DOI: 10.1002/chem.200700285

Choline-Derivative-Based Ionic Liquids

Juliusz Pernak,*[a] Anna Syguda,[a] Ilona Mirska,[c] Anna Pernak,[c] Jan Nawrot,[d] Aleksandra Prądzyńska,[d] Scott T. Griffin,[b] and Robin D. Rogers*[b]

Abstract: A total of sixty-three choline derivative-based ionic liquids in the forms of chlorides, acesulfamates, and bis(trifluoromethylsulfonyl)imides have been prepared and their physical properties (density, viscosity, solubility, and thermal stability) have been determined. Thirteen of these salts are known chlorides: precursors to the 26 water-soluble acesulfamates, 12 acesulfamates only partially miscible with water, and 12 water-insoluble imides. The crystal structures for two of the chloride salts—(2-hydroxyethyl)dimethylundecyloxymethylammonium chloride and cyclododecyloxymethyl(2-hydroxyethyl)dimethylammonium chloride—were determined. The antimicrobial (cocci, rods, and fungi) activities of the new hydrophilic acesulfamate-based ILs were measured and 12 were found to be active. The alkoxymethyl(2-hydroxyethyl)dimethylammonium acesulfamates have been shown to be insect feeding deterrents and thus open up a new generation of synthetic deterrents based on ionic liquids. The alkoxymethyl(2-decanoyloxyethyl)dimethylammonium bis(trifluoromethylsulfonyl)imides have also been shown to act as fixatives for soft tissues and can furthermore be used as substitutes for formalin and also preservatives for blood.

Keywords: blood preservation · choline derivatives · green chemistry · insect feeding deterrents · ionic liquids

Introduction

Ionic liquids (ILs)[1,2] are a class of liquids comprised entirely of ions, which have low melting points, typically lower than 100 °C, often have broad liquidus ranges and low vapor pressures, and may be noncoordinating and highly polar. Properties of ILs—such as density, melting point, viscosity, or solubility in water or other molecular solvents—can be fine-tuned by changing either the anion or cation.[3] These compounds offer unique environments for chemistry and can be used to enhance the efficiencies of a wide range of electrochemical, analytical, synthetic, and engineering processes.[4] ILs have even been used as tools in embalming and tissue preservation in histopathological diagnosis.[5,6]

Quaternary ammonium salts (quats), or inverted soaps, are well known cationic surfactants. They each contain at least one or two long (eight or more carbon atoms) alkyl chains and retain their cationic character at any pH. Particular properties of quats—surface activity, adsorption onto negatively charged solids, and biocidal activity—have commercial significance and provide the basis for their widespread use.[7–10] Quats play important roles in living processes, serving as precursors for the synthesis of vitamins (e.g., vitamin B complexes and thiamine), enzymes that participate in carbohydrate metabolism, and choline.[11,12] Choline is essential for normal functioning of all cells, and elaborate regulatory mechanisms to control its biosynthesis and hydrolysis exist.[11] In addition, choline hydroxide has been used as a basic catalyst for aldol condensation reactions.[13]

Choline derivatives with low melting points have been the subjects of many studies, and several quat analogues of choline have already been prepared.[14–20] Mixtures of $[Me_3NC_2H_4Y][Cl]$ (Y = OH, Cl, OC(O)Me, OC(O)Ph) and MCl_2 (M = Zn, Sn) yield viscous liquids that conduct at or around room temperature.[18,21] Low-melting eutectic mixtures based on choline chloride and zinc chloride have been used as alternatives to the more commonly employed alkyl-

[a] Prof. J. Pernak, Dr. A. Syguda
Poznań University of Technology, Poznań (Poland)
Fax: (+61) 665-3649
E-mail: juliusz.pernak@put.poznan.pl

[b] Dr. S. T. Griffin, Prof. R. D. Rogers
Department of Chemistry and Center for Green Manufacturing
The University of Alabama, Tuscaloosa, AL 35487 (USA)
Fax: (+1) 205-348-0823
E-mail: RDRogers@bama.ua.edu

[c] Dr. I. Mirska, A. Pernak
University of Medical Sciences in Poznań (Poland)

[d] Prof. J. Nawrot, Dr. A. Prądzyńska
Plant Protection Institute, Poznań (Poland)

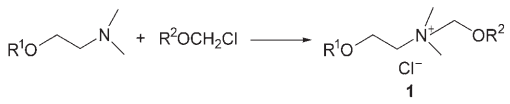
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

imidazolium/aluminium chloride ILs,[21] and have been found to be effective for carrying out *O*-acetylation reactions on a number of monosaccharides and cellulose.[19] Alkyl(2-hydroxyethyl)dimethylammonium bromides, as precursors of ILs, have also been prepared,[22] and their thermodynamic properties and partition coefficients in octan-1-ol/water binary system (log*P*) have been described, together with their solubilities in alcohols.[23] At close to ambient temperatures the vapor pressures of choline-derived ILs remain negligible, but during distillation the cholinium cation shows signs of decomposition.[24]

Here we wish to report the straightforward synthesis and multifunctional properties of novel choline derivative-based ionic liquids coupled with ammonium acesulfamate and bis(trifluoromethylsulfonyl)imide anions. Deanol, an economical commercially available compound marketed as a dietary supplement, was utilized as a cheap source of starting material.[25] Acesulfamates are nonvolatile antielectrostatic agents and noncaloric sugar substitutes, and we have successfully demonstrated their use as insect feeding deterrents. In this study we therefore sought to combine the chemical and biological properties of the cations with those of the anions and here we present the synthesis, characterization, and application of 50 new salts containing choline derivative-based cations paired with acesulfamate and bis(trifluoromethylsulfonyl)imide anions, together with 13 chloride precursors.

Results and Discussion

Synthesis and characterization: Three homologous series of chloride salts were prepared by nucleophilic substitution reactions of deanol, or its esters, with alkyl chloromethyl ethers containing two to 12 carbons in the alkoxy group under anhydrous conditions (Scheme 1). The first step in the



1

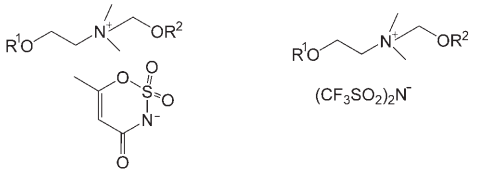
Scheme 1.

synthesis proceeded through a specific type of Menschutkin reaction involving an S_N1 mechanism, giving very high yields (95–97%) of the alkoxymethyl(2-hydroxyethyl)dimethylammonium chlorides listed in Table 1. The second step of the synthesis involves the metathesis of the chlorides either with the potassium salt of acesulfamate (K[Ace]) or with lithium bis(trifluoromethylsulfonyl)imide (Li[NTf_2]). (Potassium acesulfamate was chosen in the reaction as it is routinely used as a popular noncaloric sugar substitute.[26] Li[NTf_2] was chosen in the hope of preparing hydrophobic derivatives.) The ion-exchange reactions proceeded efficiently in distilled water, with yields greater than 75% for

Table 1. Alkoxymethyl(2-hydroxyethyl)dimethylammonium chlorides (**1**).

Chloride	R^1	R^2	Yield [%]
1a	H	C_2H_5	93
1b	H	C_3H_7	90
1c	H	C_4H_9	89
1d	H	C_5H_{11}	90
1e	H	C_6H_{13}	90.5
1f	H	C_7H_{15}	89
1g	H	C_8H_{17}	94
1h	H	C_9H_{19}	86
1i	H	$C_{10}H_{21}$	88
1j	H	$C_{11}H_{23}$	87.5
1k	H	$C_{12}H_{25}$	88
1l	H	$C_{14}H_{29}$	90
1m	H	c-$C_{12}H_{23}$	90

$[Ace]^-$ salts and of 85–99% for $[NTf_2]^-$ salts. The structures of these new choline derivatives are presented in Scheme 2.



Scheme 2. **2**: R^1 = H, R^2 = from C_2H_5 to $C_{14}H_{29}$ and $C_{12}H_{23}$; **3**: R^1 = Ac, R^2 = from C_2H_5 to $C_{14}H_{29}$ and *c*-$C_{12}H_{23}$. **4** and **5**: $R^1 = C_9H_{19}$, R^2 = from C_2H_5 to $C_{12}H_{25}$ and *c*-$C_{12}H_{23}$.

The $[Ace]^-$ salts **2** and **3** were water-miscible at room temperature and were also soluble in acetone, ethyl acetate, toluene, chloroform, methanol, butanol, and dichloromethane, but were insoluble in hexane or diethyl ether. However, $[Ace]^-$ salts **4** were only partially miscible with water and hexane but showed high solubility in chloroform. Tables 2–4 list 38 $[Ace]^-$ salts (**2**–**4**), including 20 that act as room tem-

Table 2. Analytical data for alkoxymethyl(2-hydroxyethyl)dimethylammonium acesulfamates (**2**).

IL	R^1	R^2	Yield [%]	m.p. [°C]	S_{cont}[a] [%]	ρ[b] [g mL^{-1}]	T_d [°C]
2a	H	C_2H_5	88	liquid	–	1.277	126.5
2b	H	C_3H_7	99	liquid	–	1.252	126.5
2c	H	C_4H_9	76	liquid	–	1.225	126.5
2d	H	C_5H_{11}	73	liquid	–	1.211	126.5
2e	H	C_6H_{13}	82	liquid	–	1.194	126.5
2f	H	C_7H_{15}	78	liquid	–	1.181	126.5
2g	H	C_8H_{17}	79	liquid	96	1.160	126.5
2h	H	C_9H_{19}	76	liquid	98	1.134	126.5
2i	H	$C_{10}H_{21}$	75	liquid	97	1.103	126.5
2j	H	$C_{11}H_{23}$	87	34–34.5	99.5	–	–
2k	H	$C_{12}H_{25}$	83	36–36.5	98	–	–
2l	H	$C_{14}H_{29}$	89	31–31.5	99	–	–
2m	H	c-$C_{12}H_{23}$	75	82–84	98.5		–

[a] Surfactant content. [b] At 25 °C.

Table 3. Analytical data for (2-acetoxyethyl)alkoxymethyldimethylammonium acesulfamates (**3**).

IL	R^1	R^2	Yield [%]	m.p. [°C]	S_{cont}[a] [%]	ρ[b] [g mL^{-1}]	T_d [°C]
3a	Ac	C_2H_5	89	liquid	–	1.270	122
3b	Ac	C_3H_7	87	liquid	–	1.242	122
3c	Ac	C_4H_9	91	liquid	–	1.213	122
3d	Ac	C_5H_{11}	78	liquid	–	1.202	122
3e	Ac	C_6H_{13}	82	liquid	–	1.183	122
3f	Ac	C_7H_{15}	68	liquid	93	1.159	122
3g	Ac	C_8H_{17}	77	liquid	94	1.145	122
3h	Ac	C_9H_{19}	76	liquid	95	1.123	122
3i	Ac	$C_{10}H_{21}$	75	liquid	98	1.080	122
3j	Ac	$C_{11}H_{23}$	78	liquid	99.5	1.065	122
3k	Ac	$C_{12}H_{25}$	73	liquid	99	1.041	122
3l	Ac	$C_{14}H_{29}$	78	oil	99	–	–
3m	Ac	c-$C_{12}H_{23}$	75	85–86	98	–	–

[a] Surfactant content. [b] At 25 °C.

Table 4. Analytical data for alkoxymethyl(2-decanoyloxyethyl)dimethylammonium acesulfamates (**4**).

IL	R^1	R^2	Yield [%]	m.p. [°C]	S_{cont}[a] [%]
4a	$C_9H_{19}CO$	C_2H_5	79	oil	90
4b	$C_9H_{19}CO$	C_3H_7	83	oil	91
4c	$C_9H_{19}CO$	C_4H_9	80	oil	90
4d	$C_9H_{19}CO$	C_5H_{11}	78	oil	92
4e	$C_9H_{19}CO$	C_6H_{13}	98	oil	91
4f	$C_9H_{19}CO$	C_7H_{15}	96	oil	97
4g	$C_9H_{19}CO$	C_8H_{17}	87	oil	95
4h	$C_9H_{19}CO$	C_9H_{19}	86	oil	99
4i	$C_9H_{19}CO$	$C_{10}H_{21}$	87	oil	98.5
4j	$C_9H_{19}CO$	$C_{11}H_{23}$	85	oil	99.5
4k	$C_9H_{19}CO$	$C_{12}H_{25}$	88	oil	99
4l	$C_9H_{19}CO$	c-$C_{12}H_{23}$	77	87–88	99.5

[a] Surfactant content.

perature ionic liquids (RTILs). The remaining salts were either crystalline solids or highly viscous oils.

In aqueous solutions, the surfactant contents of the $[Ace]^-$ salts **2**–**4** could be assayed by a direct two-phase back-titration technique (EN ISO 2871-2: 1990)[27] and ranged from 90 to 99.5%. The remainder was essentially water. The determinations could be conducted only for the $[Ace]^-$ salts with appropriately long R^2 substituents: in the case of compounds **2**, R^2 had to contain more than seven carbon atoms, for **3**, R^2 had to contain more than six carbons, while for **4**, R^2 had no restrictions. The surface activities of the salts depended upon the lengths of the R^1 and R^2 substituents.

At room temperature, the isolated $[NTf_2]^-$ salts (**5**) are hydrophobic liquids and these RTILs are presented in Table 5. They were characterized as colorless, nonflammable liquids, miscible with chloroform, dichloromethane, acetone, DMF, THF, ethyl acetate, and low-molecular weight alcohols, but insoluble in hexane, diethyl ether, and water. All of the prepared ILs **5** are stable in air and when in contact with water.

Anhydrous forms of the $[Ace]^-$ and $[NTf_2]^-$ salts were obtained by heating the samples at 50 °C in vacuum (8 mm Hg) for 24 h. Karl–Fisher measurements showed the water contents of these dried $[Ace]^-$ and $[NTf_2]^-$ salts to be less than 600 and 500 ppm, respectively. The densities, viscosities, and thermal degradation temperatures of the anhydrous ILs were measured and are presented in Tables 2, 3, and 5. All the prepared liquids were denser than water and, as a general rule, became less dense with increasing size of the alkoxy group. The relationships between the density and the number of carbon atoms in the alkoxy groups are approximately linear. $[Ace]^-$ salts **2** and **3** are highly viscous liquids (>1000 mPa s), while the viscosities of the $[NTf_2]^-$ salts **5** are considerably lower, between 213 and 315 mPa s (Table 5).

Table 5. Analytical data for alkoxymethyl(2-decanoyloxyethyl)dimethylammonium bis(trifluoromethylsulfonyl)imides (**5**).

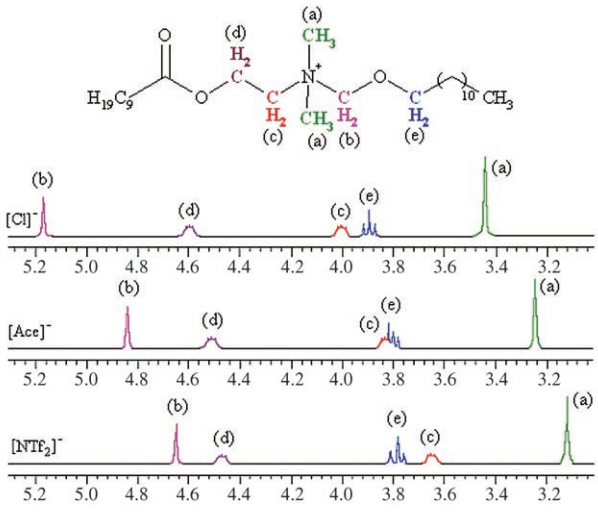
IL	R^1	R^2	Yield [%]	m.p. [°C]	ρ[a] [g mL^{-1}]	Viscosity[a] [mPa s]	T_d [°C]
5a	$C_9H_{19}CO$	C_2H_5	99	liquid	1.226	213	180.5
5b	$C_9H_{19}CO$	C_3H_7	86	liquid	1.211	221	180.5
5c	$C_9H_{19}CO$	C_4H_9	89	liquid	1.198	222	180.5
5d	$C_9H_{19}CO$	C_5H_{11}	99	liquid	1.186	226	180.5
5e	$C_9H_{19}CO$	C_6H_{13}	82	liquid	1.179	232	180.5
5f	$C_9H_{19}CO$	C_7H_{15}	91	liquid	1.174	242	180.5
5g	$C_9H_{19}CO$	C_8H_{17}	85	liquid	1.167	256	180.5
5h	$C_9H_{19}CO$	C_9H_{19}	96	liquid	1.165	269	180.5
5i	$C_9H_{19}CO$	$C_{10}H_{21}$	87	liquid	1.156	281	180.5
5j	$C_9H_{19}CO$	$C_{11}H_{23}$	99.5	liquid	1.149	297	180.5
5k	$C_9H_{19}CO$	$C_{12}H_{25}$	80	25–25.5	1.146	315	180.5
5l	$C_9H_{19}CO$	c-$C_{12}H_{23}$	98	liquid	1.194	>1000	180.5

[a] At 25 °C.

The RTILs in this study all have no distinguishable vapor pressure, although no quantitative study of this was performed. The established decomposition onset temperatures (T_ds), taken as the first thermal event detectable on TGA analysis upon heating, are presented in Tables 2, 3, and 5. The thermal stabilities were found to be dependent upon the type of anion, with the $[NTf_2]^-$ salts having slightly higher stabilities. The DSC thermograms of the RTILs **3b**, **3d**, **3h**, **3j**, **5b**, **5d**, and **5h** each exhibited a single thermal event. All formed glasses, the glass transition temperatures (T_gs) being low (for example: **3d** $T_g = -49$ °C, for **5d** $T_g = -37$ °C).

The synthesized salts were characterized by ^{1}H and ^{13}C NMR analyses and by CHN elemental analysis. Comparison of the ^{1}H NMR spectra of the chloride salts with those of their $[Ace]^-$ and $[NTf_2]^-$ counterparts indicated differences in several of the proton chemical shifts, as presented in Figure 1. These shifts were observed for the ten protons localized adjacent to the quaternary nitrogen atom and for the protons of two of the CH_2 groups ($CH_2CH_2NCH_2OCH_2$). The substitution of a small anion $[Cl]^-$ for a large one $[NTf_2]^-$ resulted in proton signal shifts of as much as 0.53 ppm. The ^{13}C NMR spectra of these salts indicated no significant variation in the carbon signal shifts.

Crystal structures: The crystal structures of two of the chloride salts—(2-hydroxyethyl)dimethylundecyloxymethylam-



No.	Group	$[Cl]^-$	$[Ace]^-$	$[NTf_2]^-$
a	$N(CH_3)_2$	3.45 (*s*)	3.25 (*s*)	3.12 (*s*)
b	CH_2	5.17 (*s*)	4.84 (*s*)	4.65 (*s*)
c	CH_2	4.01 (t, $J=4.8$)	3.82 (t, $J=4.8$)	3.65 (t, $J=4.8$)
d	CH_2	4.55 (t, $J=4.8$)	4.51 (t, $J=4.8$)	4.47 (t, $J=4.8$)
e	CH_2	3.89 (t, $J=6.6$)	3.80 (t, $J=6.6$)	3.79 (t, $J=6.6$)

In $CDCl_3$; s – singlet; t – triplet; J in Hz.

Figure 1. Chemical shifts in proton signals.

monium chloride (**1j**) and cyclododecyloxymethyl(2-hydroxyethyl)dimethylammonium chloride (**1m**)—were determined

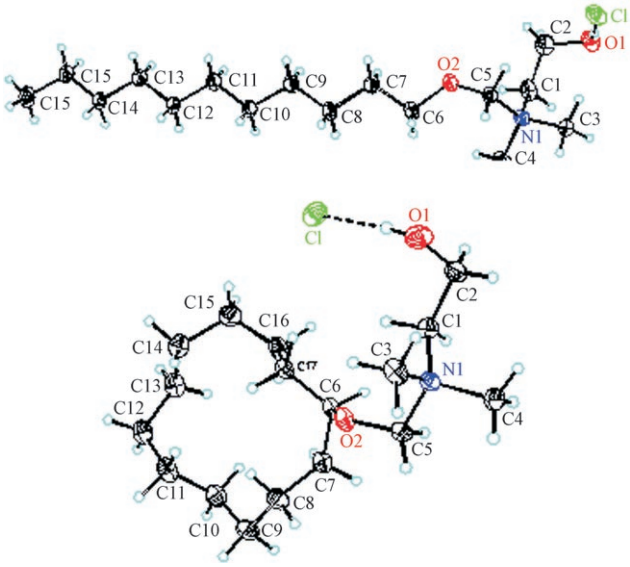


Figure 2. ORTEP illustrations of the asymmetric units observed for **1j** (top) and **1m** (bottom); ellipsoids are drawn at the 50% probability level.

(Figure 2). They both display similar packing modes (Figure 3), exhibiting double layers, with the individual cations packed in head-to-head arrangements, although in **1j** the long alkyl chains interdigitate while the cyclic alkyl groups in **1m** do not. The head-to-head orientations generate hydrophobic regions created by the aliphatic tail groups

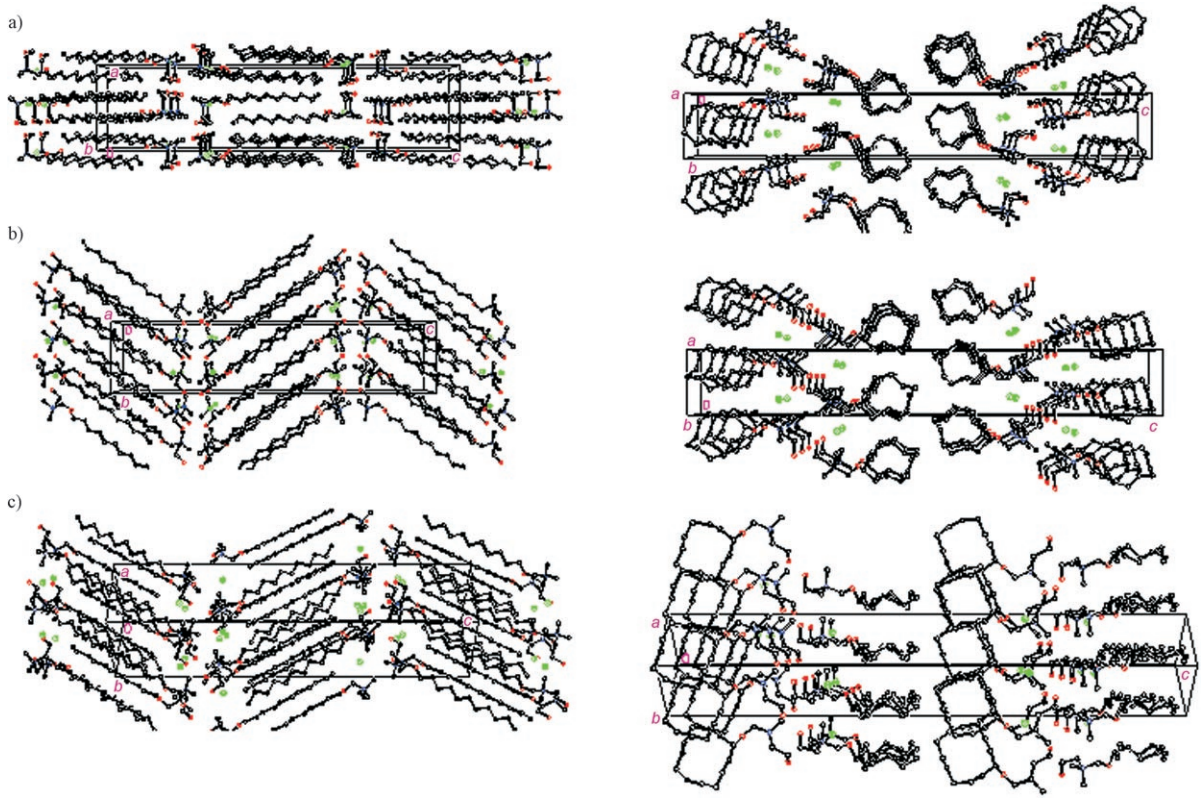


Figure 3. Packing diagrams for **1j** (left) and **1m** (right) viewed down a) the *a* axis, b) the *b* axis, and c) the *ab* diagonal.

separated by hydrophilic regions created by the polar choline end groups and the anions.

Each structure exhibits strong hydroxyl hydrogen to chloride hydrogen bonds (H···Cl and O–H···Cl = 2.18(3) Å, 174(3)° in **1j** and 2.10(3) Å, 177(2)° in **1m**), as well as close contact interactions within hydrophobic layers (same layer orientation) and across the hydrophilic region (connecting bilayers). The layers are connected by a hydrogen bond network with the chloride anions.

The first carbon atom in the undecyloxymethyl chain of **1j** is in a *gauche* position relative to the N-C-C-OH head group, followed by a kink around the hetero oxygen atom (N1-C5-O2-C6 and C5-O2-C6-C7 torsion angles of 100.8(2) and 158.7(2)°, respectively), while the rest of the long undecyloxymethyl tail adopts a linear all-*trans* configuration. The tail axes are all packed parallel to each other within each hydrophobic region, with adjacent hydrophobic regions orientated approximately 72° from each other and creating a zigzag pattern (Figure 3b, left).

The cyclododecane ring in **1m** has a slightly distorted D_4 symmetry. The fourfold axis is perpendicular to the ring plane and the two twofold axes lie within the plane (at the bisection the carbon-carbon bonds of C7–C8 to C13–C14 and C10–C11 to C16–C17). The torsion angles around the ring, beginning with C6-C7-C8-C9 followed by C7-C8-C9-C10, and others, follows the pattern $ag^-g^-ag^-g^-ag^-g^-ag^-g^-$, where $a = anti \approx 180°$ and $g^- = gauche^- \approx -60°$), in a pattern similar to those seen in other cyclododecane ring structures.[28] The head-to-head packing arrangement creates hydrophilic and hydrophobic regions similar to those in **1j**, also creating a zigzag pattern between regions; also note the orientations of the ring planes facing each other within the hydrophobic region (Figure 3c, right). The angles between the least-squares planes of opposing cyclododecyl rings are approximately 90°. This orientation and the bulkiness of the cyclododecyl rings in relation to the linear undecyloxymethyl tails in **1j** discourages the rings from interdigitation as observed in **1m** above.

Antielectrostatic properties: The antielectrostatic properties of a substance are based on two quantities: the surface resistance (R_s [Ω]) and the half-charge decay time ($\tau_{1/2}$ [s]) and are ranked according to the criteria listed in Table 6,[29] while the surface resistance and half-decay times for 55 of the prepared salts are presented in Table 7. The antielectrostatic properties depend on the R^1 substituent. For the chlorides and the $[Ace]^-$ salts with $R^1 = H$ (**2**), excellent effects were observed for only eight of the 22 compounds: those with a large R^2 group (i.e., nine, ten, 11, and 12 carbon atoms in the alkoxy group). On the other hand, for the $[Ace]^-$ salts with $R^1 = Ac$ (**3**), or for the decanoyloxyethyl $[Ace]^-$ salts (**4**) and the $[NTf_2]^-$ salts (**5**), all of the 33 compounds tested showed excellent activity over a wide range of R^2, with alkoxy group sizes ranging from two to 12

Table 6. Criteria for the estimation of antielectrostatic effects based on the surface resistances R_s [Ω] and half-charge decay times $\tau_{1/2}$ [s].

log R_s	$\tau_{1/2}$	Antielectrostatic effect
< 9	< 0.5	excellent
9–9.9	0.51–2	very good
10–10.9	2.1–10	good
11–11.9	10.1–100	sufficient
12–12.9	> 100	insufficient
≥ 13	> 600	lack of antielectrostatic properties

Table 7. Antielectrostatic effects: surface resistances R_s [Ω] and half-charge decay times [$\tau_{1/2}$; s].

Salt	log R_s	$\tau_{1/2}$	Effect
1a	> 13	> 600	lack
1b	> 13	> 600	lack
1c	13	> 100	insufficient
1d	12.5	> 100	insufficient
1e	12.5	> 100	insufficient
1f	10	2.1	good
1g	9.3	0.5	very good
1h	8.7	0.25	excellent
1i	8	0.13	excellent
1j	8.6	0.18	excellent
1k	8.3	0.25	excellent
2a	> 13	> 600	lack
2b	> 13	> 600	lack
2c	12.8	> 100	insufficient
2d	12.7	> 100	insufficient
2e	12.3	> 100	insufficient
2f	12.6	> 100	insufficient
2g	9.5	1.5	very good
2h	8.8	0.23	excellent
2i	8.5	0.43	excellent
2j	8.3	0.18	excellent
2k	8.8	0.25	excellent
3a	8.3	0.2	excellent
3b	8.3	0.15	excellent
3c	8.3	0.25	excellent
3d	8.6	0.23	excellent
3e	8	0.2	excellent
3f	7.9	0.15	excellent
3g	8.3	0.2	excellent
3h	8.5	0.23	excellent
3i	8.8	0.2	excellent
3j	8.8	0.18	excellent
3k	8	0.18	excellent
4a	8.3	0.37	excellent
4b	9	0.4	excellent
4c	8	0.35	excellent
4d	7.6	0.4	excellent
4e	7.7	0.48	excellent
4f	7.8	0.2	excellent
4g	7.8	0.23	excellent
4h	7.9	0.15	excellent
4i	8	0.13	excellent
4j	7.9	0.18	excellent
4k	7.8	0.23	excellent
5a	8.3	0.37	excellent
5b	9.0	0.40	excellent
5c	8.0	0.35	excellent
5d	7.6	0.40	excellent
5e	7.7	0.48	excellent
5f	7.8	0.20	excellent
5g	7.8	0.23	excellent
5h	7.9	0.15	excellent
5i	8.0	0.13	excellent
5j	7.9	0.18	excellent
5k	7.8	0.23	excellent

carbon atoms. Substitution of the $[Ace]^-$ anion with the $[NTf_2]^-$ anion did not affect the antielectrostatic properties even though the hydrophobicity of the compound was altered.

The excellent activities obtained were similar to that of the known antistatic agent Catanac 609 (*N*-(3′-dodecyloxy-2′-hydroxypropyl)-*N*,*N*-bis(2-hydroxyethyl)methylammonium methanesulfate; $\log R_s = 8.48$ and $\tau_{1/2} = 0.25$ s). The results indicate that the antielectrostatic effect in the prepared salts with a small R^1 group strongly depends on the length of the alkoxymethyl substituent. On the other hand, a large R^1 substituent eliminates the need for a large length in the R^2 substituent. These results indicate that many of the prepared salts can be used as antistatic agents, reducing the propensities of materials to accumulate electrostatic charges.

Biological activities: Antimicrobial activities were estimated for the hydrophilic $[Ace]^-$ salt series **2** and **3**. Minimum inhibitory concentration (MIC) values and minimum bactericidal or fungicidal concentration (MBC) values are given in Table 8. Salts with alkoxy substituents containing two, three, four, or five carbon atoms were shown to be inactive against microbes, but compounds with six or more carbon atoms became active in this respect.

In order to visualize the antimicrobial activities of these salts better, the mean MIC and MBC values were established for 12 of the tested microbes and these results are shown in Figure 4. The shapes of the curves were similar in both tested series, with optimal activities occurring for the $[Ace]^-$ salts containing dodecyloxymethyl groups (**2k** and **3k**). The efficacies of **2k** and **3k** were low (but still high enough to be effective) in comparison with that of the widely used benzal-

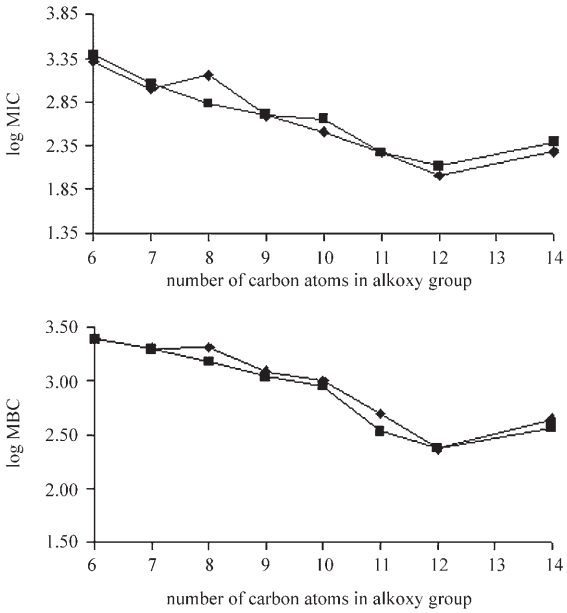


Figure 4. Mean MIC values (top) and MBC values (bottom) of acesulfamates (◆–**2**, ■–**3**) for microorganisms.

Table 8. MIC and MBC values[a] for alkoxymethyl(2-hydroxyethyl)dimethylammonium acesulfamates (**2g–l**), (2-acetoxyethyl)alkoxymethyldimethylammonium acesulfamates (**3g–l**), and of BAC.

		Acesulfamates												
Strain		**2g**	**2h**	**2i**	**2j**	**2k**	**2l**	**3g**	**3h**	**3i**	**3j**	**3k**	**3l**	**BAC**[b]
cocci														
M. luteus	MIC	317	153	74	37	18	33	71	69	67	33	16	31	7
	MBC	634	306	148	72	36	65	286	277	135	131	63	120	11
S. epidermidis	MIC	634	153	74	72	36	65	71	69	67	65	32	60	3
	MBC	1267	306	148	143	69	131	1145	555	269	131	63	120	3
S. aureus	MIC	317	153	148	72	26	65	143	139	67	65	32	60	7
	MBC	1267	1224	592	286	69	131	573	555	538	261	127	240	7
S. aureus MRSA	MIC	634	306	148	72	36	65	143	139	67	65	32	60	7
	MBC	1267	1224	296	143	69	131	1145	555	538	261	127	240	11
E. hirae	MIC	1267	306	296	72	36	65	286	139	67	65	32	60	11
	MBC	2534	1224	1183	286	139	261	1145	555	538	261	127	240	22
rods														
E. coli	MIC	1267	306	296	143	69	131	573	277	269	131	32	60	7
	MBC	2534	1224	592	286	139	261	2290	1110	538	261	63	120	11
P. vulgaris	MIC	1267	612	296	286	139	261	1145	555	269	131	63	120	22
	MBC	2534	1224	592	573	277	522	2290	1110	1076	522	254	480	22
K. pneumoniae	MIC	2534	612	592	286	139	261	1145	555	538	261	127	240	11
	MBC	2534	1224	1183	1145	555	1044	2290	2219	1076	522	254	480	11
S. marcescens	MIC	2534	1224	592	286	277	522	1145	1110	1076	522	507	960	175
	MBC	2534	2447	2366	1145	555	1044	2290	2219	1076	522	507	960	175
P. aeruginosa	MIC	>2534	1224	592	573	277	255	2290	2219	2152	522	507	960	54
	MBC	>2534	>2447	2366	1145	555	1044	>2290	>2219	2152	522	1014	960	205
fungi														
C. albicans	MIC	2534	612	592	286	139	261	573	555	538	261	127	240	7
	MBC	>2534	1224	2366	573	277	522	1145	1110	2152	522	127	240	11
R. rubra	MIC	1267	306	148	72	36	65	573	277	269	131	63	120	11
	MBC	2534	612	296	143	69	130	1145	555	538	131	127	240	11

[a] In μM, the number of microorganisms in 1 mL ranged from 10^4 to 10^5. [b] Benzalkonium chloride.

konium chloride (**BAC**)—a mixture of alkylbenzyldimethylammonium chlorides of the general formula $C_6H_5CH_2N(CH_3)_2RCl$; R = an alkyl group no shorter than n-C_8H_{17} and no longer than n-$C_{18}H_{37}$)—for which the calculated mean values are well established (log MIC = 1.43 and log MBC = 1.62).

No MIC and MBC values could be established for the $[Ace]^-$ salts **4** and $[NTf_2]^-$ salts **5**, because of their hydrophobic characters. As also shown in our previous studies,[30] high biological activities in ILs are primarily determined by the cations, the role of the anions being much less pronounced. It can therefore be surmised that the **4** and **5** series of salts should be active. It should be stressed that the most effective antimicrobial salts also demonstrate excellent antielectrostatic effects.

Insect feeding deterrent activities: The deterrent activities of the sweetener $[Ace]^-$ salts **2** and **3** toward *Tribolium confusum* (larvae and adults), *Sitophilus granarius* (adults), and *Trogoderma granarium* (larvae) are presented on the basis of the amount of food consumed. In all variants, the three deterrent coefficients were calculated as follows:

1) absolute coefficient of deterrency, calculated from the no-choice test:

$$A = (CC-TT)/(CC+TT)\ 100$$

2) relative coefficient of deterrency, calculated from the choice test:

$$R = (C-T)/(C+T)$$

3) total coefficient of deterrency:

$$T = A+R$$

where C and CC are the amount of food consumed from the control discs, and T and TT are the amount of food consumed that has been treated with the tested ILs.

The deterrent activities were estimated by the criteria listed in Table 9 and described earlier.[31] In addition, Tables 10–13 list the relative, absolute, and total coefficients with the natural deterrent azadirachtin, treated as a standard. Azadirachtin (tetranortriterpinoid) was isolated from the seeds of the neem tree *Azadirachta indica* A. Juss., *Meliaceae* and the chinaberry tree *Melia azadirachta* L. The antifeedant activity of this natural product was described previously by Gill and Lewis.[32] In general, our results show that the $[Ace]^-$ salts **2**, each containing a hydroxy group, are more active than the $[Ace]^-$ salts **3**, each containing an acetyl group. In comparison with the standard, the $[Ace]^-$ salts **2** are active deterrents against *Tribolium confusum* (beetles) and *Trogoderma granarium* (larvae). Their efficacy corresponded to that of the standard, or in three cases proved to be even higher (Table 11: ILs **2g**, **2h**, and **2j**).

Table 9. Criteria for the estimation of the deterrent activity based on the total coefficient.[31]

Total coefficient	Deterrent activity
200–151	very good
150–101	good
100–51	medium
50–0	weak

Table 10. Feeding deterrent activities of alkoxymethyl(2-hydroxyethyl)dimethylammonium and (2-acetoxyethyl)alkoxymethyldimethylammonium acesulfamates against adults of *Sitophilus granarius* (beetles).

IL	Relative coefficient	Absolute coefficient	Total coefficient	Deterrent activity
2a	77.3	−26.0	51.3	medium
2b	80.1	34.3	114.4	good
2c	82.6	−0.9	81.8	medium
2d	86.1	−16.1	70.0	medium
2e	71.6	4.0	75.6	medium
2f	96.6	14.1	110.8	good
2g	93.6	13.4	107.0	good
2h	89.0	−17.8	71.2	medium
2i	90.9	−21.3	69.6	medium
2j	95.2	−10.1	85.1	medium
2k	94.8	−13.1	81.6	medium
2m	82.4	23.9	106.3	good
3a	90.1	−7.8	82.2	medium
3b	96.9	−2.2	94.7	medium
3c	96.7	−9.4	87.4	medium
3d	96.7	4.1	100.8	medium
3e	95.3	−7.1	88.2	medium
3f	82.2	−27.4	54.9	medium
3g	96.9	−8.9	88.0	medium
3h	97.7	−24.3	73.5	medium
3i	98.1	−18.9	79.2	medium
3j	73.6	−14.3	59.3	medium
3k	95.6	−5.7	89.8	medium
3m	77.9	16.7	94.6	medium
azadirachtin[a]	100.0	74.3	174.3	very good
$LSD_{0.05}$[b]	27.0	43.9	49.8	–

[a] Natural deterrent. [b] The least significant differences at the 5% level of significance.

Figures 5–8 present the feeding deterrent relationships as the total coefficient versus the number of carbon atoms in the alkoxy group. The courses of the curves in Figure 5 and Figure 8 indicate that $[Ace]^-$ salts **2** manifest deterrent activity at satisfactory or lower levels toward *Sitophilus granarius* (beetles) and *Tribolium confusum* (larvae). On the other hand, in cases of high deterrent activities (Figures 6 and 7), the total coefficient is related to the presence of an even or odd number of carbon atoms in the alkoxy group. $[Ace]^-$ salts can be regarded as two sets: those with an even number of carbon atoms, in which **2g** showed maximum activity against *Trogoderma granarium* (larvae) and *Tribolium confusum* (beetles), and those with an odd number, in which **2h** and **2j** are the most active against *Trogoderma granarium* (larvae) and *Tribolium confusum* (beetles), respectively. The differences in efficacy linked to even/odd numbers of

Table 11. Feeding deterrent activities of alkoxymethyl(2-hydroxyethyl)dimethylammonium and (2-acetoxyethyl)alkoxymethyldimethylammonium acesulfamates against larvae of *Trogoderma granarium* (larvae).

IL	Relative coefficient	Absolute coefficient	Total coefficient	Deterrent activity
2a	80.2	27.2	107.4	good
2b	84.4	21.0	105.4	good
2c	91.2	17.1	108.3	good
2d	85.1	40.2	125.3	good
2e	97.0	62.0	159.0	very good
2f	96.3	63.8	160.1	very good
2g	95.3	93.9	189.1	very good
2h	96.3	87.6	183.9	very good
2i	97.9	83.5	181.4	very good
2j	90.0	79.2	169.2	very good
2k	93.1	10.9	104.0	good
2m	94.6	73.2	167.9	very good
3a	20.2	3.7	23.9	weak
3b	56.4	19.8	76.2	medium
3c	80.5	−28.2	52.4	medium
3d	74.2	−15.9	58.3	medium
3e	95.6	0.8	96.5	medium
3f	71.7	−6.9	64.7	medium
3g	94.0	19.9	113.9	good
3h	90.8	33.8	124.6	good
3i	96.0	10.7	106.8	good
3j	71.2	11.1	82.4	medium
3k	95.5	68.2	163.7	very good
3m	72.7	7.5	80.2	medium
azadirachtin[a]	100.0	94.2	194.2	very good
$LSD_{0.05}$[b]	18.9	24.4	26.5	–

[a] Natural deterrent. [b] The least significant differences at the 5% level of significance.

Table 12. Feeding deterrent activities of alkoxymethyl(2-hydroxyethyl)dimethylammonium and (2-acetoxyethyl)alkoxymethyldimethylammonium acesulfamates against adults of *Tribolium confusum* (beetles).

IL	Relative coefficient	Absolute coefficient	Total coefficient	Deterrent activity
2a	26.5	−7.9	18.7	weak
2b	51.2	−9.1	42.1	weak
2c	94.0	−3.9	90.1	medium
2d	95.7	−6.0	89.6	medium
2e	96.7	30.7	127.4	good
2f	95.5	−4.5	91.0	medium
2g	95.8	94.7	190.5	very good
2h	95.3	92.2	187.5	very good
2i	93.6	79.5	173.1	very good
2j	95.0	94.7	189.6	very good
2k	94.6	80.7	175.3	very good
2m	94.7	72.4	167.1	very good
3a	59.5	23.8	83.3	medium
3b	74.5	14.2	88.8	medium
3c	78.9	9.3	88.2	medium
3d	96.9	19.5	116.4	good
3e	96.7	19.7	116.4	good
3f	95.6	36.5	132.1	good
3g	93.6	25.5	119.0	good
3h	96.7	33.9	130.6	good
3i	96.2	29.2	125.5	good
3j	96.5	38.3	134.8	good
3k	96.0	66.9	162.9	very good
3m	96.6	17.1	113.7	good
azadirachtin[a]	100.0	85.0	185.0	very good
$LSD_{0.05}$[b]	14.1	23.9	28.5	–

[a] Natural deterrent. [b] The least significant differences at the 5% level of significance.

Table 13. Feeding deterrent activities of alkoxymethyl(2-hydroxyethyl)dimethylammonium and (2-acetoxyethyl)alkoxymethyldimethylammonium acesulfamates against larvae of *Tribolium confusum* (larvae).

IL	Relative coefficient	Absolute coefficient	Total coefficient	Deterrent activity
2a	5.4	38.9	44.3	weak
2b	7.5	2.8	10.2	weak
2c	21.9	6.5	28.4	weak
2d	18.1	21.8	39.9	weak
2e	57.6	24.8	82.5	medium
2f	47.4	−10.6	36.7	weak
2g	98.1	−57.1	40.4	weak
2h	97.9	−11.9	86.0	medium
2i	89.0	−23.8	65.2	medium
2j	94.5	25.9	120.4	good
2k	97.7	−8.8	88.8	medium
2m	62.8	−56.0	6.8	weak
3a	56.3	9.4	65.7	medium
3b	54.9	1.4	56.2	medium
3c	16.5	10.4	26.9	weak
3d	86.0	0.7	86.7	medium
3e	74.7	7.9	82.6	medium
3f	63.4	21.9	85.3	medium
3g	90.4	26.3	116.7	good
3h	93.6	14.9	108.5	good
3i	92.3	17.8	110.1	good
3j	84.5	16.7	101.3	good
3k	97.5	59.4	156.9	very good
3m	92.0	17.6	109.5	good
azadirachtin[a]	100.0	88.4	188.4	very good
$LSD_{0.05}$[b]	59.9	39.0	80.1	–

[a] Natural deterrent. [b] The least significant differences at the 5% level of significance.

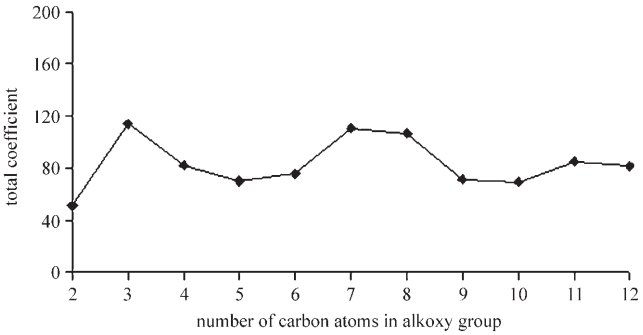


Figure 5. The deterrent activity for *Sitophilus granarius* (beetles): total coefficient as a function of the number of carbon atoms in the alkoxy groups in acesulfamates **2a**–**k**.

carbon atoms most probably result from interactions between physicochemical properties and biological activities.

Tissue and blood preservation: We tested the $[Ace]^-$ and $[NTf_2]^-$ salts for tissue (animal muscle—beef) preservation by a previously described procedure.[5,6] The $[Ace]^-$ salts proved unsuitable for fixation, while the $[NTf_2]^-$ salts proved to be very effective for tissue preservation in histopathological procedures, eliminating the requirement for formalin. The $[NTf_2]^-$ salt **4f** fixed the tissue but did not alter its structure, also preserving its elasticity and color.

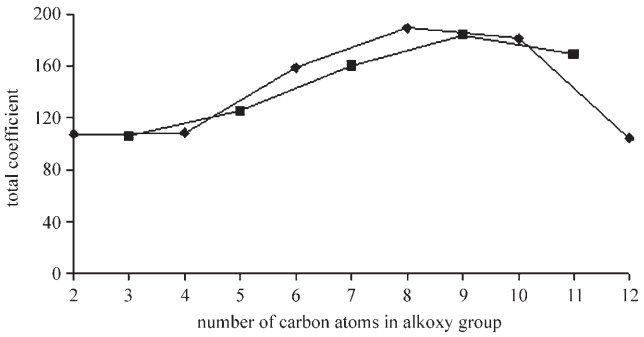


Figure 6. The deterrent activity for *Trogoderma granarium* (larvae): total coefficient as a function of the number of carbon atoms in the alkoxy groups of acesulfamates **2a**–**k**; odd vs even chain lengths are plotted separately.

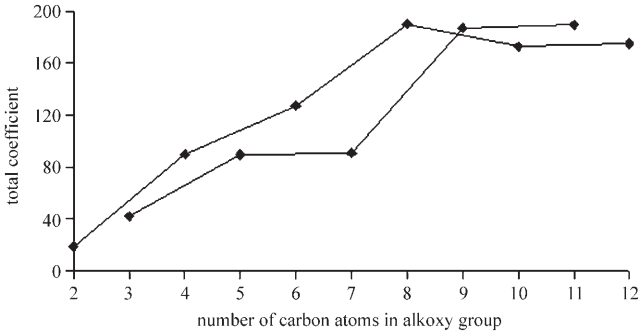


Figure 7. The deterrent activity for *Tribolium confusum* (beetles): total coefficient as a function of the number of carbon atoms in the alkoxy groups of acesulfamates **2a**–**k**; odd vs even chain lengths are plotted separately.

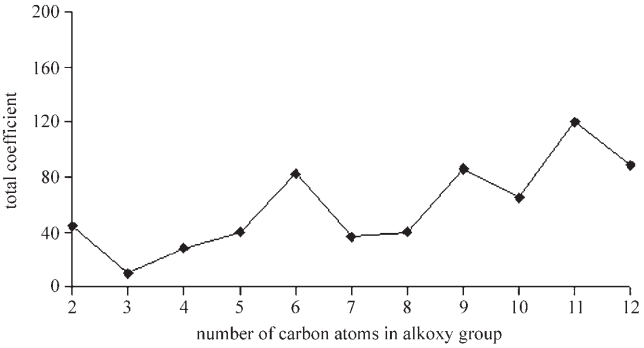


Figure 8. The deterrent activity for *Tribolium confusum* (larvae): total coefficient as a function of the number of carbon atoms in the alkoxy groups of acesulfamates **2a**–**k**.

The morphology of the tissues fixed in this IL was of higher quality than that of tissue fixed in formalin.

Since these studies had demonstrated that the $[NTf_2]^-$ salts fixed soft tissues, we decided to test whether ILs could be used in blood diagnosis. A literature survey on the subject produced no reports on fixation of blood with ILs. Our studies, performed on venous blood from a 50 year-old patient [blood group O Rh(−)], were carried out to determine the effect of the IL on the appearance of erythrocytes and the remaining blood morphotic elements under a light microscope.

After $[NTf_2]^-$ salt **4f** had been mixed with blood at a v/v ratio of 1:2, no significant alterations were observed in the macroscopic outlook of blood for the subsequent 12 h. The blood preserved its consistency and color and manifested no sedimentation. Smears were prepared and subjected to staining as described by May–Grünwald–Giemsa.[33] The pattern of blood fixed in the $[NTf_2]^-$ salt **4f** is presented in Figure 9. The sizes and shapes both of erythrocytes and of leukocytes remained normal. Moreover, light microscopy permitted monitoring of the remaining morphotic elements of the blood, such as thrombocytes, which manifested normal cellular characters. The fixed erythrocytes had not changed under microscopic examination, even after 10 months.

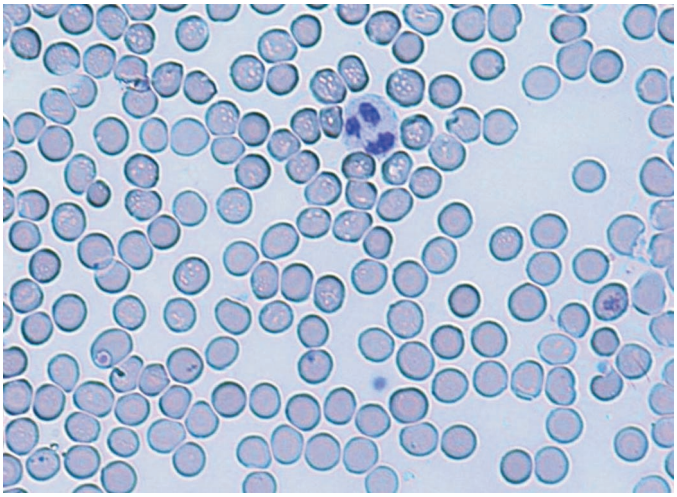


Figure 9. A blood smear showing erythrocytes and leucocytes stained by the May–Grünwald–Giemsa method (enlargement = 1000×).

Conclusion

A novel family of choline derivative-based ionic liquids has been prepared and characterized. The acesulfamate and bis(trifluoromethylsulfonyl)imide ILs are active against microbes, manifest excellent antielectrostatic effects, and have high deterrent activities. Together, the ILs prepared here include a wide range of hydrophobic to hydrophilic ILs. These preliminary studies also point to the suitability of these ILs as embalming fluid replacements and for tissue preservation. The alkoxymethyl(2-decanoylethyl)dimethylammonium bis(trifluoromethylsulfonyl)imides have abilities to fix soft tissues and can be regarded as substitutes for formalin.

Experimental Section

General: ^{1}H NMR spectra were recorded on a Mercury Gemini 300 spectrometer at 300 MHz with tetramethylsilane as the standard; ^{13}C NMR spectra were recorded on the same instrument at 75 MHz. CHN elemental analyses were performed at the Adam Mickiewicz University, Poznań, Poland. Satisfactory microanalyses were obtained: C ± 0.34, H ± 0.38, and N ± 0.29. Melting points were determined with a JA 9100 model electro-

thermal digital melting point apparatus. A Metter Toledo DA 110 M scale was used for the mass/density measurements, while a micro Ostwald viscometer was used for viscosity measurements. Thermal degradation temperatures were determined with a Büchi model B-545 automatic apparatus. Differential scanning calorimetry was carried out with a Perkin–Elmer DSC calibrated with a 99.9999 mol % purity indium sample.

General procedure for alkoxymethylation: Alkoxymethyl(2-hydroxyethyl)dimethylammonium, (2-acetoxyethyl)alkoxymethyldimethylammonium, and alkoxymethyl(2-decanoyloxyethyl)dimethylammonium compounds were prepared by a general alkoxymethylation method.[15–17] The appropriate amine (0.05 mol) was placed in anhydrous hexane (20 mL) and the chloromethyl alkyl ether (0.055 mol) was added at room temperature. The product immediately precipitated from the reaction mixture and was separated and washed with hexane. The resulting quaternary ammonium chlorides were crystallized either from acetone or from ethyl acetate.

Procedure for ion exchange: A saturated aqueous solution of K[Ace] or Li[NTf_2] was added to a stoichiometric amount of a saturated aqueous solution of the prepared quaternary ammonium chloride. The reaction mixture was stirred at room temperature for 2 h. For $[NTf_2]^-$ salts, after phase separation the aqueous phase was decanted and the product was washed with distilled water until chloride ions were no longer detectable with $AgNO_3$. For $[Ace]^-$ salts, water was removed under reduced pressure until constant weight. Anhydrous acetone was added to dissolve the product, the liquid was then filtered, and the acetone was evaporated. The products were dried for 10 h at 50 °C under vacuum (8 mmHg).

Butoxymethyl(2-hydroxyethyl)dimethylammonium acesulfamate (2c): ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (t, $J = 7.4$ Hz, 3H), 1.37 (sex, $J = 7.4$ Hz, 2H), 1.60 (q, $J = 7.0$ Hz, 2H), 2.05 (s, 3H), 3.17 (s, 6H), 3.56 (t, $J = 4.8$ Hz, 2H), 3.80 (t, $J = 6.5$ Hz, 2H), 4.05 (t, $J = 4.3$ Hz, 2H), 4.74 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 13.7$, 18.9, 19.9, 31.5, 49.2, 55.6, 62.8, 73.2, 91.3, 101.8, 161.6, 170.2 ppm; elemental analysis calcd (%) for $C_{13}H_{26}O_6SN_2$: C 46.12, H 7.76, N 8.20; found: C 46.45, H 7.52, N 8.58.

(2-Hydroxyethyl)dimethylundecyloxymethylammonium acesulfamate (2j): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.8$ Hz, 3H), 1.26 (m, 16H), 1.62 (q, $J = 6.9$ Hz, 2H), 2.05 (s, 3H), 3.18 (s, 6H), 3.59 (t, $J = 4.8$ Hz, 2H), 3.79 (t, $J = 6.5$ Hz, 2H), 4.08 (t, $J = 4.7$ Hz, 2H), 4.75 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 14.1$, 19.9, 22.7, 25.8, 29.31, 29.34, 29.52, 29.59, 29.60, 31.9, 48.4, 55.8, 63.0, 73.7, 91.5, 101.8, 161.6, 170.2 ppm; elemental analysis calcd (%) for $C_{20}H_{40}O_6SN_2$: C 55.00, H 9.25, N 6.42; found: C 55.35, H 9.57, N 6.28.

(2-Acetoxyethyl)heptyloxymethyldimethylammonium acesulfamate (3f): ^{1}H NMR ($CDCl_3$): $\delta = 0.89$ (t, $J = 6.7$ Hz, 3H), 1.29 (m, 8H), 1.63 (q, $J = 7.0$ Hz, 2H), 2.05 (s, 3H), 2.09 (s, 3H) 3.21 (s, 6H), 3.80 (t, $J = 6.6$ Hz, 2H), 3.82 (t, $J = 4.8$ Hz, 2H), 4.51 (t, $J = 4.7$ Hz, 2H), 4.79 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 14.0$, 19.9, 20.6, 22.5, 25.6, 28.8, 29.5, 31.6, 48.1, 57.4, 59.6, 73.7, 91.3, 101.8, 161.6, 169.7, 170.2 ppm; elemental analysis calcd (%) for $C_{18}H_{34}O_7SN_2$: C 51.15, H 8.13, N 6.63; found: C 51.01, H 8.22, N 6.85.

(2-Acetoxyethyl)dodecyloxymethyldimethylammonium acesulfamate (3k): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H), 1.26 (m, 18H), 1.62 (q, $J = 7.0$ Hz, 2H), 2.05 (s, 3H), 2.11 (s, 3H), 3.25 (s, 6H), 3.80 (t, $J = 6.6$ Hz, 2H), 3.82 (t, $J = 4.8$ Hz, 2H), 4.51 (t, $J = 4.8$ Hz, 2H), 4.84 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 14.1$, 19.9, 20.8, 22.6, 25.7, 29.29, 29.30, 29.49, 29.55, 29.56, 29.57, 29.60, 31.8, 48.0, 57.4, 59.5, 73.7, 91.2, 101.8, 161.6, 169.7, 170.2 ppm; elemental analysis calcd (%) for $C_{23}H_{44}O_7SN_2$: C 56.05, H 9.02, N 5.69; found: C 56.28, H 9.22, N 5.48.

(2-Decanoyloxyethyl)dimethylnonyloxymethylammonium acesulfamate (4h): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.5$ Hz, 6H), 1.27 (m, 24H), 1.60 (q, $J = 7.3$ Hz, 4H), 2.05 (s, 3H), 2.34 (t, $J = 7.7$ Hz, 2H) 3.23 (s, 6H), 3.78 (t, $J = 4.8$ Hz, 2H), 3.82 (t, $J = 6.7$ Hz, 2H), 4.51 (t, $J = 4.8$ Hz, 2H), 4.82 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 14.1$, 19.9, 22.6, 24.5, 25.7, 29.0, 29.2, 29.4, 29.5, 31.8, 33.9, 48.1, 57.3, 59.6, 73.7, 91.2, 101.8, 161.6, 170.2, 172.5 ppm; elemental analysis calcd (%) for $C_{28}H_{54}O_7SN_2$: C 59.74, H 9.69, N 4.98; found: C 59.87, H 9.42, N 4.88.

(2-Decanoyloxyethyl)dodecyloxymethyldimethylammonium acesulfamate (4k): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.5$ Hz, 6H), 1.26 (m, 30H), 1.63 (q, $J = 7.0$ Hz, 4H), 2.05 (s, 3H), 2.34 (t, $J = 7.7$ Hz, 2H) 3.25 (s, 6H), 3.80 (t, $J = 6.6$ Hz, 2H), 3.82 (t, $J = 4.8$ Hz, 2H), 4.51 (t, $J = 4.8$ Hz, 2H), 4.84 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 14.1$, 19.9, 22.6, 24.5, 25.6, 29.0, 29.1, 29.23, 29.25, 29.28, 29.35, 29.45, 29.49, 29.6, 31.6, 33.8, 48.1, 57.2, 59.6, 73.7, 91.1, 101.8, 161.6, 170.2, 172.7 ppm; elemental analysis calcd (%) for $C_{31}H_{60}O_7SN_2$: C 61.54, H 10.02, N 4.63; found: C 61.14, H 9.95, N 4.52.

(2-Decanoyloxyethyl)dimethylnonyloxymethylammonium bis(trifluoromethylsulfonyl)imide (5h): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.5$ Hz, 6H), 1.26 (m, 24H), 1.64 (q, $J = 7.3$ Hz, 4H), 2.10 (t, $J = 7.7$ Hz, 2H), 3.11 (s, 6H), 3.64 (t, $J = 4.8$ Hz, 2H), 3.79 (t, $J = 6.7$ Hz, 2H), 4.46 (t, $J = 4.8$ Hz, 2H), 4.63 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 14.0$, 22.6, 24.5, 25.6, 29.0, 29.2, 29.37, 29.39, 31.8, 33.8, 48.2, 56.9, 59.9, 73.9, 91.4, 113.2, 117.4, 121.7, 125.9, 172.6 ppm; elemental analysis calcd (%) for $C_{26}H_{50}O_7S_2N_2F_6$: C 45.85, H 7.42, N 4.11; found C 46.22, H 7.26, N 4.04.

(2-Decanoyloxyethyl)dodecyloxymethyldimethylammonium bis(trifluoromethylsulfonyl)imide (5k): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.5$ Hz, 6H), 1.26 (m, 30H), 1.63 (q, $J = 7.0$ Hz, 4H), 2.34 (t, $J = 7.7$ Hz, 2H) 3.12 (s, 6H), 3.65 (t, $J = 4.8$ Hz, 2H), 3.79 (t, $J = 6.6$ Hz, 2H), 4.47 (t, $J = 4.8$ Hz, 2H), 4.65 (s, 2H), 5.49 ppm (s, 1H); ^{13}C NMR: $\delta = 14.0$, 22.6, 24.5, 25.6, 29.0, 29.17, 29.21, 29.28, 29.33, 29.38, 29.44, 29.51, 29.6, 31.7, 33.8, 48.2, 56.9, 59.9, 73.9, 91.4, 113.2, 117.4, 121.7, 125.9, 172.7 ppm; elemental analysis calcd (%) for $C_{29}H_{56}O_7S_2N_2F_6$: C 48.17, H 7.82, N 3.88; found C 48.54, H 7.46, N 3.68.

X-ray crystallography: Data were collected on a Bruker CCD area detector-equipped diffractometer with graphite monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation and the structures were solved with the aid of the SHELXTL software package.[34] Absorption corrections were made with SADABS.[35] The structures were refined by full-matrix, least-squares on F^2. Data collection and structure refinement for crystals of **1j**[36] and **1m**[37] proceeded normally. The initial unit cell determination resulted in the orthorhombic space group *Pbca* for **1j** and $P2_12_12_1$ for **1m**. In each case the non-hydrogen atoms were readily located from the initial structure solution. The positions of all non-hydrogen atoms were anisotropically refined and all hydrogen atoms were located from the Fourier difference map and refined isotropically.

CCDC-628804 (**1j**) and -628805 (**1m**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Antielectrostatic properties: The antielectrostatic effects of $[Ace]^-$ and $[NTf_2]^-$ salts was measured on a polyethylene film (PE: LDPE II 003/GO) that did not contain any lubricants or antioxidants. The PE disks of diameter 0.125 m were washed in acetone and were then dried by placing them in an air-conditioned room. The disks were immersed for 60 s in chloroform solutions (0.5 %) of the salts to be tested and were then hung up so that the solvent could evaporate spontaneously. The discs were rubbed on their surfaces with cotton pads soaked with the solutions of the salts to ensure that the surface was covered thoroughly and were stored for 24 h in an air-conditioned room at a temperature of 20 °C and relative humidity of 65 %. Finally, the surface resistances and half-charge decay times on the film surfaces were examined. The measuring apparatus, the method of measurement, and the measurement conditions were described by Pernak et al.[29] The relative error in determination of two quantities did not exceed 5 %.

Antimicrobial activities: The following microorganisms were used: *Micrococcus luteus* ATCC 9341, *Staphylococcus epidermidis* ATCC 12228, *Staphylococcus aureus* ATCC 6538, *Staphylococcus aureus (MRSA)* ATCC 43300, *Enterococcus hirae* ATCC 10541, *Escherichia coli* ATCC 25922, *Proteus vulgaris* NCTC 4635, *Klebsiella pneumoniae* ATCC 4352, *Pseudomonas aureginosa* ATCC 27853, *Serratia marcescens* ATCC 8100, *Candida albicans* ATCC 10231, and *Rhodotorula rubra* PhB. The *Rhodotorula rubra* was obtained from the Department of Pharmaceutical Bacteriology, University of Medical Sciences, Poznań (Poland).

The antimicrobial activities of the compounds was determined by the tube dilution method in the Müller–Hinton broth medium for bacteria and in the Sabouraud broth medium for fungi. Suspensions of standard microorganisms at a concentration of 10^6 cfu mL^{-1} were prepared from

each culture. Serial twofold dilutions of a compound (2 mL) were inoculated with a standardized suspension of test microorganism to obtain a final concentration of $1–5\times10^5$ cfu mL^{-1}. Growth of the microorganism (or its lack) was determined visually after incubation for 24 h at 35 °C (bacteria) or 48 h at 22 °C (fungi). The lowest concentration at which there was no visible growth (turbidity) was taken as the minimal inhibitory concentration (MIC). Then, from each tube content, a sample (10 μL; calibrated loop) was smeared on an agar medium with inactives (0.3 % lecithin, 3 % polysorbate 80 and 0.1 % L-cysteine) and the system was incubated for 48 h at 35 °C (bacteria) or for 5 days at 22 °C (fungi). The lowest concentration of the substances to kill 99.9 % or more of the test organisms was defined as the minimum bactericidal (fungicidal) concentration (MBC).

Bioassays: The experiments were conducted with *Tribolium confusum* Duv. (larvae and adults), *Sitophilus granarius* L. (adults), and *Trogoderma granarium* Ev. (larvae). They came from laboratory colonies reared in a chamber maintained at 26 ± 1 °C and 60 ± 5 % relative humidity on wheat grain or whole-wheat meal diet.

Choice and no-choice tests for chewing insects were conducted by a previously described procedure.[31] Wheat wafer discs (1 cm in diameter × 1 mm thick) were saturated by dipping either in ethanol only (control) or in an ethanol solution (1 %) of the IL to be tested. After evaporation of the solvent (30 min of air-drying) the wafers were weighed and offered to the insects in plastic boxes as a sole food source for five days. Feeding of insects was recorded under three sets of conditions: a) on two control discs (*CC*), b) on a choice between one treated disc (*T*) and one control disc (*C*) (choice test), and c) on two treated discs (*TT*; no-choice test). Each of the three experiments was repeated five times with three adults of *Sitophilus granarius*, 20 adults and 10 larvae of *Tribolium confusum*, and 10 larvae of *Trogoderma granarium*. The number of individual insects depended on the intensity of their food consumption. Adults used for experiments were unsexed, 7–10 days old, and the larvae were 5–30 days old. After five days, the discs were reweighed and the average weight of eaten food was calculated.

Acknowledgements

This work was supported by Polish grant 3 T09B 053 29. Work at The University of Alabama was supported by the US Environmental Protection Agency's STAR program through grant number RD-83143201. (Although the research described in this article has been funded in part by EPA, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

[1] R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792–793.
[2] K. R. Seddon, *Nat. Mater.* **2003**, *2*, 363–365.
[3] M. Deetlefs, K. R. Seddon, M. Shara, *New J. Chem.* **2006**, *30*, 317–326.
[4] *Ionic Liquids III A/B: Fundamentals, Progress, Challenges, and Opportunities* (Eds.: R. D. Rogers, K. R. Seddon), *ACS Symp. Ser. 901/902*, American Chemical Society, Washington, DC, **2005**.
[5] P. Majewski, A. Pernak, M. Grzymisławski, K. Iwanik, J. Pernak, *Acta Histochem.* **2003**, *105*, 135–142.
[6] A. Pernak, K. Iwanik, P. Majewski, M. Grzymisławski, J. Pernak, *Acta Histochem.* **2005**, *107*, 149–156.
[7] E. Jugermann, *Cationic Surfactants. Surfactant Science Series, Vol. 4*, Marcel Dekker, New York, **1970**.
[8] J. M. Richmond (Ed), *Cationic Surfactants: Organic Chemistry. Surfactant Science Series, Vol. 34*, Marcel Dekker, New York, **1990**.
[9] *Cationic Surfactants: Physical Chemistry. Surfactant Science Series, Vol. 37* (Eds.: D. N. Rubingh, P. M. Holland), Marcel Dekker, New York, **1990**.
[10] *Cationic Surfactants: Analytical and Biological Evaluation. Surfactant Science Series, Vol. 53* (Eds.: J. Cross, E. J. Singer), Marcel Dekker, New York, **1994**.
[11] W. H. Meck, C. L. Williams, *Devel. Brain Res.* **1999**, *118*, 51–59.
[12] S. H. Zeisel, *Choline and phosphatidylcholine, in Nutrition in Health and Disease* (Eds.: M. Shils, J. A. Olson, M. Shike, A. C. Ross), 9th ed., Williams & Wilkins, Baltimore, **1999**.
[13] S. Abelló, F. Medina, X. Rodríguez, Y. Cesteros, P. Salagre, J. E. Sueiras, D. Tichit, B. Coq, *Chem. Commun.* **2004**, 1096–1097.
[14] A. Hamzé, E. Rubi, P. Arnal, M. Boisbrun, C. Carcel, X. Salom-Roing, M. Maynadier, S. Wein, H. Vial, M. Calas, *J. Med. Chem.* **2005**, *48*, 3639–3643.
[15] J. Pernak, P. Chwała, A. Syguda, R. Poźniak, *Polish J. Chem.* **2003**, *77*, 1263–1274.
[16] J. Pernak, P. Chwała, *Eur. J. Med. Chem.* **2003**, *38*, 1035–1042.
[17] J. Pernak, P. Chwała, A. Syguda, *Polish J. Chem.* **2004**, *78*, 539–546.
[18] V. Mévellec, B. Leger, M. Mauduit, A. Roucoux, *Chem. Commun.* **2005**, 2838–2839.
[19] A. P. Abbott, T. J. Bell, S. Handa, B. Stoddart, *Green Chem.* **2005**, *7*, 705–707.
[20] A. P. Abbott, G. Capper, D. L. Davies, H. Munro, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.* **2001**, 2010–2011.
[21] A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, *Inorg. Chem.* **2004**, *43*, 3447–3452.
[22] U. Domańska, R. Bogel-Łukasik, *J. Phys. Chem. B* **2005**, *109*, 12124–12132.
[23] U. Domańska, R. Bogel-Łukasik, *Fluid Phase Equilib.* **2005**, *233*, 220–227.
[24] M. J. Earle, J. M. S. S. Esperanc, M. A. Gilea, J. N. Canongia Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, *Nature* **2006**, *439*, 831–834.
[25] J. A. Lewis, B. S. Lewis, *Dis. Nerv. Syst.* **1977**, *38*, 21–24.
[26] G.-R. von Rymon Lipinski, *Ullman's Encyclopedia of Industrial Chemistry, Vol. 35*, Wiley-VCH Weinheim, **2003**, 6th ed., p. 407.
[27] ISO 2871–2:1990. "Surface active agents—Detergents—Determination of cationic-active matter content—Part 2: Cationic-active matter of low molecular mass (between 200 and 500)".
[28] For example, see R. Rudert, D. Vollhardt, G. Czichocki, *Acta Crystallogr. Sect. C* **1994**, *50*, 1054–1057; J. D. Dunitz, H. M. M. Shearer, *Helv. Chim. Acta* **1960**, *43*, 18; P. de Fremont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy, S. P. Nolan, *Organometallics* **2005**, *24*, 6301–6309.
[29] J. Pernak, A. Czepukowicz, R. Poźniak, *Ind. Eng. Chem. Res.* **2001**, *40*, 2379–2383.
[30] J. Pernak, K. Sobaszkiewicz, I. Mirska, *Green Chem.* **2003**, *5*, 52–56.
[31] J. Nawrot, E. Błoszyk, J. Harmatha, L. Nowotný, B Drożdż, *Acta Entomol. Bohemosl.* **1986**, *83*, 327–335.
[32] J. S. Gill, C. T. Lewis, *Nature* **1971**, *232*, 402–403.
[33] C.-Y. Li, L. T. Yam, T. Sun, *Modern Modalities for the Diagnosis of Hematologic Neoplasms*, Igaku-Shoin, New York, Tokyo, **1996**, p. 160.
[34] G. M. Sheldrick, *SHELXTL*, Version 5.05, Siemens Analytical X-Ray Instruments, Inc., **1996**.
[35] G. M. Sheldrick, *Program for Semiempirical Absorption Correlation of Area Detector Data*, University of Göttingen (Germany), **1996**.
[36] Crystal data for **1j**: formula $C_{16}H_{36}NO_2Cl$, $M=309.91$, orthorhombic, $a=9.7702(9)$, $b=9.1029(8)$, $c=41.508(4)$ Å, $V=3691.6(6)$ Å^3, $T=173$ K, space group *Pbca*, $Z=8$, $\rho_{calcd}=1.115$ Mg m^{-3}, $\mu(Mo_{K\alpha})=0.210$ mm^{-1}, 24616 reflections measured, 4501 unique ($R_{int}=0.0654$), GOF = 1.019, $R1=0.0513$, $wR2=0.1213$ ([$I>2\sigma(I)$] data), $R1=0.1010$, $wR2=0.1426$ (all data).
[37] Crystal data for **1m**: formula $C_{17}H_{36}NO_2Cl$, $M=321.92$, orthorhombic, $a=6.3087(10)$, $b=6.3900(10)$, $c=45.484(7)$ Å, $V=1833.6(5)$ Å^3, $T=173$ K, space group $P2_12_12_1$, $Z=4$, $\rho_c=1.166$ Mg m^{-3}, $\mu(Mo_{K\alpha})=0.214$ mm^{-1}, 11468 reflections measured, 4328 unique ($R_{int}=0.0339$), GOF = 1.029, $R1=0.0367$, $wR2=0.0756$ ([$I > 2\sigma(I)$] data), $R1=0.0473$, $wR2=0.0790$ (all data).

Received: February 19, 2007
Published online: May 30, 2007

