

New Chemical Family of $[n-C_xH_{(2x+1)}NEt_3]$ [BEt₃Me] Showing Ionic Plastic-Crystal (x = 4, 5), Rotator-Crystal (x = 6, 7) and Liquid-Crystal Phases (x = 8-16)

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Abstract

New ionic liquid crystals of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (abbreviated to [CxNEt₃][BEt₃Me]) were detected for species with even numbers of $8 \le x \le 16$. In contrast, plastic- and rotator-crystal phases were obtained for [CxNEt₃][BEt₃Me] species with lower x values of x = 4, 5, and 6, 7, respectively. Because we previously documented plastic phases for the $[CxNEt_3][BEt_3Me]$ (x = 1-3) species, $[CxNEt_3][BEt_3Me]$ can be classified as a novel chemical family adopting the entire range of states (mesophases) between solid and isotropic liquid phases (plastic, rotator, and liquid crystals) as a function of the alkyl chain length. Polarized optical microscope (POM) and X-ray diffraction (XRD) measurements revealed that these liquid crystals (x = 8-16 with even numbers of x) form smectic B (x = 8) and A (x = 10), and nematic phases ($x \ge 12$) in the liquid-crystal phases. In the case of x = 4, 5, XRD analysis showed that the salts form cubic crystal structures. Furthermore, the NMR line shapes revealed that both the cation and anion underwent isotropic reorientation. In contrast, the NMR spectra showed that the cations rotated about their long axis in the [C6NEt₃][BEt₃Me] and [C7NEt₃][BEt₃Me] crystals.

Keywords: Plastic crystal | Rotator crystal | Liquid crystal

1. Introduction

Mesophases between solid and isotropic liquid phases can be classified into two groups, i.e. plastic-crystals and liquidcrystals (LCs). In the plastic-crystalline phase, the constituents undergo isotropic reorientation at each crystal-lattice point (the particle orientation is fused; however, the gravity point is ordered). Isotropic reorientation occurs in the solid phases, resulting in small entropy changes at each melting point $(\Delta_{\rm mp}S < 20\,{\rm J\,K^{-1}\,mol^{-1}})$ and a large ΔS value at the temperature of transition between the solid phases.¹ In the plastic crystals, there is a rotator crystal, in which constituents undergo uniaxial rotation at each crystalline lattice point.²⁻¹⁹ Rotator phases are often obtained in crystals formed by rod-like (long chain) chemicals, e.g. $n-C_mH_{(2m+1)}NH_3Cl$ (m = 4-18),²⁻¹¹ n-1 $C_m H_{(2m+1)}COOM (M = Li (m = 14-18), K(m = 13-21)),^{12-15}$ $n-C_mH_{(2m+1)}OSO_3M$ (M = Li (m = 18, 20), Na (m = 14-20), K (m = 16)¹⁶ (where M is an alkali metal ion), etc. In the rotator phase, two-dimensional ion-translation and uniaxial rotation about the molecular long chain have been reported.²⁻¹⁹ In contrast, globular and plane-like ions frequently form ionic plastic crystals.²⁰⁻²⁹ Differential scanning calorimetry (DSC) measurements of rotator crystals show similar trends to those observed for plastic phases: Small $\Delta_{mp}S$ and large total entropy changes at the solid-solid phase transition temperatures are recorded. Conversely, calamitic- or disc-like chemicals often show LC phases in which the orientation of the constituents is ordered; however, the gravity point of the constituents is fused. Ionic LCs have been widely studied for application in the electrical, optical, biochemical, and organic science fields.³⁰⁻⁴⁷ Generally, LC materials are generated through the use of temperature (thermotropic liquid-crystals) or a solvent (lyotropic liquid-crystals). In this study, the objective is to compare LCs and plastic crystals (including rotator crystals), therefore, thermotropic LCs are treated.

Solids can transition to only one phase of plastic crystal or LC (if they have mesophases), because only one state of orientation or gravity point of the constituents is allowed to melt in the mesophase (both states are fused in an isotropic liquid state). It is, thus, interesting to determine which parameters contribute to forming rotator (plastic crystal) or LC phases, especially, in rod-like chemicals. The physical properties of $n-C_mH_{(2m+1)}$ -NH₃Cl,²⁻¹¹ n-C_mH_(2m+1)COOM¹²⁻¹⁵ n-C_mH_(2m+1)OSO₃M,¹⁶ 5-alkoxy-2-(4-alkoxyphenyl)pyrimidine,^{48,49} 4-[4-n-alkoxy cinnamoyloxy]-4-methoxy benzyl cinnamates, 50,51 etc., have previously been evaluated as a function of the alkyl-chain lengths. In the case of $n-C_xH_{(2x+1)}NH_3Cl$ ($x \ge 7$), a rotator phase transforming to a LC phase with increasing temperatures is observed,¹¹ however, no LC phase is detected in $n-C_mH_{(2m+1)}$ -COOM and $n-C_mH_{(2m+1)}OSO_3M$ salts.^{12–16} In contrast, the latter two molecular compounds of 5-alkoxy-2-(4-alkoxyphenyl) pyrimidine and 4-[4-n-alkoxy cinnamoyloxy]-4-methoxy benzyl cinnamates form only LC phases.^{48–51} This difference is considered to indicate that attractive interactions among the constituents influence which phase (rotator or LC) is formed. However, the formation of both LC and plastic-crystal phases for a chemical family is rarely observed.

For ionic plastic-crystals, we have recently proposed a new region in which chemicals assemble via weak ionic interactions, and we have successfully demonstrated the formation of twenty-four new ionic plastic-crystals of $[NEt_xMe_{(4-x)}]$ - $[BEt_2Me_{(4-z)}]$ and $[NEt_vPr_{(4-v)}][BEt_2Me_{(4-z)}]$ (x = 0-4, y = 1-3, z = 3, 4),^{52,53} [NEt₃Pr][BBu₄] and [NEt₂Pr₂][BBu₄],^{54,55} $[NEt_xMe_{(3-x)}Pr][BEt_3Me]$ (x = 1, 2),⁵⁶ and 1-alkyl-4-aza-1azoniabicyclo[2,2,2]octane salts⁵⁷ in the new region. These compounds exhibit interesting characteristics, including low temperatures of transition to the plastic phases (similar to the nature of molecular plastic-crystals) and high melting points (similar to ionic plastic-crystals). Since the $[NEt_3R]^+$ and $[BEt_3Me]^-$ ions (R = alkyl groups) can be assembled via weak ionic interactions and show several ionic plastic crystalline phases,⁵² it can be expected that several salts in this chemical family should show LC phases in a range of long alkyl-chains. In this study, we treat $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (abbreviated to $[CxNEt_3][BEt_3Me]$ with x = 4-16 with even values of x and x = 5, 7, to explore the mechanisms determining which mesophase (plastic crystal, rotator crystal, or LC) is formed by the salts and to investigate the formation of new ionic liquidcrystals in the new region.

In the case of $[CxNEt_3][BEt_3Me]$, it has been reported that the salts with x = 1, 2, and 3 exhibit plastic-crystal phases at around room temperature: the transformation temperature for conversion to the plastic phase is 232.2 K for $[C3NEt_3]$ - $[BEt_3Me]$, 227.2 K for $[C2NEt_3][BEt_3Me]$, and below 200 K for $[C1NEt_3][BEt_3Me]$. The melting point of $[C3NEt_3]$ - $[BEt_3Me]$ is 391.2 K; in contrast, $[C1NEt_3][BEt_3Me]$ and $[C2NEt_3][BEt_3Me]$ decompose at around 400 K.⁵² These salts (x = 1-3) are classified into new ionic-plastic-crystal regions with weak interaction acting on cation and anion.

2. Experimental

For the preparation of Li[BEt₃Me] and [NEt_xMe_(3-x)R]Br, reported procedures⁵² were applied. Li[BEt₃Me] crystals were obtained by adding MeLi dissolved in diethylether (Kanto

Kagaku Co.) to BEt₃ in hexane diluent at 0 °C and evaporating the solvents. During this process, the flask was continuously flushed with N₂ gas. For preparation of $[n-C_xH_{(2x+1)}NEt_3]Br$ (x = 4-8, 10, 11, 12, 14, 16), NEt₃ and $n-C_xH_{(2x+1)}Br$ were mixed in ethanol. The products were obtained by evaporating the solvent at 60 °C. After dissolving $[n-C_xH_{(2x+1)}NEt_3]Br$ in water, Li[BEt₃Me] was added to the aqueous solution at 0 °C. [CxNEt₃][BEt₃Me] (x = 4) crystallized in the solution; in contrast, liquid products were obtained for x = 5-8, 10, 12, 14, and 16. The latter materials were separated by use of dichloromethane and purified by vacuum drying. The chemical structures of all products were confirmed by ¹H and ¹³C NMR measurements in DMSO-d₆ solvent.

DSC spectra were obtained with a Shimadzu DSC-60 calorimeter using Al_2O_3 as a reference sample. The samples were heated from ca. 230 to 480 K at a rate of 5 K min⁻¹. Based on the DSC results, the transition temperatures (T_{tr}) in the solid phase were determined as well as entropy changes at these transition temperatures.

Polarized optical microscope (POM) photographs of the liquid crystal and isotropic liquid phases were obtained using an Olympus CX31P instrument with a sensitive color plate.

XRD patterns were acquired using a Bruker D8 ADVANCE instrument equipped with a Cu anticathode. A rotating stage and ttk450 probe were employed at room and other temperatures, respectively. Powder patterns were recorded over a scan range of $5-40^{\circ}$ with a step angle of 0.02° .

Solid-state ¹HNMR spectra were recorded at a Larmor frequency of 600.13 MHz using a Bruker Avance 600 spectrometer (14.10 T). The samples were packed in a ZrO_2 rotor with an outer diameter of 4.0 mm. Spectra were obtained by Fourier transformation (FT) of the free-induction-decay (FID) signals that were obtained after a $\pi/2$ pulse. The ¹H chemical shifts (CS) were calibrated relative to an external H₂O ($\delta = 2.499$ ppm) reference. A recycle time of 5s was employed for capturing the FID data. The sample temperature was controlled and recorded by a Bruker VT-2000 instrument. Solid-state ¹³C NMR spectra were recorded at a Larmor frequency of 150.92 MHz by use of the same spectrometer and temperature controller. The same sample tube used for the ¹H measurements was employed for accumulating ¹³CNMR signals. Crosspolarization (CP) and magic-angle-spinning (MAS) methods were applied to detect signals with glycine as an external reference ($\delta = 43.16$ ppm). Recycle times of 5 and 20 s were respectively employed for ¹³C NMR measurements with and without CP. In order to estimate the purity of the synthesized specimens, ¹H and ¹³C NMR measurements of the prepared sample dissolved in DMSO-d₆ were carried out in the same apparatus (analysis of samples in the solution and solid states is possible with this spectrometer by exchanging the probe). The chemical shift (CS) values of the ¹H and ¹³C nuclei were calibrated by employing tetramethylsilane (TMS) dissolved in DMSO-d₆ as an internal reference ($\delta = 0.00 \text{ ppm}$).

Density functional theory (DFT) simulation was performed to assign the NMR peaks and to estimate the line-widths observed in the ¹H and ¹³C NMR spectra. As demonstrated in a previous report,^{52–57} the B3LYP/6-311+G** function in the Gaussian 03 computer program⁵⁸ can be adequately used to explain the ¹³C NMR CS values and line-widths observed for alkylammonium and $[BEt_3Me]^-$ ions; the same procedure was applied in the present study.

3. Results and Discussion

3.1 DSC. DSC thermograms acquired for the [CxNEt₃]- $[BEt_3Me]$ (x = 4-8, 10, 12, 14, 16) samples are shown in Figure 1, where the variation appearing at around 220 K is due to instrument noise. The entropy changes and transition temperatures for each compound are listed in Table 1. In this paper, we employ the symbols T_{mI} and T_{tr1} , T_{tr2} to indicate the phasetransition temperatures from mesophase to isotropic liquid phase and in the solid phases moving from higher to lower temperatures; $\Delta_{mI}S$, $\Delta_{tr1}S$, and $\Delta_{tr2}S$ indicate entropy changes at each transition temperature; Phase I, Phase II, etc., are used from the highest-temperature solid-phase or mesophase of each salt. This table also shows the values reported for [NEt₃Me]-[BEt₃Me] (x = 1), [NEt₄][BEt₃Me] (x = 2), and [NEt₃Pr]-[BEt₃Me] (x = 3) that form plastic crystal phases⁵² for comparison with the data obtained in this study. Each phase was assigned by use of POM measurements: a liquid phase exhibiting polarizing patterns was assigned to a liquid-crystal phase, and if no POM pattern was observed, it was assigned as an isotropic liquid phase and the transition temperature for conversion to the phase was indicated as T_{mI} . Here, the compounds (x = 8-16) showed fluidity in the highest-temperature phase. The pale white colored samples had high viscosity. These macroscopic characters are often observed in LCs. The results of the present POM measurements are discussed in the following section. Small $\Delta_{ml}S$ and/or large $\Delta_{tr1}S$ values were obtained for $[CxNEt_3][BEt_3Me]$ with x = 5-7, 12, 14, 16 (Table 1). In contrast, no phase-transition peak was recorded for x = 4, 8, 10.



Figure 1. DSC thermograms of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (x = 4–16). The heating rate was 5 K min⁻¹.

In the case of x = 4, decomposition of crystals was observed instead of fusion in a test tube at ca. 350 K. For x = 8, 10, color of both liquids was changed from white to pale yellow at around 350 K. These changes (decomposition) frequency observed in some of [BEt₃Me] and [BEt₄] salts.^{52–56} In the case of x = 5-7, small $\Delta_{ml}S$ values (4.3–11.1 JK⁻¹ mol⁻¹) were recorded between solid and isotropic liquid phases. The values are similar to those reported in ionic plastic crystals.⁵²⁻⁵⁷ In addition, the [C5NEt₃][BEt₃Me] salt showed large $\Delta_{tr1}S$ values of 48.5 $JK^{-1}mol^{-1}$. Based on these results, it can be considered that motional modes with large degrees of freedom occurred in Phase I of the three crystals (x = 5-7). In the case of x = 12, the value of $(\Delta_{tr1}S + \Delta_{tr2}S)$ is similar to those of x = 2, 3 (plastic crystal), therefore it can be regarded that the ions perform overall motions with large amplitudes in Phase I (LC phase). In the case of x = 14, 16, large $\Delta_{tr1}S$ values of 110.7 and 130.7 $J\,K^{-1}\,mol^{-1}$ suggest that the constituents also have overall motions in each LC phase.

3.2 POM. POM photographs were acquired for the liquid phases of $[CxNEt_3][BEt_3Me]$ (x = 5, 6, 7, 8, 10, 12, 14, 16). In the case of x = 4, no liquid phase was detected (decomposition was observed in the solid phase at ca. 330 K as described in the above section). The POM patterns observed for the liquid-phase of the x = 8-16 species with even numbers are displayed in Figure 2. No POM texture was obtained above the T_{mI} for $[CxNEt_3][BEt_3Me]$ with x = 5-7. Since the $[CxNEt_3][BEt_3Me]$ crystals with x = 5-7 showed only isotropic liquid-phases, it can be concluded that $[CxNEt_3][BEt_3Me]$ species with x = 1-7 are not transformed to any LC phase under ambient pressures.

In the case of $[CxNEt_3][BEt_3Me]$ (x = 8-16), the POM textures indicate that these compounds have ionic LC phases. Since it is reported that $[CxNEt_3][BEt_3Me]$ (x = 1-3) salts have plastic phases,⁵² [CxNEt_3][BEt_3Me] (x = 1-16) can be regarded

Table 1. Entropy changes at phase transition temperatures of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$. Each temperature (K) is shown in parentheses, and entropies are given in J K⁻¹ mol⁻¹.

x	$\Delta_{\rm tr2}S~(T_{\rm tr2})$	$\Delta_{\rm trl}S\left(T_{\rm trl}\right)$	$\Delta_{\rm mI}S~(T_{\rm mI})$
1*			Dec.
2*	8.0 ± 0.8	19.0 ± 0.8	Dec.
	(227.2 ± 0.8)	(233.4 ± 0.5)	
2*	25.6 ± 0.4	23.2 ± 0.5	5.1 ± 0.8
3	(232.2 ± 0.7)	(243.3 ± 0.4)	(391.2 ± 0.5)
4			Dec.
5		48.5 ± 0.2	4.3 ± 0.2
5		(243.4 ± 0.5)	(270.6 ± 0.5)
(11.1 ± 0.2
0			(286.1 ± 0.5)
7			5.7 ± 0.2
/			(321.3 ± 0.5)
8			Dec.
10			Dec.
12	16.1 ± 0.2	16.8 ± 0.2	Dec
	(247.3 ± 0.5)	(252.3 ± 0.5)	Dec.
14		110.7 ± 0.2	Dec
14		(270.9 ± 0.5)	Det.
16		130.7 ± 0.2	Daa
10		(289.0 ± 0.5)	Dec.

Dec. = decomposition. *Ref. 52.



Figure 2. POM photographs of liquid crystal phases of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (x = 8-16). The photographs were obtained at 300 K.

as a rare system in which the chemicals form plastic crystal and LC phases; as the length of the alkyl-chain in the plastic crystal of [CxNEt₃][BEt₃Me] increases, ionic LC phases are obtained. Different POM textures were observed for [CxNEt₃][BEt₃Me] with x = 8 and 10 and x > 12 as displayed in Figure 2. In the case of $x \ge 12$, marble designs were obtained in the POM photographs; conversely, a mosaic texture with radial lines and focal conic fan-shaped patterns were detected for [C8NEt₃]-[BEt₃Me] and [C10NEt₃][BEt₃Me], respectively. Based on these textures, we can classify the liquid-crystalline structure of the x = 8 and 10 and $x \ge 12$ species into smectic B (SmB) and smectic A (SmA) and nematic (N) phases, respectively. Several thermotropic liquid-crystals transform to SmB, SmA, and N phases in turn with increasing temperature.48-51,59,60 Therefore, this successive transformation follows the same order in terms of increasing freedom of the constituent arrangements; as the alkyl-chain lengths of the cation increase, the ions form more disordered structures in the [BEt₃Me] salts.

3.3 DFT Simulation. In order to assign the NMR peaks observed in this study (NMR spectra are shown in section 3.5), DFT simulations were performed by using the B3LYP/ $6-311+G^{**}$ function in the Gaussian 03 computer program.⁵⁸ This function can adequately explain the ¹³C NMR CS values and line-widths observed for the [CxNEt₃]⁺ (x = 1-3) and [BEt₃Me]⁻ ions.⁵² Before calculating the CS values, all atomic coordinates in the cations and [BEt₃Me]⁻ ion were optimized by using the same B3LYP/6-311+G^{**} function. A minimum energy ionic conformation was also employed for discussion

Table 2. ¹³C NMR chemical-shift values (ppm) and ¹³C NMR line-widths (ppm) estimated for $[CxNEt_3]^+$ and $[BEt_3Me]^-$ using the B3LYP/6-311+G** function. The line-breadth is presented in parentheses. Partial data for ¹³C NMR CS values and line-widths are listed in this table.

 $[CH_{3}(Terminal)-(CH_{2})_{(x-3)}-CH_{2}(\beta)-CH_{2}(\alpha)-N-(CH_{2}(\alpha')-CH_{3}(\beta'))_{3}]^{+}$

x	α-С	β-C	Terminal-C
	α'-C	<u>β'-C</u>	
1*	44.67(60.28)		
1	65.15(79.02)	9.51(20.14)	
2*	63.03(85.40)	11.44(21.91)	
2*	62.19(70.55)	13.93(16.23)	14.65(24.87)
3	51.52(63.51)	12.63(18.33)	
4	62.86(74.45)	28.43(29.78)	15.75(27.96)
4	57.90(68.31)	8.63(17.70)	
5	62.99(74.64)	27.27(28.48)	16.22(28.63)
3	57.82(68.07)	8.62(17.73)	
C	62.95(74.88)	27.35(28.72)	16.31(28.60)
0	57.79(68.17)	8.58(17.71)	
7	62.97(74.90)	27.39(28.97)	16.47(28.73)
/	57.74(68.04)	8.59(17.74)	
o	62.95(75.06)	27.37(29.00)	16.60(28.94)
0	57.72(68.08)	8.55(17.73)	
10	62.96(75.15)	27.43(29.20)	16.71(29.08)
10	57.69(68.01)	8.51(17.74)	
12	63.01(75.28)	27.58(29.48)	16.89(29.33)
12	58.15(67.96)	8.49(17.38)	
14	63.22(75.66)	27.72(29.82)	16.98(29.36)
14	57.59(67.76)	8.37(17.83)	
16	63.00(75.35)	27.67(29.68)	16.91(29.43)
10	57.67(67.90)	8.38(17.84)	
[DEt Mal-	38.57(34.49)	19.41(24.40)	
	9.93(29.56)		

*Ref. 52.

of the XRD data (in the next section). The CS values were obtained by subtracting the isotropic value of the shielding tensors estimated for the ions from that of a tetramethylsilane (TMS) molecule, where the isotropic shielding tensors of the ¹³C nucleus in the TMS molecule were simulated by using the same process as described above (atomic coordinates were calculated by using the same B3LYP/6-311+G^{**} function). The ¹³C NMR line-widths were estimated by using the anisotropic shielding tensors. The partial CS data and line-breadth obtained by this calculation are listed in Table 2.

3.4 XRD. The XRD powder patterns observed for Phase I of $[CxNEt_3][BEt_3Me]$ (x = 4-16) are shown in Figure 3. The DSC and POM measurements revealed that Phase I is a solid state for $x \le 7$. In the case of x = 4 and 5, the XRD powder patterns could be indexed to a cubic structure. Since plastic-crystal phases are usually obtained for the cubic structure of $[NEt_xMe_{(4-x)}][BEt_3Me]$ (x = 0-4) salts,⁵² it can be considered that the $[C4NEt_3]^+$ and $[C5NEt_3]^+$ cations both form orientationally disordered phases with the $[BEt_3Me]^-$ anions. The lattice constants (*a*) estimated for these compounds are listed in Table 3. In contrast of these salts, the XRD patterns of the x = 6 and 7 species could be fitted to the trigonal and tetragonal lattice, respectively. These unit lattices are frequently observed in plastic and rotator phases;²⁻¹⁹ therefore, it can be deduced



Figure 3. XRD powder patterns observed in Phase I of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (x = 4-16).

Table 3. Crystal structure and lattice constant (*a* and *c*) of the highest-temperature solid phase of $[n-C_xH_{(2x+1)}NEt_3]$ -[BEt₃Me] (x = 4-7). In the case of x = 8, a liquid crystal state was obtained.

x	Crystal Structure	a/pm	c/pm
4	Cubic	864 ± 5	
5	Cubic	935 ± 3	
6	Trigonal	1075 ± 5	1798 ± 5
7	Tetragonal	1076 ± 5	1861 ± 5
8	Hexagonal (SmB)	630 ± 5	3775 ± 5

that the anion and cations have overall motions with large amplitudes.

In the case of the LC phase of $[CxNEt_3][BEt_3Me]$ (x = 10-16), no XRD peak without broad components was recorded as displayed in Figure 3; conversely, line patterns were obtained for [C8NEt₃][BEt₃Me]. The signals of [C8NEt₃][BEt₃Me] could be fitted to the hexagonal structure. This result is consistent with the POM photographs displayed in Figure 2: Phase I of [C8NEt₃][BEt₃Me] can be assigned to SmB in which the constituents form a hexagonal structure. Obtained lattice constants are listed in Table 3. Since ionic lengths of 1118 nm (width is 517 pm) and 741 pm were simulated for the [C8NEt₃]⁺ and [BEt₃Me]⁻ ions, respectively, it can be considered that both the cation and the anion form lamella structure in the SmB phase. The POM photograph suggested that Phase I of [C10NEt₃][BEt₃Me] is SmA; however, no XRD signal was detected in Figure 3 (in the case of SmA, a peak corresponding to the repetition length along the *c*-axis is generally observed at very small angles). Assuming that the [C10NEt₃]⁺ cation and [BEt₃Me]⁻ anion are stacked along each long axis of the molecular ion and form a layer (SmA), the DFT simulation



Figure 4. ¹HNMR spectra observed in Phase I of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (x = 4-16).

shows that the length of the layer should be ca. 2115 pm (cation length(1374 pm) + anion(741 pm)). Based on this estimation, an XRD signal indexed to (001) would be observed at ca. 3°. In actuality, the separation between the cation and anion is larger than 0 pm, therefore the signal will be observed at very small angle ($<3^\circ$). Unfortunately, we were unable to observe signals at such a small angle due to the instrumental limitations of the available XRD spectrometer.

3.5 NMR. ¹H and ¹³C NMR measurements were used to monitor the ionic motions. The ¹H and ¹³C NMR spectra observed for Phase I of $[CxNEt_3][BEt_3Me]$ (x = 4-16) are shown in Figures 4 and 5, respectively. ¹H and ¹³C signals with narrow line-widths were recorded without MAS for the crystal and LC phases. In general, broad ¹HNMR lines are obtained for ordinary solid samples because of strong dipole-dipole interaction among the H atoms. The line-width of the ¹³C NMR spectra is generally affected by chemical-shift-anisotropy (CSA) rather than by dipole-dipole interactions because the gyromagnetic ratio (γ) of ¹³C is one quarter that of the ¹H nucleus. The line-width, which is affected by dipole-dipole interactions, is proportional to both γ^2 and the inverse-cube of the distance between ¹³C nuclei, where the distance between ¹³C nuclei is long in natural abundance samples (ca. 1% ¹³C is present in ordinary samples). In contrast, the contribution of CSA to the ¹H NMR spectra is small. Therefore ¹H and ¹³C NMR measurements provide information about the inter- and intra-distance of the nucleus and motional modes, respectively.

In the case of the [C4NEt₃][BEt₃Me] crystal, the line-widths in the ¹H NMR spectrum were slightly broadened. In order to estimate full width at half-maximum ($\Delta \nu$) and the second moment (M_2) of each signal, Lorentz functions were applied to line analysis. The results are shown in Figure 6(a) and



Figure 5. ¹³C NMR spectra observed in Phase I of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (x = 4-16).



Figure 6. Spectral analysis of ¹H NMR spectra for (a) [*n*-C₄H₉NEt₃][BEt₃Me] and (b) [*n*-C₅H₁₁NEt₃][BEt₃Me]. Here, black solid lines are the observed spectra, blue solid lines are line envelope obtained by summing, and colored are analyzing lines.

Table 4. Here, the M_2 values were estimated by the following relation:

$$M_2 = \langle \omega^2 \rangle = \frac{\int d\omega (\omega_0 - \omega)^2 f(\omega_0 - \omega)}{\int d\omega f(\omega_0 - \omega)}$$
(1)

Here, ω_0 and $f(\omega_0 - \omega)$ are the angular frequency of the highest signal and the line height at $\omega_0 - \omega$ ($\omega = 2\pi\nu$), respectively. The maximum values of $\Delta\nu$ (0.96 kHz) and M_2 (0.62 G²) are similar to those reported for ionic plastic crystals of [NEt_x-

Table 4. Chemical shift ν (kHz), full width at half-maximum $\Delta \nu$ (kHz) and second moments M_2 (G²) of analyzing lines for [*n*-C₄H₉NEt₃][BEt₃Me] and [*n*-C₅H₁₁NEt₃][BEt₃Me]

[n-C ₄ H ₉ NEt ₃][BEt ₃ Me]		$[n-C_5H_{11}NEt_3][BEt_3Me]$			
ν	$\Delta \nu$	M_2	ν	$\Delta \nu$	M_2
2.34	0.57	0.38	1.77	0.05	0.03
1.55	0.96	0.62	1.68	0.07	0.05
1.19	0.24	0.16	0.80	0.06	0.04
1.01	0.24	0.16	0.59	0.07	0.05
0.83	0.24	0.16	0.34	0.07	0.04
0.59	0.48	0.31	0.19	0.07	0.05
0.29	0.28	0.19	-0.32	0.07	0.05
-0.07	0.62	0.41	-0.72	0.07	0.05



Figure 7. Spectral analysis of (a) ${}^{1}HNMR$ spectra for $[n-C_{6}H_{13}NEt_{3}][BEt_{3}Me]$ and (b) $[n-C_{7}H_{15}NEt_{3}][BEt_{3}Me]$. Here, black solid lines are the observed spectra, blue solid lines are line envelope obtained by summing, and colored are analyzing lines.

 $Me_{(4-x)}$][BEt₃Me] and [NEt_xMe_(4-x)][BEt₄] (x = 0-4).^{52,53} Therefore, it can be considered that the ions have overall motions with large amplitudes in the crystal. In addition, similar ¹³C NMR line-widths to those of plastic crystals^{52,53} were obtained, and the [C4NEt₃][BEt₃Me] crystal showed a cubic crystal structure as described in the previous section. Based on these results, it can be concluded that [C4NEt₃]-[BEt₃Me] falls into the category of ionic plastic crystals.

In the case of the [C5NEt₃][BEt₃Me] crystals, similar trends were observed in the XRD, ¹H, and ¹³C NMR spectra; therefore, [C5NEt₃][BEt₃Me] can also be classified as a new ionic plastic crystal. In addition, the small M_2 values (the maximum value of 0.005 \ll 1 G²) were estimated in [C5NEt₃][BEt₃Me] crystals as displayed in Figure 6(b) and Table 4. Based on these results, it can be suggested that isotropic reorientation and ion jump motions occur in Phase I.

In the case of the $[C6NEt_3]^+$ and $[C7NEt_3]^+$ salts, the linewidths in the ¹H NMR spectra were similar to those observed for the plastic crystals of $[CxNEt_3][BEt_3Me]$ (x = 4, 5) as shown in Figure 7 and Table 5. This result indicates that $[C6NEt_3]$ - $[BEt_3Me]$ and $[C7NEt_3][BEt_3Me]$ crystals also have overall motions with large amplitudes. However, some broad linewidths were needed to line analysis for the cation, therefore it can be regarded that the cations do not perform isotropic reorientation in both crystals. In addition, CSA lines were detected in the ¹³C NMR spectra. Based on the DFT simulation,

Table 5. Chemical shift ν (kHz), full width at half-maximum $\Delta \nu$ (kHz) and second moments M_2 (G²) of analyzing lines for $[n-C_6H_{13}NEt_3][BEt_3Me]$ and $[n-C_7H_{15}NEt_3][BEt_3Me]$

$[n-C_6H_{13}NEt_3][BEt_3Me]$		[n-C ₇ H ₁₅ NEt ₃][BEt ₃ Me]			
ν	$\Delta \nu$	M_2	ν	$\Delta \nu$	M_2
2.02	0.51	0.34	7.01	5.00	3.11
0.84	0.34	0.22	3.70	0.70	0.46
0.57	0.17	0.11	2.35	1.20	0.78
0.42	0.17	0.11	2.65	5.00	3.10
0.36	1.80	1.16	1.00	5.00	3.11
-0.06	0.34	0.22			
-0.45	0.34	0.22			



Figure 8. Spectral analysis of (a) 13 C NMR spectra for [n-C₆H₁₃NEt₃][BEt₃Me] and (b) [n-C₇H₁₅NEt₃][BEt₃Me]. Here, black solid lines are the observed spectra, blue solid lines are line envelope obtained by summing, and colored are analyzing lines.

the signals observed at around 20 and 55 ppm can be assigned to the α -carbon of the anion and the α -carbon of the cation, respectively. The ¹³CNMR line-breadths observed for these compounds are notably smaller than the simulated widths (ca. 34 and 68 ppm as listed in Table 2), and the line-envelopes observed at around 55 pm can be regarded as axial-symmetry line-shapes. In order to estimate CSA values correctly, the line analysis was carried out. The results are demonstrated in Figure 8. In these figures, some Lorentz lines and one curve with axial-symmetry line-shapes were employed for fitting each ¹³C NMR spectrum. The lines-widths obtained at around 55 ppm are 11.7 (x = 6) and 6.8 ppm (x = 7). Based on these results, it can be considered that the anion performs isotropic reorientation and the cations rotate about an axis, and the axis is liberated with large angles (tumbling motion) in the crystals. This motional model was previously proposed for [NEt₂Pr₂]-[BEt₃Me], [NEtPr₃][BEt₃Me],⁵² [NEt_xMe_(3-x)Pr][BEt₃Me],⁵⁶ and $[NEt_x Pr_{(4-x)}][BEt_4]$ (x = 1-3).⁵³ Since small $\Delta_{mp}S$ values were obtained and the crystallographic structures were skewed from cubic (lattice axes are extended) based on the DSC and XRD measurements, respectively, it can be concluded that the $[CxNEt_3][BEt_3Me]$ (x = 6, 7) salts (middle alkyl chain lengths) have rotator-crystal phase.

Among the liquid-crystals of $[CxNEt_3][BEt_3Me]$ with x = 8-16, narrow line-widths (similar to those observed for isotropic liquid phases) were observed in the ¹³C NMR spectra of the species with x = 10-16, as displayed in Figure 5. These results



- **Figure 9.** Spectral analysis of ¹H NMR spectrum of $[n-C_8H_{17}NEt_3]$ [BEt₃Me]. Here, black solid lines are the observed spectra, blue solid lines are line envelope obtained by summing, and colored are analyzing lines.
- **Table 6.** Chemical shift ν (kHz), full width at half-maximum $\Delta \nu$ (kHz) and second moments M_2 (G²) of analyzing lines for $[n-C_8H_{17}NEt_3][BEt_3Me]$

$[n-C_8H_{17}NEt_3][BEt_3Me]$					
ν	$\Delta \nu$	M_2			
1.90	0.49	0.32			
1.77	0.59	0.39			
0.75	0.29	0.19			
0.39	0.42	0.28			
-0.09	0.51	0.33			
-0.45	0.38	0.25			

showed that the CSA of the C atoms in the cations and anion was averaged by ionic motions in the SmA and N phases. In the case of x = 8, the signals were slightly broadened relative to those observed for the x = 10-16 species. Based on these lineshapes, it can be deduced that the ionic motions are slightly restricted in the SmB phase of [C8NEt₃][BEt₃Me] compared with those in the SmA and N phases of [CxNEt₃][BEt₃Me] (x = 10-16). The ¹H NMR line-shapes of the SmB phase were remarkably different from those of the other phases, as shown in Figure 4. The line-breadth of [C8NEt₃][BEt₃Me] was similar to that of the $[CxNEt_3][BEt_3Me]$ (x = 4–7) crystals as shown in Figure 9 and Table 6. Based on the ¹H and ¹³C NMR lineshapes, it can be deduced that the [C8NEt₃]⁺ and [BEt₃Me]⁻ ions are localized at the lattice points in the SmB hexagonal structure and the inter-ion dipole-dipole interactions among H atoms are maintained. In contrast with [C8NEt₃][BEt₃Me], the narrow line-breadths obtained for $[CxNEt_3][BEt_3Me]$ (x = 10-16) suggest that the dipole-dipole interactions are averaged by ionic motions with large amplitudes in the SmA and N phases. Since the ¹H NMR line-widths of $[CxNEt_3][BEt_3Me]$ (x = 10– 16) were slightly larger than those detected for the isotropic liquid phases, it is proposed that the anion and cations undergo overall motions; however, the ionic translational motions are slow in the LC phases compared with those of the ions in the isotropic liquid phases.

3.6 Discussion of Plastic Crystals, Rotator Crystals, and Liquid Crystals. Ionic plastic-crystals, rotator-crystals, and liquid-crystals were obtained for the $[CxNEt_3][BEt_3Me]$ (x = 1-16) chemical series, as summarized in Table 7. Since the entire range of intermediate states (plastic, rotator, and liquid crystals) between solid and isotropic liquid phases is rarely detected for one chemical series, the $[CxNEt_3][BEt_3Me]$ salts can be

Table 7. Phase speciation of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (x = 1-16) above 220 K

x	$T_{\rm trl}/{\rm K}$		$T_{\rm mI}/{ m K}$
1*		Plastic Crystal	Dec.
2*	227.2	Plastic Crystal	Dec.
3*	232.2	Plastic Crystal	391.2
4		Plastic Crystal	Dec.
5	243.4	Plastic Crystal	270.6
6		Rotator Crystal	286.1
7		Rotator Crystal	321.3
8		Liquid Crystal (SmB)	262.3
10		Liquid Crystal (SmA)	Dec.
12	252.3	Liquid Crystal (N)	Dec.
14	270.9	Liquid Crystal (N)	Dec.
16	289.0	Liquid Crystal (N)	Dec.

Dec.: decomposition. *Ref. 52.

categorized as a quite unique chemical family. The difference between the definition of rotator and liquid crystals lies in the lattice structure. In the case of rotator crystals, the gravity point of the constituents is located on the lattice point in three dimensions; conversely, the repetition is disordered in LCs with two (Smectic phase) or three (Nematic phase) directions. The present results indicate that Coulombic attraction (enthalpy term) between cation-anion pairs for species with $x \le 7$ dominates the heat energy (entropy term): The crystal lattice can be constructed although the particle's orientation is fused.

In the SmB phase (x = 8), the species form structures with higher repetition compared with those in the SmA (x = 10)and N phases (x = 12-16). Since it is reported that several thermotropic LCs undergo transformation to the SmB, SmA, and N phases in turn with increasing temperature, 48-51,58,59 the present [CxNEt₃][BEt₃Me] series forms more disordered structures with increasing x values. Based on these results, it can be concluded that interaction among the constituents is a key factor for forming plastic-, rotator-, or liquid-crystals as well as SmB, SmA, and N phases in LC phases. Therefore, ¹H NMR measurements were performed to evaluate the strength of the interaction between the anion and cations using samples dissolved in CDCl₃. The obtained spectra are plotted in Figure 10. In this figure, extended signals recorded at around 0.85 ppm are also displayed because the terminal H atoms of the [n- $C_x H_{(2x+1)} N(CH_2 CH_3)_3]^+$ ions with $x \ge 3$ are thought to interact with the anions in the solid phases. The signal of the terminal H successively shifted to smaller CS values with increasing alkyl-chain lengths x. The ¹HNMR CS values are linked to the electron density because the shielding tensors of the ¹H nucleus are mainly determined by diamagnetic terms rather than paramagnetic terms.^{60,61} Based on the decreasing ¹H CS values (Figure 10(b)), it can be deduced that the electron density on the H atoms increases with increasing x values of the $[CxNEt_3]^+$ ions. Thus, the positive charge on the terminal H atoms decreases gradually for longer alkyl-chains: longer alkyl-chains in the $[CxNEt_3]^+$ ions result in weaker interaction between the anion and cations, and therefore, the rod-like cations form rotator crystals (x = 6, 7) and SmB (x = 8), SmA (x = 10), and N phases (x = 12-16).



Figure 10. ¹H NMR spectra of $[n-C_xH_{(2x+1)}NEt_3][BEt_3Me]$ (x = 4–16) in CDCl₃ solution. (b) and (c) Enlarged signals of (a). (b) Signal of $[CxN(CH_2C\underline{H}_3)_3]^+$; (c) $[CxN(CH_2CH_3)_3]^+$.

4. Conclusion

Ionic plastic-crystals, rotator-crystals, and liquid-crystals were observed for the $[CxNEt_3][BEt_3Me]$ (x = 1–16) series. This rare observation of the entire range of intermediate states (plastic-, rotator-, and liquid-crystals) between solid and isotropic liquid phases for a single chemical series places the [CxNEt₃][BEt₃Me] salts in the privileged position of belonging to a quite unique chemical family. ¹³C NMR spectral analvsis revealed that the [BEt₃Me]⁻ anion and the cations of $[CxNEt_3][BEt_3Me]$ (x = 4, 5) undergo isotropic reorientation in the solid state, as also substantiated by the XRD line-patterns, which were indexed to cubic structures. In the case of x = 6and 7, ¹³CNMR spectral analysis confirmed that the constituents rotate about one axis. DSC and XRD analyses also demonstrated that these salts form rotator phases where small entropy changes ($\Delta_{mp}S$) of 11.1 (x = 6) and 5.7 J K⁻¹ mol⁻¹ (x = 7) and trigonal and tetragonal lattices were respectively recorded. POM photographs of the $x \ge 8$ species revealed that the $[CxNEt_3][BEt_3Me]$ (x = 8–16) compounds could be classified as liquid crystals. SmB, SmA, and N phases were detected for the x = 8, 10, and $x \ge 12$ species, respectively, based on the POM textures. ¹H, ¹³C NMR, and XRD analyses also suggested that the [C8NEt₃][BEt₃Me] salt forms the SmB phase. The ¹HNMR spectra of [CxNEt₃][BEt₃Me] in CDCl₃ solution showed a decline in the CS values with increasing xvalues. Based on this result, it is proposed that the successful observation of plastic-, rotator-, and liquid-crystals for this chemical series is linked to a reduction in the strength of the Coulombic interaction between adjacent ions with increasing alkyl-chain lengths. This weak interaction is an intrinsic feature of this new class of ionic plastic-crystals.

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References

1 J. Timmermans, J. Phys. Chem. Solids 1961, 18, 1.

2 A. Terreros, P. A. Galera-Gómez, E. Lopez-Cabarcos, J. Therm. Anal. Calorim. 2000, 61, 341.

3 M. G. Broadhurst, J. Res. Natl. Bur. Stand., Sect. A 1962, 66A, 241.

4 D. A. Pink, J. Chem. Phys. 1975, 63, 2533.

5 S. Fukada, H. Yamamoto, R. Ikeda, D. Nakamura, J. Chem. Soc., Faraday Trans. 1 1987, 83, 3207.

6 S. Iwai, R. Ikeda, D. Nakamura, *Can. J. Chem.* **1988**, *66*, 1961.

7 M. Hattori, S. Fukada, D. Nakamura, R. Ikeda, J. Chem. Soc., Faraday Trans. 1990, 86, 3777.

8 S. Iwai, M. Hattori, D. Nakamura, R. Ikeda, J. Chem. Soc., Faraday Trans. 1993, 89, 827.

9 M. Hattori, Y. Onoda, T. Erata, M. E. Smith, M. Hattori, H. Ohki, R. Ikeda, Z. Naturforsch., A **1994**, 49, 291.

10 S. Tanaka, N. Onoda-Yamamuro, S. Ishimaru, R. Ikeda, Bull. Chem. Soc. Jpn. **1997**, 70, 2981.

11 R. Ikeda, Recent Res. Dev. Chem. Phys. 2004, 5, 257.

12 N. A. S. White, H. A. Ellis, J. Mol. Struct. 2008, 888, 386.

13 N. A. S. White, H. A. Ellis, *Mol. Cryst. Liq. Cryst.* 2009, 501, 28.

14 N. A. S. White, H. A. Ellis, P. N. Nelson, P. T. Maragh, *J. Chem. Thermodyn.* **2011**, *43*, 584.

15 T. Hayasaki, H. Honda, S. Hirakawa, *Hyperfine Interact.* 2013, 222, 27.

16 S. Hirakawa, Y. Morimoto, H. Honda, *Hyperfine Interact.* 2015, 230, 101.

17 V. Busico, P. Cernicchiaro, P. Corradinl, M. Vacatello, J. Phys. Chem. **1983**, 87, 1631.

18 E. C. Reynhardt, A. Wozniak-Braszak, *Chem. Phys. Lett.* **1993**, *215*, 493.

19 Z. Fojud, C. Boeffel, E. Szcześniak, S. Jurga, *J. Mol. Struct.* 2000, *555*, 107.

20 M. Kenmotsu, H. Honda, H. Ohki, R. Ikeda, T. Erata, A. Tasaki, Y. Furukawa, Z. Naturforsch., A **1994**, 49, 247.

21 H. Honda, M. Kenmotsu, H. Ohki, R. Ikeda, Y. Furukawa, *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 1009.

22 H. Honda, S. Ishimaru, N. Onoda-Yamamuro, R. Ikeda, *Z. Naturforsch., A* **1995**, *50*, 871.

23 H. Honda, M. Kenmotsu, N. Onoda-Yamamuro, H. Ohki, S. Ishimaru, Y. Furukawa, R. Ikeda, *Z. Naturforsch., A* **1996**, *51*, 761.

24 H. Honda, Z. Naturforsch., A 2007, 62, 633.

25 J. Adebahr, M. Grimsley, N. M. Rocher, D. R. MacFarlane, M. Forsyth, *Solid State Ionics* **2008**, *178*, 1798.

26 A. J. Seeber, M. Forsyth, C. M. Forsyth, S. A. Forsyth, G. Annat, D. R. MacFarlane, *Phys. Chem. Chem. Phys.* **2003**, *5*, 2692.

27 H. Ono, S. Ishimaru, R. Ikeda, *Ber. Bunsen-Ges. Phys. Chem.* 1998, 102, 650.

28 H. Ono, S. Ishimaru, R. Ikeda, H. Ishida, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2049.

29 J. Huang, M. Forsyth, D. R. MacFarlane, *Solid State Ionics* 2000, *136–137*, 447.

30 B. R. Kaafarani, Chem. Mater. 2011, 23, 378.

31 J. P. F. Lagerwall, G. Scalia, *Curr. Appl. Phys.* 2012, 12, 1387.

32 W. Han, M. Tu, R. Zeng, J. Zhao, C. Zhou, *Carbohydr*. *Polym.* **2012**, *90*, 1353.

33 E. Zapp, E. Westphal, H. Gallardo, B. de Souza, I. C. Vieira, *Biosens. Bioelectron.* **2014**, *59*, 127.

34 K. Wang, F. Jian, R. Zhuang, Soft Mater. 2010, 9, 32.

35 A. Lyashchova, D. Fedorenko, Y. Garbovskiy, G. Klimusheva, T. Mirnaya, V. Asaula, *Liq. Cryst.* **2013**, *40*, 1377.

36 X. Pan, M. Wang, X. Fang, C. Zhang, Z. Huo, S. Dai, *Sci. China Chem.* **2013**, *56*, 1463.

37 F. Xu, K. Matsumoto, R. Hagiwara, J. Phys. Chem. B 2012, 116, 10106.

38 N. Yamanaka, R. Kawano, W. Kubo, N. Masaki, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, *J. Phys. Chem. B* **2007**, *111*, 4763.

39 S. Xiao, X. Lu, Q. Lu, B. Su, *Macromolecules* 2008, 41, 3884.

40 K. Binnemans, Chem. Rev. 2005, 105, 4148.

41 M. Yoshio, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* 2004, *126*, 994.

42 M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2006**, *128*, 5570.

43 H. Shimura, M. Yoshio, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2008**, *130*, 1759.

44 M. Yoshio, T. Mukai, K. Kanie, M. Yoshizawa, H. Ohno, T. Kato, *Adv. Mater.* **2002**, *14*, 351.

45 T. Mukai, M. Yoshio, T. Kato, M. Yoshizawa, H. Ohno, *Chem. Commun.* 2005, 1333.

46 N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, *Chem. Commun.* **2005**, 740.

47 C. K. Lee, H. W. Huang, I. J. B. Lin, *Chem. Commun.* 2000, 1911.

48 M. Thompson, C. Carkner, A. Bailey, N. J. Mosey, N. Kapernaum, R. P. Lemieux, *Liq. Cryst.* **2014**, *41*, 1246.

49 I. Rupar, K. M. Mulligan, J. C. Roberts, D. Nonnenmacher, F. Giesselmann, R. P. Lemieux, *J. Mater. Chem. C* 2013, *1*, 3729.

50 B. H. Patel, N. N. Vyas, A. V. Doshi, *Mol. Cryst. Liq. Cryst.* 2015, 607, 114.

51 B. H. Patel, A. A. Doshi, A. V. Doshi, *Mol. Cryst. Liq. Cryst.* **2015**, *608*, 38.

52 T. Hayasaki, S. Hirakawa, H. Honda, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 993.

53 S. Hirakawa, H. Honda, Z. Naturforsch., A 2015, 70, 521.

54 T. Hayasaki, S. Hirakawa, H. Honda, Z. Naturforsch., A 2014, 69, 433.

55 T. Hayasaki, S. Hirakawa, H. Honda, *Am. Chem. Sci. J.* 2014, *4*, 745.

56 Y. Kotani, H. Honda, *Bull. Chem. Soc. Jpn.* 2019, *92*, 768.
57 S. Hirakawa, Y. Kotani, T. Hayasaki, H. Honda, *Bull. Chem. Soc. Jpn.* 2015, *88*, 1735.

58 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03* (*Revision B.04*), Gaussian, Inc., Pittsburgh PA, **2003**. 59 T. N. Govindaiah, Nagappa, H. R. Sreepad, *Mol. Cryst. Liq. Cryst.* 2013, *574*, 1.

60 R. C. Tandel, N. K. Patel, *Mol. Cryst. Liq. Cryst.* **2014**, *593*, 114.

61 C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed., Springer-Verlag, New York, **1992**. doi:10.1007/978-3-662-09441-9.