

Scientific paper

Orthoamides LXVIII¹: *N,N',N''*-Peralkylated Guanidinium Salts by Alkylation of *N,N,N',N',N''*-Pentasubstituted Guanidines

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Dedicated to Professor Branko Stanovnik on the occasion of his 70th birthday

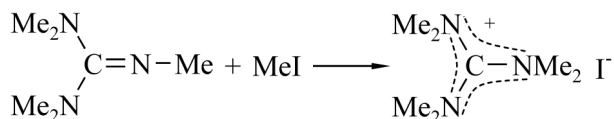
Abstract

Starting from secondary amines and *N,N*-dialkylcarbamoylchlorides or phosgene *N,N'*-peralkylated ureas **2b**, **d-k** have been prepared, which were converted by phosgene to the not isolated chloroformamidinium chlorides **3**. From these *N,N,N',N',N''*-pentasubstituted guanidines **5** could be obtained by treatment with primary amines/triethylamine and sodium hydroxide. The alkylation of the guanidines which methyl- and ethyl iodide afforded the guanidinium iodides **7a-q**. Two of them (**7m**, **g**) are room temperature ionic liquids (RTIL) (mp. < 25 °C) and another five compounds (**7c**, **f**, **h**, **i**, **p**) are ionic liquids (mp < 100 °C).

Keywords: *N,N',N''*-Peralkylated guanidinium salts, *N,N',N''*-Peralkylated guanidines, ureas, alkylation, ionic liquids

1. Introduction

From a historical point of view *N,N,N',N',N''*-hexamethylguanidinium iodide was the first *N,N',N''*-peralkylated guanidinium salt described. It was prepared by alkylation of *N,N,N',N',N''*-pentamethylguanidine with methyl iodide.^{2a}

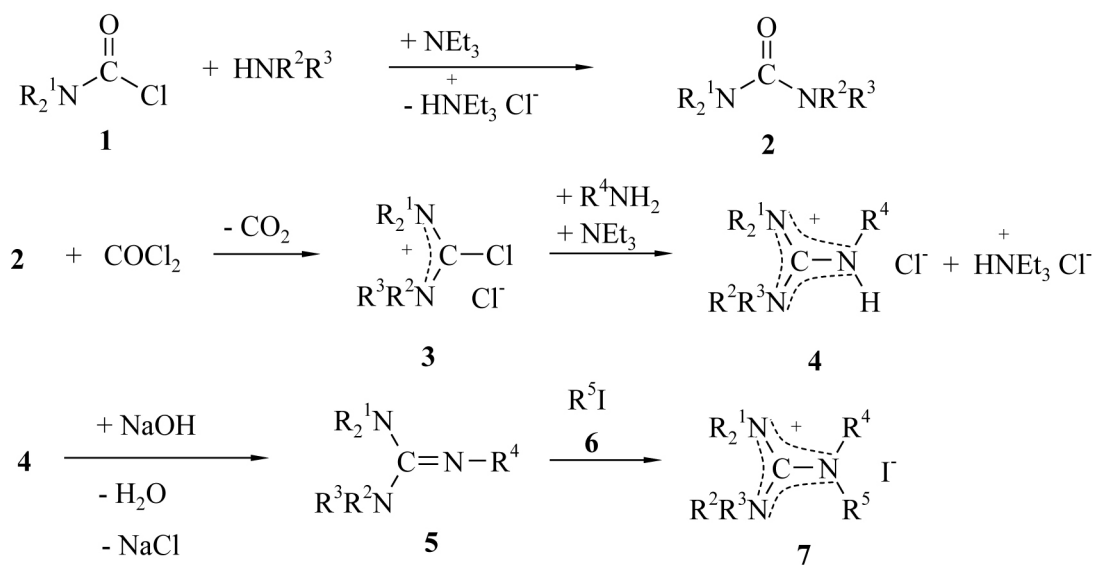


In the course of the last years *N,N',N''*-persubstituted guanidinium salts have attracted the attention of chemists for several reasons. On the one hand they are valuable building blocks for orthoamide derivatives of carbonic acid,³ formic and benzoic acid, heterocyclic carboxylic acids^{3c,4} and alkyne carboxylic acids.^{3a,4} On the

other hand guanidinium compounds can be prepared in which carbanions act as counter ion for the guanidinium ion.^{6,7,8,9,10} Such compounds can catalyze technically important processes as anionic polymerisation,⁹ polyether formation etc. Furthermore it has turned out that some *N,N',N''*-peralkylated guanidinium salts are ionic liquids which can be used advantageously as electrolytes in photoelectrochemical solar cells.¹¹

2. Results and Discussion

Since we are still working in a project which deals with guanidinium salt based ionic liquids, we tried to prepare such compounds by alkylation procedures. Usually symmetrically substituted guanidinium iodides, bearing small substituents on the nitrogens show high melting points, thus *N,N,N',N',N''*-hexamethylguanidinium iodide melts above 300 °C^{2a} and even for the chloride a melting point above 300 °C has been reported.¹² More



2	a	b	c	d	e	f	g	h	i	j	K
R ¹	Me	Me	Et	Et	Et	Et	Et	Pr	<i>sec</i> -Bu	Bu	Hex
R ²	Me	Et	Et	Pr	Allyl	Pent	Me	Bu	Hex	Bu	Hex
R ³	Me	Et	Et	Pr	Allyl	Pent	<i>c</i> -Hex	Bu	Hex	Bu	Hex

5	a	b	c	d	e	f	g	h	i	j
R ¹	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me
R ²	Me	Me	Et	Et	Et	Et	Et	Et	Et	Et
R ³	Me	Me	Et	Et	Et	Et	Et	Et	Et	Et
R ⁴	Me	Bu	Pr	<i>i</i> -Pr	Bu	<i>i</i> -Bu	<i>sec</i> -Bu	<i>t</i> -Bu	Pent	<i>i</i> -Pent

6	k	l	m	n	o	p	q
R ¹	Me	Et	Et	Et	Et	Et	Me
R ²	Et	Et	Et	Et	Et	Et	Me
R ³	Et	Et	Et	Et	Et	Et	Me
R ⁴	Hex	Bu	<i>i</i> -Bu	<i>sec</i> -Bu	<i>i</i> -Pent	Hex	C ₆ H ₅ -CH ₂ -CH ₂

7	a	b	c	d	e	f	g	h
R ¹	Me	Me	Me	Me	Me	Me	Me	Me
R ²	Et	Et	Et	Et	Et	Et	Et	Et
R ³	Et	Et	Et	Et	Et	Et	Et	Et
R ⁴	Pr	<i>i</i> -Pr	Bu	<i>i</i> -Bu	<i>t</i> -Bu	Pent	<i>i</i> -Pent	Hex
R ⁵	Me	Me	Me	Me	Me	Me	Me	Me

7	i	j	k	l	m	n	o	p	q
R ¹	Et	Et	Et	Et	Et	Et	Et	Et	Et
R ²	Et	Et	Et	Et	Et	Et	Et	Et	Et
R ³	Et	Et	Et	Et	Et	Et	Et	Et	Et
R ⁴	Bu	<i>i</i> -Bu	<i>sec</i> -Bu	<i>i</i> -Pent	Hex	<i>i</i> -Bu	<i>sec</i> -Bu	<i>i</i> -Pent	Hex
R ⁵	Me	Me	Me	Me	Me	Et	Et	Et	Et

Scheme 1

than 30 years ago when we started our investigations directed at the chemistry of *N,N,N'*-peralkylated guanidinium salts¹³ we have prepared guanidinium salts by alkylation of *N,N,N',N''*-pentasubstituted guanidines with methyl iodide, benzyl bromide and dimethyl sulfate.^{13d} So-

me of these compounds showed melting points lower than 100 °C, therefore they can be regarded as ionic liquids.

Since only a few *N,N,N'*-peralkylated guanidinium salts possessing an asymmetric pattern of substituents at the nitrogens are known and a lot of important physical

Table 1: Some physical properties and elementanalytical data for ureas **2**

Compound	yield [%]	bp [°C] n_D^{20}	Molecular Formula (Molar Mass [g/mol])	Elemental Analysis
<i>N,N</i> -Diethyl- <i>N',N'</i> -dipropylurea (2d)	92	106–110/12 Torr 1.4487	C ₁₁ H ₂₄ N ₂ O (200.33)	Calcd: C, 65.95; H, 12.08; N, 13.98. Found: C, 65.63; H, 12.07; N, 14.13.
<i>N,N</i> -Diallyl- <i>N',N'</i> -diethylurea (2e)	97	107–110/12 Torr 1.4704	C ₁₁ H ₂₀ N ₂ O (196.29)	Calcd: C, 67.31; H, 10.27; N, 14.27; Found: C, 67.36; H, 10.35; N, 14.10.
<i>N,N</i> -Diethyl- <i>N',N'</i> -dipentylurea (2f)	90	152–158/12 Torr	C ₁₅ H ₃₂ N ₂ O (256.43)	Calcd: C, 70.26; H, 12.58; N, 10.92; Found: C, 70.06; H, 12.32; N, 10.94.
<i>N</i> -Cyclohexyl- <i>N',N'</i> -diethyl- <i>N</i> -methylurea (2g)	94	94–96/0.001 Torr	C ₁₂ H ₂₄ N ₂ O (212.34)	Calcd: C, 67.88; H, 11.39; N, 3.19; Found: C, 67.69; H, 11.51; N, 13.09.
<i>N,N</i> -Dibutyl- <i>N',N'</i> -dipropylurea (2h)	87	147/12 Torr	C ₁₅ H ₃₂ N ₂ O (256.43)	Calcd: C, 70.26; H, 12.58; N, 10.92; Found: C, 70.02; H, 12.40; N, 10.87.
<i>N,N</i> -Di-(<i>sec.</i> -butyl)- <i>N',N'</i> -dihexylurea (2i)	88	148–152/0.001 Torr	C ₂₁ H ₄₄ N ₂ O (340.60)	Calcd: C, 74.05; H, 13.02; N, 8.22; Found: C, 74.22; H, 13.04; N, 8.22.
<i>N,N,N',N'</i> -Tetrahexylurea (2k)	65	213/0.1 Torr 1.4578	C ₂₅ H ₅₂ N ₂ O (396.70)	Calcd: C, 75.70; H, 13.21; N, 7.06; Found: C, 75.48; H, 13.11; N, 7.00.

properties such as viscosity, electrical conductivity etc.¹¹ of guanidinium salts depend strongly on the structure and size of the cations, we felt the need to prepare such compounds by alkylation of *N,N',N''*-peralkylated guanidines **5**. The guanidines **5**, needed as starting materials were prepared according to a procedure described by us some years ago.^{13d} Thus *N,N,N',N''*-tetrasubstituted ureas **2** were reacted with phosgene to give the non isolated chloroformamidinium chlorides **3**, which were reacted further with primary amines in the presence of triethylamine to afford mixtures of *N,N,N',N',N''*-pentasubstituted guanidinium chlorides **4** and triethylamine hydrochloride. From these mixtures the crude guanidiniumchlorides **4** can be obtained by treatment with equimolar amounts of sodium or potassium hydroxide. From the crude salts **4** the guanidines **5** can be set free by treatment with excessive sodium- or potassium hydroxide (scheme 1).

The ureas **2** used in the above described procedure were prepared either from *N,N*-dialkylcarbamoyl chlorides **1** and secondary amines (**2b-j**) or from phosgene and dihexylamine (**2k**) in the presence of triethylamine or trimethylamine, resp. in acetonitrile.

The guanidines **5** were heated to reflux with the alkyl iodides **6a, b** in dry acetonitrile to produce the guanidinium salts **7a-q**.

The experimental data, together with the values of the elemental analysis for the compounds thus obtained and additionally NMR- and IR- analytical data for selected compounds are compiled in Tables 1–6.

Ionic liquids are defined as organic salts with a melting point below 100 °C. As can be seen from the data in Table 5 some of the guanidinium iodides (**7c, 7f, 7g, 7i, 7m, 7p, 7q**) fulfil this condition and hence can be regarded as ionic liquids.

Table 2: Spectroscopic Data of *N,N,N',N''*-Tetralkylureas **2**

Compound	¹ H NMR (250 MHz, CDCl ₃) [δ ppm]	¹³ C NMR (125 MHz, CDCl ₃) [δ ppm]	IR (ATR) ν [cm ⁻¹]
<i>N,N,N',N''</i> -Tetrahexyl-urea (2d)	0.88 (t, <i>J</i> = 6.9 Hz, 12H, CH ₃); 1.21–1.32 (m, 24H, CH ₂); 1.44–1.52 (m, 8H, N-CH ₂ -CH ₂); 3.09 (t, <i>J</i> = 7.5 Hz, 8H, N-CH ₂)	105.51 (C=O); 48.31 (N-CH ₃); 31.71 (N-CH ₂ -CH ₂); 28.01 (N-(CH ₂) ₂ -CH ₂); 26.81 (N-(CH ₂) ₃ -CH ₂); 22.67 [N-(CH ₂) ₄ -CH ₂]; 14.05 (CH ₃)	1646 (C=O)
<i>N,N</i> -Diallyl- <i>N',N'</i> -diethylurea (2f)	5.75–5.90 (m, 2H, CH); 5.12–5.21 (m, 4H, NCH ₂ -CH=CH ₂); 3.71 (d, <i>J</i> = 5.6 Hz, 2H, NCH ₂ CHCH ₂); 3.20 (q, <i>J</i> = 7.1 Hz, 4H, NCH ₂ -CH ₃); 1.11 (t, <i>J</i> = 7.1 Hz, 5H, NCH ₂ -CH ₃)	164.73 (C=O); 134.33 (CH); 116.92 (NCH ₂ -CH=CH ₂); 50.46 (N-CH ₂ -CHCH ₂); 42.08 (-NCH ₂ -CH ₃); 13.18 (N-CH ₂ -CH ₃)	1655 (C=O) 1640 (C=C)

Compound	¹ H NMR (250 MHz, CDCl ₃) [δ ppm]	¹³ C NMR (125 MHz, CDCl ₃) [δ ppm]	IR (ATR) ν [cm ⁻¹]
<i>N,N</i> -Diethyl- <i>N',N'</i> -dipropylurea (2g)	3.06–3.20 (m, 8H, N-CH ₂); 1.53 (m _c , 4H, NCH ₂ -CH ₂ -CH ₃); 1.10 (t, <i>J</i> = 7.1 Hz, 6H, NCH ₂ -CH ₃); 0.87 (t, <i>J</i> = 7.4 Hz, 6H, N(CH ₂) ₂ -CH ₃)	165.30 (C=O); 49.92 (N-CH ₂ -CH ₂); 42.04 (NCH ₂ -CH ₃); 21,21 (N-CH ₂ -CH ₂); 13.26, 11.43 (CH ₃)	1645 (C=O)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dipentylurea (2h)	3.08–3.20 (m, 8H, N-CH ₂); 1.50 (tt, <i>J</i> = 7.3 Hz, 4H, NCH ₂ -CH ₂); 1.16–1.37 (m, 8H, N(CH ₂) ₂ -(CH ₂) ₂ -CH ₃); 1.10 (t, <i>J</i> = 7.1 Hz, 6H, N-CH ₂ -CH ₃); 0.89 (t, <i>J</i> = 7.0 Hz, 6H, N(CH ₂) ₄ -CH ₃)	165.27 (C=O); 48.10 (NCH ₂ -(CH ₂) ₃ -CH ₃); 42.40 (N-CH ₂ -CH ₃); 29.24 (N-CH ₂ -CH ₂); 27.68 (N-(CH ₂) ₂ -CH ₂); 22.51 (N-(CH ₂) ₃ -CH ₂); 14.07, 13.28 (CH ₃)	1645 (C=O)
<i>N,N</i> -Dibutyl- <i>N',N'</i> -dipropylurea (2i)	3.10 (t, <i>J</i> = 7.5 Hz, 4H, -CH ₂ -CH ₂ -CH ₃); 3.07 (t, <i>J</i> = 7.6 Hz, 4H, N-CH ₂ -(CH ₂) ₂ -CH ₃); 1.43–1.60 (m, 8H, N-CH ₂ -CH ₂); 1.28 (m _c , 4H, N-(CH ₂) ₂ -CH ₂); 0.91 (t, <i>J</i> = 7.2 Hz, 6H, CH ₃); 0.86 (t, <i>J</i> = 7.4 Hz, 6H, CH ₃)	165.59 (C=O); 50.01, 48.04 (N-CH ₂); 30.17 (N-(CH ₂) ₂ -CH ₂); 21.21, 20.37 (N-CH ₂ -CH ₂); 13.95, 11.45 (CH ₃)	1645 (C=O)
<i>N,N</i> -Di-(<i>sec</i> -butyl)- <i>N',N'</i> -dihexylurea (2j)	3.20–3.34 (m, 2H, CH); 2.86–3.17 (m, 4H, CH ₂ -(CH ₂) ₄ -CH ₃); 1.44–1.78 (m, 8H, CH ₂ -(CH ₂) ₃ -CH ₃ /CH-CH ₂ -CH ₃); 1.22–1.31 (m, 18H, (CH ₂) ₃ -CH ₃ /CH-CH ₃); 0.84–0.34 (m, 12H, CH-CH ₂ -CH ₃ /(CH ₂) ₅ -CH ₃)	164.99, 164.75 (C=O); 54.06, 53.78 (CH); 48.84 (CH ₂ -(CH ₂) ₄ -CH ₃); 31.74 (CH ₂ -(CH ₂) ₃ -CH ₃); 28.92, 28.50 (CH-CH ₂ -CH ₃); 28.06 (CH ₂ -(CH ₂) ₂ -CH ₃); 26.95 (N-(CH ₂) ₃ -CH ₂); 22.69 (N-(CH ₂) ₄ -CH ₂); 19.74, 19.05 (CH); 14.04 (CH ₂) ₅ -CH ₃); 12.23, 11.97 (CH-CH ₂ -CH ₃)	45 (C=O)
<i>N</i> -Cyclohexyl- <i>N',N'</i> -diethyl- <i>N</i> -methylurea (2k)	3.50–3.62 (m, CH); 3.14 (q, <i>J</i> = 7.1 Hz, 4H, CH ₂ -CH ₃); 2.69 (s, 3H, N-CH ₃); 1.62–1.83 (m, 4H, N=CH(CH ₂) ₂); 1.29–1.52 (m, 6H, CH-CH ₂ (CH ₂) ₃); 1.11 (t, <i>J</i> = 7.1 Hz, 6H, CH ₂ -CH ₃)	165.30 (C=O); 56.98 (CH); 42.31 (CH ₂ -CH ₃); 30.78 (N-CH ₃); 30.14 (N-CH(CH ₂) ₂); 26.04 (N-CH(CH ₂ -CH ₂) ₂); 25.80 (CH ₂) ₂ CH ₂); 13.28 (-CH ₂ -CH ₃)	1640 (C=O)

Table 3: Some physical properties and element analytical data for *N,N,N',N',N''*-pentasubstituted guanidines 5

Compound	yield [%]	bp [°C] n _D ²⁰	Molecular Formula (Molar Mass [g/mol])	Elemental Analysis
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -propylguanidine (5c)	83	45/0.2Torr 1.4572	C ₁₀ H ₂₃ N ₃ (185.32)	Calcd: C, 64.81; H, 12.51; N, 22.68; Found: C, 63.36; H, 12.23; N, 22.10.
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''-iso</i> -propylguanidine (5d)	89	41/0.2Torr 1.4534	C ₁₀ H ₂₃ N ₃ (185.32)	^a
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''-butyl</i> -guanidine (5e)	98	58/0.2Torr 1.4580	C ₁₁ H ₂₅ N ₃ (199.34)	Calcd: C, 66.28; H, 12.64; N, 21.08; Found: C, 64.34; H, 12.26; N, 20.43.
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''-iso</i> -butylguanidine (5f)	48	51/0.2Torr 1.4560	C ₁₁ H ₂₅ N ₃ (199.34)	^a
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''-sec</i> -butylguanidine (5g)	42	43/0.2Torr 1.4543	C ₁₁ H ₂₅ N ₃ (199.34)	^a
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''-tert</i> -butylguanidine (5h)	89	37/0.2Torr 1.4564	C ₁₁ H ₂₅ N ₃ (199.34)	^a
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''-pentyl</i> -guanidine (5i)	58	51/0.2Torr 1.4605	C ₁₂ H ₂₇ N ₃ (213.37)	Calcd: C, 67.55; H, 12.75; N, 19.70; Found: C, 67.30; H, 12.69; N, 19.56.
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''-iso</i> -pentylguanidine (5j)	92	47/0.2Torr 1.4588	C ₁₂ H ₂₇ N ₃ (213.37)	^a

Compound	yield [%]	bp [°C] n_D^{20}	Molecular Formula (Molar Mass [g/mol])	Elemental Analysis
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -hexylguanidine (5k)	60	67/0.2Torr 1.4601	C ₁₃ H ₂₉ N ₃ (227.40)	Calcd: C, 68.67; H, 12.85; N, 18.48; Found: C, 67.86; H, 12.76; N, 18.34.
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -butylguanidine (5l)	89	70/0.2Torr 1.4585	C ₁₃ H ₂₉ N ₃ (227.38)	Calcd: C, 68.67; H, 12.85; N, 18.48; Found: C, 67.75; H, 12.56; N, 18.16.
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> - <i>iso</i> -butylguanidine (5m)	92	51/0.2Torr 1.4576	C ₁₃ H ₂₉ N ₃ (227.38)	Calcd: C, 68.67; H, 12.85; N, 18.48; Found: C, 68.39; H, 12.58; N, 18.43.
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> - <i>sec</i> -butylguanidine (5n)	82	47/0.2Torr 1.4575	C ₁₀ H ₂₃ N ₃ (185.32)	Calcd: C, 68.67; H, 12.85; N, 18.48; Found: C, 68.54; H, 12.88; N, 18.45.
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> - <i>iso</i> -pentylguanidine (5o)	90	64/0.2Torr 1.4589	C ₁₄ H ₃₁ N ₃ (241.42)	Calcd: C, 69.65; H, 12.94; N, 17.41; Found: C, 69.63; H, 12.25; N, 17.44.
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -hexylguanidine (5p)	88	74/0.2Torr 1.4606	C ₁₅ H ₃₃ N ₃ (255.45)	Calcd: C, 70.53; H, 13.02; N, 16.45; Found: C, 70.28; H, 12.81; N, 16.38.
<i>N,N,N',N'</i> -Tetramethyl- <i>N''</i> -1-phenylethylguanidine (5q)	66	62/0.001Torr	C ₁₃ H ₂₁ N ₃ (219.33)	Calcd: C, 71.19; H, 9.65; N, 19.16; Found: C, 71.15; H, 9.66; N, 19.35.

^a the compound is extreme sensitive to humidity, thus no correct elementalanalytica data could be obtained deviations from the calculated C, H, N values were about 1–2%.

Table 4: NMR Spectra of *N,N,N',N'',N'''*-Pentaalkylguanidines **5**

Compound	¹ H NMR (250 MHz, CDCl ₃) [δ ppm]	¹³ C NMR (125 MHz, CDCl ₃) [δ ppm]
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -propylguanidine (5c)	3.02–3.09 (m, 6H, NCH ₂); 2.73, 2.71 (s, 6H, NCH ₃); 1.54 (qt, ³ J = 7.1 Hz; 2H, NCH ₂ -CH ₂); 1.01–1.05 (m, 6H, CH ₃); 0.89, 0.89 (t, ³ J = 7.3 Hz; 3H, C ₂ H ₅ -CH ₃)	159.17 (C=N); 51.77 (NCH ₂ -CH ₂); 42.77, 41.99 (NCH ₂ -CH ₃); 39.73, 38.71 (NCH ₃); 25.96, 25.92 (NCH ₂ -CH ₂); 13.85, 13.13, 13.12, 12.15 (CH ₃)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> - <i>iso</i> -propylguanidine (5d)	3.40–3.52 (hept, ³ J = 6.2 Hz; 1H, NCH); 3.02 (q, ³ J = 7.0 Hz; 4H, NCH ₂ -CH ₃); 2.71, 2.76 (s, 6H, NCH ₃); 1.07 (d, ³ J = 6.2 Hz; 6H, CH-CH ₃); 1.02 (t, ³ J = 7.0 Hz; 6H, CH ₃)	158.17, 157.54 (C=N); 48.30, 47.87 (NCH); 43.01, 42.07 (NCH ₂ -CH ₃); 40.16, 38.44 (NCH ₃); 5.54, 25.48 (CH-CH ₃); 13.80, 13.29 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -butylguanidine (5e)	3.00–3.19 (m, 6H, NCH ₂); 2.70, 2.73 (s, 6H, NCH ₃); 1.45–1.58 (m, 2H, NCH ₂ -CH ₂); 1.27–1.42 (m, 2H, CH ₂ -CH ₃); 0.99–1.06 (m, 6H, NCH ₂ -CH ₃); 0.90 (t, ³ J = 7.2 Hz; 3H, CH ₃)	159.18, 158.91 (C=N); 49.50, 49.40 (NCH ₂ -C ₃ H ₇); 42.72, 41.94 (NCH ₂ -CH ₃); 39.74, 38.72 (NCH ₃); 35.06, 34.98 (NCH ₂ -CH ₂); 20.67 (CH ₂ -CH ₃); 14.13, 14.01, 13.85, 13.09 (CH ₃)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> - <i>iso</i> -butylguanidine (5f)	2.89–3.08 (m, 6H, NCH ₂); 2.72 (s, 6H, NCH ₃); 1.78 (hept, ³ J = 6.6 Hz; 1H, CH); 0.99–1.07 (m, 6H, NCH ₂ -CH ₃); 0.89 (d, ³ J = 6.6 Hz; 6H, CH-CH ₃)	159.18 (C=N); 58.14, 57.94 (NCH ₂ CH); 42.74, 41.76 (NCH ₂ -CH ₃); 39.75, 38.74 (NCH ₃); 31.04, 30.97 (CH); 20.88, 20.82 (CH-CH ₃); 13.84, 13.23 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> - <i>sec</i> -butylguanidine (5g)	2.96–3.22 (m, 5H, NCH/NCH ₂); 2.71–2.80 (m, 6H, NCH ₃); 1.31–1.42 (m, 2H, NCH ₂ -CH ₂); 0.99–1.14 (m, 9H, CH ₂ -CH ₃ /CH-CH ₃); 0.80 (t, ³ J = 7.2 Hz; 3H, CH ₃)	158.89, 158.29 (C=N); 54.53, 54.20 (NCH); 42.84, 42.00, 41.61, 40.16, 38.76, 38.51, 32.88, 32.45 (NCH ₃); 32.88, 32.45 (CH ₂); 22.85, 22.79 (CH-CH ₃); 13.66, 13.30, 13.21, 11.50, 11.47 (CH ₃)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> - <i>tert</i> -butylguanidine (5h)	3.12 (m, 6H, NCH ₂); 2.72 (s, 6H, NCH ₃); 1.27 (C-CH ₃); 1.07 (t, ³ J = 7.1 Hz; 6H, CH ₂ -CH ₃)	41.99 (NCH ₂ CH ₃); 38.74 (NCH ₃); 32.12 (C(CH ₃) ₃); 31.28 (C-CH ₃); 13.30 (CH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -pentylguanidine (5i)	3.01–3.10 (m, 6H, NCH ₂); 2.70 (s, 6H, NCH ₃); 1.50–1.56 (m, 2H, NCH ₂ -CH ₂); 1.28–1.34 (m, 4H, CH ₂); 1.01–1.04 (m, 6H, NCH ₂ -CH ₃); 0.89 (t, ³ J = 6.9 Hz; 3H, CH ₃)	159.13, 158.83 (C=N); 49.86, 49.79 (NCH ₂ -C ₄ H ₉); 42.70, 41.99 (NCH ₂ -CH ₃); 39.73, 38.71 (NCH ₃); 32.58, 32.51 (NCH ₂ -CH ₂); 29.90 (CH ₂ -C ₂ H ₅); 22.71, 22.68 (CH ₂ -CH ₃); 14.24, 13.85 (C ₄ H ₉ -CH ₃); 13.30, 13.10 (CH ₃)

Compound	¹ H NMR (250 MHz, CDCl ₃) [δ ppm]	¹³ C NMR (125 MHz, CDCl ₃) [δ ppm]
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -iso-pentylguanidine (5j)	3.00–3.16 (m, 6H, NCH ₂); 2.69, 2.73 (s, 6H, NCH ₃); 1.56–1.77 (m, 1H, CH); 1.37–1.46 (m, 2H, NCH ₂ -CH ₂); 1.02 (t, ³ J = 7.1 Hz; 6H, NCH ₂ -CH ₃); 0.88 (d, ³ J = 5.4 Hz; 6H, CH-CH ₃)	159.15, 158.89 (C=N); 47.85, 47.78 (NCH ₂ CH ₂); 42.71, 41.94 (NCH ₂ -CH ₃); 39.75, 38.75 (NCH ₃); 26.08, 25.95 (CH); 22.77, 22.74 (CH-CH ₃ , NCH ₂ -CH ₂); 13.87, 13.08 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -hexylguanidine (5k)	3.00–3.13 (m, 6H, NCH ₂); 2.70, 2.73 (s, 6H, NCH ₃); 1.47–1.55 (m, 2H, NCH ₂ -CH ₂); 1.25–1.38 (m, 6H, CH ₂); 1.02, 1.03 (t, ³ J = 7.1 Hz; 6H, CH ₃)	159.15, 158.87 (C=N); 49.83, 49.76 (NCH ₂ -C ₅ H ₁₁); 42.73, 41.96 (NCH ₂ -CH ₃); 39.73, 38.72 (NCH ₃); 32.80, 32.74 (NCH ₂ -CH ₂); 32.74 (CH ₂ -C ₂ H ₅); 27.29 (NCH ₂ -CH ₃); 0.85–0.91 (m, 3H, CH ₃) (CH ₂ -C ₃ H ₇); 22.78 (CH ₂ -CH ₃); 14.13, 13.84 (C ₅ H ₁₁ -CH ₃); 13.11 (CH ₃)
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -butylguanidine (5l)	2.99–3.17 (m, 10H, NCH ₂); 1.41–1.58 (m, 2H, NCH ₂ -CH ₂); 1.41–1.58 (m, 2H, NCH ₂ -CH ₂); 0.90 (t, ³ J = 7.2 Hz; 3H, CH ₃)	158.23 (C=N); 49.62 (NCH ₂ -CH ₂); 42.67, 41.51 (NCH ₂ -CH ₃); 35.04 (NCH ₂ -CH ₂); 20.77 (CH ₂ -CH ₂ -CH ₃); 14.16 (CH ₂ -CH ₃); 13.72, 13.27, 13.00 (NCH ₂ -CH ₃)
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -iso-butylguanidine (5m)	3.16 (q, ³ J = 7.1 Hz, 4H, NCH ₂ -CH ₃); 3.03 (q, ³ J = 7.1 Hz, 4H, NCH ₂ -CH ₃); 2.90 (d, ³ J = 6.5 Hz, 2H, NCH ₂ -CH); 1.78 (hept, ³ J = 6.6 Hz, 1H, CH); 1.02, 1.03 (t, ³ J = 7.2 Hz, 12H, NCH ₂ -CH ₃); 0.89 (d, ³ J = 6.5 Hz; 6H, CH-CH ₃)	158.70 (C=N); 58.62 (NCH ₂ -CH); 42.96, 41.48 (NCH ₂ -CH ₃); 31.45 (CH); 21.28 (CH-CH ₃); 14.25, 13.42 (NCH ₂ -CH ₃)
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -sec-butylguanidine (5n)	2.94–3.33 (m, 9H, NCH/NCH ₂); 1.33–1.45 (m, 2H, NCH-CH ₂); 0.99–1.14 (m, 15H, CH ₂ -CH ₃ /CH-CH ₃); 0.82 (t, ³ J = 7.2 Hz; 3H, CH ₂ -CH ₃)	157.68 (C=N); 54.60 (NCH); 42.97, 42.36, 41.22 (NCH _x); 32.77 (CH ₂); 22.62 (CH-CH ₃); 13.64, 13.06 (NCH ₂ -CH ₃); 11.52 (CH ₃)
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -iso-pentylguanidine (5o)	3.08–3.14 (m, 6H, NCH ₂); 3.03 (q, ³ J = 7.1 Hz, 6H, NCH ₂ -CH ₃); 1.67 (hept, ³ J = 6.7 Hz, 1H, CH); 1.42 (q, ³ J = 7.1 Hz, 2H, NCH ₂ -CH ₃); 1.01–1.04 (m, 12H, NCH ₂ -CH ₃); 0.88 (d, ³ J = 6.7 Hz; 6H, CH-CH ₃)	158.41 (C=N); 54.60 (NCH); 48.43 (NCH ₂ -CH ₂); 42.96, 41.81 (NCH ₂ -CH ₃); 42.30 (NCH ₂ -CH ₂); 26.42 (CH); 23.14 (CH-CH ₃); 14.09, 13.31 (NCH ₂ -CH ₃)
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -hexylguanidine (5p)	2.98–3.17 (m, 10H, NCH); 1.47–1.55 (m, 2H, NCH ₂ -CH ₂); 1.25–1.32 (m, 6H, CH ₂); 0.99–1.05 (m, 12H, CH ₃); 0.85–0.90 (m, 3H, CH ₃)	158.17 (C=N); 49.96 (NCH ₂ -(CH ₂) ₄); 42.60, 41.49 (NCH ₂); 32.77 (CH ₂ -C ₂ H ₅); 31.91 (NCH ₂ -CH ₂); 27.36 (N-(CH ₂) ₂ -CH ₂); 22.78 (CH ₂ CH ₃); 14.10, 13.71, 13.00 (CH ₃)

Table 5: *N,N,N',N',N'',N''*-Hexaalkylguanidinium-iodides **7a–7q** from *N,N',N',N'',N''*-Pentaalkylguanidines **5** and Methyl- or Ethyliodide

Compound	yield [%]	mp [°C]	Molecular Formula (Molar Mass [g/mol])	Elemental Analysis
<i>N,N</i> -Diethyl- <i>N',N',N''</i> -trimethyl- <i>N''</i> -propyl-guanidiniumiodide (7a)	89	181	C ₁₁ H ₂₆ N ₃ I (327.25)	Calcd: C, 40.37; H, 8.01; N, 12.84; I, 38.78; Found: C, 40.37; H, 7.98; N, 12.88; I, 38.91.
<i>N,N</i> -Diethyl- <i>N',N',N''</i> -trimethyl- <i>N''</i> -iso-propyl-guanidiniumiodide (7b)	83	267–268	C ₁₁ H ₂₆ N ₃ I (327.25)	Calcd: C, 40.37; H, 8.01; N, 12.84; I, 38.78; Found: C, 40.22; H, 7.96; N, 12.80; I, 39.07.
<i>N,N</i> -Diethyl- <i>N',N',N''</i> -trimethyl- <i>N''</i> -butyl-guanidiniumiodide (7c)	82	83	C ₁₂ H ₂₈ N ₃ I (341.28)	Calcd: C, 42.23; H, 8.27; N, 12.31; I, 37.18; Found: C, 42.06; H, 8.29; N, 12.22; I, 37.32.
<i>N,N</i> -Diethyl- <i>N',N',N''</i> -trimethyl- <i>N''</i> -iso-butyl-guanidiniumiodide (7d)	72	115–116	C ₁₂ H ₂₈ N ₃ I (341.28)	Calcd: C, 42.23; H, 8.27; N, 12.31; I, 37.18; Found: C, 42.27; H, 8.36; N, 12.32; I, 37.35.
<i>N,N</i> -Diethyl- <i>N',N',N''</i> -trimethyl- <i>N''</i> -tert-butyl-guanidiniumiodide (7e)	76	267	C ₁₂ H ₂₈ N ₃ I (341.28)	Calcd: C, 42.23; H, 8.27; N, 12.31; I, 37.18; Found: C, 42.38; H, 8.24; N, 12.22; I, 37.18.
<i>vN,N</i> -Diethyl- <i>N',N',N''</i> -trimethyl- <i>N''</i> -pentyl-guanidiniumiodide (7f)	95	88	C ₁₃ H ₃₀ N ₃ I (355.31)	Calcd: C, 43.95; H, 8.51; N, 11.83; I, 35.81; Found: C, 44.06; H, 8.49; N, 11.80; I, 35.81.
<i>N,N</i> -Diethyl- <i>N',N',N''</i> -trimethyl- <i>N''</i> -iso-pentyl-guanidiniumiodide (7g)	97	122	C ₁₃ H ₃₀ N ₃ I (355.31)	Calcd: C, 43.95; H, 8.51; N, 11.83; I, 35.81; Found: C, 44.11; H, 8.53; N, 11.85; I, 35.72.

Compound	yield [%]	mp [°C]	Molecular Formula (Molar Mass [g/mol])	Elemental Analysis
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> -hexyl-guanidiniumiodide (7h)	47	70	C ₁₄ H ₃₂ N ₃ I (369.33)	Calcd: C, 45.51; H, 8.73; N, 11.38; I, 34.36; Found: C, 45.53; H, 8.79; N, 11.39; I, 34.46.
<i>N,N,N',N''</i> -Tetraethyl- <i>N'''</i> -methyl- <i>N'''</i> -butyl-guanidiniumiodide (7i)	99	77–78	C ₁₄ H ₃₂ N ₃ I (369.33)	Calcd: C, 45.53; H, 8.73; N, 11.38; I, 34.36; Found: C, 45.48; H, 8.68; N, 11.40; I, 34.11.
<i>N,N,N',N''</i> -Tetraethyl- <i>N'''</i> -methyl- <i>N'''</i> - <i>iso</i> -butyl-guanidiniumiodide (7j)	92	104	C ₁₄ H ₃₂ N ₃ I (369.33)	Calcd: C, 45.53; H, 8.73; N, 11.38; I, 34.36; Found: C, 45.79; H, 8.74; N, 11.37; I, 34.20.
<i>N,N,N',N''</i> -Tetraethyl- <i>N'''</i> -methyl- <i>N'''</i> -2-butyl-guanidiniumiodide (7k)	91	162	C ₁₄ H ₃₂ N ₃ I (369.33)	Calcd: C, 45.53; H, 8.73; N, 11.38; I, 34.36; Found: C, 45.55; H, 8.68; N, 11.26; I, 34.52.
<i>N,N,N',N''</i> -Tetraethyl- <i>N'''</i> -methyl- <i>N'''</i> - <i>iso</i> -pentyl-guanidiniumiodide (7l)	97	102	C ₁₅ H ₃₄ N ₃ I (383.36)	Calcd: C, 47.00; H, 8.94; N, 10.96; I, 33.10; Found: C, 47.10; H, 8.87; N, 10.97; I, 33.03.
<i>N,N,N',N''</i> -Tetraethyl- <i>N'''</i> -methyl- <i>N'''</i> -hexyl-guanidiniumiodide (7m)	97	liquid at 20°C n _D ²⁰ = 1.5421	C ₁₆ H ₃₆ N ₃ I (397.39)	Calcd: C, 48.36; H, 9.13; N, 10.57; I, 31.93; Found: C, 48.05; H, 9.23; N, 10.59; I, 31.97.
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N'''</i> - <i>iso</i> -butyl-guanidiniumiodide (7n)	96	124	C ₁₅ H ₃₄ N ₃ I (383.36)	Calcd: C, 47.00; H, 8.94; N, 10.96; I, 33.10; Found: C, 47.00; H, 8.80; N, 10.87; I, 33.24.
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N'''</i> - <i>sec</i> -butyl-guanidiniumiodide (7o)	55	195–196	C ₁₅ H ₃₄ N ₃ I (383.36)	Calcd: C, 47.00; H, 8.94; N, 10.96; I, 33.10; Found: C, 46.99; H, 8.93; N, 10.85; I, 33.22.
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N'''</i> - <i>iso</i> -pentyl-guanidiniumiodide (7p)	98	45	C ₁₆ H ₃₆ N ₃ I (397.39)	Calcd: C, 48.36; H, 9.13; N, 10.57; I, 31.93; Found: C, 48.48; H, 9.07; N, 10.52; I, 31.81.
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N'''</i> -hexyl-guanidiniumiodide (7q)	96	liquid at 20°C n _D ²⁰ = 1.5421	C ₁₇ H ₃₈ N ₃ I (411.41)	Calcd: C, 49.63; H, 9.31; N, 10.21; I, 30.85; Found: C, 49.51; H, 9.31; N, 10.22; I, 30.64.

Table 6: ¹³C NMR Spectra of selected Guanidiniumiodides 7

Compound	¹³ C NMR (125 MHz, CDCl ₃) [δ ppm]
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> -propyl-guanidiniumiodide (7a)	163.41 (CN ₃); 54.90, 54.55 (NCH ₂ -CH ₂); 43.94, 41.77, 41.56, 41.03, 39.31, 39.06 (NCH _x); 0.94, 20.86 (CH ₂); 13.45, 13.17, 11.40, 11.27 (CH ₃)
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> - <i>iso</i> -propyl-guanidiniumiodide (7b)	163.69 (CN ₃); 53.10, 52.85 (NCH); 43.83, 41.70, 40.83, 32.75 (NCH _x); 21.49, 19.16 (CH-CH ₃); 13.51 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> -butyl-guanidiniumiodide (7c)	163.45, 163.34 (CN ₃); 52.95, 52.66 (NCH ₂ CH ₂); 44.58, 44.07, 43.94, 41.81, 41.56, 41.36, 41.01, 39.33, 39.10 (NCH _x); 29.61, 29.47 (CH); 20.02, 19.95 (CH ₂ -CH ₃); 13.78, 13.72, 13.58, 13.49, 13.39, 13.20 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> - <i>iso</i> -butyl-guanidiniumiodide (7d)	163.74, 163.49 (CN ₃); 61.07, 60.47 (NCH ₂ CH); 44.91, 44.01, 43.70, 42.13, 41.97, 41.16, 40.72, 40.30, 40.11 (NCH _x); 26.16, 26.08 (CH); 20.57, 20.44, 20.16, 19.91 (CH-CH ₃); 13.64, 13.58, 13.26, 12.90 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> - <i>tert</i> -butyl-guanidiniumiodide (7e)	163.23 (CN ₃); 59.89 (NCH ₂); 44.72 ((H ₃ C) ₃ CNCH ₃); 41.23 (NC); 36.041 (NCH ₃); 27.95 (C-CH ₃); 13.89, 12.84 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> - <i>iso</i> -pentyl-guanidiniumiodide (7g)	163.39 (CN ₃); 51.51, 51.34 (NCH ₂ CH ₂); 44.52, 44.01, 41.93, 41.58, 41.31, 41.03, 39.44, 39.25 (NCH _x); 36.40, 36.01 (CH ₂ -CH); 25.98, 25.87 (CH ₂ -CH); 23.00, 22.71, 22.13 (CH-CH ₃); 13.44 (NCH ₂ -CH ₃)
<i>N,N</i> -Diethyl- <i>N',N''</i> -trimethyl- <i>N'''</i> -hexyl-guanidiniumiodide (7h)	163.41 (CN ₃); 53.24, 52.94 (NCH ₂ CH ₂); 44.58, 44.00, 41.92, 41.65, 41.30, 40.95, 39.42, 39.17 (NCH _x); 31.28 (CH ₂ -C ₂ H ₅); 27.59, 27.43 (NCH ₂ -CH ₂); 26.45, 26.18 (CH ₂ -C ₃ H ₇); 22.47 (CH ₂ -CH ₃); 13.98, 13.43 (CH ₃)
<i>N,N,N',N''</i> -Tetraethyl- <i>N'''</i> -methyl- <i>N'''</i> - <i>iso</i> -butyl-guanidiniumiodide (7i)	164.11 (CN ₃); 61.20 (NCH ₂ CH); 44.94, 44.66, 44.37, 43.88 (NCH ₂); 40.61 (NCH ₃); 26.36 (CH); 20.91, 20.43 (CH-CH ₃); 14.04, 13.80, 13.35 (NCH ₂ -CH ₃)

Compound	^{13}C NMR (125 MHz, CDCl_3) [δ ppm]
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -methyl- <i>N''</i> - <i>sec</i> -butyl-guanidiniumiodide (7k)	164.15 (CN_3); 59.21 (NCH); 44.39, 43.98, 43.51 (NCH_2); 33.84 (NCH_3); 28.14 (CH_2); 18.58 (CH-CH_3); 13.50, 13.38, 13.06, 12.97 ($\text{NCH}_2\text{-CH}_3$); 11.55 ($\text{CH}_2\text{-CH}_3$)
<i>N,N,N',N'</i> -Tetraethyl- <i>N''</i> -methyl- <i>N''</i> - <i>iso</i> -pentyl-guanidiniumiodide (7l)	163.61 (CN_3); 51.45 (NCH_2CH_2); 44.46, 44.29, 44.23, 43.73, 39.50 (NCH_2); 36.14 ($\text{CH}_2\text{-CH}$); 25.94 ($\text{CH}_2\text{-CH}$); 22.73, 22.10 (CH-CH_3); 13.65, 13.38, 13.22 ($\text{NCH}_2\text{-CH}_3$)
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N''</i> - <i>iso</i> -butyl-guanidiniumiodide (7n)	164.02 (CN_3); 57.21 (NCH_2CH); 45.93, 44.69, 44.62, 44.46 (NCH_2); 26.58 (CH); 21.09, 20.65 (CH-CH_3); 14.07, 13.91, 13.86, 13.47, 13.30 ($\text{NCH}_2\text{-CH}_3$)
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N''</i> - <i>sec</i> -butyl-guanidiniumiodide (7o)	163.39, 163.14 (CN_3); 60.31 (NCH); 44.26, 44.16, 43.96, 43.78, 40.19 (NCH_2); 29.40 (CH_2); 17.47, 16.49, 13.31, 13.13, 12.78, 12.59, 11.24 (CH_3)
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N''</i> - <i>iso</i> -pentyl-guanidiniumiodide (7p)	163.12 (CN_3); 47.15 (NCH_2CH_2); 44.56, 43.93, 43.89, 43.87, 43.82 (NCH_2); 35.86 ($\text{NCH}_2\text{-CH}_2$); 25.59 (CH); 22.34, 21.72 (CH-CH_3); 13.21, 13.11, 13.00, 12.98, 12.86 ($\text{NCH}_2\text{-CH}_3$)
<i>N,N,N',N',N''</i> -Pentaethyl- <i>N''</i> -hexyl-guanidiniumiodide (7q)	163.49 (CN_3); 49.29 (NCH_2CH_2); 44.94, 44.28, 44.20, 39.41 (NCH_2); 31.24 ($\text{CH}_2\text{-C}_2\text{H}_5$); 27.49 ($\text{NCH}_2\text{-CH}_2$); 26.57 ($\text{CH}_2\text{-C}_3\text{H}_7$); 22.50 ($\text{CH}_2\text{-CH}_3$); 13.94, 13.61, 13.51, 13.34, 13.26 (CH_3)

From the melting point data given in Table 5 and the compilation in Table 7 the following still preliminary conclusions concerning the guanidinium iodides **7a-h**, **7i-m** and **7n-q** can be drawn. In all cases the N-alkyl group present in the guanidinium iodides strongly influences the value of the melting point of these compounds. In the case of the salts **7a-h** branching in the alkyl group gives rise to an increase of the melting point of isomeric compounds.

Table 7: Relations between Constitution and melting points in *N,N',N''*-peralkylated guanidinium iodides

	Compounds	mp [°C]
7a	R = C_3H_7	181
7b	R = $\text{CH}(\text{CH}_3)_2$	267–268
7c	R = C_4H_9	81
7d	R = $\text{CH}_2\text{-CH}(\text{CH}_3)_2$	115
7e	R = $\text{C}(\text{CH}_3)_3$	267
7f	R = C_5H_{11}	88
7g	R = $(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	122
7h	R = C_6H_{13}	70

Additionally it can be suspected, that there is an alternation in the melting points of the salts with nonbranched alkyl groups in such a way that compounds as **7a**, **7f** with odd numbered alkyl groups show higher melting points than the subsequent compounds **7c**, **7h** possessing even numbered alkyl groups. The same seems to be valid for the series of the isopropyl compounds **7b**, **7d**, **7g**. In fact the analogous observations can be made when the melting points of the compounds in the series **7i-7m** and **7n-7q** are compared. Always the compound possessing the n-alkyl group shows the lowest melting point within a series of isomeric compounds. Usually the elongation of the alkyl group leads to a decrease of the melting point in the guanidinium salt series (c. f. mp **7i** > **7m**). The guanidinium salts **7m** and **7q** having a six membered alkyl

chain are liquid at room temperature and thus belong to the so called room temperature ionic liquids (RTIL's).

3. Experimental

N,N,N',N'-Tetraalkylureas **2a** and **2j** are commercially available. For our purposes we used products which we obtained from BASF AG, Ludwigshafen.

Preparation of the Ureas 2b-i from *N,N*-Dialkylcarbamoylchlorides and Secondary Amines in the presence of Triethylamine. General procedure. Triethylamine (106.0 g, 1.05 mol) and the corresponding secondary amine (1.05 mol) were dissolved in dry acetonitrile (500 mL). To this solution was added at -10 °C dropwise and with stirring the freshly distilled *N,N*-dialkylcarbamoylchloride (1.05 mol). The temperature of the mixture was kept by cooling with a sodium chloride-ice bath. Then the cooling bath was removed and the mixture was stirred for 16 h. The separated triethylamine-hydrochloride was filtered off and from the filtrate the acetonitrile was removed in a rotatory evaporator. To the residue was added dry ether (400 mL). The mixture was set aside in a refrigerator (2 °C) for 16 h. The separated salt was filtered off. From the filtrate the ether was removed by distillation. The residue was distilled through a 25 cm Vigreux-column with fractionation. Results and physical data for the compounds **2b-i** see Table 1, 2.

***N,N,N',N'*-Tetrahexylurea (2k).** Gaseous trimethylamine (165 g, 2.80 mol) was introduced into a mixture of dihexylamine (500 g, 2.71 mol) and dry acetonitrile (1.2 l) within 1 h at -15 to -10 °C. While the reaction mixture was cooled with an ice-sodium chloride bath was introduced phosgene (135 g, 1.36 mol) at -7 to -5 °C under vigorous stirring. The mixture was stirred for 1 h and then set

aside for 12 h at room temperature. The unreacted phosgene was removed by distilling off some acetonitrile (20 mL). The residue was stored for 12 h at 0–3 °C with exclusion of moisture and then filtered by suction. The filter cake was washed several times with ether. The combined filtrates formed a diphasic system, from which the solvents were removed in vacuo by means of a rotatory evaporator. The residue was taken up to 500 mL ether and extracted three times with water. After drying with magnesium sulphate the ethereal phase was evaporated. The thus obtained crude urea was purified by fractional distillation on a 30 cm Vigreux-column in the vacuum of an oil-pump. After a small forerun with bp 175 °C/0.7 Torr, n_D^{20} were obtained 350 g (65%) **2k** with bp 213 °C/0.3 Torr. $n_D^{20} = 1.4578$. For further details see tables 1 and 2.

***N,N,N',N',N''*-Pentaalkylguanidinium chlorides 3 from in situ prepared *N,N,N',N'*-tetraalkylchloroformamidinium chlorides 4 and primary amines in the presence of triethylamine. General procedure.** In the solution of the corresponding *N,N,N',N'*-tetraalkylurea (1.0 mol) in 200 mL dried acetonitrile was introduced phosgene (110.0 g, 1.11 mol) at –5 °C with stirring and exclusion of moisture. After the introduction of the phosgene the mixture, which was protected against moisture with a drying tube (CaCl₂) was kept for 6 h at –5 °C and then set aside in a well ventilated hood for 48 h at room temperature. To remove the excessive phosgene from the reaction mixture about 10 mL acetonitrile were distilled off at about 200 Torr. To the solution of the *N,N,N',N'*-tetraalkylchloroformamidinium chloride **3** in acetonitrile thus obtained was added dropwise without cooling an equimolar mixture of corresponding primary amine (1.00 mol) and triethylamine (101.0 g, 1.00 mol) under vigorous stirring. In the case of gaseous amines the amine (2.2 mol) were introduced into the mixture. During the amine addition the reaction mixture boiled under reflux. The mixture was stirred for 1 h at room temperature and then evaporated to dryness. To the salt mixture thus obtained was added aqueous sodium hydroxide [40 g (1.0 mol) in 100 mL water] at 0 °C. The triethylamine formed and the water were removed from the mixture in vacuo by means of a rotatory evaporator. The residue was heated to reflux with acetonitrile (200 mL) under stirring. The separated sodium chloride was filtered off. The filtrate was evaporated to complete dryness to leave the crude guanidinium salt **4** which can be purified by recrystallization from the appropriate dry solvent.

***N,N,N',N',N''*-Pentaalkylguanidines 5 from *N,N,N',N',N''*-pentaalkylguanidinium chlorides 4 and sodium hydroxide. General procedure.** To the crude salts **4** (0.1 mol) was added a layer of ether (100 mL). Sodium hydroxide (12 g, 0.3 mol) in water (100 mL) or potassium hydroxide (20 g, 0.3 mol, 84%) in water (100 mL) was added at 0 °C with vigorous stirring. The ethereal phase was

separated after 20 min and the residue stirred again with ether (50 mL). After the separation of the ether phase, the ether phases were combined and dried over potassium carbonate for 1 h. After the filtration of the carbonate the ether was removed from the filtrate and the residue distilled over a 25 cm Vigreux-column. (Details can be found in tables 3 and 4).

Preparation of *N,N,N',N',N''*-Pentamethylguanidine (5a) and *N*-butyl-*N',N',N'',N''*-tetramethylguanidine (5b). General Procedure. Into a solution of *N,N,N',N'*-tetramethylurea (58 g, 0.5 mol) in dry acetonitrile (300 mL) phosgene (54.5 g, 0.55 mol) was introduced slowly at 0–5 °C with stirring and exclusion of moisture. After 12 h of stirring at room temperature the mixture was heated to 40 °C for 2 h. Then a mixture of the butylamine (0.5 mol) and triethylamine (50.5 g, 0.50 mol) was added dropwise. In the case of methylamine the mixture was cooled at –25 °C and then the methylamine (31 g, 1.00 mol) was introduced at this temperature. After the addition of the amines was stirred for 1 h at room temperature and 1 h at 50 °C. Sodium hydroxide (20 g, 0.5 mol) in water (50 mL) was added at 0 °C with stirring. After 1 h stirring at room temperature the mixture was evaporated to dryness in a rotatory evaporator. The guanidine was set free by addition of NaOH (60 g, 1.5 mol) in water (200 mL) and extracted 3 times with ether (each portion 100 mL). The combined ethereal phases were dried (K₂CO₃). The ether was evaporated and the residue distilled in vacuo on a 25 cm Vigreux-column.

***N,N,N',N',N'',N''*-Hexaalkylguanidinium iodides 7a-q by alkylation of *N,N,N',N',N''*-pentaalkylguanidines with alkyl iodides 6a, b. General procedure.** The guanidine **5** (0.02 mol) was dissolved in dry acetonitrile (5 mL). To the solution was added dropwise the alkyl iodide **6** (0.03 mol) with stirring and exclusion of moisture. Then the mixture was heated to reflux for 12 h. The excessive alkyl iodide and acetonitrile were removed in a rotatory evaporator in vacuo. The solid residue was treated with dry ether, solid products were filtered off in vacuo and washed several times with dry ether and then carefully dried in vacuo. Liquids compounds were extracted several times with ether and then carefully dried in vacuo at 40 °C.

4. Conclusion

A series of *N,N,N',N',N'',N''*-peralkylated guanidinium iodides have been prepared from *N,N,N',N',N''*-pentasubstituted guanidines and methyl- and ethyl iodide, resp. By this procedure seven salts (**7c**, **7f**, **7h**, **7i**, **7m**, **7p**, **7q**) have been obtained which can be regarded as ionic liquids, since their melting points lay below 100 °C. Until now only a few ionic liquids consisting of *N,N',N''*-peralkylated guanidinium iodides are known.^{13d, 14}

For such compounds the lowest melting points observed are around 50 °C.^{11d, 14} Some of these compounds are reported to be glasses at room temperature.^{13d} In the present study we have described for the first time two *N,N',N''*-peralkylated guanidinium iodides (**7m**, **7q**) which represent room temperature ionic liquids.

5. References

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Povzetek

Pri reakcijah sekundarnih aminov s fosgenom ali *N,N*-dialkilkarbamoil kloridi nastanejo peralkilirane sečnine **2**, ki reagirajo s fosgenom do ustreznih kloroformamidinijevih kloridov **3**. Formamidinijeve soli **3** lahko pretvorimo naprej s primarnimi amini v prisotnosti trietilamina in natrijevega hidroksida do *N,N,N',N',N''*-pentasubstituiranih gvanidinov **5**. Alkiliranje gvanidinov **5** z metil- in etil jodidom vodi do gvanidinijevih jodidov **7**, ki so ionske tekočine.