

Supplementary materials

Molecular and segmental orientational order in a smectic mesophase of a thermotropic ionic liquid crystal

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S1. Carbon-13 NMR spectra of $C_{14}mimNO_3$

One-dimensional carbon-13 NMR spectra measured in the isotropic and aligned smectic A phase are displayed in Fig. S1. In the mesophase, proton-carbon cross-polarization was applied to enhance ^{13}C signal intensity. Spectral lines were assigned by performing 2D INADEQUATE experiment [1] in the isotropic phase and 2D dipolar INADEQUATE experiment [2] in the smectic phase.

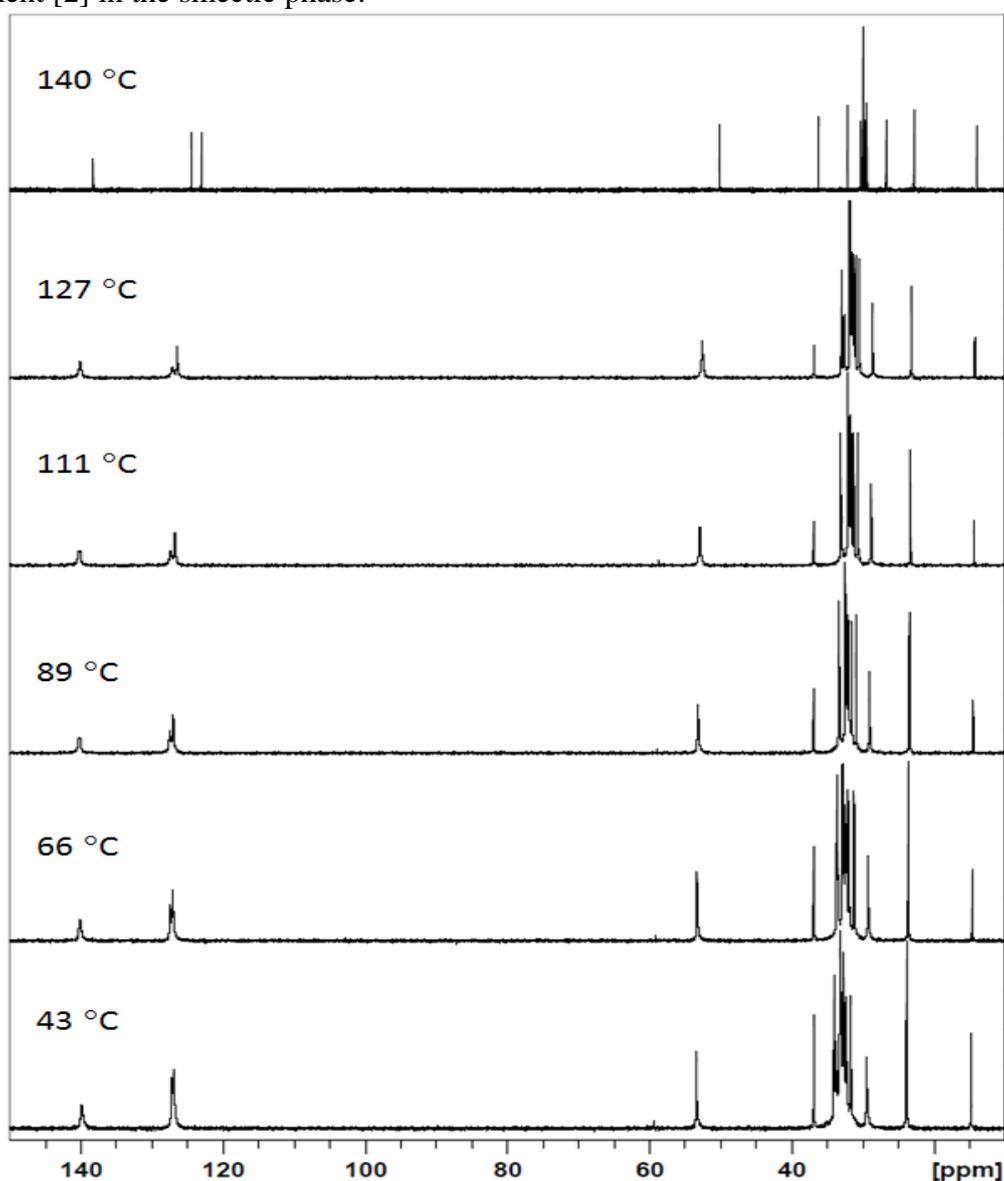


Figure S1. ^{13}C NMR spectra of $C_{14}mimNO_3$ in isotropic phase at 140 °C and at indicated temperatures in smectic A phase.

S2. Pulse sequence for PDLF experiment

In the indirect time period t_1 of the PDLF experiment [3], ^1H magnetization evolves in the presence of the local dipolar fields of rare ^{13}C . Application of the proton homonuclear decoupling sequence BLEW-48 scales the heteronuclear couplings d_{CH} with a factor of $k \approx 0.42$ [4]. A pair of 180° pulses is applied at $t_1/2$ to refocus ^1H chemical shifts while retaining the ^1H - ^{13}C couplings. The proton magnetization is transferred to ^{13}C spins via CP and the carbon signal is detected under ^1H heteronuclear decoupling.

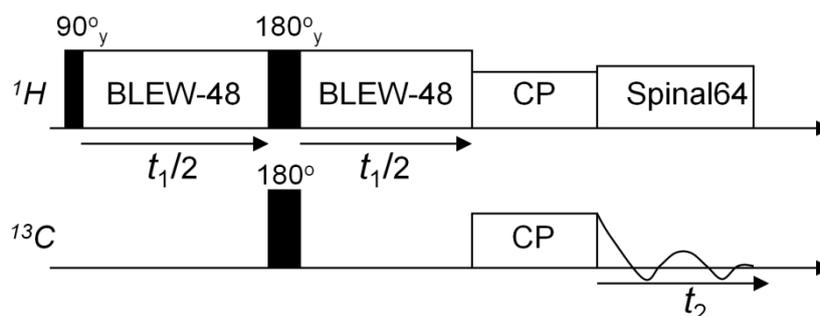


Figure S2. PDLF pulse sequence to record dipolar ^{13}C - ^1H spectra.

S3. Signal assignment for the chain carbons

In the smectic A phase of $\text{C}_{14}\text{mimNO}_3$, the core carbons exhibit signal pattern similar to that analysed previously for analogous ILC sample $\text{C}_{12}\text{mimBF}_4$ [5]. Hence, assignment was assumed the same. To unambiguously assign carbons in the chain, the dipolar INADEQUATE experiment was used.

Conventional solution state INADEQUATE pulse sequence [1] was modified by (i) using ADRF CP for ^{13}C signal enhancement [6] and (ii) setting the excitation delay to generate double quantum coherences according to range of dipolar coupling to be measured [2]. Correlations between directly bound carbons were achieved by setting relatively short excitation delay of 0.42 ms. For all spin pairs, the resolved cross peaks were observed, thus enabling the signal assignment according to conventional algorithm [1]. A part of the INADEQUATE spectrum in the smectic A phase at 66°C covering the signals of carbons from 2 to 12 is shown in figure S3. Correlation peaks between neighbouring carbons (linked by solid lines in figure S3) present pairs of antiphase doublets. The observed splittings $\Delta\nu$ are contributed by the C-C dipolar coupling and J -couplings ($J \approx 35$ Hz for the alkyl chain carbons) and are also depend on the resonance frequency difference $\Delta\delta$ between involved spins. When $\Delta\delta$ is small compared to the splitting $\Delta\nu$, the dipolar coupling is given by $d_{\text{CC}} = \Delta\nu/3$, while for the opposite case $d_{\text{CC}} = (\Delta\nu - J)/2$. For intermediate cases, numerical analysis was performed to fit the observed correlations peak patterns and calculate d_{CC} .

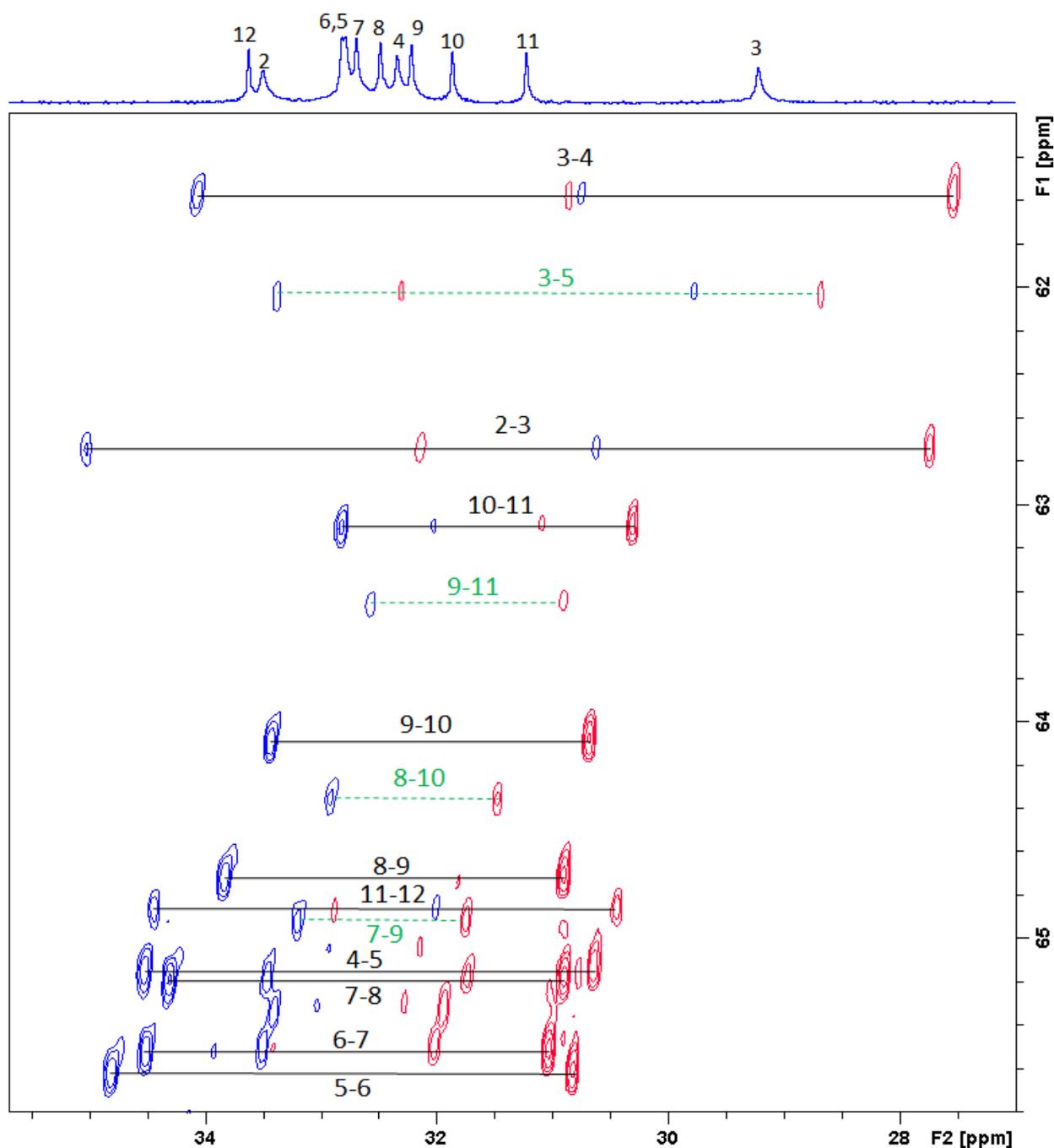


Figure S3. Dipolar INADEQUATE spectrum in the smectic A phase of the $C_{14}mimNO_3$ ionic liquid at temperature 66 °C. A part of full spectrum covering the range of signals of the carbons from 2 to 12 in the alkyl chain is shown. Blue and red contours indicate positive and negative intensities, respectively. Correlation signals along double-quantum dimension (horizontal) present pairs of antiphase doublets. Correlations peaks between neighbouring carbons are indicated by the solid black lines. Some correlations peaks for the carbons separated by two bonds are also indicated by dashed green lines.

S4. Carbon-carbon dipolar couplings

In the dipolar INADEQUATE spectrum a number of cross peaks between carbon-13 spins separated by two bonds were observed (figure S3). The corresponding experimental spectral patterns with frequency splitting $\Delta\nu$ were numerically analysed with account for chemical shift difference $\Delta\delta$ of two involved carbon spins (AB type spectra). For carbons separated by two bonds, literature values of the J -coupling are small, within 0-2 Hz range, and were neglected in the analysis [7]. The obtained dipolar couplings d_{CC} are collected in table S1.

Table S1. ^{13}C - ^{13}C dipolar splittings $\Delta\nu$ and dipolar couplings d_{CC} for alkyl chain carbons separated by two bonds. T=66 °C.

$\text{C}_n\text{-C}_{n+2}$	$\Delta\delta$ (Hz)	Splitting $\Delta\nu$ (Hz)	d_{CC} (Hz)
1-3	3200	145	72
2-4	145.5	303	71
3-5	450	137	69
4-6	57	217	65
5-7	14	186	62
6-8	41	184	57
7-9	60	183	52
8-10	77	182	46
9-11	125	77	39
10-12	222	n/a	n/a
11-13	960	55	28
12-14	2392	42	21

Dipolar coupling d_{CC} were obtained by numerical fit of experimental dipolar spectra extracted from 2D dipolar INADEQUATE spectrum. Equation S1, analogous to eq. 4 in the main article, was used to estimate molecular order parameter S .

$$d_{CC} = b_{CC} P_2(\cos \theta_{PM}) S P_2(\cos \theta_{NL}) \quad (\text{S1})$$

Rigid coupling constant is $b_{CC} = -460\text{Hz}$ (assuming distance $r=2.54\text{\AA}$ obtained from DFT optimized structure). $P_2(\cos \theta_{NL}) = -0.5$. For the methylene carbons in the beginning of the chain, the term $P_2(\cos \theta_{PM}) = 1$. Thus, average for the first three pairs results in $S \approx 0.31$.

References

- [1] S. Berger and S. Braun, *200 and More NMR Experiments: A Practical Course* (Leipzig: Wiley, 2004).
- [2] D. Sandström and M.H. Levitt, Structure and molecular ordering of a nematic liquid crystal studied by natural-abundance double-quantum ^{13}C NMR, *J. Am. Chem. Soc.* 118 (1996) 6966-6974.
- [3] B.M. Fung, K. Ermolaev, and Y. Yu, ^{13}C NMR of liquid crystals with different proton homonuclear dipolar decoupling methods, *J. Magn. Reson.* 138 (1999) 28-35.
- [4] D. P. Burum, M. Linder, and R. R. Ernst, Low-power multipulse line narrowing in solid-state NMR, *J. Magn. Reson.* 44 (1981) 173-188.
- [5] M. Cifelli, V. Domenici, V. I. Chizhik, and S. V. Dvinskikh, ^{15}N - ^{13}C Dipole Couplings in Smectic Mesophase of a Thermotropic Ionic Liquid, *Appl. Magn. Reson.* 4 (2018) 553-562.
- [6] J. S. Lee and A. K. Khitrin, Thermodynamics of adiabatic cross polarization, *J. Chem. Phys.* 128 (2008) 114504.
- [7] L. B. Krivdin and E. W. Della, Spin Spin Coupling-Constants between Carbons Separated by More Than One Bond, *Progr. Nucl. Magn. Reson. Spectrosc.* 23 (1991) 301-610.