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Masataka Tansho; Yoshito Onoda; Shoichi Kutsumizu; Shinichi Yano; Ryuji Kato

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^{14}N NMR studies on an optically isotropic liquid crystalline D phase of 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (ANBC)

by MASATAKA TANSHO*, YOSHITO ONODA, RYUJI KATO†,
SHOICHI KUTSUMIZU*‡ and SHINICHI YANO†

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba,
Ibaraki 305, Japan
†Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido,
Gifu 501-11, Japan
‡Instrumental Analysis Center, Gifu University, 1-1 Yanagido, Gifu 501-11, Japan

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^{14}N nuclear magnetic resonance (NMR) measurements have been carried out for three members of 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (ANBC-*n*, where the number of carbon atoms in the alkoxy group, *n*, is 14, 16, and 22) in the temperature range 400–500 K. ANBC-16 and -22 show an optically isotropic D phase. The ^{14}N NMR spectrum of the D phase showed a single peak, which may result from isotropically averaged quadrupole interactions around the ^{14}N nucleus. Relaxation time measurements indicate the existence of two relaxational processes, faster anisotropic and slower isotropic motions, and suggest that in both cases ANBC molecules act as a dimer. The present ^{14}N NMR results may be interpreted in the framework of the IPJR model, indicating that the structure of the D phase is a three-dimensional network continuous over the unit lattice.

1. Introduction

4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids, ANBC-*n*, (*n* is the number of carbon atoms in the alkoxy group) are known as unique thermotropic liquid crystalline compounds exhibiting an optically isotropic D phase, and thus have attracted the scientific interest of many researchers. The D phase was first discovered in two members, ANBC-16 and -18 by Gray *et al.* [1], and characterized by Demus *et al.* [2, 3]. Recently, we found that the D phase exists as a thermally stable and enantiotropic phase in all members of ANBC-*n* between $n=16$ and 22. Moreover, two kinds of isotropic liquid phases, I_1 and I_2, were observed in the members of $n=11$–22, where the I_1 phase still retains a degree of order [4]. The structure of the D phase has been investigated by X-ray diffraction (XRD) and several structural models have been proposed: the spherical micelle model by Diele *et al.* [5], the linked spherical micelle model and unconnected infinite rod model by Etherington *et al.* [6], and the interpenetrating jointed rod (IPJR) model by Tardieu and Billard [7] and Levelut and Fang [8]. In all of these models the units, such as spherical or rod-shaped micelles, are arranged in their unit cell in harmony with a cubic symmetry. Since the unit cell of the D phase consists of about 1000 molecules, and the arrangement of the molecules is fluctuating in space and time, XRD cannot give a decisive result for this system; hence structural studies of the D phase also need other physical measurements. Ukleja *et al.* [9] measured relaxation times and diffusion constants for ANBC-16 using solid state ^{1}H NMR spectroscopy and showed that in the D phase the molecular motions are isotropic on the time scale of NMR, and diffusional motions of the molecules are not fixed to one unit cell of the cubic lattice. On the other hand, Yamaguchi *et al.* [10] first measured the dynamic viscoelastic properties in the mesomorphic phases of ANBCs; they found that the D phase has a very large storage modulus of $\sim 10^7$ dyn cm^{-2} ($=10^6$ Pa), which strongly suggests the existence of a three-dimensional network structure.

This current work is undertaken to probe the structure and dynamic nature of the D phase of ANBC by the use of ^{14}N NMR spectroscopy. In ^{1}H NMR spectroscopy, the spin relaxation process is, in general, closely connected with both inter- and intra-molecular dipole interactions, which sometimes makes analysis of the spectra complicated. ^{14}N NMR spectroscopy, on the contrary, gives a very simplified spectrum because the relaxation process is related only to the quadrupole interactions [11, 12]; in the case of ANBC homologues, the ^{14}N NMR signal should only reflect molecular

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*Authors for correspondence.

motions by which the direction of the $-NO_2$ group is changed. Therefore, we can get a clearer insight into the molecular motions in the D phase, by comparison with ^1H NMR. In this work, we have measured ^{14}N NMR spectra for three members of the ANBC series, ANBC-14, -16, and -22, of which ANBC-16 and -22 have the D phase. We have also measured relaxation times in the temperature range 400–500 K to obtain information on the mode and rate of molecular motions in the D, smectic A (SmA), I_1, and I_2 phases.

2. Experimental

The ANBCs were prepared according to the established method of Gray *et al.* [1, 13]. The samples were judged to be fully pure by thin layer chromatography, differential scanning calorimetry (DSC), and elemental analysis. The phase transition temperatures determined by DSC (Seiko Denshi DSC-210) at a heating rate of $1\,K\,min^{-1}$ are as follows: $n=14$, SmC–466–SmA–475–I_1–480–I_2; $n=16$, SmC–448–D–472–SmA–473–I_1–478–I_2; $n=22$, SmC–410–D–470–I_1–477–I_2 (all temperatures in K). Solid-state ^{14}N NMR spectra were obtained using a Bruker MSL-400 spectrometer equipped with a home-built probe for high temperature measurements above 400 K. The Larmor frequency was 28·917 MHz, and the quadrupole echo pulse sequence [14] was used to obtain the spectrum of each phase. ^{14}N relaxation times were measured for the optically isotropic D, I_1, and I_2 phases and the anisotropic SmA phase. The spin–lattice relaxation time, T_1, and spin–spin relaxation time, T_2, were measured by an inversion recovery method and by the Carr–Purcell–Meiboom–Gill (CPMG) method, respectively. The samples were placed in a 10 mm diameter glass tube which was sealed under vacuum. The curve-fitting calculation was performed with a Bruker software WINFIT.

3. Results and discussion

Figure 1 shows ^{14}N NMR spectra for different phases of ANBC-16. The spectral pattern of the SmA phase changed with time after the temperature was equilibrated, suggesting a tendency for change of the molecular orientation under the magnetic field. The final signal in figure 1 shows a doublet pattern with a quadrupole splitting ($\Delta\nu_Q$) of 7·0 kHz, indicating a uni-axial property of spin one ($I=1$) nuclei [11, 15]. The signal for the SmC phase, on the contrary, is very broad but appears to show the bi-axiality of this phase [16]. No sign of magnetic orientation of the sample was detected, and for the randomly oriented sample, the observed spectral pattern was reproduced by the calculated spectrum using two parameters, $\Delta\nu_Q=26$ kHz and the asymmetry parameter $\eta=0{\cdot}6$, as shown in figure 1. In the D and I_1 phases, the ^{14}N signal shows a single peak, being isotropic on the time scale of NMR, but the linewidth in the D phase is about twice as large as that in the I_1 phase. The isotropy in the D phase is most probably due to motional averaging, which will be discussed later in detail. In the I_1 phase, our XRD studies indicated the existence of a weak organization of molecules, which vanishes in the I_2 phase [17]. The spectrum of the I_1 phase is, however, very similar in shape and linewidth to that of the I_2 phase (not shown here).

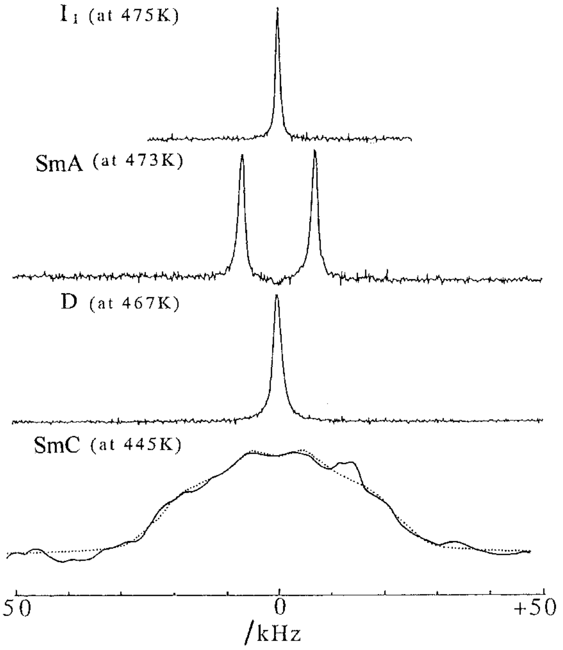

Figure 1. ^{14}N NMR spectra of the SmC, D, SmA, and I_1 phases in ANBC-16. The dotted curve is the simulated spectrum for the SmC phase (see text).

Figure 2 shows plots of T_1 versus $1/T$ for ANBC-16 and -14. The plots for ANBC-16 are divided into three regions with respect to the slope, roughly corresponding to the I_2, I_1, and S_A and D phase regions with reducing temperature. It must be said that the I_1–I_2 transition temperature does not correspond well to the temperature at which the T_1–$1/T$ curve bends, but we ascribe this small discrepancy to the difficulty of determining the I_1–I_2 transition temperature exactly because of the very broad nature of this transition in DSC [3, 4]. The plots for ANBC-14 consisted of three regions, corresponding to the I_2, I_1, and SmA phases, and almost overlap the plots for ANBC-16. Below 472 K, ANBC-16 shows the D phase while ANBC-14 has the SmA phase, but such a structural difference does not seem greatly to influence the temperature dependence of T_1, suggesting that T_1 is associated with the same type of motion for both ANBC-14 and -16. In the SmA phases, it is possible that molecules undergo a translational self-diffusion within

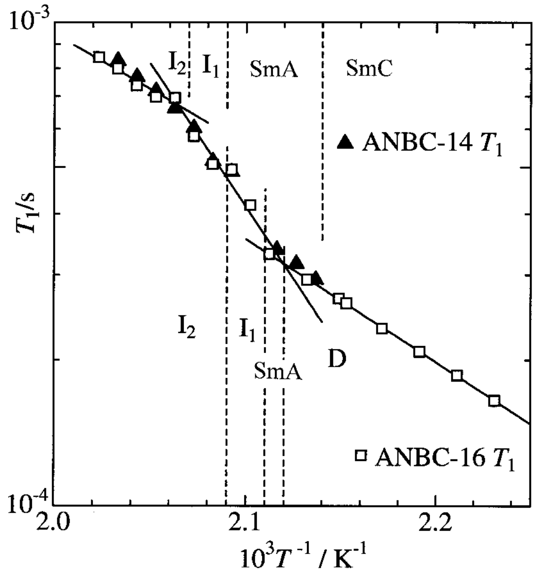

Figure 2. Plots of logarithms of T_1 versus reciprocal of the absolute temperature ($1/T$) for ANBC-14 (▲) and -16 (□). The phase types of ANBC-14 and ANBC-16 are shown at the top and the middle of the figure, respectively; the three straight lines are the linear least-squares fits for the data points of the D and SmA, I_1, and I_2 phase regions of ANBC-16.

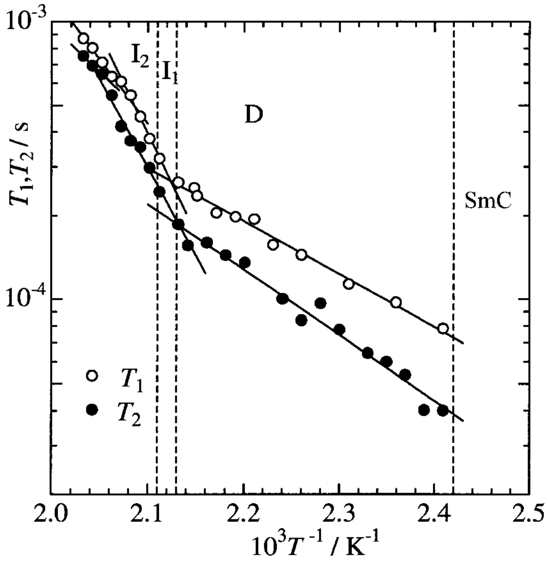

Figure 3. Plots of logarithms of T_1 (○) and T_2 (●) versus reciprocal of the absolute temperature ($1/T$) for ANBC-22. The phases observed are shown at the top, and the linear least-squares fits are also shown.

each SmA layer, but this diffusional motion can be ruled out from the motions contributing to T_1 because the diffusion does not change the electric field gradient around ^{14}N nuclei. On the other hand, a rotational motion may occur around the molecular long axis, which can contribute to T_1 in both the SmA phase of ANBC-14 and the D phase of ANBC-16. The activation energy (E_a) for T_1 was estimated as 49 ± 4 kJ mol^{-1} for the D phase of ANBC-16 (± means the standard deviation of the linear least-square fitting) and roughly 60 kJ mol^{-1} for the SmA phase of ANBC-14.

Figure 3 shows the temperature dependences of T_2 and T_1 for ANBC-22. Both T_1–$1/T$ and T_2–$1/T$ curves consist of three regions corresponding to I_2, I_1, and D phases. The E_a for T_1 was estimated as 37 ± 1 kJ mol^{-1} in the D phase region and 137 ± 6 kJ mol^{-1} in the I_1 phase region. In both phases, T_2 is slightly shorter than T_1, but equal to T_1 in the I_2 phase. The slope for T_2 is slightly larger than that for T_1 in the D phase, and both are almost identical in the I_1 phase; the apparent E_a for T_2 is estimated as 45 ± 2 kJ mol^{-1} in the D phase and 122 ± 11 kJ mol^{-1} in the I_1 phase but, as mentioned below, the temperature dependence of T_2 is not exactly characterized by the activation energy of one motional mode.

As mentioned above, comparison of the T_1–$1/T$ data below 472 K for ANBC-16 and -14 led to the conclusion that T_1 is associated with the same type of motion for both ANBC-14 and -16; the possible mode of motion contributing to T_1 in the D phase of ANBC-16 is the rotational motion around the molecular long axis. This mode of motion will, however, only partially average the anisotropic quadrupole interaction around the ^{14}N nucleus, suggesting the possibility of another motional mode averaging the residual anisotropy to zero. It is reasonable to consider that the present system is in an extremely narrow region in the framework of the Bloembergen–Purcell–Pound (BPP) theory [18], because both T_2 and T_1 increased with increasing temperature. Assuming only one mode of motion contributing to both T_2 and T_1, the slope for T_2 in the Arrhenius plots should be equal to that for T_1, but the actual behaviour was different, as shown in figure 3. For the cubic phases of lyotropic lipid systems, the two-mode model of motions has been used to explain the NMR results [19, 20]. We plotted the logarithm of $(1/T_2 - 1/T_1)$ against the inverse of temperature to confirm the applicability of this model to our system, and obtained a straight line with E_a of 61 ± 7 kJ mol^{-1} for the D phase of ANBC-22. This result encourages us to postulate an additional motional mode. If the time scale of this motion is sufficiently slower than that of the rotational mode, it is possible that this motion *contributes to* T_2 *but not to* T_1 in the temperature region of the D phase. The E_a for the *slower isotropic* motion is almost comparable to that for the (rotational) *faster anisotropic* motion, in the D phase (49 ± 4 kJ mol^{-1} for ANBC-16 and 37 ± 1 kJ mol^{-1} for ANBC-22), suggesting that the molecules act as a dimer for the slower isotropic motion in the D phase.

Ukleja *et al.* reported ^{1}H NMR studies for the D phase in ANBC-16 [9]. The ^{1}H NMR spectrum in the D phase showed four peaks, corresponding to their chemical shifts, and the temperature dependences of T_1 for the alkyl tail, phenyl ring, and acid proton in the D phase region gave E_as of 21, 28, and 41 kJ mol^{-1}, respectively; the weight-averaged E_a was estimated to be 16 kJ mol^{-1}, almost equal to the E_a values in the SmC and SmA phase regions. In our ^{14}N NMR studies, the E_a value for T_1 was 49 kJ mol^{-1} in the D phase, larger than any value obtained from ^{1}H NMR. This discrepancy may be explained by the difference between the motions monitored: the T_1 in ^{1}H NMR spectroscopy reflects both intra- and inter-molecular dipole–dipole interactions, while ^{14}N NMR detects molecular motions accompanied with the change in direction of the NO_2 groups, such as the rotational motion of the ANBC molecule itself. Ukleja *et al.* also reported that the diffusion coefficient for the D phase is 3×10^{-11} m^2 s^{-1}, suggesting that the translational diffusion of ANBC molecules is across distances of ~10 nm, greater than the unit cell length. This result rules out the spherical micelle model. They ascribed the translational self-diffusion *through regions having different directors* to the isotropy on the ^{1}H NMR because such diffusion causes a rapid re-orientation of the molecules in the time scale of NMR, completely averaging the NMR interactions, as in isotropic liquids. Here, the results of ^{1}H NMR agree with those by our ^{14}N NMR because the latter also show the isotropy of the D phase in the time scale of ^{14}N NMR.

The singlet ^{14}N NMR signal in the D phase contradicts the unconnected infinite rod model by Etherington *et al.* [6]; if their model were applicable, the D phase should produce a split peak as usually seen in a hexagonal array of rods in the lyotropic systems [11, 21, 22]. Consequently, the only remaining candidate for the structural model of the D phase is the IPJR model by Tardieu and Billard [7]. This would indicate that the D phase contains a three-dimensional network structure spreading through the unit lattice, and the slower isotropic motion with the E_a of ≈60 kJ mol^{-1} is assigned to the diffusional motion of the ANBC *dimers* through regions having different directors.

Our XRD studies for the I_1 phase showed a sharp ring in the small-angle region, in addition to a broad halo ring in the wide-angle region, indicating that a weak organization remains in the I_1 phase and that the local structure retains a layered arrangement [17]. From the ^{14}N NMR result, E_a for T_1 in the I_1 phase was 113 ± 11 kJ mol^{-1} for ANBC-16 and 137 ± 6 kJ mol^{-1} for ANBC-22. In the ^{1}H NMR data by Ukleja *et al.*, the relaxation rate ($1/T_1$) *for acid proton* significantly decreased with increasing temperature around the higher temperature side of the D phase, although this behaviour was neglected; the value of E_a estimated from their data was ≈100 kJ mol^{-1}. The temperature dependence of infrared spectra for ANBC-16 showed that the COOH dimers dissociate noticeably in the temperature region of the I_1 phase, the dissociation ceasing on going to the I_2 phase temperature region, where about 60% of COOH groups are in the dimeric state [23]. Therefore, the large activation energy suggests that the rotational motion around the molecular long axis in the I_1 phase accompanies the breaking of hydrogen-bonding formed by the end COOH groups. The breaking of the hydrogen-bonding should cause a partial destruction of smectic-like structure in the I_1 phase, resulting in a reduction in the degree of long-range ordering.

4. Conclusion

In conclusion, the present ^{14}N NMR study has shown that the D phase of ANBC is isotropic on the time scale of NMR, as in the isotropic liquid phases, I_1 and I_2. The relaxation time behaviour suggests the existence of two relaxational processes, *faster anisotropic* and *slower isotropic motions*; the former motion is rotational around the molecular long axis, while the latter is translational self-diffusion of the molecules over the unit cell length; in both motions the ANBC molecules act as a dimer. The existence of the slower isotropic motion is important because it is this motion that is responsible for averaging completely the quadrupole interactions around the ^{14}N nucleus. All these insights for the D phase agree with the ^{1}H NMR results by Ukleja *et al.*, and also support the IPJR model by Tardieu and Billard. For the I_1 phase, the activation energy for T_1 was ≈100 kJ mol^{-1}, suggesting a significant dissociation of COOH dimers. It was concluded that the I_1 phase has a locally smectic-like structure such as occurs in SmA phases, although the dissociation of COOH dimers causes partial destruction of the smectic layers.

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