行政院國家科學委員會專題研究計畫成果報告

1. 鹵醯類化合物之溶離反應及氧17核磁共振研究 (二)
(Solvolysis and Oxygen-17 NMR Studies of Acyl Halides II)

2. 錯鹽性液晶之合成研究(二)
(Synthesis of Metal Complex Liquid Crystals II)

計畫類別：☑個別型計畫　□整合型計畫
計畫編號：NSC 89-2113-M002-012
執行期間：88 年 8 月 1日 至89 年 7 月 31 日

計畫主持人：劉 廣 定
共同主持人：

處理方式：☑可立即對外提供參考
□一年後可對外提供參考
□兩年後可對外提供參考
(必要時，本會得展延發表時限)

執行單位：國 立 臺 灣 大 學 化 學 系
中華民國 89 年10 月30日

摘　要

上年度完成之工作但在本年度整理完竣，以及在本年度完成之工作，其中有已投稿者，包括：

(一) 苯甲醯溴溶離反應之溶劑效應及溶劑離子化能力 Y_{BnBr} 之應用 (附件一);

(二) 苯甲醯氯之氧 17 核磁共振研究 (附件二)；

(三) 立體效應與β-雙酮錯合物之液晶性質 (附件三);

其餘尚在整理及待補充者包括：苯甲醯溴之氧 17 核磁共振化學移差，取代基效應與β-雙酮錯合物之液晶性質等亦將報告。

關鍵詞：氧17核磁共振，溶離反應，取代基效應，溶劑效應， Y_{BnX} 和 Y_{xBnX} 值，苯甲醯溴，密度泛函理論計算，β-雙酮錯合物，液晶。

ABSTRACT

The following results were completed in this year, or were partly done last year. Those were submitted for publication including:

(1) Solvent and substituent effects on the solvolysis of benzoyl bromides, and Grunwald-Winstein correlation analysis with Y_{BnBr} scale.(Appendix 1).

(2) Density functional theory calculations of O-17 and C-13 NMR chemical shifts for aromatic acyl chlorides. (Appendix 2);

(3) Steric effect on the formation of columnar phases in β-diketoneate copper(II) complexes. (Appendix 3).

Other results are to be completed next year including: the study on nmr chemical shiftss for benzoyl bromides, substituent effects on the preparation of β-diketonate complexes and their mesomorphic properties will also be reported.

Keywords:

Oxygen-17 NMR, solvolysis, substituent effect, solvent effect, Y_{BnCl} and Y_{BnBr} values, DFT calculations, aromatic acyl bromides, β-diketonate complex, liquid crystals.

ANNUAL REPORT (1999-2000)

The following results were completed and submitted for publication:

1. 4-Methoxy-, 4-methyl-, unsubstituted and 4-chlorobenzoyl bromides were prepared and solvolysis in a variety of solvents was studied. The linear log k - Y_{BnBr} plots for 4-methoxy derivative indicates limiting S_N1 mechanism, whereas the splitting of lines for nucleophilic solvents and poorly nucleophilic solvents in the case of 4-methyl derivative suggested nucleophilic solvent participation. The mechanism for the solvolysis of unsubstituted benzoyl bromide and 4-chlorobenzyl bromide probably varies with solvents, similar to that of the corresponding chlorides. Good linear Hammett log k - σ^+ plot could be found in a few solvents. It was submitted for publication.
2. Density functional theory at the level of B3LYP/6-31+G(d) was used to calculate chemical shifts of O-17 and C-13 of the carbonyl group of a variety of aromatic acyl chlorides, including phenyl, substituted phenyl, naphthyl, furyl and thienyl derivatives. The experimental values, which were observed last year, were used for comparison. The calculated O-17 chemical shifts correlated well with the experimental values and with Hammett-type σ+ constants. Therefore, in many cases it is possible to deduce σ+ constants of substitutent or substituted aryl groups via calculation of O-17 chemical shifts of the carbonyl groups in gas phase. The σ+ constants so-obtained show the intrinsic property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of environment. Furthermore, the concept of n-π* transition can be used to understand the sensitivity of O, Cl atoms and insensitivity of C atom towards substitutent effects in aromatic acyl chlorides. (Appendix 2)
3. A systematic study of the msmomorphic properties of three series of copper(II) complexes based on β-diketonate ligands containing branched side chains was carried out. These disc-like compounds have four, six and eight flexible alkoxy side chains appended to the central core, in which two or four side chains were substituted by bulkier secondary alkoxy groups: 1-methylbutoxy or 1-methylheptoxy. The mesomorphic results indicated that at least eight side chains are required to form stable columnar mesophases; other compounds with four or six side chains were all non-mesogneic regardless of the combination of carbon chain length on the alkoxy groups of the side chains. If the diketonate ligand was 1-(3,4,5-trialkoxyphenyl)-3-(4-methylbutoxy)propane 1,3-dione, the complex was non-mesogenic. However, the presence of a longer 3-(4-methylheptoxy) side chain could make the complex to exhibit columnar phase if the trialkoxyphenyl group contained side chains of 6-12 carbons. The mesophases were characterized and identified as columnar hexagonal phases by thermal analysis and optical polarized microscopy. The presence of the introduced secondary alkoxy groups obviously appeared to influence the formation of columnar phases. The clearing points were relatively lower than similar copper(II) complexes not substituted by secondary alkoxy side chains. (Appendix 3)

Other results are:

1. The measurement of O-17 and C-13 chemical shifts in carbon tetrachloride

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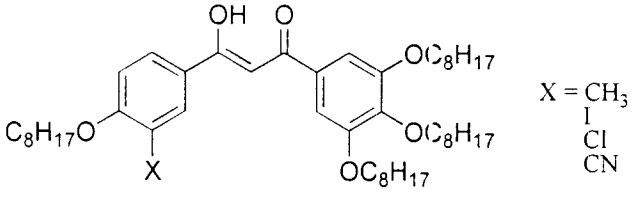
solution and the calculation of Mulliken charge distributions at B3LYP/6-31G(d) level. (Table 1)

Table 1

ArCOBr	δ, ppm (calcd)	δ, ppm (obsd)	Δδ	σ^+	Charge (O)	Charge (C)
4-$CH_3OC_6H_4$	507.8	505.2	+2.6	-0.778	-0.385	+0.352
4-$CH_3C_6H_4$	517.8	518.0	-0.2	-0.311	-0.379	+0.355
C_6H_5	524.1	522.2	+1.9	0	-0.376	+0.357
4-ClC_6H_4	524.8	523.9	+0.9	+0.114	-0.375	+0.358
3-ClC_6H_4	531.1	528.5	+2.6	+0.399	-0.373	+0.360
4-$CF_3C_6H_4$	536.9	535.5	+1.4	+0.612	-0.371	+0.361

2. Synthesis of 3"-substituted β-diketonate ligands and preparation of complexes

(1) Synthesis of ligands



From substituted acetophenone , 3,4,5-trialkoxybenzoate and sodium hydride (NaH) in tetrahydrofuran solution under reflux the following ligands were made:

(***CH_3-Ligand***) : 1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-methyl- 4"-octyloxyphenyl)propane 1,3-dione. A red, viscous liquid in 62% yield.

^{1}H-NMR (ppm, $CDCl_3$) :

δ = 0.88 (m, 12H, CH_3 in OR group), δ = 1.27-1.84 (m, 48H, -$(CH_2)_{24}$ in OR group), δ = 2.26 (s, 3H, Ar-CH_3), δ = 3.99-4.06 (m, 8H, -$(OCH_2)_4$ in OR group), δ = 6.66 (s, 1H, OHC=C**H** for keto = enol form), δ = 6.84 (d, 1H, ArH), δ = 7.16 (s, 2H, ArH), δ = 7.76 (s, 1H, ArH), δ = 7.80 (d, 1H, ArH)

^{13}C-NMR (ppm, $CDCl_3$) :

δ = 14.01 (**C**H_3 in OR group), δ = 16.23 (Ar-**C**H_3), δ = 22.61, 26.04, 29.12, 29.19, 29.25, 29.33, 29.47, 30.30, 31.78, 31.84 (**C** in OR group excluding -O**C**H_2-), δ = 68.08, 69.31, 73.46 (-O**C**H_2-), δ = 91.78(CO**C**H_2CO), δ = 105.89, 110.17, 126.94, 129.45 (**C**H in Ar), δ = 142.10, 153.01, 160.93 (Aromatic **C**-OR), δ = 126.81 (Aromatic **C**-CH_3), δ = 127.06, 130.66 (Aromatic **C**-$COCH_2CO$), δ = 184.66, 185.00 (**C**=O)

IR (cm^{-1}, Nujol) : 2960, 2928, 2858, 1607, 1462, 1379, 1342, 1261, 1135, 791, 723
HRMS (FAB) : Calcd for MH^+ $C_{48}H_{79}O_6$ 751.5876, found 751.5865

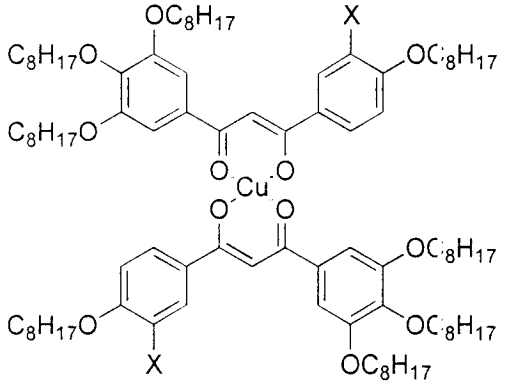
(***Cl-Ligand***) : 1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-chloro- 4"-octyloxyphenyl)propane 1,3-dione
A red, viscous liquid in 52% yield.
^{1}H-NMR (ppm, $CDCl_3$) :
δ = 0.86 (m, 12H, CH_3 in OR group), δ = 1.27-1.88 (m, 48H, -$(CH_2)_{24}$ in OR group), δ = 3.97-4.11 (m, 8H, -$(OCH_2)_4$ in OR group), δ = 6.61 (s, 1H, OHC=C**H** for keto = enol form), δ = 6.95 (d, 1H, ArH), δ = 7.15 (s, 2H, ArH), δ = 7.85 (dd, 1H, ArH), δ = 7.98 (d, 1H, ArH)
^{13}C-NMR (ppm, $CDCl_3$) :
δ = 13.94 (**C**H_3 in OR group), δ = 22.56, 25.80, 25.99, 26.02, 28.84, 29.10, 29.20, 29.31, 29.43, 30.29, 31.69, 31.74, 31.80 (**C** in OR group excluding -O**C**H_2-), δ = 69.16, 69.22, 73.38(-O**C**H_2-), δ = 91.72 (CO**C**H_2CO), δ = 105.82, 112.14, 127.09, 128.95 (**C**H in Ar), δ = 142.31, 152.98, 157.73 (Aromatic **C**-OR), δ = 123.00 (Aromatic **C**-Cl), δ = 128.26, 130.08 (Aromatic **C**-$COCH_2CO$), δ = 183.25, 184.96 (**C**=O)
IR (cm^{-1}, Nujol) : 2957, 2929, 2859, 1598, 1495, 1465, 1380, 1337, 1271, 1194, 1117, 1060, 1017, 786, 723, 698
HRMS (FAB) : Calcd for MH^+ $C_{47}H_{76}O_6{}^{35}Cl$ 771.5330, found 771.5350

(***I-Ligand***) : 1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-iodo- 4"-octyloxyphenyl)propane 1,3-dione
A red, viscous liquid in 80% yield.
^{1}H-NMR (ppm, $CDCl_3$) :
δ = 0.86 (m, 12H, CH_3 in OR group), δ = 1.27-1.87 (m, 48H, -$(CH_2)_{24}$ in OR group), δ = 4.00-4.08 (m, 8H, -$(OCH_2)_4$ in OR group), δ = 6.60 (s, 1H, OHC=C**H** for keto = enol form), δ = 6.82 (d, 1H, ArH), δ = 7.15 (s, 2H, ArH), δ = 7.93 (dd, 1H, ArH), δ = 8.37 (d, 1H, ArH)
^{13}C-NMR (ppm, $CDCl_3$) :
δ = 13.99 (**C**H_3 in OR group), δ = 22.59, 25.93, 26.00, 26.04, 28.85, 29.13, 29.17, 29.22, 29.32, 29.44, 30.30, 31.71, 31.75, 31.82 (**C** in OR group excluding -O**C**H_2-), δ = 69.33, 69.40, 73.45 (-O**C**H_2-), δ = 91.86 (CO**C**H_2CO), δ = 105.97, 110.91, 128.94, 138.33 (**C**H in Ar), δ = 142.37, 153.02, 160.74 (Aromatic **C**-OR), δ = 86.49 (Aromatic **C**-I), δ = 129.43, 130.20 (Aromatic **C**-$COCH_2CO$), δ = 183.17, 184.98 (**C**=O)
IR (cm^{-1}, Nujol) : 2958, 2923, 2858, 1593, 1462, 1379, 1341, 1265, 1117, 791, 724
HRMS (FAB) : Calcd for MH^+ $C_{47}H_{76}O_6I$ 863.4686, found 863.4688.

(***CN-Ligand***) : 1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-cyano- 4"-

octyloxyphenyl)propane 1,3-dione
A red, viscous liquid in 33% yield.
^{1}H-NMR (ppm, $CDCl_3$) :
δ = 0.86 (m, 12H, CH_3 in OR group), δ = 1.27-1.89 (m, 48H, -$(CH_2)_{24}$ in OR group), δ = 4.00-4.16 (m, 8H, -$(OCH_2)_4$ in OR group), δ = 6.61 (s, 1H, OHC=C**H** for keto = enol form), δ = 7.03 (d, 1H, ArH), δ = 7.15 (s, 2H, ArH), δ = 7.14 (d, 1H, ArH), δ = 8.16 (s, 1H, ArH)
^{13}C-NMR (ppm, $CDCl_3$) :
δ = 13.95 (**C**H_3 in OR group), δ = 22.55, 25.69, 26.02, 28.66, 29.06, 29.18, 29.27, 29.39, 30.27, 31.72, 31.78 (**C** in OR group excluding -O**C**H_2-), δ = 69.25, 69.57, 73.45 (-O**C**H_2-), δ = 91.76 (CO**C**H_2CO), δ = 105.78, 111.99, 132.83, 133.24 (**C**H in Ar), δ = 142.46, 153.04, 163.26 (Aromatic **C**-OR), δ = 102.22 (Aromatic **C**-CN), δ = 115.59 (Ar-**C**N), δ = 128.07, 129.70 (Aromatic **C**-$COCH_2CO$), δ = 182.33, 185.33 (**C**=O)
IR (cm^{-1}, Nujol) : 2958, 2928, 2858, 2233, 1607, 1589, 1465, 1379, 1338, 1282, 1199, 1118, 1013, 962, 793, 723
HRMS (FAB) : Calcd for MH^+ $C_{48}H_{76}O_6N$ 762.5672, found 762.5671

(2) Preparation of copper(II) complexes :



X = CH_3
I
Cl
CN

The β-diketone, $Cu(OAc)_2$ and K_2CO_3 were allowed to react in methanol under reflux to generate the corresponding copper(II) complex.

(***CH_3-Cu***) : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-methyl-4"-octyloxyphenyl)-propane 1,3-diketonate] copper(II)
Green solid in 89% yield
IR, (cm^{-1}, melt) : 2958, 2927, 2858, 1607, 1590, 1543, 1494, 1470, 1435, 1390, 1335, 1270, 1156, 1117, 777
MS (FAB) : Calcd for MH^+ $C_{96}H_{155}CuO_{12}$ 1563.1, found 1563.8
Anal. : Calcd for $C_{96}H_{154}CuO_{12}$: C, 73.73; H, 9.93; found:

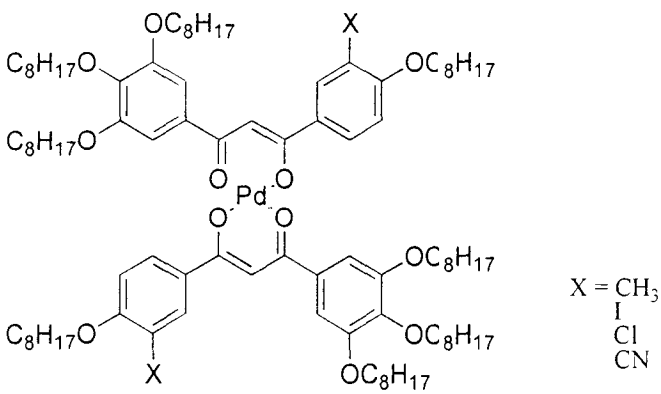
(***Cl-Cu***) : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-chloro- 4"-octyloxyphenyl)propane 1,3-diketonate] copper(II)
Green solid in 76% yield

IR (cm^{-1}, melt) : 2955, 2925, 2853, 1599, 1576, 1539, 1490, 1468, 1387, 1332, 1276, 1197, 1152, 1134, 1060, 980, 959, 773, 697
MS (FAB) : Calcd for MH^+ $C_{94}H_{149}Cl_2CuO_{12}$ 1603.0, found 1605.0
Anal. : Calcd for $C_{94}H_{148}Cl_2CuO_{12}$: C, 70.36; H, 9.30; found: C, 70.71; H, 9.35

(I-Cu) : Bis[1-(3',4',5'-Triocty oxyphenyl)-3-(3"-iodo- 4'-octyloxyphenyl)propane 1,3-diketonate] copper(II)
Green solid, in 90% yield
IR (cm^{-1}, melt) : 2958, 2928 2858, 1593, 1569, 1538, 1484, 1467, 1436, 1390, 1335, 1265, 1198, 1117, 776
MS (FAB) : Calcd for MH^+ $C_{94}H_{149}CuI_2O_{12}$ 1786.9, found 1787.7
Anal. : Calcd for $C_{94}H_{148}CuI_2O_{12}$: C, 63.16; H, 8.35; found: C, 63.40; H, 8.48

(CN-Cu) : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-cyano- 4"-octyloxyphenyl)propane 1,3-diketonate] copper(II)
Green solid in 85% yield
IR (cm^{-1}, melt) : 2959, 2929, 2859, 2229, 1606, 1583, 1544, 1487, 1470, 1441, 1387, 1335, 1281, 1117, 776
MS (FAB) : Calcd for MH^+ $C_{96}H_{149}CuN_2O_{12}$ 1585.1, found 1586.1
Anal. : Calcd for $C_{96}H_{148}CuN_2O_{12}$: C, 72.71; H, 9.41; N, 1.77 found: C, 72.70; H, 9.51; N, 1.59

(3) Preparation of palladium (II) complexes :



The β-diketone, $Pd(OAc)_2$ and K_2CO_3 were allowed to react in chloroform under reflux to generate the corresponding copper(II) complex.

(CH_3-Pd) : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-methyl-4"-octyloxyphenyl)propane 1,3-diketonate] palladium(II)
Yellow solid in 79% yield
IR (cm^{-1}, melt) : 2955, 2925, 2855, 1610, 1591, 1534, 1493, 1430, 1467, 1383, 1334, 1268, 1131, 1119, 771
MS (FAB) : Calcd for MH^+ $C_{96}H_{155}O_{12}Pd$ 1606.1, found 1606.1

Anal. : Calcd for $C_{96}H_{154}O_{12}Pd$: C, 71.77; H, 9.66; found: C, 71.70; H, 9.53

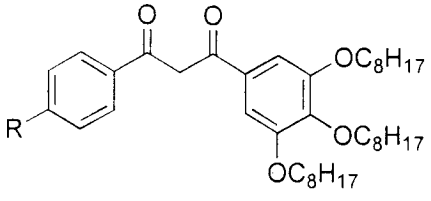
(***Cl-Pd***) : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-chloro-4"-octyloxyphenyl)propane 1,3-diketonate] palladium(II)
Yellow solid in 82% yield
IR (cm^{-1}, melt) : 2955, 2926, 2856, 1598, 1575, 1532, 1489, 1467, 1431, 1378, 1334, 1273, 1204, 1119, 1062, 770
MS (FAB) : Calcd for MH^+ $C_{94}H_{149}Cl_2O_{12}Pd$ 1645.9, found 1645.9
Anal. : Calcd for $C_{94}H_{148}Cl_2O_{12}Pd$: C, 68.53; H, 9.05; found: C, 68.70; H, 9.19

(***I-Pd***) : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-iodo-4'-octyloxyphenyl)propane 1,3-diketonate] palladium(II)
Deep yellow solid in 84% yield
IR cm^{-1} (cm^{-1}, melt) : 2959, 2928, 2858, 1594, 1566, 1531, 1504, 1485, 1469, 1433, 1380, 1337, 1263, 1202, 1118, 773
MS (FAB) : Calcd for MH^+ $C_{94}H_{149}I_2O_{12}Pd$ 1829.8, found 1828.6
Anal. : Calcd for $C_{94}H_{148}I_2O_{12}Pd$: C, 61.68; H, 8.15; found:

(***CN-Pd***) : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3"-cyano-4"-octyloxyphenyl)propane 1,3-diketonate] palladium(II)
Orange solid in 86% yield
IR (cm^{-1}, melt) : 2959, 2929, 2859, 2229, 1606, 1582, 1539, 1492, 1469, 1434, 1381, 1335, 1282, 1204, 1117, 771
MS (FAB) : Calcd for MH^+ $C_{96}H_{149}N_2O_{12}Pd$ 1628.0, found 1628.0
Anal. : Calcd for $C_{96}H_{148}N_2O_{12}Pd$: C, 70.80; H, 9.16; N, 1.72 found: C, 70.78; H, 9.26; N, 1.27

3. Synthesis of 4"- alkoxy β-diketonate ligands and preparation of complexed

(1) Synthesis of ligands



R = $OC_2H_4OC_4H_9$
$OC_4H_8OC_4H_9$
$OC_2H_4OC_2H_4OC_2H_5$
$OC_2H_4OC_2H_4OC_4H_9$

From substituted acetophenone , 3 4,5-trialkoxybenzoate and sodium hydride (NaH) in tetrahydrofuran solution under reflux the following ligands were made:

1-(3',4',5'-Trioctyloxyphenyl)-3-{4"-[({[(oxy)ethyl]oxy}butyl)yl]-phenyl}-propane-1,3-dione

^{1}H-NMR (ppm, $CDCl_3$): δ = 0.90 (m, 12H, -$(CH_3)_4$ in OR group), δ =1.27-1.81 (m,

40H, -$(CH_2)_{20}$ in OR group), δ = 3.53 (t, 2H, CH_2-O-C**H**$_2$), δ = 3.79 (t, 2H, C**H**$_2$OCH_2), δ = 4.01-4.20 (m, 8H, -$(OCH_2)_4$), δ = 6.66 (s,1H,OHC=CH for keto = enol form), δ = 6.98 (d, J= 8.88 Hz, 2H, ArH), δ = 7.16 (s, 2H, ArH), δ =7.93 (d, J = 8.84 Hz, 2H, ArH)

^{13}C-NMR (ppm, $CDCl_3$): δ = 13.87, 14.06, 19.24, 22.65, 26.09, 29.27, 29.35, 29.49, 30.32, 31.66, 31.80, 31.88, 67.66, 68.93, 69.41, 71.45, 73.58, 91.99, 105.97, 114.57, 128.09, 129.07, 130.61, 142.25, 153.11, 162.42, 184.61, 185.07
IR (cm^{-1}, Nujol): 2928, 2861, 1464, 1379, 723
Elemental Anal.: Calcd: C, 74.55; H, 10.01. Found: C, 74.54; H, 10.12.

1-(3',4',5'-Trioctyloxyphenyl)-3-{4"-[({[(oxy) butyl]oxy}butyl)yl]-phenyl}-propane-1,3-dione

^{1}H-NMR (ppm, $CDCl_3$): δ = 0.90 (m, 12H, -$(CH_3)_4$ in OR group), δ = 1.27-1.85 (m, 44H, -$(CH_2)_{22}$ in OR group), δ = 3.38 (m, 4H, C**H**$_2$OC**H**$_2$), δ = 3.97-4.08 (m, 8H, -$(OCH_2)_4$), δ = 6.66 (s, 1H, OHC=CH for keto = enol form), δ = 6.94 (d, J = 9.05 Hz, 2H, ArH), δ = 7.15 (s, 2H, ArH), δ = 7.92 (d, J = 9.02 Hz, 2H, ArH)
^{13}C-NMR (ppm, $CDCl_3$): δ = 13.88, 14.03, 19.35, 22.62, 26.03, 26.07, 26.24, 29.25, 29.32, 29.36, 29.48, 30.31, 31.79, 31.84, 67.95, 69.18, 69.37, 70.24, 70.68, 73.53, 91.88, 105.94, 107.70, 114.30, 114.38, 127.76, 129.08, 130.59, 131.32, 142.20, 152.89, 153.07, 162.65, 184.66, 184.93
IR (cm^{-1}, Nujol): 2928, 2958, 2858, 1463, 1379, 723
Elemental Anal.: Calcd: C,74.96; H,10.17. Found:

1-(3',4',5'-Trioctyloxyphenyl)-3-[4"-({[({[(oxy)ethyl]oxy}ethyl)oxy]ethyl}yl)phenyl]-propane-1,3-dione

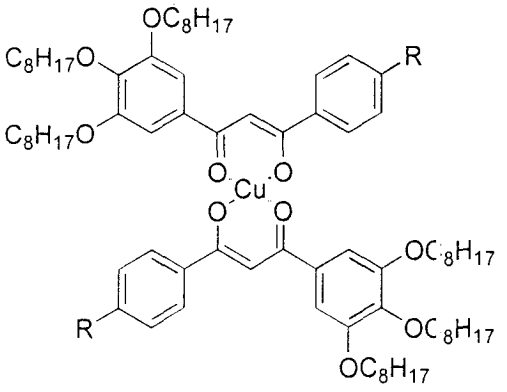
^{1}H-NMR (ppm, $CDCl_3$):
δ = 0.87 (m, 12H, -$(CH_3)_4$ in OR group), δ = 1.16-1.85 (m, 36H, -$(CH_2)_{18}$ in OR group), δ = 3.47-4.20 (m, 16H, -$(OCH_2)_8$), δ =6 .66 (s, 1H, OHC=CH for keto = enol form), δ = 6.98 (d, J = 8.95Hz, 2H, ArH), δ =7 .15 (s, 2H, ArH), δ = 7.93 (d, J = 8.86 Hz, 2H, ArH)
^{13}C-NMR (ppm, $CDCl_3$): δ = 14.06, 15.11, 22.64, 26.09, 29.25, 29.34, 29.48, 30.31, 31.79, 66.69, 67.61, 69.39, 69.54, 70.97, 73.57, 91.98, 105.96, 114.54, 128.12, 129.08, 130.54, 142.25, 153.10, 162.34, 184.58, 185.07
IR (cm^{-1}, Nujol): 2923, 2859, 1464, 1379, 723
Elemental Anal.: Calcd: C, 72.93; H, 9.79. Found: C, 73.09; H, 9.61

1-(3',4',5'-Trioctyloxyphenyl)-3-[4"-({[({[(oxy)ethyl]oxy}ethyl)oxy]butyl}yl)phenyl]-propane-1,3-dione

^{1}H-NMR (ppm, $CDCl_3$): δ = 0.83-0.93 (m, 12H, -$(CH_3)_4$ in OR group), δ =1.20-1.85 (m, 40H, -$(CH_2)_{20}$ in OR group), δ = 3.42-4.22 (m, 16H, -$(OCH_2)_8$), δ = 6.66 (s, 1H, OHC=CH for keto = enol form), δ = 6.98 (d, J = 8.90 Hz, 2H, ArH), δ = 7.16 (s, 2H, ArH), δ = 7.93 (d, J = 8.85 Hz, 2H, ArH)

^{13}C-NMR (ppm, $CDCl_3$): δ = 13.89, 14.06, 19.25, 22.64, 26.08, 29.27, 29.34, 29.49, 30.31, 31.67, 31.80, 67.63, 69.41, 69.55, 70.09, 70.94, 71.27, 73.57, 76.36, 76.99, 77.62, 91.98, 105.97, 114.55, 128.12, 129.09, 130.61, 142.25, 153.11, 162.35, 184.58, 185.07
IR (cm^{-1}, Nujol): 2927, 2957, 2858, 1464, 1379, 723
Elemental Anal.: Calcd: C,73.40; H, 9.96. Found: C,73.19;H ,9.44

(2) Preparation of Copper(II) complexes :



R = $OC_2H_4OC_4H_9$
$OC_4H_8OC_4H_9$
$OC_2H_4OC_2H_4OC_2H_5$
$OC_2H_4OC_2H_4OC_4H_9$

The β-diketone, $Cu(OAc)_2$ and K_2CO_3 were allowed to react in methanol under reflux to generate the corresponding copper(II) complex.

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4"-[({[(oxy)ethyl]oxy}butyl)yl]phenyl}-propane-1,3-dione] copper(II)

IR (cm^{-1}, KBr): 2926, 2857, 1539, 1493, 1334, 1255, 1117, 777
Elemental Anal.: Calcd: C, 71.51; H, 9.47. Found: C, 70.62; H, 8.92

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4"-[({[(oxy)butyl]oxy}butyl)yl]phenyl}-propane-1,3-dione] copper(II)

IR (cm^{-1}, KBr): 2954, 2925, 2871, 2854, 1537, 1492, 1334, 1247, 1132, 1116, 775
Elemental Anal. : Calcd: C, 72.02; H, 9.64. Found: C, 71.39 ; H, 9.01

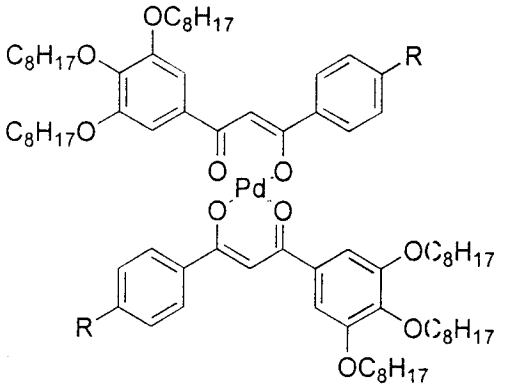
Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4"-({[({[(oxy)ethyl]oxy}ethyl)oxy]ethyl}yl)phenyl]-propane-1,3-dione} copper(II)

IR cm^{-1}(KBr):2925,2926,2872,2856,1539,1492,1437,1390,1254,1125,781
Elemental Anal. Calcd: C,70.03;H,9.27.Found:C,69.96;H,8.94

Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4"-({[({[(oxy)ethyl]oxy}ethyl)oxy]butyl}yl)-phenyl]-propane-1,3-dione} copper(II)

IR (cm^{-1}, KBr): 2925, 2928, 2854, 1538, 1492, 1444, 1335, 1253, 1133, 1117, 775

(3) Preparation of palladium(II) complexes



R = $OC_2H_4OC_4H_9$
$OC_4H_8OC_4H_9$
$OC_2H_4OC_2H_4OC_2H_5$
$OC_2H_4OC_2H_4OC_4H_9$

The β-diketone, $Pd(OAc)_2$ and K_2CO_3 were allowed to react in chloroform under reflux to generate the corresponding copper(II) complex.

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4"-[({[(oxy)ethyl]oxy}butyl)yl] phenyl}-propane-1,3-dione] palladium(II)

IR (cm^{-1}, KBr): 2926, 2857, 1531, 1491, 1334, 1254, 1117, 773
Elemental Anal : Calcd: C, 69.54; H, 9.21. Found: C, 69.89; H, 9.36

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4"-[({[(oxy)butyl]oxy}butyl)yl]Phenyl}-propane-1,3-dione] palladium(II)

IR (cm^{-1}, KBr): 2952, 2926, 2871, 2856, 1530, 1491, 1469, 1334, 1251, 1116, 773
Elemental Anal. : Calcd: C, 70.10; H, 9.39. Found: C, 69.88; H, 9.35

Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4"-({[({[(oxy)ethyl]oxy}ethyl)oxy]ethyl}yl)phenyl]-propane-1,3-dione} palladium(II)

IR (cm^{-1}, KBr): 2954, 2926, 2873, 2857, 1531, 1491, 1335, 1252, 1118, 773
Elemental Anal. : Calcd: C, 68.14; H, 9.02. Found: C, 68.09; H, 8.72

Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4"-({[({[(oxy)ethyl]oxy}ethyl)oxy]butyl}yl)phenyl]-propane-1,3-dione} palladium(II)

IR (cm^{-1}, KBr): 2956, 2928, 2871, 2855, 1530, 1492, 1469, 1388, 1335, 1252, 1133, 1122, 771

Other studies are in progress.

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Application of Grunwald-Winstein correlation analyses with Y_{BnBr} scales to the solvolysis of benzoyl bromides.

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The solvolysis of 4-methoxy- (**1**), 4-methyl- (**2**), unsubstituted (**3**) and 4-chloro- (**4**) benzoyl bromide in a variety of solvents was studied. The linear log k - Y_{BnBr} plots for **1** indicates limiting S_N1 mechanism, whereas the splitting of lines for nucleophilic solvents and poorly nucleophilic solvents in the case of **2** suggests significant nucleophilic solvent participation. The mechanism for the solvolysis of **3** and **4** probably varies with solvents, similar to that of the corresponding chlorides. Good linear Hammett log k - σ^+ plot could be found in a few solvents. A comparison of the solvolytic behavior for aromatic acyl bromides and chlorides will be discussed.

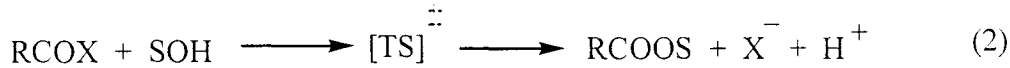
Introduction

Acyl halides are basic organic substrates with very high reactivity. Although acyl chlorides were continuously studied from both mechanistic[1] and synthetic[2] point of view, much less attention was paid to the corresponding bromides. Nucleophilic substitution of substituted aromatic acyl bromides with methanol in acetonitrile solution was examined and the mechanism was found substituent-dependent.[3] To our knowledge, little work on the solvent effect for the solvolysis of acyl bromides has been performed.

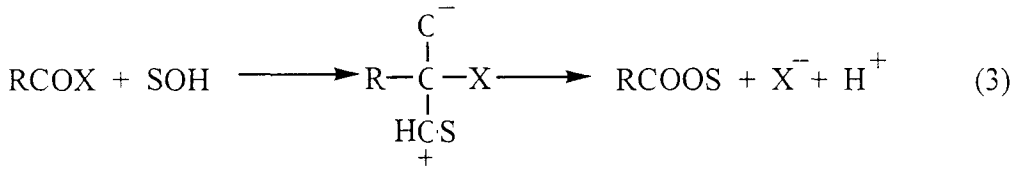
Early mechanistic studies led to a conclusion of three possible pathways for the solvolysis of acyl halides,[4] namely, the unimolecular dissociation [eqn. (1)], the

bimolecular synchronous S_N2-type [eqn. (2)] and the addition-elimination [eqn. (3)] mechanisms

(1)



(2)



(3)

In the previous report,[1] we successfully employed the single-[5] and the dual-parameter[6] Grunwald-Winstein equations [eqn. (4)[5] and eqn. (5)[6]] with Y_{BnCl}[7] and N_{OTs}[8] scales to examine solvolytic mechanisms for a series of benzoyl chlorides.

$$\log(k/k_0) = mY \quad (4)$$

$$\log(k/k_0) = mY + lN \quad (5)$$

In association with the results of Hammett-type correlation analyses and of *ab initio* calculations, it was concluded that 2,6-dimethylbenzoyl chloride solvolyzed with limiting S_N1 mechanism (eqn 1), while 2-methyl-, 4-methoxy- and 4-methylbenzoyl chloride proceeded with nucleophilic solvent participation. The solvolysis of the unsubstituted benzoyl chloride was considered on the borderline of unimolecular dissociation (eqn 2) and the addition-elimination (eqn 3) mechanisms. In addition, the solvolysis of 4-chloro- and 4-nitrobenzoyl chloride was likely to involve an S_N2 mechanism (eqn 2) in nucleophilic solvents, and an addition-elimination (eqn 3) mechanism in trifluoroethanol-ethanol.[2]

Consequently, we undertook to explore the applicability of using Y_{BnBr}[9] in the similar approach for studying the solvolytic mechanism of benzoyl bromides. The results are reported in the present paper

Results

4-Methoxylbenzoyl bromide (**1**), 4-methylbenzoyl bromide (**2**), benzoyl bromide (**3**), and 4-chlorobenzoyl bromide (**4**), were solvolysed in a variety of solvents, and the rate constants were measured by conductimetric method as described.[7a] Because of the high reactivity and the low solubility at temperature below -10°C, the rate of solvolysis in solvents of relatively large solvent ionizing power could not be measured accurately. Pertinent data at 25°C are given in Table 1.

(Structural formulas)

(Table 1)

Correlation analyses of log k values against Y_{Br}[10] using eqn. (4) or against Y_{Br} and N_{OTs} using eqn. (5) showed poor correlation with scattered data points in every case. The results of the analysis against Y_{BnBr} are shown in Table 2. An excellent linear relationship[11] (R = 0.993) was found in log k - Y_{BnBr} plots for acyl bromide **1** in all solvents where k could be measured (Figure 1). In the case of compound **2**, two lines, one in nucleophilic solvents (R = 0.995 in aqueous acetone, ethanol and methanol) and the other in poorly nucleophilic ethanol-trifluoroethanol, were observed against Y_{BnBr} (Figure 2). Only dispersed log k - Y_{BnBr} plots were found for **3** and **4**, even if only nucleophilic solvents were considered. Moreover, the analysis for log k against Y_{BnBr} and N_{OTs} or N_T[12] by using eqn 2 revealed no good linear relationship for acyl bromides **2**, **3** and **4**.

(Table 2)

(Figures 1 and 2)

Hammett-type correlation analyses of log k values against σ^+ constants[13] by using equation. 6 were carried out for those three or four rate constants were available in the same solvent system (Table 3).

$$\log(k/k_o) = \sigma^+\rho \qquad (6)$$

Among the limited number of solvent systems under examination, excellent linear correlation (R = 0.994) was observed only in 60T40E with ρ of –2.20 (Figure 3)

(Table 3)

(Figure 3)

Discussion

Correlation of rates of solvolysis using Grunwald-Winstein equations (4) and/or (5) with appropriate scales of solvent ionizing power (Y) and solvent nucleophilicity (N) has been generally applied to mechanistic studies for the solvolysis of substrates at saturated carbons.[14] Recently, it was also successfully employed in the elucidation of solvolytic mechanisms for other systems, such as styryliodonium salt,[15] *N,N*-diphenylcarbamoyl chloride[16] and aromatic acyl chlorides.[1] The usefulness of Y_{BnCl} scale in studying the solvolysis of benzoyl chlorides suggested an extension to the study of the corresponding benzoyl bromides with Y_{BnBr} would be worthwhile. Indeed, valuable information about the solvolytic mechanism for benzoyl bromides was obtained.

Owing to the high reactivity, only limited number of aromatic acyl bromides were found suitable for the study of solvent effects. Although seven substituted benzoyl chlorides were examined in the previous work,[1] the reaction kinetics for only four bromides (**1-4**) could be monitored in reasonable varieties of solvent systems, including both highly nucleophilic and poorly nucleophilic ones, for correlation analyses. In spite of their low solubility in solvents of high water-content, **1-4** could still be solvolysed in solvent systems with sufficiently large difference (ΔY_{BnBr} = 2.7 - 4.6) in solvent ionizing power and made the interpretation meaningful. However, due to insufficient kinetic data in the non-nucleophilic trifluoroethanol (100T) available, which was found necessary in correlating experimental reactivity with the energy of isodesmic reaction,[1] *ab initio* calculation for the formation of acylium ion ($ArCO^+$) from benzoyl bromides (RCOBr) was not performed in this study. Besides, the three-parameter equation (7) suggested by Kevill and coworkers[17] was not tested, as it would be meaningless to treat such regression with less than ten variables.

$$\log (k/k_o) = mY_{Cl} + lN_T + hI \qquad (7)$$

Similar to the corresponding chlorides,[1] no linear correlation with Y_{Br}, or Y_{Br} and N_{OTs} was found in any case. On the other hand, log k— Y_{BnBr} plots showed excellent

linear correlation (Figure 1; $R = 0.993$, Table 2) for the solvolysis of 4-methoxybenzoyl bromide (**1**), and therefore, a limiting S_N1 mechanism could be deduced. The lack of significant nucleophilic solvent participation as compared with the analogous 4-methoxybenzoyl chloride[1] is likely due to the presence of the better leaving group, bromide, in **1**.

In the case of the 4-methyl derivative (**2**), two separate lines, one for nucleophilic solvents (AEM) and the other for poorly nucleophilic solvents (TE), were observed (Figures 2). The use of isodielectric trifluoroethanol-ethanol mixture[18] has been shown to be a diagnostic probe for nucleophilic solvent participation in solvolyses of various substrates.[19] Therefore, the downward splitting of line for data points obtained in TE from that in AEM suggests the intervention of nucleophilic solvents in the solvolysis of **2**. The poor regression for **2** with respect to all solvents ($R = 0.926$, $n = 11$, Table 2) by using the single-parameter eqn. (4) could be improved ($R = 0.964$, $n = 9$) from the dual-parameter eqn. (5), $\log (k/k_0) = 0.458\ Y_{BnBr} + 0.301\ N_{OTs}$. Although no excellent linear correlation ($R \geq 0.99$)[11] was obtained, the low m value and the high l value could also indicate significant nucleophilic solvent participation in the solvolysis of **2**. Unlike **1** (*vide supra*), but similar to 4-methoxylbenzyl halides,[19(c)] the reactivity of the bromide leaving group is not good enough to yield a unassisted solvolysis.

The solvolysis of benzoyl bromides **3** and **4** gave nonlinear relationship for eqns. (4) or (5). Scattered data points were resulted from $\log k - Y_{BnBr}$ plots. Poor correlation with Y_{BnBr} and N_{OTs} by using the dual-parameter eqn. (5), $R = 0.7$ to 0.8, was found in both cases. The results show some similarities with those found for the corresponding benzoyl chlorides,[1] indicating changing mechanisms in different solvent. Logarithm plots of rate data for 4-chlorobenzoyl bromide (**4**) in this work against those for the corresponding chloride in the literature[20] give a linear correlation ($n = 7$, $R = 0.987$) if the data point in 100T is discarded. However, the limited variety of solvents available causes the result less conclusive. In the case of parent benzoyl bromide (**3**) and chloride, similar treatment of rate data gave less satisfactory linear relationship ($R = 0.96$). It is possible that different types of non-S_N1 reactions are involved in the solvolysis of **3** and **4** in nucleophilic solvents, similar to the corresponding chlorides.[1]

The results of Hammett plots against σ^+ constants (Table 3) are also interesting. The solvolysis of **1** to **4** showed linear $\log k$ - σ^+ relationship in 60T40E (Figure 3), but

not in other nucleophilic solvents. Bromide **1** was too reactive in 80T20E to yield a reliable rate constant. Nevertheless, linear plot was observed for **2** – **4** in 80T20E, and presumably for **1** – **4** as well. In 40T60E, significant deviation was found for the 4-chloro derivative **4** and linear regression for **1** – **3** was realized as a marginal case. In the present study, the rate constant for **4** in 70A or in 80E could not be measured conductimetrically due to the low solubility at the temperature below 0°C. But linear plots were obtained for **1** – **3** in these solvents. Pertinent data for log k - σ^+ regression are listed in Table 3. For the corresponding acyl chlorides, linear relationships were found only in solvents containing high percentage of water (50A, 50E and 60M) or high percentage of trifluoroethanol (100T and 80T20E) if all of the four substrates were considered.[1] But for chlorides corresponding to **1-3**, linear log k - σ^+ plots were observed in solvents containing less water (60A, 60E and 70M) or trifluoroethanol (60T40E).[1] Apparently, the more reactive acyl bromides will display linear Hammett log k - σ^+ plots in solvents of smaller ionizing power as compared with corresponding chlorides. The small negative ρ values in 60T40E and 80T20E, and even smaller in nucleophilic solvents could be considered as an indication of less charge development at the transition state, similarly to that found in the solvolysis of acyl chlorides.[1]

In conclusion, solvolytic mechanisms for benzoyl bromides could be understood by means of Grunwald-Winstein type correlation analysis using Y_{BnBr} scales, in association with Hammett-type plots against σ^+ constants. 4-Methoxybenzoyl bromide (**1**) solvolyzes with limiting S_N1 mechanism (eqn 1), whereas 4-methylbenzoyl bromide (**2**) proceed with nucleophilic solvent participation. Different types of S_N1 and non-S_N1 reactions are probably involved in the solvolysis of benzoyl chloride (**3**) and 4-chlorobenzoyl bromide (**4**). The presence of the better leaving group, bromide as comparing with chloride, leads benzoyl halides more likely to solvolyze via limiting S_N1 mechanism and to exhibit linear Hammett log k - σ^+ plots in solvents of smaller ionizing power

Experimental

Materials

Spectral-grade or reagent-grade solvents (E. Merck) were purified following conventional methods[21] for kinetic studies. Doubly deionised water was used to prepare

aqueous solvent mixtures for solvolytic studies. Benzoyl bromide (**3**) was commercially available (Across) and other acid bromides **1**, **2** and **4** were prepared from corresponding acids and thionyl bromide,[22] respectively. The IR and NMR spectra were found to agree with the assigned structure. All of the acid bromides were freshly distilled for kinetic studies.

Kinetic measurements

Rate constants were measured by conductimetric method at least in duplicate. The conductivity cells containing about 1.8 mL of 1×10^{-4} to 1×10^{-5} M solution of substrate and 1 μL of 2,6-lutidine were placed in a thermostat with a temperature variation of ± 0.02℃. The maximum error for the measurement of k is ±2%.

Rate constants (in s^{-1}) were monitored at 25°C or at appropriate temperatures. For those measured at low temperatures are listed as follows:

For **1** in 90E, k (-10°C) = 1.79 × 10^{-2}, k(-5°C) = 3.04 × 10^{-2} and k(0°C) = 5.10 × 10^{-2}; in 80E, k(-10°C) = 2.77 × 10^{-2}, k(-5°C) = 5.10 × 10^{-2} and k(0°C) = 9.19 × 10^{-2}; in 80A, k (-10°C) = 1.62 × 10^{-2}, k(-5°C) = 2.63 × 10^{-2} and k(0°C) = 4.20 × 10^{-2}; in 70A, k(-10 ℃) = 2.54 × 10^{-2}. k (-5℃) = 4.45 × 10^{-2} and k(0℃) = 8.30 × 10^{-2}; in 100M, k (-10°C) = 3.15 × 10^{-2}, k(-5°C) = 5.31 × 10^{-2} and k(0°C) = 8.79 × 10^{-2}; in 60T40E, k (-10°C) = 4.02 × 10^{-2} and k(-5°C) = 8.08 × 10^{-2}; in 40T60E, k (-10°C) = 2.92 × 10^{-2}, k(-5°C) = 5.24 × 10^{-2} and k(0°C) = 9.22 × 10^{-2}.

For **2**, in 80E, k (-10°C) = 5.03 × 10^{-3}, k(-5°C) = 8.99 × 10^{-3} and k(0°C) = 1.57 × 10^{-2}; in 70A, k (-10°C) = 4.83 × 10^{-3}, k(-5°C) = 8.47 × 10^{-3} and k(0°C) = 1.46 × 10^{-2}; in 100M, k (-10°C) = 4.48 × 10^{-3}, k(-5°C) = 8.07 × 10^{-3} and k(0°C) = 1.42 × 10^{-2}; in 90M, k (-10°C) = 6.05 × 10^{-3}, k(-5°C) = 1.14 × 10^{-2} and k(0°C) = 2.10 × 10^{-2}; in 80T20E, k (-10°C) = 5.64 × 10^{-3}, k(-5°C) = 1.08 × 10^{-2} and k(0°C) = 2.10 × 10^{-2}; in 60T40E, k (-10°C) = 4.47 × 10^{-3}, k(-5°C) = 8.03 × 10^{-3} and k(0°C) = 1.43 × 10^{-2}.

For **3**, in 100M, k (-10°C) = 4.67 × 10^{-3}, k(-5°C) = 7.90 × 10^{-3} and k(0°C) = 1.31 × 10^{-2}; in 90M, k (-10°C) = 5.54 × 10^{-3}, k(-5°C) = 9.71 × 10^{-3} and k(0°C) = 1.67 × 10^{-2}; in 80M, k (-10°C) = 7.03 × 10^{-3}, k(-5°C) = 1.31 × 10^{-2}, k(0°C) = 2.39 × 10^{-2}.

For **4**, in 90E, k (-10°C) = 3.14 × 10^{-3}, k(-5°C) = 6.09 × 10^{-3} and k(0°C) = 1.15 × 10^{-2};

in 100M, k (-10°C) = 7.31 × 10^{-3}, k(-5°C) = 1.40 × 10^{-2} and k(0°C) = 2.62 × 10^{-2}.

The rate constants measured at 25°C and those from extrapolation to 25°C by using Arrhenius plot are given in Table 1.

Acknowledgment

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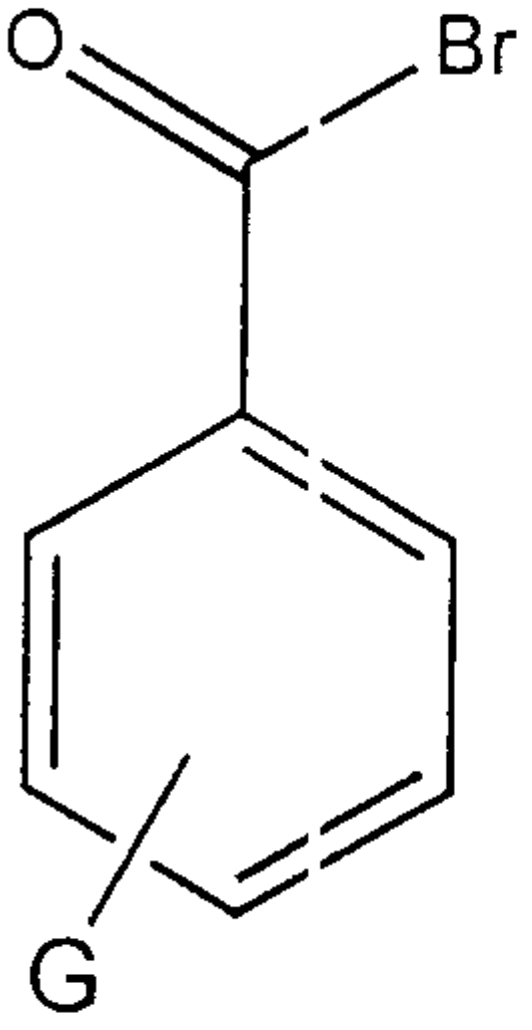


1 G = 4-OCH_3
2 G = 4-CH_3
3 G = H
4 G = 4-Cl

(structural formulas)

Table 1. Solvolysis rate constants ($\times 10^2$) for aromatic acyl bromides (**1-4**) at 25°C

Solvent [a]	**1**	**2**	**3**	**4**
100E	9.53	3.16	5.90	9.22
90E	50.2 [b]	8.87	7.12	20.4 [b]
80E	130 [b]	19.5 [b]	8.44	
90A	4.09	1.96	3.26	2.52
80A	34.3 [b]	6.94	5.77	6.10
70A	113 [b]	16.6 [b]	8.38	
100M	84.5 [b]	18.3 [b]	12.8 [b]	43.8 [b]
90M		32.7 [b]	18.9 [b]	
80M			35.5 [b]	
100T			8.12	2.03
80T20E		33.8 [b]	6.07	2.78
60T40E	327 [b]	19.2 [b]	5.51	3.54
40T60E	117 [b]	9.88	4.71	4.73

[a] For abbreviation of solvents: A = acetone, E = ethanol, M = methanol, T =2,2,2-trifluoroethanol. Figures shown are percentages of volume in water; 80T20E indicates T-E
of 80:20 v/v and likewise for 60T40E and 40T60E. [b] From data at other temperatures.

Table 2. Correlation analyses using single parameter equation (1)

Substrate	Parameters	n^a (solvent)	R	m (s.d.) [b]
1	Y_{BnBr}	9 (All)	0.993	0.702 (0.031)
		7 (AEM)	0.995	0.745 (0.032)
2	Y_{BnBr}	11 (All)	0.926	0.359 (0.049)
		8 (AEM)	0.995	0.509 (0.020)
3	Y_{BnBr}	13 (All)	0.397	0.086 (0.060)
		9(AEM)	0.923	0.299 (0.047)
4	Y_{BnBr}	9 (All)	0.383	-0.115 (0.105)
		5 (AEM)	0.882	0.597 (0.184)

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

Table 3. Hammett plots of selective log *k* values against σ+ constants.

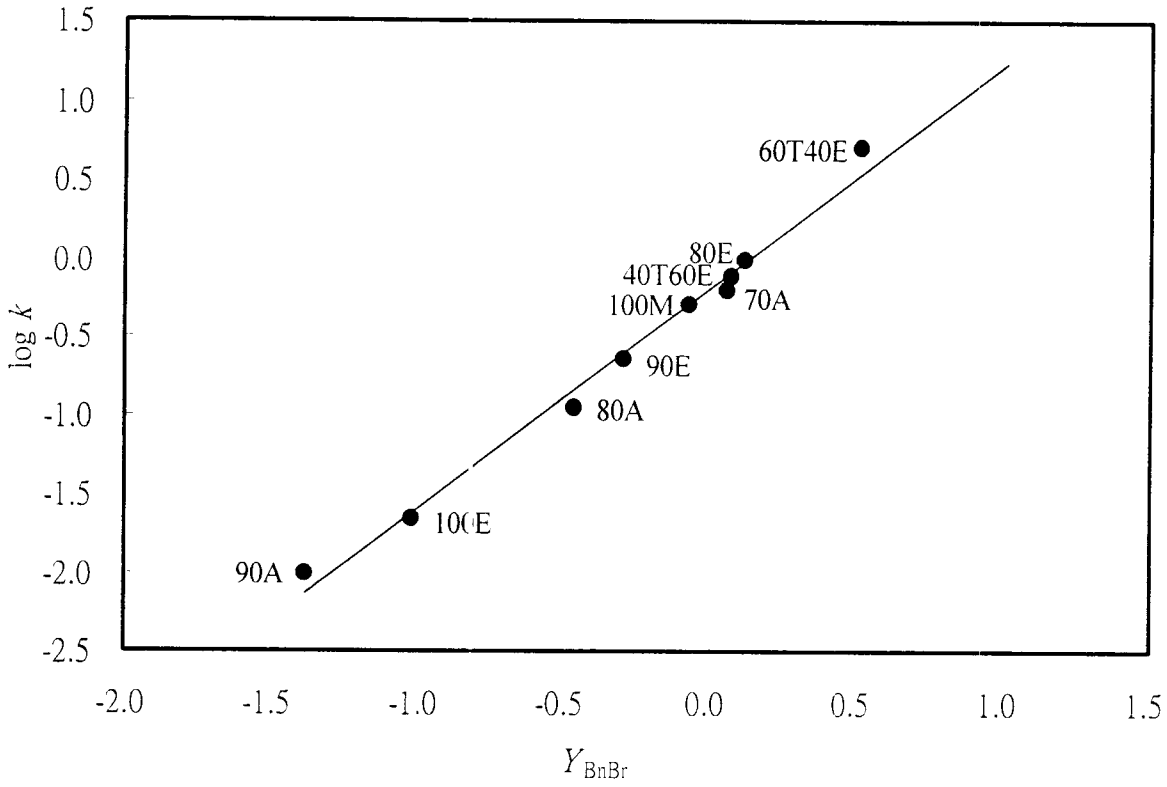
Solvent	substrate	*n*	ρ	*R*
90E	**1-3**	3	-1.13	0.954
80E	**1-3**	3	-2.03	0.995
80A	**1-4**	4	-0.859	0.927
80A	**1-3**	3	-1.03	0.951
70A	**1-3**	3	-1.48	0.988
100M	**1-3**	3	-1.08	0.974
80T20E	**2-4**	3	-2.52	0.999
60T40E	**1-4**	4	-2.20	0.994
40T60E	**1-4**	4	-1.60	0.968
40T60E	**1-3**	3	-1.83	0.983

Captions for the figures:

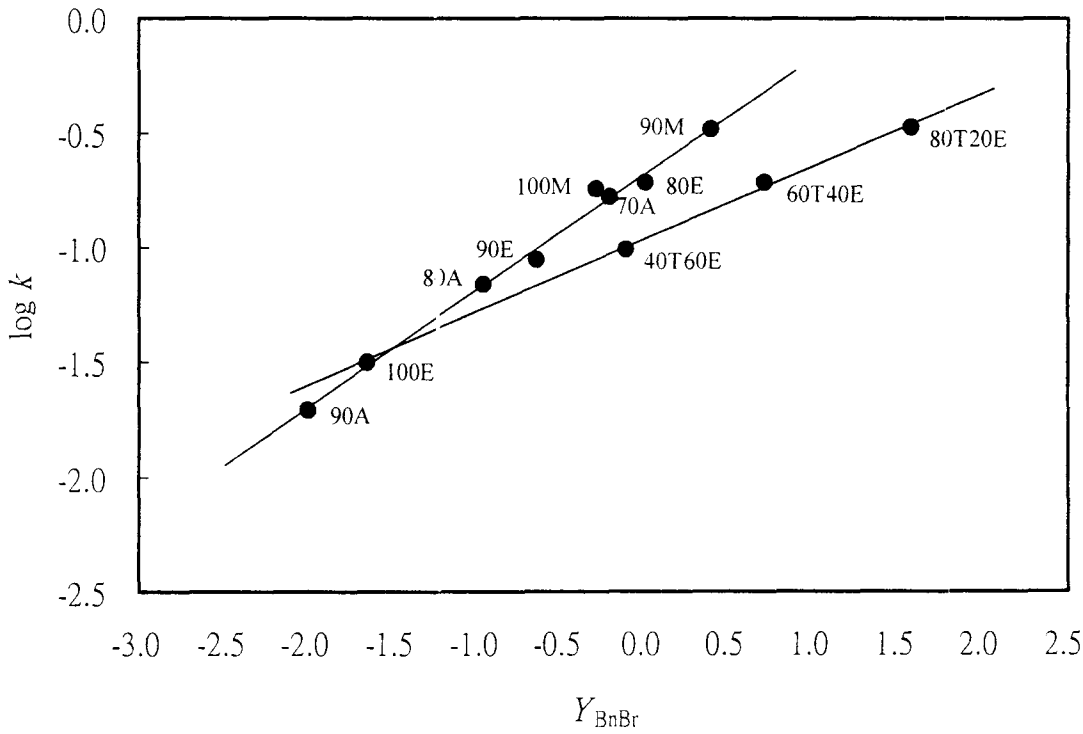
Figure 1: Plots of log k for **1** against Y_{BnBr}.

Figure 2: Plots of log k for **2** against Y_{BnBr}.

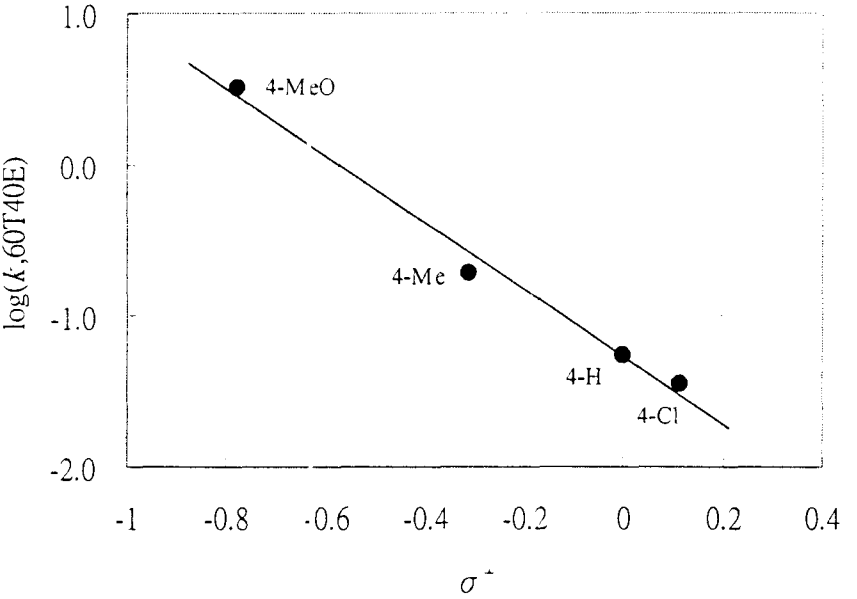
Figure 3. Plots of log k in 60T40E for **1** to **4** against σ^+ constants.


1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
log k
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
Y_{BnBr}
60T40E
80E
40T60E
100M
70A
90E
80A
100E
90A

(Figure 1)


0.0
-0.5
-1.0
-1.5
-2.0
-2.5
log k
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
Y_{BnBr}
90M
80T20E
100M
80E
70A
60T40E
90E
40T60E
80A
100E
90A

(Figure 2)



(Figure 3)

Density functional theory calculations of ^{17}O and ^{13}C NMR chemical shifts for aromatic acyl chlorides

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ABSTRACT: Density functional theory (DFT) at the level of B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) was used to calculate NMR chemical shifts of ^{17}O and ^{13}C of the carbonyl group of aromatic acyl chlorides **1a–1n**. The aryl groups include substituted phenyl, furyl, thienyl and naphthyl. The calculated ^{17}O chemical shifts correlated well with the experimental values and with Hammett-type σ^+ constants. Therefore, in many cases it is possible to deduce σ^+ constants of substituted aryl groups via gas phase calculation of ^{17}O chemical shifts of the carbonyl groups. The σ^+ values obtained in the gas phase calculation show the intrinsic property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of environment. Furthermore, the concept of n–π* transition can be used to understand the sensitivity of O, Cl atoms and insensitivity of C atom towards substituent effects in aryl acyl chlorides.

KEYWORDS: ^{17}O chemical shift; theoretical calculation; substituent constant; n–π* transition; solvolysis; solvent effect

INTRODUCTION

With the use of substituted acetophenones and benzaldehydes, it is has been shown that the ^{17}O NMR chemical shift $\delta(^{17}O)$ of a carbonyl group is sensitive to substituents of the neighboring phenyl group [1,2] Studies of acyl containing compounds such as acids, amides, esters, and other derivatives of carboxylic acids (YC(=O)X) have also confirmed the sensitivity of ^{17}O chemical shifts in reflecting the electronic nature of substituents X and Y.[3-9] Owing to this sensitivity, ^{17}O chemical shifts have been studied from different points of view. Dahn et al. used them to establish a scale of

electrophilicity of the carbonyl group[3-5]. Others used them to study the effectiveness of transmission of the substituent effect.[9-13] It was found that an excellent linear correlation existed between σ^+ constant and ^{17}O chemical shifts measured in nonpolar solvent CCl_4 for twelve α,α,α-trifluoroacetophenones (correlation coefficient R = 0.998).[7] Extending the study of benzene derivatives of trifluoroacetyl compounds to heteroaromatic derivatives such as furyl and thienyl, the same correlation between σ^+ constants and ^{17}O chemical shifts was also observed, except in the case of 3-furyl.[14] More recently, we demonstrated that density functional theory (DFT) calculations of ^{17}O chemical shifts at the level of B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) of the above trifluoroacetyl compounds were compatible with the experimental values measured in CCl_4.[15] The small deviation (absolute values of less than 5 ppm in most cases) of the calculated values from the experimental values might be fortuitous, but the good correlation between calculated and observed values is important. Excellent linear correlation (R = 0.993) between calculated and observed ^{17}O chemical shifts of 15 trifluoroacetyl compounds was obtained when the data for 3-furyl compound was excluded. Therefore, for functional groups of which the σ^+ values are difficult to deduce experimentally, theoretical calculation of ^{17}O chemical shifts of corresponding carbonyl compounds seems to be a potential substitute.

In contrast to the high sensitivity of oxygen atom to the donor/acceptor ability of a neighboring group, the ^{13}C chemical shift of the carbonyl carbon atom is less dependent on the electronic nature of a neighboring group.[11,12,16,17] Analysis of components of shielding tensors of HCOX with ab initio calculation has revealed that n–π^* transition contributes to the sensitivity of ^{17}O chemical shifts toward the nature of X.[16] As the n orbital is basically localized on the oxygen atom, the sensitivity observed on the oxygen atom does not occur on the carbon atom.

In order to find out whether the good correlations between calculated and observed ^{17}O chemical shifts, and between σ^+ constants and calculated ^{17}O chemical shifts also exist in systems other than the trifluoroacetyl compounds, we have studied other carbonyl compounds. In this article, we present results of aryl acyl chlorides (compound **1a–1n**). The aryl groups also include furyl, thienyl and naphthyl, not just limited to substituted phenyl of which the σ^+ constants *vs.* observed ^{17}O chemical shift correlation has been reported in literature.[8] In addition to the analysis of ^{17}O chemical shifts of acyl chlorides, the ^{13}C chemical shifts of the acyl carbon atom is also analyzed to verify if the explanation deduced from the calculation of HCOX can be invoked to explain the sensitivity difference of ^{17}O and ^{13}C chemical shifts in ArCOCl.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

The ^{17}O spectra were recorded on a Bruker AM-300 WB spectrometer equipped with a 10-mm broad-band probe operating at 40.670 MHz. The 0.5 M solution in carbon tetrachloride was prepared in a dry-box. Perdeuterated benzene was used as the external lock. The recording temperature (51°C) was corrected by using 80% ethylene glycol in DMSO-d_6 as the standard. The ^{13}C spectra were recorded on a Bruker AM-300 spectrometer for chloroform-d solution at ambient temperature (uncertainty: 0.5 ppm). The observed chemical shifts at natural abundance are listed in Table 1.

Stable conformers of aryl acyl chlorides were searched at the AM1 level[18] with the verification of frequency analysis. Structures of the stable conformers were further optimized at the B3LYP/6-31G(d) level.[19] Single point energy calculations and GIAO NMR chemical shift calculations[20] were carried out at the B3LYP/6-31+G(d,p) level based on the B3LYP/6-31G(d) optimized structures. The energy differences at the

B3LYP/6-31+G(d,p) level between conformers were used to calculate the population of conformers according to Boltzmann distribution (T = 298 K). The chemical shifts of conformers were all taken into account according to the population. All the semiempirical calculations were carried out with program SPARTAN 4.1[21] and the ab initio calculations were carried out with Gaussian 94, D4.[22]

To calculate the shielding tensor components(σ_{xx}, σ_{yy}, and σ_{zz}), the convention of Dahn and Carrupt was followed.[23] In brief, the direction of C=O bond is defined as the z-axis, the direction perpendicular to the acyl chloride plane is defined as the x-axis. Because the σ^+ constants for the ortho-substituted **1l–1n** are not available, we only calculate the tensor components for **1a–1k** in their lowest energy conformations.

RESULTS AND DISCUSSION

The calculated chemical shifts are analyzed in two directions. The degree of similarity between gas phase calculated values and chemical shifts observed in nonpolar CCl_4 is examined by plotting δ_{calc} against δ_{obs}. The sensitivity of calculated chemical shifts toward substituent effects in solvolysis reactions is checked by plotting δ_{calc} against σ^+ constants. Table 1 shows the ^{17}O NMR chemical shifts of **1a–1n**. The range of the ^{17}O NMR chemical shifts in CCl_4 is 470.6 to 536.3 ppm. The deviations between calculated ($\delta(^{17}O)_{calc}$) and observed ($\delta(^{17}O)_{obs}$) chemical shifts are rather small (ca. 2 ppm) for benzoyl chlorides **1a-1h** and the calculated values are consistently at downfield relative to the observed ones. The $\delta(^{17}O)_{calc}$–$\delta(^{17}O)_{obs}$ correlation is excellent (R = 0.999) for **1a–1h**. As the observed values correlate well with σ^+ constants (R = 0.995), the calculated correlate equally well with σ^+ (R = 0.996). If *ortho*-substituted phenyl (**1m**, **1n**), naphthyl (**1k**, **1l**) and hetero aromatic (**1i**, **1j**) acyl chlorides are all

taken into account, the $\delta(^{17}O)_{calc}$–$\delta(^{17}O)_{obs}$ correlation (Figure 1) is still respectable (R = 0.984). Among the fourteen compounds, calculated chemical shifts of **1j** (2-furyl) and **1n** (2,6-dimethylphenyl) show the largest deviation (9–10 ppm) from the observed. For compounds without significant steric congestion on carbonyl group, **1a–1k**, the correlation coefficient for $\delta(^{17}O)_{calc}$–σ^+ correlation is 0.988, and for $\delta(^{17}O)_{obs}$–σ^+ is 0.993. The reason for large deviations of **1j** and **1n** is not clear. With two *ortho* methyl groups, **1n** (2,6-dimethylphenyl) possesses the most serious steric congestion among the fourteen acyl chlorides; the dihedral angle between the phenyl ring and the acyl plane is 58.5° in calculated geometry. Since proper treatment of electron correlation is important for NMR calculations,[24] it is likely that better electron correlated theory levels are needed to handle sterically congestive systems such as **1n**.

In literatures, the ^{17}O chemical shifts measured in polar acetonitrile (CH_3CN) solvent[8,10] were reported for **1a**, **1c**, **1d**, **1f–1h**, and **1k–1n**, and found more upfield than that in the nonpolar CCl_4 by several ppm in most cases (Table 1). The sterically congestive **1n** has a larger deviation ($\delta(^{17}O)_{obs,CCl_4} - \delta(^{17}O)_{obs,CH_3CN}$ = 13 ppm). The correlation between gas phase calculated chemical shifts ($\delta(^{17}O)_{calc}$) and those measured in CH_3CN ($\delta(^{17}O)_{obs,CH_3CN}$) is fair ($R$ = 0.968). With the exclusion of **1n**, the correlation improves (R = 0.985). The corresponding R value of $\delta(^{17}O)_{calc}$–$\delta(^{17}O)_{obs}$ correlation in CCl_4 with the same set of compounds (also excluding **1n**) is 0.992. The better correlation between calculated values and chemical shifts in nonpolar solvent demonstrate that gas phase calculated chemical shifts are reasonable enough and they may be used as a control group to contrast the influence of solvent on solutes.

The ^{13}C chemical shifts of the carbonyl carbon atom of **1a–1n** in $CDCl_3$ are in the range of 154.6 to 177.0 ppm (Table 1, $\delta(^{13}C)_{obs}$). Although the calculated chemical shifts deviate from the observed by less than 5.9 ppm, the relatively small variation

range of $\delta(^{13}C)_{obs}$ (ca. 23 ppm) makes the $\delta(^{13}C)_{calc}$–$\delta(^{13}C)_{obs}$ correlation (R = 0.906) much worse than that of ^{17}O chemical shift. Scattered $\delta(^{13}C)_{obs}$–σ^+ and $\delta(^{13}C)_{calc}$–σ^+ plots were obtained (R < 0.77) even if the sterically congested compounds **1l-1n** were not included.

Chemical shift is the difference of isotropic shieldings (σ_{iso}; $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, σ_{xx}, σ_{yy}, and σ_{zz} are the shielding tensor components in the x, y, and z directions, respectively) between the reference compound and the measured compound. In the study of HCOX (X = SiH_3, H, Me, SH, Cl, F, OMe, OH, NH_2, and O^-), Dahn et al. found that σ_{zz} of ^{17}O is far more sensitive than σ_{xx} and σ_{yy} to the electronic nature of X.[23] The range of σ_{zz} is –1649 (X = SiH_3) to –9 ppm (X = O^-), whereas the range of σ_{xx} is 414 to 215 ppm and that of σ_{yy} is –604 to –126 ppm. Shielding tensor component σ_{zz} is related to charge circulation in the x,y plane. Analysis of IGLO[25,26] calculation results of mixing of unoccupied and occupied ground state orbitals in the presence of magnetic field, Dahn et al. found that the low energy n(in the y direction)–π*(in the x direction) transition is the major cause for large variation of σ_{zz} and is therefore responsible for the sensitivity of ^{17}O chemical shift. On the other hand, the magnitudes of σ_{xx}, σ_{yy}, and σ_{zz} of ^{13}C do not differ so much as in the case of ^{17}O. Furthermore, although some sensitivity towards X has been found for σ_{xx} and σ_{yy} of ^{13}C, the irregular variation of σ_{zz} results in poor overall sensitivity of carbonyl carbon atom towards X.[23] In brief, the ^{17}O shift values are strongly influenced by the low energy n–π* transition, whereas the ^{13}C shift values are determined by multiple factors. The n–π* transition does not affect ^{13}C chemical shift because the lone pair is located on the O atom.

In comparison with HCOX, the ArCOCl system, with the presence of the aryl group, is more complex in terms of mixing of orbitals under the influence of magnetic field. Whether a specific shielding tensor component still dominates the sensitivity of

an atom is unclear. Using the same definition of x, y, z, directions as in Dahn's study, we calculated σ_{xx}, σ_{yy}, and σ_{zz} of carbonyl oxygen and carbon atoms and plotted them against σ^+ constants to examine whether the tensor components are sensitive to the substituent effect. As shown in Figure 2, the slopes for σ_{xx}, σ_{yy}, and σ_{zz} of ^{17}O are 6.68, –23.30, and –33.62, respectively; the correlation coefficients are 0.489, 0.993, and 0.921, respectively. Therefore, although σ_{zz} is inferior to σ_{yy} in correlating with σ^+, it is the most sensitive component toward substituent effects, judged by the slopes. This result is similar to that of HCOX in that σ_{yy} correlates the best with σ_{R^+}, but is less sensitive than σ_{zz}.[23] Because the substituent effect is controlled by groups not directly bonded to the carbonyl group, unlike in the HCOX series, the variation ranges of the components are smaller in ArCOCl than in HCOX. When only the phenyl analogs **1a-1h** ($\sigma^+ = 0.612 \sim -0.311$) are considered, all three components correlate well with σ^+ constants (R = 0.985, 0.997, 0.998 for σ_{xx}, σ_{yy}, and σ_{zz}, respectively). The slopes are 9.77, –24.43, –42.47 for σ_{xx}, σ_{yy}, and σ_{zz}, respectively, so σ_{zz} still contributes significantly to the variation of σ_{iso}.

Figure 3 shows the correlation between shielding tensor components of ^{13}C and σ^+ constants. All correlation coefficients are less satisfactory (< 0.9) than that of ^{17}O. The slopes do not differ much from each other, so the variation of σ_{iso} is not dominated by any specific component. Therefore, it will not be possible to describe the variation of ^{13}C chemical shift qualitatively by a specific argument. Unlike for ^{17}O chemical shift, the dominance of σ_{zz} makes the argument of n–π^* transition plausible.

Examination of frontier orbitals of the lowest energy conformer of **1a–1h** shows that HOMO and HOMO–1 are π orbitals largely distributed on the phenyl ring. The HOMO–2 contains the oxygen lone pair along y-axis (in the acyl chloride molecular plane and perpendicular to the C–O bond). The LUMO is consisted of π^* of C–O and

the phenyl ring. Therefore, the HOMO–2 to LUMO transition has the least energy gap among transitions that are responsible to the magnitude of $\sigma_{zz}(^{17}O)$. Plotting the energy gap of n–π* transition against σ_{zz} and σ_{iso} of ^{17}O afforded fair correlation (both R = 0.958).[27] The HOMO–LUMO π–π* transition is irrelevant to the O atom, so it is not surprising that when the HOMO–LUMO gaps are plotted against σ, the correlation is very poor (R = 0.303 for σ_{zz} and 0.294 for σ_{iso}).

Since HOMO–2 contains not only lone pair of the oxygen atom, but also lone pair of the chlorine atom on the y,z plane, we postulate that chlorine may also exhibit sensitivity toward substituent effect with similar n–π* transition mechanism. Plotting calculated σ_{zz} of the chlorine atom of sterically unhindered **1a–1k** against σ^+ constants indeed shows a fair correlation (R = 0.952). Because the σ_{xx} of the two 5-membered hetero aryl **1i** and **1j** deviate significantly from the trend of other aryl acyl chlorides (Figure 4), it makes the σ_{iso} of these two compounds much smaller than what one would expect on the basis of the σ^+ value (Table 1). To have a fair comparison between O, C and Cl, we use **1a–1h** again to examine how well σ_{iso} of Cl reflects substituent effects. Plotting σ_{iso} of Cl against σ^+ gives a correlation coefficient 0.929. This is worse than the $\delta(^{17}O)_{calc}$–σ^+ correlation, but significantly better than the $\delta(^{13}C)_{calc}$–σ^+ correlation.

CONCLUSION

We have shown that calculation of ^{17}O chemical shifts at the B3LYP/6-31+G**//B3LYP/6-31G* level, as previously reported for $ArCOCF_3$, also affords good results for ArCOCl. In general, the correlation between calculated and observed ^{17}O chemical shifts is good, especially when unhindered phenyl analogs are considered. Therefore, the calculation of ^{17}O chemical shifts has the potential to determine the σ^+

constant for a given group. It is known that σ^+ values, and other substituent constants as well, for certain groups observed in different solvent systems are at significant variance.[28] The σ^+ values obtained in the gas phase calculation show the intrinsic property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of environment.

The calculated absolute deviation of ^{13}C chemical shift from the observed value is similar to that of ^{17}O. Nevertheless, the significantly smaller variation range of observed ^{13}C chemical shifts of the carbonyl carbon atom makes the analysis of $\delta(^{13}C)$ not worthwhile in terms of detecting substituent effect. Our results demonstrated that for ArCOCl the sensitivity of $\delta(^{17}O)$ and the insensitivity of $\delta(^{13}C)$ could be understood in terms of n–π^* transition, in line with the conclusion obtained from HCOX by Dahn and coworkers. Furthermore, this concept leads us to analyze the σ_{iso} of Cl and we have found correlation between σ_{is}, and σ^+ for closely related compounds.

Acknowledgements

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Supporting Information:

Table S1. Calculated shielding tensors.

Table S2. Orbital energies of HOMO–2, HOMO, and LUMO of lowest energy conformers of **1a–1h**.

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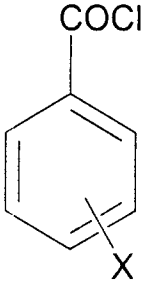
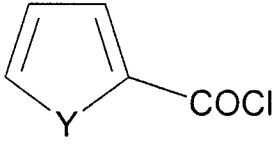
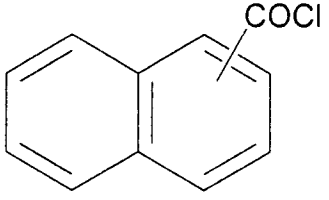


1a X = 4-CF_3
1b X = 3-Cl
1c X = 4-Cl
1d X = H
1e X = 3-CH_3
1f X = 4-F
1g X = 4-CH_3
1h X = 4-OCH_3
1m X = 2-CH_3
1n X = 2,6-$(CH_3)_2$



1i Y = S
1j Y = O



1k 2-COCl
1l 1-COCl

Table 1. Calculated and experimentally observed chemical shifts of aromatic acyl chlorides.

ArCOCl	Ar	σ^+	$\delta(^{17}O)_{calc}$	$\delta(^{17}O)_{obs,CCl_4}$	$\delta(^{17}O)_{obs,CH_3CN}$	$\Delta\delta_{CCl_4}$ [a]	$\Delta\delta_{CH_3CN}$ [b]	$\delta(^{13}C)_{calc}$	$\delta(^{13}C)_{obs}$	$\Delta\delta$ [c]	$\delta(Cl)_{calc}$
1a	4-$CF_3C_6H_4$	0.612	506.7	505.2	497.5	1.5	9.2	169.9	167.9	2.0	518.4
1b	3-ClC_6H_4	0.399	501.2	499.2		2.0		169.4	167.4	2.0	523.6
1c	4-ClC_6H_4	0.114	495.6	494.6	487.7	1.0	7.9	168.9	167.0	1.9	525.6
1d	C_6H_5	0	494.8	493.6	485.5	1.2	9.3	170.1	168.0	2.1	531.5
1e	3-$CH_3C_6H_4$	-0.066	493.4	492.3		1.1		170.1	167.8	2.3	533.5
1f	4-FC_6H_4	-0.073	492.0	490.6	483.6	1.4	8.4	168.6	166.9	1.7	525.1
1g	4-$CH_3C_6H_4$	-0.311	489.2	487.7	479.3	1.5	9.9	169.3	167.6	1.7	534.2
1h	4-$CH_3OC_6H_4$	-0.778	479.4	477.4	468.9	2.0	10.5	168.2	165.3	2.9	540.4
1i	2-thienyl	-0.928	479.5	476.7		2.8		160.2	159.3	0.9	511.3
1j	2-furyl	-1.03	479.9	470.6		9.3		156.1	154.6	1.5	512.2
1k	2-Naphthyl	-0.126	493.7	489.0	485.3	4.7	8.4	170.1	172.2	-2.1	534.5
1l	1-Naphthyl		508.2	508.3	505.8	-0.1	2.4	169.3	175.2	-5.9	510.4
1m	2-$CH_3C_6H_4$		514.7	511.6	505.5	3.1	9.2	169.7	167.3	2.4	514.1
1n	2,6-$(CH_3)_2C_6H_3$		547.1	536.3	523.3	10.8	23.8	175.6	177.0	-1.4	423.0

a: $\Delta\delta_{CCl_4} = \delta(^{17}O)_{calc} - \delta(^{17}O)_{obs,CCl_4}$

b: $\Delta\delta_{CH_3CN} = \delta(^{17}O)_{calc} - \delta(^{17}O)_{obs,CH_3CN}$

c: $\Delta\delta = \delta(^{13}C)_{calc} - \delta(^{13}C)_{ob}$

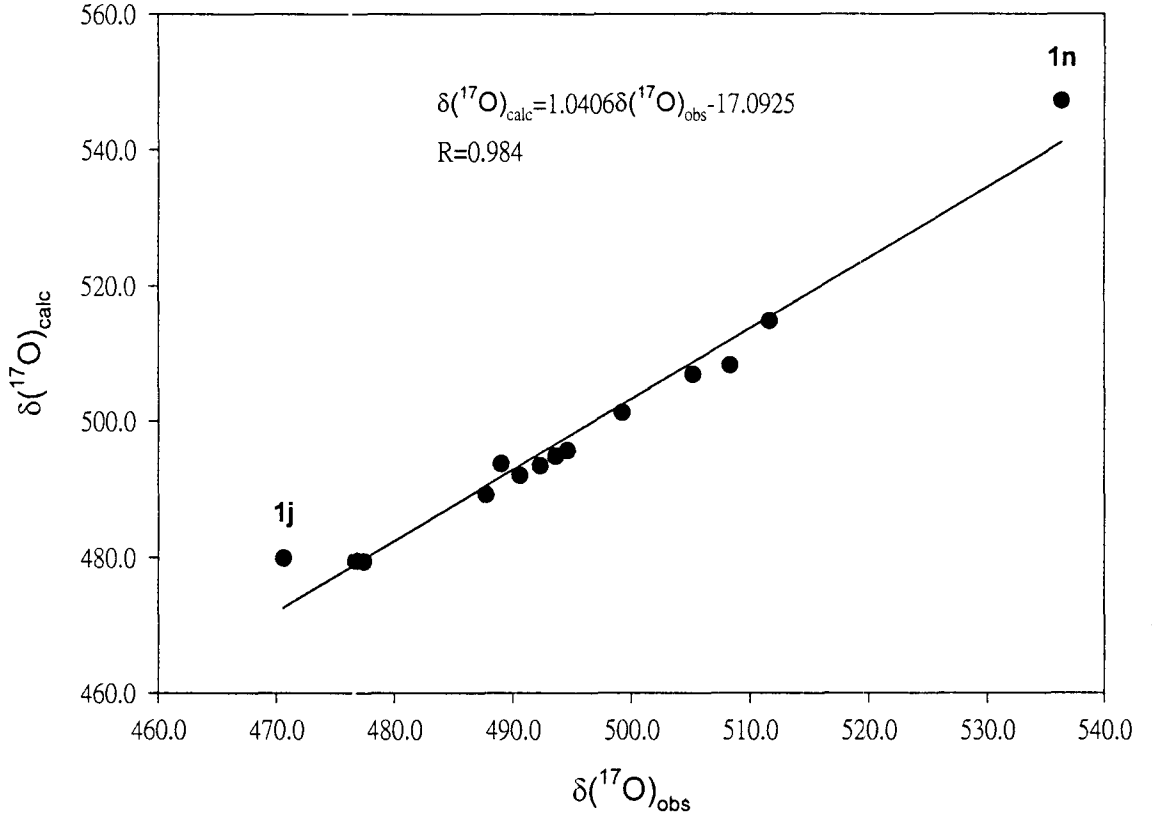
Figure caption:

Figure 1. Correlation between $\delta(^{17}O)_{calc}$ and $\delta(^{17}O)_{obs}$ for compounds **1a–1n**.

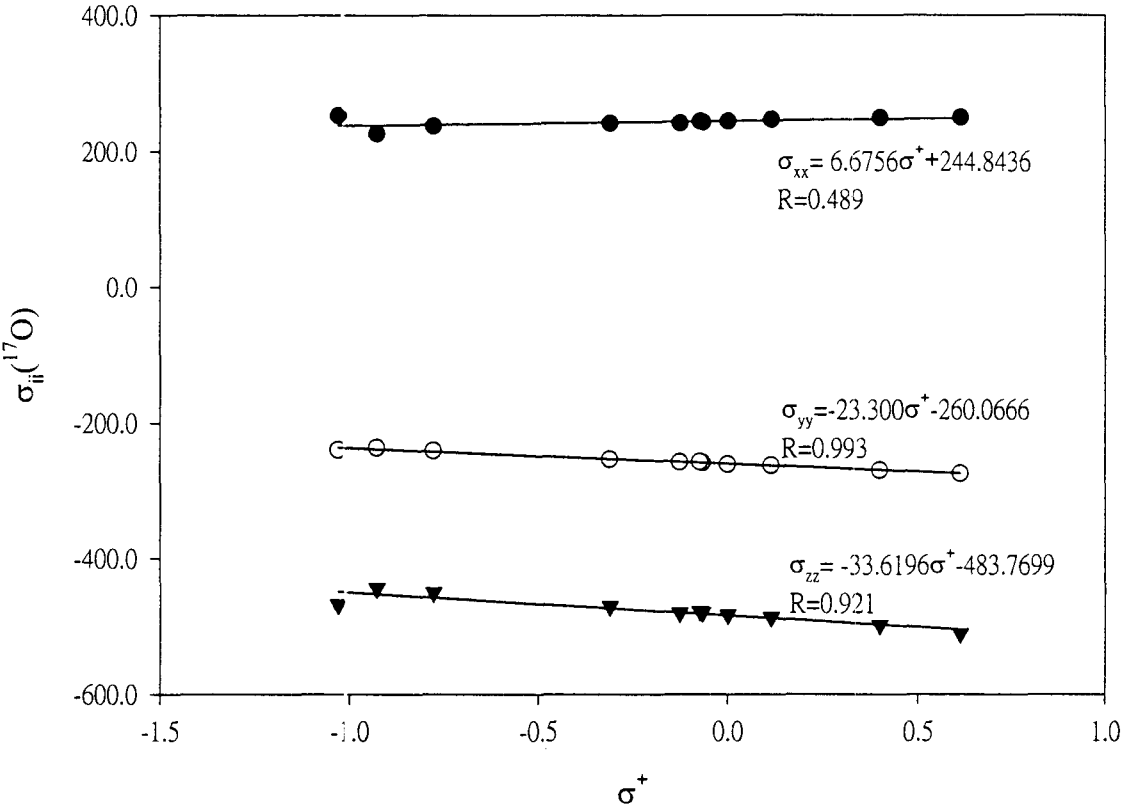
Figure 2. Plot of calculated σ_{ii} of ^{17}O against σ^+ constants for compounds **1a–1k**.

Figure 3. Plot of calculated σ_{ii} of ^{13}C against σ^+ constants for compounds **1a–1k**.

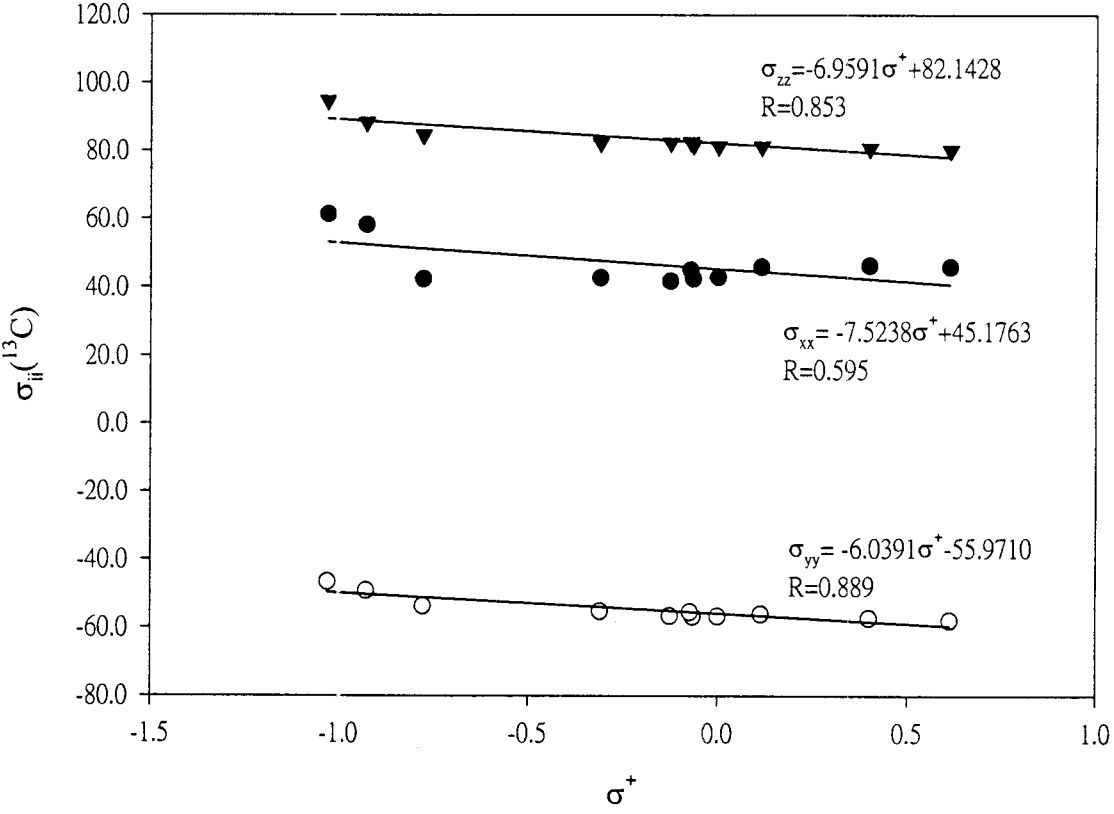
Figure 4. Plot of calculated σ_{ii} of Cl against σ^+ constants for compounds **1a–1k**; the correlation is determined without the consideration of **1i** and **1j**.



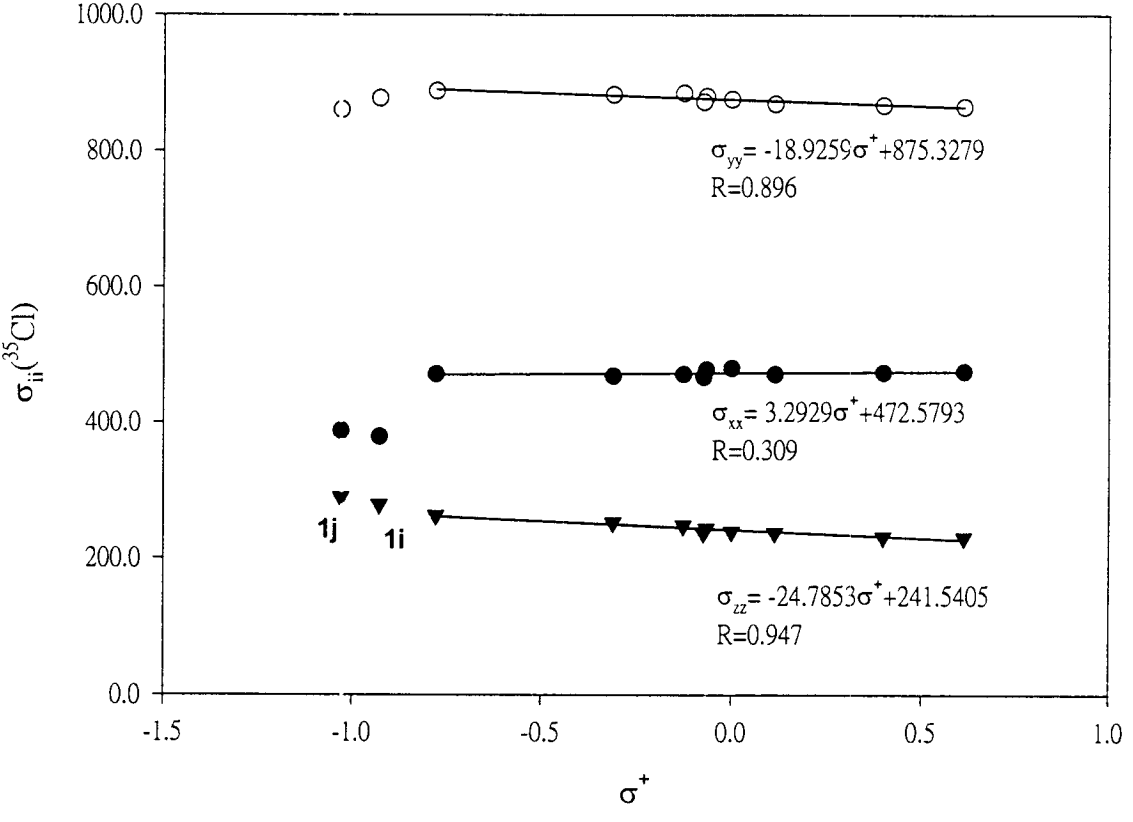
Ito Chao Figure 1



Ito Chao Figure 2



Ito Chao Figure 3



Ito Chao Figure 4

Table S1. Calculated shielding tensors.

ArCOCl	Ar	^{17}O			^{13}C			^{35}Cl		
		σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}	σ_{xx}	σ_{yy}	σ_{zz}
1a	4-$CF_3C_6H_4$	250.16	-274.70	-510.67	45.71	-57.98	80.01	474.84	864.32	230.26
1b	3-ClC_6H_4	249.46	-269.65	-498.13	46.10	-57.37	80.58	472.86	866.83	230.97
1c	4-ClC_6H_4	247.10	-262.14	-486.49	45.66	-56.17	81.18	470.84	868.75	237.20
1d	C_6H_5	244.53	-260.74	-482.94	42.80	-56.77	81.25	479.76	875.60	239.10
1e	3-$CH_3C_6H_4$	243.09	-258.55	-479.45	42.37	-56.82	81.60	477.52	879.82	243.04
1f	4-FC_6H_4	244.22	-256.92	-477.99	44.82	-55.53	82.45	466.77	871.79	236.68
1g	4-$CH_3C_6H_4$	241.48	-253.42	-470.50	42.66	-55.36	82.26	468.04	882.46	252.11
1h	4-$CH_3OC_6H_4$	237.47	-240.33	-450.05	42.25	-53.79	84.46	471.10	887.92	262.28
1i	2-thienyl	226.56	-236.22	-443.72	58.09	-49.29	88.15	378.77	876.91	278.12
1j	2-furyl	252.93	-239.41	-467.99	61.22	-46.73	94.57	387.50	860.03	288.94
1k	2-Naphthyl	241.69	-257.71	-480.00	41.71	-56.68	82.28	470.74	884.80	247.91

Table S2. Orbital energies (eV) of HOMO-2 (n), HOMO (π), LUMO(π^*) of lowest energy conformers of **1a**–**1h**.

ArCOCl	Ar	n	π	π^*
1a	4-$CF_3C_6H_4$	-0.31658	-0.30336	-0.10957
1b	3-ClC_6H_4	-0.31117	-0.27867	-0.09996
1c	4-ClC_6H_4	-0.31001	-0.28281	-0.09814
1d	C_6H_5	-0.30403	-0.28542	-0.09062
1e	3-$CH_3C_6H_4$	-0.30134	-0.27349	-0.08811
1f	4-FC_6H_4	-0.30868	-0.28757	-0.09339
1g	4-$CH_3C_6H_4$	-0.3001	-0.27644	-0.08558
1h	4-$CH_3OC_6H_4$	-0.29697	-0.25717	-0.07911

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Steric effect on the formation of columnar phases in β-diketonate copper(II) complexes

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A systematic study of the mesomorphic properties of three series of copper(II) complexes based on β-diketonate ligands containing branched side chains is reported. These disc-like compounds have four, six and eight flexible alkoxy side chains appended to the central core, in which two or four side chains were substituted by bulkier secondary alkoxy groups: 1-methylbutyloxy $R' = C_5(2°)$ or 1-methylheptyloxy $R' = C_8(2°)$. The mesomorphic results indicated that at least eight side chains are required to form stable columnar mesophases; other compounds with four or six side chains are not mesogenic regardless of the combination of the carbon length on the alkoxy or secondary alkoxy groups of the side chains. The compounds **3** with shorter $R' = C_5(2°)$ side chains were all non-mesogenic regardless of the carbon length of three alkoxy side chains ($R = C_8$, C_{10}, C_{12}) used. However, when the longer 1-methylheptyloxy side chain $R' = C_8(2')$ was substituted, the compounds **3b–3e** with various alkoxy groups ($R = C_6$, C_7, C_8, C_{10}, C_{12}) exhibited columnar phases. The mesophases were characterized and identified as columnar hexagonal phases (Col_h), as expected, by thermal analysis and optical polarized microscopy. The presence of the introduced secondary alkoxy groups apparently appeared to influence the formation of columnar phases. The clearing points were relatively lower than other similar copper(II) compounds not substituted by secondary alkoxy side chains.

1. Introduction

The formation of columnar mesophases [1] is often accomplished by molecules with a variety of overall molecular shapes, such as disc-like, half-disc or possibly rod-like molecules. In this phase the central core is stacked to form columns surrounded by numerous disordered flexible side chains. The organization of antiparallel correlation, as a result of dipolar forces, by half-disc or rod-like molecules to form columnar phases is also feasible, particularly in metallomesogenic structures due to intermolecular coordinative forces. In general the stability of the columnar mesophases formed by these molecules is determined and/or controlled by the number of flexible side chains (i.e. side chain density) attached to the central core. On the other hand more flexible side chains or longer carbon length of side chains are frequently needed to stabilize a larger central core. Among many metallomesogenic structures bis(β-diketonate)-metal(II) complexes [2–6] are the ones most studied. Various mesophases [1] exhibited by these metal complexes are known: discotic lamellar (D_L), columnar hexagonal (Col_h), columnar rectangular (Col_r) and nematic (N) phases. Studies of mesomorphic properties indicated that in this particular metallomesogenic structure six or more flexible alkoxy side chains are found to be required for the formation of stable columnar phases. The introduction of chiral side chains in metallomesogenic structures to generate tilted columnar mesophases [7, 8] with a helical structure has also been studied recently.

In order to understand the effect of steric substituent groups attached to the phenyl ring of β-diketones on the formation of columnar phases, we systematically prepared three series of copper(II) β-diketonate complexes **1–3**. These compounds have four, six and eight alkoxy side chains, respectively. In series **1** and **3**, two flexible side chains were substituted by secondary alkoxy

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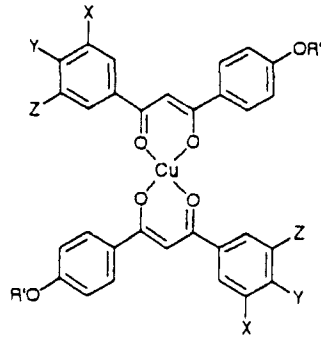
groups: 1-methylbutyloxy $C_5(2°)$ or 1-methylheptyloxy $C_8(2°)$. In series **2** four side chains were similarly substituted.



1 Y = OR; X = Z = H
1a R' = $C_5(2^0)$, R = C_{10}
1b R' = $C_8(2^0)$, R = C_{10}
2 X = Z = OR; Y = H
2a R' = $C_8(2^0)$, R = C_{12}
2b R' = $C_8(2^0)$, R = C_{16}
2c R' = C_{16}, R = $C_5(2^0)$
2d R' = C_{16}, R = $C_8(2^0)$
3 X = Y = Z = OR
3a R' = $C_5(2^0)$, R = C_{12}
3b R' = $C_8(2^0)$, R = C_8
3c R' = $C_8(2^0)$, R = C_7
3d R' = $C_8(2^0)$, R = C_8
3e R' = $C_8(2^0)$, R = C_{12}
3f R' = $C_8(2^0)$, R = C_{14}

2. Results and discussion

2.1. *Synthesis and characterization*

The compounds 4-(1-methylbutyloxy)acetophenone and 3,5-di(1-methylheptyloxy)acetophenone were prepared by analogous methods by Mitsunobu reactions [9, 10]. They were obtained by the reaction of 4-hydroxyacetophenone or 3,5-dihydroxyacetophenone with 2-pentanol or 2-octanol in the presence of triphenyl phosphine (TPP) and disopropyl azodicarboxylate (DIAD) in dried THF at room temperature. These secondary ether ketones were isolated as light yellow oils in yields of 70–83%. The β-diketonate ligands were prepared by Claisen condensation of the appropriate methyl benzoate ester and the acetophenone in the presence of sodium hydride. The products were separated and purified by flash column chromatography, eluting with a mixture of ethyl acetate/*n*-hexane (v/v 1/19). These compounds were obtained as viscous dark yellow to orange pastes; yields were 67–87%. All these organic compounds were characterized by ^1H and ^{13}C NMR spectroscopy.

The reaction of β-diketonate ligands with $Cu(OAc)_2$ produced the copper(II) complexes in yields of 72–85%. These copper(II) complexes were obtained as light green solids or green pastes depending on the carbon length of the side chains. The solid complexes were purified by recrystallization from CH_2Cl_2/CH_3OH (v/v 1/1); the oily paste complexes were separated by flash column chromatography, eluting with a mixture of ethyl acetate/*n*-hexane (v/v 1/9). These complexes were characterized by IR spectroscopy and elemental analysis. Satisfactory elemental analyses for all compounds were obtained, see table 1.

2.2. *Mesomorphic properties of compounds 1 and 2*

All known metal β-diketonate complexes (M = Cu, Pd, VO) appended with four symmetric or unsymmetrical alkoxy side chains, are reported to be non-mesogenic [1]. The lack of liquid crystallinity is attributed to strong intermolecular forces between the neighbouring molecules in the columns, and the mesomorphic properties are often improved by increasing the numbers of flexible side chains (i.e. side chains density) attached to the central core. The numbers of the side chains were increased to, for example, six, eight, ten or twelve, and all reported compounds with eight, ten or twelve side chains exhibited better mesomorphic properties. Our initial thought was to increase the side chain steric hindrance, in hope that the bulkiness of substituent groups might weaken the intermolecular attraction. Therefore, three series of copper(II) complexes based on unsymmetrical β-diketonate ligands have been prepared. In these compounds a systematic combination of various carbon length chains on either side of the two phenyl rings was applied to alter the steric bulkiness of the whole molecules. In compounds **1** and **2**, in two or four side chains were substituted by bulkier secondary 1-methylbutyloxy [$C_5(2°)$] or 1-methylheptyloxy [$C_8(2°)$] groups. The mesomorphic properties for all the copper complexes was studied by thermal analysis (DSC) and polarizing microscopy. The phase behaviour for copper complexes **1** and **2** are summarized in table 2. All the compounds exhibited crystalline phases regardless of the combination of the carbon length of alkoxy side chains (R = C_{10}, C_{12}, C_{16}) or secondary side chains [R' = $C_5(2°)$ or $C_8(2°)$] used. Crystal-to-isotropic transitions were all

Table 1. Elemental analysis of complexes 1–3 with calculated values in parentheses.

Compds	C/%	H/%
1a	72.28 (72.44)	8.24 (8.31)
1b	73.44 (73.47)	8.86 (8.78)
2a	74.62 (75.08)	9.74 (10.05)
2b	76.49 (76.45)	10.36 (10.61)
2c	73.83 (73.75)	9.60 (9.51)
2d	74.58 (75.08)	9.97 (10.53)
3a	75.45 (75.23)	10.29 (10.48)
3b	71.82 (72.02)	9.48 (9.28)
3c	72.56 (72.81)	9.81 (9.58)
3d	73.48 (73.52)	9.86 (9.84)
3e	75.82 (75.70)	10.67 (10.66)
3f	76.45 (76.51)	10.80 (10.96)

Table 2. Phase behaviour of the compounds **1–3**. K = crystal phase; Col_{hd} = columnar disordered hexagonal phase; I = isotropic. The transition temperature (°C) and enthalpies (in parenthesis, kJ/mol) are determined by DSC at a scan rate of 10.0°C/min.

1a			Cr	154.6 (57.9) / 124.5 (44.0)	I	
1b			Cr	133.5 (36.0) / 115.0 (32.1)	I	
2a			Cr	90.3 (54..) / 55.5 (45..)	I	
2b			Cr	83.2 (51.) / 55.2 (51.)	I	
2c			Cr	83.5 (20.) / < 20.0	I	
2d			Cr	62.6 (73.) / < 20.0	I	
3a			Cr	67.0 (131) / 32.0[a]	I	
3b	Cr	73.1 (24.6)	Col_{hd}	82.2 (4.1.) / 32.6 (0.76)[a]	I	
3c	Cr	33.5[a]	Col_{hd}	78.1[a] / 50.0[a]	I	
3d	Cr	48.5 (1.56)	Col_{hd}	68.3 (74.) / 53.0[a]	I	
3e	Cr	62.9 (111)	Col_{hd}	68.3 (2.7.) / < 20.0	I	
3f			Cr	69.2 (67..) / 30.2 (55.)	I	

[a] Values observed by microscopy.

observed. The clearing points were all apparently lower than those reported for complexes without secondary side chains.

2.3. *Mesomorphic properties of compounds 3*

When side chain numbers were increased to eight, the mesomorphic properties was greatly improved. Complexes **3b–3e** exhibited columnar phases and the compounds **3b** and **3f** formed crystalline phases. Compounds **3** with secondary 1-methylbutyloxy side chains $R' = C_5(2°)$ were all non-mesogenic regardless of the carbon length of three alkoxy side chains ($R = C_8, C_{10}, C_{12}$) used. However when secondary 1-methylheptyloxy side chains $R' = C_8(2°)$ were used compounds **3b–3e** exhibited columnar phases ($R = C_6, C_7, C_8, C_{10}, C_{12}$). These compounds melt to give a birefringent fluid phase with an optical texture of pseudo focal-conics, with linear birefringent defects and large areas of uniform homeotropic domains, typically of hexagonal columnar discotic structures. In contrast to columnar rectangular phases, mosaic textures with wedge-shaped defects were often observed. In DSC analysis, compounds **3c** and **3d** formed monotropic phases, and **3b** and **3e** formed enantiotropic phases. DSC showed a larger enthalpy for the crystal-to-liquid crystal transition at lower temperature and a relatively lower enthalpy for the liquid crystal-to-isotropic transition at higher temperature, indicating the mesophase to be in highly disordered state. The temperature range of mesomorphism is narrow. The identification of columnar hexagonal columnar phases was characterized by optical textures, and confirmed by variable-temperature X-ray powder diffraction (XRD).

The results showed that recurrence of liquid crystallinity depended not only on the numbers and type of side chains but also on the distribution of electron polarization. As a result, four or six side chains does not contribute enough electron density for β-diketonate cores to form stable discotic mesophases. Dipole interaction between cores is relatively weak.

3. Summary and conclusion

Copper(II) β-diketonate complexes with a combination of various numbers and/or secondary [$R' = C_5(2°)$ or $C_8(2°)$] substitution of alkoxy side chains were prepared. Their mesomorphic properties were investigated, to understand the steric effect of substitution on the formation of columnar phases. We have found that the numbers of side chains played an important role in controlling the core–core interactions which determined the formation of the liquid crystallinity. In addition, the degree of polarization distribution of side chain density, by choosing steric secondary side chains, apparently influenced the formation and stability of the mesophases. Although eight side chains are required to form stable mesophases, the introduction of more steric secondary side chains reduced the core–core interaction and lowered the clearing points.

4. Experimental

All chemicals and solvents were reagent grades (Aldrich Chemical Co.) and used without further purification. THF and dimethoxyethane (DME) were dried over sodium benzophenone ketyl. ^1H and ^{13}C NMR spectra were measured on a Bruker AC-300F instrument. Infrared spectra were recorded on a Nicolet Magna II 550 spectrometer using polystyrene as standard. DSC thermographs were carried out on a Perkin-Elmer DSC-7. All phase behaviours were determined at a scan rate of 10°C min^{-1}. Optical polarized microscopy was carried out on a Nikkon Microphot-FXA with a Mettler FP90/FP82HT hot stage system. XRD studies were conducted on an Inel MPD-diffractometer with a 2 kW CuK_α X-ray source equipped with an INEL CPS-120 position sensitive detector.

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4.1. *4-(1-Methylbutyloxy)acetophenone*

4-Hydroxyacetophenone (5.0 g, 36.7 mmol), 2-pentanol (3.24 g, 36.7 mmol) and triphenyl phosphine (12.0 g, 0.046 mol) were mixed and dissolved in 175 ml of dried THF. To this solution was added dropwise diisopropyl azodicarboxylate (DIAD, 9.30 g, 0.046 mol) dissolved in 25 ml of THF at 0°C. The reaction mixture was stirred at room temperature for 2 days. Water (*c.* 5 drops) was added to the solution, and the mixture stirred for 1 h. The solution was concentrated to give a yellow liquid and white solids. The solids were filtered off, and the yellow liquid was purified by flash chromatography with an eluant of ethyl acetate/hexane (1/10). Yield 83%, light yellow oil. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 3H), 1.30 (d, CH_3CHO, 3H), 1.31–1.77 (m, $-CH_2$, 4H), 2.55 (s, $COCH_3$, 3H), 4.46 (m, $-OCH$, 1H), 6.91 (d, $-C_6H_4$, 2H), 7.91 (d, $-C_6H_4$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.63, 18.31, 19.19, 38.10, 25.82, 73.34, 114.7, 129.5, 130.3, 162.0, 196.1. IR (neat): 2961, 2874, 1677, 1600, 1507, 1254, 1111 cm^{-1}.

4.2. *4-(1-Methylheptyloxy)acetophenone*

Yield 79%, light yellow oil. ^{1}H NMR (ppm, $CDCl_3$): 0.79 (t, $-CH_3$, 3H), 1.22 (d, CH_3CHO, 3H), 1.29–1.69 (m, $-CH_2$, 4H), 2.43 (s, $COCH_3$, 3H), 4.34 (m, $-OCH$, 1H), 6.80 (d, $-C_6H_4$, 2H), 7.81 (d, $-C_6H_4$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.79, 19.31, 22.32, 25.15, 28.96, 31.50, 36.06, 25.93, 73.72, 114.8, 129.6, 130.3, 162.1, 196.2. IR (neat): 2961, 2874, 1677, 1600, 1507, 1254, 1111 cm^{-1}.

4.3. *3,5-Di(1-methylheptyloxy)acetophenone*

Yield 78%, light yellow oil. ^{1}H NMR (ppm, $CDCl_3$): 0.85 (t, $-CH_3$, 3H), 1.27 (d, CH_3CHO, 3H), 1.35–1.73 (m, $-CH_2$, 20H), 2.53 (s, $COCH_3$, 3H), 4.36 (q, $-OCH_2$, 2H), 6.58 (t, $-$ph, 1H), 7.01 (d, $-$ph, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.75, 15.81, 23.71, 27.05, 27.27, 29.87, 30.05, 32.40, 73.73, 113.51, 115.75, 129.68, 129.65, 130.67, 163.87, 196.44 (C=O). IR (neat): 2960.7, 2873.6, 1678.4, 1600.1, 1507.2, 1254.4, 1110.8 cm^{-1}.

4.4. *1-(4-Decyloxyphenyl)-3-(4-methylbutyloxyphenyl)-propane 1,3-dione*

4-(1-Methylbutyloxy)acetophenone (5.0 g, 0.024 mol) and methyl, 4-decyloxybenzoate (6.70 g, 0.024 mol) were mixed in 150 ml of dried THF. The solution was slowly added to NaH (1.75 g, 0.073 mol) suspended in 30 ml of TFH, and the reaction mixture was gently refluxed for 24 h. A few drops of 95% ethanol was added to quench the excess NaH, and the solution was neutralized with dilute hydrochloric acid. The solution was extracted twice with chloroform, and the organic layers were combined and dried over $MgSO_4$. The solution was concentrated to give a dark brown paste. The product was obtained as an orange paste by flash chromatography with an eluant of ethyl acetate/hexane (1/20). Yield 81%. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (m, $-CH_3$, 6H), 1.26–1.81 (m, $-CH_2$, 23H), 4.00 (t, $-OCH_2$, 6H), 4.45 (m, $-$OCH, 1H), 6.70 (s, HC=CH, 1H), 6.92 (m, $-C_6H_4$, 4H), 7.90 (m, $-C_6H_4$, 4H). ^{13}C NMR (ppm, $CDCl_3$): 13.98, 14.08, 18.67, 19.59, 22.64, 25.96, 29.10, 29.29, 29.52, 31.86, 38.45, 68.21, 73.75, 91.30, 114.4, 115.3, 127.7, 128.0, 129.0, 129.1, 131.4, 161.8, 162.6, 184.5. IR (neat): 2964, 2872, 1605, 1460, 1255, 1117 cm^{-1}.

4.5. *1-(3,5-Didodecyloxyphenyl)-3-(4-methylheptyloxy phenyl)-propane 1,3-dione*

Yield 85%, orange oily paste. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (m, $-CH_3$, 9H), 1.25–1.81 (m, $-CH_2$, 53H), 3.98 (t, $-OCH_2$, 4H), 4.40–4.49 (m, $-$OCH, 1H), 6.60 (s, $-$ph, 1H), 6.71 (s, HC=CH, 1H), 6.92 (d, $-$ph, 2H), 7.06 (s, $-$ph, 2H), 7.92 (d, $-$ph, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.09, 19.61, 22.57, 22.67, 25.42, 26.02, 29.22, 29.35, 29.61, 31.75, 31.90, 36.31, 68.31, 74.09, 92.49, 105.11, 105.36, 115.35, 127.50, 129.31, 137.62, 160.38, 162.09, 184.31, 185.67. IR (neat): 2924.1, 2853.6, 1604.0, 1463.4, 1255.2, 1116.9 cm^{-1}.

4.6. *1-[3,5-Di(methylheptyloxyphenyl)]-3-(4-hexadecyloxy phenyl)-propane 1,3-dione*

Yield 78%, orange oily paste. ^{1}H NMR (ppm, $CDCl_3$): 0.88 (m, $-CH_3$, 9H), 1.26–1.81 (m, $-CH_2$, 54H), 3.99 (t, $-OCH_2$, 2H), 4.38–4.44 (m, $-$OCH, 2H), 6.59 (s, $-$ph, 1H), 6.73 (s, HC=CH, 1H), 6.93 (d, $-$ph, 2H), 7.06 (s, $-$ph, 2H), 7.93 (d, $-$ph, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.04, 19.68, 22.58, 22.66, 25.48, 25.97, 29.10, 29.27, 29.35, 29.66, 31.78, 31.91, 36.45, 68.20, 74.09, 92.38, 106.55, 107.40, 114.36, 127.76, 129.18, 137.68, 159.51, 162.84, 184.38, 185.55.

4.7. *1-(3,4,5-Trihexyloxylphenyl)-3-(4-methylheptyloxyphenyl)propane 1,3-dione*

Yield 83%, orange oily paste. ^{1}H NMR (ppm, $CDCl_3$): 0.88 (m, $-CH_3$, 12H), 1.25–1.84 (m, $-CH_2$, 37H), 3.95–4.06 (m, $-OCH_2$, 6H), 4.41–4.49 (m, $-$OCH, 1H), 6.65 (s, HC=CH, 1H), 6.92 (d, $-$ph, 2H), 7.16 (s, $-$ph, 2H), 7.91 (d, $-$ph, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.04, 19.63, 22.61, 25.43, 25.78, 29.21, 29.32, 30.27, 31.56, 31.74, 36.32, 69.38, 73.58, 74.11, 91.91, 105.91, 115.17, 127.47, 129.18, 130.66, 142.15, 152.92, 161.99, 184.75, 18491. IR (neat): 2927.3, 2855.9, 1602.9 (C=O), 1491.4, 1466.0, 1254.0, 1115.4 cm^{-1}.

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