. DSC thermographs were carried out on a Mettler DSC-820 calibrated with pure indium. All phase behaviour was determined at a scan rate of 10.0°C min^{-1}. Polarizating

microscopy was carried out on Nikkon MICROPHOT-FXA with a Mettler FP-90/FP82HT hot stage system. Elemental analysis for carbon, hydrogen, and nitrogen was conducted on a Heraeus CHN-O-Rapid elemental analyser. The compounds 4-alkoxyacetophenones [11 *a*], 3,4-dialkoxy acetophenones [11 *b*], 3,4-dialkoxybenzaldehydes [11 *c*], 3,4,5-trialkoxybenzoic acids [11 *a*] 3,4,5-trialkoxyacetophenones [11 *a*], 3,4,5-trialkoxybenzoylalcohols [11 *c*] and 3,4,5-trialkoxybenzaldehydes [11 *c*] were prepared by literature methods.

4.1. *4-Dodecyloxyacetophenone (**10a**, n = 12)*

White crystals, yield 86%, m.p. 48–49°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 3H), 1.24–1.81 (m, $-CH_2$, 16H), 2.52 (s, $-COCH_3$, 3H), 3.98 (t, $-OCH_2$, 2H), 6.87 (d, –Ar, 2H), 7.88 (d, –Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.88, 15.49, 23.26, 26.95, 27.31, 29.67, 29.93, 30.21, 32.50, 68.78, 113.50, 115.85, 129.60, 129.70, 130.64, 163.38, 196.36. IR (KBr): 2960, 2873, 1678 (CO), 1600, 1507, 1254, 1111 cm^{-1}.

4.2. *4-Dodecyloxybenzonitrile (**11a**, n = 12)*

White crystals, yield 87%, m.p. 42–43°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 3H), 1.24–1.80 (m, $-CH_2$, 20H), 3.96 (t, $-OCH_2$, 2H), 6.86 (d, –Ar, 2H), 7.52 (d, –Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.76, 13.82, 22.42, 25.67, 28.72, 29.09, 29.32, 29.39, 31.67, 68.14, 103.38, 114.90, 118.89, 133.55, 162.20. IR (KBr): 2919, 2859, 2223 (CN), 1613, 1513, 1261, 1182, 844, 552 cm^{-1}.

4.3. *3,4-Didodecyloxyacetophenone (**10b**, n = 12)*

White crystals, yield 75%, m.p. 60–62°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 6H), 1.23–1.81 (m, $-CH_2$, 40H), 2.52 (s, $-CH_3$, 3H), 4.03 (t, $-OCH_2$, 4H), 6.86 (d, –Ar, 1H), 7.49 (s, –Ar, 1H), 7.53 (d, –Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 14.06, 14.11, 15.44, 22.64, 25.94, 26.14, 29.00, 29.12, 29.33, 29.58, 30.13, 31.88, 32.54, 68.97, 69.17, 111.48, 112.30, 123.12, 130.20, 148.78, 153.47, 196.82. IR (KBr): 2939, 2866, 1676 (CO), 1593, 1520, 1434, 1281, 1215, 1149, 1082, 804, 651 cm^{-1}.

4.4. *3,4-Didodecyloxybenzaldehyde*

White crystals, yield 69%. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, J = 5.46 Hz, $-CH_3$, 6H), 1.23–1.81 (m, $-CH_2$, 40H), 4.05 (t, J = 4.38 Hz, $-OCH_2$, 4H), 6.92 (d, –Ar, J = 7.74 Hz, 1H), 7.36 (s, –Ar, 1H), 7.41 (d, –Ar, J = 1.99 Hz, 1H), 9.80 (s, –CHO, 1H). ^{13}C NMR ($CDCl_3$): δ 14.03, 22.31, 22.63, 25.30, 25.94, 28.98, 29.06, 29.31, 29.57, 31.21, 31.88, 68.92, 69.10, 111.03, 111.92, 126.54, 130.16, 149.81, 154.83, 190.27. IR (KBr): 29.32, 2853, 1699 (CO), 1600, 1520, 1467, 1434, 1393, 1281, 1241, 1149, 811 cm^{-1}.

4.5. *3,4-Didecyloxybenzonitrile (**11b**, n = 12)*

Light yellow crystals, yield 69%, m.p. 81–83°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 6H), 1.24–1.81 (m, $-CH_2$, 40H), 3.98 (t, $-OCH_2$, 4H), 6.85 (d, –Ar, 1H), 7.04 (s, –Ar, 1H), 7.21 (d, –Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 13.80, 22.42, 23.05, 24.87, 25.70, 28.62, 28.72, 29.02, 29.06, 30.55, 31.54, 31.56, 68.58, 69.10, 103.36, 112.54, 115.46, 125.60, 148.62, 152.72, 119.07. IR (KBr): 2932, 2853, 2229 (CN), 1600, 1513, 1467, 1281, 1241, 1142, 996, 804 cm^{-1}.

4.6. *3,4,5-Tridecyloxybenzoic acid (**13**, n = 10)*

White crystals, yield 75%. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, J = 4.30 Hz, $-CH_3$, 9H), 1.18–1.84 (m, $-CH_2$, 48H), 3.99 (m, $-OCH_2$, 6H), 7.33 (s, –Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.68, 26.05, 29.61, 30.30, 31.91, 69.07, 73.49, 108.39, 123.66, 143.00, 152.77, 172.21 (CO). IR (KBr): 3460 (OH), 2936, 2848, 1685 (CO), 1590, 1471, 1435, 1335, 1219, 1119, 970 cm^{-1}.

4.7. *3,4,5-Tridecyloxyacetophenone (**14a**, n = 10)*

White crystals, yield 78%, m.p. 37–38°C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 4.30 Hz, $-CH_3$, 9H), 1.24–1.84 (m, $-CH_2$, 48H), 2.53 (s, $COCH_3$, 3H), 3.97–4.03 (m, $-OCH_2$, 6H), 7.15 (s, –Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.98, 22.55, 26.28, 29.21, 30.21, 31.49, 31.64, 25.67, 69.25, 73.44, 107.14, 132.04, 142.88, 152.85, 196.98 (CO). IR (KBr): 2925, 2854, 1679 (CO), 1585, 1472, 1434, 1333, 1122, 724 cm^{-1}.

4.8. *3,4,5-Tridecyloxybenzylalcohol (**15**, n = 10)*

White solid, yield 90%, m.p. 44–45 C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, J = 4.90 Hz, $-CH_3$, 9H), 1.24–1.80 (m, $-CH_2$, 48H), 3.94 (m, $-OCH_2$, 6H), 4.59 (s, $-CH_2OH$, 2H), 6.51 (s, –Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.67, 26.13, 29.40, 29.68, 29.75, 31.98, 62.25, 68.85, 73.25, 115.0, 136.0, 137.6, 153.0. IR (KBr): 3323 (OH), 2952, 2872, 1593, 1507, 1440, 1341, 1235, 1116, 830, 704 cm^{-1}.

4.9. *3,4,5-Tridecyloxybenzaldehyde (**16**, n = 10)*

Light yellow paste, yield 79%. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, J = 4.70 Hz, $-CH_3$, 9H), 1.30–1.85 (m, $-CH_2$, 48H), 4.02 (m, $-OCH_2$, 6H), 7.02 (s, –Ar, 2H), 9.80 (s, –CHO, 1H). ^{13}C NMR ($CDCl_3$): δ 14.10, 22.60, 26.34, 29.23, 29.67, 30.32, 31.91, 69.30, 73.62, 108.78, 123.76, 143.37, 152.92, 191.04 (CHO). IR (KBr): 2920, 2840, 1690, 1580, 1490, 1460, 1440, 1370, 1320, 1220, 1110, 740 cm^{-1}.

4.10. *3,4,5-Tridecyloxybenzonitrile (**17**, n = 10)*

A mixture of 3,4,5-tridecyloxybenzaldehyde (5.00 g, 8.76 mmol) and pyridine hydrochloride (1.52 g, 13.1 mmol) was heated under gentle reflux in dried nitroethane (100 ml) for 12 h. The reaction was monitored by TLC.

Methylene chloride (100 ml) was added to the solution, and the reaction mixture was then extracted with 100 ml dilute hydrochloric acid (0.1M). The collected organic layers were washed three times with water. The organic layers were combined and dried with anhydrous $MgSO_4$, then concentrated to give a crude yellow oil. The final product was isolated as a yellow solid by recrystallization from methylene chloride/methanol (1/3), or by silica gel chromatography eluting with hexane/ethyl acetate (40/1). Light yellow solid, yield 77%, m.p. 50.6–52.0°C. ^{1}H NMR ($CDCl_3$), δ 0.85 (t, $J = 4.90$ Hz, $-CH_3$, 9H), 1.24–1.85 (m, $-CH_2$, 48H), 3.91–4.00 (m, $-OCH_2$, 6H), 6.78 (s, -Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 13.81, 22.50, 25.85, 29.03, 29.18, 29.35, 29.40, 29.43, 29.43, 29.55, 30.13, 31.74, 69.14, 73.37, 106.09, 110.21, 118.84 (CN), 141.25, 153.25. IR (KBr): 2923, 2866, 2236 (CN), 1586, 1507, 1474, 1434, 1248, 1135, 844, 625 cm^{-1}.

4.11. *2,4,6-Tri(3',4'-didodecyloxyphenyl)pyrimidine (**2**, n = 12)*

A mixture of 3,4-didodecyloxybenzonitrile (4.95 g, 10.5 mmol) dissolved in dried methylene chloride (30 ml and trifluoromethanesulphonic anhydride (1.61 g, 5.70 mmol) was prepared under nitrogen. 3,4-Didodecyloxyacetophenone (2.44 g, 5.00 mmol) dissolved in dried methylene chloride (75 ml) was added dropwise during 1 h. The solution turned reddish, and was stirred for 48 h at room temperature. The solution was extracted with saturated sodium bicarbonate (50 ml), and the organic layer was collected and dried over anhydrous $MgSO_4$. This solution was concentrated to give a black paste which was purified by flash chromatography eluting with hexane/ethyl acetate (40/1). The product was obtained as light yellow crystals after recrystallization from methylene chloride/methanol (1/3). Yield 26%, m.p. 106–108°C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $J = 4.20$ Hz, $-CH_3$, 18H), 1.25–1.87 (m, $-CH_2$, 120H), 4.07–4.16 (m, $-OCH_2$, 12H), 6.98 (d, $J = 8.50$ Hz, -Ar, 3H), 7.74–7.77 (d, $J = 600$ Hz, 2H), 7.77 (s, 1H), 7.88 (d, $J = 7.50$ Hz, 2H), 8.25 (s, -Ar, 1H), 8.25–8.28 (d, $J = 7.60$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.63, 26.02, 26.09, 26.11, 29.25, 29.28, 29.35, 29.43, 29.70, 29.88, 31.66, 31.82, 69.10, 69.45, 108.20, 112.75, 113.03, 113.62, 120.37, 121.75, 130.30, 131.04, 148.75, 149.22, 151.43, 151.60, 163.83. FAB-MS (*m/z*) 1414.3 (MH^+, 100%). IR (KBr): 2956, 2854, 1605, 1576, 1517, 1464, 1394, 1374, 1273, 1224, 1121, 800, 722 cm^{-1}. Anal: calcd for $C_{94}H_{160}N_2O_6$, C 79.83, H 11.40, N 1.98; found, C 79.54, H 11.17, N 1.93%.

4.12. *2,4,6-Tri(4'-dodecyloxyphenyl)pyrimidine (**4**, n = 12)*

White crystals, yield 51%, m.p. 64.0–66.0°C. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, $J = 4.38$ Hz, $-CH_3$, 9H), 1.21–1.90 (m, $-CH_2$, 60H), 3.93–4.02 (m, $-OCH_2$, 6H), 6.09–7.04 (m, -Ar, 6H), 7.74 (s, Ar, 1H), 8.20 (d, $J = 8.40$ Hz, ArH, 4H), 8.68 (d, $J = 8.50$ Hz, ArH, 2H). ^{13}C NMR ($CDCl_3$): δ 14.09, 22.68, 26.03, 29.22, 29.28, 29.34, 29.40, 29.58, 29.63, 30.11, 31.90, 68.08, 68.18, 107.82, 114.20, 114.68, 128.74, 129.78, 130.07, 130.61, 161.36, 161.41, 163.76, 163.80. HRMS (FAB): calcd. for MH^+ $C_{58}H_{88}N_2O_3$ 861.6874, found 861.6898. IR (KBr): 2926, 2857, 1608, 1587, 1568, 1529, 1512, 1419, 1368, 1255, 1176, 1042, 825, 783, 523 cm^{-1}. Anal: calcd for $C_{58}H_{88}N_2O_7$, C 80.88, H 10.30, N 3.25; found, C 80.60, H 10.29, N 3.02%.

4.13. *2,4-Bis(3',4'-didecyloxyphenyl)-6-(3',4',5'-tridecyloxyphenyl)pyrimidine (**3**, n = 10)*

Light yellow solid, yield 14%. m.p. 105°C. ^{1}H NMR ($CDCl_3$): δ 0.83 (t, $-CH_3$, 21H), 1.24–1.91 (m, $-CH_2$, 112H), 4.01–4.16 (m, $-OCH_2$, 14H), 6.98 (d, 1H), 7.43 (s, 2H), 7.73 (s + d, 2H), 7.89 (s, pyrimidine–H, 1H), 8.24 (s + d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.66, 26.03, 26.14, 29.36, 29.60, 30.36, 31.90, 69.17, 69.56, 73.59, 106.23, 108.66, 113.01, 113.70, 118.66, 120.06, 121.75, 130.39, 131.33, 132.85, 140.06, 148.83, 149.30, 151.49, 151.73, 153.44, 164.13. FAB-MS (*m/z*): calcd 1402.19, found 1402.3 IR (KBr): 2926, 2853, 1573, 1520, 1474, 1361, 1269, 1116, 844, 753, 778 cm^{-1}. Anal: calcd for $C_{92}H_{156}N_2O_7$, C 78.80, H 11.21, N 2.00; found, C 78.54, H 10.96, N 2.26%.

4.14. *2,4-Bis(3',4',5'-tridecyloxyphenyl)-6-phenylpyrimidine (**4**, n = 10)*

Off white solid, yield 10%, m.p. 83.0°C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 18H), 1.25–1.89 (m, $-CH_2$, 96H), 4.02–4.15 (m, $-OCH_2$, 12H), 7.45 (s, -Ar, 2H), 7.55 (t, -Ar, 3H), 7.84 (s, pyrimidine–H, 1H), 7.93 (s, 2H), 8.21–8.24 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.01, 22.63, 26.14, 29.34, 29.48, 29.60, 30.36, 31.88, 68.94, 69.16, 73.38, 105.83, 106.93, 109.24, 127.14, 128.69, 130.47, 132.24, 132.99, 137.62, 140.67, 140.86, 152.98, 153.34, 163.84, 163.96, 164.35. FAB-MS (*m/z*): calcd 1246.04, found 1246.1. IR (KBr): 2926, 2860, 1573, 1540, 1467, 1368, 1229, 1123, 851 cm^{-1}. Anal: calcd for $C_{82}H_{136}N_2O_6$, C 79.05, H 11.00, N 2.25; found, C 78.91, H 10.97, N 2.19%.

4.15. *2,4-Bis(3',4',5'-tridecyloxyphenyl)-6-(4'-decyloxyphenyl)pyrimidine (**5**, n = 10)*

Off white solid, yield 11%, m.p. 114.0°C. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, $-CH_3$, 21H), 1.25–1.88 (m, $-CH_2$, 112H), 4.00–4.16 (m, $-OCH_2$, 14H), 7.01–7.06 (d, -Ar, 2H), 7.46 (s, -Ar, 2H), 7.77 (s, pyrimidine–H, 1H), 7.92 (s, 2H), 8.17–8.22 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 26.03, 26.20, 29.21, 29.38, 29.51, 29.61, 29.67, 30.37, 31.91, 68.21, 69.11, 69.34, 73.48, 73.50, 106.04, 107.07,

108.69, 114.75, 128.69, 129.80, 132.63, 133.25, 140.70, 140.84, 153.07, 153.43, 161.48, 163.98, 164.07. FAB-MS (*m/z*): calcd 1402.19, found 1402.3. IR (KBr): 2926, 2853, 1573, 1534, 1501, 1474, 1361, 1116, 771 cm^{-1}. Anal: calcd for $C_{92}H_{156}N_2O_7$, C 78.80, H 11.21, N 2.00; found, C 78.51, H 11.29, N 1.83%.

4.16. *2,4-Bis(3',4',5'-tridecyloxyphenyl)-6-(3',4'-didecyloxyphenyl)pyrimidine (6, n = 10)*

Light yellow solid, yield 12%, m.p. 131.4°C. ^1H NMR ($CDCl_3$): δ 0.85 (t, $-CH_3$, 24H), 1.49–1.89 (m, $-CH_2$, 128H), 4.01–4.15 (m, $-OCH_2$, 16H), 7.00 (s, 2H), 7.45 (s, 2H), 7.76 (s, 1H), 7.90–7.92 (s + d, 3H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.69, 26.03, 26.13, 26.17, 29.21, 29.38, 29.50, 29.63, 29.75, 30.36, 31.91, 69.00, 69.18, 69.38, 69.47, 73.50, 73.60, 106.13, 106.92, 108.85, 112.87, 113.14, 120.36, 130.24, 132.64, 133.15, 140.64, 140.89, 149.28, 151.74, 153.04, 153.44, 163.77, 164.05. FAB-MS (*m/z*): calcd 1558.34, found 1558.0. IR (KBr): 2926, 2853, 1573, 1507, 1474, 1361, 1116, 874, 753 cm^{-1}. Anal: calcd for $C_{102}H_{176}N_2O_8$, C 78.61, H 11.38, N 1.80; found C 78.42, H 11.02, N 1.62%.

4.17. *2,4,6-Tri(3',4',5'-tridecyloxyphenyl)pyrimidine (7, n = 10)*

Reddish-brown solid, yield 13%, m.p. 140.5°C. ^1H NMR ($CDCl_3$): δ 0.85 (t, $J = 4.40$ Hz, $-CH_3$, 27H), 1.25–1.86 (m, $-CH_2$, 144H), 4.01–4.12 (m, $-OCH_2$, 18H), 7.44 (s, 4H), 7.72 (s, 1H), 7.92 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.66, 26.14, 29.36, 29.48, 29.61, 29.66, 30.36, 31.91, 68.99, 69.51, 73.51, 73.63, 106.37, 106.93, 109.41, 132.60, 133.00, 140.70, 141.06, 153.05, 153.46, 163.78, 164.32. FAB-MS (*m/z*): calcd 1714.49, found 1714.59. IR (KBr): 2926, 2860, 1573, 1534, 1501, 1361, 1229, 1116, 862, 750 cm^{-1}. Anal: calcd for $C_{112}H_{196}N_2O_9$, C 78.45, H 11.52, N 1.63; found C 78.52, H 11.41, N 1.74%.

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Solvolyses of naphthoyl chlorides. Solvent effect and Grunwald–Winstein correlation analyses with Y_{xBnCl} scales†

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ABSTRACT: The solvolyses of 1-naphthoyl (**2**), 2-naphthoyl (**3**), 4-methyl-1-naphthoyl (**4**) and 6-methoxy-2-naphthoyl (**5**) chlorides in a variety of solvents were studied, and correlation analyses by using the single- and dual-parameter Grunwald–Winstein equations were examined. An excellent linear relationship ($R = 0.995$) for **4**, log $(k/k_0) = 0.733Y_{xBnCl} + 0.269N_{OTs}$, was observed. An S_N1-like mechanism with decreasing extent of nucleophilic solvent participation was found in the solvolysis of **2** and **4**. 2-Naphthoyl chloride is likely to have a mechanism at the borderline of S_N1-like dissociation and an addition–elimination process. 6-Methoxy-2-naphthoyl chloride shows more S_N1-like character than **3** and is associated with nucleophilic solvent intervention more pronounced than that for **2** and **4**. The applicability and the advantages of using the Y_{xBnCl} scale for different types of substrates are discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: naphthoyl chlorides; solvolysis; solvent effect; Grunwald–Winstein correlation analysis

INTRODUCTION

Acyl chlorides are fundamental organic substrates with high reactivity towards many kinds of transformations.[1] Recent examples of physical organic[2] and synthetic[3] studies illustrate continuing interest in research on this category of compounds. Concerning the kinetics and mechanisms of the solvolysis of acyl chlorides, early work by Hudson and co-workers suggested a dependence of the mechanism on solvent composition.[4] The failure of employing the single-parameter Grunwald–Winstein equation [Eqn. (1)],[5] with the original Y values, to the solvolysis of 4-nitrobenzoyl chloride[6] and acetyl and benzoyl chlorides[4c] in hydroxylic solvents was reported.

$$\log(k/k_0) = mY \qquad (1)$$

Mechanistic studies of the solvolysis of benzoyl chlorides have advanced since the 1980s. Bentley *et al.* proposed a limiting S_N1 mechanism for the solvolysis of 4-methoxybenzoyl chloride,[7] and different mechanisms of solvolysis for aromatic acyl chlorides containing different substituents were suggested from rate–product selectivity studies.[8] Non-linear log k vs mY_{Cl}[9] plots were observed again.[10] On the other hand, the solvent effect on the solvolytic reactivity of a series of substituted benzoyl chlorides (**1**) was examined[2c] using the Y values, Y_{BnCl}, derived from the solvolysis rate constants of α-*tert*-butyl(4-methylphenyl)methyl chloride and 2-aryl-2-chloroadamantane,[11a,b] specific to benzylic substrates.[11] An S_N1 mechanism was realized in the case of 2,6-dimethylbenzoyl chloride (**1a**), and S_N1 mechanisms with various extents of nucleophilic solvent participation were found in the solvolysis of **1b–d**, while different types of non-S_N1 reaction mechanisms were suggested for the parent and deactivated benzoyl chlorides **1e–g**.[2c] The successful application of the Y_{BnCl} scale to the benzoyl system made it desirable to explore the possibility of employing the Y_{xBnCl} scale, the parameter of solvent ionizing power suitable for the benzylic system with extended charge delocalization based on the use of α-*tert*-butyl(2-naphthyl)methyl chloride as the reference standard,[12,13] to the solvolysis of naphthoyl chlorides.

Consequently, the solvolysis of naphthoyl chlorides **2–5** in a variety of solvents was studied. The applicability of the Y_{xBnCl} scale in Grunwald–Winstein-type correlation analyses with single- and dual-parameter equations [Eqns (1) and (2)[14]] can be confirmed, and the mechanism of solvolysis may be understood.

$$\log(k/k_0) = mY + lN \qquad (2)$$

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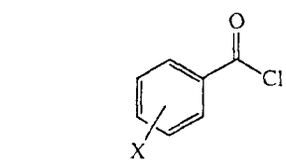
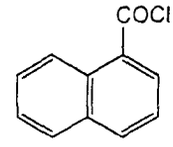


1a : X = 2,6-$(CH_3)_2$
1b : X = 2-CH_3
1c : X = 4-CH_3O
1d : X = 4-CH_3
1e : X = 4-H
1f : X = 4-Cl
1g : X = 4-NO_2



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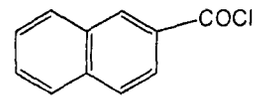

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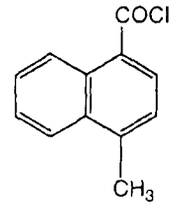

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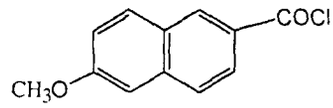

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RESULTS AND DISCUSSION

1-Naphthoyl chloride (**2**), 2-naphthoyl chloride (**3**), 4-methyl-1-naphthoyl chloride (**4**) and 6-methoxy-2-naphthoyl chloride (**5**) were purified or prepared, and were solvolyzed in a variety of solvents. The rates of solvolysis were monitored conductometrically at appropriate temperatures. First-order kinetics were observed up to at least 80% of the reaction. The rate constants at 25 °C are shown in Table 1.

The solvolysis of **2** and **3** in acetone–methanol and in acetonitrile–methanol has also been studied by Yoon *et al.*[15] For rate constants of methanolysis, the variation of the two sets of data is within about 10%. Correlation analyses using the single-parameter Grunwald–Winstein equation [Eqn. (1)] against Y_{Cl},[9] Y_{BnCl}[11] and Y_{xBnCl}[12] were carried out. The results for all solvents (All), nucleophilic solvents (AEM) and iso-dielectric solvents (TE) are listed in Table 2. From this table it is clear that, similarly to those reported previously,[2c,10] poor correlations and scattered data points for log k–Y_{Cl} plots were found in all four cases.

With the exception of 2-naphthoyl chloride (**3**), in other cases the log k–Y_{xBnCl} plots yielded two lines with excellent correlations ($R \geq 0.99$),[16] one for aqueous acetone–ethanol–methanol (AEM) and the other for the trifluoroethanol–ethanol (TE) mixtures. The log k–Y_{xBnCl} plot for **2** is shown in Fig. 1 as an example. The appearance of a downward splitting line for poorly nucleophilic trifluoroethanol–ethanol mixtures from that for nucleophilic solvents suggests significant nucleophilic solvent intervention in solvolysis, as was illustrated in recent examples.[2c,17] Moreover, the difference between m_{AEM} and m_{TE} was found to exhibit various extents of nucleophilic solvent intervention.[18] From Table 2, Δm ($m_{AEM} - m_{TE}$) of log k–Y_{xBnCl} plots increased from **4** (0.052) to **2** (0,127) to **5** (0.230). Therefore, regression analyses of log k values in Table 1 employing the dual-parameter equation [Eqn. (2)] were carried out. Since the

Table 1. Solvolytic rate constants at 25 °C[a]

Solvent[b]	2	3	4	5
100E	2.05×10^{-3}	7.30×10^{-4}	7.00×10^{-3}	7.45×10^{-4}
90E	6.70×10^{-3}	2.08×10^{-3}	2.37×10^{-2}	2.18×10^{-3}
80E	1.69×10^{-2}	3.37×10^{-3}	6.56×10^{-2}	5.46×10^{-3}
70E	4.03×10^{-2}	5.58×10^{-3}	–	1.07×10^{-2}
60E	9.08×10^{-2}	9.33×10^{-3}	–	2.44×10^{-2}
100M	1.51×10^{-2}	4.55×10^{-3}	4.35×10^{-2}	5.40×10^{-3}
90M	2.69×10^{-2}	8.54×10^{-3}	1.52×10^{-1c}	1.29×10^{-2}
80M	9.34×10^{-2}	1.49×10^{-2}	5.13×10^{-1c}	2.60×10^{-3}
70M	3.12×10^{-1c}	2.13×10^{-2}	–	5.97×10^{-2}
90A	5.14×10^{-4}	3.37×10^{-4}	1.10×10^{-3}	–
80A	1.96×10^{-3}	7.58×10^{-4}	5.30×10^{-3}	1.05×10^{-3}
70A	7.21×10^{-3}	1.43×10^{-3}	1.96×10^{-2}	3.16×10^{-3}
60A	2.68×10^{-2}	3.28×10^{-3}	7.81×10^{-2}	9.94×10^{-3}
50A	–	9.24×10^{-3}	–	3.44×10^{-2}
100T	5.36×10^{-1c}	8.96×10^{-3}	–	3.33×10^{-2}
80T20E	1.26×10^{-1}	3.29×10^{-3}	1.02[c]	1.59×10^{-2}
60T40E	2.88×10^{-2}	1.13×10^{-3}	1.59×10^{-1c}	4.74×10^{-3}
40T60E	9.63×10^{-3}	7.38×10^{-4}	5.00×10^{-2}	2.24×10^{-3}

[a] In s^{-1}.
[b] Abbreviations of solvents: A = acetone, E = ethanol, M = methanol, T = 2,2,2-trifluoroethanol. Figures shown are percentages by volume in water; 80T20E indicates T–E 80:20 (v/v) and likewise for 60T40E and 40T60E.
[c] Extrapolated from the data at lower temperatures (see text).

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Table 2. Correlation analyses using the single-parameter equation [Eqn. (1)]

Substrate	Parameter	n[a] (solvent)[b]	R[c]	m (SD[d])
2	Y_{Cl}	17 (All)	0.968	0.553 (0.037)
		13 (AEM)	0.871	0.531 (0.090)
		5 (TE)	0.990	0.448 (0.037)
	Y_{BnCl}	17 (All)	0.957	0.532 (0.042)
		13 (AEM)	0.987	0.666 (0.033)
		5 (TE)	0.996	0.470 (0.024)
	Y_{xBnCl}	17 (All)	0.968	0.533 (0.036)
		13 (AEM)	0.993	0.657 (0.024)
		5 (TE)	0.997	0.530 (0.025)
3	Y_{Cl}	18 (All)	0.694	0.254 (0.066)
		14 (AEM)	0.794	0.320 (0.071)
		5 (TE)	0.886	0.201 (0.061)
	Y_{BnCl}	18 (All)	0.708	0.260 (0.065)
		14 (AEM)	0.962	0.445 (0.037)
		5 (TE)	0.910	0.215 (0.057)
	Y_{xBnCl}	18 (All)	0.737	0.278 (0.064)
		14 (AEM)	0.982	0.448 (0.025)
		5 (TE)	0.912	0.243 (0.030)
4	Y_{Cl}	13 (All)	0.831	0.653 (0.112)
		10 (AEM)	0.764	0.517 (0.163)
		4 (TE)	0.998	0.620 (0.055)
	Y_{BnCl}	13 (All)	0.970	0.633 (0.048)
		10 (AEM)	0.973	0.720 (0.061)
		4 (TE)	0.999	0.583 (0.016)
	Y_{xBnCl}	13 (All)	0.989	0.650 (0.029)
		10 (AEM)	0.996	0.715 (0.022)
		4 (TE)	0.999	0.663 (0.016)
5	Y_{Cl}	17 (All)	0.846	0.355 (0.058)
		13 (AEM)	0.870	0.414 (0.071)
		5 (TE)	0.992	0.314 (0.023)
	Y_{BnCl}	17 (All)	0.832	0.364 (0.063)
		13 (AEM)	0.994	0.594 (0.020)
		5 (TE)	0.996	0.328 (0.017)
	Y_{xBnCl}	17 (All)	0.842	0.391 (0.065)
		15 (AEM)	0.992	0.600 (0.018)
		5 (TE)	0.996	0.370 (0.066)

[a] Number of data points.
[b] Abbreviations of solvents as in Table 1.
[c] Correlation coefficient.
[d] Standard deviation.

solvent nucleophilicity scale N_{OTs}[19] was found to be superior to N_T[20] for substrates bearing anionic leaving groups, such as in the solvolysis of various benzylic[12] and benzoyl chlorides,[2c] only the former scale was used. A few rate data could not be included owing to the shortage of N values for the corresponding solvents. Nevertheless, it still covers a wide range of both Y (5.76 for Y_{xBnCl}[12] and 5.83 for Y_{BnCl}[11]) and N (3.00 for N_{OTs}[19]) values, and has 11–15 data points, which make the outcome of a dual-parameter regression analysis acceptable. The results are given in Table 3.

Table 3 clearly indicates that an excellent correlation ($R \geq 0.99$)[16] can be found only in the case of **4** if the parameters Y_{xBnCl} and N_{OTs} were applied. A poor correlation ($R < 0.90$) is realized for **3**, whereas the correlations are satisfactory ($R = 0.95$–0.98)[16] for **2** and **5** no matter whether the Y_{BnCl} or Y_{xBnCl} scale was

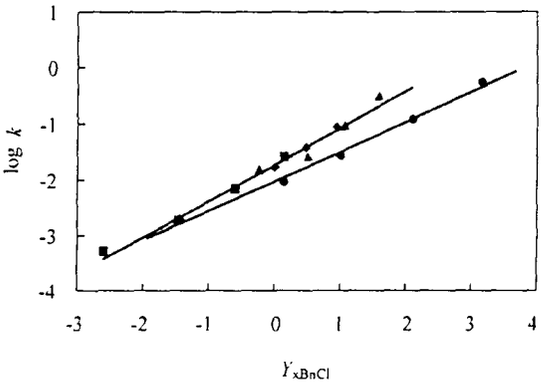


Figure 1. Plots of log k for **2** against Y_{xBnCl}. Data points for (◆) aqueous ethanol (E), (■) aqueous acetone (A), (▲) aqueous methanol (M) and (●) trifluoroethanol–ethanol (TE)

employed. Therefore, the data in Tables 2 and 3 suggest the superiority of using Y_{xBnCl} over other Y values in the correlation analysis for the solvolysis of naphthoyl chlorides.

There are three possible pathways generally considered for the solvolysis of acyl halides, namely the unimolecular S_N1-type dissociation [Eqn. (3)], the bimolecular synchronous S_N2-type reaction [Eqn. (4)] and the stepwise addition–elimination reaction [Eqn. (5)], as have been discussed.[21]

$$RCOX \longrightarrow RC{=}O^{+}\,X^{-} \xrightarrow{SOH} RCOOS + H^{+} \quad (3)$$

$$RCOX + SOH \longrightarrow [TS]^{\ddagger} \longrightarrow RCOOS + X^{-} + H^{+} \quad (4)$$

$$RCOX + SOH \longrightarrow RC(O^{-})(SOH)X \longrightarrow RCOOS + X^{-} + H^{+} \quad (5)$$

Previous work on the mechanism of solvolysis for benzoyl chlorides (**1**) indicated a dependence of the reaction pathways on the nature of the substitutents, based on the results of Grunwald–Winstein-type correlation analyses [Eqns (1) and (2)], Hammett-type correlation analysis [Eqn. (6)] and *ab initio* calculations.[2c] The most reactive and sterically hindered 2,6-dimethylbenzoyl chloride (**1a**) was found to solvolyze with a limiting S_N1 mechanism [Eqn. (3)], whereas the less reactive 2-methyl- (**1b**), 4-methoxy- (**1c**) and 4-methylbenzoyl chloride (**1d**) proceed via an S_N1 mechanism with a significant extent of nucleophilic solvent intervention.[2c] The unsubstituted benzoyl chloride (**1e**) was considered to solvolyze with a mechanism at the borderline of unimolecular dissociation [Eqn. (3)] and the addition–elimination [Eqn. (5)].[2c] However, for benzoyl chlorides containing a deactivating substitutent, such as 4-chloro- (**1f**) and 4-nitro- (**1g**), an S_N2-like

Table 3. Correlation analyses using the dual-parameter equation [Eqn. (2)]

Substrate	Parameter	n^a	R	m (SD[b])	l (SD[b])
2	Y_{BnCl},N_{OTs}	14	0.986	0.656 (0.044)	0.335 (0.069)
	Y_{xBnCl},N_{OTs}	14	0.984	0.648 (0.046)	0.241 (0.068)
3	Y_{BnCl},N_{OTs}	15	0.850	0.454 (0.082)	0.505 (0.131)
	Y_{xBnCl},N_{OTs}	15	0.844	0.454 (0.082)	0.443 (0.125)
4	Y_{BnCl},N_{OTs}	11	0.985	0.745 (0.055)	0.432 (0.117)
	Y_{xBnCl},N_{OTs}	11	0.995	0.733 (0.031)	0.269 (0.062)
5	Y_{BnCl},N_{OTs}	15	0.964	0.587 (0.051)	0.500 (0.081)
	Y_{xBnCl},N_{OTs}	15	0.957	0.568 (0.066)	0.403 (0.099)

[a] Number of data points.
[b] Standard deviation.

mechanism [Eqn. (4)] was found in nucleophilic solvents and an addition–elimination mechanism [Eqn. (5)] in trifluoroethanol–ethanol.[2c] Similar variation of mechanisms would be expected to proceed in the solvlolysis of naphthoyl chlorides.

$$\log(k_X/k_H) = \sigma^+\rho \qquad (6)$$

Among the four substrates investigated, 2-naphthoyl chloride (**3**) is the least reactive, as shown from Table 1. A comparison of its rate constants with those for benzoyl chlorides[2c] indicates that the reactivity lies between those of **1d** and **1e** in the more ionizing solvents, i.e. 70E, 60E, 80M, 70M, 70A to 50A and 100T to 40T60E, in line with the trend of σ^+ constants (−0.311 for CH_3,[22] −0.126,[23] −0.135[24] or −0.18 (K.-T. Liu, unpublished data) for 2-naphthyl and zero for H). Although the result of correlation analysis using the single-parameter equation [Eqn. (1)] showed similar behavior in nucleophilic solvents for **1d** ($m = 0.662$, $R = 0.990$ against Y_{BnCl})[2c] and for **3** ($m = 0.448$, $R = 0.982$ against Y_{xBnCl}, Table 2), the correlation was different between **1d** ($R = 0.967$ against Y_{BnCl} and N_{OTs})[2c] and **3** ($R = 0.844$ against Y_{xBnCl} and N_{OTs}, Table 3) if the rate data in all solvents were considered and Eqn. (2) was used. Logarithmic plots of rate data for **3** in the present study against that for **1d** in the literature[2c] also exhibit scattered points (Fig. 2). On the other hand, a poor correlation ($R = 0.924$) was observed for **1e**[25] in all solvents by using the dual-parameter equation [Eqn. (2)] against Y_{BnCl} and N_{OTs}. Furthermore, the plot of log$k$(**3**) vs log$k$(**1e**)[2c] gave excellent linear relationships ($R = 0.997$) only in aqueous acetone, ethanol and methanol (Fig. 3), and showed significant deviations in 100T and 80T20E. Therefore, the solvolysis mechanism of **3** in nucleophilic solvents might be close to that of benzoyl chloride (**1e**), at the borderline of unimolecular dissociation [Eqn. (3)] and the addition–elimination process [Eqn. (5)], as was suggested.[2c] The observed acceleration of solvolysis rates for **3** compared with **1e** in weakly nucleophilic solvents (100T and 80T20E, Fig. 3) indicates that the mechanism is closer to the unimolecular dissociation in the case of **3** than **1e**.

Table 1 indicates that 6-methoxy-2-naphthoyl chloride (**5**) is slightly more reactive than the unsubstituted substrate **3** with a rate ratios k(**5**)/k(**3**) of 1.3–4.8. However, large rate enhancements, 100–1000-fold, due to increasing resonance stabilization in the cationic transition state by the 6-methoxy group, were found in the solvolysis of the corresponding α-*tert*-butyl(6-methoxy-2-naphthyl)methyl chloride (**6**)[26] versus the parent α-*tert*-butyl(2-naphthyl)methyl chloride (**7**).[12] The σ^+

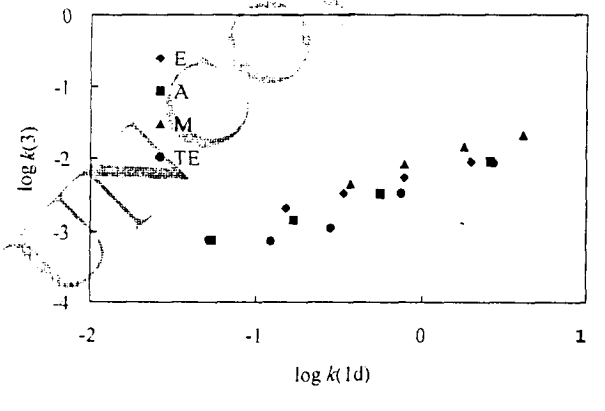


Figure 2. Plots of log k for **3** against log k for **1d**. Symbols as in Fig. 1

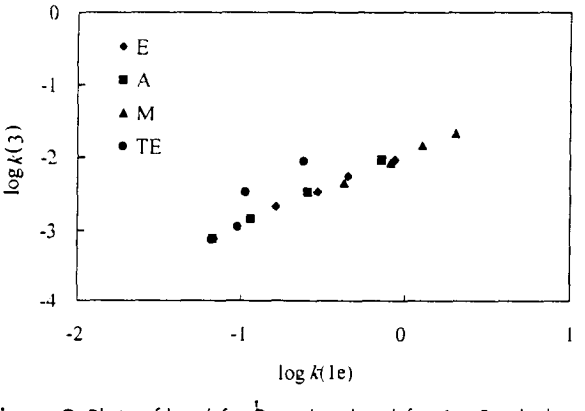
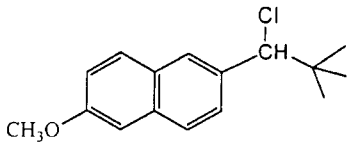


Figure 3. Plots of log k for **3** against log k for **1e**. Symbols as in Fig. 1

constant for the 6-methoxy-2-naphthyl group was estimated as −0.57 (K.-T. Liu, unpublished data). Probably **5** solvolyzed with a mechanism different from that for **3**, but similar to that for **1c** and **1d**. Although no good linear relationship was observed for **5** in the dual-parameter correlation analysis (Table 3), two separate lines, one for nucleophilic solvents (AEM) and the other for poorly nucleophilic solvents (TE), were found in the single-parameter plots (Table 2, Figure 4). Therefore, the downward splitting of line for data points obtained in TE ($m = 0.370$) from that in AEM ($m = 0.600$), i.e. $\Delta m = 0.230$, suggests the intervention of nucleophilic solvents in the ionization process of **5** (see above). The low m values (≤ 0.6) in Tables 2 and 3 obtained from both single-parameter [Eqn. (1)] and dual-parameter [Eqn. (2)] regression analyses also revealed deviations from an S_N1 process. The observation of an excellent linear log$k$(**5**)–log$k$(**1d**) plot with $R = 0.994$ and $m = 0.933$ (Figure 5), but a poor correlation for the log$k$(**5**)–log$k$(**1e**) plot (Fig. 6), provides additional evidence for the similarity of solvolytic mechanisms between **5** and **1d**.



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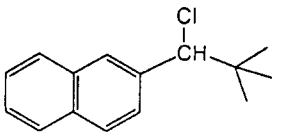

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A comparison of k(**2**) and k(**3**) (Table 1) reveals that 1-naphthoyl chloride (**2**) is more reactive than 2-naphthoyl chloride (**3**) in all solvents employed. The rate ratios are

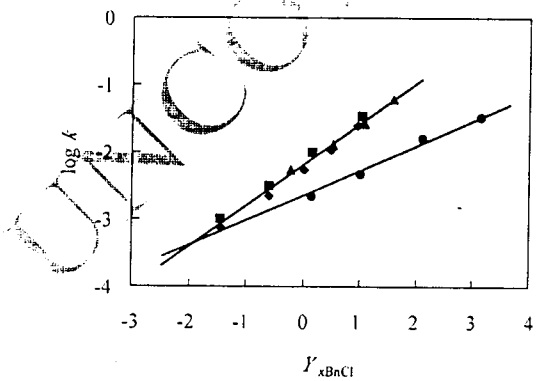


Figure 4. Plots of log k for **5** against Y_{xBnCl}. Symbols as in Fig. 1

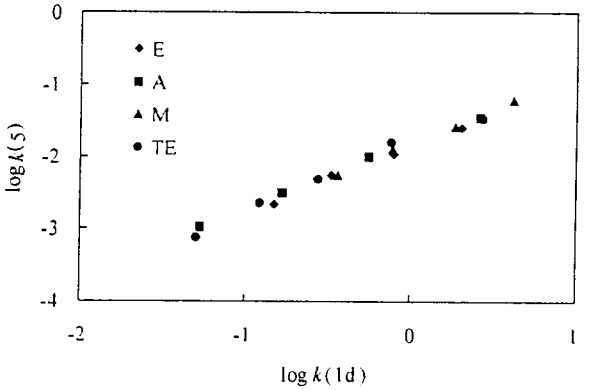


Figure 5. Plots of log k for **5** against log k for **1d**. Symbols as in Fig. 1

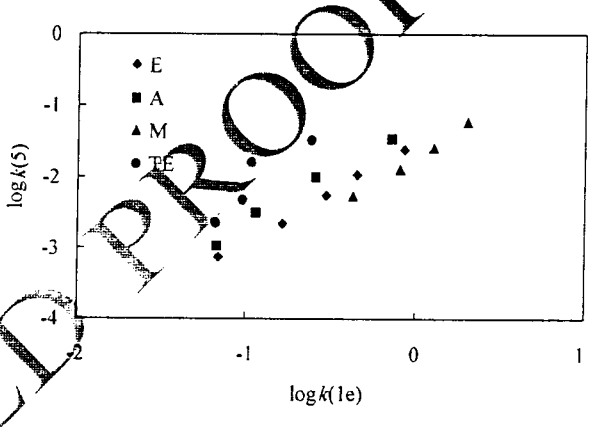
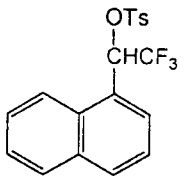


Figure 6. Plots of log k for **5** against log k for **1e**. Symbols as in Figure 1

1.5–5.0 in less ionizing but more nucleophilic solvents, about 10–15 in others, and the largest (ca 60) in the least nucleophilic trifluoroethanol. On the other hand, the solvolysis of secondary 1-naphthylmethyl tosylate (**8**) was found to be about 10–25-fold more reactive than the 2-naphthylmethyl analogue **9** in a variety of solvents.[27] Both **2** and **3** could therefore be proposed to solvolyze, at least in part, via an ionization mechanism [Eqn. (3)] in solvents such as 60E, 70M, 100T and some other TE mixtures. Indeed, Fig. 1 exhibits a splitting of lines, and



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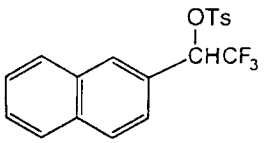

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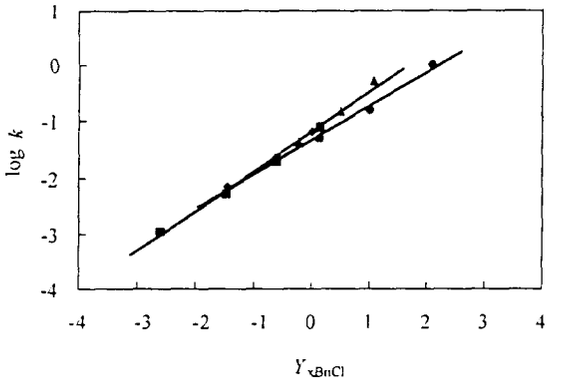


Figure 7. Plots of log *k* for **4** against Y_{xBnCl}. Symbols as in Fig. 1

Table 3 shows a fairly good linear relationship ($R = 0.984$) from the dual-parameter correlation with Y_{xBnCl} and N_{OTs} in the case of **2**. In other words, **2** is likely to solvolyze via S_N1 mechanisms involving a certain extent of nucleophilic solvent intervention, although it could be partially hindered by the *peri*-hydrogen at C-8.

Table 1 shows a small increment of the solvolytic reactivity, 2–8, for 4-methyl-1-naphthoyl chloride (**4**) over that for 1-naphthoyl chloride (**2**). The log*k*–Y_{xBnCl} plot gave two lines in both cases (Figs 1 and 7), and Table 2 reveals a smaller difference in the slopes for **4** ($m_{AEM} - m_{TE} = 0.052$) than that for **2** (0.127). Obviously, the introduction of a 4-methyl substituent gives rise to increased stability of the cationic intermediate, probably due to a resonance effect (**10**) (Scheme 1), and thus a decreased extent of nucleophilic solvent intervention in solvolysis. Since good to excellent linear relationships in the dual-parameter correlation [Eqn. (2)] were observed for **4** ($R = 0.995$) and **2** ($R = 0.984$), and the N_{OTs} scale was defined from the reaction of methyl tosylate,[17] the intervention of nucleophilic solvents in this study would probably be a kind of 'participation'[28] but not 'nucleophilic solvation.'[29] A discussion on the criteria for nucleophilic solvent participation will be reported elsewhere.

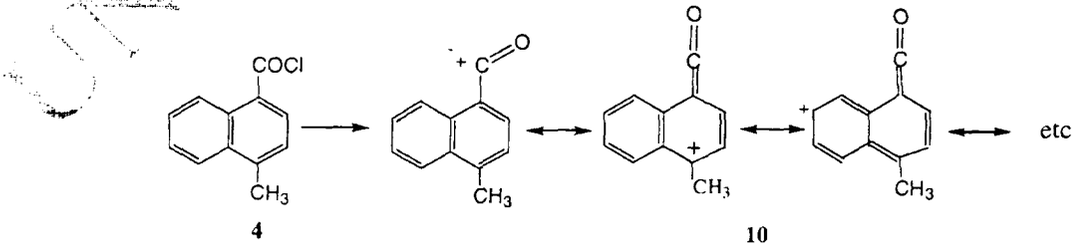
Accordingly, a spectrum of the change in solvolytic mechanisms for the four naphthoyl chlorides **2–5** could be suggested. The least reactive 2-naphthoyl chloride (**3**) is likely to have a mechanism at the borderline of unimolecular dissociation [Eqn. (3)] and the addition–elimination process [Eqn. (5)]. The more reactive 6-methoxy-2-naphthoyl chloride (**5**) shows more S_N1-like character but is associated with significant nucleophilic solvent participation. Similarly to **5**, S_N1-like mechanisms are involved for 1-naphthoyl chloride (**2**) and the most reactive 4-methyl-1-naphthoyl chloride (**4**) and with decreasing extent of nucleophilic solvent participation from **5** to **2** to **4**, in line with the observed Δm ($m_{AEM} - m_{TE}$) of log *k*–Y_{xBnCl} plots discussed previously.

Furthermore, the present results demonstrate a further example that the observation of excellent linear correlations in the Grunwald–Winstein-type correlation analysis using the Y_{xBnCl} scale [Eqn. (1)] and Y_{xBnCl} and N_{OTs} scales [Eqn. (2)] as solvent parameters could be regarded as a criterion for the elucidation of solvolysis mechanisms for naphthoyl chlorides **2–5**, in addition to other systems already reported, such as benzhydryl,[12,13b,c] 9-fluorenyl[12,13a,30] and *N,N*-diphenylcarbamoyl.[11c] Although Kevill and co-workers proposed the use of the aromatic ring parameter *I* together with Y_X and N_T scales [Eqn. (7)] for studying the solvolytic behavior of benzylic substrates,[31] its inferiority compared with Y_{BnX} for the solvolysis of benzylic[32] and benzoyl[2c,17a] derivatives has already been shown in our previous work. Utilization of Y_{xBnX} was also found to be superior to Y_X and Y_X in benzhydryl and 9-fluorenyl solvolyses.[12,13,27,33] It is therefore desirable to compare these two approaches in the solvolysis of naphthoyl chlorides. A regression analysis using Eqn. (7), for example, yielded less satisfactory results for **2** [$n = 15$ and $R = 0.955$, Eqn. (8)] and **4** [$n = 12$ and $R = 0.981$, Eqn. (9)] than those listed in Table 3. The small magnitudes of *h* and their large difference (0.767 vs 1.26) also seem to be unreasonable for interpreting the contribution of the naphthalene ring.

$$\log(k/k_0) = mY + lN + hI \quad (7)$$

$$\log(k/k_0) = 0.558\ Y_{Cl} + 0.670\ N_T + 0.767I \quad (8)$$

$$\log(k/k_0) = 0.697\ Y_{Cl} + 0.636\ N_T + 1.26I \quad (9)$$



4 **10**

Scheme 1

CONCLUSION

From single- and dual-parameter Grunwald–Winstein-type correlation analyses with Y_{xBnCl}, or Y_{xBnCl} and N_{OTs} scales, the solvolytic mechanisms for naphthoyl chlorides **2–5** could be deduced. Along with the increasing trend of reactivity from **3** to **5** to **2** and to **4**, the mechanism changes from that at the borderline of S_N1-like unimolecular dissociation [Eqn. (3)] and the addition–elimination process [Eqn. (5)] for **3**, to a more S_N1-like route and involving significant nucleophilic solvent intervention for **5**. A purely unimolecular process is associated with a decreasing extent of such a participation for **2–4**. Substituent effects enhancing resonance stabilization of the cationic transition state might be responsible for the increasing reactivity and the changing mechanisms. The present results also demonstrate the wide applicability and the advantage of using the Y_{xBnCl} scale to elucidate the mechanism of solvolysis for different types of substrates.

EXPERIMENTAL

Spectra. Proton and carbon-13 NMR spectra were recorded on a Bruker Model DMX-300 instrument. IR spectra were measured on a Nicolet MANGA-IR 550 spectrometer.

Materials. Spectral-grade or reagent-grade solvents (Merck) were purified following conventional methods[34] for kinetic studies. Doubly deionized water was used to prepare aqueous solvent mixtures for solvolytic studies. Commercially available naphthoyl chlorides (**2** and **3**) were purchased from TCI. 4-Methyl-1-naphthoyl chloride (**4**) was synthesized from 1-bromo-4-methylnaphthlene (Aldrich) to 4-methylnaphthalene-1-carboxylic acid[35] and then by treating with thionyl chloride.[36] 6-Methoxy-2-naphthoyl chloride (**5**) was prepared from the corresponding acid (Aldrich) and thionyl chloride.[37] The IR and NMR spectra were found to be in accord with the assigned structures. All chlorides were freshly purified prior to kinetic measurements.

Kinetic measurements. Rate constants were measured by a conductimetric method at least in duplicate. The conductivity cells containing solution of about 1×10^{-4}–1×10^{-5} M were placed in a thermostat with a temperature variation of ±0.02 °C. The error for the measurement of k was ±3%.

Most of the rate constants were monitored at 25 °C. For those measured at low temperatures the values are as follows (in s^{-1}): for **2** in 100T $k(-10\,°C) = 2.53 \times 10^{-2}$, $k(-5\,°C) = 3.44 \times 10^{-2}$ and $k(0\,°C) = 6.70 \times 10^{-2}$, and in 70M $k(-5\,°C) = 9.58 \times 10^{-3}$, $k(0\,°C) = 1.79 \times 10^{-2}$ and $k(5\,°C) = 3.33 \times 10^{-2}$; for **4** in 90M $k(-10\,°C) = 3.46 \times 10^{-3}$, $k(-5\,°C) = 6.30 \times 10^{-3}$ and $k(0\,°C) = 1.15 \times 10^{-2}$, in 80M, $k(-10\,°C) = 1.41 \times 10^{-2}$, $k(-5\,°C) = 2.81 \times 10^{-2}$ and $k(0\,°C) = 4.26 \times 10^{-2}$, in 80T20E $k(-10\,°C) = 2.58 \times 10^{-2}$, $k(-5\,°C) = 4.19 \times 10^{-2}$ and $k(0\,°C) = 8.20 \times 10^{-2}$, and in 60T40E $k(-5\,°C) = 8.20 \times 10^{-3}$, $k(0\,°C) = 1.47 \times 10^{-2}$ and $k(5\,°C) = 2.35 \times 10^{-2}$. These data were extrapolated to 25 °C by the use of an Arrhenius plot. The results at 25 °C are summarized in Table 1.

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1956 年之 20 人增加至 1984 年之 291 人。其中化學及應用化學碩士班畢業生 92 人，在學生 244 人；博士班畢業生 3 人，在學生 49 名。可見其盛況。

關於化學研究方面，二十世紀初以前，極少記載。丁守存曾於 1845 年仿西人配方試製雷酸銀，然非屬研究。第一篇勉強稱得上的中文化學研究報告的，是 1877 年同文館法籍教習畢利幹（Anatole Billiguin）所寫的〈化分中國鐵礦〉，也就是鐵礦的化學分析報告。可不是中國人寫的。1901 年徐建寅在湖北鋼藥廠研製無煙火藥失敗喪生，表示有國人從事研究。惜無紀錄。1920 年代之東南大學已展開化學研究，1931 年以後，國民政府在教育與學術建設方面有相當成就，然近代史書甚少道及其中之科學成就。作者乃耗費許多時間撰寫三篇論文，重建自清末到民國 80 年的化學研究和發展情形。分期（清末、民初、戰時、戰後）、分地（兩岸），詳細介紹各研究機構、大學化學系所師資及碩博士研究生成長、著名化學家人數、研究題目範圍，及個人與機構發表化學論文的名稱及篇數，幾近錙銖不遺，極有參考價值。

於介紹本書各篇內容後，應有所批評，惟在化學專業方面，無我置嘴餘地，僅從歷史寫作方面提出些淺見。前面說過，作者劉廣定教授，不僅是位化學專家，也是一位歷史考古的漢學家。他抱者不信「成說」與懷疑「權威」的科學精神，腳踏實地，從古今中外歷史文獻和地下

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