acylium ion generates **11**-O, from which tautomerization gives **4**-O.

The chemistry of metallacycle complexes has been largely dominated by reactivity at the metal–carbon bonds. The mechanistic work described herein indicates that metallacycle substituents provide a rich source of new chemical reactivity and points the way to the further development of this unprecedented alkyne cyclization chemistry.

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Supplementary Material Available: Full spectroscopic and analytical data for compound **4** and spectroscopic data for **7**, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters for **4**, ^{13}C NMR spectra of isotopic shift resonances for **3**-O, **4**-O, and **7**-O, and mass spectral data for **3**-O, **4**-O, **4**/**4**-d_{12}, **5**-O, and **6**-O (53 pages); table of observed and calculated structure factors for **4** (28 pages). Ordering information is given on any current masthead page.

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Stereochemical Aspects of the Hydration of Carbohydrates. Kinetic Medium Effects of Monosaccharides on a Water-Catalyzed Hydrolysis Reaction

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The hydration characteristics of carbohydrates in aqueous solution represent an intriguing and challenging problem[2] and are of direct relevance for understanding the role of glycolipids and glycoproteins in molecular recognition.[3,4] Previous attempts to rationalize carbohydrate hydration have been couched in terms of hydration numbers,[5,6] the ratio of equatorial vs axial OH groups,[7,8] the anomeric effect,[9] the hydrophobic/hydrophilic index,[10] and the hydrophilic volume of the carbohydrate.[11] No comprehensive theory has yet emerged.

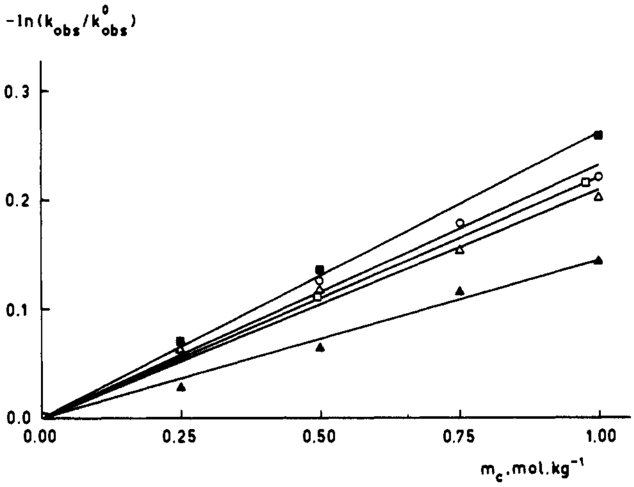
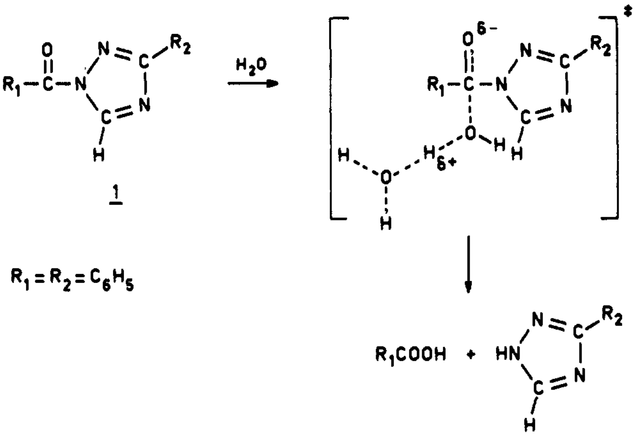


Figure 1. Plots of ln ($k_{obsd}/k^{\circ}_{obsd}$) vs molality of hexose for the neutral hydrolysis of **1** at 25 °C: D-glucose (△), D-mannose (○), D-allose (□), D-galactose (▲), and D-talose (■).

Scheme I



Herein we report a new endeavor to frame a picture of the hydration of monosaccharides as a function of their stereochemistry. To this end we have measured pseudo-first-order rate constants for the water-catalyzed hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (**1**) in aqueous solutions in the presence of 0–1.00 mol·kg^{-1} of a series of aldohexoses (**2a–e**), ketohexoses (**3a,b**), and aldopentoses (**4a–d**) (Table I). The neutral hydrolysis of **1** proceeds via an activated complex containing two water molecules in which three OH bonds are stretched (Scheme I).[12] As shown previously, medium effects of mono- and polyhydric alcohols on this reaction can be understood by considering hydration shell overlap effects between the alcohol and the initial and transition states of the hydrolytic process.[13] In a similar approach, we quantify the kinetic medium effect of a carbohydrate via eq 1,[14] in which k_{obsd} is the pseudo-first-order rate constant for hydrolysis of **1** in an aqueous carbohydrate solution (molality m_c) and k°_{obsd} refers to $m_c = 0$. The number of water molecules

$$\ln (k_{obsd}/k^{\circ}_{obsd}) = (2/RT)G(C)m_c - n\Phi M_1 m_c \qquad (1)$$

in the transition state is n ($n = 2$), Φ is the practical osmotic

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Table I. Medium Effects on the Neutral Hydrolysis of **1** in Dilute Aqueous Solutions of Monosaccharides[a] at 25.0 ± 0.1 °C

carbohydrate[a]	dominant conformation[b]	G(C),[c] J·kg·mol^{-2}	G(CHOH,endo),[d] J·kg·mol^{-2}	$K°_2$(s) × 10^4,[e] cm^3·mol^{-1}·bar^{-1}
2a, D-glucose	1e2e3e4e6e	−201 (12)	−45	−17.8 (0.3)[f]
2b, D-galactose	1e2e3e4a6e	−142 (11).	−31	−20.8 (0.5)[f]
2c, D-mannose	1a2a3e4e6e	−227 (12)	−52	−16.0 (0.5)[f]
2d, D-allose	1e2e3a4e6e	−228 (15)	−52	
2e, D-talose	1a2a3e4a6e	−280 (10)	−65	−11.9 (0.3)
3a, D-fructose	1e2a3e4e5a	−202 (12)	−45	−21.6 (0.4)
3b, L-sorbose	1e2a3e4e5e	−212 (23)	−49	−21.8 (0.4)
4a, D-xylose	1e2e3e4e	−253 (18)	−52	−12.9 (0.5)[f]
4b, L-arabinose	1a2e3e4a	−129 (10)	−21	−19.3 (0.5)[f]
4c, D-lyxose	1a2a3e4e	−241 (18)	−49	−13.1 (0.1)
4d, D-ribose	1e2e3a4e	−223 (10)	−45	−12.5 (0.2)[f]

[a] 0–1.00 mol·kg^{-1}. [b] Axial (a) or equatorial (e) position of OH is indicated. [c] Experimental value. [d] Calculated from experimental data assuming that G(−0−) = 91.8 J·kg·mol^{-2} and $G(CH_2)$ = −136 J·kg·mol^{-2}; e.g., G(D-glucose) = 4 × G(CHOH,endo) + G(CHOH,exo) + G(−0−) + $G(CH_2)$. [e] Isentropic partial molar compressibility. [f] Reference 18.

coefficient of water ($\Phi = 1$ for $m_c = 0$), and G(C) depicts the overall effect of the carbohydrate on the Gibbs energy of activation for the hydrolytic process.[15] Excellent straight lines were obtained by plotting $\ln (k_{obsd}/k°_{obsd})$ vs m_c, and the G(C) values calculated from the slopes of these lines are listed in Table I. Some representative plots are shown in Figure 1.

All carbohydrates cause a rate retardation which is quantitatively expressed in the negative G(C) values. Interestingly, these G(C) values are almost invariant for many of the hexoses and pentoses and do not respond to the presence of a keto- or aldohexose, the anomer distribution, and the number of equatorial OH groups in the molecule.[16] A significantly different G(C) is only found when the OH at C-4 is axial (e.g., D-galactose, D-talose, and L-arabinose), but the effect depends on the relative orientation of the next nearest neighbor,[17] the OH moiety at C-2. When OH(4) and OH(2) are trans toward each other, G(C) is markedly less negative, for the corresponding cis orientation G(C) is markedly more negative (Table I). In fact, the G(C) value for D-talose is even more negative than that for the relatively hydrophobic monohydric alcohol 1-propanol (−258 ± 6 J·kg·mol^{-2}),[13] indicating that D-talose is recognized by the hydrolytic probe as a relatively hydrophobic solute.

On the next level of sophistication, one can calculate group interactions[14] for the overall effect of the carbohydrate on the Gibbs energy of activation. The calculations were performed for the pyranose form, which is the dominant conformer in aqueous solution. From the difference in G(C) between hexoses and pentoses one obtains G(CHOH,exo) = +25 J·kg·mol^{-2}, a value comparable to that found for a similar group in vicinal dihydric alcohols.[13] Now G(CHOH,endo) values (Table I) can be calculated. These are all negative, which means that intermolecular interactions of these groups lead to rate retardation and are, therefore, dominated by the methine moieties in the endocyclic CHOH function. We note that the limiting isentropic compressibilities of the carbohydrates[18] (Table I), which are a measure of the water compatibility of the solute,[19] follow the same trends as the G(CHOH,endo) values. Taken together, these results indicate that the better the carbohydrate fits into the three-dimensional hydrogen-bond structure of water, the more the OH groups are camouflaged[20] for interaction with the kinetic probe and the more negative G(CHOH,endo) is found.

We gather from the present results that the carbohydrates can be classified into three groups in order of decreasing hydration and diminished fit into the water structure: (1) both OH(2) and OH(4) are axial (D-talose); (2) OH(4) is equatorial and OH(2) is either axial or equatorial (**2a**, **2c**, **2d**, **3a**, **3b**, **4a**, **4c**, and **4d**); (3) OH(4) is axial and OH(2) is equatorial (D-galactose and L-arabinose). Our results suggest that molecular recognition in aqueous carbohydrate solutions is probably governed by an interplay between the rigid polyol structure of the carbohydrate, dictated by its detailed stereochemistry, and the flexible three-dimensional hydrogen-bond structure of water, apt to respond to subtle structural variations in a solute. Additional studies are underway aimed at further modeling of the stereochemical aspects of carbohydrate hydration in aqueous solution.

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(15) Careful analysis of the reaction mixtures by GC (Varian 3700 instrument) and combined GLC/MS (Carlo-Erba GC/Kratos MS80/Kratos DS 55 system) revealed the absence of carbohydrate-derived esters. Full experimental details will be given in a full paper.

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Template-Synthesized Polyacetylene Fibrils Show Enhanced Supermolecular Order[†]

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We have recently described the synthesis of nanoscopic fibrils of heterocyclic polymers.[1] These fibrils were synthesized via a template method, in which the pores in a nanoporous membrane act as templates for the nascent polymer. Such fibrils show electronic conductivities (along the fibril axis) which are substantially higher than conductivities of bulk films of the analogous polymer.[1] We suggested that this enhanced conductivity resulted from preferential orientation of the polymer chains parallel to the fibril axis;[1] however, we had no experimental data to support this contention.

This paper provides experimental proof for such enhanced supermolecular order in template-synthesized conductive polymer fibrils. We describe (for the first time) the template synthesis of nanoscopic polyacetylene fibrils. We then present results of a polarized infrared absorption experiment which prove that the polyacetylene chains in these fibrils are preferentially oriented

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