

Orientation of the Chemical Shielding Anisotropy Tensor of the Carbonate Carbon in Diphenyl Carbonate and Its Consequences for NMR Studies on Polycarbonate

P. Robyr,^{*,†} M. Utz,[†] Z. Gan,[‡] C. Scheurer,[‡] M. Tomaselli,^{‡,‡} U. W. Suter,[†] and R. R. Ernst[‡]

Departement Werkstoffe, Institut für Polymere and Laboratorium für Physikalische Chemie, ETH-Zürich, CH-8092 Zürich, Switzerland

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ABSTRACT: The orientation of the chemical shielding anisotropy tensor of the carbonate carbon in diphenyl carbonate was determined by using solid state NMR spectroscopy. The same tensor orientation was obtained from quantum mechanical calculation based on density functional theory. The most shielded direction of the tensor is along the C=O double bond. The least shielded direction is for the carbonate plane perpendicular to the C=O double bond. Chemical shielding calculations in diphenyl carbonate fragments with different conformations show that the tensor orientation measured in crystalline diphenyl carbonate also applies to the carbonate groups of bisphenol A polycarbonate. However, this orientation is not identical to that assumed so far in the work on bisphenol A polycarbonate. The consequences of this incorrect assumption in previous studies are examined.

1. Introduction

Many nuclear magnetic resonance (NMR) techniques make use of chemical shielding anisotropy (CSA) to gain structural or dynamical information.^{1–3} Knowing the orientation of the CSA tensors in the molecular frame, one may determine angular relationships between molecular fragments or get information on the fragments' dynamics. In this paper, we concentrate on fragments containing a carbonate group. For example, bisphenol A polycarbonate has repeatedly been investigated using the CSA tensor of the carbon atom in the carbonate group. The reorientations of this tensor at different temperatures were studied to understand the dynamics of the carbonate groups.⁴ More recently, the two dihedral angles between the aromatic ring and the carbonate group were characterized by using this tensor.^{5,6} The molecular orientation in bisphenol A polycarbonate resulting from plastic deformation was also probed by using the CSA tensor of the carbonate carbon.⁷ The conclusions drawn from these experiments rely on the accurate knowledge of the orientation of the CSA tensor with respect to the local molecular frame.

Several NMR techniques exist to measure CSA tensors.^{8,9} In the traditional method,^{8–10} the resonance frequencies of the different sites in a single crystal are monitored as functions of the crystal orientation with respect to the static magnetic field. From the trajectories of the resonance frequencies, the principal values and the principal axes of the CSA tensors can be obtained. This technique provides accurate values but is quite tedious and requires single crystals. Alternatively, the principal directions of a CSA tensor in the molecular frame can be evaluated from powder spectra sensitive to the relative orientations of the CSA tensors of neighboring molecules.^{11–15}

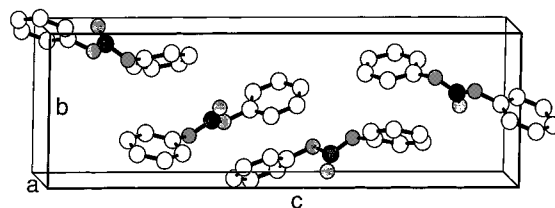


Figure 1. Unit cell of diphenyl carbonate measured by X-ray diffraction at 164 K.²⁰ The crystal structure is orthorhombic and belongs to the space group $P2_12_12_1$. The lattice parameters are $a = 6.062$, $b = 7.242$, and $c = 23.375$ Å.

In the past decade, *ab initio* calculation of CSA tensors have progressed^{16,17} and new approaches based on density functional theory (DFT) were proposed. One of these is called sum-over-states density-functional perturbation theory (SOS-DFPT).^{18,19} It yields principal values of carbon CSA tensors which lie within 10 ppm of the experimental results for many aromatic compounds.¹⁹ Unfortunately, the principal axes of the calculated CSA tensors have not been systematically documented in the literature. Therefore, a comparison with empirical rules for CSA orientations is often impossible.^{1,8} Since deviations from these rules are not uncommon,^{8,12} reliable predictions based on calculations would be valuable.

In this paper we focus on the carbon CSA tensor of the carbonate group in the model compound diphenyl carbonate (Figure 1). This substance is a low-molecular-weight analogue of bisphenol A polycarbonate. Hitherto, the most shielded principal axis of the CSA, x_{CSA} , has been assumed to be perpendicular to the carbonate plane and the least shielded axis, z_{CSA} , to be along the direction defined by the two ether oxygen atoms.^{4–7} This puts the intermediately shielded axis along the C=O double bond. This assumption is mainly based on the fact that in carbonyl and carboxylic groups the most shielded direction is perpendicular to the sp^2 plane.^{1,8} No experimental evidence for carbonate groups was available so far.

[†] Departement Werkstoffe, Institut für Polymere.

[‡] Laboratorium für Physikalische Chemie.

[‡] Present address: Material Sciences Division, Lawrence Berkeley National Laboratories, Berkeley, CA, 94720, and Department of Chemistry, University of California, Berkeley, CA, 94720.

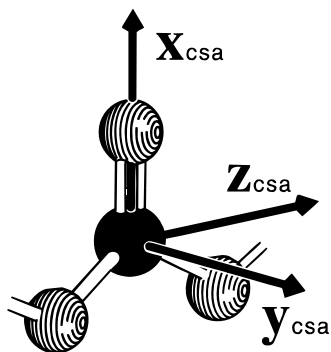


Figure 2. Orientation of the chemical shielding anisotropy tensor of the carbonate carbon in diphenyl carbonate. The most shielded direction x_{csa} is along the C=O double bond. The least shielded axis z_{csa} is parallel to the direction defined by the two ether oxygen atoms.

The experimental results presented in this contribution demonstrate that the most shielded and the intermediately shielded directions of the CSA tensor of the carbonate carbon have to be interchanged compared to the traditional assumption. The correct CSA tensor orientation in the molecular frame is shown in Figure 2. The same orientation is predicted by quantum mechanical calculations based on the SOS-DFPT approach.^{18,19} In addition, we present calculations on diphenyl carbonate fragments with different conformations, as they may exist in amorphous polycarbonate. These additional calculations show that for very different conformations between the aromatic ring and the carbonate group, the CSA orientation of Figure 2 is preserved. Finally, the consequences of the incorrect orientation assumed in previous work on polycarbonate⁴⁻⁷ are discussed.

2. NMR Measurements

In order to determine the relative orientation of the four CSA tensors of the carbonate carbons in the unit cell of diphenyl carbonate, a two-dimensional (2D) ^{13}C polarization-transfer NMR experiment of a powder sample of diphenyl ^{13}C -carbonate was recorded. A long mixing time of 5 s was used so that, in the resulting quasi-equilibrium spectrum of Figure 3a, all frequency pairs within the randomly oriented microcrystallites show cross peaks. From the powder pattern, it is possible to determine the relative orientations of the four CSA tensors. Since the four CSA tensors are related in pairs by three orthogonal twofold screw axes,²⁰ the orientation of the tensors with respect to the local molecular frames can also be determined from the NMR spectrum.¹¹⁻¹³

The analysis of the spectrum in Figure 3a was performed in two steps. First, from a 2D experiment with zero mixing time, the three principal values of the CSA tensor of the labeled carbon and the width of the homogeneous broadening represented by a 2D Gaussian function were determined. A full width at half-height of 4.34 ppm (325 Hz) was obtained for the 2D Gaussian function together with the principal values listed in Table 1. In a second step, the three Euler angles (α , β , γ), which define the rotation of the principal axis system of the CSA tensor into the system of axes (x_m , y_m , z_m) attached to the molecule, were determined. The axis z_m is parallel to the direction O_2O_3 defined by the two ether oxygens numbered as in ref 20; y_m is perpendicular to the plane defined by the three oxygen atoms and its

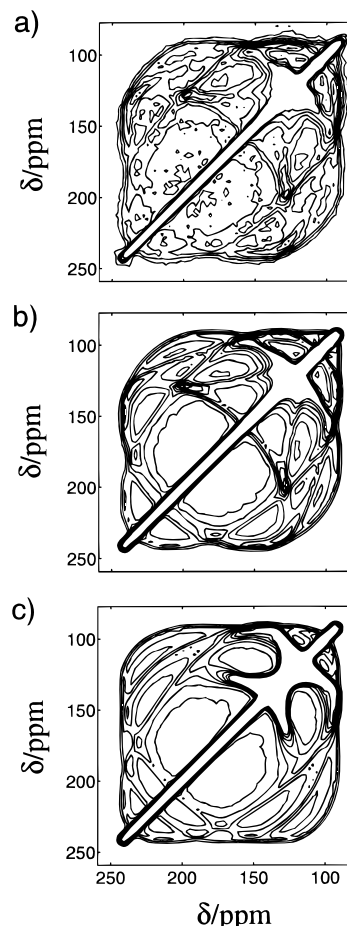


Figure 3. (a) Two-dimensional NMR polarization-transfer spectrum under slow magic-angle sample spinning²¹ of diphenyl ^{13}C -carbonate (Isotech Inc., Miamisburg, OH) at 298 K. The spectrum was measured on a home-built spectrometer working at a proton frequency of 300 MHz using a Chemagnetics (Fort Collins, CO) 6-mm double resonance MAS probe. The rf fields on the ^{13}C and the ^1H channels were both matched at 62 kHz. The spinning frequency was 50 Hz. The mixing time was set to 5 s in order to obtain nearly complete polarization exchange between the four differently oriented sites. (b) Best fit of the spectrum in (a). The Euler angles that define the orientation of the chemical shielding anisotropy (CSA) tensor of the carbonate carbon with respect to the molecule were optimized. The resulting orientation of the tensor is shown in Figure 2. (c) 2D polarization-transfer spectrum calculated under the assumption that the x and the y axis of the CSA tensor of the carbonate carbon are interchanged compared to the situation depicted in Figure 2.

Table 1. Principal Values of the Chemical Shift Tensor of the Carbonate Carbon in Diphenyl Carbonate Fragments^a

	T/K	δ_{xx}/ppm	δ_{yy}/ppm	δ_{zz}/ppm
diphenyl carbonate (exptl)	298	88 ± 2	125 ± 2	239 ± 2
diphenyl carbonate (calcd)		78	133	228
bisphenol A polycarbonate (ref 5) ^b	298	90 ± 2	120 ± 2	231 ± 2
bisphenol A polycarbonate (ref 5) ^b	135	84 ± 1	124 ± 1	234 ± 1

^a All values are given with respect to TMS. ^b After interchanging the incorrectly assigned axes.

direction is such that x_m points along the C=O double bond. Several least squares fits of the spectrum in Figure 3a using the CSA eigenvalues and line width mentioned above were performed with different initial values of (α , β , γ). They systematically converged to

$\beta = -0.3^\circ \pm 1.5^\circ$. For such a value of β , α and γ are ill-defined and only their sum can be fitted. Including this restriction, we obtained $\beta = -0.3^\circ \pm 1.5^\circ$ and $\alpha + \gamma = -1.1^\circ \pm 2.0^\circ$. The corresponding computed spectrum is shown in Figure 3b. Thus, the principal axis system of the CSA tensor is oriented as shown in Figure 2 and coincides, within experimental accuracy, with the molecular frame defined above. The 2D spectrum calculated by using the traditional tensor orientation, where x_{csa} and y_{csa} are swapped compared to the orientation of Figure 2, is shown in Figure 3c. It differs conspicuously from the experimental spectrum in Figure 3a.

3. Calculations of CSA Tensors

3.I. Computational Details. All the calculations were carried out by using the SOS-DFPT approach of Malkin et al.^{18,19} as implemented in the *deMon-NMR* code.^{22–24} The shieldings were calculated using the Loc.1 SOS-DFPT¹⁸ approximation and individual gauges for localized orbitals (IGLO¹⁶). The molecular orbitals were localized by the method of Boys.²⁵ The underlying Kohn-Scham calculations employed the gradient-corrected Perdew-Wang-91 (PW91) exchange-correlation potential.²⁶ IGLO-II basis sets¹⁶ were used on all atoms of the carbonate group and on the two carbon atoms directly connected to the carbonate group. For all other atoms DZ basis sets²⁷ were used. The electronic density and the exchange-correlation potential were fitted with auxiliary basis sets^{22,23} of the sizes 5,1 (H) and 5,2 (C,O). The numerical quadrature was carried out on FINE RANDOM^{22,23} angular grids with 64 radial grid points.

3.II. Crystalline Diphenyl Carbonate. The crystal structure obtained from X-ray diffraction²⁰ does not contain the coordinates of the protons. These were added to the phenylene groups along the lines bisecting the angles defined by three consecutive carbon atoms. The distance of the C–H bonds was set to the standard value of 1.10 Å.^{28,29} This geometry was used to compute the CSA tensor of the carbonate carbon in an isolated molecule. The calculation yielded the principal values of the CSA tensor listed in Table 1 and the following eigenvectors in the molecular frame:

$$x_{\text{csa}} = (0.997, 0.076, -0.001)$$

$$y_{\text{csa}} = (-0.076, 0.997, -0.002)$$

$$z_{\text{csa}} = (-0.001, 0.002, 1.000)$$

The transformation, which rotates the principal axis system of the CSA tensor into the molecular frame, amounts to a rotation of -4.4° about the axis z_{csa} . This value differs from $-1.1^\circ \pm 2.0^\circ$ obtained experimentally. The calculated principal values and principal axes both deviate from the experimental results. However, considering the difficulties in calculating CSA tensors, the agreement is satisfactory. In addition, the accuracy is sufficient for the next step in our study, namely, for investigating the variation of the orientation of the CSA tensor as a function of the conformation of diphenyl carbonate fragments. Therefore, no attempt was made to improve the agreement by using different basis sets or different exchange-correlation potentials or by including neighboring molecules in the CSA calculation.

3.III. Diphenyl Carbonate Fragments. In amorphous bisphenol A polycarbonate, the diphenyl carbonate fragments can adopt different conformations.^{6,30} Therefore, it is important to know if the orientation of the CSA tensor changes with the fragment conformation. Diphenyl carbonate fragments with different conformations were obtained from an atomistic simulation of bisphenol A polycarbonate.³¹ In the simulated polymer chain, consisting of 20 monomer units, the two dihedral angles φ_c and φ_p (Figure 4) spread over many tens of degrees. Each of the 20 diphenyl carbonate units was cut out from the simulated chain and terminated at both ends by

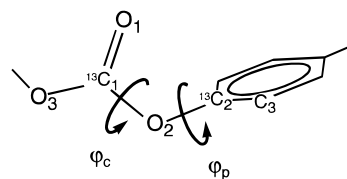


Figure 4. Two dihedral angles φ_c ($\text{O}_1\text{C}_1\text{O}_2\text{C}_2$) and φ_p ($\text{C}_1\text{O}_2\text{C}_2\text{C}_3$) in doubly ^{13}C -labeled polycarbonate.

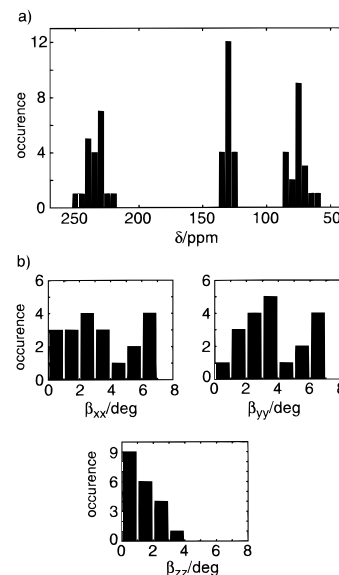


Figure 5. Histograms of the calculated CSA tensor parameters of the carbonate carbon in diphenyl carbonate fragments. The 20 fragments were obtained from an atomistic simulation of bisphenol A polycarbonate. The polymer structure was generated by the amorphous cell algorithm followed by a molecular dynamics annealing procedure using the force field pcff91.³² (a) Distribution of the principal values of the CSA tensor. The values are given relative to TMS. (b) Angles between each principal axis of the CSA tensor and the respective molecular frame axis. The z axis of the molecular frame is parallel to the direction defined by the two ether oxygen atoms and the y axis is perpendicular to the plane defined by the three oxygen atoms of the carbonate group.

adding two protons in the same way as described in section 3.II. For each fragment, the CSA tensor of the carbon in the carbonate group was computed according to the procedure mentioned above. The resulting CSA principal values are shown in Figure 5a, and the angles between each principal axis of the CSA tensor and the corresponding molecular axis are given in Figure 5b. None of the angles between the CSA axes and the respective axes of the molecular frame exceeds 7° . Therefore, the orientation of the CSA tensor shown in Figure 2 appears to be an intrinsic property of the diphenyl carbonate fragment, which does not significantly depend on the conformation. In addition to a wide spread of the dihedral angles between the carbonate and the phenylene groups, the fragments also have distorted carbonate groups with atoms out of plane by more than 0.2 Å. In view of these large geometric distortions, the differences between the CSA tensors calculated from the fragments and the tensor obtained from the X-ray geometry might be considered as an upper bound for the variations of the CSA tensor in amorphous bisphenol A polycarbonate.

4. Consequences for Previous Works on Bisphenol A Polycarbonate

In ref 4, the dynamics of the carbonate group in bisphenol A polycarbonate was studied by analyzing the shape of the NMR line caused by the modulation of the

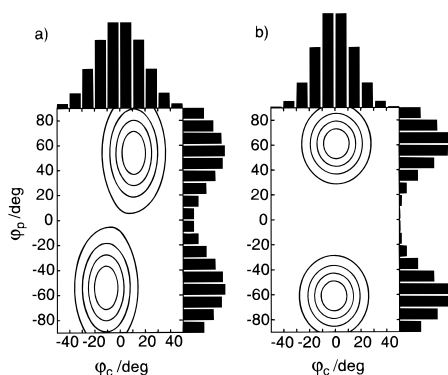


Figure 6. Distribution function $P(\varphi_c, \varphi_p)$ of the two dihedral angles φ_c and φ_p in bisphenol A polycarbonate. The distributions were obtained from a fit of a Gaussian function model to a 2D separated local field NMR spectrum.⁶ The model consists of a centrosymmetric arrangement of two 2D Gaussian functions. The optimal values of the parameters are given in Table 2. (a) Fitted distribution function obtained in ref 6 assuming that the x and the y axis of the CSA tensor of the carbonate carbon are interchanged compared to the situation depicted in Figure 2. (b) Fitted distribution function using the same procedure as in ref 6, but assuming the orientation the CSA tensor of the carbonate carbon shown Figure 2.

CSA of the carbonate carbon at different temperatures. From this work, a motional model emerged whose main feature is a reorientation of the carbonate group about the direction defined by the two ether-oxygen atoms. This direction coincides with Z_{CSA} , which is left unchanged by the revision of CSA tensor orientation. Therefore, the conclusions on the dominant motion remain unchanged. It was also proposed that the carbonate group could undergo small amplitude motions about the C=O double bond.⁴ In principle, the effect of this type of motion on the line shape is different for the old and the revised tensor orientations. However, the manifestation of this motion in the line shape could hardly be detected.⁴

In refs 5 and 6, the distribution of dihedral angles between the carbonate and the phenylene groups in bisphenol A polycarbonate was studied by using a doubly ^{13}C -labeled polymer. The chain contained isolated carbon-13 pairs, with one label in the carbonate group and the other two bonds away in one of the adjacent phenylene rings (Figure 4). The distribution function of the two dihedral angles φ_c and φ_p was measured by correlating the orientation of each of the two carbon CSA tensors with that of the dipolar coupling tensor in a 2D separated-local-field NMR experiment.⁹ The distribution function $P(\varphi_c, \varphi_p)$ was assumed to consist of two centrosymmetrically arranged 2D Gaussian functions. The fit parameters were the position of the maximum (φ_c^0, φ_p^0) and the standard deviations σ_c and σ_p along the φ_c and φ_p axes of the function with $-90^\circ \leq \varphi_p^0 \leq 0^\circ$. We have fitted again the original 2D spectrum using the same procedure and the same assumptions as described in refs 5 and 6, except that the CSA tensor of the carbonate carbon was assumed to take the orientation of Figure 2. The old and the new optimal distribution functions are shown in parts a and b of Figure 6, and their parameters are listed in Table 2. Overall, the two distribution functions differ little. The probability of the conformation $\varphi_c = \varphi_p = 0^\circ$ is smaller in the new distribution. This change is sensible since a large sterical overlap exists between the phenylene ring and the carbonate group when both dihedral

Table 2. Parameters of the Bimodal Gaussian Distribution Function of the Dihedral Angles in Bisphenol A Polycarbonate

parameter	original fit ⁶	new fit
position of max: φ_p^0 , deg	-54 ± 20	-61 ± 10
position of max: φ_c^0 , deg	-11 ± 10	-1 ± 9
width: σ_p , deg	26 ± 10	18 ± 13
width: σ_c , deg	14 ± 5	15 ± 5

angles are zero. The main conclusion of the original study,^{5,6} namely that the trans conformation around the carbonate group ($\varphi_c \approx 0^\circ$) largely predominates, remains unchanged. However, the slight correlation found therein between the two dihedral angles is no longer significant.

In ref 7, the orientational distribution of the carbonate groups resulting from uniaxial compression of a bisphenol A polycarbonate sample was measured by analyzing the CSA line shape of the resonance of the carbonate carbon. The results suggested that the direction defined by the C=O double bond would orient preferentially along the deformation axis. In light of the correct orientation of the CSA tensor, this conclusion has to be revised. After compression, the carbonate planes tend to orient perpendicular to the deformation axis, in agreement with the corresponding findings for the phenylene planes.⁷

5. Conclusions

The most shielded direction of the CSA tensor of the carbonate carbon in diphenyl carbonate is along the C=O double bond and not perpendicular to it as is the case in carbonyl and carboxylic groups.^{1,8} This illustrates the danger of applying empirical rules for CSA tensor orientations^{1,8} derived for one type of local bonding environment to a similar one. The rules for orientation of carbon CSA tensors in carbonyl or carboxylic groups do not apply to the carbonate group of diphenyl carbonate. This particularity might extend to all carbonate groups.

This work shows that carbon CSA tensors can be accurately oriented in polycrystalline compounds using 2D polarization-transfer NMR. It also demonstrates that recent quantum mechanical methods to calculate chemical shielding can be remarkably precise. One of the many applications of such calculations^{17,33,34} consists in analyzing the dependence of the orientation of CSA tensors on molecular conformation.³⁵ The analysis of the CSA tensor of the carbonate carbon in diphenyl carbonate fragments indicates that the orientation of the CSA tensor varies at most by a few degrees as a function of the conformation and that the tensor orientation measured in crystalline diphenyl carbonate is also valid in amorphous bisphenol A polycarbonate.

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