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## H/D Isotope Effect of $^1\text{H}$ MAS NMR Spectra and $^{79}\text{Br}$ NQR Frequencies in Piperidinium and Pyrrolidinium p-Bromobenzoate

Piperidine and pyrrolidinium molecules form two kinds of O—H—N type hydrogen bonding with a p-bromobenzoic acid in each crystal. These crystals take the same space group of Pbca as piperidinium and pyrrolidinium p-chlrobenzoate (abbreviated to PIC(H) and PYC(H)) crystals[1-3]. Deuterium substitution samples of piperidinium and pyrrolidinium p-chlrobenzoate-d2 (PIC(D) and PYC(D)) have shown anomalous H/D isotope effects: large shifts of  $^{35}\text{Cl}$  NQR frequencies reaching to ca. 290 kHz have been recorded, although Cl atoms makes no hydrogen bond in the crystals. In addition,  $^1\text{H}$  MAS NMR lines have displayed significant changes, while in contrast, little shifts of  $^{13}\text{C}$  CP/MAS NMR signals have been obtained[1,2]. Since it is expected that anomalous H/D isotope effects are also detected in piperidinium and pyrrolidinium p-bromobenzoate,  $^{79}\text{Br}$  NQR and  $^1\text{H}$  MAS spectra measurements were carried out. Piperidinium and pyrrolidinium p-bromobenzoate (PIB(H) and PYB(H)) were prepared by adding piperidinine and pyrrolidine to a hot benzene solution of p-bromobenzoic acid and by evaporating the solvent. The crude specimens obtained were recrystallized from benzene. PIB(D) and PYB(D) were prepared by crystallizing three times from a hot CH<sub>3</sub>OD and recrystallization from dried benzene. Measurements of  $^{79}\text{Br}$  NQR frequency were performed using a handmade super-regenerative spectrometer. Solid-state high-resolution  $^1\text{H}$  MAS NMR experiments were carried out at a Larmor frequency of 600.13 MHz with a Bruker Avance 600 spectrometer. The samples were packed in a ZrO rotor with an outer diameter of 2.5 mm and the spinning rate was kept at 30 kHz through the acquisition of FID. Temperature dependences of  $^{79}\text{Br}$  NQR frequencies obtained for PIB(H) and PIB(D) are shown in Fig. 1. Small H/D isotope shifts of ca. 70 kHz were recorded although large  $^{35}\text{Cl}$  NQR shifts have been detected for PIC[1]. Moreover  $^1\text{H}$  MAS NMR spectra of PIB and PYB showed little changes by deuterium substitution. In order to reveal these differences between PIB, PIC, PYB and PYC, DFT calculations were carried out using the Gaussian 03w computer program. DFT estimation suggests that H/D changing of atomic arrangements contribute to EFG of Br atoms and shielding tensors of H atoms. References[1] R Nakano, H. Honda, T. Kimura, et. al., Hyperfine Interactions, 181, 59-68 (2008).[2] R Nakano, H. Honda, T. Kimura, et. al., Bull. Chem Soc. Jpn., in press (2010).[3] S. Kashino, Y. Sumida, M. Haisa, Acta Cryst., B28, 1374(1972).

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### Summary

Temperature dependences of  $^{79}\text{Br}$  NQR frequencies obtained for PIB(H) and PIB(D) showed small H/D isotope shifts of ca. 70 kHz, although large  $^{35}\text{Cl}$  NQR shifts have been detected for PIC. Moreover  $^1\text{H}$  MAS NMR

spectra of PIB and PYB showed little changes by deuterium substitution. DFT calculations with the Gaussian 03w computer program suggests that H/D changing of atomic arrangements contribute to EFG of Br atoms and shielding tensors of H atoms.

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