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Abstract
The isotope effect of hydrogen motion in an organic ferroelectric, phenazine (Phz)–chloranilic acid (H_2ca and D_2ca for normal and deuterated compounds, respectively) co-crystal, was studied by ^{35}Cl nuclear quadrupole resonance (NQR). Besides a ferroelectric transition at $T_c = 253$ K (303 K), a neutral-to-ionic transition was found below 170 K (200 K) for Phz–H_2ca (Phz–D_2ca). ^1H–^{14}N nuclear quadrupole double resonance measurements were also made in order to study the temperature dependent electronic state of Phz–$(H/D)_2ca$. ^{14}N NQR parameters suggested that donor orbital populations of the two nitrogen atoms in a phenazine molecule become nonequivalent (1.78 and 1.97) in the ferroelectric phase, while they are both equal to 1.89 in the paraelectric phase. In the ionic phase of Phz–D_2ca, which was obtained by cooling below 188 K, they became 1.50 and 1.95, suggesting a proton transfer from D_2ca to Phz.

1. Introduction

The microscopic origin of the spontaneous electric polarization for the recently developed hydrogen-bonded ferroelectric, phenazine–chloranilic acid (Phz–H_2ca), involves very interesting aspects of crystal polarization [1–3]. In this compound, the two hydrogen atoms of chloranilic acid (H_2ca) do not hop to the nitrogen of phenazine (Phz), but stay chemically bonded within H_2ca even in the ferroelectric phase. Therefore, the conventional pictures of the hydrogen-bonded ferroelectrics cannot be applied to this system. The observed spontaneous electric polarization of 0.76 $\mu C\,cm^{-2}$ is huge compared with the theoretical

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estimation of $0.10\ \mu\text{C cm}^{-2}$ by the quantum mechanical calculation of dipole moment for isolated molecules [3]. The polarization is explained for the first time by taking into account the hydrogen bond mediated covalency between the acid and base molecules forming a supramolecular chain in the crystal, as well as the molecular distortion in cooperation with the hydrogen-bond-distance change [3]. This process is related to the calculation of the Berry phase of Bloch wavefunctions [4, 5]. That is, the displacement induced electric charge transfer or the electric polarization induced by the hydrogen-bond mediated covalency is important especially in the hydrogen-bonded ferroelectrics consisting of electrically neutral molecular components.

For the experimental investigation of hydrogen-bond mediated covalency between Phz and $H_2\text{ca}$, nuclear quadrupole resonance (NQR) spectroscopy is expected to be a very powerful tool, since NQR frequency is very sensitive to charge distribution around the resonant nucleus. We attempt to estimate the displacement induced electric charge transfer between Phz and $H_2\text{ca}$ by NQR. Such experimental efforts will be important to verify the theory of electric polarization of the solid.

Although the Phz–$H_2\text{ca}$ co-crystal is believed to be a displacive-type ferroelectric [1], there is also some indication of hydrogen motion in the crystal. Recently, we have reported temperature dependences of ^{35}Cl NQR spin–lattice relaxation time T_1 of Phz–$H_2\text{ca}$, in which T_1 decreases with decreasing temperature in the ferroelectric phase [6]. This can be explained by a fast motion of a nearby atomic group, which is a cause of electric field gradient (EFG) fluctuation. This motion is very likely to be related to that of hydrogen atoms involved in the hydrogen-bonded chain. In this paper, we report the isotope effect of the atomic motion responsible for the ^{35}Cl NQR relaxation, as well as a neutral-to-ionic phase transition found in the ferroelectric phase. The results of ^{1}H–^{14}N nuclear quadrupole double resonance measurements are also reported, attempting to elucidate the temperature variation of the electronic state of the phenazine–chloranilic acid co-crystal from the base molecular side.

2. Experimental details

2.1. Sample preparation and identification

The Phz–$D_2\text{ca}$ co-crystals were prepared by the diffusion of Phz and $D_2\text{ca}$ in $CH_3\text{OD}$ in an H-shaped glass tube. $D_2\text{ca}$ was obtained by twofold recrystallization of $H_2\text{ca}$ from $CH_3\text{OD}$. The nondeuterated compound is the same sample as used in the previous study [6]. The sample was identified by comparing the observed x-ray powder pattern with the expected one from the crystal data [2]. Elemental analysis was made by the Center for Organic Elemental Microanalysis, Kyoto University. Analysis calculated for $C_{12}H_8N_2 \cdot C_6D_2O_4Cl_2$: C, 55.2; H/D, 3.1; N, 7.2; O, 16.4; Cl, 18.2. Found: C, 55.2; H/D, 3.0; N, 7.1; O, 16.4; Cl, 18.3. The degree of deuteration was determined by the infrared vibrational spectra on the KBr disc [2] to be about 90% for the NQR sample ($T_c = 303$ K).

2.2. ^{35}Cl NQR

A pulsed spectrometer based on the Matec gated amplifier 525 was used. The spin–lattice relaxation time T_1 was determined by the inversion recovery method. The signal intensity was monitored by the echo height. The sample temperature was controlled within ± 0.5 K over the sample volume using an Oxford DTC 2 electronic controller and measured with an accuracy of ± 0.5 K by use of a gold $+ 0.07\%$ iron versus chromel thermocouple.

2.3. ^1H NMR

The pulsed spectrometer consists of a home-made probe, a flow cryostat (CRYO Industries RC152), a superconducting magnet (Cryomagnetics), and a Thamway's spectrometer (PROT3100MR) was used at Larmor frequency of 45.7 MHz. The spin–lattice relaxation time T_1 was determined by use of a comb-τ-90° pulse sequence.

2.4. ^2H NMR

^{2}H NMR spin–lattice relaxation time T_1 was measured in a 4.7 T superconducting magnet (Oxford Instruments) at the Larmor frequency of 30.701 MHz. An Oxford CF1200 helium continuous-flow cryostat with the temperature resolution of 0.1 K was used employing liquid nitrogen instead of liquid helium as a coolant, and T_1 was determined by use of a comb-τ-90° pulse sequence with the 90° pulse length of 7 μs.

2.5. ^1H–^{14}N nuclear quadrupole double resonance

A ^{14}N nucleus has a spin $I = 1$ and hence three nondegenerate nuclear quadrupole energy levels in zero external magnetic field. The three NQR frequencies are given as

$$\nu_+ = \frac{e^2Qq}{4h}(3+\eta) \tag{1}$$

$$\nu_- = \frac{e^2Qq}{4h}(3-\eta) \tag{2}$$

$$\nu_0 = \nu_+ - \nu_- = \frac{e^2Qq}{2h}\eta. \tag{3}$$

Here e^2Qq/h is the quadrupole coupling constant and η is the asymmetry parameter of the EFG tensor.

The ^{14}N NQR frequencies have been measured with a magnetic field cycling ^{1}H–^{14}N nuclear quadrupole double resonance technique [7, 8]. Here the sample was first kept in a magnet with $B_0 \approx 0.8$ T until the equilibrium magnetization of the proton spin system was reached. Then the sample was pneumatically moved into a second magnet with a variable low magnetic field B. After $\tau = 0.5$ s the sample was pneumatically moved back into the first magnet and the proton NMR signal S was measured. The double resonance process consisted of three steps. In the first step we applied during the time τ a series of frequency sweeps of the rf magnetic field covering the frequency range where the two higher ^{14}N NQR frequencies ν_+ and ν_- are expected to be found. A single sweep lasted for 10 ms and the amplitude of the rf magnetic field was approximately 3 mT. The magnetic field cycles were repeated at various values of B. A decrease of the proton NMR signal S at the end of the magnetic field cycle was observed when the resonance condition $\nu_{LH} = \nu_0$ was reached. Here $\nu_{LH} = \gamma_H B/2\pi$ is the proton Larmor frequency and ν_0 is the lowest ^{14}N NQR frequency.

In the second step the proton Larmor frequency was fixed equal to ν_0 and the limits of the frequency sweeps were varied. A train of the frequency sweeps is namely effective only when it covers both ν_+ and ν_-. When it covers only a single NQR frequency it usually produces only a minor change of the proton magnetization. In such a way the ^{14}N NQR frequencies ν_+ and ν_- were determined with a precision of ± 20 kHz.

In the third step we simultaneously applied two rf magnetic fields with the frequencies ν_1 and ν_2 during the time τ. One of the frequencies, say $\nu_1 \approx \nu_+$, was fixed and the scan was performed with the second frequency ν_2. The lowest proton NMR signal S was observed when $\nu_2 = \nu_-$. Then ν_2 was fixed at $\nu_2 = \nu_-$ and the scan was performed with the frequency
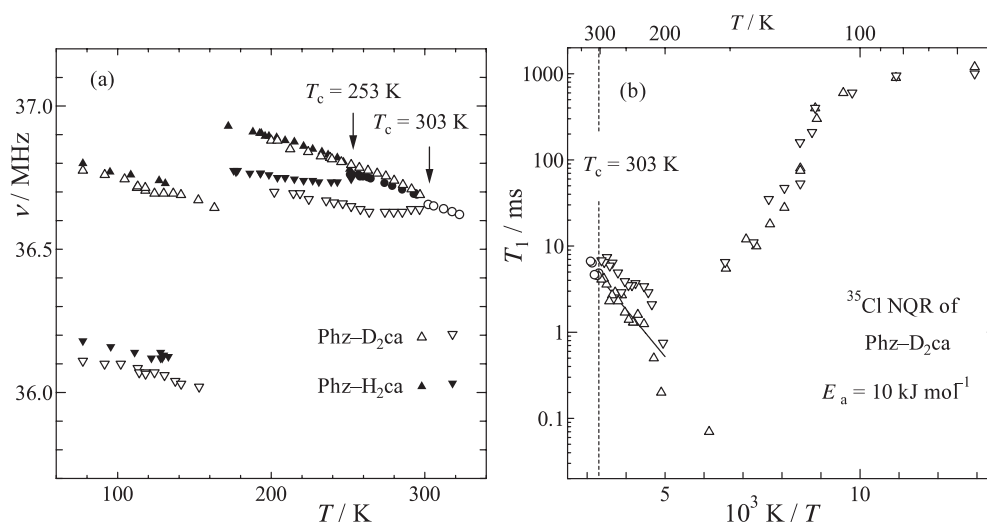
Figure 1. (a) Temperature dependence of ^{35}Cl NQR frequencies of phenazine–chloranilic acid (1:1); normal and deuterated compounds. (b) Temperature dependence of ^{35}Cl NQR spin–lattice relaxation time T_1 of deuterated phenazine–chloranilic acid (1:1). The same symbols are used for the data of the respective NQR lines in (a) and (b).

ν_1. The lowest proton NMR signal was observed at $\nu_1 = \nu_+$. The ^{14}N NQR frequencies were determined with the two-frequency irradiation technique with the precision of ± 5 kHz or better. In addition, the three ^{14}N NQR frequencies corresponding to a given nitrogen position were simultaneously determined by the above technique.

3. Results and discussion

3.1. ^{35}Cl NQR, ^{1}H NMR, and ^{2}H NMR

The temperature dependence of ^{35}Cl NQR frequencies ν of Phz–D$_2$ca is shown in figure 1(a) together with that of Phz–H$_2$ca partly reported in [6]. Below $T_c = 303$ K or 253 K, respectively, for Phz–D$_2$ca and Phz–H$_2$ca, the frequency split into a doublet in accord with the inversion-symmetry breaking at the molecular centre of chloranilic acid (36.650 MHz at 306 K, 36.795 and 36.650 MHz at 252 K for Phz–D$_2$ca, and 36.689 MHz at 295 K, 36.880 and 36.750 MHz at 209 K for Phz–H$_2$ca). Although the NQR signals of Phz–D$_2$ca (Phz–H$_2$ca) once disappeared below ca. 200 K (ca. 170 K) with decreasing temperature, they could be detected again below ca. 160 K (ca. 130 K) in the lower-frequency region as shown in figure 1(a). This result clearly indicates that another phase transition takes place at low temperature and is consistent with the recent heat capacity measurements, which have indicated new phase transitions at 136 and 146 K in Phz–H$_2$ca [9].

Let us denote the phase sequence of Phz–H$_2$ca as follows: phase IV $<$ 136 K $<$ phase III $<$ 146 K $<$ phase II $<$ 253 K $<$ phase I. ^{35}Cl NQR frequencies in phase I and phase II suggest that the chloranilic acid molecule has an almost electrically neutral electronic state in these phases. This is because the NQR frequency at 77 K decreases as 37.145 MHz in H$_2$ca [10], 36.400 MHz in C$_4$H$_4$N$_2$H$^+\cdot$Hca$^-\cdot$C$_4$H$_4$N$_2$ [11], and 35.538 and 34.853 MHz (35.20 MHz on average) in Na$_2^+$ca^{2-} [10] when the negative formal charge of chloranilic acid increases. On the other hand the NQR frequencies in phase IV (36.775 and 36.110 MHz at 77 K
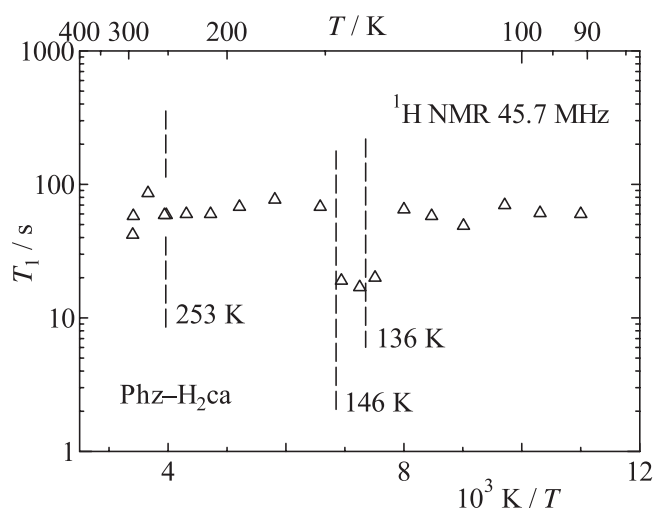
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Figure 2. Temperature dependence of ^{1}H NMR spin–lattice relaxation time T_1 of phenazine–chloranilic acid (1:1). The T_1 of the long component of the magnetization recovery is shown (see the text).

for Phz–D_2ca, and 36.800 and 36.180 MHz at 77 K for Phz–H_2ca) show that the chloranilic acid molecule is in an electronic state of the monovalent anion in the crystal. The occurrence of a neutral-to-ionic transition was also suggested by infrared spectra. The broad band assigned to the O–D stretching vibration (2273 cm^{-1} at 320 K) moved to the lower wavenumber side with decreasing temperature and the bands observed at around 1600 and 1245 cm^{-1}, which can be assigned to –C–C–OD skeleton deformation vibration, showed a splitting below ca. 200 K. In the temperature range corresponding to phase III, no NQR line could be detected. This is probably due to too short spin–lattice relaxation time T_1 as expected from figure 1(b), which shows the temperature dependence of T_1 of Phz–D_2ca.

T_1 decreases with decreasing temperature in phases I and II. No remarkable anomaly was observed at T_c = 303 K. In phase IV, T_1 increased with decreasing temperature. This temperature dependence of T_1 was ascribed to electric field gradient modulation due to motion of a nearby atomic group, probably including hydrogen atoms in the hydrogen-bond network [6]. From the slope of the plot of figure 1(b) in the range $3.3 \leqslant 10^3$ K/$T \leqslant 4.5$, the activation energy of the fast motion was estimated as 10 kJ mol^{-1} for Phz–D_2ca. The 'fast' means that the correlation time of the motion is much shorter than the inverse of the resonance angular frequency of the NQR. This value is considerably larger than the value of 6.6 kJ mol^{-1} [6] derived for the motion of the nondeuterated compound, suggesting a connection of the acid hydrogen with the motion.

We have also measured ^{1}H NMR T_1, attempting to detect the hydrogen motion. The magnetization recovery curve of the proton indicated the existence of two components with long and short T_1. The long component was expected to be assigned to a group of hydrogens which includes the acid hydrogen, since the relative importance of the long component was decreased for Phz–D_2ca as compared with Phz–H_2ca. In figure 2 only the temperature dependence of T_1 of the long component of Phz–H_2ca is shown. The T_1 was almost temperature independent, showing no clear motion of hydrogen atoms. However, in the narrow temperature range which corresponds to phase III, a recognizable shortening of T_1 was observed. This may suggest an increase of amplitude of a lattice vibration which is related to the successive phase transition II–III–IV.
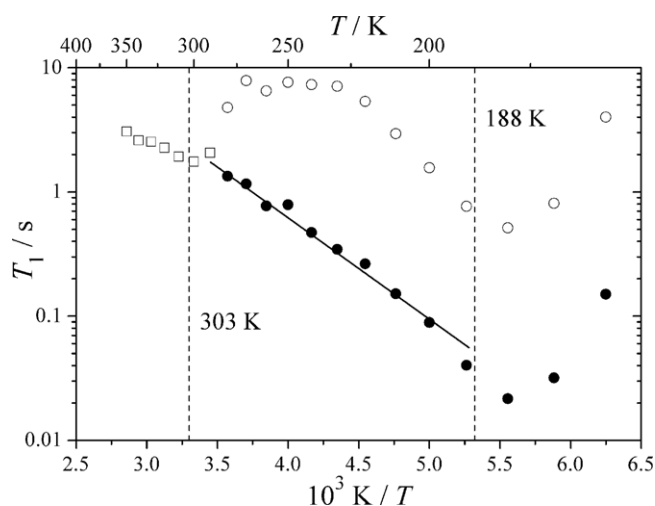
Figure 3. Temperature dependence of ^{2}H NMR spin–lattice relaxation time T_1 of deuterated phenazine–chloranilic acid (1:1). Above the ferroelectric transition at 303 K the magnetization recovery is monoexponential (open squares), whereas below the transition T_1 becomes two component (solid and open circles). The solid line yields the activation energy $E_a = 15$ kJ mol^{-1}.

In contrast to the ^{1}H T_1, which is predominantly determined by the proton–proton magnetic dipole interaction and is thus insensitive to the motion of nearby ions, the ^{2}H T_1 is determined by the electric quadrupole interaction, which is highly sensitive to the motion of nearby ionic electric charges via the fluctuating EFGs. ^{2}H T_1 is expected to be sensitive to the same kind of atomic motion as the ^{35}Cl T_1. Below the ferroelectric transition at 303 K, the ^{2}H magnetization–recovery curves showed the existence of two components with long and short T_1 (where we can adopt the same assignation as for the ^{1}H T_1), whereas above the transition the magnetization decay was monoexponential. The temperature dependence of T_1 is displayed in figure 3. Below the 303 K transition, the T_1 values decrease towards the low-temperature phase transition at 188 K, where a minimum is observed. In the temperature range between the two phase transitions, shortening of T_1 values indicates that ionic fluctuations in the vicinity of the ^{2}H nuclei slow down, but are still in the fast motion regime with respect to the nuclear Larmor frequency. The activation energy was determined on the short T_1 component in the temperature interval $3.5 \leqslant 10^3$ K$/T \leqslant 5$ (thus between 285 and 200 K), where we have $E_a = 15 \pm 2$ kJ mol^{-1}. This is roughly the same as the E_a value estimated from the ^{35}Cl T_1 in this temperature interval. The minimum in T_1 at 10^3 K$/T \approx 5.5$ (thus at $T \approx 182$ K) allows us to extract the correlation time τ_c from the condition $\omega\tau_c = 1$, wherefrom we get τ_c (182 K) $= 5 \times 10^{-9}$ s, and, adopting the Arrhenius form $\tau_c = \tau_0 \exp(E_a/k_B T)$, the prefactor $\tau_0 = 2.5 \times 10^{-13}$ s. The ionic motion that determines the ^{2}H T_1 temperature dependence below the ferroelectric phase transition at 303 K is thus thermally activated and slows down continuously.

3.2. ^{1}H–^{14}N nuclear quadrupole double resonance

3.2.1. Nondeuterated compound. In the nondeuterated compound the measurements were performed between room temperature and 173 K. The temperature dependences of the ^{14}N NQR frequencies ν_+ and ν_-, quadrupole coupling constant e^2Qq/h and asymmetry parameter η are shown in figures 4(a), 5(a), and 6(a), respectively. At room temperature we observe three ^{14}N NQR frequencies corresponding to a single nitrogen position. Thus both nitrogen
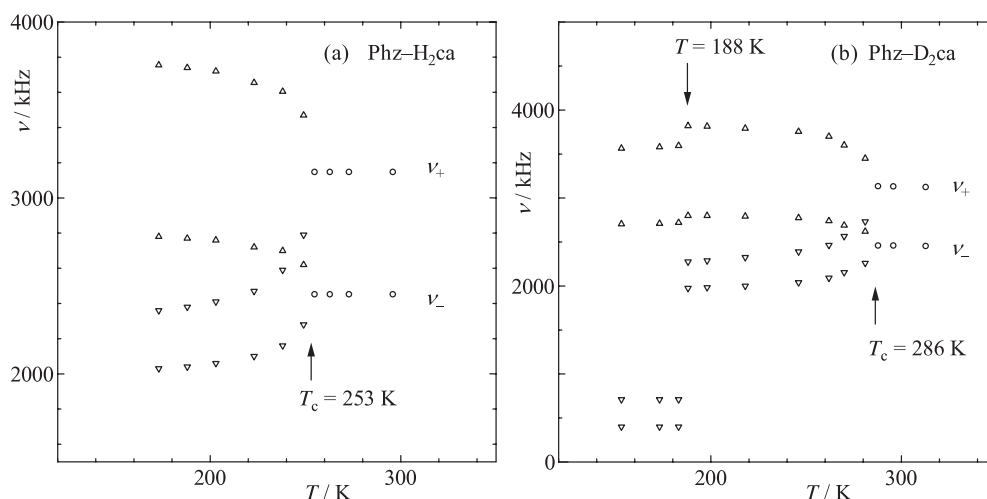
Figure 4. (a) Temperature dependence of ^{14}N NQR frequencies ν_+ and ν_- in phenazine–chloranilic acid (1:1). (b) Temperature dependence of ^{14}N NQR frequencies ν_+ and ν_- in deuterated phenazine–chloranilic acid (1:1). Frequencies assigned to crystallographically equivalent nitrogen atoms are shown by the same symbol.
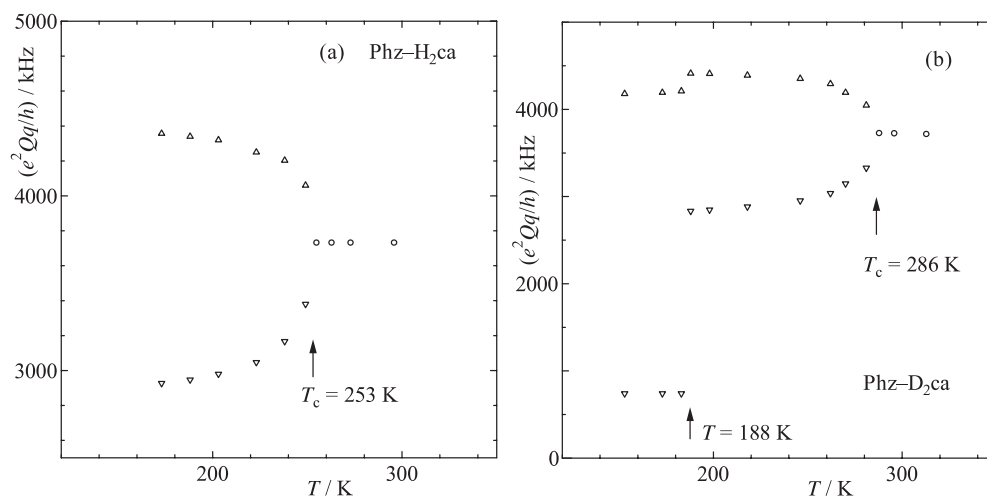

Figure 5. (a) Temperature dependence of ^{14}N quadrupole coupling constant e^2Qq/h in phenazine–chloranilic acid (1:1). (b) Temperature dependence of ^{14}N quadrupole coupling constant e^2Qq/h in deuterated phenazine–chloranilic acid (1:1).

positions in a phenazine molecule are equivalent. The quadrupole coupling constant $e^2Qq/h = 3730$ kHz and the asymmetry parameter $\eta = 0.373$. This may be compared to the ^{14}N NQR data for phenazine [12], where $e^2Qq/h = 4572$ kHz and $\eta = 0.443$ (in table 1 of [12] the data of phenazine and *s*-triazine seem to be exchanged by mistake). The presence of the O–H $\cdots$ N hydrogen bonds decreases the quadrupole coupling constant. On decreasing temperature in the paraelectric phase both e^2Qq/h and η remain constant within the experimental resolution. Below $T_c = 253$ K we observe two sets of three ^{14}N NQR frequencies, corresponding to two nonequivalent nitrogen positions. At one nitrogen position the quadrupole coupling constant
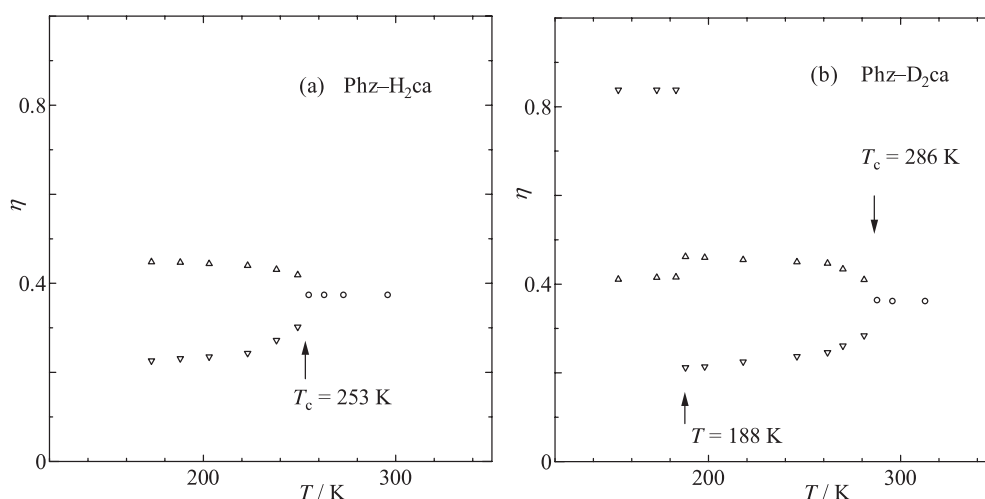
Figure 6. (a) Temperature dependence of ^{14}N asymmetry parameter η in phenazine–chloranilic acid (1:1). (b) Temperature dependence of ^{14}N asymmetry parameter η in deuterated phenazine–chloranilic acid (1:1).

e^2Qq/h increases, whereas at the other nitrogen position e^2Qq/h decreases. At 173 K we obtain $e^2Qq/h = 4357$ kHz and $\eta = 0.448$ at one nitrogen position and $e^2Qq/h = 2927$ kHz and $\eta = 0.226$ at the other nitrogen position. An increase of e^2Qq/h may be associated with the weakening of the $O–H\cdots N$ hydrogen bond, whereas in the case of a stronger $O–H\cdots N$ hydrogen bond the quadrupole coupling constant is expected to decrease.

3.2.2. Deuterated compound. In the deuterated compound the NQR frequencies have been measured between 313 and 153 K. The temperature dependences of the ^{14}N NQR frequencies ν_+ and ν_-, quadrupole coupling constant e^2Qq/h and asymmetry parameter η are shown in figures 4(b), 5(b), and 6(b), respectively. At room temperature we observe a single nitrogen position with the ^{14}N quadrupole coupling constant $e^2Qq/h = 3721$ kHz and the asymmetry parameter $\eta = 0.361$. These results are close to the ones observed in the nondeuterated compound in the paraelectric phase. On decreasing temperature e^2Qq/h slightly increases and at approximately 286 K the sample undergoes the phase transition into the ferroelectric phase. The phase transition temperature in an 89% deuterated compound is reported as being $T_c = 304$ K [2]. The lower phase transition temperature in the present compound is the consequence of partial deuteration. Assuming a linear relationship between the phase transition temperature and the degree of deuteration, we calculate the degree of deuteration as being approximately 60%. In the ferroelectric phase the ^{14}N NQR spectra closely resemble the ones observed in the nondeuterated compound. At 188 K we observed two nitrogen positions, one characterized with $e^2Qq/h = 4413$ kHz and $\eta = 0.462$ and another nitrogen position characterized with $e^2Qq/h = 2833$ kHz and $\eta = 0.212$.

Below 188 K a low-temperature phase transition occurs. In contrast to the ferroelectric phase transition, the low-temperature phase transition seems to be rather slow, which is clearly seen on the proton spin–lattice relaxation in the low magnetic field. When the sample was for example cooled to 178 K it took about one hour until the proton spin–lattice relaxation time T_1 in the magnetic field of 4 mT stabilized. During this time we observed a continuous increase of the proton T_1.
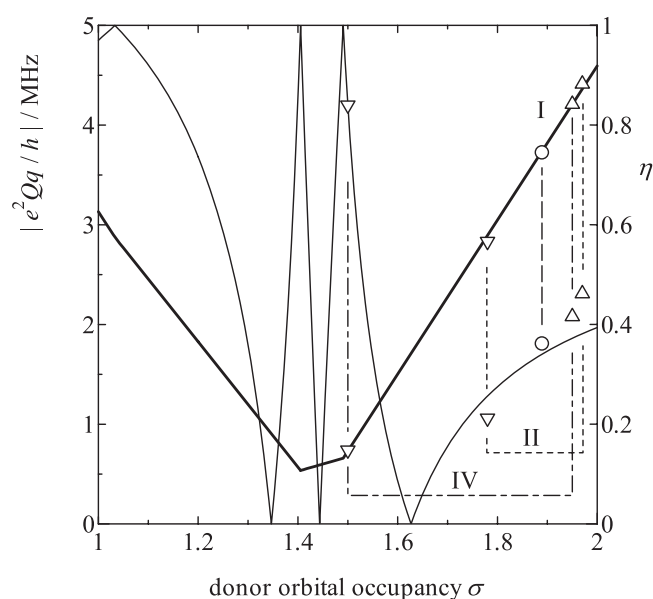
Figure 7. ^{14}N quadrupole coupling constant $|e^2 Qq/h|$ (thick line) and asymmetry parameter η (thin line) as a function of donor orbital occupancy σ, which were derived by Rubenacker and Brown [14] applying an extended Townes–Dailey analysis to a series of coordinated pyridine compounds. Experimental data of Phz–D$_2$ca in phases I, II, and IV are shown by the same symbols as used in figures 5(b) and 6(b). σ can be estimated from the abscissa where the experimental data fit to the calculated curves.

At 183 K we observe a completely different ^{14}N NQR spectrum. There are still two nonequivalent nitrogen positions. At one nitrogen position the ^{14}N NQR parameters, $e^2 Qq/h = 4210$ kHz, $\eta = 0.416$, are close to the ones observed in the ferroelectric phase. At the other nitrogen position the ^{14}N quadrupole coupling constant is rather low, $e^2 Qq/h = 740$ kHz, and the asymmetry parameter is large, $\eta = 0.84$. Such a low quadrupole coupling constant has been observed in pyridinium chloride and some other compounds, where the nitrogen position is protonated. The ^{14}N NQR data agree with the crystallographic data [13], which show that in the low-temperature phase two types of hydrogen bonds occur, N–H $\cdots$ O and O–H $\cdots$ N. This is formed by the donation of one hydrogen atom from chloranilic acid to phenazine.

3.2.3. Nitrogen donor orbital population. Below the ferroelectric transition temperature T_c, the two nitrogen atoms in a phenazine molecule become crystallographically nonequivalent. Let us evaluate the change of electronic state of the nitrogen atom from the ^{14}N NQR data. According to the Townes–Dailey type analysis of electron populations of valence atomic orbitals for coordinated pyridine compounds [14], donor orbital occupancy, σ, which represents the population of the nitrogen orbital in the acid–base σ bond to the Lewis acid (chloranilic acid in the present case), could be estimated from $e^2 Qq/h$ values as shown in figure 7. In the paraelectric phase I, the two nitrogen atoms are crystallographically equivalent and have $\sigma = 1.89 \pm 0.01$. In phase II, they become nonequivalent with $\sigma = 1.78 \pm 0.01$ and $\sigma = 1.97 \pm 0.01$. In phase IV, obtained by further decreasing of temperature, $\sigma = 1.50 \pm 0.01$ and $\sigma = 1.95 \pm 0.01$ were obtained. This means a proton transfer from the chloranilic acid to the phenazine molecule.

In phase II, the displacement induced electric charge transfer from one of the nitrogen atoms of Phz to the oxygen atom of H_2ca may be evaluated as about $-0.2e$, where $e = 4.8 \times 10^{-10}$ esu $= 1.6 \times 10^{-19}$ C, while that of the other nitrogen atom of Phz may be negligible. Assuming electric charges of $+0.2e$ and $-0.2e$ on the nitrogen and oxygen atoms, respectively, which are located at a distance of 0.264 nm apart from each other [13], the crystal polarization which results along the crystal b axis can be evaluated as about 1.0 μC cm^{-2} from the crystal structure [13]. This result agrees fairly well with the observed spontaneous polarization of 0.76 μC cm^{-2} and the theoretical value of 0.55 μC cm^{-2} calculated from the Berry phase [3]. For phase IV, a similar calculation with electric charges of $+0.5e$ and $-0.5e$ on the nitrogen and oxygen atoms, respectively, results in the crystal polarization of 2.5 μC cm^{-2}.

4. Conclusion

Phenazine–chloranilic acid (1:1) shows a neutral-to-ionic phase transition associated with a proton transfer from chloranilic acid to phenazine in ferroelectric phase. Electron populations σ of the donor orbitals of the two nitrogen atoms in a phenazine molecule were estimated as $\sigma = 1.89$, $\sigma = 1.78$ and 1.97, and $\sigma = 1.50$ and 1.95, in the paraelectric, ferroelectric neutral, and ionic phases, respectively.

Acknowledgments

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