

Journal of Molecular Structure 355 (1995) 121-133



### Carbon-13 NMR studies of solid bisphenol-A alkanoates

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Received 1 March 1995; accepted 16 March 1995

### Abstract

Magic-angle spinning <sup>13</sup>C spectra are reported for six bisphenol-A alkanoates, usually with cross-polarisation. These reveal effects arising from crystallographic non-equivalence, molecular motion (phenylene ring-flipping) and non-crystalline forms. The data are complemented by DSC and solution-state NMR measurements. Apparently inhomogeneous ring-flipping for some of the compounds is discussed.

#### 1. Introduction

Bisphenol compounds are important components of a wide range of resins and polymers with considerable industrial use. The solid polymers themselves have been extensively studied by NMR, especially using the magic-angle spinning (MAS) technique [1-4]. Both their chemical microstructure and motion at the molecular level can be explored by NMR, though their generally amorphous nature frequently limits the amount of detail that can be obtained. Generally their glass transition temperatures are well above ambient, so that motional averaging of NMR interactions is far from complete. Recently, it has been shown [4] that NMR studies at high temperature (above  $T_g$ ) can significantly increase the chemical information available by improving the resolution attained.

In contrast to the polymer systems, monomeric bisphenol compounds have not been the subject

of so much study by NMR in the solid state, but we have embarked on a series of investigations of these materials. We have shown that both molecular motion and polymorphism influence the appearance of spectra, which are thus strongly dependent on the temperature of measurement.

The present paper deals with a series of bisphenol-A alkanoates I. The numbering scheme indicated in structure I will be used in this paper for discussion of the NMR, but a different notation



(a) Formate, R=H; (b) Acetate, R=CH<sub>3</sub>; (c) Propionate, R=CH<sub>3</sub>CH<sub>2</sub>; (d) iso-Butyrate, R=(CH<sub>3</sub>)<sub>2</sub>CH; (e) Pivalate, R=(CH<sub>3</sub>)<sub>3</sub>C; (f) n-Valerate, R=CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>.

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is used for X-ray work. In a previous paper [5] we have given some information about our work on **Ib** ( $\mathbf{R}$ =CH<sub>3</sub>). A principal aim for the study of the full series is to determine how the bulkiness of the alkyl groups influences motional processes, such as flipping of the phenylene rings. Other questions of interest are the conformations (both the mutual orientations of the rings and the orientation of the ester side-chains), the molecular symmetries in the crystalline environments, and polymorphism. In some cases quenching from high temperatures was used to promote the occurrence of amorphous (glassy) forms.

Carbon-13 MAS NMR is readily able to address matters of molecular structure for crystalline solids, making use of isotropic chemical shifts in much the same way as for NMR of solutions. A number of techniques can assist in assigning resonances to chemical sites. For instance, the dipolar dephasing experiment selects signals from quaternary and mobile carbons, the latter generally being in methyl groups [6]. Mobility also affects the process of cross-polarisation (CP), rendering it less efficient, so that comparison of CP spectra with those obtained by single pulse excitation (SPE) can be informative. The effectiveness of CP also depends on the contact time (CT) used, so that variation of CT and/or the use of delayed contact can be of value. As for molecular symmetry in the crystal site, simple information can be obtained from <sup>13</sup>C MAS NMR in favourable cases by counting the number of resonances — in principle this yields the number of atoms in the crystallographic asymmetric unit directly. Solution-state <sup>13</sup>C NMR spectra of the bisphenol-A alkanoates are relatively simple because of molecular motion (both inter- and intra-molecular). Both side-chain and ring-flipping motions are rapid on the NMR timescale. Therefore the two halves of each molecule are equivalent and only a single signal is seen for the four ring carbons ortho to the phenolic oxygens (and correspondingly for the meta carbons). For instance, for the formate Ia only seven <sup>13</sup>C signals are expected in the solution state: one C=O, one CH<sub>3</sub>, one aliphatic quaternary and four aromatic carbons (ipso, ortho, meta and para to the phenolic oxygens). The ortho and meta carbons will have ideal relative

intensities double those of the other aromatic signals. For the solid, however, even if the asymmetric unit consists of no more than a single molecule, four ortho-carbon signals will be observed in principle unless ring-flipping is rapid. Phenylene ring-flipping, however, is known to be detectable on the NMR timescale for a number of solid systems (see below).

In the present study, some use has been made of techniques other than MAS NMR of the solids. In particular, DSC measurements help in the understanding of crystallisation and possible polymorphism, while solution-state NMR can clarify some questions of spectral assignments. Moreover, brief details of the crystal structure of the pivalate **Ie**, obtained from X-ray diffraction studies, are given. In the discussions that follow, the numbering scheme of the structure **I** will be adopted for the central part of the molecules.

The crystal structures of a number of bisphenol-A compounds (and of related systems with hydrogen atoms replacing the central methyl groups) have been determined [7]. The dihedral angles which the phenylene rings make with the central C2-C1-C2' link vary considerably. In some cases the rings nearly eclipse the C1-CH<sub>3</sub> bonds whereas in others this is far from the case. Moreover, although for several systems the two halves of the molecule are related (or nearly related) by symmetry, in other compounds the two relevant dihedral angles are very different. For unsymmetrical cases, in principle, motional averaging causing coalescence of signals could occur via simultaneous phenvlene ring rotation to give a mirror-image conformation, involving dihedral angle changes of substantially less than 180°. However, for most compounds, rotations of at least  $120^{\circ}$  (if not the full ring-flip of 180°) would be required to completely average the four ortho sites, say. We have demonstrated [4] the existence of ring-flipping in bisphenol-A diglycidyl ether and shown that it is an apparently inhomogeneous process.

We have already published [5] the solid-state NMR spectra of the acetate Ib ( $R=CH_3$ ). We have shown that there are apparently two polymorphs and that the NMR spectra show considerable variation with temperature, attributable to molecular motion. The crystal structure of one of

the polymorphs was reported, and it was found that the asymmetric unit consisted of two entire molecules, so that in principle (in the absence of molecular motion) there should be eight resonances for the ortho sites (and correspondingly for the other carbons). The magnitudes of the relevant ring-to-central bond dihedral angles are 20.6° and 67.0° for one molecule and  $23.0^{\circ}/65.3^{\circ}$  for the other. Thus in each case one ring almost eclipses (within 9°) a Cl-CH<sub>3</sub> bond whereas the other is in a significantly different situation.

### 2. Experimental

### 2.1. Synthesis and purification

Compounds **Ib**, **Ic**, **Id** and **Ie** were prepared according to the general procedure outlined in our earlier publication [5]. The formate **Ia** was synthesised as follows: 1,3-dicyclohexylcarbodiimide (0.13 mol) was added to an ethyl acetate solution of bisphenol-A (44.0 mmol) and formic acid (0.10 mol) at room temperature and the mixture was stirred overnight. The white solid precipitate was filtered off and the remaining solution was concentrated. The crude product was purified by chromatography using a column of silica gel eluted with a solution of *n*-hexane/diethyl ether (3:1). The product (9.5 g) was obtained as white crystals. The valerate **If** was prepared analogously, using valeric acid in place of formic acid.

Compounds Ia, Ic, Id and Ie were crystallised by slow evaporation at room temperature from a solution of  $Et_2O/n$ -pentane. However, all attempts to crystallise If (R=Bu<sup>n</sup>) failed, and the NMR experiments were carried out on a sample of glassy solid obtained by freezing the viscous liquid at  $-50^{\circ}C$ .

### 2.2. Differential scanning calorimetry

The DSC traces were obtained using a Perkin Elmer DSC7 calorimeter. In a typical experimental session a sample of approximately 10 mg was heated at a rate of  $10^{\circ}$ C min<sup>-1</sup> and kept for 10 min  $10-15^{\circ}$ C above the melting point.

Afterwards, the sample was quenched at  $200^{\circ}$ C min<sup>-1</sup> to  $-60^{\circ}$ C, held at that temperature for 10 min and then reheated above the melting point with a scanning rate in the range  $2-10^{\circ}$ C min<sup>-1</sup>. The heating and quenching runs were repeated several times in order to observe a reproducible thermal behaviour of the solid. The integration of the peaks supplied the enthalpies of rearrangement and fusion observed in the solids.

#### 2.3. Solution-state NMR

The samples were dissolved in  $CDCl_3$  and spectra were recorded using a Varian Gemini spectrometer operating at 199.97 MHz (<sup>1</sup>H) and 50.29 MHz (<sup>13</sup>C). The <sup>13</sup>C peak assignments were based on chemical shifts for similar compounds [8] and were substantiated by DEPT experiments. As usual, shifts are reported relative to the signals for tetramethylsilane (TMS), using the highfrequency-positive convention.

### 2.4. Solid-state NMR

Magic-angle spinning spectra were obtained using a Bruker CXP300 spectrometer, operating at 75.45 MHz for carbon-13. The crystalline samples were finely ground and packed into a 7 mm o.d. zirconia rotor. Spin rates were of the order of 3-4 kHz and where necessary spinning sidebands were recognised by the effects of changing the spinning rate. The <sup>1</sup>H pulse duration for a 90° flip angle was 5  $\mu$ s, which was also the value for <sup>13</sup>C as set by the Hartmann-Hahn condition. For cross-polarisation contact times were generally set at  $\approx 3$  ms though in some instances a wide variation was used. Recycle delays for CP were  $\approx 5$  s. Hartmann-Hahn matching became difficult to set for situations where mobility was high [5]. For SPE substantially longer recycle delays ( $\approx 30$  s) were necessary. The number of transients required to achieve good S/N varied with the circumstances but was typically between 200 and 500. The spectrometer was equipped with a BVT-1000 variable temperature device. The low temperatures were obtained by a flow of dry nitrogen precooled in a heat exchanger immersed in

R	Crystalline		Quenched		Quenched		Quenched	
	m.p.(°C)	(J/g)	$T_{g}(^{\circ}C)$	(J/g °C)	$T_{\text{rearr}}$ (°C)	(J/g)	m.p.(°C)	(J/g)
н	101	114	-29	0.89	36	-92	98	112
Me	93	96	-13	0.59	15	-40	81	89
Et	50	86	-29	0.38	_	-	49 <sup>a</sup>	39 <sup>a</sup>
<i>i</i> -Pr	78	64	-35	0.38	15	-38	78	64
t-Bu	129	69	-17	0.67	24	-9	121	53

 Table 1

 DSC information for the bisphenol-A alkanoates

<sup>a</sup> From the melted solid slowly crystallised at room temperature.

liquid nitrogen. They were calibrated using the shifts of samarium acetate resonances [9]. High temperatures were obtained by direct heating of the air flow used to spin the sample and were calibrated [10] using the proton shifts of ethylene glycol absorbed in an inert material filling the 7 mm o.d. ZrO<sub>2</sub> rotor which was spun at 3.5 kHz. In the range 233-343 K calibrated temperatures did not differ from the nominal ones by more than  $\pm 5^{\circ}$ , whereas above that range real temperatures are below nominal. In this paper, nominal temperatures are given throughout. Dipolar dephasing experiments were used to confirm peak assignments to quaternary carbons and mobile methyl groups. Chemical shifts are quoted with respect to TMS as for the solution state <sup>13</sup>C data. but they are measured via the signal for adamantane at 29.4 ppm (by replacement).

### 2.5. X-ray diffraction

The crystal structure of the pivalate Ie was determined by the X-ray Structural Center (INEOS) of Moscow on a crystal  $0.5 \times 0.3 \times$  $0.1 \text{ mm}^3$  using a Siemens P3/PC diffractometer with MoK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). The value of F(000) was 428. Of 2853 independent reflections collected at 293 K, 1230 were used in calculations (having  $|F| > 4.0\sigma(F)$ ). The final agreement index was R = 9.86% (observed data), wR = 11.28%, maximum  $\Delta/\sigma = 0.010$ . The final difference Fourier map features were 0.42 to -0.30 e Å<sup>-3</sup>. Details of the X-ray determination and the structural parameters have been deposited at the Cambridge Crystallographic Data Centre.

### 3. Results

# 3.1. Differential scanning calorimetry and related matters

Table 1 gives information about the melting points, glass transition temperatures and other significant events. The enthalpies of fusion are listed and show a general decrease with perceived steric hindrance from the alkyl substituent. However, the DSC traces do not show any simple correlation between substituent bulk and the melting point, although increasing chain length is associated with a lowering of the m.p. (culminating in the difficulty experienced in attempting to crystallise the *n*-valerate, If, referred to above). Moreover, a melted sample of the propionate Ic (R=Et) remained liquid for approximately 15 min at ambient temperature before recrystallising, and a sample frozen (cooling rate  $200^{\circ}$ C min<sup>-1</sup>) to  $-60^{\circ}$ C gave rise to a glassy solid, which, in DSC measurements, showed only a transition point at  $-27^{\circ}C$  and not a normal fusion peak. This behaviour may be attributed to the high mobility of the ethyl group, which perhaps inhibits the process of ordered molecular packing. The difficulty of producing a crystalline form of the *n*-valerate, If, is probably a related phenomenon. In fact all the samples could be obtained as glassy solids by rapidly quenching from the melt.



Fig. 1. DSC traces for bisphenol-A formate Ia: (a) Crystalline form; (b) Quenched form (cooled from the melt to  $-40^{\circ}$ C at 200°C min<sup>-1</sup>). The scan rate was 20°C min<sup>-1</sup> for (a) and 10°C min<sup>-1</sup> for (b). Trace (b) shows the small endotherm at  $T_g = -29^{\circ}$ C and a strong crystallisation exotherm at 41°C before the melting point at 101°C. Note: The scales of (a) and (b) differ.

These quenched samples (except for the *n*-valerate **If**, which was not tested in this way) gave DSC traces which indicated glass transition temperatures below room temperature. The DSC plots also showed (with the exception of the propionate, **Ic**,) an exothermic rearrangement at about room temperature or a little above, following which

melting occurred for Ia, Ib and Ie at temperatures slightly below the ones shown by the original crystalline materials, presumably indicating some residual disorder in the quenched samples (see Fig. 1). Indeed, for the pivalate Ie a sample quickly crystallised in the DSC showed two melting endotherms approximately 3°C apart, probably because of a disordered fraction in the solid (since the ratio of the two peaks depended on the conditions of the crystallisation). However, no depression in the eventual melting point was seen for the quenched isobutyrate Id, suggesting that the original crystalline form had been fully restored, whereas in contrast there was no apparent melting endotherm from the quenched propionate Ic, as expected because of the lack of exothermic crystallisation.

### 3.2. Crystal structure of bisphenol-A pivalate, le

The pivalate crystallises (habit: colourless plates) in the monoclinic system, with space group  $P2_1$ . The unit cell dimensions are a = 6.427(3), b = 10.297(3), c = 17.747(4) Å,  $\beta = 96.27(2)^{\circ}$ , with two molecules in the unit cell, giving a calculated density of 1.128 g cm<sup>-3</sup> and a unit cell volume of 1167.5 Å<sup>3</sup>. Unlike the methyl system, there is only one molecule in the asymmetric unit (Fig. 2)<sup>1</sup>. Atomic coordinates are listed in Table 2 and bond lengths given in Table 3. The two aromatic rings are substantially twisted from each other, as can be seen from Table 4. One ring almost eclipses

<sup>&</sup>lt;sup>1</sup> The atomic numbering scheme for the crystal structure differs from that in the rest of this article.



Fig. 2. Molecular structure of bisphenol-A pivalate Ie, obtained from single-crystal X-ray diffraction measurements.

Table 3

Table 2 Atomic coordinates<sup>a</sup> (×10<sup>4</sup>) and equivalent isotropic displacement coefficients ( $\mathring{A}^2 \times 10^3$ ) for bisphenol-A pivalate, **le** 

_	x	у	Z	$U (eq)^{b}$
O(1)	9027(26)	-2493(22)	5829(7)	179(8)
O(2)	6397(19)	-1283(19)	5502(5)	136(6)
O(3)	9404(10)	-70(17)	10987(3)	103(4)
O(4)	12214(12)	543(20)	10527(5)	152(7)
C(1)	9970(46)	-2402(46)	4399(9)	379(37)
C(2)	7697(65)	-904(34)	4098(16)	296(29)
C(3)	6430(40)	-2640(38)	4102(12)	285(23)
C(4)	8083(21)	-1971(19)	4499(6)	79(5)
C(5)	7800(26)	-1887(23)	5356(10)	105(7)
C(6)	5896(18)	-1118(16)	6260(5)	61(4)
C(7)	4072(20)	-1620(16)	6409(5)	68(4)
C(8)	3332(15)	-1297(15)	7105(5)	57(4)
C(9)	4408(13)	-473(14)	7611(4)	39(3)
C(10)	6309(13)	-13(15)	7426(5)	49(3)
C(11)	7041(15)	-308(14)	6748(5)	56(4)
C(12)	3552(11)	0	8338(4)	44(3)
C(13)	1760(13)	-881(16)	8542(5)	63(4)
C(14)	2617(16)	1372(15)	8150(6)	61(4)
C(15)	5259(12)	70(15)	8992(4)	37(3)
C(16)	5946(15)	1217(17)	9371(5)	63(4)
C(17)	7420(19)	1093(20)	10006(6)	82(6)
C(18)	8166(14)	-42(21)	10285(5)	68(5)
C(19)	7618(14)	-1157(16)	9919(5)	52(4)
C(20)	6192(15)	-1089(15)	9273(5)	49(4)
C(21)	11385(14)	202(17)	11047(5)	56(4)
C(22)	12413(11)	109(15)	11869(4)	39(3)
C(23)	11844(20)	-1209(16)	12188(7)	75(5)
C(24)	14763(14)	214(17)	11866(6)	68(4)
C(25)	11609(22)	1200(17)	12320(7)	83(5)

<sup>a</sup> Using the numbering scheme of Fig. 1.

<sup>b</sup> Equivalent isotropic U defined as one third of the trace of the orthogonalised  $U_{ii}$  tensor.

one of the central methyl groups, whereas the other is nearly at right angles to the same methyl. For both moieties the OCO plane is considerably twisted from the adjacent ring and the carbonyl oxygen points towards the ring, with the Bu<sup>t</sup> group stretched outward from the ring. However, the methyl carbons of one of the *t*-butyl groups are disordered, suggesting relatively facile internal rotation.

### 3.3. Solution-state NMR spectra

Proton spectra were recorded largely to check the purity of the samples, and details are not given here. Carbon-13 solution-state NMR data

Bond lengths <sup>a</sup> (Å) for bisphenol-A pivalate, Ie								
O(1)-C(5)	1.253(25)	O(2)-C(5)	1.14					
O(2)–C(6)	1.428(14)	O(3) - C(18)	1.40					
O(3)–C(21)	1.297(12)	O(4) - C(21)	1.16					
C(1)–C(4)	1.321(35)	C(2)-C(4)	1.31					

18(25) 15(10) 18(15)

J(3) = C(21)	1.297(12)	O(4) - O(21)	1.100(15)
C(1)–C(4)	1.321(35)	C(2) - C(4)	1.317(37)
C(3)–C(4)	1.391(32)	C(4) - C(5)	1.555(21)
C(6)–C(7)	1.333(18)	C(6)-C(11)	1.359(17)
C(7)-C(8)	1.411(15)	C(8)–C(9)	1.367(16)
C(9)–C(10)	1.383(13)	C(9)-C(12)	1.536(12)
C(10)-C(11)	1.372(13)	C(12) - C(13)	1.540(14)
C(12)-C(14)	1.557(15)	C(12)-C(15)	1.510(10)
C(15)-C(16)	1.406(20)	C(15)-C(20)	1.402(19)
C(16)-C(17)	1.397(14)	C(17)-C(18)	1.337(27)
C(18)–C(19)	1.347(24)	C(19)-C(20)	1.389(12)
C(21)-C(22)	1.538(12)	C(22)-C(23)	1.530(21)
C(22)–C(24)	1.514(12)	C(22)-C(25)	1.503(20)

<sup>a</sup> Using the numbering scheme of Fig. 1.

are, however, given in Tables 5 and 6. The variations of the ring-carbon and central  $CMe_2$  shifts are not significant. The carbonyl shifts increase from Ia to Ib and then increase further with the connectivity of the carbon bonded to C=O, as is usual for alkanoic acids and their esters [11]. The shifts of the alkyl substituents are unremarkable.

## 3.4. Solid-state carbon-13 NMR spectra of the crystalline samples

### (a) Evidence of the non-aromatic carbons (Table 5)

For the formate **Ia** a pair of peaks of equal intensity is seen for the central methyls under all circumstances, suggesting that the two halves of the molecule are not related by symmetry in the

Table 4							
Selected	torsional	angles <sup>a</sup>	(deg)	for	bisphenol-A	pivalate.	Ie

Ring 1	Angle	Ring 2	Angle
C8C9C12C13	18.1	C13C12C15C16	-120.3
C8C9C12C14	-98.4	C13C12C15C20	57.0
C8C9C12C15	141.3	C14C12C15C16	-1.3
C10C9C12C13	-165.0	C14C12C15C20	176.0
C10C9C12C14	78.5	C9C12C15C16	116.1
C10C9C12C15	-41.9	C9C12C15C20	-66.6
C5O2C6C7	-115.7	C21O3C18C17	-81.7
C5O2C6C11	75.3	C21O3C18C19	102.8
C6O2C5O1	1.6	C18O3C21O4	3.7
C6O2C5C4	179.2	C18O3C21C22	180.0

<sup>a</sup> Using the numbering scheme of Fig. 1.

Table 5 Carbon-13 chemical shifts (expressed as  $\delta$ /ppm) for solutions in CDCl<sub>3</sub> of the bisphenol-A alkanoates (except for the alkyl resonances)<sup>a</sup>

R	н	Me <sup>b</sup>	Et	Pr <sup>i</sup>	Bu <sup>t</sup>	Bu <sup>n</sup>
Cl	42.8	42.5	42.3	42.4	42.4	42.9
C2	148.4	147.8	147.9	148.0	147.9	148.2
C4/C6	128.6	127.8	127.9	127.9	127.9	128.2
C3/C7	121.1	121.0	121.0	121.1	121.0	121.4
C5	148.9	148.8	148.8	149.1	149.2	149.2
C8	160.0	169.1	173.6	175.9	177.5	172.7
C9/C10	31.1	31.0	30.8	30.9	30.9	31.4

<sup>a</sup> See structure I, noting that in solution the primed atoms are indistinguishable from those unprimed.

<sup>b</sup> Ref. [5].

crystal and so the asymmetric unit is the whole molecule. The carbonyl carbons likewise give a pair of peaks, but these are often of substantially unequal intensity (Fig. 3): the one at high frequency has the greater intensity when CP is used with short contact times. However, under longer contact conditions (>30 ms) at elevated temperature (353 K), the lines become equal in intensity (Fig. 4). Moreover, at the same temperature, under SPE conditions with short recycle delays (<30 s), the low frequency peak is substantially the more intense (though this may arise from a new mobile phase — see below). These facts point to a very considerable difference in intramolecular mobility at the two ends of the molecule, but we have not been able to quantify this difference. An alternative explanation for the appearance of peaks of unequal intensity is that there may be two different crystallographic sites for the molecule (with different abundances), but variations in

Table 6

Carbon-13 chemical shifts (expressed as  $\delta$ /ppm) for the alkyl substituents of the bisphenol-A alkanoates in solution in CDCl<sub>3</sub>

Position <sup>a</sup>	Me	Et	Pr <sup>i</sup>	Bu <sup>t</sup>	Bu <sup>n</sup>
α-C	21.0	27.6	34.0 <sup>b</sup>	38.9 <sup>c</sup>	34.6
β <b>-</b> C		8.8	18.8	27.0	22.7
$\gamma$ -C					27.5
δ-C					14.1

<sup>a</sup> With respect to the carbonyl group.

<sup>b</sup> CH.

° Quaternary carbon.



Fig. 3. Carbon-13 CPMAS spectra of bisphenol-A formate Ia (aromatic and carboxylic region only): (a) At ambient temperature (298 K); (b) at 313 K; (c) at 333 K. This shows the changes in the aromatic CH region caused by molecular motion. Spectrometer operating conditions: Contact time 2 ms; recycle delay 3 s; number of transients 200(a), 251(b), 344(c); spin rate 3.95 kHz (a), 3.85 kHz(b), (c).

mobility would still be required and it should be noted that C1 displays a single sharp signal under all conditions.



Fig. 4. Carbon-13 MAS spectra of bisphenol-A formate Ia (aromatic and carboxylic region only) at 353 K, showing the effect of contact time (CT) and of SPE operation: (a) CP, CT = 2 ms; (b) CP, CT = 15 ms; (c) CP, CT = 45 ms; (d) SPE. The asterisks indicate peaks arising from compound degradation. Spectrometer operating conditions: recycle delay 3 s (a), (b) and (c), 4 s (d); number of transients 400(a),(b) and (c), 300(d); spin rate 3.8 kHz.

NMR data for two polymorphs of the acetate Ib have been reported previously. The crystal structure of one of these (form I) has been determined, and the asymmetric unit was found to consist of two molecules. The <sup>13</sup>C NMR is correspondingly complex. Thus, whereas C1 still appears to give a single resonance, there are four peaks of apparently unequal intensity assignable to C9/C10 and two of very different intensity ascribed to C8/C8'. Some of the variability in intensity may be a function of contact time and/or spinning speed (via spinning sidebands). The second polymorph (form II) gives a far simpler spectrum, with only a single peak for each of the non-aromatic carbons, suggesting that the asymmetric unit is only half a molecule. The resonance frequencies for this second form are very close to those for a solution in  $CDCl_3$ .

The propionate Ic shows (Fig. 5) two equallyintense carboxyl (C8/C8') signals, and a single resonance for C1, but the CH<sub>2</sub> region overlaps the C9/C10 region, complicating detailed



Fig. 5. Carbon-13 MAS spectra of bisphenol-A propionate Ic: (a) CP at ambient probe temperature, contact time 5 ms; (b) SPE at 325 K. Spectrum (b) shows peaks due to the crystalline phase ( $\Delta$ ), a mobile phase (+) and the melt (×). Spinning sidebands in (a) are indicated by asterisks. Spectrometer operating conditions: Recycle delay 3 s(a), 4 s(b); number of transients 200(a), 400(b); spin rate, 4.1 kHz.



Fig. 6. Carbon-13 CPMAS spectra of bisphenol-A isobutyrate Id: (a) 298 K; (b) 265 K; (c) 253 K. These show, in particular, the influence of ring-flipping. Asterisks indicate spinning sidebands. Spectrometer operating conditions: Contact time 5 ms(a), 3 ms(b) and (c); recycle delay 3 s; number of transients 300(a), 200(b) and (c); spin rate 4.3 kHz(a), 2.9 kHz(b) and (c).

interpretation. However, the indications are that the asymmetric unit is a whole molecule.

At room temperature the  ${}^{13}C$  spectrum of the isobutyrate Id (Fig. 6) shows single signals for



Fig. 7. Carbon-13 CPMAS spectra of bisphenol-A pivalate **Ie** (aromatic CH region only), showing the effect of ring-flipping: (a) 273 K; (b)  $\approx 298$  K; (c) 306 K. The asterisks indicate spinning sidebands. Spectrometer operating conditions: Contact time 2 ms(a), 5 ms(b) and (c); recycle delay 3 s; number of transients 200(a), 400(b), 1000(c); spin rate 3.0 kHz(a) and (b), 4.3 kHz(c).

Table 7

NMR chemical shifts (expressed in  $\delta$ /ppm) for the non-aromatic and quaternary aromatic carbons of the solid bisphenol-A alkanoates

	Н	Ме	Et	Pr <sup>i</sup>	Bu <sup>t</sup>	Bu <sup>n f</sup>
CI	43.5	42.0	40.8	42.8	42.7	42.2 43.0
C2/C2 <sup>′ c</sup>	147.2 148.3	144.7 146.0	146.8 147.6	149.0	146.3 149.7 <sup>b</sup>	148.4 <sup>e</sup>
C5/C5'°	149.3 150.1	147.7 148.7 150 1	149.0 <sup>a</sup>	150.2	149.7	148.4 <sup>e</sup>
C8/C8′	160.6 162.1	168.3 169.0	173.8 174.6	175.1	175.0 175.5	170.8 171.6
C9/C10	30.6 32.2	171.4 29.0 31.0	28.7	31.3	30.5 34.1	30.5
α <b>-</b> C	_	32.2 20.9 21.7 <sup>d</sup>	27.5	34.2	38.7	34.1
β-C		21.7	9.1 10.4	18.4 20.1	27.6	26.8
γ-C δ-C						22.3 14.2

<sup>a</sup> Double the intensity of each C2/C2' peak.

<sup>b</sup> See the text.

 $^{\rm c}$  In some cases there is ambiguity about the assignments to C2/C2' and C5/C5'.

<sup>d</sup> Intensity  $\approx$  3 times that of the peak at  $\delta$  20.9

<sup>e</sup> Not resolved at 173 K.

<sup>f</sup> At 223 K.

C1, C8/C8' and C9/C10, suggesting the asymmetric unit is half a molecule. However, a CP spectrum at  $-70^{\circ}$ C shows a narrow splitting into two components for C1 and apparently four overlapping resonances for C8/C8', which hints at an asymmetric unit of two molecules. Clearly there is motional averaging at room temperature which affects the whole molecule.

For the pivalate **Ie** the crystal structure shows that the asymmetric unit is a whole molecule. The isopropylidenic methyls C9/C10 give a well-spaced pair of lines. This is presumably the result of different orientations of the phenylene rings in relation to the methyls, as revealed by the structure determined using X-ray diffraction. The quaternary carbon C1 gives rise to a single resonance as expected. However, whereas C8/C8' shows two signals, the one at high frequency is distinctly more intense than the other, possibly for reasons of CP efficiency as for Ic (though spectra with contact times 5 ms and 30 ms show similar relative intensities for these signals).

The aliphatic side-chain resonances are, on the whole, less informative. The <sup>13</sup>C shifts are reported in Table 7, using the notation  $\alpha$ ,  $\beta$  etc. to refer to the position of the relevant carbon with respect to the carbonyl group. For the isobutyrate Id the existence of two  $\beta$ -CH<sub>3</sub> signals at room temperature shows the two methyls on the same Pr<sup>1</sup> group have non-equivalent environments. At low temperature, the  $\delta 18.4$  peak splits into two (Fig. 6(b) and (c)), confirming that there is an averaging process that is rapid on the NMR timescale at room temperature. Surprisingly, the methyls of the *t*-butyl group of **Ie** give rise to a single peak under all conditions. Thus, not only does this imply no observable difference between the two halves of the molecule, but it also suggests rapid reorientation of each t-butyl group about the C(O)-C axis. The disorder for the methyls of one t-butyl group detected by the X-ray study is consistent with this implication. Of course if the motion is by 120° jumps, it would not be detectable by X-ray diffraction.

### (b) Evidence of the quaternary aromatic carbons

Chemical shifts for C2/C2' and C5/C5' in the crystalline samples are given in Table 7. These resonances are sufficiently close together that assignment and interpretation are sometimes difficult. However, in general they confirm the conclusions obtained from the non-aromatic carbons regarding the asymmetric units. Thus, for the formate Ia four signals are seen (Fig. 3), which is consistent with the asymmetric unit being one molecule. Admittedly the resonances are of distinctly different intensity, but this is at least partly accounted for by the variations in shielding anisotropy causing differences in spinning sideband intensities. However, the alternative suggestion for the appearance of peaks of unequal intensity, mentioned above, should be borne in mind. The relevant centreband region for the acetate form Ib (polymorphic form I) is complex, with at least five resolved peaks, as reported earlier. For the second polymorph only two signals were observed. The propionate Ic showed three peaks (Fig. 5), with one at least twice the intensity of the others. The isobutyrate **Id** gives only two peaks in the appropriate region (Fig. 6), the high frequency one being of substantially greater intensity. The low frequency lineshape is not simple and this peak shows a distinct incipient splitting at low temperatures. In the case of the pivalate **Ie** only two peaks are seen between  $\delta 140$  and  $\delta 160$ , with the low frequency one much less intense than the other. Since we know the asymmetric unit is one molecule, it is likely that only half the C2/C2' resonance is at  $\delta 146.3$ , the other half being hidden by the C5/C5' band at  $\delta 149.7$ .

### (c) Evidence of the aromatic CH carbons

Motion of the phenylene rings will affect the appearance of the signals for the eight CH aromatic carbons in each molecule. It is expected that variable-temperature spectra may prove informative, and we have shown previously [12] that for bisphenol-F diglycidyl ether (and probably also for **Ib**) motion of the rings is spatially inhomogeneous. The effect of such motion can be observed in principle for a two-site system by the appearance of a line between the low-temperature doublet peaks which augments in relative intensity as temperature increases, in contrast to the more usual coalescence phenomenon [13].

For the formate Ia the aromatic CH region (corresponding to eight non-equivalent carbons if the asymmetric unit is one molecule) consists of six peaks (Fig. 3), one of which is noticeably more intense than the others, at ambient probe temperature. As T increases to 353 K (nominal) these coalesce to give a doublet at high frequency  $(\delta = 127.0 \text{ and } 130.2)$  and an intense singlet to lower frequency ( $\delta = 121.9$ ). Remarkably, in this process the three peaks mentioned do not appear to have shifted, but those at  $\delta$ 132.5, 125.9 and 124.0 have disappeared. Moreover, the quaternary aromatic resonances remain essentially unchanged over this temperature range so that the asymmetric unit remains a complete molecule. At 353 K a small peak appears (Fig. 4(a)) at  $\delta$ 128.5 (between the doublet), which is barely visible with a contact time of 1 ms but appears much more intensely when this is increased to 45 ms (Fig. 4(c)), when, in addition a small sharp shoulder is seen at  $\delta 121.0$ ,

together with a sharp peak at  $\delta \approx 115.5$ . At the same temperature a SPE spectrum with a short recycle delay (4 s) shows (Fig. 4(d)) only three peaks in the range  $\delta 110-140$ , at  $\delta = 115.6$ , 121.0 and 128.4. The ones at 121.0 and 128.4 ppm are close to those seen for a solution in CDCl<sub>3</sub>, and the whole phenomenon is reminiscent of the observations on bisphenol-F diglycidyl ether reported earlier. This suggests spatially inhomogeneous motions of the phenylene rings which average the environments of  $C_3/C_3'/C_7/C_7'$  (and correspondingly of C4/C4'/C6/C6'). We cannot account for the signal at  $\delta = 115.6$  in terms of structure Ia, but believes it arises from degradation caused by the heating. Such degradation did not occur for the other samples.

The variable-temperature spectra of the acetate **Ib** (polymorphic form **I**) have been described already. They show similar phenomena but are more complex than for **Ia** because of the larger asymmetric unit for **Ib** and because of its polymorphism.

Room-temperature spectra for the propionate Ic show (Fig. 5(a)) an intense peak at  $\delta 123.0$ , which we assign to C4/C4'/C6/C6', with three signals ( $\delta = 129.7$ , 125.5 and 124.6, the firstmentioned being more intense than the others) assignable to C3/C3'/C7/C7'. This is, in our view, good evidence that the asymmetric unit is one molecule. When the temperature is increased to 320 K the peaks at 129.7, 125.5 and 124.6 broaden somewhat and decrease in intensity, and a sharp peak appears at  $\delta = 127.7$ . Single pulse experiments (Fig. 5(b)) show mainly sharp signals at  $\delta = 121.2$  and 127.7. The interpretation is analogous to that for Ia, but the temperature required for motional effects to be observed is lower for Ic. The isobutyrate Id behaves rather differently. At room temperature the aromatic CH carbons show (Fig. 6(a)) two broad peaks at  $\delta = 121.7$  and 128.4. The significant changes in the spectrum occur below room temperature. As the temperature is lowered the peak at 121.7 ppm sharpens slightly (Fig. 6(b) and (c)), and the situation at room temperature for this carbon may result from MAS or decoupling modulating a motional effect. By contrast, the peak at 128.4 ppm broadens further below room temperature (Fig. 6(b) and (c)) and eventually splits into two ( $\delta = 127.5$  and 132.5 at 253 K). This can be treated as a classical decoalescence phenomenon arising from rotation of the phenylene ring. Simulation with a two-site exchange model [14] yields an activation energy of  $50.3 \text{ kJ mol}^{-1}$ , which is in line with values for similar systems [15]. The appearance of the spectrum of the aromatic CH carbons for the pivalate Ie at 298 K (Fig. 7) is similar to that observed for Id at 253 K, with peaks at  $\delta = 121.6$  (double intensity), 127.6 and 130.1. Heating to 303 K causes coalescence of the latter two, indicating phenylene ring flips with a higher activation energy for the pivalate than for the isobutyrate. Treatment on a classical coalescence basis, however, does not provide such a good fit to the spectra for Ie as for Id. Conversely, decreasing the temperature to 272 K not only causes further sharpening of the signals at 127.6 and 130.1 ppm but also splits the other band into two ( $\delta = 122.3$  and 123.4).

The observations of apparent "classical" coalescence/decoalescence involving ring-flipping for Id and Ie raises the question of the nature of the supposedly inhomogeneous processes reported for Ib and now for Ia and Ic also. There are three possible origins of the effects observed:

- (a) a genuinely inhomogeneous process, with populations of mobile molecules increasing with temperature because activated creation of such a mobile fraction is required;
- (b) a similar process but involving a polymorphic change to a mobile phase;
- (c) melting of part of the sample because of temperature gradients (and/or pressure gradients) across the rotor.

We are unable to come to an absolutely unequivocal conclusion on this matter but we believe (c) is unlikely because, in the case of the propionate, measurements near the melting point (Fig. 5(b)) using SPE show not only sharp peaks from a mobile (presumably solid) phase, but also *additional* signals assigned to C1 and C9/C10 which are significantly shifted but which are at frequencies very close to those of the CDCl<sub>3</sub> solution. Note that for this system the DSC gives no indication of any rearrangements above  $0^{\circ}$ C until the melting point. Moreover, four other observations further support conclusions (a) or (b). Firstly, it is possible

to cross-polarise to the "averaged" peaks in the spectrum of the acetate Ib, as reported earlier. Secondly, the apparently inhomogeneous averaging process for the formate Ia can be seen to commence  $\approx 30^{\circ}$  below the melting point for modest spinning speeds, e.g. 3.8 kHz (and this compound has the highest heat of fusion in the series). Thirdly, the DSC shows that rearrangements do occur for Ia and Ib between 0°C and the melting point (though these do not correlate well with the spectral changes). Finally, we have observed that, in cases where a substantial fraction of a sample has melted (i.e. at about the m.p.), magic-angle spinning becomes unstable, but this did not normally occur in the cases considered here. However, in addition to the fact that Id and Ie do not show the inhomogeneous phenomenon, a contrary view to the above arises from the similarity of the high-temperature solid-state spectra of Ia and Ib to those of the solution state. We plan further experiments in an attempt to resolve this question, but believe the present evidence is in favour of a genuine inhomogeneous process.

It will be noted from the data quoted above that the splitting of the C3/C7 signals below coalescence, arising from the conformational influence of the two substituents on the phenylene ring, is in the range 3–5 ppm, whereas for the only compound (Ie) showing a non-equivalence for the C4/C6 pair of nuclei it is only  $\approx 1.5$  ppm. This observation is in line with literature results for condensed bisphenol-A compounds and suggests a major influence arising from the second phenylene group.

Our observations of motional processes in the bisphenol-A alkanoates should be set in the context of related studies in the literature. Thus Schaefer et al. investigated molecular motion in bisphenol-A polycarbonate and other polymers containing aromatic groups using NMR methods [16]. They concluded that the dominant motions are indeed  $180^{\circ}$  ring-flips, occurring over a broad range of frequencies, but that these are super-imposed on  $30^{\circ}$  ring oscillations about the same axes. Chemical changes reduced motion, in some cases preventing a fraction of the rings from flipping. They considered that rotational freedom of the phenylene rings, predicted to be nearly free in

isolated molecules, is partially blocked by adjacent chains in the solid glassy polymers. Further theoretical work by Yaris and co-workers [17] confirmed that flexibility in the lattice provides a mechanism which allows the rings to flip and computer simulations were extended to the simpler case of benzene [18]. Our own studies certainly show that the motional phenomena encountered in polymeric systems are also found in molecular systems. It should also be noted that Luss and Henrichs [19] have proposed that in bisphenol-A diphenyl carbonate the carbonyl groups interact strongly with neighbouring molecules, thus acting as a turnstile with respect to ring motion. When the carbonate group becomes distorted, the turnstile opens and ring-flipping takes place. The implication of all these studies is that mobility in the rest of the molecule, and in the lattice as a whole, is required to account for the observed effects of ring-flipping on NMR spectra. This in turn suggests that substituent bulk will have a substantial influence, as our results testify.

### 3.5. Solid-state <sup>13</sup>C NMR of the quenched samples

Data for the *n*-valerate If are included in Table 5. This system could not be obtained in crystalline form and it was necessary to cool below 0°C to get reasonable CP spectra. At 173 K resonances were seen for most carbon sites, though only a single peak was found for the quaternary carbons C2, C2', C5 and C5'. Signals for the aromatic CH carbons were broad, in the region  $\delta =$ 120–130, a maximum at  $\delta$ 121.0 being attributed to C3/C3'/C7/C7'. No peak from C9/C10 can be seen, though a broad band would be obscured by signals from the Bu<sup>n</sup> groups. As the temperature is increased to 223 K a strong C9/C10 signal emerges, and its apparent absence at lower temperatures probably involves modulation of the carbonproton dipolar interaction by the MAS or proton decoupling in conjunction with C-CH<sub>3</sub> internal rotation. The aromatic CH signals are less visible at 223 K than at 173 K, perhaps for motional reasons, whereas the C1 and C8/C8' resonances each become doublets, which may indicate lack of molecular symmetry.

The only other compound to be studied in the

quenched state was the pivalate Ie. At room temperature, the ring CH carbons already show only two relatively narrow bands, indicating a small lowering in the barrier to ring-flipping compared to the crystalline material. At low temperatures (e.g. 223 K), however, the flipping is slowed even for the quenched samples. The major differences between the crystalline and quenched samples are (a) the apparent lack of a peak at  $\delta = 146.3$  in the latter, and (b) the appearance of only one peak (at  $\delta = 31.1$ ) for the C9/C10 methyl carbons for the quenched material, in marked contrast to the case for the crystalline sample — surprising in view of the fact that the remaining signals are at very similar chemical shifts for all the other carbons.

### 4. Conclusions

Carbon-13 MAS NMR studies have been used to derive information about the crystallographic asymmetric unit of bisphenol-A alkanoates, with results that are in agreement with X-ray diffraction work in the two known cases (**Ib** and **Ie**, the latter reported for the first time herein). Evidence of phase changes has been obtained by DSC measurements, again paralleled by NMR work in some cases. The *n*-valerate was only available in glassy form.

The resonances of the aromatic ring CH carbons, studied under variable-temperature conditions, have been used to investigate motion of the phenylene rings about their para axes. For the lower members of the series (Ia, Ib and probably Ic) this motion appears to develop inhomogeneously above room temperature, as shown by the gradual appearance, as temperature increases, of a central line, together with a doublet of decreasing intensity. A combination of cross-polarisation and single-pulse experiments has been used to study this phenomenon, which may be complicated by the existence of temperature and pressure gradients across the sample under MAS conditions.

For the formate Ia there is a second process occurring in the range 298-333 K which simplifies the CH spectra by an as-yet unexplained mode. Apparent changes in the asymmetric unit of the lower members of the series of compounds I at low temperatures probably arise from the complexity of molecular and lattice motions in these compounds.

The iso-butyrate (Id) and pivalate (Ie) compounds, however, show apparently classical coalescence/decoalescence of the relevant resonances, with energy barriers  $\approx 50 \text{ kJ mol}^{-1}$  in the former case and a little higher for the latter. It would seem that barriers of this sample type are higher for the more densely packed compounds Ia, Ib and Ic, which have less bulky alkyl groups (correlating with the heats of fusion). As pointed out previously, ring-flipping for bisphenol-A compounds does not necessarily involve 180° motion of each ring since cooperative movement of the two rings in a given molecule may occur so as to reach an equivalent state. Indeed, there may be wide cooperative motions covering a number of unit cells, which might explain the apparently inhomogeneous changes observed.

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