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High-Resolution Solid-State Cross-Polarization Magic-Angle Spinning ^{13}C NMR of Metal-Free Phthalocyanines

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Synopsis. The high-resolution solid-state cross-polarization magic-angle spinning ^{13}C NMR spectra of α, β, τ and X-form metal-free phthalocyanines (H_2pc) were investigated. Chemical shifts differed according to crystal forms. As a result of the temperature dependence of chemical shifts, we could observe the change in the spectra because of the inner protons.

Phthalocyanines are a very interesting class of organic compounds owing to their highly functional properties. In particular, metal-free phthlocyanines (H_2pcs) have specific phenomena. The H_2pc molecule has two inner protons; their locations are somewhat controversial. Cross-polarization magic-angle spinning (CP-MAS) ^{13}C nuclear magnetic resonance (NMR) has been developed as an effective method to investigate the state of a solid and its morphology. Thus, many researchers have been investigating the relationship between inner protons and phthalocyanine rings.[1,2] An especially, important theme is whether the two inner protons are directly bonded with a diagonally opposed pair of nitrogens (bonded type) or are shared by four equivalent pyrrole nitrogens (bridged type). The proton dynamics in an α-form H_2pc were observed using a two-dimensional chemical exchange in the solid-state by Meier et al.[1] They demonstrated the utility of two-dimensional exchange spectroscopy, and proposed that the way to obtain kinetic information about this system is through difficult isotope labeling. Toscano studied electrically conductive metallo-macrocyclic assemblies.[2]

This paper describes ^{13}C NMR spectroscopy that can be applied to detect and identify the difference in crystal forms of H_2pc (α, β, X, and τ-forms). Moreover, the ^{13}C NMR spectra change between −100 °C and room temperature; a peak shift, disappearance and reappearance can be found in the exchange reaction of two inner protons between the two tautomeric positions, depending upon the temperature.

Experimental

Samples. The β-H_2pc used in this work was prepared from crude H_2pc by vacuum sublimation in a zone furnace at 470 °C under a pressure of 10^{-5} Torr (1 Torr=133.322 Pa) for 8 h. Acid pasting of this β-H_2pc gave a fine powder of α-H_2pc. The X-H_2pc was prepared as previously described.[3,4] Conversion to the τ-form was achieved by a wet milling method.[5] All samples were purified by a solvent-extraction technique with methyl ethyl ketone and methanol. The individual crystal forms were checked by their powder X-ray diffraction patterns as well as infrared absorption spectra.

Spectroscopy. High-resolution CP-MAS ^{13}C NMR spectra were obtained on a JOEL GSX-270W spectrometer at a frequency of 67.5 MHz with accessories. The techniques of magic-angle spinning, cross-polarization and dipole dephasing delay were employed in order to enhance the single-to-noise ratio as well as the spectral resolution. The resolution was within 5 Hz at a spinning speed of 4.5 kHz within the temperature range used. Admantane was used for measurements of the resolution. The temperature was measured with a thermocouple positioned close to the spinner in the range the −100—25 °C. The repetition time was within 10 seconds. The ^{13}C chemical shifts were determined by using liquid tetramethyl silane (TMS) as an external reference.

Results and Discussion

H_2pc has four representative polymorphic forms: the β-form is thermodynamically stable and the α-form is metastable, while the X- and τ-forms are quite differently packed in the middle energy states between the α- and β- forms. The differences in the crystal forms found by crystallographic, spectroscopic, and photoconducting methods are attributable to a distinct stacking of phthalocyanine molecules and to the state of the inner protons.

Chemical Shifts of H_2pc at Room Temperature. The CP-MAS ^{13}C NMR spectra of H_2pcs measured at room temperature are shown in Fig. 1. The chemical shifts and their assignments are summarized in Table 1. In order to assign the quaternary carbons, the dipole dephasing delay method was used. The assignments followed the described methods by Meier et al.[5]

In the case of α-H_2pc having four equivalent central nitrogens, one resonance line comprises a contribution from four equivalent carbons (Scheme 1), due to a fast hydrogen exchange rate between the inner nitrogens. These broad lines suggest a lower regularity and a wide distribution of the crystalline structure, compar-

Table 1. Chemical Shifts and Assignments of ^{13}C NMR Spectra with Metal-Free Phthalocyanines at Room Temperature (ppm)[a]

α	β	τ	X
	119.6 (4,4′)	118.6 (4′)	118.7 (4′)
122.1 (4,4′)	121.9	122.9 (4)	
	124.5 (3,3′)	125.8 (3′)	126.2 (3,3′,4)
128.2 (3,3′)	126.8	128.9 (3)	
	130.6	131.6 (2′)	131.2 (2′)
132.6 (2,2′)	133.8 (2,2′)	137.2 (2)	137.3 (2)
	136.7		
145.6 (1,1′)	142.8	145.1 (1′)	144.9 (1′)
	146.3 (1,1′)	150.6 (1)	150.4 (1)
	149.8		

a) Numerals in parentheses present the assignment of carbon atoms which exhibit in Scheme 1.

ed with the other three forms. We have observed four broad resonance lines of oxo(phthalocyaninato)titanium (IV) ([TiO(pc)] in CP-MAS ^{13}C spectra.[6] It is known that metallophthalocyanines possess four central nitrogen atoms equivalently bonded to the hydrogen atoms.[7,8] This result may support the fact that four resonance lines appear for α-H_2pc. The β-H_2pc actually has a much more complicated tautomerism, and the molecules tend to be packed as close as their geometry allows. Thus, the β-H_2pc have a number of chemical shifts, possibly due to the diversity of carbon atoms in the molecules. The τ-H_2pc are assigned to the eight well-split carbon atoms. The chemical shifts of the same numerals differ by approximately 5.5 ppm in relation to whether the bridge nitrogens are bonded with the inner hydrogens or not. The resonance lines, which bond with hydrogen-bonded nitrogen, appear in the lower magnetic field. Since two inner protons of τ-H_2pc are directly bonded with a diagonally opposed pair of nitrogens in a molecule, the N–H bonds may further weaken the overlapping of the π-electrons and induce differences in their chemical shifts. Though X-H_2pc has relatively similar shifts compared to the τ-form above 140 ppm, a broad shift can be seen from 120 to 130 ppm. The structures of the crystal packing of τ-H_2pc may be stable, and the distances of each molecule are in suppose to be longer than those of X-H_2pc.

Variation of the Chemical Shifts as a Function of the Temperature. The temperature dependences of the CP-MAS ^{13}C NMR spectra with H_2pcs are given in Fig. 2. These shifts are attributable to a change in the

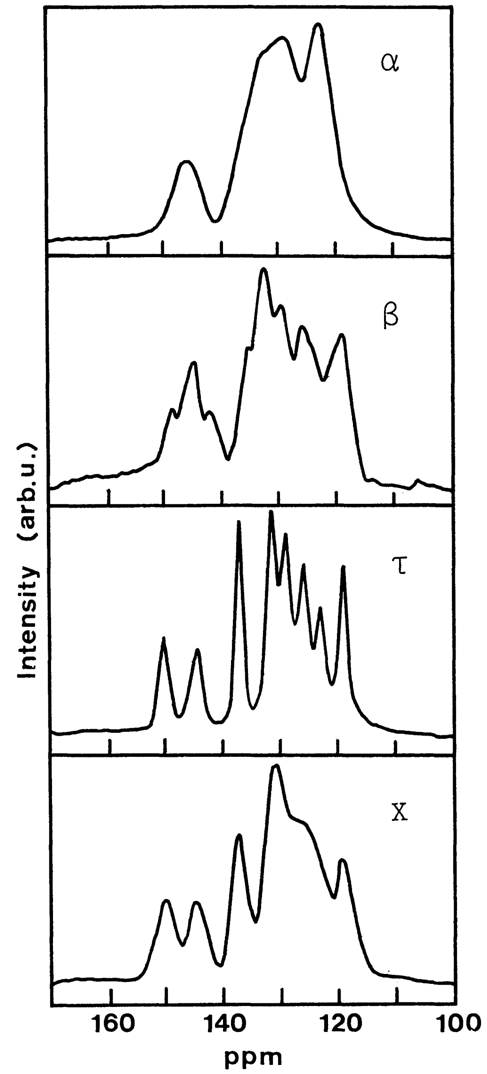


Fig. 1. Solid-state ^{13}C NMR spectra of four kinds of metal-free phthalocyanines using the CP-MAS method at 27 °C.

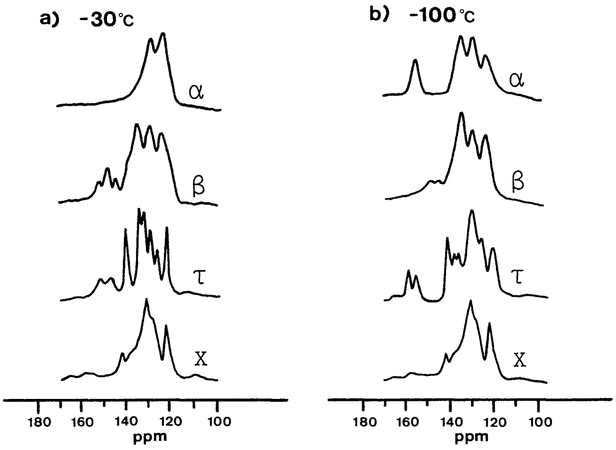
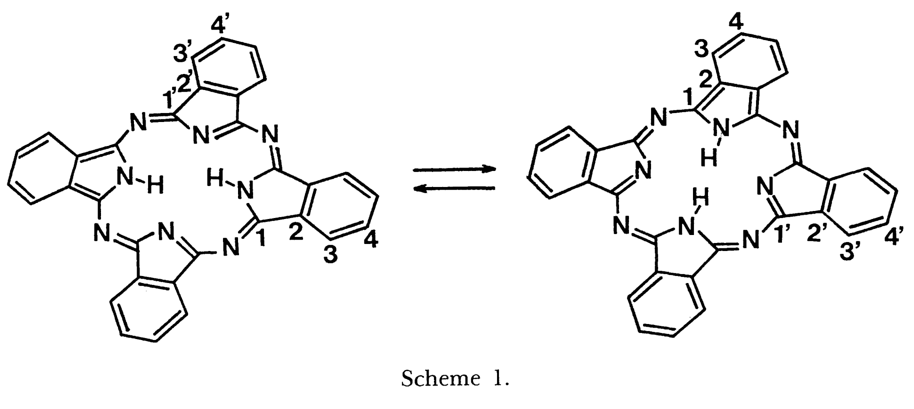


Fig. 2. Solid-state ^{13}C NMR spectra of four kinds of metal-free phthalocyanines using the CP-MAS method. a) −30 °C, b) −100 °C.



Scheme 1.

exchange limits between −30 °C and −100 °C. The chemical shifts from 130 to 150 ppm of α-H_2pc progressively decrease from room temperature to −30 °C, because of a decreasing intermolecular interaction, while the intermolecular interaction increases. Below −30 °C, these shifts increase with decreasing temperature under a smaller magnetic field (151 ppm). The temperature dependence of β-H_2pc is rather low until −100 °C. It can be concluded that a proton exchange reaction with an intramolecular interaction will occur at the same time in β-H_2pc, due to these complicated spectra. The change in the shifts of τ-H_2pc accompanied by temperature differences is remarkable. Two lines assigned to two kinds of carbons, which bond with nitrogens, shift downfield as for α-H_2pc; they disappear at −40 °C, but appear again below −60 °C. The distance of the two shifts varied at −30 °C (6.2 ppm) and −100 °C (3.0 ppm), resulting from the proton exchange velosity. The narrow distance of two equivalent spins suggests a faster exchange regime. Below −60 °C, the intermolecular interaction becomes greater due to the weakened forces of the intermolecular interaction. The influence is larger than other H_2pcs due to the high sensitivity of τ-H_2pc to the nuclear magnetic moments. Moreover, the chemical shifts of carbon in resonating benzene rings are well separated in this temperature region. The chemical shifts of resonating carbon atoms are not well separated compared with those of τ-H_2pc, and the distances of chemical shifts with carbon 2 and 2′ are 5.0 ppm at −30 °C and 4.2 ppm at −100 °C. The energy stage of X-H_2pc may be located near that of τ-H_2pc. However, the lines of the inner carbons cannot separate like those of τ-H_2pc, probably at −100 °C, because of inperfections in crystal packing.

Though the α, X and τ-H_2pcs show a changed limit at a temperature of approximately −30 °C, we can not observe this situation for the β-H_2pc. This result may be because the strong interaction of molecular packing prevents the formation of intramolecular N–H bonding, instead of the intermolecular N–H bonding with neighbor molecules.

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