Solid-State ²H NMR Study of Phase Transitions in Deuterated Crystals of 5-Methyl-9-hydroxyphenalen-1-one and 5-Bromo-9-hydroxyphenalen-1-one

Tomoyuki Mochida,*,†,‡ Daisuke Kuwahara,‡,¶ Seiichi Miyajima,‡,# and Tadashi Sugawara§

Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan, Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan, and Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153-8902, Japan

The nature of the phase transitions and proton−deuteron dynamics in the crystals of 9-hydroxyphenalenone derivatives have been investigated by means of solid-state ²H NMR spectroscopy. It was found that the antiferroelectric ordering of deuterons along the hydrogen bonds in 5-methyl-9-deuterioxyphenalenone (**1**-*d*) and 5-bromo-9-deuterioxyphenalenone (**2**-*d*) occurs below the phase transition temperatures at T_C = 44 K and T_I = 34 K, respectively. The microscopic origin of the incommensurate modulation in **2**-*d* below T_I = 34 K is attributable to slight rotational displacements, which are fixed at commensurate angles below the lock-in transition at T_C = 22 K.

1. Introduction

Hydrogen-bonded materials exhibit a variety of phase transition phenomena.[1] In particular, the phase transitions in hydrogen-bonded ferroelectrics have been explained in terms of statistical mechanics based on the tunneling states of protons,[2,3] and the proton-tunneling model has accounted for the large deuterium isotope effects on the transition temperatures.[1−10] To elucidate the role of proton-tunneling in hydrogen-bonded ferroelectrics, we focused on 9-hydroxyphenalenone derivatives as a model system (Figures 1 and 2),[11] because the tunneling phenomenon in these molecules in the gas phase is well documented.[12−14] The molecular system has several advantages over conventional inorganic ferroelectrics, such as the suppression of the "geometrical isotope effect"[15,16] due to an intramolecular hydrogen bond within a fixed molecular framework[17] and the clarity of the polarity inversion mechanism based on proton tautomerism.[11,18]

The phase sequences of 5-methyl-9-hydroxyphenalen-1-one (**1**-*h*), 5-bromo-9-hydroxyphenalen-1-one (**2**-*h*), and their deuterioxy analogues (**1**-*d* and **2**-*d*) have been examined so far. The crystal of **1**-*h* exhibits a phase transition at 41 K, whereas no phase transitions are observed in the crystal of **2**-*h*.[11] Upon deuteration, however, **2**-*d* exhibits successive phase transitions at T_I = 34 K and T_C = 22 K, as demonstrated by dielectric,[19] calorimetric,[20] and diffraction[21−24] studies. The former phase transition is a second-order transition from the normal phase to the incommensurate phase, and the latter transition is a lock-in transition to the commensurate phase. Quantum aspects of such deuteration-induced phase transitions have been discussed,[25] and we interpret the absence of phase transitions in **2**-*h* in terms of quantum paraelectricity based on proton-tunneling.[11] Direct
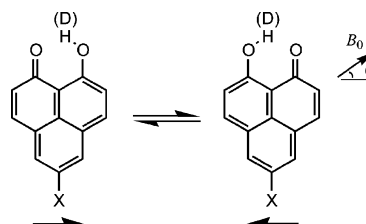

Figure 1. Tautomerization of 9-hydroxyphenalen-1-one derivatives. The arrows below the tautomers indicate the transverse dipole moments, which invert coupling with tautomerization. Also shown is the direction of the magnetic field B_0 with respect to the orientation of the deuterated tautomers (see text).
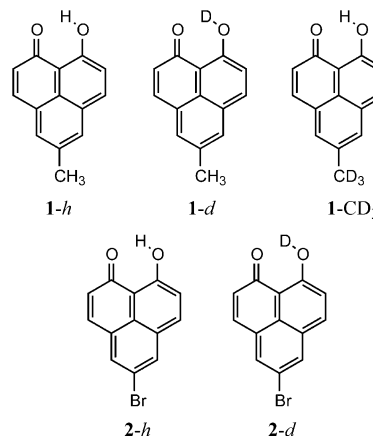

Figure 2. Structural formula of 9-hydroxyphenalen-1-one derivatives.

evidence for the tunnel mode has been obtained in the crystal of **2**-*h* by far-infrared spectroscopy.[26] Furthermore, a 5-iodo-derivative turned out to have a phase sequence similar to **2**.[27,28]

To understand the origin of the intriguing phase behaviors of these compounds, it is important to determine the order−disorder behavior of the proton dynamics along the hydrogen bond. In particular, the origins of (i) the paraelectricity at low temperatures in **2**-*h*, (ii) the deuteration-induced phase transitions in **2**-*d*, and (iii) the incommensurate modulation in **2**-*d* are of interest. Thus, we have performed low temperature ²H NMR

* Corresponding author. Tel.:+81-47-472-4406; fax.: +81-47-472-4406; e-mail: mochida@chem.sci.toho-u.ac.jp.
† Toho University.
‡ Institute for Molecular Science.
§ The University of Tokyo.
¶ Present address: Center for Instrumental Analysis, The University of Electro-Communications, Chofu, Tokyo 182−8585.
# Present address: Miyajima Syoyu Co., Ltd., 2318, Funamiya, Karatsu, Saga 847-0062, Japan.

experiments on solid samples of **1**-*d*, **2**-*d*, and 5-methyl-*d₃*-hydroxyphenalen-1-one (**1**-CD₃). This paper presents firm evidence for the coupling between the deuterium-induced phase transition in the crystal of **2**-*d* and the order−disorder of deuterons. This finding conversely gives further support for the proton-tunneling in protio compound **2**-*h* in the solid state. We also describe the tautomerization dynamics in the crystal of **1**-*d* as well as the methyl rotation in **1**-CD₃ and discuss the deuteron dynamics with reference to the low-temperature structure of **2**-*d*.

2. Experimental Section

Compounds **1**-*h* and **2**-*h* were synthesized by the literature methods.[11,29] The methyl-deuterated compound, 5-methyl-*d₃*-hydroxyphenalenone, was synthesized from 2-bromo-6-methyl-*d₃*-naphthalene, which was prepared by the Kumada coupling[30] of methyl iodide-*d₃* and 2-bromonaphthalene. Deuterium substitution of the hydroxyl hydrogens of **1**-*h* and **2**-*h* was performed by repeated recrystallization from benzene solutions containing a small amount of D₂O under nitrogen. Single crystals of **1**-*d* or **2**-*d* were grown by slow cooling of saturated benzene solutions in the presence of a small amount of D₂O within sealed glass tubes under nitrogen. The deuterium concentration was checked by measuring infrared spectra, and complete deuteration (>99%) was confirmed. ²H NMR experiments were performed on a Bruker DSX-400 spectrometer operating at the resonance frequency of 61.25 MHz. Low-temperature measurements were conducted with a Doty Ultra-low-temperature probe (Penguin Probe) in the temperature range 300−5 K. Powder spectra were measured using a spin−echo pulse sequence. Single-crystal experiments were performed using a single-pulse sequence on deuterated crystals of **1**-*d* and **2**-*d* sealed in glass tubes. Typical sample dimensions were 0.3 × 0.3 × 4.0 mm³. Spectra for **2**-*d* were measured for two different sample orientations as schematically shown in Figures 5 and 6. The numbers of acquisitions were 4−20. With lowering temperature, the relaxation time of the deuteron in **1**-*d* and **2**-*d* became extremely long.

3. Results and Discussion

Phase Transition in 5-Methyl-9-deuterioxyphenalen-1-one (1-d). A-1. Order−Disorder Dynamics of Deuterons. The crystals of **1**-*h* and **1**-*d* exhibit only a small deuterium substitution effect in their phase transition temperatures: T_C = 41 and 44 K, for **1**-*h* and **1**-*d*, respectively. To investigate the order−disorder state of deuterons in **1**-*d*, we performed single-crystal ²H NMR experiments on **1**-*d*. While a pair of resonance lines will be observed because of the motional averaging if a deuteron undergoes fast exchange, each line will split into a doublet because the quadrupole coupling constants of the tautomers become unequal if the tautomerization is ordered, provided that B_0 is applied along a direction other than the transverse direction ($\theta \neq 0$, in Figure 1).[31−33] The degree of the splitting is dependent on θ, and it is expected to become a maximum when B_0 coincides with the O−D vector of either of the tautomers, considering the orientation of the electric field gradient (EFG) tensors in general hydrogen bonds.[34] Figure 3 shows the spectra of **1**-*d* recorded at 50 and 35 K. At 50 K, a pair of resonance peaks is observed, indicating that rapid tautomerization takes place. Below the phase transition temperature of T_C = 44 K, the peaks become doubled, indicating that an ordering of the deuteron occurs associated with the antiferroelectric phase transition.

A-2. Deuterium Quadrupole Coupling Constants. We further carried out ²H NMR experiments on powder samples of **1**-*d* because deuterium quadrupole coupling constant, asym-
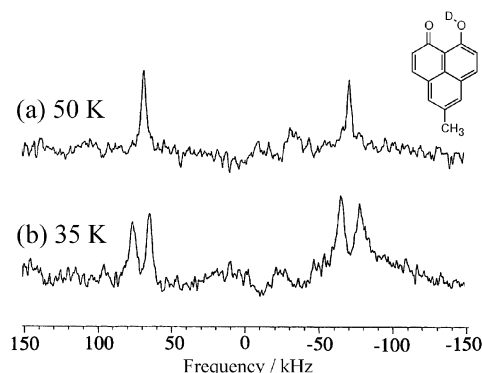

Figure 3. ²H NMR spectra of a single crystal of 5-methyl-9-deuterioxyphenalen-1-one (**1**-*d*) recorded at 50 K (above T_C) and 35 K (below T_C).
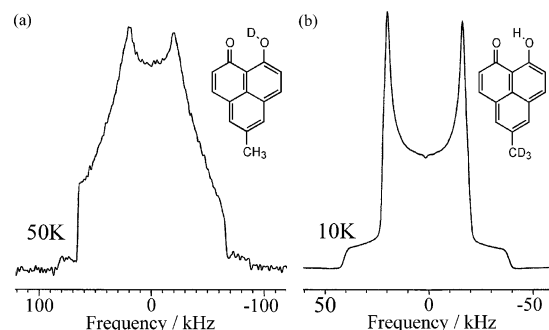

Figure 4. (a) ²H NMR spectrum of a powdered sample of 5-methyl-9-deuterioxyphenalen-1-one (**1**-*d*) recorded at 50 K. (b) ²H NMR spectrum of a powdered sample of 5-methyl-*d₃*-9-hydroxyphenalen-1-one (**1**-CD₃) recorded at 10 K.

metric parameters, and principal values of EFG tensors can be derived from the analysis of powder spectra.[33,35] Figure 4 a shows the ²H powder spectrum of **1**-*d* recorded at 50 K. Fitting of the spectrum yielded the quadrupole coupling constant e^2Qq/h = 122 kHz and the asymmetric parameter η = 0.46, which are reasonable values for a hydrogen-bonded system undergoing fast deuteron exchange.[36] If we assume η = 0.46, an O−D...O angle of 140°, and an O...O distance of 2.5 Å, an inherent value of $\eta \sim 0.2$ can be estimated for the tautomer of **1**-*d* in a static state, using the method of Soda and Chiba.[38] Consistent with this, fitting of the spectrum below T_C yielded e^2Qq/h = 140 kHz and η = 0.23. The principal values of EFG tensors of **1**-*d* could be derived from the spectrum at 15 K, despite the poor signal-to-noise ratio: V_{xx} = −41, V_{yy} = −66, and V_{zz} = 107 kHz. Overall, the quadrupole coupling constant and the asymmetric parameters are reasonable for a static hydrogen bond with an O...O distance of 2.5 Å.[36] As a related example, values for the enol tautomer of propane-1,3-dione at 77 K have been reported: e^2Qq/h = 120.7 kHz, η = 0.326, V_{xx} = −30.5, V_{yy} = −60.0, and V_{zz} = 90.5 kHz.[34] At this temperature, the tautomerization equilibrium is mostly shifted to a dominant component. The smaller value of e^2Qq/h than the present case is ascribable to the shorter O...O distance.[34] The e^2Qq/h value of 9-hydroxyphenalen-1-one in solution has been reported to be ca. 140 kHz,[37] on the basis of analysis of spin−lattice relaxation times. This value is larger than the present value of 122 kHz, and the difference may arise partly because of the assumption of a zero asymmetry parameter in the solution measurement.[34]

A-3. Rotation of the Methyl Group. To check whether the phase transition in **1**-*h* is associated with the motion of the methyl group, we measured variable-temperature ²H NMR spectra on a methyl-deuterated compound, 5-methyl-*d₃*-
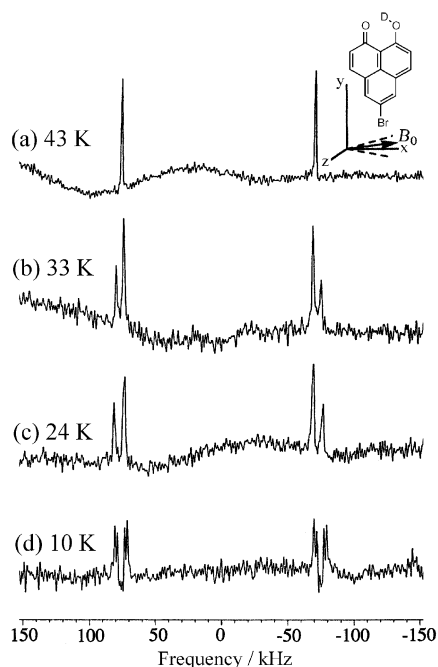
Solid-State ^{2}H NMR Study of Phase Transitions

J. Phys. Chem. B, Vol. 107, No. 44, 2003 **12317**

Figure 5. ^{2}H NMR spectra of a single crystal of 5-bromo-9-deuterioxyphenalen-1-one (**2**-*d*) recorded at various temperatures. The inset shows the direction of the magnetic field B_0 with respect to the molecular orientation in the crystal; the *x*−*y* plane denotes the molecular plane, where the molecule's long axis points to the *y*-axis.

hydroxyphenalen-1-one. Figure 4b shows the powder spectrum of **1**-CD$_3$ recorded at 10 K, which displays a typical Pake doublet, characterized by e^2qQ/h = 52 kHz and η = 0. The e^2qQ/h value is ca. one-third of that of a static methyl group, indicating that the methyl group undergoes fast rotation or reorientation. The line shape was temperature independent in the temperature range of 100−4 K, which means that the methyl group is rotating very rapidly probably by the tunneling mechanism,[39,40] being independent of the phase transition. Thus, it was demonstrated that the phase transition of **1** was an order−disorder transition and was not being related to the motion of the methyl group.[41] However, the substituents play a crucial role on the contrasting phase behaviors in **1**-*h* and **2**-*h*. In contrast to the spherical bromo substituent, the methyl group is symmetry-breaking with respect to the molecular plane. This effect reduces the tunneling frequency in **1**-*h*[42] and leads to the appearance of the ordering phase transition.[11] Although the symmetry-breaking effect is known to be slight in the gas phase,[14] it may become significant under unsymmetrical crystal environments.

Phase Transitions in 5-Bromo-9-deuterioxyphenalen-1-one (2-d). B-1. Order−Disorder Dynamics of Deuterons. The crystal of **2**-*d* exhibited successive phase transitions at T_I = 34 K and T_C = 22 K, whereas **2**-*h* showed no phase transitions. To investigate the nature of the deuterium-induced phenomena, we measured the ^{2}H NMR spectra of single crystals of **2**-*d*. The temperature dependence of the spectra is shown in Figure 5. In the room-temperature phase, a pair of resonance lines was observed. With lowering temperature, each line split into doublets below T_I = 34 K, and the splitting widths increased with decreasing temperature.[43] Thus, it was concluded that the phase transition at T_I was associated with the antiferroelectric ordering of the deuterons, as in the case of **1**-*d*. The result is consistent with the interpretation obtained from calorimetric studies, and the observed phenomenon reasonably accounts for the entropy change associated with the phase transitions.[20]
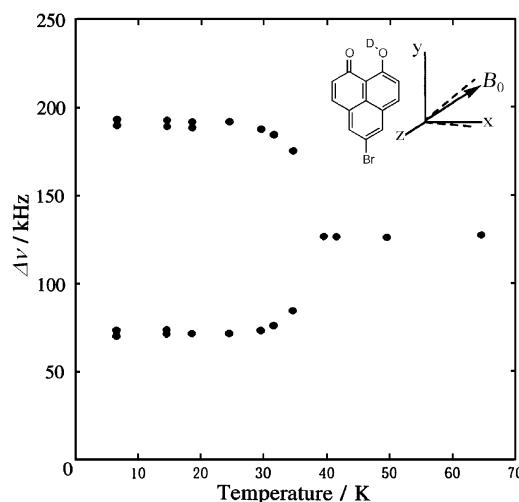

Figure 6. Temperature dependence of the quadrupole splitting of a single crystal of 5-bromo-9-deuterioxyphenalen-1-one (**2**-*d*). The direction of B_0 with respect to the molecular orientation is shown in the inset.

Figure 6 shows the temperature dependence of the quadrupole splitting measured for a different orientation of the sample. The angles between B_0 and the transverse direction with reference to the molecule's long axis (angle θ in Figure 1) were ca. 5° and ca. 35°, for the orientations in Figures 5 and 6, respectively, and thus the splitting of the signals associated with the ordering process is larger in the latter because of the closer direction of B_0 to the O−D vector of the tautomer. The temperature dependence of the splitting indicates that the origin of the phase transition at T_I is attributable to the dipole−dipole interaction, in agreement with the second-order nature of the phase transition.

We also carried out powder ^{2}H NMR experiments on **2**-*d*, although spectra of a sufficient S/N ratio were difficult to obtain because of the extremely long relaxation time. The powder ^{2}H spectrum of **2**-*d* displays essentially the same pattern as that of **1**-*d*, and it may be reasonable to assume that the EFG tensors of **2**-*d* are almost identical to those of **1**-*d*. The principal values of EFG tensors of **1**-*d* as estimated above can explain the angular dependence of the quadrupole splittings of **2**-*d* in Figures 5 and 6 well, assuming that the *y*-axis of the principal axes is normal to the molecular plane and that the *z*-axis is parallel to the O−D bond. The directions of the principal axes are typical for an asymmetrically hydrogen-bonded system.[34]

B-2. Structure of Low-Temperature Phases. As discussed above, the splitting of the ^{2}H signals in **2**-*d* appearing below T_I originates from the antiferroelectric ordering of tautomerization. With further lowering of temperature below T_I, each signal becomes broadened in the temperature range of T_I–T_C (Figure 5b, c), and they further split into four doublets in the commensurate phase, below T_C = 22 K (Figure 5d). The spectrum below T_C indicates that there are four molecules in the unit cell with different O−D vectors with respect to the direction of B_0. This is consistent with the space group $P2_1/c$ (Z = 8) of the low-temperature phase determined by Noda et al.[21] The space group is centrosymmetric, and thus there are four independent molecules with respect to inversion symmetry. The tilt of the O−D vector is presumably derived from a rotational displacement of the molecule rather than from an out-of-plane displacement of only the deuteron atom from the molecular plane because the latter is energetically highly unfavorable. Thus, when the antiferroelectric nature is taken into account, the four independent molecules are considered to be composed of two

12318 *J. Phys. Chem. B, Vol. 107, No. 44, 2003*

Mochida et al.

pairs of antiferroelectrically coupled molecules with slightly different orientations. The widths of the fine splitting appearing below T_C are ca. 3.5 kHz for both orientations in Figures 5 and 6. If we assume that the EFG values of **2**-*d* are the same as those determined for **1**-*d* and that the C−O−D angle is 110°, the splitting widths can be explained by the rotation of the molecular planes by ca. ±1.5 degrees about the molecular long axis.

On the basis of these results, it may be reasonable to assume that the incommensurate wave appearing between T_I and T_C is derived from incommensurate rotational displacements of the molecules. Indeed, the line broadening with decreasing temperature in this phase is consistent with the incommensurate feature,[44] where the molecular tilt or rotational displacement becomes larger with decreasing temperature. The fine splitting of the resonance signals below T_C can be interpreted in terms of the lock-in phase transition, which accompanies the fixation of the molecular tilt at a particular commensurate angle. However, no information can be obtained from the present data on possible translational displacements, which may occur in addition to the rotational displacements. On the other hand, such a molecular tilt may also occur in **1**-*d* below T_C, considering the similarities of the low-temperature structures (space group $P2_1/c$),[24] although no fine splitting was observed in the spectra of **1**-*d* as in **2**-*d* (Figure 3). Such a splitting, if any, may be hidden by the broadness of the signals, probably because of the poorer quality of the crystal.

The above experiments demonstrate that the ordering of tautomerization as well as incommensurate rotational displacements of the molecules occur below T_I. In most incommensurate materials, such as thiourea, the molecular displacement causes both the dielectric polarity and incommensurate modulation.[45] In contrast, the present materials provide an interesting example in which the origins of the incommensurate modulation and dielectric polarization are different. However, the deuteron ordering and the incommensurate modulation are by no means independent; the incommensurate molecular orientation should be correlated with the dielectric polarization associated with deuteron ordering, because incommensurate modulation results from the balance among various intermolecular dipole−dipole interactions.

4. Conclusion

The order−disorder characters of the phase transitions in **1**-*d* and **2**-*d* have been established by the present single-crystal ^{2}H NMR experiments. Thus, the phase transitions in these materials are rather classical phenomena based on dipole−dipole interactions. Conversely, the absence of ordering phenomena in the hydrogen compound **2**-*h* is considered to be unusual. The crystals of **2**-*h* have a disordered (or delocalized) state of the proton that forms the zero-entropy ground state. The paraelectricity down to cryogenic temperatures is derived from the quantum nature of the protons. Deuteration of the hydrogen bond decreases the tunneling splitting, or the delocalization energy, which stabilizes the ground state through the classical ordering process, that is, the order−disorder phase transition at T_I. Being consistent with these interpretations, theoretical studies of 0-dimensional hydrogen-bonded crystals including **2**-*h*/**2**-*d* based on a quantum mechanical model have successfully accounted for the isotope effect and the appearance of incommensurate phases.[6,46] On the other hand, the appearance of the ordering phase transition in **1**-*h* is ascribable to the reduction of the tunneling frequency because of symmetry-breaking caused by the methyl group.[11] Therefore, the introduction of the methyl group causes a similar effect as deuterium substitution of the hydrogen bond on the proton tunneling state. The origin of the incommensurate wave in **2**-*d* is ascribable to rotational molecular displacements, which are only indirectly related to deuteron dynamics. In summary, the molecular crystals of 9-hydroxyphenalenones provide an interesting system for investigating proton−deuteron dynamics and its consequences on phase transitions in hydrogen-bonded materials.

References and Notes

(1) For example, Matsuo, T.; Inaba, A.; Yamamuro O.; Onoda-Yamamuro, N. *J. Phys.: Condens. Matter* **2000**, *12*, 8595, and references therein.

(2) Blinc, R. *J. Phys. Chem. Solids* **1960**, *13*, 204.

(3) Blinc, R.; Pirc, R. *Theoretical Treatments of Hydrogen Bonding*; Hadzi, D., Ed.; John Wiley and Sons: Chichester, U.K., 1997; Chapter 11.

(4) de Gennes, P. G. *Solid State Commun*. **1963**, *1*, 132.

(5) Tokunaga, M.; Matsubara, T. *Prog. Theor. Phys.* **1966**, *35*, 581.

(6) Totsuji, C.; Matsubara, T. *Solid State Commun*. **1994**, *89*, 677.

(7) Moritomo, Y.; Tokura, Y.; Nagaosa, N.; Suzuki, T.; Kumagai, K. *Low Temp. Phys.* **1995**, *99*, 55.

(8) Yamada, Y. *J. Korean Phys. Soc.* **1996**, *29*, S393.

(9) Totsuji, C.; Matsubara, T. *Solid State Commun*. **1998**, *107*, 741.

(10) Moritomo, Y.; Tokura, Y.; Nagaosa, N.; Suzuki T.; Kumagai, K. *Phys. Rev. Lett.* **1993**, *71*, 2833.

(11) Mochida, T.; Izuoka, A.; Sugawara, T.; Moritomo, Y.; Tokura, Y. *J. Chem. Phys.* **1994**, *101*, 7971.

(12) Bondybey, V. E.; Haddon R. C.; English, J. H. *J. Chem. Phys*. **1984**, *80*, 5432.

(13) Nishi, K.; Sekiya, H.; Hamabe, H.; Nishimura, Y.; Mochida T.; Sugawara, T. *Chem. Phys. Lett.* **1996**, *257*, 499.

(14) Nishi, K.; Sekiya, H.; Mochida, T.; Sugawara T.; Nishimura, Y. *J. Chem. Phys.* **2000**, *112*, 5002.

(15) Ichikawa, M.; Motida, K.; Yamada, N. *Phys. Rev.* **1987**, *B36*, 874.

(16) Ichikawa, M.; Gustafsson, T.; Olovsson, I.; Tsuchida, T. *J. Phys. Chem. Solids* **1999**, *60*, 1875.

(17) Noda, Y.; Tamura, I.; Hayashide, T.; Mochida T.; Sugawara, T. *J. Korean Phys. Soc.* **1996**, *29*, S436.

(18) Takasu, I.; Sugawara, T. *Adv. Phys. Org. Chem.* **1999**, *32*, 219.

(19) Moritomo, Y.; Tokura, Y.; Mochida, T.; Izuoka, A.; Sugawara, T. *J. Phys. Soc. Jpn.* **1995**, *64*, 1892.

(20) Matsuo, T.; Kohno, K.; Inaba, A.; Mochida, T.; Izuoka, A.; Sugawara, T. *J. Chem. Phys.* **1998**, *108*, 9809.

(21) Tamura, I.; Noda, Y.; Kuroiwa, Y.; Mochida, T.; Sugawara, T. *J. Phys. Condens. Matter* **2000**, *12*, 8345.

(22) Noda, Y.; Tamura, I.; Kuroiwa, Y.; Mochida, T.; Sugawara, T. *J. Phys. Soc. Jpn.* **1994**, *63*, 4286.

(23) Noda, Y.; Hayashide, T.; Tamura, I.; Mochida, T.; Sugawara, T. *J. Korean Phys. Soc.* **1998**, *32*, S8.

(24) Kiyanagi, R.; Kimura, H.; Watanabe, M.; Noda, Y.; Kojima, A.; Hayashide, T.; Mochida, T.; Sugawara, T.; Kumazawa, S. *J. Korean Phys. Soc.* **2003**, *42*, S1279.

(25) Matsuo, T. *Pure Appl. Chem.* **2003**, *75*, 913.

(26) Matsuo, T.; Kohno, K.; Ohama, M.; Mochida, T.; Izuoka, A.; Sugawara, T. *Europhys. Lett.* **1999**, *47*, 36.

(27) Matsuo, T.; Baluja, S.; Koike, Y.; Ohama, M.; Mochida, T.; Izuoka, A.; Sugawara, T. *Chem. Phys. Lett.* **2001**, *342*, 22.

(28) Mochida, T.; Suzuki, S.; Takasu, I.; Sugawara, T. *J. Phys. Chem. Solids* **2003**, *64*, 1257.

(29) Haddon, R. C. *J. Org. Chem.* **1986**, *46*, 4588.

(30) Kumada, M.; Tamao, K.; Sumitani, K. *Org. Synth.* **1988**, *6*, 407.

(31) Bjorkstam, J. L. *Phys. Rev.* **1967**, *153*, 599.

(32) Kasahara, M. *J. Phys. Soc. Jpn.* **1978**, *44*, 537.

(33) Vold R. R. *Nuclear Magnetic Resonance Probes of Molecular Dynamics*; Tycko, R., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1994; Chapter 2.

(34) Brown, T. L.; Butler, L. G.; Curtin, D. Y.; Hiyama, Y.; Paul, I. C.; Wilson, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 1172.

(35) Gall, C. M.; DiVerdi, J. A.; Opella, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5039.

(36) Butler, L. G.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6541.

(37) Jackman, L. M.; Trewella, J. C.; Haddon, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 2519.

Solid-State ^{2}H NMR Study of Phase Transitions

J. Phys. Chem. B, Vol. 107, No. 44, 2003 **12319**

(38) Soda, G.; Chiba, T. *J. Chem. Phys.* **1969**, *50*, 439.

(39) Torchia, D. A.; Szabo, A. *J. Magn. Reson.* **1982**, *49*, 107.

(40) Takeda, S.; Kataoka, H.; Ikeda, S.; Yamaguchi, K. *Physica B* **1996**, *226*, 174.

(41) An indirect effect of the phase transition was observed in the single-crystal ^{2}H NMR spectra of **1**-CD_3. Slight broadening of the peaks appeared below T_C, which is ascribable to the recovery of the nuclear dipolar interactions between the deuterons in CD_3 and the hydroxyl proton, associated with the ordering of the proton.

(42) Busch, J. H.; de la Vega, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 3984.

(43) In Figure 5b and 5c, unequal intensities of the deuterium doublets are seen, but they are not related to the phase transition phenomena. The intensity ratio depended on acquisition numbers and intervals, and the inequality presumably originates from the anisotropy of relaxation time. See Mehring, M. *Principles of High-Resolution NMR in Solids,* 2nd ed.; Spinger-Verlag: New York, 1983; p 276.

(44) Agranovich, V. M.; Blinc, R.; Levanyuk, A. P. *Incommensurate phases in dielectrics l. fundamentals*; North-Holland: Amsterdam, 1986.

(45) Blinc, R.; Levanyuk A. P.; Agranovich, V. M. *Incommensurate phases in dielectrics 2. materials*; North-Holland: Amsterdam, 1986.

(46) Nakanishi, A.; Kato, M. *J. Phys. Soc. Jpn.* **2001**, *70*, 2321.