

Molecular Motions in Solid 1,6-Anhydro- β -D-glucopyranose by ^1H Nuclear Magnetic Resonance

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When crystalline 1,6-anhydro- β -D-glucopyranose is heated, the low-temperature form (phase II) is transformed to a 'plastic crystal' (phase I). ^1H Nuclear magnetic resonance studies have shown that phase II possesses an effectively rigid lattice. After a transition to phase I which takes place at ca. 385 K the molecules begin to reorient about their centres of gravity and, as the temperature is raised further, measurable molecular self-diffusion occurs with an activation energy of 18 ± 2 kcal/mol.

1,6-ANHYDRO- β -D-GLUCOPYRANOSE (levoglucosan) formed from the pyrolysis of cellulose and starch is of considerable theoretical and practical interest in relation to the problems of the combustion and utilization of cellulosic materials.¹ The crystalline material when heated displays some unusual changes in its physical properties.^{2,3} While similar anhydro-sugars such as 3,6-anhydro-D-glucose,⁴ 1,6-anhydro- β -D-glucofuranose,⁵ and 1,4-anhydro- α -D-glucopyranose⁶ melt at 395, 384, and 358 K respectively, 1,6-anhydro- β -D-glucopyranose melts at a much higher temperature of 453 K. Thermal analysis indicates that at 385 K levoglucosan undergoes a strong reversible endothermic transition ($L_t = 6$ kcal/mol) which is followed by a minor endotherm on melting ($L_t = 0.85$ kcal/mol). Since the entropy of melting is only 1.8 e.u., levoglucosan qualifies as a 'plastic crystal' according to Timmermans' definition⁷ ($\Delta S_f < 5$ e.u.).

The significance of the phenomenon of 'plasticity' is best understood by considering that normally the melting process consists of the superposition of diffusional motion (with loss of crystal coherence) and isotropy or randomization of orientation. For certain stiff elongated molecules, after liquefaction some orientations are favoured and the liquid remains anisotropic until it is expanded by a transition at a higher temperature. The anisotropic liquid state is characteristic of liquid crystals. The situation is reversed for many globular molecules such as triethylenediamine,⁸ pentaerythritol,⁹ camphor,¹⁰ and levoglucosan which give a 'plastic crystal' phase transition. In this case molecules gain the freedom of rotation and movement by a first- or second-order transition, before the coherence of the crystal is broken by fusion at a higher temperature, and the plastic crystal is isotropic.

The increased molecular motion in the plastic crystal-line phase of levoglucosan is accompanied by reduction of hydrogen bonds that lead to changes in the conformational entropy and i.r. spectra of the molecule. It also

results in increased heat capacity and softening of the crystals as discussed before.³ A further indication of molecular motion and anisotropy within the plastic-crystal phase is provided by X-ray crystallography. Below the transition levoglucosan has a sharp diffraction pattern, which disappears above the transition and reappears when the process is reversed by cooling.¹¹ It is also interesting to note that the same transition is displayed by stereoisomers of the anhydro-D-glucose compound, with minor differences due to the variation of the conformational entropy.³

Here we report the ^1H n.m.r. investigation of the molecular motions in solid 1,6-anhydro- β -D-glucopyranose, including self-diffusion which apparently is one of the characteristics of plastic crystals.^{12,13}

^1H N.m.r. experiments on molecular crystals generally yield a resonance line, the width (in gauss) of which is determined by the magnetic dipolar interactions among the protons and by the motions of the molecules in the crystal. An important parameter in such experiments is S , the second moment or mean square line width (in gauss²). When the molecules are rigidly fixed in their lattice sites, the rigid lattice second moment S_{rig} is determined solely by the interproton spacings according to relation (1) (for a polycrystalline sample)

$$S_{\text{rig}} = 358.082 N_0^{-1} \sum_{i \neq j} r_{ij}^{-6} \quad (1)$$

where N_0 is the number of protons per molecule, r_{ij} is the distance (in Å) between proton i on a given molecule and any other proton j . Techniques for simplifying the calculation by breaking S_{rig} into intra- and inter-molecular contributions are well known and are described elsewhere.^{8,9,13}

As the molecules begin to move, the large anisotropic interaction originating from the magnetic dipole moments of the protons are averaged; consequently the ^1H n.m.r. line narrows and the second moment is reduced. The line narrowing may be analyzed using the modified

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⁷ J. Timmermans *J. Chim. phys.*, 1938, **35**, 331; *Phys. and Chem. Solids*, 1961, **18**, 1.

⁸ G. W. Smith, *J. Chem. Phys.*, 1965, **43**, 4325.

⁹ G. W. Smith, *J. Chem. Phys.*, 1969, **50**, 3595.

¹⁰ J. E. Anderson and W. P. Slichter, *J. Chem. Phys.*, 1964, **41**, 1922.

¹¹ Personal communication from Professor G. A. Jeffrey.

¹² G. W. Smith, *Internat. Sci. Tech.*, 1967, **61**, 72.

¹³ G. W. Smith, *J. Chem. Phys.*, 1969, **51**, 3569.

¹ F. Shafizadeh, *Adv. Carbohydrate Chem.*, 1968, **23**, 419.

² F. Shafizadeh, G. D. McGinnis, C. W. Philpot, and R. A. Susott, *Carbohydrate Res.*, 1970, **13**, 184.

³ F. Shafizadeh, G. D. McGinnis, R. A. Susott, and C. W. Philpot, *Carbohydrate Res.*, 1970, **13**, 165.

⁴ W. N. Haworth, L. N. Owen, and F. Smith, *J. Chem. Soc.*, 1941, 88.

⁵ R. J. Dimler, H. A. Davis, and G. E. Hilbert, *J. Amer. Chem. Soc.*, 1946, **68**, 1377.

Bloembergen, Purcell, and Pound¹⁴ theory described previously^{8,9,13,15,16} to obtain the correlation frequency ν_c and the activation energy for the molecular motion, through equation (2) where $\alpha = (8 \ln 2)^{-1}$, γ is the

$$2\pi\nu_c = \alpha\gamma\delta H(\tan\{\frac{1}{2}\pi[(\delta H^2 - B^2)/(C^2 - B^2)]\})^{-1} \quad (2)$$

gyromagnetic ratio, δH is the linewidth in the transition region, B is the linewidth at temperatures higher than the transition region, and C is the linewidth at temperatures below the transition region. Calculated values of ν_c are then least squares fitted to the Arrhenius expression (3).

$$\nu_c = \nu_\infty \exp(-E/RT). \quad (3)$$

In addition the magnitude of the second moment as reduced by molecular motions can be used to evaluate the nature of the motion.^{8,9,13,15,16} Thus ¹H n.m.r. experiments allow us to determine details of both molecular structure (from the second moment) and molecular motions (from the linewidth and the second moment). Such experiments should be of interest to organic chemists who find subtle manifestations of molecular motion in spectral and other properties of organic compounds.¹⁷

EXPERIMENTAL

Apparatus and Methods.—The apparatus is the General Motors Research Laboratories 40 MHz instrument described previously.^{8,9,15,16} The levoglucosan was prepared by pyrolysis of starch¹⁸ and was purified by recrystallization from methanol solution. A small amount of mobile impurity was still present in the recrystallized sample, as was evident by a very narrow ¹H n.m.r. line superimposed on the sample line in the high-temperature phase. However, this impurity was driven off by keeping the sample at elevated temperatures (ca. 400 K) in a flow of dry nitrogen for several hours. This final purification was performed in the ¹H n.m.r. probe itself as was done previously for hexamethylenetetra-amine.¹⁵ The reduction of mobile impurity was verified by the absence of the very narrow component in the high-temperature phase. All ¹H n.m.r. measurements were taken on polycrystalline levoglucosan in an open-topped glass sample holder which allowed good thermal contact between the sample and the flowing nitrogen exchange gas.^{8,9,15} Data for levoglucosan before and after final purification are reported here.

Our measurements were restricted to line width (δH) and second moment (S) as a function of temperature. Data analysis techniques reported previously^{8,9} were used. Signal-to-noise problems were greater in the present work than previously with a resultant greater experimental scatter. Because of the phase-sensitive detection techniques used, derivatives of ¹H n.m.r. lines were recorded (see Figure 1). Care was taken not to overmodulate the line when δH was measured (between points of slope extreme) and the usual Andrew¹⁹ modulation correction of S was used.

The experimental values of second moment, were derived

from recorder tracings of the line-shape derivative, $g'(H)$, by means of the expression (4)^{8,19} where H_0 is the resonance

$$S = \frac{1}{3} \frac{\int_0^\infty g'(H)(H - H_0)^2 dH}{\int_0^\infty g'(H)(H - H_0) dH} - \frac{h_m^2}{4} \quad (4)$$

field value and h_m is the amplitude of the sinusoidal field modulation. A GE BASIC program has been written to derive S from this equation.

RESULTS

Line Shape and Line Width.—The ¹H n.m.r. derivative line maintained a constant shape (Figure 1a) over a temperature range from 298 K to at least 381 K. At ca. 383 K a narrow central component began to appear at the expense of the broader component (Figure 1b). At 386 K the central component was well resolved (Figure 1c), and by 390 K the broad component had almost disappeared (Figure 1d). It is assumed that the dramatic line-shape change actually occurs discontinuously at the phase transition and the measured temperature range covered by the line-shape change of ca. 4–5 K, is due to temperature drifts and long equilibration times. The same phenomenon is observed on thermal analysis and the temperature is slightly raised so that the transition could proceed to completion after it is started. From the ¹H n.m.r. line-shape change therefore it is concluded that the transition temperature is 385 ± 2 K, in good agreement with the calorimetric result.^{1,2}

At a temperature of 415 K (well into phase I) the line shape was approximately Lorentzian. This is shown in Figure 1e, in which the magnetic field scan has been narrowed by ca. 10 times that for Figures 1a–d. Thus the line width in Figure 1e is ca. 0.67 G while that in Figure 1a is ca. 12 G.

A plot of line width (δH) versus temperature is given in Figure 2. The three types of symbols shown represent data taken on a sample after preparation and recrystallization (■), the same sample after further purification by heating it in the ¹H n.m.r. apparatus (○ and ●). The open circles are data taken with increasing temperature, the closed circles with decreasing temperature.

As the sample is warmed from 298 to 385 K, δH is constant at the rigid lattice value of 11.4 ± 0.5 G. Above 385 K, δH drops to ca. 2 G (signifying the onset of motion) and continues to decrease as the temperature is raised further. It is possible to supercool phase I a few degrees, as shown by the data of Figure 2; however, under these experimental conditions nothing approaching the large effect seen in references 1 and 2 was noted. An expansion of the linewidth plot in phase I is shown in Figure 3. It can be clearly seen that around 395 K the as-prepared sample has a narrower line than the purified sample. However at higher temperatures there is no linewidth difference.

Second Moment.—At 298 K the experimental second moment S is 15.6 ± 1 G², a value which can be ascribed to a rigid lattice, as we shall see; S does not decrease until the temperature is raised to the transition at which point S drops abruptly to 0.7 G². As the temperature is increased further in phase I, S continues to decrease, attaining a

¹⁴ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 1948, **73**, 679.

¹⁵ G. W. Smith, *J. Chem. Phys.*, 1962, **36**, 3081.

¹⁶ G. W. Smith, *J. Chem. Phys.*, 1965, **42**, 4229.

¹⁷ As an example see J. E. Katon, J. T. Miller, jun., and F. F. Bentley, *Carbohydrate Res.*, 1969, **10**, 505.

¹⁸ R. B. Ward, *Methods of Carbohydrate Chem.*, 1962, **2**, 394.

¹⁹ E. R. Andrew, *Phys. Rev.*, 1953, **91**, 425.

value of *ca.* 0.2 G² at 429 K. As shown below, these values of *S* are characteristic of molecules undergoing general reorientation about the centre of gravity, followed by self-diffusion.

Considerations of Structure and Motions from Second Moment.—As mentioned above, the theoretical value of the rigid lattice second moment (*S*_{rig}) can be calculated from

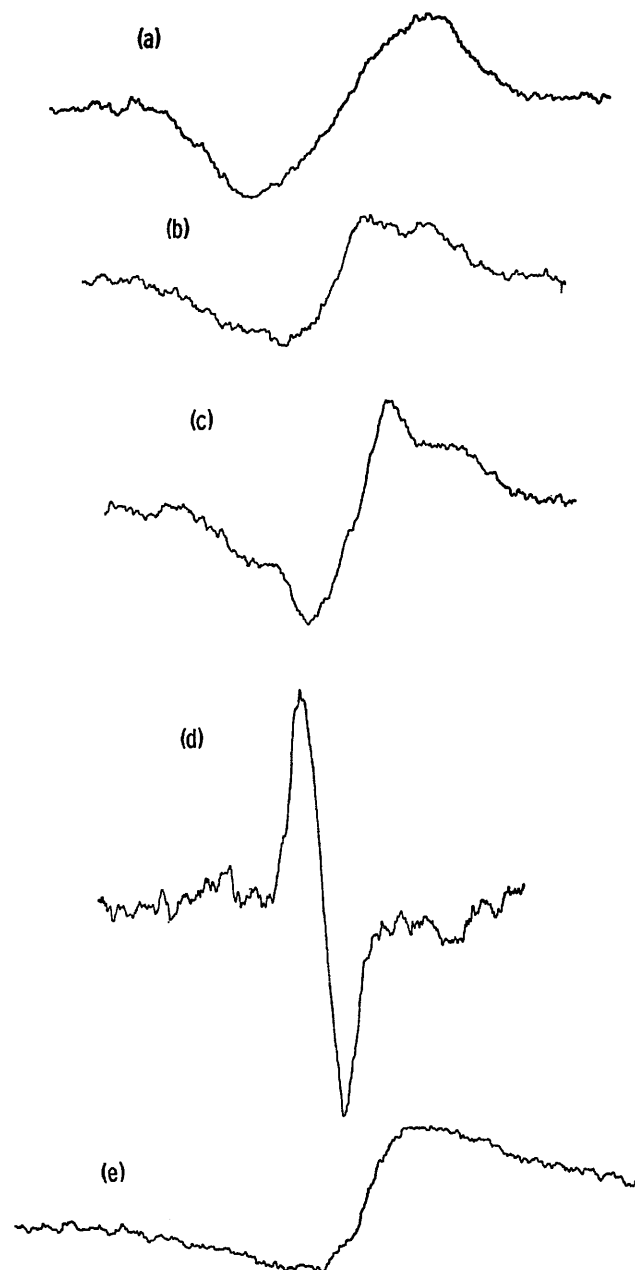


FIGURE 1 ¹H N.m.r. derivative line shapes of levoglucosan at various temperatures: (a) 298–381 K, (b) 383 K, (c) 386 K, (d) 390 K, and (e) 415 K. [The field scan for (e) is over a range *ca.* 10 times smaller than for (a) to (d).]

the hydrogen positions.⁹ The data required for these calculations are provided by crystallographic investigations of Jeffrey and co-workers²⁰ which shows the crystal structure of the low-temperature phase of levoglucosan to be

*P*2₁2₁2₁ (*V*⁴) with *a* = 6.684 Å, *b* = 13.266 Å, and *c* = 7.547 Å. A computer program was used to generate hydrogen positions on neighbouring molecules on the

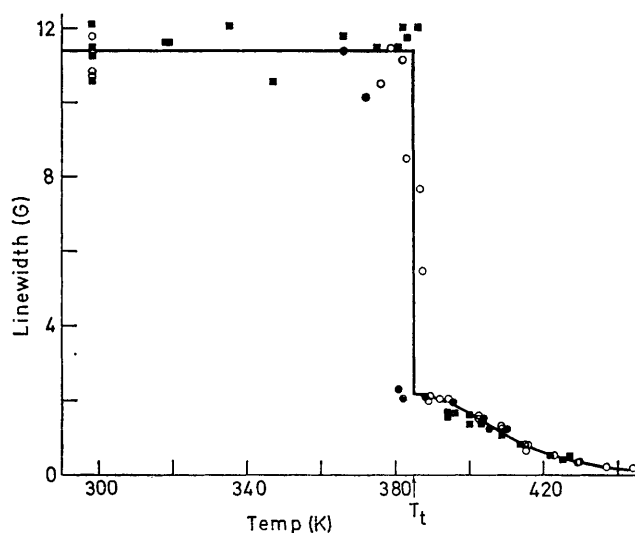


FIGURE 2 Plot of line width *versus* temperature for levoglucosan. As explained in text, symbols represent data for sample as prepared (■), repurified sample, heating (○), repurified sample, cooling (●)

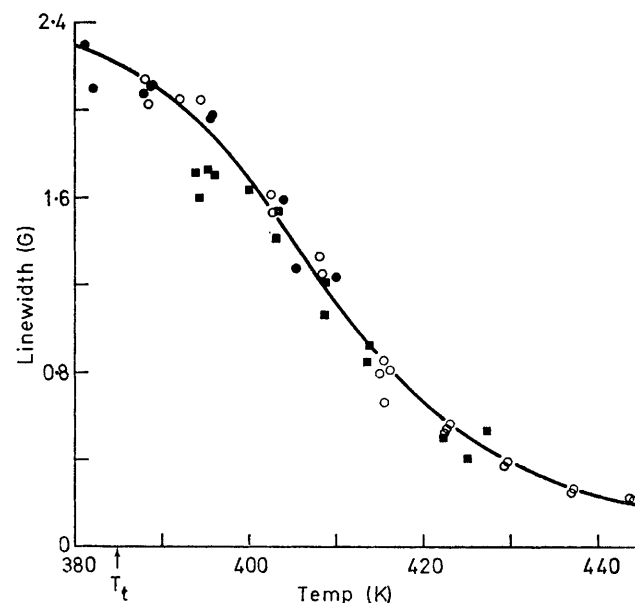


FIGURE 3 Plot of line width *versus* temperature for levoglucosan in plastic crystalline phase (phase I). Symbols are as in Figure 2. Solid line is least-squares fit to the modified BPP expression of ref. 9 with *E* = 18 kcal/mol.

lattice and to calculate the second moment from equation (1).

We found the intramolecular and intermolecular contributions to the rigid lattice second moment to be 8.3 and 6.8 G² for a total of 15.1 G², in satisfactory agreement with the experimental value of 15.6 ± 1 G² at room temperature.

Although it is possible to visualize a number of intra-
²⁰ Y. J. Park, H. S. Kim, and G. A. Jeffrey, *Acta Cryst.*, to be published.

molecular modes of motion in which hydroxy hydrogens reorient about C-O bond axes, it appears from the value of S immediately above the transition that the dominant mode of motion at that point is general molecular reorientation about the molecular centre of gravity. Such motions generally produce ^1H n.m.r. second moments of less than 1 G^2 (see references 8, 9, 13, 15, 16, and 21). In fact, if we assume that the lattice of phase II persists in phase I and estimate S_{reor} , the second moment for general molecular reorientation, by the methods of reference 9, we obtain $S_{\text{reor}} \approx 0.9\text{ G}^2$. For a more open lattice, which prevails after the first-order transition, S_{reor} would be further reduced toward the experimental value of 0.7 G^2 at 385 K .

The decrease in S and δH as temperature is further increased in phase I indicates that molecular self-diffusion is occurring at frequencies on the order of 10^4 Hz .^{8,13} It is well known that for completely isotropic motion the second moment approaches zero.^{8,9,13,15,16}

Evaluation of Diffusion Activation Energy from δH .—The gradual line narrowing which occurs in phase I of levoglucosan as we have seen above, is due to molecular self-diffusion. From the temperature dependence of δH and equations (2) and (3) we evaluated E_D , the activation energy for self-diffusion, obtaining $18 \pm 2\text{ kcal/mol}$. The large error is due, not to scatter in the data, but to uncertainty in the value of C , the asymptotic low-temperature value of δH which appears in equation (2). It is reasonable to suppose that C is somewhat less than the 2.8 G for hexamethylenetetramine.¹⁵ A value of 2.5 G seemed suitable and yielded the quoted value of E_D . However, a change of 0.1 G in C produces a swing of $1\text{--}2\text{ kcal/mol}$ in E_D .

²¹ G. W. Smith, *J. Chem. Phys.*, to be published.

²² E. R. Andrew, 'Defects in Crystalline Solids,' The Physical Society, London, 1955, p. 60.

DISCUSSION AND CONCLUSIONS

The ^1H n.m.r. data seem for the most part to be consistent with the previous calorimetric and crystallographic studies. In the low-temperature phase (phase II) the levoglucosan lattice is rigid with the structure found by Jeffrey and his co-workers.²⁰ As the temperature is raised above 385 K , the high-temperature 'plastic crystalline' phase (phase I) is entered. In this phase the molecules are reorienting about their centres of gravity sufficiently frequently to narrow the ^1H n.m.r. line and reduce the second moment from the rigid lattice value to 0.7 G^2 . Self-diffusion, with activation energy $E_D = 18 \pm 2\text{ kcal/mol}$, also occurs in phase I.

Andrew,²² Van Liempt,²³ and Nachtreib and Handler²⁴ have suggested methods for estimating E_D . The Andrew relation is $E_D \approx L_m + L_v$, where L_m and L_v are the heats of melting and vapourization. Lacking data for L_v , we cannot test this method. The Van Liempt expression is $E_D \approx 32 T_m\text{ cal/mol}$, where T_m is the melting temperature. This expression yields $E_D = 14.5\text{ kcal/mol}$. The Nachtreib-Handler expression ($E_D = 16.5 L_m\text{ kcal/mol}$) gives $E_D = 13\text{ kcal/mol}$. The agreement of these two methods with the experimental value is about as good as one might expect.

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²³ J. Van Liempt, *Z. Physik*, 1935, **96**, 534.

²⁴ N. H. Nachtreib and G. S. Handler, *Acta Met.*, 1954, **2**, 797.