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# Influence of *N*-Alkyl Substituents and Counterions on the Structural and Mesomorphic Properties of Guanidinium Salts: Experiment and Quantum Chemical Calculations

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A series of N-4-(4'-alkoxybiphenyl)-N',N',N",N"-tetramethylguanidinium salts was synthesized with varying alkoxy chain lengths and additional N-alkyl substituents, each with a number of different counterions. X-ray crystal-structure analyses of 1b l, 1b PF<sub>6</sub>, 2a I, and 4a I reveal bilayer structures in the solid state and, for the 1b and 1b PF<sub>6</sub> salts, a hydrogen-bond-type connectivity between the guanidinium N-H group and the anion is found. For the N-alkyl homologues 2a I and 4a I the anion is still oriented close to the head group, although at a larger distance. Ion pairs are present also in solution, as demonstrated by <sup>1</sup>H NMR: the *N*-H chemical shift shows a good linear correlation with the radius, and hence the hardness, of the anion. The intramolecular conformational flexibility of 1b I, 2b I, 3b I, and 4b I was studied by temperature-dependent <sup>1</sup>H NMR spectroscopy and discrete activation barriers were determined for rotations about each of the three C-N partial double bonds of the

1. Introduction

Based on a seminal observation by Knight and Shaw that longchain alkyl pyridinium halides display liquid-crystalline properties,<sup>[1]</sup> and more detailed investigations on the mesophase type by Bruce, Maitlis, Seddon and Holbrey,<sup>[2,3]</sup> ionic liquid crystals have gained increasing interest among material scientists.<sup>[4]</sup> Several groups have studied counterion effects on mesomorphic properties<sup>[5]</sup> and correlated, for example, the liquidcrystalline behavior of pyridinium salts with the formation of charge-transfer complexes between the pyridinium cation and a counterion.<sup>[6,7]</sup> However, the effect of the anion on the structure–property relationship in ionic liquid crystals requires further investigation.

Recently, we have reported that changing the anion of the *N*-4-(4'-dodecyloxybiphenyl)-*N'*,*N'*,*N''*,*N''*-tetramethylguanidinium salt **1b Cl** affects the stability of the smectic A (SmA) mesophases more critically than variations in the alkoxy chain length R<sup>1</sup> (Scheme 1).<sup>[8,9]</sup> Bruce et al. have observed the same behavior for silver stilbazole complexes.<sup>[10]</sup> Crystallographic data for **1b Cl** show a tilted bilayer structure in the solid state as well as a hydrogen-bond-type connectivity between the chloride anion and the guanidinium *N*-H.<sup>[8a]</sup> Hence, it was expected that *N*-alkylation might lead to a decisive change in the mesomorphic properties because hydrogen bonding is no longer possible, and also because the electronic (+1) and steric effects of the different alkyl substituents will change the over-

guanidinium core. The relative heights of the individual barriers change between the *N*-H and the *N*-alkylguanidinium salts. A fourth barrier is observed for the rotation about the *N*-biphenyl bond. DFT calculations of charge densities show that the positive charge resides primarily on the central carbon atom. Rotational barriers were calculated for *N'*-substituted 2amino-1,3-dimethylimidazolidinium cations as models, and are in qualitatively good agreement with the NMR data. Mesomorphic properties were studied by differential-scanning calorimetry, polarizing optical microscopy, and X-ray diffraction (WAXS/ SAXS). All liquid-crystalline guanidinium salts exhibit smectic A mesophases. Clearing temperatures show a linear correlation with the anionic radius. Substitution of the *N*-H group with methyl, ethyl, or propyl results in decreasing mesophase widths and a concomitant shrinkage of the layer spacings.

all charge distribution in the guanidinium moiety. Combined dynamic NMR investigations and charge-density calculations should provide a deeper insight into the relation between *intra*molecular organization and mesomorphic, that is, *inter*molecular properties of guanidinium salts. A comparative study of the *N*-H guanidinium salts **1X** and the corresponding *N*-alkyl homologues **2–41** might even provide a probe for assessing ionic-liquid-crystal properties in general. We report the results herein.

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#### 2. Results and Discussion

#### 2.1. Experimental

Synthesis (Scheme 2) and analytical characterization of the compounds **1c,d,f,g Cl** and **1a,d,e X** (X  $\neq$  Cl; see Scheme 1), **2–41**, **7**, **8c,d,f,g** and **9c,d,f,g** are described in the Supporting Information. Synthetic details for the compounds **1a,b,e Cl** and **1b X** (X  $\neq$  Cl), **5**, **6**, **8a,b,e**, **9a,b,e** have been reported previous-ly<sup>[8]</sup> and these compounds are included here for comparative investigations. Tridecyl bromide,<sup>[11a]</sup> (S)-1-bromo-3,7-dimethyl-octane,<sup>[11b-e]</sup> 1-bromo-3,7,11,15-tetramethylhexadecane,<sup>[11b,c,f-h]</sup> and tetramethylchloroamidinium chloride<sup>[12]</sup> were prepared according to literature procedures.

#### 2.2. Synthesis of Guanidinium Salts

The synthesis of N-4-(4'-alkoxybiphenyl)-N',N',N",N"-tetramethylguanidinium chlorides 1Cl (Scheme 2) started from 4-nitrobiphenyl-4'-yl benzoate 5, available in two steps from 4-hydroxybiphenyl by following our previously published procedure.<sup>[8]</sup> Saponification of 5 with KOH, rather than with K<sub>2</sub>CO<sub>3</sub>, to obtain the alcohol **6** as reported,<sup>[8]</sup> yielded the corresponding potassium biphenolate 7 in 93% yield, which was then directly reacted with alkyl bromides in refluxing acetonitrile to give the ethers 8 in 71-94% yield. Catalytic hydrogenation of the nitro group (85–95%), treatment of amines **9**<sup>[13]</sup> with tetramethylchloroamidinium chloride<sup>[8,12]</sup> in the presence of NEt<sub>3</sub>, and subsequent neutralization with NaOH afforded the guanidinium chlorides 1Cl in an overall yield of 86-97%. The chlorides 1Cl were then submitted to salt metathesis with Nal, NaBr, NaBF<sub>4</sub>, KPF<sub>6</sub>, KSCN, and KBPh<sub>4</sub>, respectively, in MeCN to give the corresponding quanidinium salts 1X (X  $\neq$  Cl) (Scheme 2, for yields



**Scheme 2.** Synthesis overview (for details on alkyl chain length and yields see the Supporting Information).

see Table S1 in the Supporting Information). Mixed-anion guanidinium salts  $1 \operatorname{Cl}_{x} \operatorname{I}_{1-x}$  were obtained by incomplete salt exchange.

The corresponding pentaalkylarylguanidinium iodides 2–41 were obtained by reaction of the chlorides 1Cl with methyl, ethyl, and *n*-propyl iodide, respectively, in acetonitrile at room temperature or 100 °C in the presence of  $K_2CO_3$ .

#### 2.3. Single-Crystal X-Ray Diffraction Studies

Suitable single crystals could be grown for compounds **1b I**, **1b PF**<sub>6</sub>, **2a I**, and **4a I**. The corresponding X-ray structures of the single molecules and packing diagrams are presented in Figures 1-4.<sup>[14]</sup>

All packing diagrams displayed bilayer structures with interdigitated alkyl chains as reported before,<sup>[8]</sup> but also revealed interesting interactions between the guanidinium cations and

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Figure 1. a) X-ray structure of 1b l in the solid state (numbering of atoms given here is used only for the X-ray diffraction studies); b) Packing diagram for 1b l.





**Figure 2.** a) X-ray structure of **2a I** in the solid state (numbering of atoms given here is used only for the X-ray diffraction studies); b) Packing diagram for **2a I**.

the anions. Hydrogen-bond-type connectivities were detected in the solid state for **1b** Cl<sup>[8a]</sup> and **1b** I (Figure 1), with 'hydrogen-bond' distances of d=225 pm for (N-1)–H···Cl and 270 pm for (N-1)–H···I. The hexafluorophosphate **1b** PF<sub>6</sub> (Figure S1 in the Supporting Information) features a bifurcated hydrogen bond with distances of d=244/231 pm for (N-1)–H···F<sub>2</sub>PF<sub>4</sub>.

For the *N*,*N'*,*N''*,*N''*,*P*''-pentaalkylguanidinium salts **2–41**, hydrogen-bond formation is no longer feasible, yet some weak interactions still remain between the guanidinium head group and the anions. An atomic distance of d=317 pm was determined for (C-3)–H···I in the case of **2aI** (Figure 2) and of d=297 pm for (C-8)–H···I for **4aI** (Figure S2 in the Supporting Information). The anion thus is located close to the guanidinium head group, regardless of whether the guanidinium moiety is *N*-protonated or *N*-alkylated.

With such detailed information available about the structural organization of the *N*-alkylguanidinium salts in the crystalline state (Figure 2 and Figure S2), it appeared interesting to compare the intramolecular organization (relative orientation, conformation) of the individual, single cations in solution using <sup>1</sup>H NMR spectroscopy. As in the case of the X-ray diffraction studies, the *N*-H guanidinium salts were included for comparison.

#### 2.4. <sup>1</sup>H NMR Studies

The first observation was that the anion exchange reactions of the salts **1Cl** were easy to monitor by <sup>1</sup>H NMR since the *N*-H proton resonance shifts upfield in a significant manner upon replacement of chloride by other anions. Typical spectra of **1a X** are shown in Figure 3. The following tendency of  $\delta_{(N-H)}$  is preserved in all four series **1a X**, **1b X**,<sup>[15]</sup> **1d X**, and **1e X** (**X** = Cl, Br, I, BF<sub>4</sub>, PF<sub>6</sub>, SCN), regardless of the alkyl chain lengths R<sup>1</sup>:  $\delta_{(N-H)}$  Cl<sup>-</sup> > Br<sup>-</sup> > SCN<sup>-</sup> > l<sup>-</sup> > BF<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup>. All other signals appear virtually unchanged upon anion exchange.



**Figure 3.** Low-field section of the <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>, 296 K,  $c = 45 \text{ mmol L}^{-1}$ ) of the guanidinium salts **1a X** with different anions **X**.

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**Figure 4.** Correlation of the *N*-H chemical shifts for **1b X** and **1e X** ( $\delta$  [ppm], CDCl<sub>3</sub>, 296 K, c = 15.4 mmol L<sup>-1</sup>) with the anionic radii.

The observed upfield shift shows a fairly good linear correlation with the anionic radius<sup>[16]</sup> (Figure 4; tetraphenylborates 1b,e BPh4 were not included because of the large additional anisotropic effect of the phenyl rings). This finding indicates that the anion is positioned quite close to the N-H group of the guanidinium ion, presumably by hydrogen bonding (also in solution), and is consistent with the X-ray structures of, for example, 1b I and 1b PF<sub>6</sub> (Figure 1 and Figure S1 in the Supporting Information). These results are in good agreement with previous work by Seddon and others on imidazolium salts, which revealed the position of the anion to be controlled by hydrogen bonds rather than Coulomb attractions, that is, by close proximity of the anion to the area of greatest positive charge.<sup>[17]</sup> To strengthen this point, we investigated whether there is a pronounced solvent and/or temperature effect on the N-H chemical shift, and hence on the hydrogen-bond formation within the ion pairs. The N-H signal of 1b Cl is in fact shifted upfield by up to 2ppm with increasing solvent polarity (CDCl<sub>3</sub> to DMSO, see Figure S3 in the Supporting Information). The  $\alpha$ -OCH<sub>2</sub> signal, on the other hand, stays more or less constant. This deshielding effect in less polar solvents was previously observed by Saielli with octyl viologen salts.<sup>[18]</sup> Temperature, in contrast, affects the N-H signal much less. From -50 °C to +50 °C, the *N*-H resonance of **1b Cl** in CDCl<sub>3</sub> is shifted downfield by only ~0.5 ppm (Figure S4 in the Supporting Information).

For mixed guanidinium salts in  $CDCl_{3}$ , for example **1a**  $Cl_{0.25}l_{0.75}$ , one single signal was observed for the *N*-H proton, with the average chemical shift corresponding to the molar ratio (Figure S5 in the Supporting Information). Even though hydrogen bonds seem to fix the anion at a certain distance to the guanidinium cation, there still is a rapid exchange between the different halide ions. The same behavior is found even in DMSO.

The *N*-H guanidinium salt **1b I** and the *N*-alkyl homologues **2b I**, **3b I**, and **4b I** also display a pronounced conformational mobility. At 196 K, the <sup>1</sup>H NMR spectrum (500 MHz,  $CD_2CI_2$ ) of **1b I** shows four discrete signals for the four topologically different *N*-CH<sub>3</sub> groups which are spread over almost 1ppm



Figure 5. Temperature-dependent  ${}^{1}$ H NMR spectral traces (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, expansion 2.4–3.6 ppm) for the *N*-H guanidinium iodide 1b I.<sup>[21]</sup>



Scheme 3. Numbering scheme for the topologically different positions in the compounds 1b I-4b I (the numbering given here differs from that employed for the X-ray diffraction studies, but is maintained consistently from here on).

(Figure 5; for characterization of the positions, see Scheme 3). At 300 K, these four lines have coalesced into one single, but still rather broad resonance. The *N*-alkyl homologues **2b I**, **3b I**, and **4b I** display the same spectral pattern, with the final coalescence, however, shifted to higher temperatures by ~40 K to 338K compared to **1b I** (<sup>1</sup>H NMR spectra of **2b I** at various temperatures are shown in Figure 6). The different sites are equilibrated by rotation around the three partial double bonds between C<sup>1</sup> and N<sup>2</sup>, N<sup>3</sup>, and N<sup>4</sup>, respectively. These intramolecular dynamics were evaluated by temperature-dependent <sup>1</sup>H NMR spectroscopy.<sup>[19]</sup>

Calculating the free energy of activation,  $\Delta G_c^{\dagger}$ , for any given dynamic process requires precise values for the coalescence temperature ( $T_c$ ) and the line separation at this temperature ( $\delta v_c$ ).<sup>[20]</sup> In the case of the *N*-H compound **1b I**, for instance, spectra were therefore recorded within 1°-intervals from 237– 248K to exactly determine the coalescence point for the first pair of *N*-CH<sub>3</sub> signals (~2.60/3.07 ppm) at 247K (see Figure S7 in the Supporting Information for the spectral traces). The experimentally not accessible  $\delta v_c$  value has to be obtained from a  $\delta v$  versus *T* plot. All guanidinium salts studied herein displayed a small to negligible temperature dependence of  $\delta v$ .



Figure 6. Temperature-dependent <sup>1</sup>H NMR spectral traces (500 MHz, 196–296 K in  $CD_2CI_2$ , 296–343 K in  $CI_2CD$ – $CDCI_2$ , expansion 2.4–3.6 ppm, not all traces are shown) for the *N*-methylguanidinium iodide **2b** I.

Nevertheless,  $\delta v_c$  values extrapolated to  $T_c$  were always used for the calculations (Table 2).

Already at 250 K, the signal of C<sup>2</sup>/C<sup>6</sup>-H, in the *ortho* position of the N<sup>3</sup> aryl ring and high-field part of an AA'XX' spin system, appears severely broadened relative to the signals of the C<sup>3</sup>/C<sup>5</sup>-H (low-field half of the AA'XX' system) and also to those of the second aryl ring of the 4'-decyloxybiphenyl moiety. At 186 K, this signal is split into two distinct and widely separated resonances. Thus, rotation around the C<sup>1'</sup>–N<sup>3</sup> bond can likewise be frozen out. For all four guanidinium salts **1b** I–**4b** I, this rotation 1 (Scheme 3) has the lowest energy barrier. The frequency separation  $\delta v$  and the coalescence temperature both cannot be determined with the same precision as for the other dynamic processes. The calculated activation barrier,  $\Delta G_c^{\dagger}$ , is ~ 35 kJ mol<sup>-1</sup>, that is, 10–15kJ mol<sup>-1</sup> lower than for the other rotational processes (Table 2).

One of the methyl resonances appears shifted upfield by  $\geq 0.5$  ppm for all four guanidinium iodides **1b I–4b I**. It can be assigned to 4<sub>5</sub>-CH<sub>3</sub>. In the crystal structure of **1b I** (see Figure 1) this methyl group is located directly above the aromatic ring. The distance between the 4<sub>5</sub>-CH<sub>3</sub> carbon and the

Table 1. Selected structural parameters from the X-ray diffraction analy-ses of the guanidinium iodides 1b I, 2a I, and 4a I (numbering as given inScheme 3, not as in the ORTEP plots).

R <sup>2</sup>	1a I H	<b>2b Ι</b> C <sup>α</sup> H <sub>3</sub>	<b>4b I</b> C <sup>α</sup> H <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
RMS deviation <sup>[a]</sup> [pm] dihedral angle <sup>[b]</sup> (+) [°]	0.87	0.16	0.00
for C <sup>4S</sup> N <sup>4</sup> C <sup>4A</sup>	29.3	31.9	28.2
for C <sup>25</sup> N <sup>2</sup> C <sup>2A</sup>	28.6	30.0	33.6
for C <sup>1′</sup> N <sup>3</sup> H/C <sup>α</sup>	34.9	46.9	48.2
distance <sup>[c]</sup> [pm]	306	299	297
distance <sup>[d]</sup> [pm]	354	366/351	319/351

[a] RMS deviation from coplanarity for the central guanidinium core (N<sup>2</sup>N<sup>3</sup>N<sup>4</sup>C<sup>1</sup>). [b] Twist of the three amino groups relative to the guanidinium core plane. [c] Distance between 4<sub>5</sub>-CH<sub>3</sub> and the *ipso* aryl carbon atom C<sup>1'</sup>. [d] Distance between closest/two closest 4<sub>5</sub>-CH<sub>3</sub> hydrogens and the center of the aryl ring.

**Table 2.** Coalescence temperatures  $T_{cr}$  frequency separations  $\delta v_{cr}$  rate constants k, and enthalpy barriers  $\Delta G_c^{+}$  for the guanidinium iodides **1b I**, **2b I**, **3b I**, and **4b I** (Scheme 3, for details see the Supporting Information).

	rotational proc.	Т <sub>с</sub> [К]	$\delta v_{\rm c}$ [Hz]	<i>k</i> [Hz]	$\Delta G_{c}^{\dagger}$ [kJ mol <sup>-1</sup> ]
1b I	2	247	224	498	47
	3	271	187	415	52
	4	277	223	495	53
2b I	4	231	81	180	46
	4	245	350	778	46
	2, 3	324	138	307	64
3b I	4	240	109	242	46
	4	257	389	864	47
	2, 3	320	135	300	63
4b I	4	232	93	206	46
	4	249	384	853	47
	2, 3	317	143	318	63

*ipso* carbon C<sup>1'</sup> of the phenyl ring is 306 pm (Table 1). One hydrogen atom of the 4<sub>s</sub>-CH<sub>3</sub> group is located 354 pm above the center of the aromatic ring, and thus deep within the shielding cone of the ring current. Upon raising the temperature, the 4<sub>s</sub>-CH<sub>3</sub> resonance (2.597 ppm) coalesces with the *N*-CH<sub>3</sub> signal at 3.073 ppm for **1b I** ( $T_c$ =247 K,  $\Delta G_c^{\dagger}$ =47 kJ mol<sup>-1</sup>). Coalescence for the other two methyl signals at 3.124 and 3.494 ppm, respectively, was observed at 271 K ( $\Delta G_c^{\dagger}$ =52 kJ mol<sup>-1</sup>). The final coalescence of the two broad merged resonances could be fixed at 277 K. All coalescence temperatures and the enthalpy barriers, calculated from the coalescence data, are summarized in Table 2.

If the first coalescence was due to rotation 4 around the C<sup>1</sup>–N<sup>3</sup> partial double bond, this would exchange positions 4<sub>s</sub>-CH<sub>3</sub> and 2<sub>5</sub>-CH<sub>3</sub> as well as 4<sub>A</sub>-CH<sub>3</sub> and 2<sub>A</sub>-CH<sub>3</sub>. Different coalescence temperatures are expected for these two exchange processes since the frequency separations  $\delta v$  for the two pairs of lines involved differ sufficiently (Table 2). The free activation barriers, however, calculated from the coalescence data, should be identical because the same intramolecular motion mutually interchanges positions  $4_s/2_s$  and  $4_A/2_A$ , respectively. Since this is not the case, the first intramolecular motion detected upon raising the temperature from 196K must be assigned to rotation 2 around  $C^1-N^4$ , followed by that around  $C^1-N^2$ . In the last stage, rotation 4 around  $C^1-N^3$  finally equilibrates all four N-CH<sub>3</sub> positions. With the first dynamic process fixed as rotation 2, involving  $4_{s}$ - and  $4_{A}$ -CH<sub>3</sub>, the resonance at 3.073 ppm can be assigned unequivocally to  $4_{A}$ -CH<sub>3</sub>.

For the *N*-methylguanidinium iodide **2b I** (Figure 6),  $4_{s}$ -CH<sub>3</sub> displays an even more pronounced upfield shift, and hence must dip even deeper into the aromatic shielding cone. Coalescence links this resonance to the *N*-methyl signal at 3.272 ppm, corresponding to a frequency separation  $\delta \nu$  of almost 360 Hz. The second pair of coalescing *N*-CH<sub>3</sub> signals is more closely spaced ( $\delta \nu \sim 80$  Hz). Nevertheless, identical  $\Delta G_c^{\dagger}$  values were calculated for both exchange processes. This is expected if rotation 4 around the C<sup>1</sup>–N<sup>3</sup> bond now is the intramolecular motion with the lowest activation barrier. The *N*-ethyl and *N*-propyl homologues, **3b I** and **4b I**, show compara-

ble line patterns, and almost identical  $\Delta G_{c}^{\dagger}$  values were calculated for all three coalescence phenomena (Table 2).

The drastic change in intramolecular dynamics between the N-H and the N-alkyl derivatives can be rationalized by closer inspection of the crystal structures of 1b I, 2a I, and 4a I (Figures 1,2 and Figure S2 in the Supporting Information). The RMS deviation from coplanarity for the central C<sup>1</sup>N<sup>2</sup>N<sup>3</sup>N<sup>4</sup> moiety is <1 pm for the *N*-H and <0.2 pm for the *N*-alkylguanidinium salts (Table 1). The molecular core thus can be considered as perfectly planar. Overlap between the three nitrogen lone pairs and the central carbon C<sup>1</sup>, that is, delocalization of the positive charge, and the concomitant partial double-bond character of the individual C<sup>1</sup>-N bonds thus depends only upon the twist of the three amino moieties relative to the guanidinium plane. As the values for the dihedral angles in Table 1 show, both dimethylamino groups are twisted uniformly by  $\sim 30^{\circ}$  in the crystalline state. For the more bulky N-arylamino group, the dihedral angle is  $35^{\circ}$  in the *N*-H compound.

With an additional alkyl substituent at N<sup>3</sup>, that is, for **2a I** and **4a I**, however, the *N*-alkyl-*N*-arylamino group is twisted by almost 50° (Table 1), severely reducing the  $p_{\pi}$ -overlap between C<sup>1</sup> and N<sup>3</sup> (cos<sup>2</sup> function) and thus the partial double-bond character of this bond. Consequently, the corresponding internal motion now has the lowest activation barrier even though a much bulkier group has to be rotated around the C<sup>1</sup>–N<sup>3</sup> bond. With the *N*-alkyl-*N*-arylamino moiety contributing less to the stabilization of the positive charge, the electronic demand upon the two dimethylamino groups is increased concomitantly. The barrier for rotation around the C<sup>1</sup>–N<sup>4</sup> and C<sup>1</sup>–N<sup>2</sup> bonds, which now are topologically equivalent, is in fact raised by > 10 kJ mol<sup>-1</sup> for all three *N*-alkylguanidinium iodides relative to the *N*-H compound.

The internal dynamics of protonated guanidines and especially of *N*,*N'*,*N''*,*N''*-pentamethylguanidinium salts have been firmly established by the fundamental work of Kessler and Leibfritz.<sup>[22a-b]</sup> These authors have also demonstrated that for both classes of compounds the topological interchanges are due to distinct rotational processes around the three C–N partial double bonds rather than to nitrogen inversion or a deprotonation/reprotonation sequence. With the higher chemical shift dispersion at 11.74 Tesla compared to 1.408 Tesla, we evaluated even the lowest of the three coalescence processes (see Table 2), and thus verified that the two lowest coalescence processes in, for example, the pentamethylarylguanidinium iodide **2b I** are linked to identical energy barriers.<sup>[23]</sup>

This constitutes direct proof that in the *N*-alkyl, other than in the corresponding *N*-H guanidinium salts, rotation around the  $C^1-N^3$  bond indeed has the lowest barrier. The  $\Delta G_c^+$  values for the three coalescence processes, and hence all rotational barriers, remain unaffected within the error limit<sup>[24]</sup> of  $\pm 0.5$  kJ mol<sup>-1</sup> (Table 2) when the size of the  $N^3$ -alkyl substituent R<sup>2</sup>, and hence steric interaction with the aryl group, is increased from methyl to propyl. For the pentamethylarylguanidinium salts, Kessler and Leibfritz have found that two *ortho* methyl groups, on the other hand, already lead to a dramatic increase in this barrier.<sup>[22a-b]</sup>

#### 2.5. Quantum Chemical Calculations

Quantum chemical calculations were expected to provide a more detailed understanding of charge distribution, conjugation effects, and intramolecular dynamics in this type of guanidinium cations. The Gaussian 03 program suite<sup>[25,26]</sup> was used for all calculations. The DFT hybrid functional  $\mathsf{B3LYP}^{\scriptscriptstyle[27]}$  and the standard 6-31G(d,p) basic set were used for all calculations. We calculated the optimized structures for the isolated guanidinium cations 1b, 2a, and 4a (Tables S11-S13 in the Supporting Information) for a direct comparison with the crystal structure data for the corresponding iodides 1b I, 2a I, and 4a I. Generally, good agreement was found between experimental and calculated C–C and C–N bond lengths ( $\Delta r_{max} = |6|$  pm) and bond angles ( $\Delta \delta_{max} = |2|^{\circ}$ ). The dihedral angles C<sup>1</sup>-N<sup>3</sup>-C<sup>1</sup>- $C^{2'/6'}$ , for instance, are ~40°, ~50°, and ~45° for the calculated structures 1b, 2a, 4a, respectively. The corresponding X-ray diffraction values are  $27^{\circ}$ ,  $34^{\circ}$ , and  $36^{\circ}$ . The agreement of the torsion angle for the calculated isolated molecule and the experimental data for the solid state is guite reasonable since this dihedral angle comprises two intramolecular motions, the twist of the N<sup>3</sup>R<sup>2</sup>R<sup>3</sup> amino group around the C<sup>1</sup>-N<sup>3</sup> bond with respect to the guanidinium core plane, and the torsion of the biphenyl moiety around the N<sup>3</sup>-C<sup>1'</sup> bond relative to the  $C^{1'}N^{3}H(C^{\alpha})$  plane.

For all further calculations, the long alkoxy chain  $R^1$  in the biphenyl moiety was replaced by an OMe group to minimize computational costs. The following set of model guanidinium cations was used for the quantum chemical studies (Scheme 4): the *N*-4-(4'-methoxybiphenyl)-*N'*,*N'*,*N''*,*N''*-tetrame-



Scheme 4. Model structures 10-20 used for quantum chemical calculations.

thylguanidinium cation (**10**) and the homologous cations with an additional *N*-methyl, *N*-ethyl, and *N*-propyl substituent (**11**– **13**). As smaller models, the *N*-4-(4'-methoxyphenyl)guanidinium cations, **15** and **16**, and the penta- and hexamethylguanidinium cations, **18** and **19**, as well as the corresponding neutral guanidines **14**, **17**, and **20** were included for comparison. Only small deviations between the X-ray structural data and comparable calculated bond lengths ( $\Delta r_{max} = |5|$  pm) and bond angles ( $\Delta \delta_{max} = |10|^{\circ}$ ) were observed in all the model structures.

The minimum structures for the guanidinium cations **1b**, **2a**, **4a**, **10–13**, **15**, **16**, **18**, and **19** have a twisted right- or lefthanded propeller-type arrangement of the planar NR<sub>2</sub> groups around the central carbon C<sup>1</sup>. Optimum resonance stabilization of the cationic center C<sup>1</sup> would require a close to coplanar arrangement whereas repulsive steric interaction between alkyl and aryl substituents induces torsion of the NR<sub>2</sub> group plane relative to the guanidinium core plane (C<sup>1</sup>N<sup>2</sup>N<sup>3</sup>N<sup>4</sup>). Table 3

**Table 3.** Torsional angles  $\phi$  between the guanidinium core plane  $(C^1N^2N^3N^4)$  and the planes of the three amino functions, and torsional angles  $\theta$  between the plane of the amino group  $N^3R^2R^3$  and the plane  $(C^{\ell}C^{1'}C^{2'})$  of the aryl substituent.

Structure	Structure $\phi$ [°]				
	$N^3 - R^2$	N <sup>2</sup> (Me) <sub>2</sub>	$N^3C^{1'}R^{2''}$	N <sup>4</sup> (Me) <sub>2</sub>	
1b I	Н	29	35	29	37
1b	Н	31	30	33	44
10	Н	30	29	32	44
2a l	Me	30	47	32	40
2a	Me	35	37	34	54
11	Me	35	37	34	54
12	Et	36	40	33	44
4a l	<i>n</i> -Pr	34	48	28	30
4a	<i>n</i> -Pr	36	42	33	45
13a	<i>n</i> -Pr	35	38	35	46
13b	<i>n</i> -Pr	36	42	33	44

shows a comparison of corresponding measured and calculated interplane angles  $\phi$ . The calculated interplane angles  $\phi$  between the NR<sub>2</sub>-group planes and the C<sup>1</sup>N<sup>2</sup>N<sup>3</sup>N<sup>4</sup> plane of the central guanidinium moiety vary between 29–42°. Calculated and experimental diffraction angles  $\phi$  for the two N(Me)<sub>2</sub> groups are in fairly good agreement. The calculated torsion angles for the cations are marginally larger ( $\phi \sim 2-5^\circ$ ) than

of the N(Me)<sub>2</sub> groups and the guanidinum main plane is  $\phi$ = 35°. The coordinates for all minimum structures **1b**, **2a**, **4a**, and **10–20** are collected in Tables S14–S40 in the Supporting Information.

The calculated interplane torsion angle  $\theta$  of the substituted aryl ring of the biphenyl substituent with respect to the C<sup>1</sup>N<sup>3</sup>R<sup>2</sup> plane is  $\theta = 44^{\circ}$  for the guanidinium cations **1b** and **10**, similar to the experimentally determined angle for the crystalline salt **1b I** of  $\theta = 37^{\circ}$ . For **2a** and **11** a torsion angle of  $\theta =$  $54^{\circ}$  is calculated as compared to the experimentally measured angle of  $\theta = 40^{\circ}$  in **2a I**. For the guanidinium cations **4a**, **12**, and **13** the alkyl substituent R<sup>3</sup> (Et, *n*-Pr) can adopt different conformations which lead to minimum structures of similar energy but different interplane torsion angles  $\theta$  [for **13** for example, **13a** (R<sup>3</sup>=*anti*-*n*-Pr,  $\theta = 46^{\circ}$ ) and **13b** (R<sup>3</sup>=*gauche*-*n*-Pr,  $\theta = 44^{\circ}$ ,  $\Delta E = +6 \text{ kJ mol}^{-1}$ ) see the Supporting Information]. A torsion angle of  $\theta \approx 45^{\circ}$  is calculated for **4a**, **12**, and **13** with an alkyl-group conformation analogous to that experimentally observed for the solid guanidinium salt **4a I**, where  $\theta = 30^{\circ}$ .

Atomic charges for the guanidinium cations **10–13**, **15**, **16**, **18**, and **19** were calculated using the natural bond orbital (NBO) method (Table 4).<sup>[28]</sup> In all eight guanidinium cations, an identical positive charge (0.70) is localized at the central carbon C<sup>1</sup> (Table 4a). The charge distribution is identical for the three *N*-H guanidinium cations **10**, **15**, **18**, and thus independent of the *N*<sup>3</sup>-substituent, 4'-methoxybiphenyl, 4-methoxyphenyl, or methyl. The negative charge density at the secondary nitrogen N<sup>3</sup> is higher than that at the dimethyl-substituted nitrogens N<sup>2</sup> and N<sup>4</sup> and is equal for all nitrogens of the hexasubstituted guanidinium cations **11–13**, **16**, and **19**.

Group charges for the structural fragments, the guanidinium core G and the different R<sup>3</sup> substituents (4'-methoxybiphenyl, 4-methoxyphenyl, methyl), are the same for all eight guanidinium cations (Table 4b). The total charge for the guanidinium moiety G is constant, independent of the N<sup>3</sup> substitution. This implies that the N<sup>3</sup>-aryl and N<sup>3</sup>-Me substituents have the same effect, and thus there is no evidence for delocalization of the

those determined experimentally for the corresponding salts. The plane of the secondary imino/ amino group ( $N^{3}R^{2}C_{arvl}$ ,  $R^{2} = H$ ) of 1b and 10 is twisted  $\sim\!30^\circ$  from the guanidinium main plane, somewhat less than measured in the crystal structure 1b I. This interplane angle increases with increasing steric demand of the substituent  $R^2$  (2a, 11,  $R^2 = Me$ ,  $\phi = 37^{\circ}$ ; **12**, R<sup>2</sup> = Et,  $\phi = 40^{\circ}$ ; **4a** and **13b**,  $R^2 = n$ -Pr,  $\phi = 42^{\circ}$ ). Experimentally, this angle increases from **1b I** ( $R^2 = H$ ,  $\phi = 35^\circ$ ) to **2a I** ( $R^2 = Me$ ,  $\phi = 47^\circ$ ) and **4a I** ( $R^2 =$ *n*-Pr,  $\phi = 48^{\circ}$ ). For the hexamethyl-substituted guanidinium cation 19 the calculated interplane angle between the plane

**Table 4.** NBO charge distribution in the guanidinium cations **10**, **11**, **15**, **16**, **18**, and **19**: 4a) for the guanidinium core atoms, 4b) for the two structural fragments G (total guanidinium core  $C^1N^2N^3N^4$ ) and  $R^3$  (aryl/methyl substituent at  $N^3$ ), and 4c) for  $C^1$  and the three individual amino groups ( $\Sigma$ =total charge).

		10	11	12	13	15	16	18	19
4a)	<b>C</b> <sup>1</sup>	+0.70	+0.70	+0.70	+0.70	+0.70	+0.70	+0.70	+0.70
	N <sup>2</sup>	-0.44	-0.44	-0.44	-0.44	-0.43	-0.44	-0.43	-0.43
	N <sup>3</sup>	-0.61	-0.44	-0.44	-0.45	-0.61	-0.44	-0.61	-0.43
	$N^4$	-0.43	-0.43	-0.43	-0.42	-0.43	-0.43	-0.44	-0.43
	other	+1.78	+1.61	+1.61	+1.61	+1.77	+1.61	+1.78	+1.59
	$\Sigma$	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00
4b)	G	+0.75	+0.74	+0.75	+0.75	+0.74	+0.74	+0.73	+0.73
	R <sup>3</sup>	+0.25	+0.26	+0.25	+0.25	+0.26	+0.26	+0.27	+0.27
	$\Sigma$	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00
4c)	C1	+0.70	+0.70	+0.70	+0.70	+0.70	+0.70	+0.70	+0.70
	$N^2(Me)_2$	+0.10	+0.09	+0.09	+0.09	+0.10	+0.09	+0.11	+0.10
	$N^{3}(R^{2},R^{3})$	+0.09	+0.10	+0.10	+0.09	+0.10	+0.10	+0.10	+0.10
	N <sup>4</sup> (Me) <sub>2</sub>	+0.11	+0.11	+0.11	+0.12	+0.09	+0.10	+0.11	+0.10
	Σ	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00	+1.00

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positive charge in the N<sup>3</sup>-aryl  $\pi$ -system. The group charges for the central carbon C<sup>1</sup> and the three groups N<sup>2</sup>(Me)<sub>2</sub>, N<sup>3</sup>(R<sup>2</sup>,R<sup>3</sup>), and N<sup>4</sup>(Me)<sub>2</sub> confirm equal and predominant localization of the positive charge at carbon C<sup>1</sup> independent of different *N*-substituents (Table 4c).

In the guanidines 14, 17, and 20 calculated for comparison, the imino-nitrogen  $N^3$  carries slightly more negative charge than the amino-nitrogens  $N^2$  and  $N^4$ , independent of aryl or methyl substitution (see Table 5a). The NBO group charges for

<b>Table 5.</b> NBO charge distribution in the guanidines <b>14</b> , <b>17</b> , and <b>20</b> : 5a) for the guanidine core atoms, 5b) for C <sup>1</sup> and the three individual amino/ imino groups ( $\Sigma$ =total charge).							
		14	17	20			
5a)	C <sup>1</sup>	+0.64	+0.64	+0.62			
	N <sup>2</sup>	-0.48	-0.48	-0.49			
	N <sup>3</sup>	-0.57	-0.57	-0.57			
	N <sup>4</sup>	-0.50	-0.50	-0.52			
	other	+1.91	+1.91	+1.96			
	$\Sigma$	+1.00	+1.00	+1.00			
5b)	<b>C</b> <sup>1</sup>	+0.64	+0.64	+0.62			
	N <sup>2</sup> (Me) <sub>2</sub>	-0.05	-0.06	-0.09			
	N <sup>3</sup> R <sup>3</sup>	-0.52	-0.50	-0.42			
	N <sup>4</sup> (Me) <sub>2</sub>	-0.07	-0.08	-0.11			
	$\Sigma$	$\pm$ 0.00	$\pm$ 0.00	$\pm 0.00$			

the central carbon C<sup>1</sup> and the three amino/imino substituents N<sup>2</sup>(Me)<sub>2</sub>, N<sup>3</sup>R<sup>3</sup>, and N<sup>4</sup>(Me)<sub>2</sub> show strong C<sup> $\delta+-N^{\delta-}$ </sup> polarization of the imino double bond C<sup>1</sup>=N<sup>3</sup> (Table 5b). The C<sup>1</sup>–N<sup>2</sup> and C<sup>1</sup>–N<sup>4</sup> bond lengths (140 pm) calculated for **14**, **17**, and **20** are slightly shorter than a C–N single bond (147 pm in Me–NH<sub>2</sub>). The imino bond C<sup>1</sup>–N<sup>3</sup> (129 pm) is close to the length of a C=N double bond (127 pm in Me=NH). The similar calculated NBO charge distribution (Table 5b) for **14**, **17**, and **20** suggests no significant conjugation of the 4'-methoxy(bi)phenyl substituent at N<sup>3</sup> with the guanidine core.

The larger calculated negative charge density at the iminonitrogen atom N<sup>3</sup> compared to the amine-nitrogen atoms N<sup>2</sup> and N<sup>3</sup> in **14**, **17**, **20** is in accord with earlier findings that N<sup>3</sup> is the preferred protonation site in guanidines.<sup>[22]</sup>

#### 2.6. Modeling Rotational Barriers

Guanidinium cations in principle can show bond rotations around the three different  $[C^1]^+$ –N bonds impeding calculation of individual rotational barriers. Thus, we have chosen the 2-amino-substituted imidazolidinium cations **22–29** with different substituents R<sup>2</sup> and R<sup>3</sup> at the nitrogen N<sup>3</sup> as computational models. These structures have fewer degrees of freedom and allow one to single out specific rotational barriers around the  $[C^1]^+$ –N<sup>3</sup>(R<sup>2</sup>R<sup>3</sup>) bond which then can be compared with the experimentally determined rotational barriers in the guanidinium salts **1b1** and **2b1**. Stationary points, the energy minimum structures **22–29** and transition state structures **TS-22–TS-29**, were verified by analysis of vibrational frequencies. Starting geometries for the optimization of transition state structures were obtained by calculations scanning the dihedral angle. Transition state structures were confirmed to have imaginary frequencies only for the torsional vibration associated with the corresponding C<sup>1</sup>–N<sup>3</sup> bond rotation. Intrinsic reaction coordinate (IRC) calculations proved that the transition state structures for the C<sup>1</sup>–N<sup>3</sup> bond rotation connect the corresponding minima. The calculated rotational barriers for the C<sup>1</sup>–N<sup>3</sup> bond rotation in **22–29** are listed in Table 6 (see also Scheme 5).

<b>Table 6.</b> Calculated barriers of the $C^1-N^3$ bond rotation for the imidazol- idinium cations <b>22–29</b> (for numbering refer to Scheme 5).						
imidazolidinium	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	$\Delta G^{\ddagger}$ [kJ mol <sup>-1</sup> ]		
22	Н	Me	Н	63		
23	Н	anisyl	Н	71		
24	Me	Me	н	63		
25	Me	anisyl	Н	76		
26	Н	Me	Me	34		
27	Н	anisyl	Me	39		
28	Me	Me	Me	24		
29	Me	anisyl	Me	29		

The minimum structures of the  $N^2$ , $N^4$ -H imidazolidinium ions **22– 25** have a coplanar arrangement of the  $N^2C^1N^4$  plane of the imidazolidine ring and the planar exocyclic amino group ( $R^2N^3R^3$  plane). This allows p–n-orbital  $\pi$ -type conjugative interaction between the formally positively charged C<sup>1</sup> and all three planar nitrogen atoms. The anisyl ring in the model structures **23, 25, 27,** and **29** is oriented



Scheme 5.

almost perpendicular to the imidazolidin ring, thus  $\pi$ -aryl resonance delocalization of the positive charge at C<sup>1</sup> is lacking. In the transition state structures for C<sup>1</sup>–N<sup>3</sup> bond rotation (**TS-22**–**TS-25**) the exocyclic amino group N<sup>3</sup> is no longer planar (sp<sup>2</sup> bond angle sum 360°) but pyramidalized (338–346°) towards sp<sup>3</sup>-hybridization (327°). The R<sup>2</sup>N<sup>3</sup>R<sup>3</sup> plane is orthogonal to the imidazolidine ring plane (N<sup>2</sup>C<sup>1</sup>N<sup>4</sup>). Thus overlap between the vacant p-orbital at C<sup>1</sup> and the n-orbital at N<sup>3</sup> is interrupted in the transition state for C<sup>1</sup>–N<sup>3</sup> bond rotation. The barriers for C<sup>1</sup>–N<sup>3</sup> bond rotation vary between 63 and 76 kJ mol<sup>-1</sup> for **22**–**25** (Table 6).

The *N*,*N*-dimethylimidazolidinium model structures **26** and **27** are sterically more congested due to methyl substitution of the nitrogen of the imidazolidine amino group. The exocyclic secondary amino group ( $R^2 = H$ ) yet adopts in the ground state an almost coplanar orientation (7–10°) relative to the N<sup>2</sup>C<sup>1</sup>N<sup>4</sup> plane. In the transition state structures **TS-26** and **TS-27**, the nitrogen is pyramidalized (bond angle sum 348° and 345°), and the R<sup>2</sup>N<sup>3</sup>R<sup>3</sup> plane and the ring plane are almost orthogonal (87–83°). Structures **28** and **29** have a bulkier, disubstituted exocyclic amino group ( $R^2 = Me$ ) and the minimum structures of **28** and **29** no longer adopt a coplanar conformation. The

 $R^2N^3R^3$  plane and the imidazolidinium ring plane are twisted (~36°). This reduces  $n-p-\pi$  conjugation in the ground state. Accordingly, ~10 kJ mol<sup>-1</sup> lower barriers for rotation around the  $[C^1]^+-N^3$  bond are calculated for **28** (24 kJ mol<sup>-1</sup>) and **29** (29 kJ mol<sup>-1</sup>) as compared to **26** and **27**. The transition state structures **TS-28** and **TS-29** have a pyramidalized exocyclic nitrogen N<sup>3</sup> (bond angle sum 350° and 356°) and the interplane angle between the  $R^2N^3R^3$  and the  $N^2C^1N^4$  planes is close to 90°. Some conformational effects of the anisyl group in **TS-29** are subject to further studies.

The model calculations of a barrier of about  $10 \text{ kJ mol}^{-1}$ lower for rotation around the  $[C^1]^+-N^3$  bond for **28** and **29** as compared to **26** and **27**, respectively, are in very good agreement with the barrier of ~7 kJ mol<sup>-1</sup> lower in energy determined experimentally by <sup>1</sup>H NMR spectroscopy for the guanidinium salt **2b I** (R<sup>2</sup>=Me,  $\Delta G_c^{\dagger} = 46 \text{ kJ mol}^{-1}$ ) compared to **1b I** (R<sup>2</sup>=H,  $\Delta G_c^{\dagger} = 53 \text{ kJ mol}^{-1}$ ). Explorative calculations using other DFT functionals which include dispersion terms such as X3LYP<sup>[29]</sup> and B97D<sup>[30]</sup> give within  $\pm 3 \text{ kJ mol}^{-1}$  the same results as B3LYP. Further computational studies on the structure and dynamics of this type of guanidinium cations are in progress.

#### 2.7. Mesomorphic Properties

The mesomorphic properties of the guanidinium salts **1X** and **2–41** were studied by differential-scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (WAXS, SAXS).



**Figure 7.** DSC curves of guanidinium chloride **1a Cl** during first and second heating (bottom and middle traces) and first cooling (upper trace), heating/ cooling rate  $10 \text{ Kmin}^{-1,[31]}$ 

A typical DSC curve for **1a Cl** is shown in Figure 7. At 60 °C, an exothermal crystal-to-crystal transition was observed, but without any attempt for a more detailed investigation (additional crystal-to-crystal transitions were observed during the first heating cycle for some derivatives; for details see Tables S3–S10 in the Supporting Information). A melting transition at 101°C (onset temperature) and a clearing transition at 194°C were detected upon first heating. The transition from the isotropic into the smectic A phase was observed at 194°C

upon cooling. No recrystallization peak was identified because compound **1a CI** presumably undergoes a steady transition into the glassy state. The corresponding glass transition at 33°C and a clearing transition at 193°C were observed during the second heating. Compound **1a CI** thus displays enantiotropic mesomorphism. All *N*-H guanidinium chlorides **1 CI** showed similar behavior, irrespective of the R<sup>1</sup> chain length (Figure 8). It appears noteworthy that the guanidinium chlorides **1 f CI** and **1g CI**, with branched side chains, displayed increased mesophase widths, combined with decreasing first melting temperatures, compared to the derivatives with corresponding linear side chains, **1h CI** (R<sup>1</sup> = C<sub>8</sub>H<sub>17</sub>)<sup>[8]</sup> and **1e CI**.



**Figure 8.** Phase behavior of guanidinium chlorides **1 Cl** with varying chain length (heating/cooling rate 10 K min<sup>-1</sup>; data for **1h Cl** are taken from ref. [8]; compound **1f Cl** and **1g Cl** can be found in the Supporting Information).

A possible influence of the anion on the mesomorphic properties was studied next for four different linear alkyl chain lengths [C<sub>10</sub> (**a**), C<sub>12</sub> (**b**), C<sub>14</sub> (**d**), and C<sub>16</sub> (**e**)]. The temperature range of the SmA phase is similar for the guanidinium chlorides, bromides, and iodides, with a trend towards an increasing mesophase width with longer chain length (Figure 9). The two tetraphenylborates 1b,e BPh4 were non-mesomorphic, on the other hand, the bulky anion completely suppressing a SmA double-layer organization. For the tetrafluoroborate, hexafluorophosphate, and thiocyanate salts, the situation appeared less clear-cut. For the derivatives 1a,b X with a C10- and C12-alkyl chain, respectively, these counterions induced a considerable shrinking of the mesophase width relative to that for the corresponding halides. In the C14-alkyl chain series, however, the tetrafluoroborate salt 1d BF<sub>4</sub> behaves like the halide salts, with the SmA phase ranging over 188K, whereas the SmA phases of the corresponding hexafluorophosphate 1d PF<sub>6</sub> and thiocyanate 1d SCN span only 61 and 77 K, respectively. For the guanidinium salts 1e X, the hexadecyl chain determines the mesophase properties and all salts show SmA phase behavior over a wide temperature range.



Figure 9. Phase behavior of the guanidinium salts 1a,b,d,e X depending on the different anions X.



**Figure 10.** Correlation of clearing temperature T with the anionic radius for the guanidinium salts **1a,b,d,e X** (data for **1 SCN** salts were omitted for clarity, but can be found in the Supporting Information).

The clearing temperatures in fact display a linear correlation with the anionic radius for the salts **1a,b,d,e X**.<sup>[16]</sup> As Figure 10 shows, they decrease with increasing anionic radius; for the bulkiest anion tetraphenylborate, the SmA phase is lost completely. Presumably due to the ellipsoid structure of the thiocyanate anion, the clearing temperatures of the salts **1SCN** were always lower than those for the other anions.

Since the *N*-H chemical shift was found to be anion-dependent as well, clearing points might possibly be deduced from chemical shift data or, in other words, phase transition temperatures could be obtained by <sup>1</sup>H NMR. Clearing points were determined by DSC for a series of guanidinium salts **1b X** and **1b Cl**<sub>x</sub>**I**<sub>1-x</sub> with a varying chloride/iodide ratio to probe this hypothesis. Figure S6 (Supporting Information) shows that the clearing points indeed decrease with a higher molar ratio of iodide. When all clearing temperatures *T* were plotted against  $\delta_{NH}$  for the different anions and chloride/iodide ratios, a fairly good direct, linear relationship was obtained (Figure 11). With



the corresponding graph in Figure 11, clearing points can in principle be derived directly from <sup>1</sup>H NMR shift data.

As the last parameter, we studied the influence of *N*-alkylation on the mesomorphic properties of the guanidinium iodides **2–41**. The data in Figure 12 clearly reveal that the presence of the N–H moiety in the guanidinium head group is a crucial factor for mesophase stability. The SmA phase of **1a I** with a  $C_{10}$  chain, for example, ranges from



**Figure 11.** Correlation between clearing temperature *T* and *N*-H chemical shifts (300 MHz, 296 K, CDCl<sub>3</sub>,  $c = 15.4 \text{ mmol L}^{-1}$ ) for **1b X** and mixed guanidinium salts **1b Cl<sub>x</sub>I<sub>1-x</sub>** with different chloride/iodide ratios.



**Figure 12.** Phase-transition temperatures for the *N*-methyl-, *N*-ethyl-, and *N*-propylguanidinium iodides **2–41** depending on the alkoxy chain length R<sup>1</sup>.

9 to 141°C (132K), for 1e I with a  $C_{16}$  chain from 41 to 237°C (196 K). In contrast, the N-methylguanidinium iodides 2a,b I with the shorter  $C_{10}$  and  $C_{12}$ -chain lengths are nonmesomorphic, and for the salt 2eI with a  $C_{16}$  chain the mesophase range is reduced to 114K (143-257°C). This destabilizing effect appears even more pronounced for the N-ethyl- and N-propylguanidinium iodides 31 and 41. It should be noted that Hunt<sup>[32a]</sup> and Zahn et al.<sup>[32b]</sup> have independently studied by computational methods the counterintuitive increase of melting points and viscosity upon methylation of C-2 in imdiazolium ionic liquids. They propose that the loss of hydrogen-bond connectivity leads to a reduced free movement of the corresponding anion relative to the imidazolium cation. The reduction in entropy results in a greater ordering, thus raising the melting points. Presumably, similar effects are operative in our case.

The mesophases of the guanidinium salts **1X** and **2–41** were studied by polarizing optical microscopy (POM) and displayed spontaneous homeotropic alignment over large areas during cooling from the isotropic melt to the smectic mesophase, giving rise to the homeotropic textures typical for SmA phases.<sup>[33]</sup> Representative POM textures are shown in Figure 13.



**Figure 13.** a) SmA texture of **1d Cl** at 242°C with large, homeotropically aligned areas; b) Bâtonette texture of **1f Cl** at 150°C; c) focal conic texture of **1d SCN** at 175°C with the homeotropic alignment disturbed around the edges of air bubbles; d) SmA texture of **2b I** at 215°C (all with magnification  $\times$  200 and a cooling rate of 30 Kmin<sup>-1</sup>).

#### 2.8. X-Ray Powder Diffraction Studies

In a previous publication,<sup>[8]</sup> we have proposed a smectic bilayer for the guanidinium salts **1 CI**, similar to the packing situation in the corresponding single crystals. However, one should not draw too great parallels between X-ray information from the solid state and the organization in the liquid-crystal mesophases. The X-ray measurements for compounds **2d I–4d I** likewise displayed characteristic diffraction patterns with a strong fundamental diffraction peak (001) typical for smectic mesophases (shown in Figure 14 for **3d I**). In conjunction with the POM results, the mesophases of the *N*-alkyl salts **2–41**, as well as those



Figure 14. WAXS experiment for  $3d\,I$  at 190  $^\circ\text{C}$  with the corresponding diffraction pattern.

of all *N*-H salts **1**X<sup>[8]</sup> thus can unequivocally be characterized as SmA phases.

If one compares the layer spacings, obtained by X-ray diffraction studies for the *N*-alkylguanidinium iodides **2d I-4d I** in the liquid-crystalline phase with the calculated length of the molecules **2d-4d** (~3100 pm for an *all-trans* conformation),<sup>[34]</sup> an analogous bilayer structure with strongly interdigitated alkyl chains becomes apparent. The smectic layer spacing of the bilayers was also temperature-dependent and decreased with increasing temperature (Figure 15). This effect was found



**Figure 15.** Temperature dependence of the  $d_{001}$  layer spacing for **1d I–4d I** obtained from SAXS experiments.

to be much more pronounced for the *N*-H compound **1d I** than for the *N*-alkyl homologues **2d I**-**4d I**.

For a quantitative comparison of the guanidinium salts 1d I - 4d I, despite the observed temperature dependence, layer spacings were compared at a reduced temperature ( $T_{red} = 0.95$   $T_{iso}$ ). These reduced layer spacings  $d_{red}$  showed a general shrinking in the order 2d I > 1d I > 3d I > 4d I (Table 7), keeping in mind that there was no common mesophase range at a given temperature. Just before the clearing point, the layer

<b>Table 7.</b> Reduced layer spacings $d_{\rm red}$ of the guanidinium salts 1d I-4d I.						
compound	$T_{iso}$ [°C]	$T_{\rm red}$ [°C]	d <sub>red</sub> [pm]			
1d I	210	200	4170			
2d I	232	220	4240			
3d I	187	178	4090			
4d I	138	131	4060			

spacing  $d_{red}$  is smaller for **1d I** than for **2d I** even though at lower temperatures compound **1d I** displayed a much larger layer spacing. The polarity of the polar guanidinium head group decreases with increasing *N*-alkyl chain length; ionic repulsion between the guanidinium moieties thus is reduced, resulting in an overall shrinkage of the layer spacings.

#### 3. Conclusions

For the penta-substituted guanidinium salts 1 X, a direct hydrogen-bond-type connectivity was found in the crystalline solid state between the anion and the N-H group. This ion-pair contact is conserved even in solution. The N-H resonance is shifted to higher field by ~4 ppm (in dilute solution) when the anion is changed from Cl<sup>-</sup> (12ppm) to PF<sub>6</sub><sup>-</sup> (8ppm). For the mixedanion guanidinium salts **1b**  $Cl_x l_{1-x}$ , the *N*-H proton chemical shift shows a linear correlation with the chloride/iodide molar ratio. These findings clearly demonstrate that the anion cannot be located directly above the central carbon atom C<sup>1</sup> of the guanidinium functionality where NBO calculations predict the highest positive charge (+0.7).<sup>[35]</sup> Rather, the anion must be oriented along the axis of the N-H bond, just as found in the solid state. The hydrogen bonding of the anion to N-H guanidinium cations in 1X also directly affects their liquid-crystalline properties. The observed anion effects on hydrogen bonding in solution and in the solid state, as well as their stabilizing effect on the liquid-crystalline properties, agree well with previous experimental and theoretical studies by Seddon,<sup>[17]</sup> Bruce,<sup>[10]</sup> and others working on imidazolium and pyridinium ionic liquid crystals. Thus, large anions destabilize the mesophases as they reduce the anisotropy. Comparison with the literature cited above also shows the general trend that the anion effect overrules the side-chain effect with regard to mesophase stabilities. Along these lines it was demonstrated that the anion-dependent <sup>1</sup>H NMR chemical shift of the *N*-H signal could be correlated with the clearing transition temperature even for guanidinium salts with a mixture of anions. In other words, <sup>1</sup>H NMR data might be used as a surrogate for determining clearing temperatures by DSC. It must be demonstrated in future experiments whether this correlation is limited for this specific class of compounds or can be extended to other ionic liquid crystals.

*N*-alkylation also has a decisive influence on the liquid-crystalline properties. With hydrogen bonding no longer possible, the mesophase stability is reduced or even lost completely. The suppression of mesophases—by eliminating hydrogen bonding by alkylation of the cation—has also had ample precedence in the literature.<sup>[32]</sup>

The influence of the N-alkyl substituent is also manifest in intramolecular processes in solution, as demonstrated by variable-temperature NMR studies. A number of rotational degrees of freedom exist within the guanidinium moiety. In all N-H guanidinium structures, the two dimethylamino functions have the lowest barriers of rotation, with the N(Me)<sub>2</sub> group syn to the  $N^3$ -aryl substituent even lower than with the N(Me)<sub>2</sub> group in anti position. In the N-alkylguanidinium iodides 2b I, 3b I, and 4b I, in contrast, the lowest rotational barrier is found for the C<sup>1</sup>-N<sup>3</sup> bond, and hence the smallest partial double-bond character is derived for this C<sup>1</sup>–N<sup>3</sup> bond. The inversion of the relative heights of these three rotational barriers can be deduced directly from the crystal structure data and is confirmed by calculations for imidazolidinium model cations. In order to get insight into the electronic (and dynamic) behavior of guanidinium salts, NBO charge distributions were calculated. The results reveal that the replacement of the mesogenic *p*-alkoxybiphenly moiety by *p*-alkoxyphenly or even methyl at the guanidinium core does not change the charge density particulary on atom  $N^3$ , whereas the replacement of N-H by N-Me, N-Et, and N-nPr results in a decreased charge density at N<sup>3</sup>. Thus, the computional results gave no indication for a delocalization of the positive charge in various  $N^3$ -aryl  $\pi$ -systems and therefore the N-C aryl bond behaves like a spacer between the cationic head group and the mesogenic biaryl substituent.

Besides the extensively investigated pyridinium and imidazolium salts, guanidinium salts constitute an alternative class of thermotropic ionic liquid crystals. Their properties can be adjusted by several structural parameters, thus opening a wide field for future applications.

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