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Studies of the series of cellooligosaccharide peracetates as a model for cellulose triacetate by ^{13}C CP/MAS NMR spectroscopy and X-ray analyses

Hiroyuki Kono *, Yukari Numata, Nobuhiro Nagai, Tomoki Erata, Mitsuo Takai

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

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Abstract

The series of crystalline oligomers from α-cellobiose octaacetate through α-cellohexaose eicosaacetate, listed as below, was prepared from homogeneous acetylation of the corresponding cellooligosaccharides and characterized by ^{13}C CP/MAS NMR spectroscopy and X-ray analysis in order to obtain the structural models of cellulose triacetate (CTA) in solid state. Progressing toward the hexamer, the NMR spectral feature of the oligomers, in comparison with two allomorphs of CTA I and CTA II, gradually approached that of CTA I. Specifically, chemical shifts of both the hexamer and the pentamer were in considerable respective agreement with those of CTA I. In addition, X-ray diffraction patterns of the oligomers established that the crystalline pentamer and hexamer have a CTA I lattice in spite of recrystallization from ethylacetate–hexane. We therefore concluded that the pentamer and hexamer would be useful models for the CTA I structure.

Keywords: Cellulose triacetate; Crystal structure; ^{13}C CP/MAS NMR spectroscopy; X-ray diffraction; Oligomeric compound

1. Introduction

When compared with the other synthetic polymers, the fundamental properties [1–4] of cellulose triacetate (CTA), such as the structure–property relationships, crystallization behavior, and molecular dynamics, are poorly understood due to the existence of two allomorphs, denoted CTA I and CTA II. In X-ray crystallographic studies of the CTAs, diffraction patterns of CTA I and CTA II can be distinguished from each other [5–7]; the structural model of CTA I has a parallel-chain packing [8], and that of CTA II has an antiparallel structure [9,10]. In a study by Sprague et al. [6], CTA I is only produced by heterogeneous acetylation from cellulose I, while the crystalline state of CTA can be produced by homogeneous acetylation from cellulose or by heterogeneous acetylation from cellulose II in CTA II. The authors also demonstrated that cellulose I and cellulose II were respectively obtained from the corresponding polymorphs of CTA by saponification; thus, they concluded that the polymorphism of the CTAs was in absolute relation to that of cellulose [6]. However, recent opinions have differed over the polymorphism relationships between cellulose and CTA suggested by Sprague et al. In previous reports [7,11] by authors in our group, it was shown that typical CTA I was

* Corresponding author. Tel./fax: +81-11-706-6568.
E-mail address: kohno@dove-mc.eng.hokudai.ac.jp (H. Kono)

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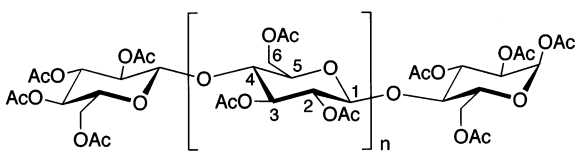
obtained from prehydrolyzed cellulose II by heterogeneous acetylation without any dissolving process. In addition, CTA I derived from heterogeneously acetylated cotton is reported [12] to transform CTA II in the presence of formic acid, and the resultant CTA II product is saponified into cellulose I. Roche et al. [13] reported that CTA I was produced from a CTA in a solution state in trifluoroacetic acid. Discussion regarding the crystal structures of allomorphs of both CTA and cellulose are currently in progress, though the most important question remains whether reversals of chain direction on areas of neighboring chains are required for the transformation of one allomorph of CTA into another.

In order to investigate crystal structures of CTAs, it is important to have determined the structures of cellooligosaccharides acetates in the solid state; examination of the homologous series of oligomeric compounds, which asymptotically approach a polymer structure, has revealed some polymer properties [14]. Regarding CTA oligomers, crystal structures of β anomer of the CTA dimer and trimer were discussed by Pérez and Brisse [15], who concluded that glycosidic torsion angles of the middle and nonreducing end units in the trimer were close to those of the CTA I and CTA II, respectively. Buchanan et al. [16] compared physical properties of the cellooligosaccharide acetates from a degree of polymerization (DP) of 2–9 with those of CTA by differential scanning calorimetric analysis. However, thus far, surprisingly few studies have examined the relationship between the crystal structure of CTAs and that of CTA oligomers.

Herein, we describe preparation of the series of crystalline α-D-cellooligosaccharide acetates from the dimer through the hexamer, where $n = 0–4$, by homogeneous acetylation and characterize their crystal structures by analyses of ^{13}C cross polarization–magic angle sample spinning (CP/MAS) NMR spectroscopy and X-ray diffraction.

Comparisons of the crystal structures of the CTA oligomers with those of the two allomorphs of CTA were made in order to obtain a simplified oligomer model of CTA, which is also described herein.



n = 0, α-Cellobiose octaacetate
n = 1, α-Cellotriose hendecaacetate
n = 2, α-Cellotetraose tetradecaacetate
n = 3, α-Cellopentaose heptadecaacetate
n = 4, α-Cellohexaose eicosaacetate

2. Results and discussion

Characterization of CTAs and CTA oligomers.—CTA I and CTA II were prepared by heterogeneous acetylation [17] of cellulose powder and pre-mercerized cellulose, respectively. The titration method [18] gave a degree of substitution (DS) of 2.95 acetyls/glucose repeat unit for the CTA I, and one DS of 2.93 for CTA II. The CTAs were subsequently exposed to heat treatment at 210 °C for 15 min in order to increase their crystallinities, then air-dried. The products showed typical X-ray diffraction patterns and CP/MAS NMR spectra of the corresponding allomorphs of CTA, which will be described later.

The CTA oligomers were all obtained by acetylation of the corresponding respective cellooligosaccharide and purified by recrystallization twice from ethylacetate–hexane. Complete substitution of the acetyl group for the hydroxyl group on the oligomers was estimated by the disappearance of OH-group adsorption at about 3200 cm^{-1} as determined by FTIR spectroscopy and compound purity was confirmed in each case by thin-layer chromatography (TLC) analysis. As shown in Table 1, elemental and mass spectroscopic analyses data of the CTA oligomers are completely coincident with the theoretical values, which indicates that the initial hydroxyl groups of the oligomers have been completely acetylated. The complete ^{13}C NMR spectral assignments for the oligomers, as well as those for CTA I in chloroform-*d* are summarized in Table 2. The ^{13}C NMR chemical shifts of the CTA I and CTA oligomers are in agreement with the previous report [16]. Regarding C-1 resonances of reducing end units, chemical shifts of α anomeric carbons are in the region 88–90 ppm [19], and those of β anomeric carbons are downfield in the region 90–92 ppm

[19]. As shown in Table 2, the spectral data of the oligomers gave no signals at the β anomeric C-1 region, while C-1 resonances of reducing end units of all the oligomers were observed in the α anomeric carbon region. This finding established that these products were α-cellooligosaccharide peracetates. As can be seen in Table 2, the chemical shifts of

Table 1
Yields and analyses of the cellooligosaccharide peracetates (DP = 2–6)

Compound	DP	Yield (%)	Formula	M_r: Calcd (Found)	Calcd (Found) (%)		
					C	H	N
Dimer	2	81	$C_{28}H_{38}O_{19}$	678.6 (679)	49.56 (49.52)	5.64 (5.64)	0 (0)
Trimer	3	76	$C_{40}H_{54}O_{27}$	966.8 (967)	49.69 (49.42)	5.63 (5.58)	0 (0)
Tetramer	4	74	$C_{52}H_{70}O_{35}$	1255.1 (1255)	49.76 (49.54)	5.62 (5.63)	0 (0)
Pentamer	5	69	$C_{64}H_{86}O_{43}$	1543.3 (1543)	49.81 (49.60)	5.62 (5.59)	0 (0)
Hexamer	6	73	$C_{76}H_{102}O_{51}$	1831.6 (1831)	49.84 (49.69)	5.61 (5.58)	0 (0)

Table 2
^{13}C NMR spectral data (δ, ppm) for CTA I and cellooligosaccharide peracetates in $CDCl_3$

Compound	CTA I	Dimer	Trimer	Tetramer	Pentamer	Hexamer
DP		2	3	4	5	6
Reducing end unit						
C-1		89.2	89.1	89.1	89.1	89.1
C-2		70.7	69.6	69.6	69.6	69.6
C-3		70.7	69.6	69.6	69.6	69.6
C-4		76.0	76.0	76.0	76.2	76.2
C-5		71.8	70.8	70.9	70.8	70.8
C-6		61.8	61.5	61.8	61.8	61.7
C-1 Ac		168.8	168.8	168.8	168.8	168.8
C-2 Ac		169.6	169.7	169.7	169.7	169.7
C-3 Ac		169.5	169.6	169.6	169.7	169.6
C-6 Ac		170.2	170.1	170.2	170.2	170.2
Internal unit(s)						
C-1	100.5		100.6	100.5	100.5	100.5
C-2	72.0		72.5	72.1	72.1	72.1
C-3	72.7		72.9	72.5	72.4	72.7
C-4	76.2		76.2	76.2	76.2	76.2
C-5	73.1		72.8	73.0	73.0	73.1
C-6	62.2		62.4	62.2	62.2	62.2
C-2 Ac	169.3		169.3	169.3	169.3	169.3
C-3 Ac	169.7		169.7	169.7	169.7	169.7
C-6 Ac	170.2		170.1	170.2	170.2	170.2
Nonreducing end unit						
C-1		100.7	100.8	100.8	100.8	100.8
C-2		72.2	71.8	71.8	71.8	71.8
C-3		73.1	72.9	72.8	72.7	73.1
C-4		68.2	68.1	68.1	68.1	68.1
C-5		72.6	72.2	72.2	72.1	72.1
C-6		61.8	61.8	61.8	61.8	61.7
C-2 Ac		169.0	169.0	169.1	169.1	169.1
C-3 Ac		170.2	170.1	170.2	170.2	170.2
C-4 Ac		169.3	169.3	169.3	169.3	169.3
C-6 Ac		170.4	170.4	170.4	170.4	170.5
C-Me	20.5	20.5	20.5	20.5	20.5	20.5
	20.7	20.7	20.7	20.8	20.8	20.8
	20.9					

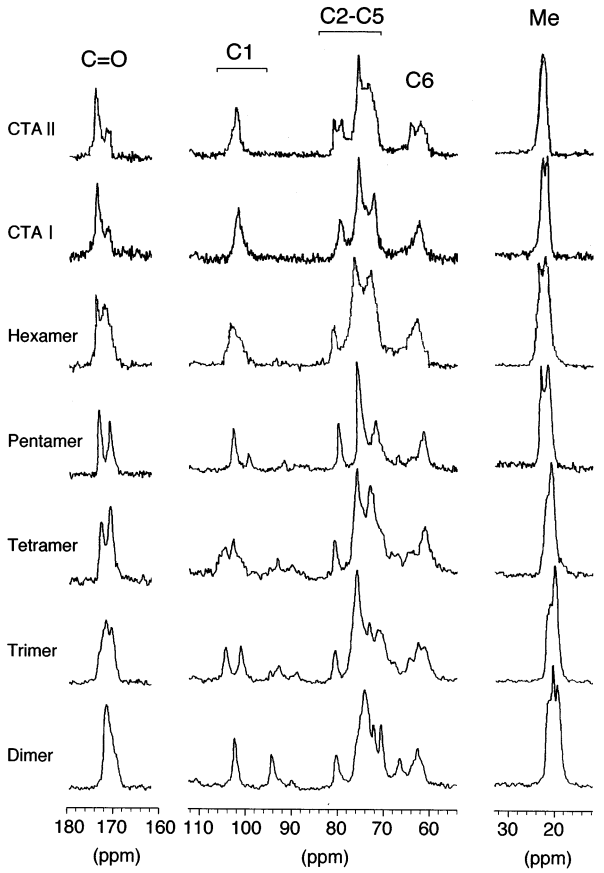


Fig. 1. ^{13}C CP/MAS spectra of CTA I, CTA II, and cellooligosaccharide peracetates (DP = 2–6). Peak intensities of the methyl region are shown at 40% reduction.

the ring carbons and of the carbonyl carbons of the CTA oligomers show little variation with increasing DP. Specifically, when the DP of the oligomers reach a value higher than that of tetramer, the ^{13}C chemical shifts of internal units of the oligomer are in reasonable agreement with those of CTA. This finding suggests that the chemical circumstances of internal residues of the CTA oligomers (DP > 3) are approximately identical to those of CTA, which could be applied to conformational analyses of CTA in solution state.

Solid-state NMR spectra.—The ^{13}C CP/MAS NMR spectra of the CTA oligomers are shown in Fig. 1, arranged from the dimer to the hexamer and indicating the assignments of resonances to various carbons. Assignments are based on the chemical shift data for the oligomers in chloroform-*d* (Table 2). Progressing toward the hexamer, the spectra of the oligomers simplify because the signal intensities of the internal residues of the oligomers gradually increase with the increase of their DP relative to those of the reducing end and nonreducing end units. The number of ^{13}C resonances in the ring carbon region (61–104 ppm) converged to five when the DP of the oligomers reached a value equal to that of the pentamer. Strong similarities were observed between the pentamer and the hexamer in the chemical shifts of the predominant five resonances. The C-1 region (88–106 ppm) for the oligomers shows a remarkable tendency for the C-1 resonance(s) of internal residue at about 103 ppm to become dominant, while two resonances, at 90 and 99 ppm, derived from a reducing and nonreducing end, respectively, become diminished, then finally negligible. Because carbonyl carbon and methyl carbon regions of the oligomers show a more

Table 3
Solid-state ^{13}C NMR spectral data (δ, ppm) for CTA I, CTA II, and α-D-cellohexaose eicosaacetate

Compound	Carbonyl carbon	Ring carbon			Me
		C-1	C-2–C-5	C-6	
CTA I	170.9 172.2	103.2	80.6 76.3 72.9	62.7	23.2 22.3
CTA II	169.8 170.6 172.6 172.9	101.8	80.8 78.2 76.0 75.0 73.2	65.8 61.9	21.8
Hexamer	170.9 173.0	103.2	80.6 76.3 73.0	62.6	23.2 22.3

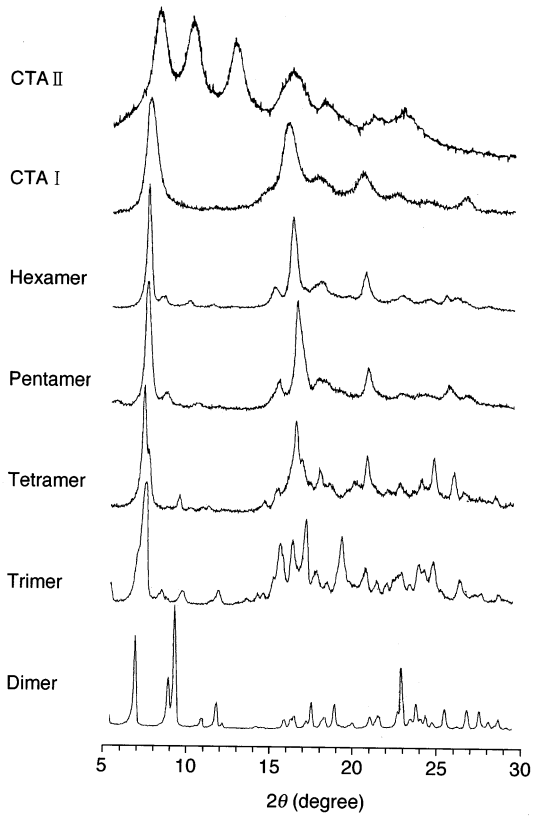


Fig. 2. X-ray diffractograms of CTA I, CTA II, and cellooligosaccharide peracetates (DP = 2–6).

complex version of variation, trends in the spectral features of the methyl regions were not established.

The ^{13}C CP/MAS spectra of CTA I and CTA II are also shown in Fig. 1. Chemical shifts of the CTAs and the hexamer are summarized in Table 3. The two allomorphs of CTA could be distinguished from each other by the chemical shifts and crystallographic splittings, as previously reported [11,20]. In a comparison of the CP/MAS spectrum of the hexamer with the spectra of CTAs, conspicuous similarities between the orientation of acetyl groups in the hexamer and of those in CTA I were observed. A sharper doublet for Me (21–24 ppm) of the hexamer and of CTA I, with splitting of 0.91 and 0.89 ppm, respectively, was observed, while that for the CTA II spectrum has a broad single peak (21.8 ppm). In the carbonyl carbon resonance regions (169–173 ppm), there is a doublet splitting for both CTA I and the hexamer. Carbonyl carbons of CTA II, on the other hand, gave shoulder peaks characteristic of a partially resolved quartet. Significant multiplicity of CTA I and the hexamer was also confirmed in the spectral features of the C-2–C-5 (71–82 ppm) and the C-6 (66–61 ppm) region. In the C-2–C-5 region of these spectra, the predominant signals numbered three for both CTA I and the hexamer, in contrast to five for CTA II. In the C-6 region of the spectra, both CTA I and the hexamer show a single peak. Doublet splitting for the C-6 carbon of CTA II was also detected. Table 3 shows the close correspondence of chemical shifts of ring carbon between the hexamer and CTA I in the crystalline phase. From these results, it was suggested that the crystalline pentamer and hexamer both have the crystal CTA I lattice, which was confirmed by X-ray diffraction analyses.

X-ray diffraction.—In order to firmly establish the crystal structures of the oligomers suggested by solid-state NMR analysis, we measured X-ray powder diffractograms for the two allomorphs of CTA and for the CTA oligomers by the refraction method, the results of which are shown in Fig. 2. Heat treatment of the CTAs results in sharp and typical X-ray patterns [7] for CTA I and CTA II, respectively. CTA I gave three sharp equatorial diffractions at 11.6 ($2\theta = 7.6°$), 5.6 (15.9°), and 4.37 Å (20.3°), while CTA II gave strong diffractions at 10.48 ($2\theta = 8.4°$), 8.5 (10.4°), 6.7 (13.4°), 5.4 (16.3°), 5.3 (16.7°), 4.8 (18.6°), and 3.8 Å (23.4°). These diffraction spots of both crystalline CTAs were in complete agreement with those previously reported [7]. On the other hand, although the diffractograms of both the CTA dimer and the trimer show a number of sharp peaks, the number of diffractions of CTA oligomers decreased with an increase of their DP. The spots and relative intensities of diffractions detected on the crystalline CTA and on the oligomers (DP > 3) are summarized in Table 4 with their Miller indexes. In contrast to findings on the X-ray diffraction behavior of the dimer and trimer, many similarities were observed between the CTA oligomer (DP > 3) and CTA I. Three remarkably strong diffractions appear in the CTA oligomers (DP > 3) at approximately 11.6 ($2\theta = 7.6°$), 5.5 (16.1°), and 4.3 Å (20.3°), which correspond to the

(001), (202), and (500) plane for the crystal CTA I [7]. Although very weak diffractions are observed in some spots in the diffractograms of the tetramer and pentamer, there are no diffractions at these spots in CTA I or CTA II. Differences between the weak diffractions of the oligomers and those of CTAs may arise from an effect of the end-unit forms of these samples. CTAs are composed of a number of 2,3,6-tri-*O*-acetyl-β-D-glucose residues, while the reducing and nonreducing end of the oligomers are 1,2,3,6-tetra-*O*-acetyl-α-D-glucose residues and 2,3,4,6-tetra-*O*-acetyl-β-D-glucose residues, respectively. However, the pentamer and the hexamer gave approximately similar diffractograms for CTA I, and, notably, the hexamer was in complete agreement with CTA I in terms of interplanar spacing values and diffraction intensities, except in the case of a very weak diffraction at 10.1 Å (8.8°). On the basis of the X-ray analysis data considered in conjunction with the results of the ^{13}C CP/MAS spectra, it is evident that the crystal pentamer and hexamer have a crystalline CTA I lattice.

The assumption that CTA I is not at all obtained from the homogeneous acetylation of cellulose I, as well as from cellulose II, is now widely accepted [6], whereas our findings here prove clearly that crystal CTA oligomers (DP > 4) exhibit a crystalline CTA I structure despite the homogeneous acetylation of the corresponding cellooligosaccharides. To clarify any apparent contradiction with our previous study employing X-ray analysis [7] in which a mixed pattern of CTA I and CTA II was obtained from CTA prepared by heterogeneous acetylation of a previously acid-hydrolyzed cellulose II, one must consider that the proportions of the CTA I and CTA II were dependent on cellulose sources as well as on conditions for prehydrolysis of cellulose II [7]. Although the distinct relationship between the crystal structure of CTA and its DS has not yet been proved, our findings herein suggest that the crystal structure of oligomeric

Table 4
Interplanar spacing values (δ) and relative intensity of equatorial diffractions for CTA I, CTA II, and cellooligosaccharide peracetates (DP = 4–6)

Compound	2θ (°)	δ (Å)	Intensity [a]	Miller index [b]	Compound	2θ (°)	δ (Å)	Intensity [a]
CTA I	7.64	11.56	v.s.	(001)	pentamer	7.64	11.56	v.s.
	14.58	6.07	w.	(102)		8.75	10.09	w.
	15.90	5.57	v.s.	(202)		14.60	6.05	w.
	17.80	4.95	w.			15.92	5.55	v.s
	20.30	4.37	s.	(500)		17.76	4.97	w.
	22.37	3.97	w.	(103)		20.40	4.33	s.
	26.50	3.36	w.			22.65	3.90	w.
						25.17	3.51	w.
CTA II	8.43	10.48	v.s.	(110)				
	10.42	8.48	v.s.	(210)	tetramer	7.49	11.78	v.s.
	13.14	6.73	v.s.	(310)		9.56	9.23	w.
	16.28	5.44	s.	(410)		14.31	6.17	w.
	16.74	5.29	s.	(220)		15.91	5.55	v.s.
	18.59	4.77	s.	(320)		17.61	5.01	w.
	21.39	4.15	w.	(600)		18.19	4.85	w.
	23.39	3.80	s.	(130)		20.40	4.33	s.
	26.50	3.36	w.			22.60	3.91	w.
						23.61	3.74	w.
Hexamer	7.64	11.56	v.s.			24.12	3.66	s.
	8.75	10.09	w.			25.31	3.49	s.
	14.63	6.03	w.			28.70	3.08	w.
	15.91	5.55	v.s.					
	17.76	4.97	w.					
	20.35	4.34	s.					
	22.48	3.92	w.					
	26.42	3.34	w.					

[a] The abbreviations used are as follows: v.s., very strong; s., strong; w., weak.
[b] Previously reported value [7].

CTA, prepared by homogeneous acetylation, may be same as that of CTA I. We therefore conclude that the crystalline state of the CTA hexamer and pentamer is identified with the crystalline CTA I lattice. Further, the crystal hexamer would be a useful model for CTA I. Provided that the oligomers could be grown to appropriate crystal size, this single crystal could facilitate complete elucidation of the molecular order of CTA I.

3. Experimental

Preparation of CTAs and CTA oligomers.—CTA I and CTA II were prepared from CF-11 cellulose powder (Whatman International Ltd., UK) by mercerization of the cellulose powder, respectively, by heterogeneous acetylation using the method of Tanghe et al. [17]. The mercerization of the cellulose was carried out as follows: a 2 g sample of the cellulose powder was mixed at 20 °C in a solution of 20% (w/v) NaOH in water. After standing for 20 min, the powder was filtered, washed in a continuous stream of water for 1 h, and dried in vacuum overnight. The two allomorphs of CTAs were recrystallized by heat treatment under nitrogen at 210 °C for 15 min as previously described [7]. The DS of the CTAs were determined according to the usual method [18]. A 0.2 g sample was transferred to a flask containing 0.2 mol/L potassium hydroxide in 30 mL of 50% (v/v) aq MeOH at 23 °C. After 24 h 30 mL of 0.2 mol/L HCl was added, and after a further 30 min the solution was titrated with aq 0.1 mol/L NaOH, phenolphthalein being used an indicator.

α-Cellooligosaccharide acetates (DP = 2–6) were prepared from the corresponding cellooligosaccharides (Seikagaku Co., Japan) by homogeneous acetylation as follows: a 200 mg sample of the cellooligosaccharide was added to a mixture of 12 mL of pyridine and 8 mL of Ac_2O. After stirring at 100 °C for 3 h, the mixture was poured into ice water and filtered, and the water was evaporated. The oligomer acetate was obtained by recrystallization twice from 1:1 ethylacetate–hexane. All the products were assayed for homogeneity by TLC using Silica Gel 60 plates (E. Merck, Germany) with toluene–ethyl acetate in appropriate proportions.

General methods.—Fast-atom-bombardment mass spectra (FABMS) were obtained on a Joel JMX-HX110 mass spectrometer operated at 1.0 keV. The spectrometer was calibrated with cesium iodide, and samples were prepared by wetting the FABMS probe tip with 3-nitrobenzyl alcohol. Elemental analyses were carried out with a Hewlett–Packard model 185 analyzer. FTIR spectra were recorded on samples on KBr pellets on a Jasco FTIR-350 spectrometer at a resolution of 4 cm^{-1}. NMR spectral data were obtained on a Bruker MSL 400 spectrometer at 23 °C operating at 400 MHz for proton and at 100.6 MHz for carbon. The sample concentrations were ca. 10 mg/mL of $CDCl_3$. Double-quantum filtered ^1H–^1H-correlated spectroscopy (DQFCOSY) and total correlation spectroscopy (TOCSY) with a spin-lock time of 60 ms were used to assign ^1H resonances. Heteronuclear single quantum coherence (HSQC) and ^1H-decoupled multiple-bond heteronuclear multiple quantum coherence (HMBC) were used to assign ^{13}C resonances. All the NMR experiments were performed according to standard pulse sequences. Chemical shifts were reported in ppm from tetramethylsilane (TMS), with $CHCl_3$ as an internal reference. For ^1H NMR spectra, residual $CHCl_3$ was taken as 7.24 ppm. For ^{13}C NMR spectra, the center peak of the triplet resonance of $CDCl_3$ was taken as 77.0 ppm.

Solid-state ^{13}C NMR spectra.—Solid-state NMR spectra were recorded on the Bruker MSL 400 spectrometer in the usual way [21] by combining the techniques of CP, high-power proton decoupling, and MAS. All of those CP/MAS spectra were taken at 23 °C with a uniform set of parameters: 2 ms CP time and 3460–3800 Hz MAS frequency. The spectra were usually accumulated 2000–3000 times to achieve a reasonable signal-to-noise ratio. Chemical shifts were calibrated through the carbonyl carbon resonance of glycine as an external reference at 176.03 ppm and converted to values downfield from TMS (ppm).

X-ray diffraction analyses.—X-ray diffractograms were measured on a Rigaku Rint-2000 diffractometer by the refraction method

using nickel-filtered Cu K_α radiation operated in $\omega - 2\theta$ scanning mode between 5 and 30° (2θ). Slit systems were set at 1° for divergence, 0.15 mm for receiving, and 1° for scatter.

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