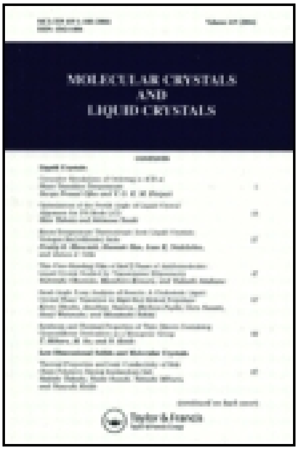

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Conformational and Crystallographic Effects on Solid-State CP/MAS ^{13}C NMR Spectra of Thermotropic Phenyl Benzoates

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Conformational and Crystallographic Effects on Solid-State CP/MAS ^{13}C NMR Spectra of Thermotropic Phenyl Benzoates

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The crystalline structures of thermotropic ester compounds, 4-cyanophenyl 4-pentoxybenzoate (CPPOB), 4-cyanophenyl 4-heptylbenzoate (CPHB), 4-cyanophenyl 4-pentylbenzoate (CPPB), and 4-nitrophenyl 4-octyloxybenzoate (NPOOB) have been examined by high-resolution CP/MAS (cross polarization/magic angle spinning) solid-state ^{13}C NMR. The spectral features were correlated with the crystalline structures. Conformational and crystallographic effects were observed in the solid-state spectra. The resonances of aromatic carbons showed more distinct conformational effects when the molecule adopted a high degree of symmetry, that is, the exact C_s symmetry for CPPOB. As for aliphatic end groups, conformational effects were clearly observed for longer alkyl chains, that is, the heptyl group of CPHB and the octyloxy group of NPOOB. It is assumed that these differences are due to different features of crystal packings.

INTRODUCTION

Intensive work has been focused on liquid crystalline low-molecular-weight esters and polyesters because of their high potential as functional materials.[1,2] It is important to investigate solid-state structures of these compounds since solid-state structures have close relations to properties in solids and to liquid crystalline characteristics.

Solid-state CP/MAS (cross polarization/magic angle spinning) ^{13}C NMR is a powerful method to study solid-state structures of organic molecules.[3–6] It has been possible to obtain information about conformations and crystal packings of various solid samples, e.g., single crystal, amorphous, polycrystalline, and semicrystalline samples by using CP/MAS NMR.

In our previous work,[7,8] solid-state structures of thermotropic polyesters were examined by solid-state NMR and conformations of these polymers were proposed on the basis of the CP/MAS spectra. In order to examine such semicrystalline polymers by using CP/MAS NMR, it is useful to obtain more information about

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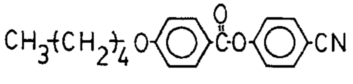
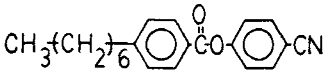
relationships between crystalline structures of low-molecular-weight compounds and their solid-state spectra.

X-Ray crystalline structure studies of thermotropic phenyl benzoates were reported for 4-cyanophenyl 4-pentoxybenzoate (CPOOB) by Baumeister *et al.*,[9] 4-cyanopheyl 4-heptylbenzoate (CPHB) by Mandal *et al.*,[10] 4-cyanophenyl 4-pentyl benzoate (CPPB) by Baumeister *et al.*,[11] and 4-nitrophenyl 4-octyloxybenzoate (NPOOB) by Kaiser *et al.*[12]

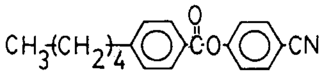
In the present work, crystalline structures of these phenyl benzoate derivatives have been examined by solid-state CP/MAS ^{13}C NMR. The spectral features were correlated with the crystalline structures.



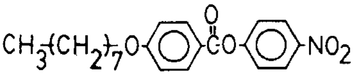
CPPOB



CPHB



CPPB



NPOOB

EXPERIMENTAL

Materials

Phenyl benzoates were prepared from the corresponding benzoyl chloride and phenol in dry pyridine. Recrystallized samples of CPPOB, CPHB, and NPOOB from ethanol and CPPB from acetone were used for NMR measurements. These crystallization conditions were the same as those used for X-ray analyses. Samples of CPPB and CPHB crystallized from melt state were also measured by CP/MAS NMR. Transition temperatures of CPPOB: crystal-isotropic 86°C (lit.[9] 85–85.5°C); isotropic-nematic 77°C (lit.[9] 76.5–77°C). CPHB: crystal-nematic 43.5°C (lit.[10] 43.5°C); nematic-isotropic 55°C (lit.[10] 56°C). CPPB: crystal-isotropic 60.5°C (lit.[11] 60.5°C); isotropic-nematic 56°C (lit.[11] 56°C). NPOOB: crystal-smectic A 50°C (lit.[13] 49°C); smectic A-nematic 62°C (lit.[13] 62°C); nematic-isotropic 68°C (lit.[13] 68°C). Visual observation of phase transitions was performed by a polarizing microscopic equipped with a Mettler FP 84 hot stage.

NMR measurements

Solid-state CP/MAS ^{13}C NMR spectra were obtained on a JEOL JNM-GX270 spectrometer (6.34 T magnetic field, ^{13}C frequency 67.8 MHz) with a CP/MAS unit at room temperature. A bullet-type Kel-F rotor was spun at the rate of 3.6–

3.8 MHz. Conventional[14] and TOSS[15] pulse sequences were used for measurements. Dipolar dephasing spectra[16] were measured with a delay time of 40 μs. Pulse parameters were: contact time of 2 ms and recycle time of 5 s. F.I.D.s were accumulated 300–500 times. The resonance of the CH of solid adamantane was used as an external reference for chemical shift referencing (29.5 ppm downfield from tetramethylsilane).[17]

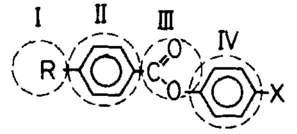
Solution spectra were recorded on the same spectrometer. The sample was measured at 27°C on 5% (w/v) solution of $CDCl_3$ or DMSO-d_6. Tetramethylsilane was used as an internal standard. The assignment of the aromatic ring resonances was performed on the basis of additive rules.[18] The alkyl and alkoxy carbon resonances were assigned according to the result of Poon et al.[19]

RESULTS AND DISCUSSION

Cyanophenyl alkyl and alkoxy benzoates were first reported by Boller *et al.*[20,21] The X-ray crystalline structure studies of 4-cyanophenyl 4-pentoxybenzoate (CPPOB),[9] 4-cyanophenyl 4-heptylbenzoate (CPHB),[10] 4-cyanophenyl 4-pentylbenzoate (CPPB),[11] and 4-nitrophenyl 4-octyloxybenzoate (NPOOB)[12] have shown that the conformational features of these thermotropic compounds are different,

TABLE I

Conformations of phenyl benzoate derivatives in the crystalline state[9–12]



CPPOB R:Pentoxy X:Cyano
CPHB R:Heptyl X:Cyano
CPPB R:Pentyl X:Cyano
NPOOB R:Octyloxy X:Nitro

	Dihedral Angle (°)				
Planes	CPPOB[a)]	CPHB[b)]	CPPB[c)]		NPOOB[d)]
I/II	0	53.4	3.6	0.5	17.0
II/III	0	14.7	9.1	1.3	2.0
III/IV	90	62.1	68.2	58.8	58.1
II/IV	90	47.5	60.0	59.4	57.1

a) 4-Cyanophenyl 4-pentoxybenzoate. Ref. 9.

b) 4-Cyanophenyl 4-heptylbenzoate. Ref. 10.

c) 4-Cyanophenyl 4-pentylbenzoate. Ref. 11. Two independent molecules with different conformations exist in the crystalline state.

d) 4-Nitrophenyl 4-octyloxybenzoate. Ref. 12.

although these molecules generally adopt stretched forms in the crystalline state. Table I summarizes conformational features of these four aromatic esters. It is noteworthy that only CPPOB shows the exact C_s symmetry, whereas CPPB, CPHB, and NPOOB show C_1 symmetry.

The crystalline structure of CPPOB was examined by CP/MAS NMR at first because highly resolved and well-split solid-state spectra which would help to interpret spectra of the phenyl benzoates were expected for CPPOB because of C_s symmetry. The conformation of CPPOB in the crystalline state[9] is depicted in Figure 1. The solid-state spectrum of CPPOB obtained by conventional pulse sequence is shown in Figure 2A; the spinning sideband free spectrum obtained by TOSS pulse sequence in Figure 2B. Figure 2C shows the solution spectrum obtained in $CDCl_3$ at 27°C. Chemical shifts and assignments are shown in Table II.

In the solid-state spectra, the resonance of ortho carbons was clearly split into a doublet separated by 6.4 ppm, that is, C2 resonance at 111.4 ppm and C2′ resonance at 117.8 ppm. This splitting is due to a locked orientation of the pentoxy group with respect to the benzene ring. Maricq and Waugh studied[22] the chemical shift values of 1,4-dimethoxybenzene in the solid state and found that the resonance of the ortho carbon shielded by the methoxy group appeared at 113 ppm; the deshielded ortho carbon resonance at 119 ppm. (In our previous communication,[23] the assignment of these ortho carbon resonances was interchanged.)

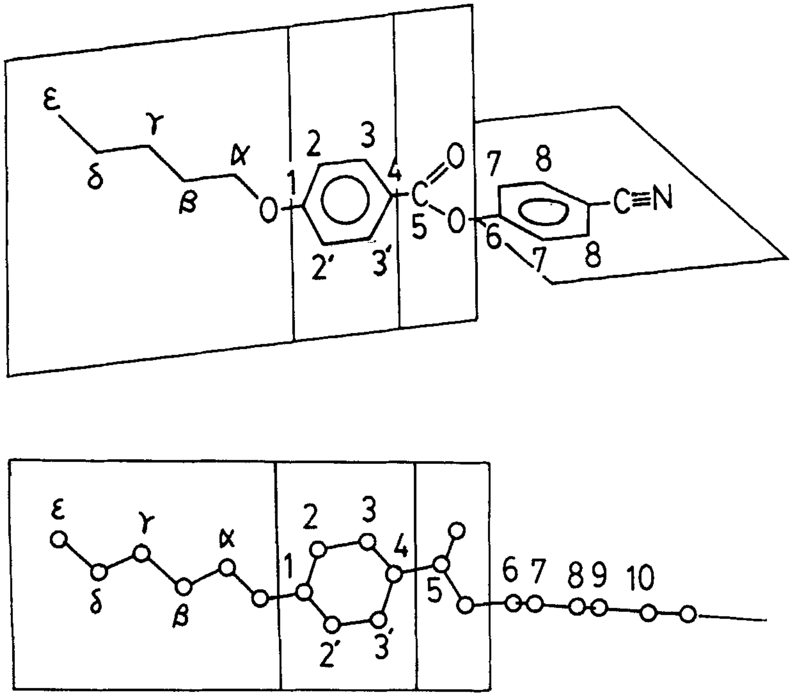


FIGURE 1 Conformation of CPPOB in the crystalline state (Reference 9).

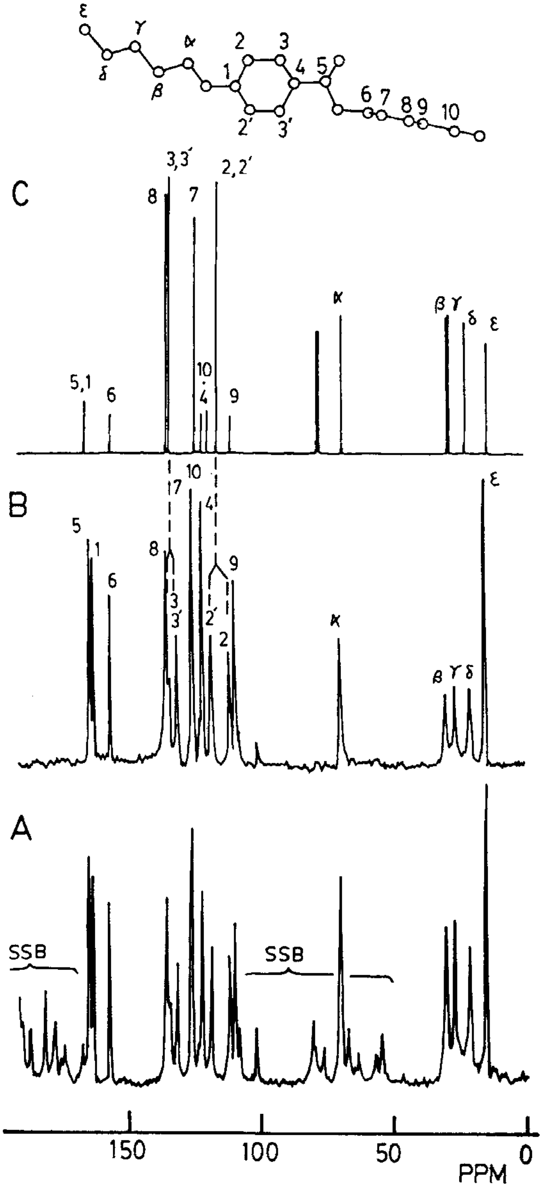


FIGURE 2 67.8 MHz ^{13}C NMR spectra of CPPOB: (A) solid-state CP/MAS spectrum obtained by conventional pulse sequence; (B) solid-state spinning sideband free spectrum; (C) solution spectrum obtained in $CDCl_3$ at 27°C.

TABLE II

^{13}C chemical shifts[a] of 4-cyanophenyl 4-pentoxybenzoate (CPPOB) in the crystalline and solution states

	1	2	2'	3,3'	4	5	6	7
Solid	162.4	111.4	117.8	131.0, 134.0	121.4	163.0	156.1	125.4
Solution[b)]	164.0	114.5		132.5	120.6	164.0	154.5	123.0

	8	9	10	α	β	γ	δ	ε
Solid	135.2	109.3	122.6	69.7	30.4	27.0	21.5	15.6
Solution[b)]	133.7	109.6	118.4	68.4	28.8	28.1	22.4	14.0

a) Chemical shifts (ppm) from tetramethylsilane. b) In $CDCl_3$ at 27 ℃.

The splitting into C3 and C3′ at 131.0 and 134.0 ppm was observed in the solid-state spectra since the pentoxyphenyl group (planes I and II) and the ester linkage group (plane III) are coplanar, and C3 and C3′ become nonequivalent. The resonance of C7 showed no splitting and complete equivalency since the cyanophenyl group (plane IV) and the ester group (plane III) are perpendicular, as shown in Figure 1 and Table I.

No appreciable conformational effect was observed for the resonances of the pentoxy group which forms the all-trans conformation in the crystalline state. The resonances of C_α, C_β, and C_ε were shifted downfield in the solid-state spectra compared with the solution spectrum whereas the resonances of C_γ and C_δ showed upfield shifts. Discussions about the chemical shifts of alkyl chain carbons will be given below.

4-Cyanophenyl 4-heptylbenzoate (CPHB) and 4-cyanophenyl 4-pentylbenzoate (CPPB) which have similar chemical structures to CPPOB have been examined by CP/MAS NMR. CPHB exhibits an enantiotropic nematic phase whereas CPHB

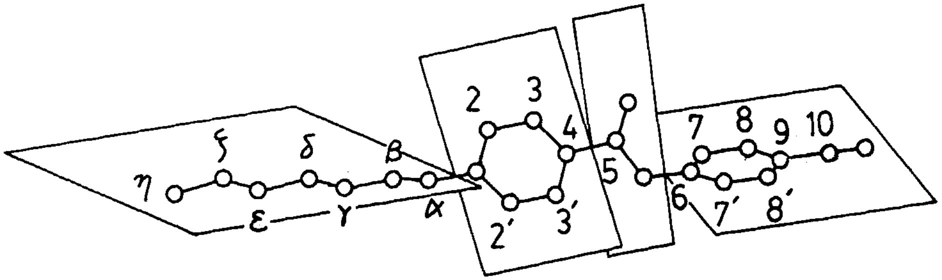


FIGURE 3 Conformation of CPHB in the crystalline state (Reference 10).

forms a monotropic nematic phase. X-Ray crystalline structure studies of CPHB[10] and CPPB[11] have shown that the conformations of these compounds are not of a high degree of symmetry. Figure 3 illustrates the conformation of CPHB in the crystalline state. The conformational feature of CPPB is similar to that of CPHB. However, for CPPB, two independent molecules with different conformations exist in the crystalline state. The dihedral angles between the phenylene ring and the ester linkage plane of CPPB and CPHB are not extreme values like 0° and 90° of CPPOB (Table I). Most of phenyl benzoates adopt C_1 symmetry.[10–12,24]

Figures 4A and 5A show conventional CP/MAS spectra of CPHB and CPPB, respectively. Dipolar dephasing spectra with delayed time of 40 μs have been measured to assign quarternaly aromatic carbons as shown in Figures 4B and 5B. Spinning sideband free spectra are shown in Figures 4C and 5C. Both samples, crystallized from solution and melt states, were measured by CP/MAS NMR, and no difference was observed between spectra of these samples. Solution spectra obtained in $CDCl_3$ at 27°C are shown in Figures 4D and 5D. Chemical shifts and assignments are given in Table III. For CPHB, DMSO-d_6 was also used as a solvent to study solvent effects on chemical shifts (Table III). Chemical shift differences between two solvents were within 0.9 ppm.

In the solid-state spectra, different features of aromatic carbon resonances among these analogous phenyl benzoates, i.e., CPPOB (Figure 2), CPHB (Figure 4), and CPPB (Figure 5), were observed. These differences reflected the differences in molecular conformation and molecular packing in the crystalline state. In solution spectra, resonances of the cyanopheyl benzoate units showed no difference. Although resonances of aromatic ortho carbons of CPHB and CPPB were not so well resolved and split as those of CPPOB because of only C_1 conformation, the spectral features gave us information about crystalline structures.

For CPHB, nonequivalency of C3 and C3′ resonances (131.3 and 132.7 ppm) was observed in the solid-state spectra. This was caused by the conformational effect of the ester group and the aromatic ring which make an angle of 14°. The peaks at 120.4 and 123.9 ppm might be due to the resonances of C7 and C7′. The splitting was asymmetric and relatively large, which suggests that it was not only due to conformational effects. Mandal et al. reported[10] that there is a close contact between C7 and the oxygen of the ester linkage of a neighboring molecule. It is assumed that the intermolecular (crystallographic) effect and conformational nonequivalency caused the split resonances of C7 and C7′.

Figure 5B (CPPB) clearly shows the splitting of C4 resonance into a doublet separated by 1.5 ppm. This splitting is due to a crystallographic nonequivalency of C4 of two independent molecules. Aromatic carbon resonances were not well split and resolved in the CP/MAS spectra. It is considered that this complexity of the resonances is due to the effects of both crystallographic and conformational nonequivalencies of aromatic ortho carbons.

The alkyl chains of CPHB and CPPB adopt the all-trans form in the crystalline state. For the heptyl chain resonances of CPHB, conformational effects were noticeable. The internal methylene carbons, i.e., C_β–C_ε appeared at 33.2 ppm in the solid-state spectrum. These resonances were shifted downfield by 1.4–4.1 ppm from those in the solution spectrum. These differences can be explained in terms of the

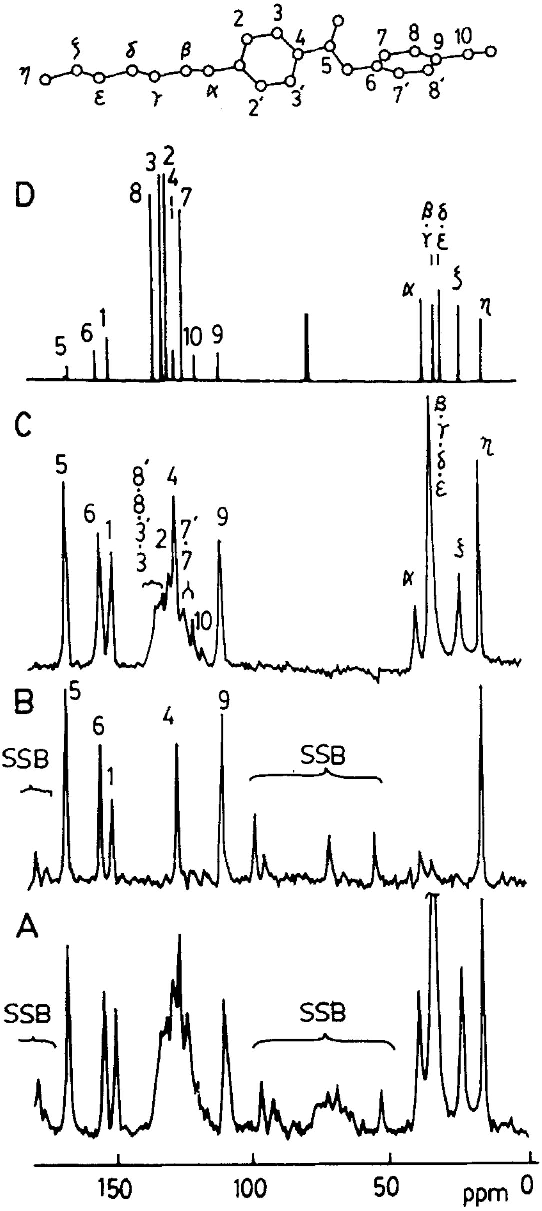


FIGURE 4 67.8 MHz ^{13}C NMR spectra of CPHB: (A) solid-state CP/MAS spectrum; (B) dipolar dephasing solid-state spectrum; (C) solid-state spectrum (spinning sideband free); (D) solution spectrum obtained in $CDCl_3$ at 27°C.

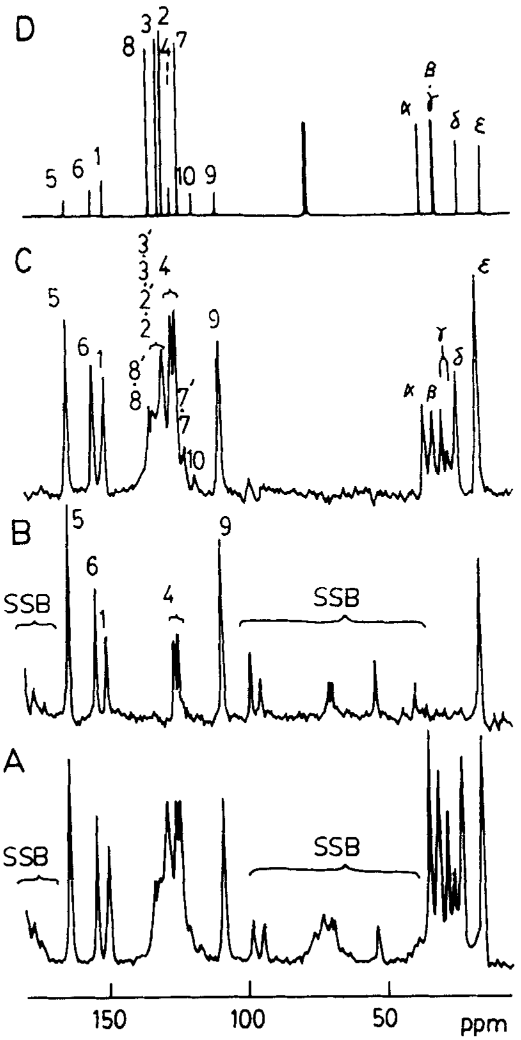


FIGURE 5 67.8 MHz ^{13}C NMR spectra of CPPB: (A) solid-state CP/MAS spectrum; (B) dipolar dephasing solid-state spectrum; (C) solid-state spectrum (spinning sideband free); (D) solution spectrum obtained in $CDCl_3$ at 27°C.

γ-gauche effect.[25,26] In solution, trans-gauche conformational changes occur rapidly and averaged resonances are shifted upfields by the existence of some gauche conformations. For polyethylene and *n*-alkanes in the crystalline state, the methylene carbon resonances of all-trans conformation were observed at 33.0–34.0 ppm,[27–30] which was in good agreement with those of the heptyl chain. On the other hand, for the pentyl chain of CPPB, the features were complicated. The resonances of C_α and C_γ were shifted upfield in the solid-state spectra and C_γ resonance showed splitting into a doublet. This splitting shows that C_γ of two

TABLE III

^{13}C chemical shifts[a] of 4-cyanophenyl 4-pentylbenzoate (CPPB) and 4-cyanophenyl 4-heptylbenzoate (CPHB) in the crystalline and solution states

		1	2,2'	3,3'	4	5	6	7,7'	8,8'
CPHB	Solid	150.0	129.0	131.3 132.7	126.6	166.6	154.2	120.4 123.9	133.8
	Soln[b)]	150.1	128.9	130.4	126.1	164.4	154.4	123.0	133.7
	Soln[c)]	149.6	128.9	130.0	125.8	163.9	154.1	123.4	134.0
CPPB	Solid	150.5	129.4	131.8	124.7 126.2	164.4	154.5	121.3	134.0
	Soln[b)]	150.1	128.9	130.4	126.1	164.4	154.4	123.0	133.7

		9	10	α	β	γ	δ	ε	ξ	η
CPHB	Solid	110.5	117.0	39.2	33.2				23.5	15.7
	Soln[b)]	109.7	118.3	36.1	31.8	31.1	29.2	29.1	22.6	14.1
	Soln[c)]	108.8	118.3	35.2	31.2	30.5	28.5	28.4	22.0	13.8
CPPB	Solid	109.2	117.5	35.3	31.8	28.8 26.4	23.4	15.9		
	Soln[b)]	109.7	118.3	36.1	31.4	30.8	22.5	14.0		

a) Chemical shifts (ppm) from tetrametylsilane. b) In $CDCl_3$ at 27 ℃. c) In DMSO-d_6 at 27 ℃.

independent molecules were affected by an appreciably different crystallographic (intermolecular) effect.

The crystalline structure of 4-nitrophenyl 4-octyloxybenzoate (NPOOB) has been examined by CP/MAS NMR.[31] NPOOB shows both smectic A and nematic phases. X-Ray structure study of NPOOB was performed by Kaiser *et al.*,[12] revealing that NPOOB adopts a stretched conformation (C_1 symmetry) in the crystalline state, as illustrated in Figure 6. The dihedral angles are shown in Table I. It is interesting

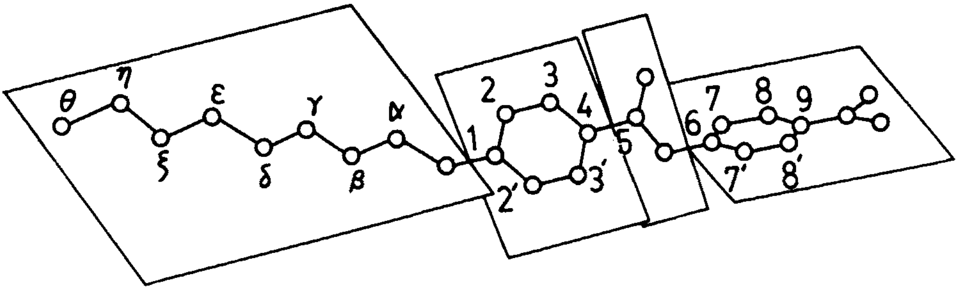


FIGURE 6 Conformation of NPOOB in the crystalline state (Reference 12).

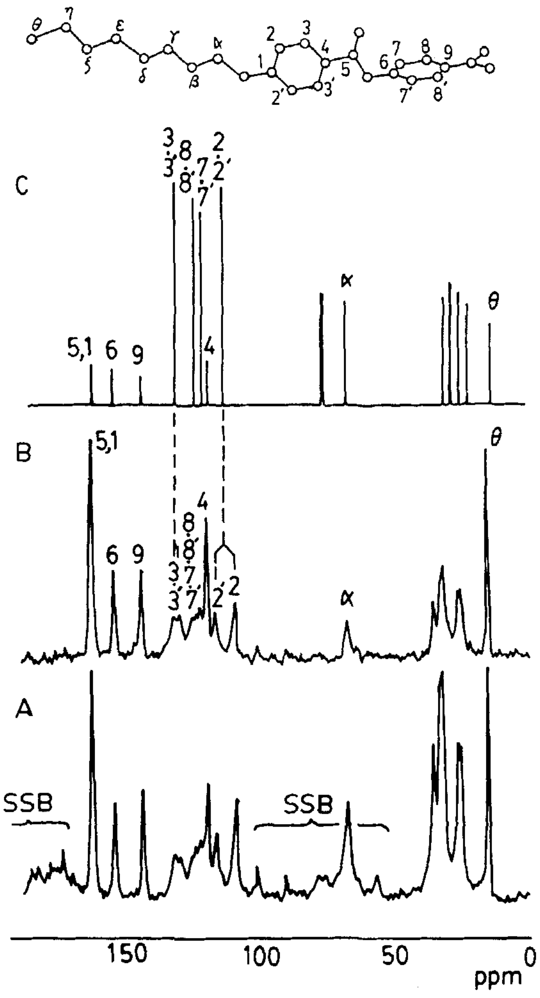


FIGURE 7 67.8 MHz ^{13}C NMR spectra of NPOOB: (A) solid-state CP/MAS spectrum; (B) solid-state spectrum (spinning sideband free); (C) solution spectrum obtained in $CDCl_3$ at 27°C.

to compare spectral features of NPOOB with those of CPPOB because both of them have the oxyphenylbenzoyl unit. The solid-state conventional spectrum is shown in Figure 7A; the spinning sideband free spectrum in Figure 7B. The solution spectrum obtained in $CDCl_3$ at 27°C is shown in Figure 7C. The chemical shifts and assignments are listed in Table IV. Comparison of solution spectra of CPPOB and NPOOB showed that the resonances of the ortho carbons of the oxybenzoyl unit (C2 and C3) appeared at the same chemical shifts, respectively (Tables II and IV). This suggests that the different spectral features of these resonances in the solid-state spectra reflect the differences of conformations about the alkoxy group and the ester linkage.

TABLE IV

^{13}C chemical shifts[a] of 4-nitrophenyl 4-octyloxybenzoate (NPOOB) in the crystalline and solution states

	1	2	2'	3,3'	4	5	6	7,7'
Solid	163.5	110.4	117.0	130.7, 132.5	120.4	163.5	155.5	123.4, 124.9
Solution[b)]	164.0	114.6		132.5	120.4	164.1	156.0	122.7

	8	9	α	β	γ	δ	ε	ζ	η	θ
Solid	126.6	144.9	68.2	33.3	26.9	32.4	32.4	36.0	25.7	15.4
Solution[b)]	125.2	145.3	68.5	29.0	26.0	29.3	29.2	31.8	22.7	14.1

a) Chemical shifts from tetramethylsilane. b) In $CDCl_3$ at 27 ℃.

The nonequivalency of C2 and C2′ in the solid-state spectra showed that conformational effects of the alkoxy group were observed appreciably in the small torsion angle of 17° between the plane of the alkoxy group and the benzene ring. As for the ester linkage, the angle between planes II and III is 2.0°, while the angle between planes III and IV is 58.1° as listed in Table I. The ortho carbon resonances of the octyloxyphenyl group appearing at 132.5 ppm in solution showed nonequivalency at 130.7 and 132.5 ppm (C3, C3′). The resonances at 123.4 and 124.9 ppm were due to the nonequivalency of C7 and C7′.

For the octyloxy group, conformational effects were observed clearly. All aliphatic carbons except for C_α showed downfield shifts in the solid-state spectra. For example, internal methylene carbon resonances (C_δ and C_ε) which can be affected by double γ-gauche shielding effects from both sides (C_α and C_η for C_δ; C_β and C_θ for C_ε) were shifted downfield by 3.2 ppm in the solid-state spectra from the solution spectrum.

In these four phenyl benzoates, conformational effects were observed clearly only for longer alkyl chains, that is, the heptyl group of CPHB and the octyloxy group of NPOOB. On the contrary, for the pentoxy group of CPPOB and the pentyl group of CPPB which also form all-trans conformations, the conformational effects between solid-state and solution spectra were not noticeable.

One possible explanation for these differences is that they are due to different features of the molecular packing. Figure 8 illustrates schematic molecular packings in the crystalline state of CPHB (A), NPPOB (A), CPPOB (B), and CPPB (C). For CPHB[10] and NPOOB,[12] the molecules are packed in layered structures, where the aliphatic chains and the aromatic units are stacked separately as shown in Figure 8A. For CPPOB[9] (Figure 8B) and CPPB[11] (Figure 8C), aliphatic carbons are close to the aromatic units of neighbouring molecules. These molecular packings suggest that the intermolecular (crystallographic) effects of aromatic rings causing upfield

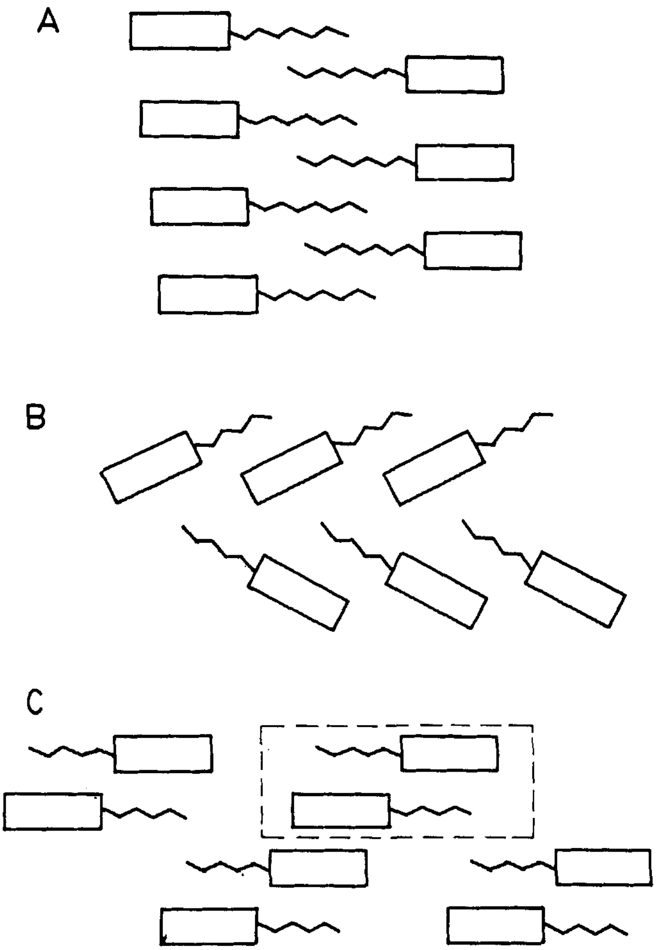


FIGURE 8 Schematic crystal packings of phenyl benzoate derivatives: (A) NPOOB and CPHB; (B) CPPOB; (C) CPPB.

shifts of some aliphatic carbon resonances cancel the deshielding effects of the trans conformation and no simple conformational effects were observed.

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