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^{13}C–^{1}H INTER-RESIDUE COUPLING IN DISACCHARIDES, AND THE ORIENTATIONS OF GLYCOSIDIC BONDS*

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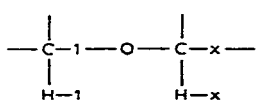
ABSTRACT

In examining orientations of glycosidic linkages, measurements of three-bond coupling between ^{13}C-1 and ^{1}H-4′, or ^{13}C-4′ and ^{1}H-1, have been made from natural abundance, ^{1}H-coupled, ^{13}C-n.m.r. spectra of maltose, cyclohexaamylose, and related compounds. Maltose and cyclohexaamylose in water exhibit inter-residue ^{13}C–O–C–^{1}H couplings of close to 3 Hz. In terms of torsional angles, ϕ and ψ, these findings suggest that, in aqueous solution, the molecules favor conformations that are appreciably more staggered than those known to exist in the solid state. Analogous measurements on *O*-acetyl derivatives suggest that ϕ is smaller, and ψ larger, than in maltose. Data are also presented for sucrose, maltosan, and α,α-trehalose.

INTRODUCTION

Disaccharides, particularly maltose and cellobiose, have received a good deal of attention as models for assessing the conformations of structurally related polysaccharides. A comparison of X-ray crystallographic data[1–4] with free-energy calculations[5,6] suggests that the linkage orientations of disaccharides in the solid state may be closely similar to those in solution, and support for this possibility has come from spectroscopic[7] and optical rotatory[8] measurements.

An alternative approach for examining disaccharide conformations in solution is offered[9] by the measurement of spin–spin coupling between a ^{13}C nucleus of one residue and a proton of the other. As depicted in structure **1**, inter-residue, three-bond



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coupling is possible between C-1 of the nonreducing-end group and the nearest ^1H of the reducing-end residue ($^3J_{C_1-H_x}$), and between the linkage carbon of the latter and the glycosidic proton ($^3J_{C_x-H_1}$). The dihedral (torsional) angles represented by these two spin–spin interactions correspond, respectively, to[10] angles ψ and ϕ that are commonly used in depicting linkage orientations. As the magnitude of $^3J_{C-H}$ varies with the size of the dihedral angle[11–13], inter-residue $^{13}C-^1H$ coupling should reflect the orientation of the two residues relative to each other[9].

For experimental reasons, $^{13}C-^1H$ coupling data have usually been obtained from ^1H-spectra of ^{13}C-enriched compounds (see, *e.g.*, refs. 11–13). However, recent improvements in instrumentation have greatly facilitated the acquisition of ^1H-coupled ^{13}C-spectra at natural-abundance levels, permitting the alternative of measuring $^{13}C-^1H$ coupling without the need for ^{13}C-labelling. In examining this latter possibility, the current article deals with data furnished by ^1H-coupled ^{13}C-spectra of maltose, cyclohexaamylose, and related disaccharides and derivatives.

RESULTS

Coupling between C-1 and H-4'. — A given ^{13}C nucleus may exhibit splitting due to interactions with several protons, and hence may produce a highly complex signal. However, the anomeric carbon atoms of D-glucose and derivatives, as shown both with ^{13}C-enriched and natural-abundance samples[9,11,13,14], give relatively simple spectra (which served initially as a stimulus for examining the present approach). The C-1α signal appears essentially as a doublet, with a spacing of 170 Hz due to coupling (^1J) with H-1, whereas the C-1β signal is a doublet of doublets, exhibiting $^1J = 160$ Hz and a coupling with H-2 of -5.5 Hz (see Table I). Protons-3, -4, and -6 have no detectable effect on C-1, whereas H-5 couples to the extent of 2 Hz: but the latter interaction has been detected only with ^{13}C-enrichment[13], and was not evident in the C-1α or C-1β signal under the conditions described here. Its existence was suggested, nevertheless, by the fact that the line widths at half-height ($\nu^{1/2}$) of these signals were narrower by 1–1.5 Hz when H-5 of D-glucose was replaced by deuterium[15] (see Table I).

In dealing here with α-D-glucopyranosides*, it has been assumed *a priori* that the coupling characteristics of C-1 of α-D-glucose remain essentially intact when an aglycon is bonded to it, and hence, that any additional splitting or broadening of the C-1 signal is due to a proton of the aglycon moiety. A test of this assumption in a disaccharide model was furnished by the α-D-glucopyranosyl group of sucrose (**2**): *i.e.*, carbon-1, which cannot engage in inter-residue (^3J) coupling as there is no proton at the point of linkage to the D-fructose moiety, produced a signal that was closely akin to the C-1 signal of α-D-glucose in both shape (see Figs. 1A and 1B) and line width (see Table I).

*Preliminary observations on cellobiose have been reported[9], but it appears that, in the β-D-*gluco* series, the data are sufficiently complex to merit separate treatment.

TABLE I

INTER-RESIDUE, $^{13}C-^{1}H$ COUPLING (^{3}J) DATA FOR MALTOSE, CYCLOHEXAAMYLOSE, AND RELATED COMPOUNDS

Compound	*Signal observed*	δ	^{1}J (*Hz*)	$\nu^{1/2}$ (*Hz*)[a]	^{3}J (*Hz*) ($\Delta\nu^{1/2}$)	
					C-1–H-4′	*C-4–H-1*
D-Glucose	C-1 (α)	93.3	169.5	4.0		
				2.5[b]		
	C-1 (β)	97.1	162.0	10.0 (5.5)		
				8.5[b] (5.5)		
	C-4	70.8	145.0	10.0		
Sucrose	C-1 (α)	92.8	169.0	4.0		
Maltose	C-1 (α,β)	100.9	172.5	7.5	<3.5	
	C-1′ (α)	93.2	171.5	4.0		
	C-1′ (β)	97.2	162.5	9.5 (5.5)		
	C-4′ (α,β)	78.9, 78.6	~140	13.5		<3.5
Methyl β-maltoside	C-1 (α)	100.4	173.0	6.5	2.5	
	C-4′	77.8	146.0	11.5		3.0
	C-4	70.1	145.0	8.5		
Phenyl β-maltoside	C-4′	78.0	145.5	12.5		2.5
	C-4	70.2	144.0	10.0		
Cyclohexaamylose	C-1 (α)	102.6	168.5	8.5 (3.5)	3.5	
	C-4	82.6	143.5	14.0		4–5
Maltosan	C-1 (α)	98.6	168.0	8.0 (4.5)	4.5	
α,α-Trehalose	C-1 (α)	94.5	171.5	7.0 (2.5)	2.5	

[a]Line width of signal at half height; numbers in parentheses are observed splittings. [b]Measured with ^{15}D-glucose-5,6,6′-d_3.

The spectrum of α,β-maltose (**3**+**4**) in solution in deuterium oxide permitted an internal comparison of anomeric signals: *i.e.*, the C-1 signal of the nonreducing-end groups with the C-1′ signal due to the α-reducing-end residue. It was found that the latter signal is 3.5 Hz wider at half-height than* C-1′, and it is reasonable to attribute this substantial line-broadening to inter-residue coupling with H-4′. However, the C-1 signal consists of contributions from the nonreducing-end groups of both the α and β forms (**3** and **4**) and, although the two C-1 signals are coincident in the ^{1}H-decoupled spectrum[18], the $\Delta\nu^{1/2}$ value of 3.5 Hz obtained from the coupled spectrum is regarded as a maximum value – hence, the <3.5 entry in Table I.

Methyl β-maltoside (**5**) furnished a C-1 signal representative of the non-reducing-end group of a single anomeric form of the disaccharide (see Fig. 1D). In this instance, the line width was 6.5 Hz, which, in comparison with the reference

*A consistent trend is seen in the fact that the C-1′ signal, and the C-1 signals of α-D-glucose and sucrose, are all virtually indistinguishable (see Table I). Also noteworthy are the ^{1}J data for maltose (see Table I), which show that the coupling between C-1 and H-1, or C-1′α and H-1′α, is larger than that between C-1′β and H-1′β, by about the same amount (~10 Hz) as has been found by comparing other α and β anomers[11,13,16,17]. Coupling data for related compounds are included.

signals, indicates that this signal incorporates a coupling of 2.5 Hz due to interaction across the glycosidic bond with H-4′.

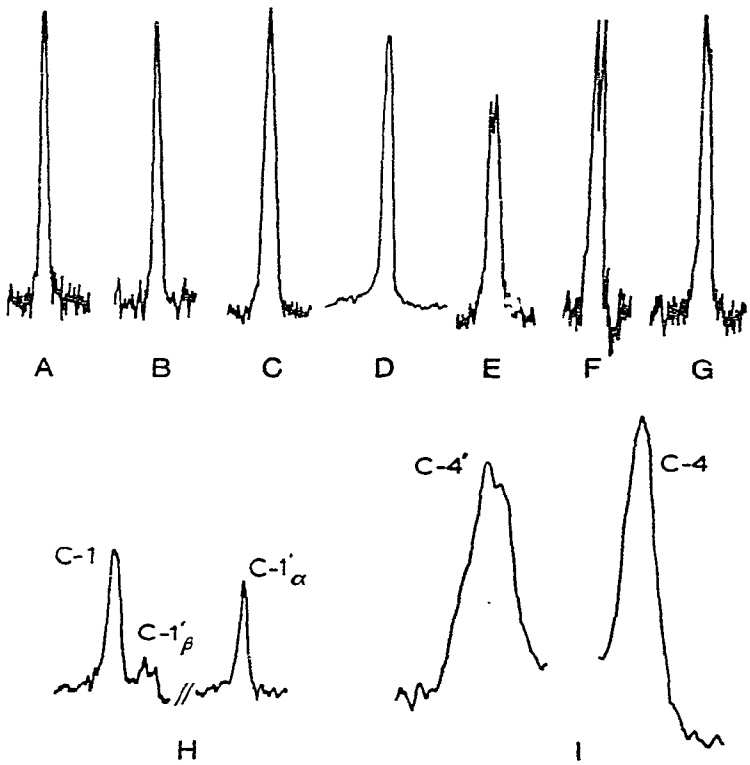
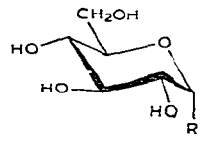


Fig. 1. Signals from ^{1}H-coupled, ^{13}C-n.m.r. spectra at 22.63 MHz (1500-Hz sweep-width). [(A) C-1 signal (downfield half) of α-D-glucose in D_2O. Signals B to G (downfield half of each): C-1 of the α-D-glucopyranosyl group of (B) sucrose, (C) maltose, (D) methyl β-maltoside, (E) cyclohexaamylose, (F) 1,6-anhydro-4-*O*-α-D-glucopyranosyl-β-D-glucopyranose, and (G) α,α-trehalose; each in D_2O. (H) Anomeric signals (downfield half of each) of 2,3,4,6,2′,3′,6′-hepta-*O*-acetyl-α,β-maltose, in $CDCl_3$. (I) C-4′ (downfield half) and C-4 (upfield half) signals of methyl β-maltoside, in D_2O (scale expansion, 3X).]

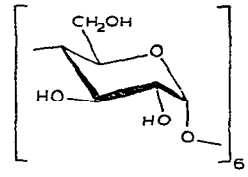
Cyclohexaamylose (**6**), a cyclic trimer of α-maltose, provided more-direct evidence of ^{13}C–^{1}H coupling across the glycosidic bond. In this instance, the C-1 signal (see Fig. 1E) appeared as a well defined doublet of doublets: ^{1}J was 169 Hz, in accord with the α configuration, and the spacing seen in Fig. 1E amounted to 3.5 Hz. Moreover, the latter splitting was shown to be caused by coupling with H-4, as the doublet structure of the signal collapsed when low-power irradiation was applied selectively at the resonance frequency of H-4.

The fact that splitting of the C-1 signal was observed in one instance and not in the other does not appear to be due to lesser rotational freedom about the glycosidic bond in cyclohexaamylose than about that in maltose. Evidence of this was provided

by the fact that the C-1 signal (see Fig. 1F) of maltosan (1,6-anhydro-4-*O*-α-D-glucopyranosyl-β-D-glucopyranose) (7) showed a well defined splitting of 4.5 Hz, attributable to coupling between C-1 and H-4′; yet inspection of models suggested that there may be even greater rotational freedom about the linkage of this molecule than about that of maltose.



2 R = 2-*O*-substituted β-D-fructofuranose
3 R = 4-*O*-substituted α-D-glucopyranose
4 R = 4-*O*-substituted β-D-glucopyranose
5 R = 4-*O*-substituted methyl β-D-glucopyranoside
7 R = 4-*O*-substituted 1,6-anhydro-β-D-glucopyranose
8 R = 1-*O*-substituted α-D-glucopyranose



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An additional example of an α-D-glucopyranosyl-containing structure was provided by the disaccharide α,α-trehalose (α-D-glucopyranosyl α-D-glucopyranoside) (8). In this instance, the C-1 signal (see Fig. 1G) common to both residues had a line width 3.0 Hz wider than that of sucrose, and it also exhibited a shallow splitting amounting to a spacing of ~2.5 Hz.

Coupling between C-4′ and H-1. — The C-4 signal of α- or β-D-glucose consists of a doublet of multiplets; its major spacing ($^1J_{C\text{-}4-H\text{-}4}$) is 145 Hz, and the line width of each multiplet is* 9–10 Hz. These characteristics appear to be maintained in the shape of the C-4′ signal of maltose in deuterium oxide (see Table I); see Fig. 1C of ref. 9. However, the two signals due to the α and β reducing-end residues differ in chemical shift[18] by several Hz, and, as they coalesced in the ^{1}H-coupled spectrum, they could not yield a reliable measurement of line width. Instead, a half-height line-width value for the C-4′ signal was taken from the spectra of methyl and phenyl β-maltoside: the C-4′ width was 2–3 Hz greater than that of the C-4 signal in the same spectrum (see Fig. 1I and Table I), suggesting that this is approximately the magnitude of coupling between C-4′ and H-1 in maltose. The C-4′ signal for cyclohexaamylose was noticeably broader than that for the maltosides, indicative of an inter-residue coupling, with H-1, of ~4 Hz.

O-Acetyl derivatives. — The crystal structure of maltose is characterized by hydrogen bonds between the two residues[1–4], and there is spectroscopic evidence[7] that such bonding is maintained when the compound is dissolved in dimethyl sulfoxide. As this would not apply for the peracetate of the disaccharide, it was of interest to compare inter-residue ^{13}C–^{1}H coupling in such a derivative with data obtained for the parent biose.

*This dimension is accounted for[19] mainly by couplings of close to −5 Hz each with H-3 and H-5, although the protons on C-6 are also likely to contribute.

TABLE II

INTER-RESIDUE, $^{13}C-^{1}H$ COUPLING (^{3}J) DATA FOR PERACETATES OF MALTOSE AND RELATED COMPOUNDS

Peracetate of	*Signal observed*	δ	^{1}J (*Hz*)	$\nu^{1/2}$ (*Hz*)[a]	^{3}J (*Hz*) ($\Delta\nu^{1/2}$)	
					C-1–H-4′	*C-4′–H-1*
α-D-Glucose	C-1 (α)	87.5	177.5	5.5		
	C-4	66.4	151.0	10.5		
Sucrose	C-1 (α)	93.5	175.0	5.0		
β-Maltose	C-1 (α)	95.3	174.0	8.5	3.5	
	C-4′	74.6	164.0	12.5		2.0
α-Maltose (heptaacetate)	C-1 (α)	95.3	174.0	9.5	4.0	
	C-1′ (α)	89.6	174.0	5.5		
Methyl β-maltoside	C-1 (α)	95.4	175.0	9.0 (3.0)	~4.0	
	C-4′	75.2	153.0	12.5		2.0
Phenyl β-maltoside	C-1 (α)	95.3	174.0	9.0 (2.5)	~4.0	
	C-1′ (β)	98.1	165.0	12.0 (5.0)		
	C-4′	75.3	156.0	11.0		
Cyclohexaamylose	C-1 (α)	97.0	171.8	9.5	<4.5	
	C-4	77.0	148.0	14.5		<4.0
Maltosan	C-1 (α)	97.7	171.0	9.0 (4.0)	4.0	

[a]Line width of signal at half height; numbers in parentheses are observed splittings.

As shown in Table II for line-width measurements on peracetates in solution in deuteriochloroform, the C-1 signal of β-maltose octaacetate was 3.5 Hz greater than that of sucrose octaacetate. A related derivative of maltose, the α anomer of the 2,3,4,6,2′,3′,6′-heptaacetate, permitted a direct comparison of the line widths of signals produced in the same spectrum by two α anomeric carbon atoms. For its preparation, the crystalline β anomer was allowed to mutarotate in deuteriochloroform (which was the spectral solvent): after some weeks, the α anomer had become the preponderant (>80%) species*. Essentially, then, the spectrum examined was that of a single species. Comparing line widths of the C-1 and C-1′α signals in this spectrum (see Fig. 1H), a difference of 4.0 Hz was found, indicative of a C-1, H-4′ inter-residue ^{3}J of this magnitude.

The C-1 signal produced by methyl or phenyl β-maltoside heptaacetate exhibited a shallow splitting of 2.5–3.0 Hz, and a line width 4.0 Hz larger than that of the C-1 signal of sucrose octaacetate, which suggested that inter-residue coupling between C-1 and H-4′ in these compounds is close to 4 Hz.

In contrast to unsubstituted cyclohexaamylose, its hexa-(2,3,6-triacetate) did not produce a split, C-1 signal. Furthermore, the line width of C-1 and of other signals in the *decoupled* spectrum was unusually broad. Hence, it is unlikely that the

*That is, although the α:β ratio for maltose in water is ~2:3, the anomeric effect is apparently enhanced in chloroform (possibly also by the presence of *O*-acetyl substituents), and a correspondingly large increase in the proportion of the α anomer is observed.

$\nu^{1/2}$ value of 9.5 Hz (see Table II) can be compared directly with the value of 5.0 Hz for sucrose, and, therefore, it probably represents inter-residue coupling of less than 4.5 Hz. Maltosan hexaacetate, however, gave a well-split C-1 signal closely resembling that shown in Fig. 1F for maltosan itself, affording a $^3J_{C\text{-}1-H\text{-}4'}$ value of 4.0 Hz.

In assessing coupling between C-4′ and H-1 of the acetylated maltose derivatives, line-width comparisons could not be made within the same spectra (as for the non-acetylated compounds) for the C-4 signals, because the latter were heavily overlapped by the C-6 and C-6′ signals. Furthermore, the C-4′ signals themselves were partially obscured by the $CDCl_3$ triplet; but the latter problem was circumvented by the use of ^{13}C-depleted deuteriochloroform, in which the solvent peak was virtually eliminated. As shown in Table II, the C-4′ line-widths have been compared with the value of $\nu^{1/2} = 10.5$ Hz for α-D-glucose pentaacetate, and, on this basis, suggest that $^3J_{C\text{-}4'-H\text{-}1}$ does not exceed 2 Hz.

By analogy with the foregoing comments on the C-1 signal of cyclohexaamylose hexa(triacetate), it is probable that inter-residue coupling between C-4 and H-1 in this molecule contributes less to the line-width of the C-4 signal than is suggested by the observed value of $\nu^{1/2} = 14.5$ Hz (see Table II), and, hence, that $^3J_{C\text{-}4-H\text{-}1}$ is less than 4.0 Hz.

DISCUSSION

The current approach offers an experimentally facile approach to the measurement of inter-residue $^{13}C-^1H$ coupling. However, there are a number of potential limitations to be considered. Signals of ^1H-coupled ^{13}C-spectra can be highly complex, because several protons might be favorably situated for coupling, and higher-order effects[20] could add to this complexity. Another consideration is that an apparent increase in line width ($\Delta\nu^{1/2}$), measured as already described (by comparing carbon atoms in structurally analogous environments), can be influenced by differences in solution characteristics, and also by fluctuations in the stability of the spectrometer during the long acquisition periods (> 12 h) needed for recording these ^1H-coupled spectra. Nevertheless, the spectra of individual compounds have shown good reproducibility, and the overall data contain many instances of self-consistency, as discussed later, suggesting that these various factors need not play a major role.

As already noted, the C-1 signal of α-D-glucose appears essentially as a singlet (aside from its large ^1J spacing). Although it should incorporate[13] a coupling of 2 Hz due to H-5, and, possibly, smaller couplings (< 1 Hz) due to H-2 and H-3, splitting is not observed, but there is an overall broadening of the signal, *i.e.*, $\Delta\nu^{1/2} = 4.0$ Hz. Nevertheless, the existence of coupling between C-1 and H-5 was shown by the fact that the corresponding signal of α-D-glucose deuterated at C-5 had a line width of only 2.5 Hz. This latter value, then, must be close to the natural line-width of the C-1 signal.

Characteristics of the C-1 signal of α-D-glucose are reproduced in the corresponding signals of sucrose (C-1) and maltose (C-1′), in that the line widths and ^1J

values are the same (see Table I), and this consistency is maintained in the acetate series (see Table II). However, a substantial change becomes evident (see Fig. 1) when additional coupling is possible with a proton (H-4′) located across the glycosidic bond. This extra coupling is seen most clearly in the C-1 resonance of maltosan, which exhibits a splitting of 4.5 Hz attributable to H-4′. A separation of peaks is also evident for the C-1 atoms of cyclohexaamylose, although $^3J_{C\text{-}1-H\text{-}4}$ is probably closer to 4.0 Hz than to the measured spacing of 3.5 Hz, because the signal has a relatively shallow valley[21]. Particularly noteworthy for cyclohexaamylose is the fact that it proved possible to confirm experimentally (by spin-decoupling) the existence of coupling between its anomeric carbon atom and the 4-proton located across the glycosidic bond.

Lines comprising the C-1 signal of maltose or various derivatives of it are less well resolved, and, in these instances, $\Delta\nu^{1/2}$ has been taken as a measure of coupling with H-4′. Relative to sucrose or its octaacetate, a signal-broadening of 2.5–4.0 Hz is observed, with the higher value occurring in the acetate series. Among the latter, also, the line shapes strongly suggest incipient splitting. Furthermore, a line shape akin to that of C-1 of maltose (see Fig. 1C) or methyl β-maltoside has been observed in computer simulations*, by assuming that $^3J_{C\text{-}1-H\text{-}4'}$ is 3.0 Hz, whereas a value of 4.0 Hz more nearly reproduced the C-1 signal (see Fig. 1H) of α-maltose heptaacetate. Hence, it appears that the data reported here provide a moderately reliable description of inter-residue coupling between C-1 and H-4′ in the maltose series.

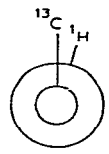
Coupling across the glycosidic bond in the opposite sense, *i.e.*, between C-4 and the anomeric proton, is less readily evaluated, because, even for α- or β-D-glucose, the C-4 signal is an unresolved multiplet. For methyl or phenyl β-maltoside, the C-4′ signal was compared with that of C-4, as an internal reference: in both instances, the C-4′ and C-4 signals had markedly different line-shapes (see Fig. 1I), and C-4′ was the wider by 2–3 Hz. However, an analogous comparison was not possible in the acetate series, because, invariably, the C-4 signal was heavily overlapped by other signals, and a reference line-width of 10 Hz (see Table I) was assumed to be reasonable. With cyclohexaamylose, C-4′ obviously could not be compared internally with an analogous carbon atom, but the broadness of its signal implies a relatively strong, inter-residue coupling between C-4′ and H-1.

Aside from limitations associated with these measurements of $^{13}C\text{–}^1H$ coupling, there is the question of how to relate the coupling values obtained to the orientations of the glycosidic linkages. Variations in the magnitude of $^3J_{C-H}$ with torsional angle are known[11–13,22,23] to follow a "Karplus-type" curve, but the relatively limited body of coupling data now available allows for only rough estimates of the geometry involved. In addition, a given value of ^3J corresponds to two widely-different possibilities. For example, the coupling of 4.5 Hz between C-1 and H-4′ of maltosan—which is relatively large in terms of an overall maximum value of ~6 Hz for $^3J_{C-H}$ involving sp^3 carbon atoms[13]—implies that these two nuclei subtend a

*Kindly performed by G. K. Hamer.

torsional angle not far removed from 0° or 180° (or both). Similarly, the slightly smaller $^3J_{C\text{-}1-H\text{-}4'}$ and $^3J_{C\text{-}4'-H\text{-}1}$ values of 3.5–4 Hz for cyclohexaamylose could correspond to torsional angles of ~20° or 160° (or both). Of these possibilities, it is more reasonable to deal with the smaller values, because large angles are wholly inconsistent with previous experimental and theoretical findings (already cited) for molecules in the maltose series, and would be incompatible with the ring structure of cyclohexaamylose.

Accordingly, the glycosidic bonds of maltosan and cyclohexaamylose may be represented (on the average) by such projections as **9** (ψ, ~10°) and **10** (ϕ and ψ, ~20°), respectively; the mirror images of **9** and **10** would be equally applicable. As maltose and its glycosides exhibit even smaller ^3J values than cyclohexaamylose, the glycosidic bonds in these molecules may be depicted by rotamers having a somewhat larger, average torsional angle, *e.g.*, **11** (or its mirror image, or both), corresponding to ϕ and ψ of, perhaps, 30–40°.



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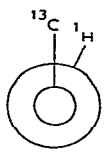

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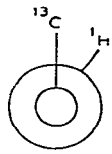

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Therefore, the current findings suggest that, in aqueous solution, the two residues of maltose favor a more staggered disposition towards each other than in the solid state, for which ϕ and ψ are[1,3] in the region of only 0–15°.

Inter-residue hydrogen-bonding is a prominent feature of the crystal structures of these disaccharides and, according to p.m.r.-spectroscopic evidence[7], occurs also in dimethyl sulfoxide solution. An aqueous medium might be more effective than dimethyl sulfoxide in competing for these hydrogen-bonding sites and, as suggested by optical rotatory measurements on maltose[8], could favor important contributions from other conformations*. For this reason, an attempt was made to obtain comparative data for solutions in dimethyl sulfoxide, but the resolution of the spectra recorded with this solvent was generally unsatisfactory.

As hydrogen bonding is not a factor when all of the hydroxyl groups are acetylated, it is noteworthy that the $^3J_{C\text{-}1-H\text{-}4'}$ values obtained for acetates of maltose and derivatives are consistently 1.0–1.5 Hz larger than for the parent compounds. Hence, the presence of these acetyl substituents, and the change in solvent to chloroform, appear to favor linkage orientations in which ψ is prominently represented by torsional angles smaller than in the unsubstituted biose. By contrast, the values (~2 Hz) measured for $^3J_{C\text{-}4'-H\text{-}1}$ of the acetates suggest that ϕ changes in the opposite

*Hydrophobic bonding between the two residues of maltose is another possible source of stabilization, favoring a folded conformation for this disaccharide, but not for cellobiose[2,4].

sense, so that the time-averaged, torsional angle is larger than for maltose itself. It appears, nevertheless, that these changes in orientation are, overall, relatively minor, and this suggests that, if inter-residue hydrogen-bonds exist in water, such bonding is not a major factor in determing the conformation of maltose. The observed effects of *O*-acetylation could, therefore, be largely one of a difference in bulk as between the hydroxyl and the acetoxyl group.

EXPERIMENTAL

^{13}C-N.m.r. spectra. — Spectra were recorded in the "gated", decoupling mode[25] at 22.63 MHz with a Bruker WH-90 spectrometer. The 8K memory of its B-NC 12 computer was used for Fourier transformation of the accumulated spectra. The repetition time was ~2.0 sec, the decouple time ~0.6 sec, and the pulse width 90° (~18 μsec). Sweep widths of 1500–2400 Hz were used, giving a computer resolution of 0.4–0.6 Hz, and the number of scans was usually >20,000. Deuterium oxide was the solvent for unsubstituted compounds, and $CDCl_3$ (in some instances, ^{13}C-depleted) for acetate derivatives, at concentrations of 0.2–0.4 g/ml.

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