NMR Spectroscopic Study of Orientational Order in Imidazolium-Based Ionic Liquid Crystals

Jing Dai [1], Debashis Majhi [1], Boris B. Kharkov [2] and Sergey V. Dvinskikh [1,2,*]

[1] Department of Chemistry, KTH Royal Institute of Technology, 11428 Stockholm, Sweden; jdai@kth.se (J.D.); majhi@kth.se (D.M.)

[2] Laboratory of Biomolecular NMR, Saint Petersburg State University, Saint Petersburg 199034, Russia; st036820@student.spbu.ru

[*] Correspondence: sergeid@kth.se

Abstract: We report on molecular and local orientational order of a series of imidazolium-based ionic liquid crystals exhibiting layered smectic A mesophase. Materials constituting of 1-dodecyl-3-methylimidazolium cation, and different counter-ions, were investigated. We apply two-dimensional ^{13}C-^{1}H dipolar NMR spectroscopy to quantify orientational order of C-H bonds of the organic cation. The experimental data supported the structural model of the interdigitated chains aligned with the smectic layer normal. Molecular order parameter S was found to increase in the anion sequence $BF_4^- < I^- < Br^- < Cl^-$. This trend correlates well with ionic radius, negative charge delocalization, and hydrogen-bonding properties of the anions.

---

1. Introduction

Ionic liquids (ILs) are considered today as key materials in a broad range of emerging technological applications in the areas of electrochemistry, synthesis, catalysis and separation, and lubrication. ILs are commonly built up of bulky organic cations and smaller anions of organic or inorganic origin. The size difference contributes in decreasing melting point by hindering crystallization of the material. Ionic liquid crystals (ILCs) are ionic liquids capable of self-assembly into thermodynamically stable liquid-crystalline phases [1–3]. They thus can be defined as anisotropic liquids consisting entirely of ions as mesogenic units. ILCs exhibit the typical properties of ionic liquids such as ionic conductivity, as well as nano-scale structures with partial molecular ordering. Generally, mesophase formation is predetermined by a pronounced anisotropy of interparticle interactions, which in the case of molecular liquid crystals (LCs) with prevailing van der Waals interaction is a consequence of molecular anisotropic shape. In contrast, in ionic LCs with dominant electrostatic interparticle interactions, the essential factor contributing to mesophase stability is an anisotropic charge distribution.

ILCs typically form layered, columnar, and bicontinuous cubic phases while least-ordered nematic phases are rare. The properties of ILCs, including phase behaviour, are readily modified by selecting cations and anions [1]. Typically, ionic mesogenic materials are composed of positively charged heterocyclic cores linked to long *n*-alkyl chains and small inorganic or organic anions. Phase segregation of incompatible, charged (anions and cationic heads), and hydrophobic nonpolar moieties (aliphatic chains) induces the formation of layered smectic phases. Imidazolium-based ILCs have been most extensively investigated [4]. Charge delocalization in the imidazolium core reduces ionic interaction and thus promotes low transition temperatures. Imidazolium salts with a length of the alkyl chain of $n \geq 12$ display interdigitated smectic A bilayer phases. Systematic trends in the

thermodynamic phase properties depending on ionic/molecular structure have been revealed [1,2]. Mesophase temperature range and clearing temperature T_C (mesophase-to-isotropic phase transition temperature) increase with the chain length of the organic cation. Similarly, the mesophase temperature changes with the type of anions. For example, mesophase temperature range decreases in the anion order $Cl^- > Br^- > I^-$ [1,5,6]. Larger size fluorinated anions with delocalized charge and lower capability to build hydrogen bonds, such as BF_4^- and PF_6^-, lead to further decrease of melting and clearing temperatures [6–8]. Additionally, the phase diagram in hydroscopic ILCs is affected by water-anion hydrogen bonding [1,6,9].

Theoretical and experimental studies of orientational order in ILCs [1,10–14] revealed that, due to the contribution of the electrostatic interactions to the stabilization of layered structures, smectic phases in ILCs exhibit significantly lower value of the molecular orientational order parameter *S* as compared to that in its non-ionic counterparts. However, systematic studies of the orientational order parameter depending on ILCs structure and ionic composition are still lacking. In the present work, we report detailed investigation of the molecular and local bond orientational ordering in a series of ILCs with a fixed imidazolium-based cation and number of anions varying in structure, ionic radius, negative charge localization, and hydrogen bonding properties.

Orientational ordering in LCs is most directly studied by nuclear magnetic resonance (NMR) spectroscopic technique [15–17]. Molecular and local bond molecular order parameters are estimated via measurement of the anisotropic spin couplings, such as dipolar and quadrupolar interactions and chemical shift anisotropy. A large anisotropy of diamagnetic susceptibility of mesogenic molecules/ions often leads to macroscopic molecular alignment with respect to direction of the magnetic field applied during NMR measurement. In this case, NMR spectra are obtained with high resolution, and site-specific anisotropic spin couplings are most straightforwardly accessed. In the present study, we apply two-dimensional (2D) ^{13}C-^{1}H dipolar NMR spectroscopy to quantify orientational order of C-H bonds of a long-chain imidazolium-based cation in an ionic smectic phase. Molecular order parameter *S* is also estimated. The observed trends of the measured bond and molecular order parameter values depending on counter-ion are discussed.

2. Materials and Methods

Four samples of ionic mesogenic materials with the same cation C_{12}mim (1-dodecyl-3-methylimidazolium) and different anions, Cl^-, Br^-, I^-, and BF_4^-, were obtained from commercial sources: C_{12}mimCl, C_{12}mimBr, and C_{12}mimBF$_4$ were purchased from ABCR GmbH, Karlsruhe, Germany, and C_{12}mimI was received from Sigma-Aldrich Sweden AB, Stockholm, Sweden. All samples were tested for water content by recording the ^{1}H NMR spectra in the isotropic phase. As received, the C_{12}mimBr sample exhibited non-negligible water content of 1.3 wt % (23 mol %). The sample was dehydrated by equilibrating for 7 days in a desiccator with P_2O_5 powder. The water contents in the samples used for NMR measurements are indicated in Table S1 in the Supplementary Materials.

NMR measurements (in smectic phase were performed in samples aligned in the magnetic field on the NMR spectrometer with the phase director distributed in the plane perpendicular to the magnetic field vector. Experiments were performed using the Bruker 500 Avance III spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) at Larmor frequencies of 500.1 and 125.7 for ^{1}H and ^{13}C, respectively. Dipolar [1]H-^{13}C spectra were recorded using proton detected/encoded local field (PDLF) NMR spectroscopy [18,19] (Figure S1 in Supplementary Materials). Other details of NMR experiment were described in a previous publication [13] and also included in the Supplementary Materials.

Radio frequency (rf)-induced sample heating effects and hardware performance limited the rf power level in our experiments. Applied heteronuclear and homonuclear decoupling powers were not sufficient to achieve high resolution and sensitivity simultaneously for all carbon sites in the molecules. Hence ^{1}H and ^{13}C offset frequencies were set to the values corresponding to optimal signal resolution in the alkyl chain region.

3. Results and Discussion

3.1. Dipolar Spectra

Representative carbon-13 cross-polarization spectrum of the C_{12}mimBF$_4$ in the smectic phase is shown in Figure 1. Spectra of other samples (displayed in Supplementary Materials, Figure S2) exhibited similar structure and peak positions. The observed chemical shifts are given by the component $\delta_{\perp}^{LC}$ of the chemical shift tensor [13,16]. Unambiguous assignment of the spectral lines was obtained from the dipolar ^{13}C-^{13}C double-quantum correlation 2D spectra and was further confirmed by dipolar PDLF spectra with dipolar splittings and carbon chemical shifts correlated in orthogonal directions. Due to the high spectral resolution in the static samples, ^{13}C-^{1}H dipolar couplings for all in-equivalent directly bound ^{13}C and ^{1}H pairs could be directly measured in a 2D PDLF experiment. Representative dipolar cross-sections from PDLF spectrum of C_{12}mimBF$_4$ are displayed in Figure 2.
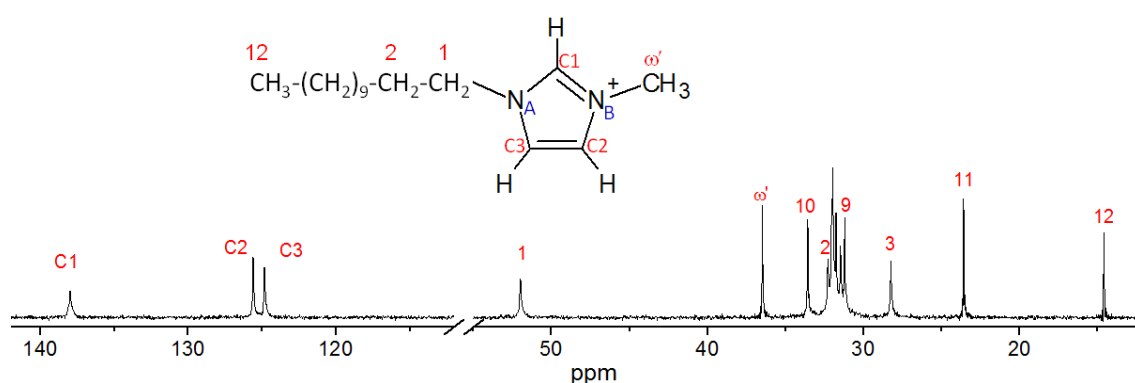
Figure 1. Carbon-13 cross-polarization (CP) spectrum of C_{12}mimBF$_4$ at 38 °C in smectic A phase. Spectrum is superposition of two spectra obtained with decoupler offset optimized either for aromatic or aliphatic carbons.

The spectral splitting in the PDLF experiment is resulted from the contribution of direct dipolar coupling d_{CH} and indirect spin coupling J_{CH}

$$\Delta \nu = \left| k(2d_{CH} + J_{CH}) \right| \tag{1}$$

where $k = 0.418 \pm 0.04$ is the experimentally calibrated dipolar scaling factor of the applied homonuclear decoupling sequence BLEW48 [20]. The dipolar coupling constant d_{CH} in a mesophase is the orientational average of the rigid lattice coupling constant $b_{CH} = -(\mu_0/8\pi^2)(\gamma_H\gamma_C\hbar/r_{CH}^3)$ (r_{CH} is atomic distance and the γ_H, γ_C gyromagnetic ratios). For a single C-H bond in aliphatic moieties the generally accepted b_{CH} value, corrected for vibration effects, is −21.5 kHz [21,22]. The orientational averaging of the local C-H vector in the director frame is described by the local bond order parameter

$$S_{CH} = \langle P_2(\cos \theta_{PN}) \rangle, \tag{2}$$

with $P_2(\cos \theta_{PN}) = (3\cos^2 \theta_{PN} - 1)/2$, where θ_{PN} is the angle between the C-H vector (principal frame) and the phase director N. For the samples with the director perpendicular to the external magnetic field and assuming uniaxial symmetry of the molecular motion, one thus obtains [23]

$$d_{CH} = -\frac{1}{2}b_{CH}S_{CH} \tag{3}$$

The values of the isotropic coupling J_{CH}, the sign of which is known to be positive, were measured in the carbon-13 spectra in the isotropic phase. The sign of the coupling constant d_{CH} was possible to infer considering director alignment and C-H bond angle to the main molecular axis.
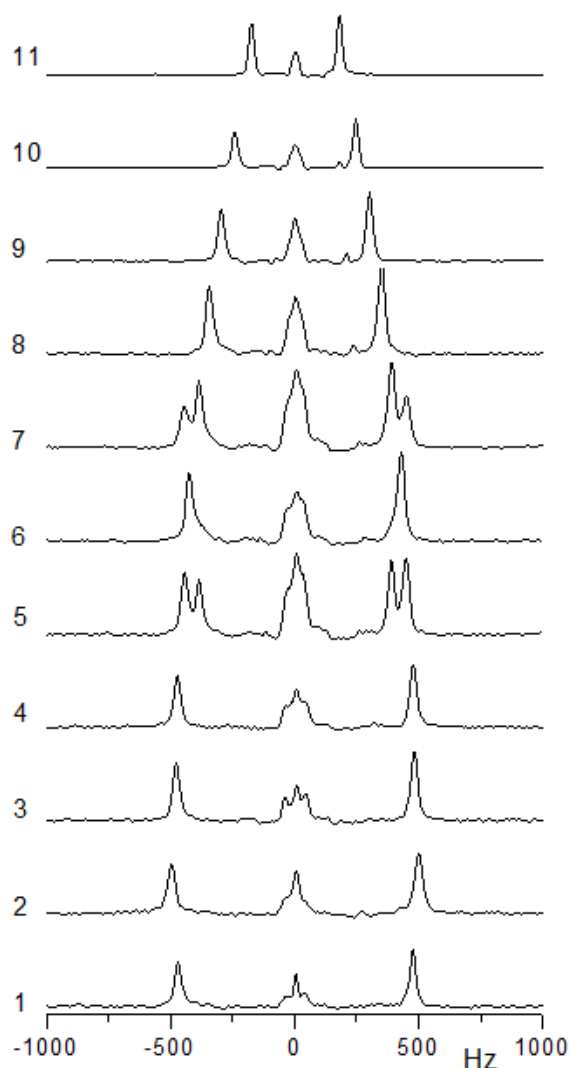
Figure 2. Dipolar cross-sections in two-dimensional proton detected/encoded local field (PDLF) spectrum of C_{12} mimBF$_4$ sample in smectic A phase at 38 °C for the methylene carbons 1–11 of the alkyl chain. Signals of carbons 5 and 7 exhibit partial overlap.

3.2. C-H Bond Orders

Bond order parameter profiles of all four ILC samples in the smectic A phase were measured at similar temperature difference $\Delta T = T_C - T$ with respect to clearing point T_C (Figure 3). The C-H bond order parameter (S_{CH}) values for the alkyl chains were negative because of the directions of the C-H bond on average perpendicular to the long molecular axis. The samples exhibited common trends in the variation of the S_{CH} values. With decreasing temperature, the magnitudes of S_{CH} parameters of all groups were consistently increasing. Besides, at a fixed temperature, S_{CH} values, being nearly constant for a few first chain segments, dropped gradually towards the chain terminal. Similar trends have been reported in the recent experimental study of the longer alkyl chain cation in the C_{14}mimNO$_3$ material [13], and also in a molecular dynamics (MD) study of C_{16}mimNO$_3$ homologue [14]. The S_{CH} profiles were analyzed by applying a model of the alkyl chain with predominant trans conformation of the groups in vicinity of the aromatic core and with the symmetry axis of this part parallel to a long molecular axis. This model was further supported by measuring (in some of the samples) the C-C order parameter (S_{CC}) for the alkyl carbons separated by two bonds: Since the vectors C-H and C_n-C_{n+2} were perpendicular to and along the molecular axis, respectively, the experimentally obtained ratios $S_{CC} \approx -2S_{CH}$ confirmed the validity of the model assumption [13].
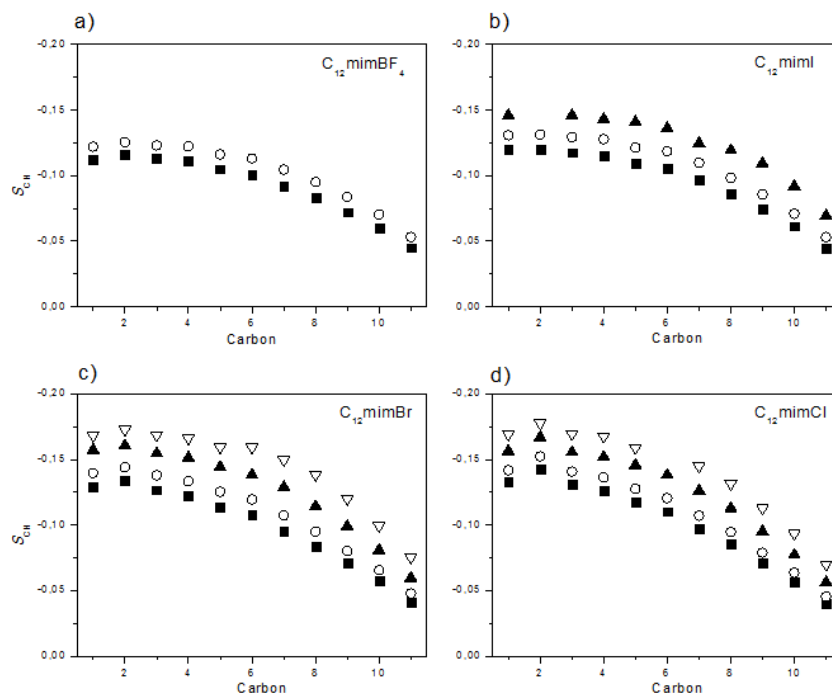
Figure 3. Bond order parameter profiles of four ionic liquid crystals (ILCs) in the smectic A phase at different temperatures. (**a**) $C_{12}mimBF_4$ at 38 °C (■) and 27 °C (○). (**b**) $C_{12}mimI$ at 55 °C (■), 44 °C (○), and 22 °C (▲). (**c**) $C_{12}mimBr$ at 91 °C (■), 79 °C (○), 58 °C (▲), and 35 °C (▽). (**d**) $C_{12}mimCl$ at 107 °C (■), 96 °C (○), 73 °C (▲), and 50.5 °C (▽).

Comparing the S_{CH} data in different samples at the same relative temperatures ΔT, one finds that the alkyl chains became more ordered in the following anion sequence: $BF_4^- < I^- < Br^- < Cl^-$. This suggests that the molecular order parameter S is also increasing in the same anion order as discussed in the next section.

3.3. Molecular Order S

Considering statistical independence of the conformational and molecular rotational dynamics and assuming the validity of the described above model of the chain dynamics, one can estimate the molecular order parameter S using the following equation for the chain segments in trans conformation

$$S_{CH} = \langle P_2(\cos \theta_{PM}) \rangle S \approx -0.5\,S \qquad (4)$$

where $\theta_{PM} \approx 90°$ is the angle between the C-H internuclear vector and long molecular axis [13,16]. Thus, we calculated the order parameter applying Equation (4) to chain carbons C1-C3 and taking the average value. The results for four samples are compiled in Figure 4, where S values are plotted against the reduced temperature $T_{red} = T/T_C$.

The values of the order parameters were found in the range of 0.22 to 0.35 depending on the temperature and anion type. These values are significantly lower when compared to typical $S > 0.5$ in conventional smectic A phases of non-ionic LCs [24,25]. Similarly low S values in smectic phase were found in an analogous ILC with longer alkyl chain imidazolium-based cation and NO_3 anion, $C_{14}mimNO_3$ [13]. Likewise, MD simulation predicted the same range of S values in the homologue sample $C_{16}mimNO_3$ [12]. A relatively low value of the parameter S in ILCs was explained by the contribution of electrostatic interactions to molecular segregation. In neutral LCs, a high molecular order is essential for mesophase stability since the molecular mutual alignment is resulted from weak van der Waals interactions of particles of anisotropic shape. In contrast, in ILCs the dominant contribution is electrostatic interaction of particles with anisotropic charge distribution while van

der Waals interaction is less important. Hence stable layer structure can form with relatively low orientational order.

The order parameter *S* was increasing in the anion sequence $BF_4^- < I^- < Br^- < Cl^-$ (Figure 4). The observed trend correlated well with changes in the physicochemical properties of the anions. For example, the anions ability to build extended hydrogen-bond network within ionic sublayer increased in the same order [2,6]. This property contributed to thermodynamic stability of the phase and hence to increasing the order parameter *S*. The anion size (Table S1) and negative charge delocalization increased in the opposite sequence [26,27]. For more bulky anions, the occupied area of the imidazolium group should match the increased negative charge delocalization and weaker hydrogen bonding. The alignment of the imidazolium core in the ionic sub-layer can affect the ordering and conformation of the chains [2,28]. In fact, in a recent ^{2}H NMR and MD study, there had been suggested a dramatic change in the headgroup conformation in the C_{12}mim cation when bulky BF_4^- was replaced by compact Cl^- [29]. The observed change in the values of the order parameter also correlates with the variation in the interlayer spacing, which is increasing in the same order [6]. Thus, the increasing interlayer spacing contributes to more extended chains with higher ordering.
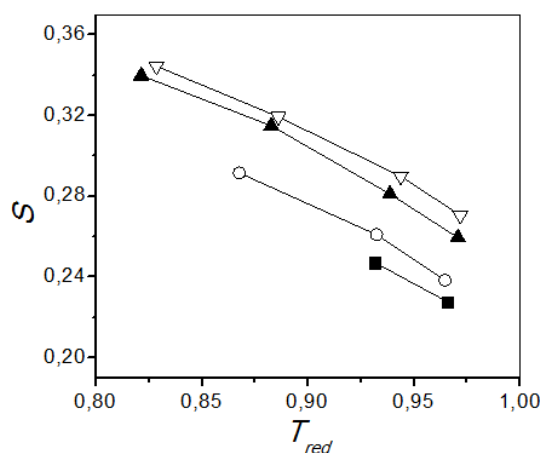
Figure 4. Order parameter *S* for four samples plotted against the reduced temperature $T_{red} = T/T_C$: C_{12}mimBF$_4$ (∇), C_{12}mimI ($\blacktriangle$), C_{12}mimBr ($\bigcirc$), and C_{12}mimCl ($\blacksquare$).

While the order parameter characterizes the re-orientational molecular dynamics, anisotropy of translational mobility in LCs is also directly affected by the orientational order [30,31]. Having obtained in the present work, the data on the order parameters in studied ILC series, we are now in the position to explain some previously found trends in translation diffusion results. Molecular self-diffusion in the smectic phase of two ionic mesogens, C_{12}mimCl and C_{12}mimBF$_4$, had been investigated by Cifelli et al. [32]. Translational diffusion coefficients $D_\perp$ and $D_\parallel$ of the organic cation were measured in directions perpendicular and parallel to the phase director. At comparable temperature, cation diffusion was slower in C_{12}mimCl sample. Interestingly, a significantly higher anisotropy ratio $D_\perp/D_\parallel$ was observed in C_{12}mimCl compared to that in the sample C_{12}mimBF$_4$. This is consistent with the larger values of the molecular order parameter in C_{12}mimCl (Figure 4). Moreover, larger diffusion anisotropy implies faster diffusion of the cations within the layer and more restricted mobility between the layers. This contributes to better defined layers of the otherwise highly dynamic structure in agreement with higher mesophase stability of the material with Cl^-.

4. Conclusions

We have applied NMR dipolar spectroscopic techniques to obtain quantitative information on molecular and local bond orientational order parameters in smectic A phase of a series of ionic mesogens. Materials constituting of the same long alkyl-chain imidazolium cation, and varying counter-ions, were

investigated. The experimental data were consistent with the structural model of the interdigitated chains aligned with the smectic layer normal. In agreement with previous experimental and MD studies [12,13], the molecular alignment was characterized by a low molecular order parameter S in the range of 0.20 to 0.35. Since the ionic interactions contribute to the layer stabilization by inducing a 'charge-ordered' nanoscale segregation of ions, thermodynamically stable smectic structure in ILCs can be assembled with lower orientational order compared to that in molecular LCs [1,10–12]. Remarkably, the values of the order parameter S exhibited a consistent increase in the anion sequence $BF_4^- < I^- < Br^- < Cl^-$. This new finding was rationalized by relating the S values to the trends in physicochemical properties of the anions such as ionic radius, charge delocalization, and increasing ability to build hydrogen bonds. Higher order was also observed for the salts with increasing interlayer spacing in the smectic A phase. Higher molecular orientational order, which is associated with the phase stability, presents an advantage in designs of ionic materials for anisotropic ion transport in various technological applications. In future studies, it would be interesting to study orientational order in hydrated mesogenic salts, where hydrogen bonds to water molecules contribute further to the structure stabilization.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/9/10/495/s1, Table S1: Ionic liquid crystals samples $C_{12}mimX$ data, Figure S1: PDLF pulse sequence to record dipolar ^{13}C-^1H spectra, Figure S2: 1D ^{13}C CP NMR spectra in smectic phase of $C_{12}mimCl$, $C_{12}mimBr$, $C_{12}mimI$, and $C_{12}mimBF_4$.

Author Contributions: S.V.D. designed and proposed the methods. J.D., D.M. and S.V.D. performed the NMR measurements. B.B.K. performed the numerical analysis. All authors contributed to the preparation of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Goossens, K.; Lava, K.; Bielawski, C.W.; Binnemans, K. Ionic liquid crystals: Versatile materials. *Chem. Rev.* **2016**, *116*, 4643–4807. [CrossRef] [PubMed]
2. Fernandez, A.A.; Kouwer, P.H.J. Key Developments in ionic liquid crystals. *Int. J. Mol. Sci.* **2016**, *17*, 731. [CrossRef] [PubMed]
3. Axenov, K.V.; Laschat, S. Thermotropic ionic liquid crystals. *Materials* **2011**, *4*, 206–259. [CrossRef] [PubMed]
4. Douce, L.; Suisse, J.M.; Guillon, D.; Taubert, A. Imidazolium-Based liquid crystals: A modular platform for versatile new materials with finely tuneable properties and behaviour. *Liq. Cryst.* **2011**, *38*, 1653–1661. [CrossRef]
5. Wang, M.; Pan, X.; Xiao, S.F.; Zhang, C.N.; Li, W.X.; Dai, S.Y. Regulating mesogenic properties of ionic liquid crystals by preparing binary or multi-component systems. *J. Mater. Chem.* **2012**, *22*, 2299–2305. [CrossRef]
6. Bradley, A.E.; Hardacre, C.; Holbrey, J.D.; Johnston, S.; McMath, S.E.J.; Nieuwenhuyzen, M. Small-angle X-ray scattering studies of liquid crystalline 1-alkyl-3-methylimidazolium salts. *Chem. Mater.* **2002**, *14*, 629–635. [CrossRef]
7. Holbrey, J.D.; Seddon, K.R. The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals. *J. Chem. Soc. Dalton Trans.* **1999**, *13*, 2133–2139. [CrossRef]
8. Gordon, C.M.; Holbrey, J.D.; Kennedy, A.R.; Seddon, K.R. Ionic liquid crystals: Hexafluorophosphate salts. *J. Mater. Chem.* **1998**, *8*, 2627–2636. [CrossRef]
9. Puntus, L.N.; Schenk, K.J.; Bunzli, J.C.G. Intense near-infrared luminescence of a mesomorphic ionic liquid doped with lanthanide beta-diketonate ternary complexes. *Eur. J. Inorg. Chem.* **2005**, *23*, 4739–4744. [CrossRef]
10. Ganzenmuller, G.C.; Patey, G.N. Charge ordering induces a smectic phase in oblate ionic liquid crystals. *Phys. Rev. Lett.* **2010**, *105*, 137801. [CrossRef]
11. Gorkunov, M.V.; Osipov, M.A.; Kapernaum, N.; Nonnenmacher, D.; Giesselmann, F. Molecular theory of smectic ordering in liquid crystals with nanoscale segregation of different molecular fragments. *Phys. Rev. E* **2011**, *84*, 051704. [CrossRef] [PubMed]

12. Saielli, G. MD simulation of the mesomorphic behaviour of 1-hexadecyl-3-methylimidazolium nitrate: assessment of the performance of a coarse-grained force field. *Soft Matter* **2012**, *8*, 10279–10287. [CrossRef]

13. Dai, J.; Kharkov, B.B.; Dvinskikh, S.V. Molecular and segmental orientational order in a smectic mesophase of a thermotropic ionic liquid crystal. *Crystals* **2019**, *9*, 18. [CrossRef]

14. Saielli, G. Fully atomistic simulations of the ionic liquid crystal [C(16)mim][NO$_3$]: Orientational order parameters and voids distribution. *J. Phys. Chem. B* **2016**, *120*, 2569–2577. [CrossRef] [PubMed]

15. Dong, R.Y. *Nuclear Magnetic Resonance Spectroscopy of Liquid Crystals*; Worlds Scientific: London, UK, 2010.

16. Dvinskikh, S.V. Characterization of Liquid-Crystalline Materials by Separated Local Field Methods. In *Modern Methods in Solid-State NMR: A practitioners' Guide*; Hodgkinson, P., Ed.; Royal Society of Chemistry: Abingdon, UK, 2018.

17. Dvinskikh, S.V.; Sandström, D.; Zimmermann, H.; Maliniak, A. Carbon-13 NMR spectroscopy applied to columnar liquid crystals. *Progr. Nucl. Magn. Reson. Spectrosc.* **2006**, *48*, 85–107. [CrossRef]

18. Dvinskikh, S.V.; Zimmermann, H.; Maliniak, A.; Sandström, D. Separated local field spectroscopy of columnar and nematic liquid crystals. *J. Magn. Reson.* **2003**, *163*, 46–55. [CrossRef]

19. Dvinskikh, S.V.; Dürr, U.H.N.; Yamamoto, K.; Ramamoorthy, A. High-Resolution 2D NMR spectroscopy of bicelles to measure the membrane interaction of ligands. *J. Am. Chem. Soc.* **2007**, *129*, 794–802. [CrossRef]

20. Burum, D.P.; Linder, M.; Ernst, R.R. Low-Power multipulse line narrowing in solid-state NMR. *J. Magn. Reson.* **1981**, *44*, 173–188. [CrossRef]

21. Dvinskikh, S.V.; Zimmermann, H.; Maliniak, A.; Sandström, D. Measurements of motionally averaged heteronuclear dipolar couplings in MAS NMR using R-type recoupling. *J. Magn. Reson.* **2004**, *168*, 194–201. [CrossRef]

22. Dvinskikh, S.V.; Sandström, D. Frequency offset refocused PISEMA-type sequences. *J. Magn. Reson.* **2005**, *175*, 163–169. [CrossRef]

23. Fung, B.M. ^{13}C NMR studies of liquid crystals. *Prog. Nucl. Magn. Reson. Spectrosc.* **2002**, *41*, 171–186. [CrossRef]

24. Constant, M.; Decoster, D. Raman-Scattering-Investigation of nematic and smectic ordering. *J. Chem. Phys.* **1982**, *76*, 1708–1711. [CrossRef]

25. Fung, B.M.; Poon, C.D.; Gangoda, M.; Enwall, E.L.; Diep, T.A.D.; Bui, C.V. Nematic and smectic ordering of 4-n-octyl-4′-cyanobiphenyl studied by carbon-13 NMR. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 267–277. [CrossRef]

26. Marcus, Y. Ionic and molar volumes of room temperature ionic liquids. *J. Mol. Liq.* **2015**, *209*, 289–293. [CrossRef]

27. Nelyubina, Y.V.; Shaplov, A.S.; Lozinskaya, E.I.; Buzin, M.I.; Vygodskii, Y.S. A New Volume-Based approach for predicting thermophysical behavior of ionic liquids and ionic liquid crystals. *J. Am. Chem. Soc.* **2016**, *138*, 10076–10079. [CrossRef] [PubMed]

28. Downard, A.; Earle, M.J.; Hardacre, C.; McMath, S.E.J.; Nieuwenhuyzen, M.; Teat, S.J. Structural studies of crystalline 1-alkyl-3-methylimidazolium chloride salts. *Chem. Mater.* **2004**, *16*, 43–48. [CrossRef]

29. Di Pietro, M.E.; Margola, T.; Celebre, G.; De Luca, G.; Saielli, G. A combined LX-NMR and molecular dynamics investigation of the bulk and local structure of ionic liquid crystals. *Soft Matter* **2019**, *15*, 4486–4497. [CrossRef] [PubMed]

30. Dvinskikh, S.V.; Furó, I. Nuclear magnetic resonance studies of translational diffusion in thermotropic liquid crystals. *Russ. Chem. Rev.* **2006**, *75*, 497–506. [CrossRef]

31. Dvinskikh, S.V. Nuclear Magnetic Resonance Studies of Translational Diffusion in Thermotropic Ionic Liquid Crystals. Available online: https://www.tandfonline.com/doi/full/10.1080/02678292.2019.1647569 (accessed on 23 September 2019).

32. Cifelli, M.; Domenici, V.; Kharkov, B.B.; Dvinskikh, S.V. Study of translational diffusion anisotropy of ionic smectogens by NMR diffusometry. *Mol. Cryst. Liq. Cryst.* **2015**, *614*, 30–38. [CrossRef]