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POLYMORPHISMS OF 4,5-BIS(4-METHOXYPHENYL)-2-(3-NITROPHENYL)-1H-IMIDAZOLE AS STUDIED BY SOLID STATE NMR

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Abstract

Solid state NMR measurements are carried out for polymorphs and inclusion complexes of 4,5-bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1H-imidazole. Observed ^{13}C and ^{15}N chemical shifts are characteristic of each polymorph A, B, C and D. In addition, ^{15}N chemical shift was a good index for understanding hydrogen bond. VT measurements revealed that B transforms to C between 93 and 113°C. From PSTMAS and ^{1}H solid echo measurements for AcOET inclusion complex, host molecules have almost same structure as B and guest molecules have the highest mobility of all inclusion complexes.

INTRODUCTION

It has already been reported that 4,5-bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1H-imidazole [I] crystallizes in several colored states by changing the crystallization solvents[1]. From X-ray diffraction, DSC and IR spectra, these colored states have been attributed to polymorphic forms of [I]. Recently we found that polymorphs can be obtained from removal of guest molecules from inclusion complex [I] in organic vapor. The polymorphisms are based on differences in the hydrogen bond. It is known that NMR chemical shift is sensitive to the hydrogen bond, especially in the solid state[2]. In this study, solid state NMR measurements are carried out for [I] in order to obtain information about structures, hydrogen bond and molecular mobility of polymorphic crystals of [I] and relation between structures of pure polymorphic crystals and inclusion complexes.

Experimental

NMR measurements

^{13}C NMR spectra were measured by JNM-EX270WB (67.5MHz) spectrometers with a CPMAS accessory at the temperature range from ambient temperature to 113°C. The sample was contained in a cylindrical ceramic rotor. The rotor was spun at about 6 kHz. The contact time was 2 ms and the repetition time was 5 s. Pulse sequences used are cross polarization mangle spinning (CPMAS), pulse saturation (PSTMAS) and dipolar dephasing (MASDL). The spectral widths were 27 kHz. ^{13}C NMR chemical shifts were calibrated indirectly using the adamantane upfield peak (29.5 ppm) relative to tetramethylsilane.

^{15}N NMR spectra were measured by JNM-EX270WB spectrometer (27.4 MHz). Magic angle spinning was carried out at about 3 kHz. The contact time was 5 ms and the repetition time was 20 s. NH_4Cl was used as a reference for ^{15}N NMR chemical shift (the peak of NH_4Cl was set to be 18 ppm).

^1H solid echo measurements were carried out using a JEOL μ25 (25 MHz) NMR spectrometer. The obtained solid echo signals were analyzed by assuming a sum of Weibull functions.

Results and discussion

Structure of polymorphic crystals

In Fig.1 are shown MASDL NMR spectra of polymorphic crystals A, B, C and D. Only CH_3 and quaternary carbons which are not bonded to hydrogens give peaks in MASDL spectrum. Chemical shift data and peak assignments are summarized in Table 1 and numbering of atoms in [I] are shown in Fig.2. From Fig.1 and Table 1, it is clear that MASDL spectra and chemical shifts are characteristic of each polymorphic crystal. As seen from Fig.1, a signal at about 55 ppm clearly splits into two peaks for B and C, but does not so for A and D. These peaks are assigned to OCH_3, C_{30} and C_{22}. Similar trend is observed for C_{26} and C_{18} which are directly bonded to OCH_3. As the chemical shift is determined by relatively local structure, peaks of $C_{30,22}$ and $C_{26,18}$ should not be split if local

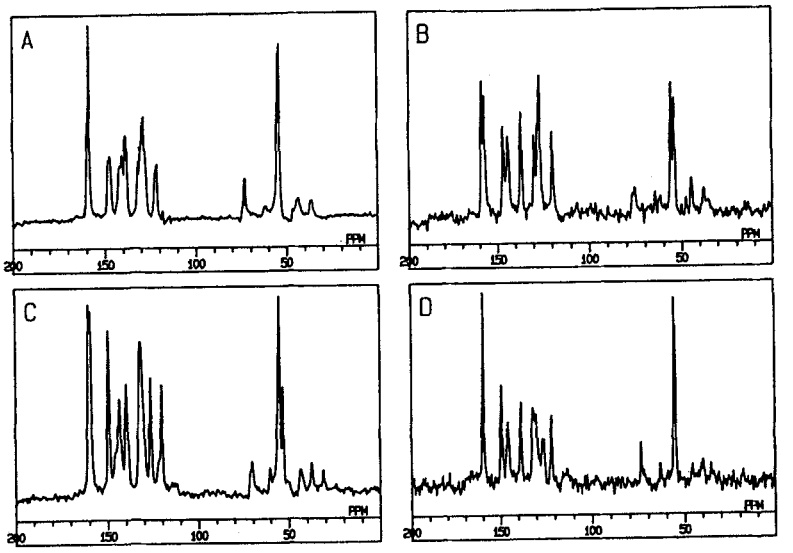

Fig.1 MASDL NMR spectra of polymorphic crystals A, B, C and D.

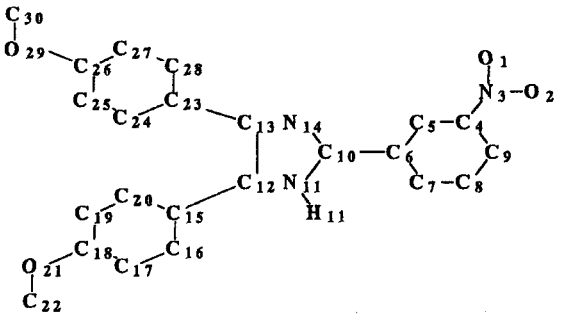

Fig.2 Numbering of [I]

Table 1 Observed ^{13}C chemical shifts of polymorphic crystals and inclusion complexes of [I]

Sample	$C_{26,18}$		C_4		C_6	C_{10}			$C_{12,13}$		$C_{15,23}$	$C_{22,30}$	
A	158.7		148.1	147.2	140.8	138.8	138.5	131.9	130.5	129.0	121.5	54.6	54.0
B	159.8	158.4	147.5		144.8	137.6			130.3	127.5		56.4	54.7
C	160.3	159.2	149.5		143.4	139.7		132.3		126.2	120.0	55.0	53.0
D	159.6		149.3		145.3	138.2		131.8	130.0	126.5	121.3	55.3	54.9
t-BuOH	159.2		148.8		143.3	137.9		129.8	127.2	125.7		55.5	
MeOH	160.6	158.9	146.6		142.9	137.2			128.9	127.0		56.8	53.6
Benzene	159.1		148.4		145.2	138.0			130.4	129.0	121.2	56.8	54.6
CH_2Cl_2	159.9		149.4	147.5	144.1	139.9	138.1		128.9	126.1	121.1	55.8	52.6
AcOET	159.8	158.8	147.3		144.5	137.3			129.8	127.1	120.3	56.6	54.5
Dioxane-H_2O	160.4		149.5		143.9	140.1			133.5	128.1		58.8	56.1

structure around C30,22 and C26,18 are same. In general NMR chemical shift is expressed as follows[3]

$$\sigma = \sigma^{dia} + \sigma^{para} + \sigma' \quad (1)$$

where σ is total chemical shift, σ^{dia} diamagnetic term, σ^{para} paramagnetic term and σ' contribution from neighboring nuclei. For ^{13}C nuclei, σ^{dia} and σ' contributions are small and σ^{para} plays most important role. Since σ^{para} is sensitive to the electronic structure around the nucleus noted, the splitting means there is a nonequivalence of geometrical structure such as conformations between the dihedral angles around C_{21}-C_{18} and C_{29}-C_{26} for B and C.

From Table 1, chemical shifts of most carbons change dependent on the polymorphic crystals, especially, chemical shifts of C_6, C_{12}, and C_{13} considerably vary with the polymorphic crystals. Since these are quaternary carbons which connect imidazole ring with phenyl rings, the considerable chemical shift changes result from differences of dihedral angles around C_6–C_{10}, C_{12}-C_{15} and C_{13}-C_{23}. These dihedral angles are strongly related to the planarity of [I]. Therefore, the dihedral angles which are correlated with conjugation of π electron are dependent on the polymorphic crystals and corresponding chemical shift can be used to identify the polymorphic crystals.

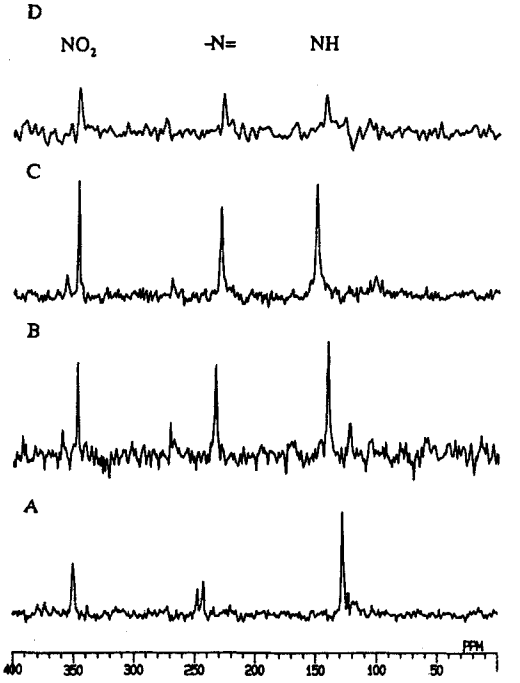

Fig.3 ^{15}N CPMAS spectra of A,B,C and D.

For polymorphic crystal A, peaks between 100 and 150 ppm are more complicated than other polymorphic

crystals. Chemical shifts in this range are attributed to phenyl and imidazole rings. Each peak in this range splits into two peaks for polymorphic crystal A, indicating that two independent molecules are present in an asymmetric unit. This result is in agreement with that of X-ray crystal analyses.

Table 2 ^{15}N chemical shifts of polymorphic crystals [I]

sample	NO_2	-N=	NH
A	341.81	239.07	119.57
		234.07	
B	346.72	232.92	140.18
C	346.72	229.36	150.16
D	345.64	227.21	142.67

In Fig.3 are shown ^{15}N CPMAS NMR spectra of polymorphic crystals A, B, C and D. From reference data, peaks at about 140, 230 and 340 ppm are assigned to $_{NO}$, N_{14} and N_3, respectively. ^{15}N chemical shifts are summarized in Table 2. From Fig.3, it is clear that -N= peak for polymorphic crystal A splits into two peaks, but those for polymorphic crystals B, C and D do not. As discussed in ^{13}C chemical shift, two nonequivalent molecules exist in a unit cell for polymorphic crystal A. The nonequivalence strongly appeared in -N= chemical shift. ^{15}N chemical shifts of N_{11} and N_{14} for polymorphic crystal A appear at upfield by about 20-30 ppm and downfield by about 7-12 ppm , respectively, compared with those for B, C and D. It is known that upfield shift of NH chemical shift and downfield shift of -N= chemical shift arise from weak hydrogen bond[4]. From X-ray crystal analyses, it is reported that oxygen atom of the nitro group in one moelcule bonds to the H-N of imidazole ring in the other molecule and N—O distance of hydrogen bond is 3.199 Å for polymorphic crystal A. On the other hand, the polymorphic crystal B has another type of hydrogen bond, N-H—N=. The distance N—N is 2.89 Å. Only from the standpoint of hydrogen bond length, the hydrogen bond in polymorphic crystal A is weaker than that in polymorphic crystal B, which is in agreement with ^{15}N chemical shift behavior.

Although it has not been reported about ^{15}N chemical shift behavior of hydrogen bond for nitro group, it is clear from Table 2 that an effect of hydrogen bond appears in ^{15}N chemical

shift of nitro group. ^{15}N chemical shift of nitro group for A appears at upper field by about 5 ppm than those for polymorphic crystals B, C and D. As there is a hydrogen bond between nitro group and NH, it is found that strong hydrogen bond of ntiro group gives upfield shift. Thus, from the above results it can be concluded that ^{13}C and ^{15}N chemical shifts are good indeces for identification of polymorphic crystals A, B, C and D.

Structural change by temperature

Variable temperature solid state measurements were carried out for polymorphic crystals B and C. Temperature dependence of chemical shift is shown in Figs.4 and 5 for peaks which are characteristic of polymorphic crystals. As seen from Fig.4, chemical shift of C_6 for polymorphic crystal C moves to down field from 143.4 to 144.7 ppm. Chemical shift of C6 after cooled from 113 to room temperature (closed circle) is 143.4 ppm, which is same as the chemical shift before raising temperature. Peaks of C_{30} and C_{22} split into two peaks at room temperature(Fig.5). Up to 93°C, these peaks move to downfield slightly. At 113°C, the higher field peak decreased in its strength. Cooling from 113°C, peaks split into two again and chemical shifts (closed circle) are same as those before heating. In other words, structure of polymorphic crystal C does not change by heating to 113°C.

For polymorphic crystal B, from Fig.3, chemical shift of C_6 is independent of temperature up to 93°. At 113°C, chemical shift of C_6 for B moves upfield by about 2.4 ppm. After cooled form 113°C, chemical shift of C_6 for polymorphic crystal B (closed triangle) is same as that for polymorphic crystal C. Similar trend was observed for C_{30} and C_{22} chemical shifts from Fig.5. From these results, polymorphic crystal B transforms to polymorphic crystal C between 93 and 113°C, which is in agreement with DSC results.

Inclusion complexes

In Table 2, chemical shift values of inclusion complexes are shown together with pure polymorphic crystals. ^{13}C chemical shifts of AcOET inclusion complex are very close to those of polymorphic crystal B. Polymorphic crystal B can be obtained by heating AcOET inclusion complex. Therefore, the structure of AcOET inclusion complex is similar to that

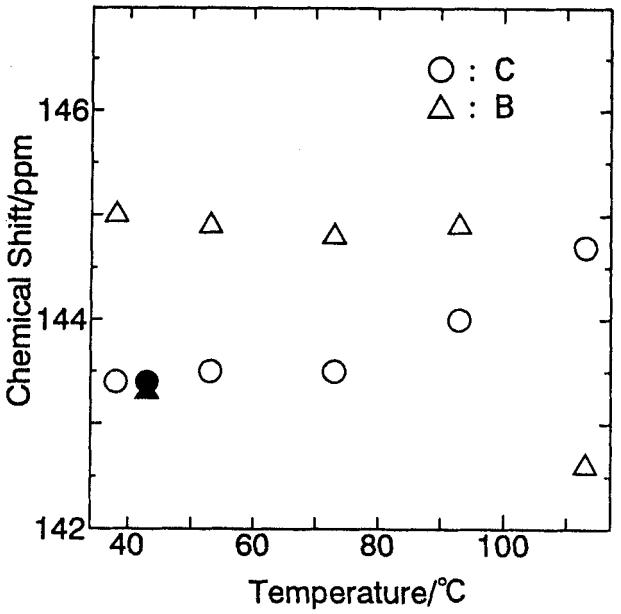

Fig.4 Temperature dependence of observed ^{13}C chemical shifts of C_6 for polymorphic crystal B and C.

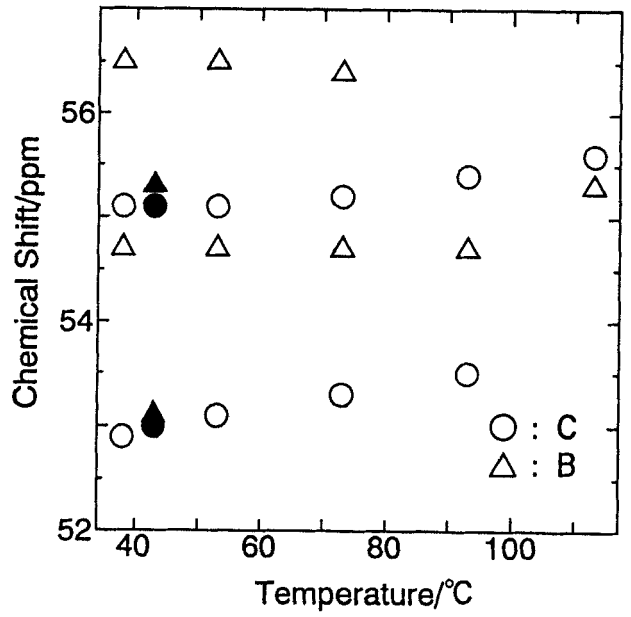

Fig.5 Temperature dependence of observed chemical shifts of C_{30} and C_{22} for polymorphic crystals B and C.

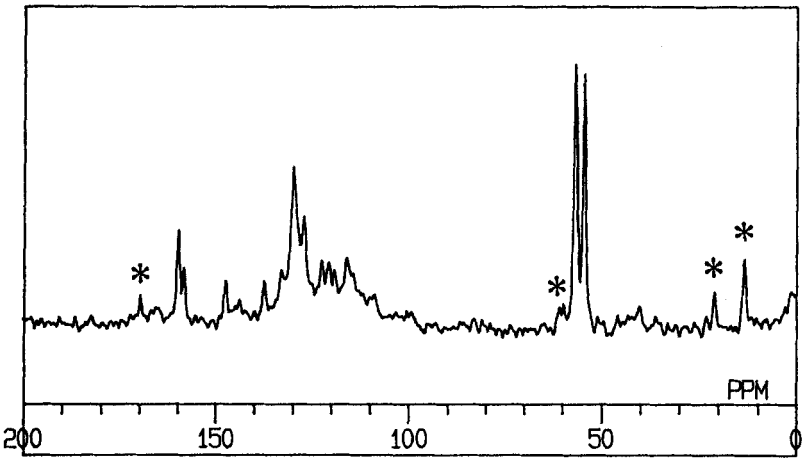

Fig.6 PSTMAS spectrum of AcOET inclusion complex.
*:Peaks of guest molecules.

of B. By heating AcOET inclusion complex, only AcOET molecules are removed from crystal without changing [I]'s position. For other inclusion complexes, chemical shifts do not necessary coincide with those of polymorphic crystals A, B, C and D. As only B can be obtained by heating inclusion complex, a structural change occurs when other inclusion complexes transform to pure polymorphic crystals.

In Fig.6 is shown the PSTMAS NMR spectrum of AcOET inclusion complex. In the PSTMAS spectrum, ^{13}C signals of relatively mobile carbon atoms are enhanced by the nuclear overhauser effect (NOE) with ^{1}H. In Fig.6, peaks of guest molecules are enhanced. In addition, peaks of host molecule appear clearly. For other inclusion complexes, peaks of host molecules hardly appear. From this spectrum, there exist mobile part in the inclusion complex AcOET. In Table 3 are listed T_2s of ^{1}H obtained by solid echo measurements for polymorphic crystals and inclusion complexes.

Table 3 T_2 of polymorphic crystals and inclusion complexes of [I]

Sample	T_2/μsec	
A	21.5	
B	22.2	
C	23.4	
D	26.9	
t-BuOH	23.4	84.9
Benzene	24.1	101.0
CH_2Cl_2	22.9	131.0
AcOET	22.9	167.0

It is known that an increase of T_2 means increased molecular mobility. For polymorphic crystals A, B, C and D, T_2s range from 21.5 to 26.9 μsec. This means [I]s of A, B, C and D are rigid. For inclusion complexes, two components were observed for T_2. Short and long components of T_2 correspond to T_2 of host and guest molecules, respectively. Short components range from 19.3 to 24.1μsec and are close to those for polymorphic crystal A, B, C and D. Therefore, mobility of [I] was not appreciably changed even in inclusion complexes. Long component of AcOET complex is 167.0 μsec and longest T_2 of all inclusion complexes. AcOET molecules in the inclusion complex have relatively high molecular mobility. This high mobility caused strong peaks of [I] in PSTMAS spectrum.

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