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THERMODYNAMIC PROPERTIES OF 1,6-ANHYDROHEXOPYRANOSE CRYSTALS

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ABSTRACT

When crystalline 1,6-anhydrohexopyranoses are heated, they all undergo closely similar, first-order transitions in the solid phase; these transitions are accompanied by major changes in the entropy and heat capacity of the compounds. The high-temperature phase has a very low entropy of fusion, and can be classified as a plastic crystal. With levoglucosan it has been shown that the transition is accompanied by softening of the crystal and changes in the i.r. and broad-line n.m.r. spectra that indicate a decrease in hydrogen bonding and increased molecular motion. The nature of these transformations is discussed in the light of the information available from other examples of phase transition to plastic crystal.

INTRODUCTION

In a preliminary communication from this laboratory[1] it was shown that crystalline 1,6-anhydro-β-D-glucopyranose (levoglucosan), when heated, undergoes a strong transition at 113°, readily detectable by differential thermal analysis (d.t.a.) as an endothermic peak. The phenomenon is reversible at 50° and the material melts at 180°. The latent heats of transition (ΔH_t), reverse transition (ΔH_{rt}), and fusion (ΔH_f) are 6, −4.9, and 0.85 kcal.mole^{-1}, respectively.

In this paper we provide further information about the solid-state transitions of levoglucosan and related 1,6-anhydrohexopyranoses.

Although a variety of organic and inorganic compounds exhibit polymorphism accompanied by distinct thermal transitions, the phenomenon observed for levoglucosan is unique because ΔH_t is several times greater than ΔH_f. Amongst the carbohydrates and related compounds, such a transition has, to our knowledge, been observed only with pentaerythritol. The transition of this compound has been investigated extensively by thermodynamic[2-5], crystallographic[6-10], and spectroscopic[11-14] methods. It has been shown that, below the transition at about 188°, pentaerythritol has a tetragonal crystalline structure. At the temperature of transition it undergoes a restricted reorientation to give a cubic, crystalline structure. The

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thermodynamic investigations reported included measurements of the heat capacity (C_p), ΔH_t, and ΔH_f. This gave the entropies of transition and fusion (in cal.mole^{-1}.degree):

$$\Delta S_t = \frac{\Delta H_t}{T_t} = \frac{10500}{461} = 22.8, \text{ and } \Delta S_f = \frac{\Delta H_f}{T_f} = \frac{1700}{539} = 3.2$$

The significance of these data and their bearing on our subject is indicated by the following consideration.

Melting of organic compounds generally involves a change in entropy of about 12 cal.mole^{-1}.degree^{-1} or more, according to the molecule's complexity. This change occurs because on melting, the molecules are set free from the lattice to move as individual particles, and various parts of the molecules that were previously restrained are also allowed to reorient and randomize. However, the entropy of fusion is lowered it the material is associated (hydrogen bonded) in the liquid state or if the molecules have freedom of rotation in the solid state[15]. According to Timmermans[16], compounds showing an entropy of fusion of less than 5 cal.mole^{-1}.degree^{-1} are considered to have a mesomorphic state called a plastic crystal. It has been shown that the molecules in plastic crystals possess an unusual degree of freedom of movement[17]. Consequently, molecules in a plastic-crystal phase are randomly distributed between the different possible orientations and show the phenomenon of self diffusion. The plastic crystals are soft and can be extruded under low pressures ,and may even flow under gravity. Transition to the plastic-crystalline phase is usually shown by molecules that are symmetrical, such as pentaerythritol and adamantane, or become spherical by rotation, such as camphor[16–19]. Despite these unique properties, it is hard to establish any criteria for definition of plastic crystals other than the arbitrary value of ΔS_f <5 cal. mole^{-1}.degree^{-1} designated by Timmermans[16,17], and molecular self-diffusion as discussed below.

Observation of changes in heat capacity at the transition temperature is also useful for the study of molecular motion[20]. It has been pointed out that a first-order transition, indicated by increased heat capacity, is observed when self diffusion[18,19] in the plastic phase is taking place, whereas a continuous heat-capacity curve (which is characteristic of second-order transitions) is noted when heating causes increased orientational freedom without self diffusion[21]. Furthermore, it has been suggested that molecular self-diffusion is the *sine qua non* characteristic of the plastic-crystalline state[22]. On this basis, an abrupt increase in the heat capacity may be considered as one of the requirements for transition into a plastic-crystalline phase.

RESULTS

Fig. 1 shows the d.t.a. curves for a number of 1,6-anhydro-β-D-hexopyranoses, including 1,6-anhydro-2-deoxy-β-D-*arabino*-hexopyranose, the related 1,6-anhydro-α-D-galactofuranose, the 1,6:2,3 and 1,6:3,4-dianhydro-β-D-hexopyranoses, and methyl α- and β-D-glucopyranosides. As can be seen, all of the 1,6-anhydrohexopyr-

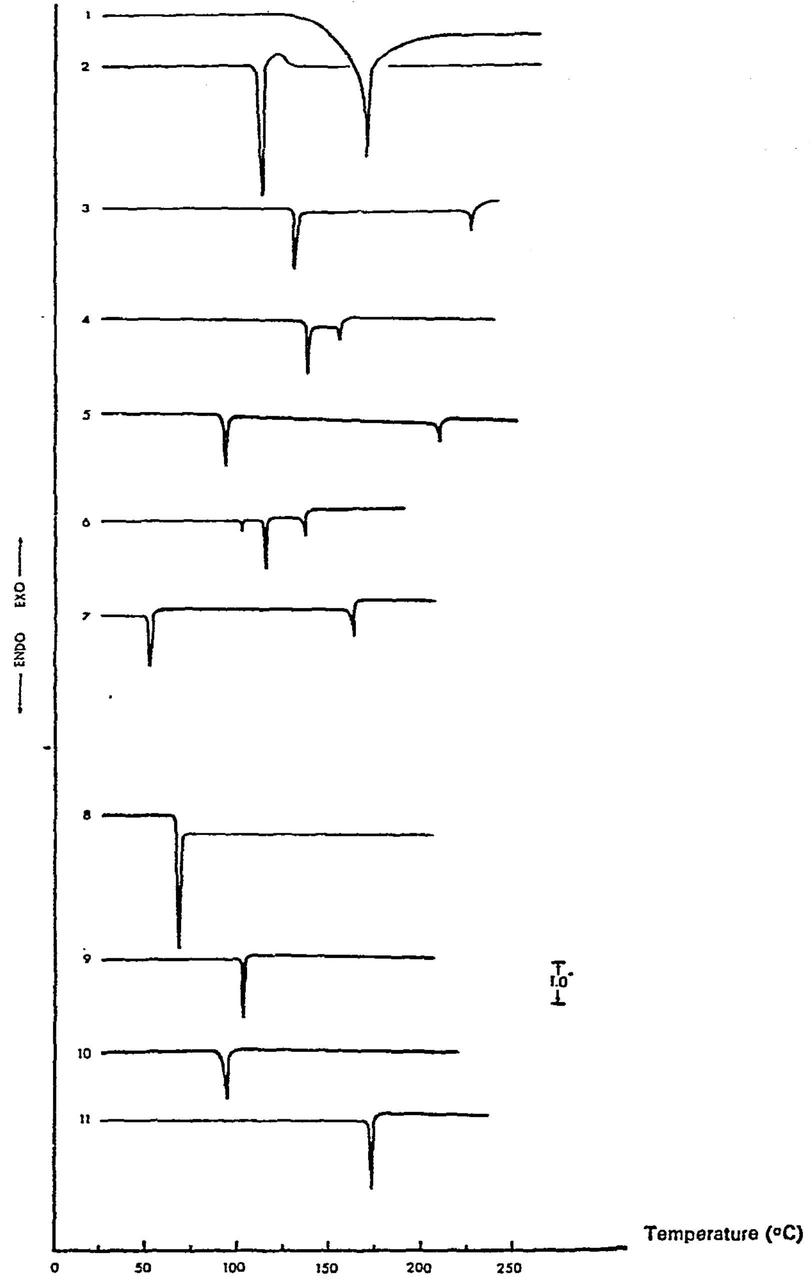


Fig. 1. The d.t.a. curves for: methyl α-D-glucopyranoside (1), methyl β-D-glucopyranoside (2), 1,6-anhydro-β-D-galactopyranose (3), 1,6-anhydro-β-D-gulopyranose (4), 1,6-anhydro-β-D-mannopyranose (5), 1,6-anhydro-β-D-altropyranose (6), 1,6-anhydro-2-deoxy-β-D-*arabino*-hexopyranose (7), 1,6:3,4-dianhydro-β-D-galactopyranose (8), 1,6:3,4-dianhydro-β-D-allopyranose (9), 1,6:2,3-dianhydro-β-D-allopyranose (10), and 1,6-anhydro-α-D-galactofuranose (11).

anoses tested show an endothermic transition-peak before melting, except for 1,6-anhydro-β-D-altropyranose, which gave two transitions. However, the closely related methyl D-glucopyranosides, the 1,6-anhydrohexofuranose, and the dianhydro sugars show only the melting point. The close proximity of the transition and melting points, 103, 115, and 137°, for the altrose derivative (Fig. 1, number 6) explains the extensive sintering of this compound before melting, that has been known for many years[23,24].

The latent heats of transition (ΔH_t) and melting (ΔH_f) for the various compounds were measured by differential-scanning calorimetry (d.s.c.) and are given in Table I, together with the temperatures of transition (T_t) and melting (T_f) and the corresponding changes in entropy (ΔS_t and ΔS_f). Methyl α-D-glucopyranoside, which shows normal melting properties, was used as a reference.

TABLE I

THERMODYNAMIC DATA ON PHASE TRANSITIONS IN 1,6-ANHYDROHEXOSES

Compound	T_t *°K*	ΔH_t *kcal.mole*$^{-1}$	ΔS_t *cal.mole*$^{-1}$*.deg.*$^{-1}$	T_f *°K*	ΔH_f *kcal.mole*$^{-1}$	ΔS_t *cal.mole*$^{-1}$*.deg.*$^{-1}$
1,6-Anhydro-β-D-glucopyranose	385	5.96	15.5	453	0.80	1.8
1,6-Anhydro-β-D-gulopyranose	404	5.85	14.5	430	0.69	1.6
1,6-Anhydro-β-D-galactopyranose	401	5.45	13.5	491	0.99	2.0
1,6-Anhydro-β-D-altropyranose	388	4.30	11.1			
				410	0.55	1.3
	375	0.58	1.5			
1,6-Anhydro-β-D-mannopyranose	364	4.37	12.0	481	0.90	1.8
1,6-Anhydro-2-deoxy-β-D-*arabino*-hexopyranose	323	3.00	9.2			
Methyl α-D-glucopyranoside				440	9.00	20.4

Most of the known cases of transition in plastic crystals take place at lower temperatures and have been discovered with calorimeters operating from room temperature and below[17,25]. It is interesting to note that a combination of d.t.a. and the recently developed d.s.c. provide an efficient system for study of this relatively unexplored transition of organic compounds, especially carbohydrates, at elevated temperatures. Furthermore, d.t.a. provides a graphic and more accurate description of the melting behavior of carbohydrates than a simple determination of melting point, which is often accompanied by decomposition, sintering, and other phenomena (compare 1, 2, 4, 6, and 8 in Fig. 1).

As noted in the previous communication[1], the d.t.a. and d.s.c. experiments indicate that the transition of levoglucosan could be reversed, with a sharp exotherm at 50°. The same phenomenon was also observed with the D-gulose derivative, which showed the reverse transition at 85°. In the case of levoglucosan it was observed that the extensive supercooling or hysteresis effect takes place after completion of the phase change. While the phase change is still in progress, the process can be reversed with only a minor lag or hysteresis. The equilibrium and reversibility was also studied by the broad-line nuclear magnetic resonance (n.m.r.) of solid levoglucosan (shown in Fig. 2).

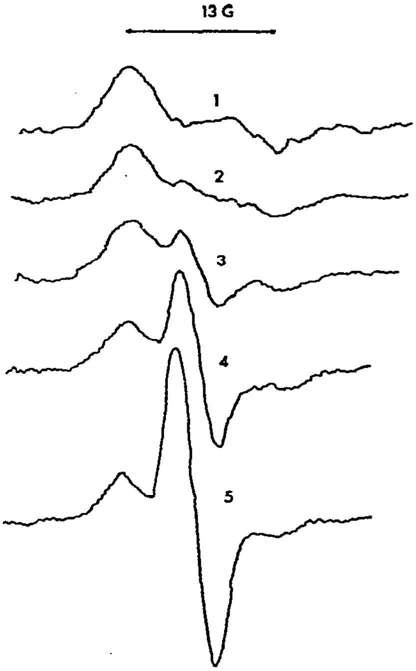


Fig. 2. The broad-line n.m.r. spectra of levoglucosan at: 100° (1), 103° (2), 105° (3), 106° (4), and 108° (5).

From room temperature up to about 103° there was no discernible change in the n.m.r. spectrum. At that temperature there began a line-narrowing that indicated the onset of increased molecular motion[17,26]. On cooling, while the transition was still in progress, the process was reversed, with a small hysteresis. The low-temperature spectrum was restored at 97°.

The plasticity or waxiness of the crystals has been attributed to the greater volume occupied by rotating molecules after the transition[17,27], or to a high proportion of vacancies at the lattice sites, which also accounts for the self diffusion[17,28]. Although this phenomenon is hard to explain and to measure quantitatively, in a qualitative way it could be seen readily that levoglucosan crystals before the transition are hard and brittle and are soft and waxy afterwards.

The transition was also reflected in a major change in the heat capacity (ΔC_p) of the 1,6-anhydrohexopyranoses. As shown in Fig. 3, the C_p values for all of these sugars were found to fall very nearly on one line before the transition, but were displaced to a higher line after the transition. The C_p values for 1,6-anhydro-2-deoxy-β-D-*arabino*-hexopyranose, on a molecular basis, were different because of the difference in molecular composition. However, the values for ΔC_p in terms of cal.g^{-1}.degree^{-1} were very nearly the same for all of the 1,6-anhydro sugars, indicating for each a similar transition. Because of the large hysteresis effect (after the complete transition), it was possible to measure, for both phases, the C_p value at temperatures below the transition point. Methyl α-D-glucopyranoside, used as a reference compound, gave a continuous C_p line.

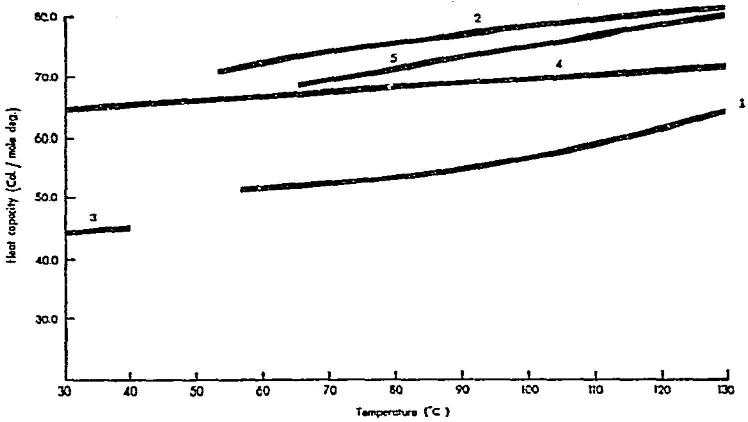


Fig. 3. The heat capacity curves for: 1,6-anhydrohexopyranose before the transition (1) and after the transition (2), 1,6-anhydro-2-deoxy-β-D-*arabino*-hexopyranose before transition (3) and after transition (4), and methyl α-D-glucopyranoside (5).

As discussed later, changes in the entropy and molecular motion indicated by the above data should involve variation in the hydrogen bonding of the molecule that may give rise to detectable changes in the i.r. spectra. However, investigation of i.r. spectra of levoglucosan at different temperatures showed transitions more complex than the phase change alone that is indicated by thermal analysis.

The i.r. spectrum of methyl α-D-glucopyranoside, again selected as a reference material, did not show any major change from 35 to 132°, other than a gradual flattening of the bands, apparently due to the unavoidable increased opacity of the KBr pellets (see Fig. 4). However, the i.r. spectrum of levoglucosan (shown in Fig. 5) indicated certain changes both before and after the transition. After the transition, the spectrum rather abruptly became broad and flat and there was a shift towards higher frequency in the region of 3400 cm^{-1}. Before the transition there were noticeable changes in the 900, 2900, and 3400-cm^{-1} region. In Fig. 5, the spectrum numbered 1 was obtained from a Nujol mull, and the rest were made from KBr pellets. Apparently the grinding and pressure required for preparation of the KBr pellets was sufficient to produce a change in the spectrum that was further enhanced by heating. In the region of 900 cm^{-1}, strong bands initially present at 892 and 922 cm^{-1} gradually disappeared in favor of other bands at 896 and 934 cm^{-1}. In the region

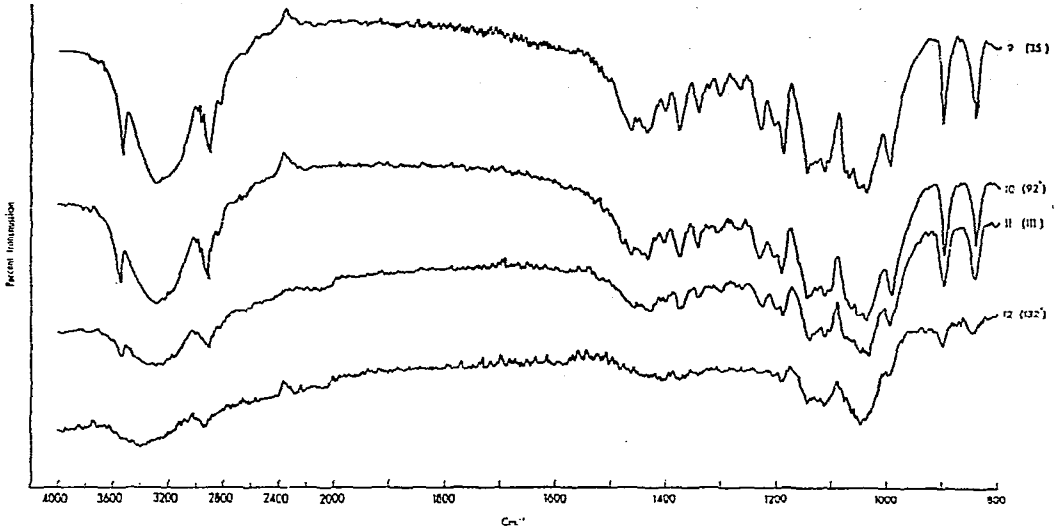


Fig. 4. The changes in the i.r. spectrum of methyl α-D-glucopyranoside over the range of 35–132°.

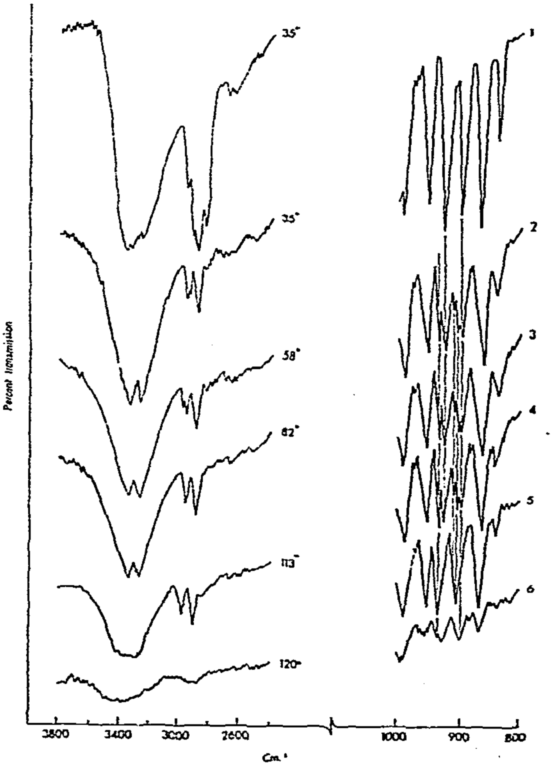


Fig. 5. The changes in the i.r. spectrum of levoglucosan over the range 35–120°. The spectrum number 1 was obtained from a Nujol mull and the rest from KBr pellets.

of 2900 cm^{-1}, the strong band at 2910 cm^{-1} remained constant (spectra 2 to 5) but the band at 2960 cm^{-1} gradually increased and the next band (at 2980 cm^{-1}) decreased. In 3400-cm^{-1} region there seemed to be a minor shift towards the lower frequencies.

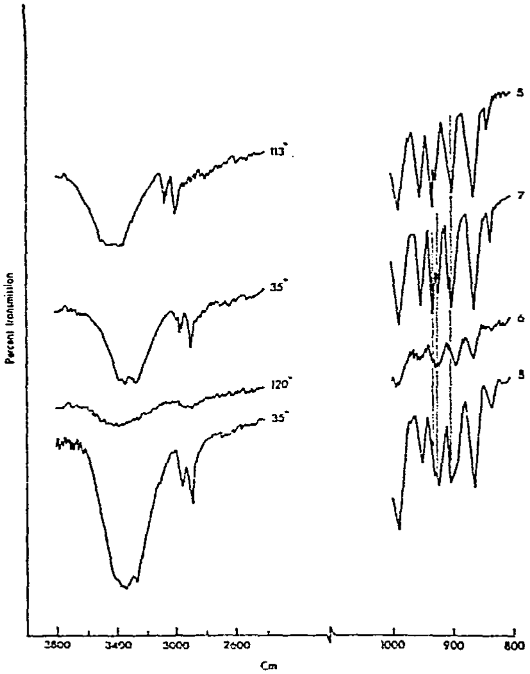
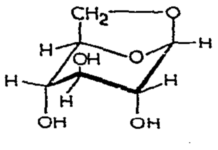


Fig. 6. The partial reversal of the changes in the i.r. spectrum of levoglucosan on cooling a sample that had been heated to the transition temperature (5→7) or past the transition (6→8).

As seen in Fig. 6, attempts to reverse the changes in the i.r. spectra by cooling the samples that had been heated to the transition temperature (5→7), or past the transition (6→8), were only partially successful.

Similar changes in the i.r. spectrum of levoglucosan has been observed previously by Nikitins and associates[29], who have attributed them to the transformation of the *1C* (D) chair (**1**) into the *3B* (D) boat (**2**) conformation of levoglucosan.



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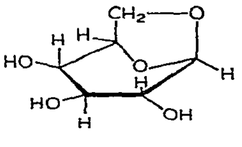

2

Such a change in the conformation of the molecule in solution may be detected by changes in the n.m.r. coupling constants of H-2, H-3, and H-4, which are equatorial in the *1C* (D) and axial in the *3B* (D) conformations. However, the n.m.r.

spectrum of levoglucosan, which was investigated by comparison with the data obtained from the tri-*O*-acetyl[30] and 2-*O*-methyl derivative[31], showed no pertinent change at temperatures up to 130°.

DISCUSSION

A first-order transition, with major changes in entropy, an exceptional low entropy of fusion, a major increase in heat capacity, the corresponding changes in the broad-line n.m.r. and i.r. spectra, and the softening of crystalline levoglucosan, indicate a transition of this material into the plastic-crystal[14,16,17] phase. This observation applies also to other 1,6-anhydrohexopyranoses; which also have low entropies of fusion and show very similar transition properties.

As noted before, the molecules in a plastic crystal possess a high degree of freedom of movement, including rotational and translational movements, as well as vibrational and intermolecular motions. Therefore, a complete understanding of this phenomenon requires information about the molecular shape and packing, as obtained by X-ray and neutron diffraction , and analysis of the molecular movements by n.m.r. spectroscopy according to the BPP theory[14,17,32]. However, lacking all of these data, considerable information can still be derived from thermodynamic considerations and by comparisons with other organic compounds. The molecules that give rise to plastic crystals are usually "globular". To meet this requirement, the levoglucosan molecules most probably become "globular" by rotation around an axis, in a manner similar to camphor, which is a known example in this group. A major difference between camphor[17,18] (T_t $-23°$, ΔS_t 7.6 cal.mole^{-1}. degree^{-1}, T_f 180°, and ΔS_f 2.8 cal.mole^{-1}.degree^{-1}) and levoglucosan is obviously the presence of hydroxyl groups and the possibilities for hydrogen bonding. This factor could also account for the difference in the ΔS_t values (given in Tables I) for the anhydro sugars and the anhydro-2-deoxy sugar, which has one less hydroxyl group*.

The change in entropy resulting from transition to the plastic-crystal phase may be considered to be partly derived from the possible reorientation of the molecule and partly from the increased freedom of movement. Assuming that the latter contributions is small, ΔS_t can be used for estimating the possible number of distinguishable orientations of the molecules after the transition. When the molecule, in addition to possible reorientation, can also gain conformational disorder or intramolecular flexibility due to the breaking of hydrogen bonding or otherwise, the ΔS_t value will be proportionately larger. A good example is found in the comparison between $\Delta S_t = 22.8$ for pentaerythritol and $\Delta S_t = 12.7$ cal. mole^{-1}. degree^{-1} for tetrafluoropentaerythritol. Part of the difference ($4R\ln 3$) is attributed to the statistical consideration that, at high temperature, the hydrogen atom from each of the four hydroxyl groups in pentaerythritol could have three potential minima (corresponding

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*Since this manuscript was written, the molecular motions of levoglucosan have been investigated by the n.m.r. method and will be reported separately.

to the possibilities for hydrogen bonding). The remainder ($R\ln 2$) is because the CH_2OH tetrahedra could have two sets of mutual arrangements[4,5,17]. On this basis, the ΔS_t value can be related to the number of hydroxyl groups and possibilities for hydrogen bonding, which is a function of stereoisomerism.

In the instances that have been measured, the entropy change on melting of the 1,6-anhydro sugars has been about 2 or $R\ln 3$, which corresponds to the communal entropy of melting. This value means that molecules have obtained before melting most of the rotational and some of the translational degrees of freedom associated with the liquid state. However, it should be noted that the very low ΔS_f values could be due in part to the persistence even in the liquid state of some hydrogen bonding. Furthermore, the physical significance of very small ΔS_f values is not well understood, and there is some skepticism about the meaning of a communal entropy of melting[17].

The extensive increase in the degree of freedom and molecular motion is also shown by the large change in the heat capacity after the transition. These factors also account for the softness of crystals after the transition, and are apparently related to the rapid changes in the i.r. absorption spectra, as discussed below.

Theoretically, the randomization, and especially the increase in configurational entropy, should be accompanied by decrease in hydrogen bonding. Furthermore, it is known that hydroxyl groups having weaker hydrogen-bonding absorb at higher frequencies[33] and that hydroxyl groups indicated to be free (by crystallographic data) appear from their i.r. spectra to be weakly hydrogen-bonded[34]. These considerations are consistent with the observation that heating of levoglucosan through the transition causes the hydroxyl band at 3400 cm^{-1} to be flattened and shifted to a higher frequency, indicating a decrease in hydrogen bonding after the transition.

The broad-line n.m.r. data (see Fig. 2) provides independent verification of the increased molecular motion[17,26]. However, the transition, as indicated by thermal analysis, may start at a higher temperature than the molecular motion shown by n.m.r. data[14], due to a surface-diffusion phenomenon[35].

Another subject that should be considered is the difference between the latent heats of transition for levoglucosan at 113° ($\Delta H_t = 6$ kcal.mole^{-1}) and the reversal at 50° ($\Delta H_{rt} = -4.9$ kcal.mole^{-1}). This datum shows that, despite the extensive supercooling, the change of entropy on reverse transition ($\Delta S_{rt} = -15.2$) very nearly equals the value for the original phase change of $\Delta S_t = 15.5$. Furthermore, the difference between heat capacity before and after the transition can be estimated from the following equation:

$$\Delta C_p = \frac{\Delta H_t - \Delta H_{rt}}{T_t - T_{rt}} = \frac{1{,}100}{63} = 17.5 \text{ cal.mole}^{-1}\text{. degree}^{-1}$$

This value is again very close to the experimental result (see Fig. 3).

Nikitin and coworkers[29] have suggested that the changes in the i.r. spectra of levoglucosan below 100° are due to the conversion of the chair (**1**) into the boat (**2**) conformation. Their conclusion is based on the observation that the vibrational frequency of C–O bonds for axial groups in steroids is slightly smaller than that of the equatorial isomers, and the reverse is true for C–D bonds[36–39].

This conclusion led us initially to reason that a small energy-barrier between the two conformations of minimal potential energy could allow the continuous interconversion of the molecule between them at the elevated temperatures. In other words, the solid-state transition of levoglucosan is of the order–disorder type[15,40,41]. In support of this theory, it was shown that the transition (see Fig. 1) disappears with the introduction of (2,3 or 3,4) epoxy groups in the pyranose ring, or by conversion into a furanose structure, which destroy the restricted flexibility of the ring system and interconvertibility of the two conformations. However, a second-order transition of that type is not consistent with the C_p data. Also, the bulk of the information available on the plastic–crystal transition indicates that this phenomenon is related to the overall symmetry or "globular" shape of the molecule, and its motion within the lattice, rather than the conformational stability of the molecule as such. This is supported by the observation that the n.m.r. spectrum of levoglucosan in solution does not show any conformational change at temperatures up to 130°. Furthermore, the conclusions of Nikitin and coworkers are open to question because of the vagaries in conformational analysis of carbohydrates on the basis of i.r. spectra of unrelated materials[42] and other reported instances of the variation of i.r. spectra with temperature[43].

Under these circumstances there is no evidence to establish a relationship between the transition of levoglucosan and the changes in the i.r. spectra at the lower temperatures. Further data are required to establish the cause of the latter phenomenon.

EXPERIMENTAL

Dynamic thermal analysis. — The d.t.a. scans were obtained with a DuPont 900 thermal analyzer, programmed at the rate of 5°.min^{-1}. The experiments were conducted in a nitrogen atmosphere by using silica beads as the reference and 20 mg of powdered levoglucosan as the sample. The curves obtained are shown in Fig. 1.

The d.s.c. data were obtained with a Perkin–Elmer DSC-1B differential-scanning calorimeter programmed at the rate of 1.25°.min^{-1} in a nitrogen atmosphere. The ΔH determinations were made on 10 mg of powdered samples. The system was calibrated against the heat of fusion of indium at 156.6°, $\Delta H_f = 6.75$ cal.g.$^{-1}$. The results are summarized in Table I.

Measurements of heat capacity. — These data were obtained with the DSC-1B instrument by the method of O'Neill[44]. A 10-mg sample was heated at 10°.min^{-1} for 10 or 20 degree intervals and then kept isothermally for 2 min before heating again. The area under the heat-capacity curve was measured with a disc integrator and, after subtraction of a blank area, was compared with the area under the curve obtained with a sapphire standard of known mass and heat capacity. The heat capacity was averaged over the temperature interval by dividing the ΔH value by the change in temperature. The temperature was determined from a calibration curve by using as fixed points the fusion points of benzophenone (48.25°), benzoic acid (122.4°), indium (156.6°), ammonium nitrate (170.0°), and tin (213.9°). These results gave the data presented in Table II, from which the heat-capacity curves shown in Fig. 3 are derived.

TABLE II

THE HEAT CAPACITY OF 1,6-ANHYDROHEXOSES

	T(°*K*)	*1,6-Anhydro-β-*D*-hexopyranose*						*Methyl α-*D*-glucoside*
		gluco	*gulo*	*galacto*	*altro*	*manno*	*2-deoxy*-arabino	
before transition	308.5						0.306[a]	
	335.1					0.319		
	339.6	0.325	0.306	0.327	0.316			0.352
	344.1					0.319		
	353.2				0.327	0.335		
	357.8	0.337	0.323	0.336				0.371
	362.4				0.335			
	371.6	0.353						
	376.2		0.346	0.357				0.390
	390.2			0.376				
	394.8		0.377					0.407
	413.7							0.421
after transition	308.5						0.440	
	317.5						0.453	
	335.1					0.446	0.457	
	344.1					0.457		
	357.8	0.476		0.465		0.473	0.470	
	376.2	0.494		0.483	0.486	0.483	0.481	
	394.8	0.503	0.496	0.493	0.482	0.496	0.488	
	413.7	0.513	0.511	0.500		0.499	0.495	

[a] C_p in cal.g^{-1}.degree^{-1}.

Mechanical properties. — Crystals of levoglucosan were poured into a melting-point capillary tube and packed by tapping. A piece of hard steel wire was then introduced into the tube, which was heated in a Mel-Temp melting-point apparatus. Before the transition the crystals were hard and brittle, and pressing the steel wire resulted only in crushing of the surface layer. After the transition and while the tube was still hot the crystals were waxy in appearance and could be readily penetrated by the wire.

I.r. spectroscopy. — Lightly ground levoglucosan was mixed with Nujol and the mull was placed on sodium chloride plates, or levoglucosan was finely ground with potassium bromide and the mixture was formed into pellets *in vacuo* under 12000 lb. in^{-2}. The samples were investigated with a Beckman IR-7 instrument.

The high-temperature measurements were made with an i.r. cell wrapped with a heating tape, and temperature control was effected by use of a Variac and a thermocouple.

N.m.r. spectroscopy. — The n.m.r. spectra were recorded with a Varian HA-60 spectrometer, equipped with a variable-temperature probe accessory. Solvents used were CCl_4 for levoglucosan triacetate and methyl sulfoxide-d_6 and D_2O for levoglucosan. The concentration of solution was 10–20%. Tetramethylsilane was used as the internal or external standard. The solution of levoglucosan in methyl sulfoxide-d_6 had the following bands at room temperature: δ 5.13 (1H, singlet),4.9–4.6 (3H, multiplet), 4.29 (1H, doublets of doublets) (J 1.2 and 0.2 Hz), 3.87 (1H) (J 1.7 and 0.2 Hz), 3.56 (1H) (J 1.3 and 0.2 Hz), and 3.4–3.0 (3H, multiplet). There was no discernible change in this spectrum on heating the solution to 130° other than the increased chemical exchange shown by the δ 4.9–4.6 multiplet.

When a few drops of D_2O were added to the above solution, the δ 4.9–4.6 multiplet (OH group) coalesced into a singlet at δ 4.6 (DOH). On heating up to 90°, there was only an expected upfield shift[45] in the DOH band to δ 4.3.

The broad-line n.m.r. data were obtained through the courtesy of Varian Associates using a Varian WL-15 spectrometer and variable-temperature accessory.

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