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DETERMINATION OF THE ^{13}C CHEMICAL-SHIFT TENSORS IN A SINGLE CRYSTAL OF METHYL α-D-GLUCOPYRANOSIDE.

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ABSTRACT

The chemical shielding tensors and their direction cosines of the ^{13}C nuclei in a single crystal of methyl α-D-glucopyranoside were determined by the high-resolution solid state n.m.r. technique. The results were used to assign the ^{13}C cross-polarization, magic angle spinning (c.p.-m.a.s.) spectrum of a polycrystalline sample of that compound. The differences between the ^{13}C chemical shifts observed in the c.p.-m.a.s. spectrum of the solid and of solutions of methyl α-D-glucopyranoside are discussed in terms of the different types of hydrogen bonds formed in the crystalline state and in solution.

INTRODUCTION

The most comprehensive information about the structures of carbohydrates has come from X-ray and neutron-diffraction studies[1]. Nuclear magnetic resonance spectroscopic studies of these compounds have, however, yielded much important knowledge. Most of the earlier studies were confined to these compounds in solution[2]. Only comparatively recently have solid-state n.m.r. techniques been applied to investigate the structural properties of carbohydrates. So far, the application of solid-state n.m.r. studies to carbohydrates has been largely confined to the use of cross-polarization and magic angle spinning (c.p.-m.a.s.) ^{13}C spectroscopic methods on polycrystalline samples[3]. It has been shown[4] that ^{13}C solid-state n.m.r. spectra and X-ray diffraction studies on polycrystalline carbohydrates are complementary. The former may, however, more readily disclose the existence of any conformational multiplicity in the crystalline state.

Some earlier studies on carbohydrates were based on the näive assumption that there is a direct correspondence between the isotropic chemical shifts of both the ^{13}C solution spectra and the solid-state c.p.-m.a.s. n.m.r. spectra, but more-recent, careful, detailed investigations have shown clearly that that assumption is not warranted[3b]. Pfeffer *et al.*[3b,4] carried out detailed studies of various poly-

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crystalline carbohydrates. For lactulose and maltulose, they showed that there are "cross-overs" in chemical shifts of certain of the carbon resonances when the spectra obtained for solution are compared with those obtained for the solid state by the c.p.-m.a.s. method. These cross-overs were found to be most prominent in the case of lactulose[3b,4]. This phenomenon has also been observed for α-D-glucose and β-D-glucose[5,6]. Chemical shifts obtained from c.p.-m.a.s. n.m.r. studies are determined to various extents by molecular conformations frozen in the solid state, as well as effects from such phenomena as hydrogen bonding and crystal packing. For these reasons, solution spectra cannot always be assumed to be a reliable guide to the assignment of the chemical shifts observed in the c.p.-m.a.s. spectra. This is particularly the case for carbohydrates, because of the different types of hydrogen bonding in the solution and in the crystalline state. To obtain satisfactory spectral assignments, it is often necessary to rely on such techniques as deuterium substitution[7], dipolar dephasing[8,9], and ^{13}C enrichment[5,6].

Earlier, from solution n.m.r. studies, Walker *et al.*[10] had shown that the resonances observed could be assigned by studying compounds which were ^{13}C-enriched at specific sites, and adjacent ^{13}C resonances could be identified from observation of ^{13}C–^{13}C scalar coupling interactions. This method was employed by Pfeffer *et al.*[5,6] to assign observed resonances in ^{13}C c.p.-m.a.s. spectra of ^{13}C-enriched α-D-glucose. This is a satisfactory method for the assignment of ^{13}C resonances in the solid-state n.m.r. spectra of organic compounds, but it is difficult to carry out. Deuterium-induced ^{13}C isotropic shifts have been used to assign the resonances observed in the solution n.m.r. spectra of mono- and di-saccharides[7,11].

So far as we are aware, there have been no previously published determinations of the individual ^{13}C chemical-shift tensors in single crystals of any carbohydrate derivative. Because pyranose-ring structures are of fundamental importance in carbohydrate chemistry, we have chosen to determine the ^{13}C chemical-shift tensors of all of the carbon nuclei in methyl α-D-glucopyranoside, which, we found, readily forms single crystals suitable for n.m.r. studies. The results from the single-crystal study were used in the assignment of the c.p.-m.a.s. n.m.r. spectrum of a polycrystalline sample of that compound.

EXPERIMENTAL

Crystals of suitable size (20 × 5 × 3 mm) were grown from an aqueous solution of pure methyl α-D-glucopyranoside. We thank Professor G. G. S. Dutton of this Department for the gift of that compound, and also for a sample of methyl α-D-glucopyranoside tetraacetate. The crystals of methyl α-D-glucopyranoside belong to the orthorhombic space-group $P2_12_12_1$, with four molecules per unit cell. The cell parameters are[12] $a = 11.311$, $b = 14.781$, $c = 5.281$ Å. The crystals grew in the form of elongated parallelopipeds with the long axis being the c axis, and exhibited predominant (110) faces. The morphology of the crystals is shown in Fig. 1. The a and b axes, which are along the body diagonal, were identified by

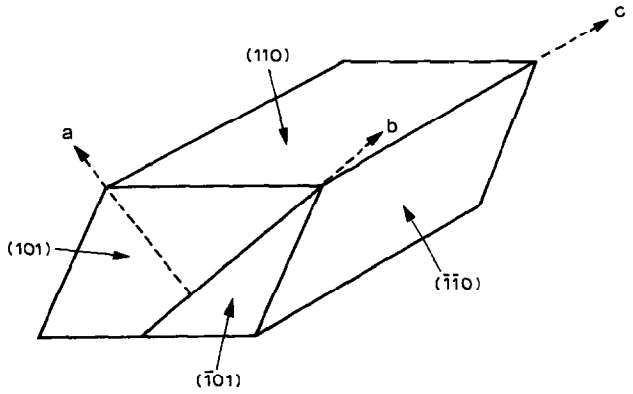

Fig. 1. Morphology of a single crystal of methyl α-D-glucopyranoside.

X-ray diffraction methods[13]. The orthogonal *abc* crystallographic axes were chosen as an experimental axis system.

Proton-enhanced, ^{13}C-n.m.r. resonances were observed by employing a Bruker CXP200 n.m.r. spectrometer operated at resonance frequencies of 200 MHz for protons, and of 50.3 MHz for the ^{13}C nuclei. We used a double-resonance probe equipped with a specially designed goniometer that could orient the crystals at any chosen angle to within ± 0.1°. A single-contact, spin-locking, cross-polarization, pulse sequence was applied with rf fields of 1 mT for the protons and 4 mT for the ^{13}C nuclei in the rotating frame, as required in order to satisfy the Hartmann–Hahn condition[14]. Contact times of 2.0 ms and recycle times of 10 s were used in the pulse sequence. Appoximately 100 transients were sufficient at each orientation to give good S/N ratios. The crystals were rotated about the three crystallographic axes chosen and the spectra were recorded at 5-degree intervals in each of the three planes. Spectra were also recorded in a general plane in which the magnetic fields was rotated from the *c*-axis to the *a* direction in the *ab* plane, which made an angle of 37.5° with the *a* axis. In the general plane, spectra were recorded with angular increments of 2°, in order to facilitate the accurate determination of the angular dependence of the different ^{13}C resonances.

The cross-polarization, magic angle spinning (c.p.-m.a.s.) spectra were determined by using the aforementioned conditions for the Hartmann–Hahn relation. A plexiglass rotor was used, and the spinning frequency was ~3.2 kHz. The magic angle spinning as established by using a small pellet of KBr embedded in the sample and monitoring the ^{79}Br resonance[15]. The chemical shifts were measured with respect to an external reference of benzene which is 128.5 p.p.m. downfield from tetramethylsilane (Me_4Si). To check the resolution of the c.p.-m.a.s. spectra, we measured the spectrum of polycrystalline methyl α-D-glucopyranoside tetra-acetate, and it was found to be in excellent accord with that published recently by Vanderhart[16]. All of the chemical shifts recorded in Tables I and II are given relative to Me_4Si.

Crystals of methyl α-D-glucopyranoside belong to the space group $P\,2_12_12_1$, and there are four molecules in the unit cell. These molecules are chemically equivalent, but magnetically nonequivalent. One can therefore expect to find four chemical shielding tensors for each chemically different nucleus in the molecule. The tensors all have the same principal values, but their direction cosines differ. The sets of direction cosines mutually satsify the symmetry operations, namely, *I* (*l,m,n*), *II* (−*l*, −*m*,*n*), *III* (*l*, −*m*, −*n*), and *IV* (−*l*,*m*, −*n*). Here, *l*, *m*, and *n* are the direction cosines of the molecules in the unit cell, which are represented by *I*, *II*, *III*, and *IV*. Only one set of direction cosines is shown in Table 1. The direction cosines of the principal values with respect to the molecular frame, calculated by using the atomic coordinates determined from neutron-diffraction studies[12], are also given in Table I.

TABLE I

PRINCIPAL VALUES OF ^{13}C CHEMICAL-SHIELDING TENSORS IN A SINGLE CRYSTAL OF METHYL α-D-GLUCOPYRANOSIDE[a].

Carbon nucleus	*Principal value of tensor*	*Direction cosines with respect to*						l_i (i = 1,2,3)
		a	*b*	*c*	*X*	*Y*	*Z*	
C-1	σ_{33} 90.0	−0.4628	−0.5453	−0.6990	−0.9812	0.0217	−0.1923	C-1
	σ_{22} 95.1	0.0741	−0.8095	0.5824	0.0178	0.9996	0.0219	O-1
	σ_{11} 119.7	0.8834	−0.2177	−0.4150	−0.1926	−0.0180	0.9811	O-5
C-2	σ_{33} 51.0	0.0041	−0.9781	0.2082	−0.9930	0.0473	0.1084	C-2
	σ_{22} 75.6	−0.9905	0.0247	0.1359	−0.0804	−0.9418	−0.3264	O-2
	σ_{11} 89.8	0.1375	0.2068	0.9687	−0.0867	0.3328	−0.9390	C-1
C-3	σ_{33} 61.2	−0.7002	0.4339	−0.5670	0.9451	−0.2302	−0.2320	C-3
	σ_{22} 68.7	−0.6548	−0.7069	0.2676	0.2874	0.9235	0.2544	O-3
	σ_{11} 94.5	0.2847	−0.5586	−0.7790	−0.1557	0.3070	−0.9388	C-4
C-4	σ_{33} 59.4	0.7422	0.1444	−0.6544	−0.9766	0.2032	0.0705	C-4
	σ_{22} 73.9	−0.5659	0.6584	−0.4962	−0.1745	−0.9402	0.2926	O-4
	σ_{11} 95.8	−0.3590	−0.7386	−0.5706	−0.1257	−0.2734	−0.9536	C-5
C-5	σ_{33} 53.7	−0.5919	−0.1394	0.7938	−0.9948	−0.0516	−0.0875	C-5
	σ_{22} 79.3	−0.3349	0.9384	−0.0849	0.0343	−0.9815	0.1880	O-5
	σ_{11} 86.8	−0.7331	−0.3161	−0.6022	−0.0995	0.1840	0.9783	C-6
C-6	σ_{33} 32.6	−0.7594	0.4159	−0.5004	−0.9867	−0 1322	−0.0951	C-6
	σ_{22} 69.2	−0.4257	−0.8992	−0.1013	−0.1559	0.5979	0.7863	O-6
	σ_{11} 88.8	−0.4920	0.1360	0.8599	−0.0469	0.7906	−0.6105	H-2 (C-7)
C-7	σ_{33} 11.5	0.9341	0.1316	0.3319	−0.9955	0.0667	0.0668	C-7
	σ_{22} 72.3	0.3361	0.0107	−0.9418	0.0061	−0.6608	0.7506	O-1
	σ_{11} 87.1	−0.1204	−0.9913	−0.0542	−0.0943	−0.7476	−0.6574	H-2 (C-7)

[a]Direction cosines with respect to the *a*,*b*,*c* crystallographic axes, as well as *X*, *Y*, *Z* axes. The *X*, *Y*, *Z* axes system is defined by the three atoms listed in this Table as follows: l_1 is taken as origin, *X* axis is along the direction $l_1 - l_2$, and the *XY* plane is spanned by $l_1 - l_2 - l_3$.

RESULTS AND DISCUSSION

When a single crytal of methyl α-D-glucopyranoside is so oriented that the magnetic field points along one of the crystallographic axes, all of the molecules in the unit cell become equivalent and seven ^{13}C resonances can be observed. However, because of the residual broadening of the resonances and the small range in which all the peaks occur, at no orientation were all the expected lines observed without overlap. Fig. 2 shows the experimental spectra when the magnetic field (H_0) is aligned along the *a*, *b*, and *c* cyrstallographic axes. Because the spectra were recorded at 5-degree intervals, all of the resonances could be identified by monitoring their angular-variation plots in each of the three main crystallographic planes. The experimentally observed angular-variation plots are shown in Fig. 3. The observed chemical-shift values are described by the equation.

$$\sigma(\Theta) = \sigma_{ii} \cos^2\Theta + \sigma_{ij} \sin 2\Theta + \sigma_{jj} \sin^2\Theta,$$

where σ_{ij} is an element of the ^{13}C chemical-shielding tensor, and Θ is the angle between the direction of the static magnetic field and the *i* axis in the *ij* plane. The values of σ_{ij} were calculated by using a least-squares fit to the angular-dependent, experimental chemical-shift values*.

In the general case in which there are two magnetically nonequivalent sites for each plane, eight possible tensors should be obtained; of these, four are correct. In the present case, some of the carbon nuclei exhibited only one resonance value in a particular plane, indicating that the off-diagonal elements of the chemical-shift tensor in that plane are close to zero, thus making both of the sites degenerate in that plane. For such carbon nuclei, either four or two tensors, were obtained depending on whether the two sites become degenerate in one plane or two. In the case of

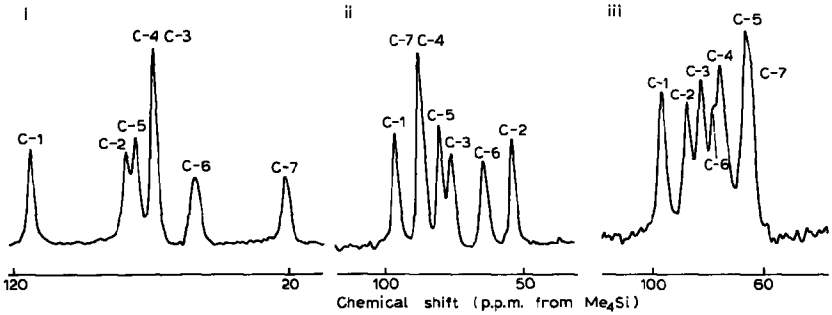

Fig. 2. High-resolution solid-state ^{13}C-n.m.r. spectra of ^{13}C in methyl α-D-glucopyranoside single crystal. [Key: (i) H_0//*a*-axis, (ii) H_0//*b*-axis, and (iii) H_0//*c*-axis.]

* The principal axis system is defined by $\sigma_{11} > \sigma_{22} > \sigma_{33}$. It might be appropriate to use δ instead of σ in this definition; however, the review article[18] and other recent articles prefer to use σ rather than δ.

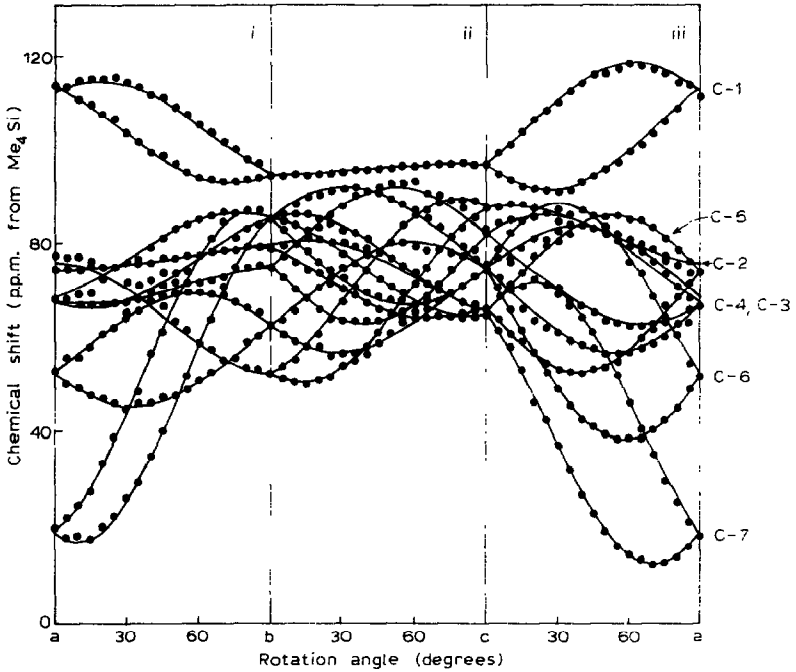

Fig. 3. Angular dependence of the high-resolution solid-state, spectra of ^{13}C in methyl α-D-glucopyranoside single crystal in the (i) *ab*, (ii) *bc*, and (iii) *ca* planes.

carbon nuclei for which all eight combinations are obtained, a choice of the correct four tensors has to be made. The direction cosines of these four are related by the crystallographic point-group symmetry. The correct choice of four tensors can be verified by calculating the angular-variation plots in the general plane, and comparing with the experimentally obtained angular variation in that plane.

In our work, the assignment of each tensor to a particular carbon nucleus was made by adopting the following procedures. Because the solution values of the isotropic chemical-shifts are known, some of the tensors could be immediately assigned to a particular carbon nucleus by comparing the isotropic values of the chemical-shift tensor with the solution value. By this means, the C-1, C-6, and C-7 tensors could be immediately assigned, but some caution had to be exercised in assigning the tensors of the C-2, C-3, C-4, and C-5 nuclei, as their isotropic-tensor values lie within a close range. For this purpose, we made use of knowledge regarding the orientation of the σ tensor of a hydroxylated carbon nucleus (all of which have sp_3-hybridized atomic orbitals) with respect to the molecular frame. So far, there have been only a few reports in which a hydroxylated carbon tensor was determined from single-crystal studies[17].

It is known from local molecular symmetry arguments that the most shielded value σ_{33}, should be closely parallel to the C–O bond direction[18]. By using this knowledge, the correct choice of the tensor was made by comparing the orientation

of the tensor elements with the local molecular symmetry. The tensors could be assigned to particular carbon nuclei by choosing the tensor whose maximum shielded component σ_{33}, was oriented to be approximately in the C–O bond direction.

The tensor of the C-1 atom was easy to assign to the molecular frame, because only one of the four tensors obtained reflected the local configuration reasonably well. This tensor has the most shielded value (σ_{33}) oriented approximately along the C-1–O-1 bond. The intermediate value (σ_{22}) was close to the C-1–O-5 bond. The least shielded direction σ_{11}, is found to be nearly perpendicular to the O-5–C-1–O-1 plane. The same orientation had been found for the σ_{11} value of the tensor of the similar carbon nucleus in Meldrum's acid[19]. After the correct tensor for each of the carbon nuclei in the molecule had been identified, diagonalization of the tensor led to the principal values, which are given in Table I. It should be noted that, in Table I, the direction cosines are listed with respect to the crystallographic axes *a*, *b*, and *c*, and also with respect to the *X*, *Y*, and *Z* axes defined with respect to the molecular frame (local symmetry). An ORTEP plot showing the orientation of the chemical shielding tensor with respect to the molecular frame is shown in Fig. 4.

In methyl α-D glucopyranoside, the anomeric carbon atom (C-1) has all of the

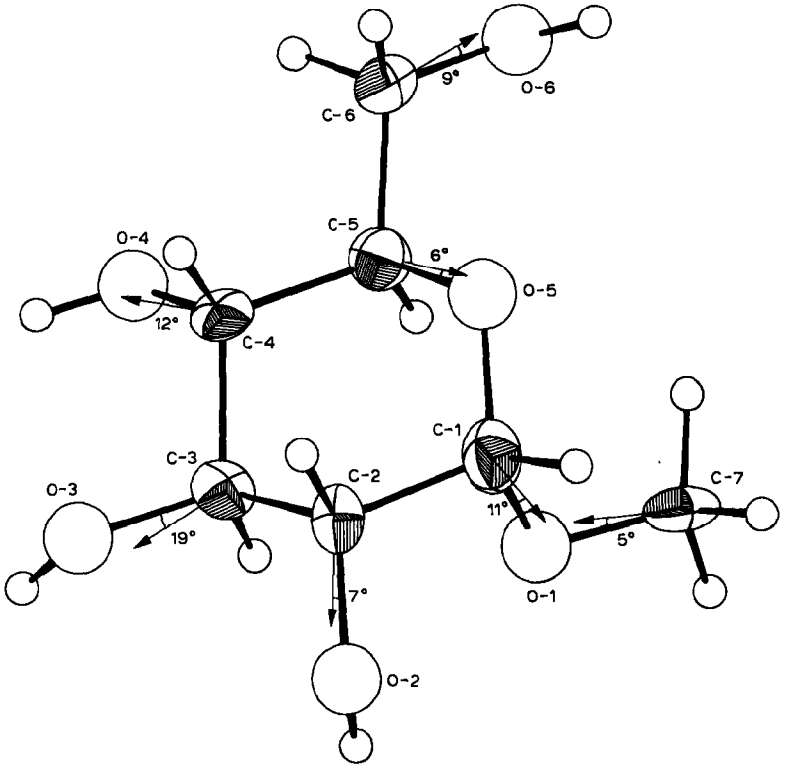

Fig. 4. ORTEP representation of the orientation of the ^{13}C chemical-shielding tensors with respect to the molecular frame of methyl α-D-glucopyranoside. [View is along the *c*-axis.]

three principal values of its chemical-shielding tensor shifted downfield compared to those of any other carbon nucleus in this compound. Besides, the chemical-shielding tensor of this carbon nucleus exhibits the smallest anisotropy, η, and maximum axial symmetry [$\eta = (\sigma_{22} - \sigma_{33})/\sigma_{11} = 0.05$]. The most-shielded direction for the anomeric carbon atom is along the C-1–O-1 bond, which is shorter[12b] than the C-1–O-5 bond by 0.012 Å.

Although the chemical shielding tensors of all of the hydroxylated carbon nuclei possess similar features, there are differences. The tensors for the C-3 and C-4 nuclei are less anisotropic [$\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22}) = -20.4$ and -25.5], and are closer to axial symmetry [$\eta = 0.08$ and 0.15, respectively]. Moreover, the values of σ_{33} for these tensors deviate more from the C–O bond direction (19 and 12°, respectively). The chemical-shift tensor of the C-5 nucleus, which is attached to the ring-oxygen atom, is similar to that of the hydroxylated carbon nucleus C-2. The asymmetries (η values) of the chemical-shift tensors of the C-5 and C-2 nuclei are 0.29 and 0.27, respectively. The respective $\Delta\sigma$ values are -29.4 and -31.7. The direction of σ_{33} for these carbon nuclei derviates from C–O bond direction by 6° and 7°, respectively.

Methylene and methyl carbon nuclei, C-6 and C-7, usually exhibit larger downfield shifts in their chemical-shift values when they are bonded to oxygen. In the present case, the methylene ^{13}C tensor is less shielded in its σ_{11} and σ_{22} directions, when compared to the corresponding values in the tensors of CH_2 carbon nuclei not bonded to oxygen[18]. Similarly, the σ_{11}, σ_{22}, and σ_{33} values of the methyl carbon tensor are less shielded, as can be seen by comparison with the corresponding values of the C–CH_3 tensors[18].

The c.p.-m.a.s. n.m.r. spectrum of polycrystalline methyl α-D-glucopyranoside obtained in the present studies is shown in Fig. 5. The ^{13}C resonances in the c.p.-m.a. spectrum are given in Table II. Without recourse to single-crystal work, one can assign the C-1, C-6, and C-7 resonances, which are well separated from the other resonances, by comparison with the corresponding solution values. However,

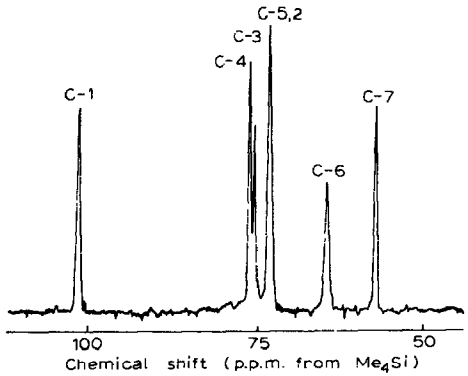

Fig. 5. ^{13}C-c.p.-m.a. spectrum of methyl α-D-glucopyranoside polycrystalline powder. [Number of scans, 25; repetition time, 10 s mixing time, 2 ms; and acquisition time, 25 ms.]

TABLE II

^{13}C CHEMICAL-SHIFT VALUES OF METHYL α-D-GLUCOPYRANOSIDE IN SOLUTION AND IN THE SOLID STATE.

Carbon nucleus	*Solution value*[a]	*Solid-state values*	
		C.p.-m.a.s.	*Single crystal*
	(σ_{iso})	(σ_{iso})	(σ_{av}[b])
C-1	100.6	101.8	101.6
C-2	72.7	73.2	72.1
C-3	74.7	75.3	74.8
C-4	71.2	76.0	76.4
C-5	73.0	73.2	73.3
C-6	62.2	64.5	63.6
C-7	56.5	57.2	57.0

[a]From ref. 10. [b]$\sigma_{av} = 1/3(\sigma_{11} + \sigma_{22} + \sigma_{33})$.

such an assignment for the ring-carbon atoms, namely C-2, C-3, C-4, and C-5 is not possible without additional information from single-crystal work, or from some of the techniques already mentioned, such as the dipolar dephasing method. We found that the resonances of C-6 and C-7 could be readily identified by dipolar dephasing experiments[8] because the C-6 (CH_2) signal decays after a dephasing period of 25 μs, whereas the C-7 (CH_3) signal is still present, even after a dephasing time of 100 μs. All of the ring-carbon nuclei dephase more or less simultaneously, and decay within a dephasing time of 100 μs. Hence, the assignment of the latter resonances was made as mentioned previously, by comparing with the isotropic values of the tensors obtained from the single-crystal measurements. These assignments are shown in Table II. When the isotropic values from the single-crystal data and the c.p.-m.a.s. values are compared with those from solution studies, it can be seen that there is some crossing over of the values of certain of the ring-carbon resonances. In solution, the order of the chemical shifts is C-1 > C-3 > C-5 > C-2 > C-4 > C-6 > C-7, whereas, from the solid-state studies, we have the sequence C-1 > C-4 > C-3 > C-2 ≈ C-5 > C-6 > C-7. The most noticeable change is in the isotropic value for C-4, which is 71.2 p.p.m. in solution, whereas the corresponding value in the solid state is 76 p.p.m. This considerable change illustrates the influence of the crystal-field effects and, most certainly, the effects of the different hydrogen-bondings found in solution and in the crystalline state. In this connection, it is interesting that in the methyl α-D-glucopyranoside structure there are, along the *c*-axis, spirals of strong hydrogen-bonds that involve three of the hydroxyl groups in approximate threefold symmetry, but the remaining one, H[O4], has the H atom in a position suitable for the formation of a bifurcated bond with the primary alcohol group (HO-6) and the ring OH of an adjacent molecule, although the distance is somewhat long[12].

Despite many attempts, we were unable to resolve the resonance that occurs at 73.2 p.p.m. in the c.p.-m.a. spectrum. It was assigned to C-2, C-5, assuming that

TABLE III

^{13}C CHEMICAL-SHIFT VALUES[a] OF RING-CARBON ATOMS IN METHYL α-D-GLUCOPYRANOSIDE TETRAACETATE IN SOLUTION AND IN THE SOLID STATE.

Carbon atom	*Solution value* [b] σ_{iso}	*Solid-state values* σ_{iso}
C-1	96.54	97.8
C-2	70.54	72.0
C-3	69.87	69.2
C-4	68.39	67.8
C-5	66.94	67.2
C-6	61.71	62.4
C-7	55.10	56.2

[a]All chemical-shift values are in p.p.m. with respect to Me_4Si. [b]In deuteriochloroform, using a Bruker WH400 n.m.r. spectrometer.

these two resonances overlap, even though our single-crystal data showed that the isotropic value of those resonances differ by 1.1 p.p.m. (which should be resolvable). It was for this reason that we measured the c.p.-m.a. spectrum of methyl α-D-glucopyranoside tetraacetate, and we were able to resolve the corresponding peaks in that compound, which differ[16] by 0.6 p.p.m. The explanation for our failure to resolve the C-2 and C-5 peaks for methyl α-D-glucopyranoside may be the larger-than-expected experimental errors in the determination of σ_{iso} from the chemical-shift tensor of these two nuclei, because of overlapping of the resonances observed at several angles in the three crystallographic planes during the single-crystal n.m.r. experiments.

The resonance positions of the ring-carbon atoms of methyl α-D-glucopyranoside tetraacetate, which we measured in the solid state as well as in solution, are given in Table III. The assignments follow the earlier report of solution n.m.r. studies made on this compound[20]. We find good correspondence between the solid state and solution n.m.r. resonance positions of the ring-carbon atoms of this compound. This can be understood as arising from the lack of strong hydrogen-bonding in the crystalline state involving the ring-carbon atoms in the tetraacetates of the methyl D-glucopyranosides[21] compared* with the parent compound[12]. This observation supports our view that it is the presence of strong hydrogen-bonding in methyl α-D-glucopyranoside that causes considerable change in the ring-carbon resonances observed in the solution and in the solid state, the hydrogen bonding being quite different in the crystalline state from that present in the solution.

* Reference 21 reports the crystal and molecular structure of methyl tetra-*O*-acetyl-β-D-glucopyranoside. The crystal structure of methyl tetra-*O*-acetyl-α-D-glucopyranoside has not yet been determined. We assume, however, that the hydrogen bonding is similar in the two compounds.

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