CHEMISTRY LETTERS, pp. 211-214, 1987.

Conformational Effects in High Resolution Solid State CP/MAS ^{13}C NMR Spectra of Thermotropic Ester Compound, 4'-Cyanophenyl-4-n-pentoxybenzoate

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The crystalline solid state structure of thermotropic ester compound, 4'-cyanophenyl-4-n-pentoxybenzoate (CPPOB) was examined by high resolution solid state CP/MAS (Cross Polarization /Magic Angle Spinning) ^{13}C NMR. Conformational effects were revealed by line splittings in the solid state spectra.

In recent years, high resolution solid state CP/MAS (Cross Polarization/ Magic Angle Spinning) ^{13}C NMR has been a strong tool for investigating organic molecules in the solid state.[1)] Conformational information can be obtained by CP/MAS ^{13}C NMR.[2)]

Ester low molecular compounds and thermotropic polyesters have attracted much attention because of their high potentials as functional materials. It is important to investigate solid state structures of these compounds. However, to our knowledge, no systematic work was reported on conformation of the aromatic ester compounds.

In the present work, the crystalline solid state structure of thermotropic ester compound, 4'-cyanophenyl-4-n-pentoxybenzoate (CPPOB)[3,4)] was examined by 67.8 MHz solid state CP/MAS ^{13}C NMR. The solution spectrum was also obtained and it was useful to interpret the spectra in the solid state. CPPOB was prepared from 4-n-pentoxybenzoylchloride and 4-cyanophenol. The sample recrystallized from ethanol was used for NMR measurements. CPPOB showed monotropic behaviour and nematic phase.[5)] X-Ray crystal structure study of CPPOB was performed by Baumeister et al.[6)] The conformation of the crystalline solid state is shown in Fig. 1. The molecule exhibits an exact C_s symmetry,[4)] whereas analogous series compound exhibits only a C_1 symmetry.[6,7] Therefore highly resolved resonances of individual carbons were expected for this compound.

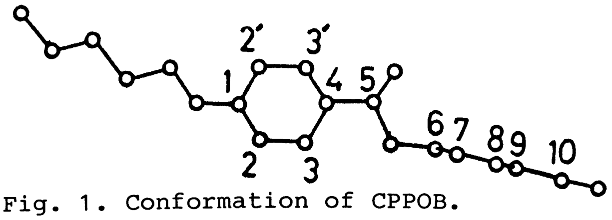

Fig. 1. Conformation of CPPOB.

The solid state spectrum of CPPOB[8] obtained by conventional pulse sequence[9] is shown in Fig. 2A; the spectrum which is free of spinning sideband was obtained by TOSS pulse sequence[10] in Fig. 2B. TOSS pulse sequence is a useful technique to eliminate spinning side bands. Fig. 2C shows the solution spectrum obtained in $CDCl_3$ at 27 °C. Comparison of the solid state spectra with the solution spectrum gave us informaton about the solid state structure. The chemical shifts and assignments were shown in Table 1.

The resonance of aromatic carbon ortho to pentoxy group at 114.5 ppm in the solution was separated into doublet by 6.4 ppm, that is, resonances of C2 at 111.4 ppm and C2' at 117.8 ppm in the solid state. In the solid state, the pentoxy group is locked at one position with respect to the benzene ring to which it is attached, whereas it rotates freely about O-C1 axis in solution. The splitting is due to the conformational effect of the fixed orientation of the pentoxy group. Hays[2] reported that splittings of the carbons ortho to alkoxy groups of p-alkoxy benzoic acids were observed in the solid state spectra

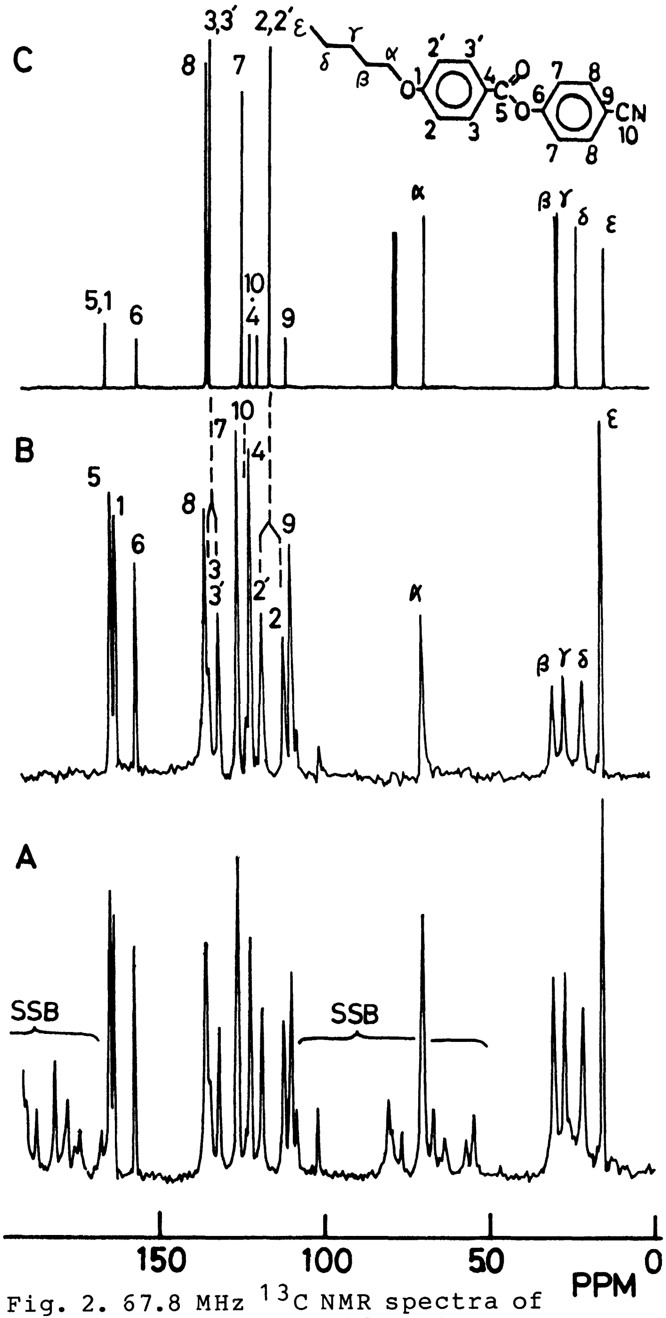

Fig. 2. 67.8 MHz ^{13}C NMR spectra of CPPOB :(A) solid state CP/MAS spectrum obtained by conventional pulse sequence; (B) solid state CP/MAS spectrum which is free of spinning sideband obtained by TOSS pulse sequence; (C) solution spectrum in $CDCl_3$ at 27 °C.

Table 1. ^{13}C Chemical Shifts of 4'-Cyanophenyl-4-n-Pentoxybenzoate (CPPOB) in the Solid State and Solution[a)]

	1	2	2'	3	3'	4	5	6	7	8
Solid	163.6	111.4	117.8	131.0	134.0	121.4	162.4	156.1	125.4	135.2
Solution[b)]	164.0	114.5		132.5		120.6	164.0	154.5	123.0	133.7

	9	10	α	β	γ	δ	ε
Solid	109.3	122.6	69.7	30.4	27.0	21.5	15.6
Solution[b)]	109.6	118.4	68.4	28.8	28.1	22.4	14.0

a) ppm from tetramethylsilane. b) In CDCl, 27 °C.

and concluded that they were due to the fixed orientation of the alkoxy groups with respect to the benzene ring on the basis of X-ray structure analyses.[11-13)]

We also observed the same type of conformational effects in the solid state spectra of thermotropic aromatic polyesters containing flexible spacer in the main chain and the model compound.[14)]

The splitting into C3 at 131.0 ppm and C3' at 134.0 ppm by 3.0 ppm was observed in the solid state spectra since the pentoxyphenyl group and the ester linkage group are coplanar and C3 and C3' became nonequivalent. The resonance of C6 showed no splitting and complete equivalency since the cyanophenyl group and the ester linkage group are perpendicular, as depicted Fig. 1.

As for aliphatic carbons of the pentoxy group, the resonances of Cα, C_β and C_ε in the solid state spectra showed downfield shifts by 1.3-1.6 ppm and those of C_γ and C_δ showed upfield shifts by 1.1 ppm and 0.9 ppm respectively compared to the solution spectra. The pentoxy group has an all-trans planar conformation in the solid state. In solution, the conformation changes rapidly, giving averaged chemical shifts. However, more studies are necessary to explain these chemical shift changes.

CPPOB has an exceptional C_s conformation for the class of phenyl benzoates. The angles formed by the ester linkage and the phenyl rings are extreme values of 0° and 90°, respectively. Compounds of the analogous series do not have these extreme values. The exceptional conformation showed distinct conformational effects by line splittings in the solid state spectra. Further studies are in progress to reveal the relationship between the conformational effects and the angles of the ester linkage groups and the phenyl rings.

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(Received November 4, 1986)