The data were compared with those obtained from the analogous quinoxaline derivative **9** analyzed previously[13] and which showed J_{ab} = 3.0 Hz and J_{bc} = 8.5 Hz. The Karplus equation[15] predicts dihedral angles of 45° for two protons coupled by 3.9 Hz and 51° for those where J = 3.0 Hz. The coupling constants for J_{bc} in **8** and **9** correspond, respectively, to dihedral angles of 158 and 164°. These data suggest that there may be slightly more deviation from the ideal staggered conformation in the triazole **8** than in the quinoxaline **9**. The difference between the two seems relatively minor as compared with the deviation from ideal. The data, of course, merely reflect an average of a large number of conformations and suggest only that of the extremes possible the staggered conformation predominates.

The nmr data for the tetraacetate derivative **7** which has the *lyxo* stereochemistry (H_{ab} *erythro*) instead of the *arabino* stereochemistry of **8** and **9** (H_{ab} *threo*) showed in pyridine-d_5 τ 1.72 (1 H, osotriazole proton), a complex aromatic region centered approximately at 2.24 (5 H), and four acetyl groups at 7.88 (3 H), 7.92 (3 H), and 7.98 (6 H). The five aliphatic protons showed signals for H_a at τ 3.30 (d) (J_{ab} = 7.5 Hz); H_b at 3.76 (q) (J_{ab} = 7.5 Hz, J_{bc} = 3.5 Hz); H_c at about 4.0 (m); and H_d at 5.40 (q). The quartet for H_d shows the nonequivalence of these methylene protons ($J_{dd'}$ = 13 Hz, J_{cd} = 7 Hz). The dihedral angles for the H_{ab} and H_{bc} bonds are calculated to be approximately 155 and 48°, respectively, which suggests the staggered conformation very similar to that shown by the osotriazole **7** and reflecting the enantiomeric configuration at C-4.

Optical rotatory dispersion data were recorded on a Cary 60 spectropolarimeter in methanol solution.

4-(D-*glycero*-Dihydroxyethyl)-2-phenyl-1,2,3-osotriazole (**1**), mp 64–65°, *c* 0.07, had the following ORD values: $[\Phi]_{350}$ +435, $[\Phi]_{282.5}$ +3280, $[\Phi]_{235}$ −4550, $[\Phi]_{222}$ −1640.

4-(D-*threo*-Trihydroxypropyl)-2-phenyl-1,2,3-osotriazole (**2**), mp 87–88.5° (lit.[22] mp 88–89°), *c* 0.043, had the following ORD values: $[\Phi]_{350}$ −670, $[\Phi]_{285}$ −3240, $[\Phi]_{241}$ +3880, $[\Phi]_{220}$ 0.

4-(L-*erythro*-Trihydroxypropyl)-2-phenyl-1,2,3-osotriazole (**3**), mp 65–68.5° (lit.[20] 69–70°), *c* 0.084, had the following ORD values: $[\Phi]_{350}$ −296, $[\Phi]_{289}$ −1340, $[\Phi]_{270-265}$ +894, $[\Phi]_{250}$ +2350, $[\Phi]_{242.5}$ +1670. $[\Phi]_{237}$ +2900, $[\Phi]_{220}$ +190.

4-(D-*lyxo*-Tetrahydroxybutyl)-2-phenyl-1,2,3-osotriazole (**4**) mp 108–109° (lit.[22] 110–111°), *c* 0.045, had the following ORD values: $[\Phi]_{350}$ −284, $[\Phi]_{284}$ −1154, $[\Phi]_{234}$ +1036, $[\Phi]_{220}$ −1508.

4-(D-*lyxo*-Tetraacetoxybutyl)-2-phenyl-1,2,3-osotriazole (**7**), *c* 0.085, had the following ORD values: $[\Phi]_{350}$ −589, $[\Phi]_{285}$ −2117, $[\Phi]_{270}$ +1650, $[\Phi]_{264}$ +1303, $[\Phi]_{236}$ +5781, $[\Phi]_{221}$ 0.

4-(L-*xylo*-Tetrahydroxybutyl)-2-phenyl-1,2,3-osotriazole (**5**), mp 151–152° (lit.[22] mp 158–159°), *c* 0.0045, had the following ORD values: $[\Phi]_{350}$ −559, $[\Phi]_{285}$ −3108, $[\Phi]_{245}$ +3768, $[\Phi]_{240}$ +2828, $[\Phi]_{235}$ +3676, $[\Phi]_{225}$ +1884.

4-(D-*arabino*-Tetrahydroxybutyl)-2-phenyl-1,2,3-osotriazole (**6**), *c* 0.131, had the following ORD values: $[\Phi]_{350}$ −910, $[\Phi]_{283}$ −5250, $[\Phi]_{245}$ +6410, $[\Phi]_{241}$ +5830, $[\Phi]_{239}$ +6700, $[\Phi]_{217}$ 0, $[\Phi]_{207}$ +12,800, $[\Phi]_{205}$ +7860.

Circular dichroism data were recorded in methanol on a Jouan Dichrograph Model 185. The following values were recorded: for compound **6**, 300 nm ($\Delta\epsilon$ 0), 277 (−1.43), 274 (−1.24), 270 (−1.84), 265 (−1.42), 258 (−1.93), 244 [−0.90 (sh)], 227 (0), 223 (+0.27), 219 (0), 213 (−1.52); for **1**, 295 nm ($\Delta\epsilon$ 0), 277 (+0.90), 273 (+0.66), 265 (+1.28), 262 (+0.96), 258 (+1.26), 248 [+0.60 (sh)], 236 (0), 222 (−0.58), 213 (0), 210 (0.24).

Ultraviolet absorption spectra were recorded in 95% ethanol on the Cary 15 or Perkin-Elmer 4000 instrument. The λ_{max} (ϵ) values for the osotriazole derivatives follow: **1**, 265 nm (20,150); **2**, 267 (20,240); **3**, 266 (19,830); **4**, 266 (19,550); **5**, 266 (18,810); **6**, 267 (24,450); **7**, 264 (22,070).

Registry No.—**1**, 16336-37-1; **2**, 15476-33-2; **3**, 15476-35-4; **4**, 15476-32-1; **5**, 15476-34-3; **6**, 16346-56-8; **7**, 6341-06-6; **8**, 7770-63-0; **9**, 4710-99-0.

The Conformation of α-D-Idopyranose Pentaacetate[1,2]

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The proton nmr spectrum of α-D-idopyranose pentaacetate (**1**) at 220 MHz in acetone-d_6 or chloroform-*d* is completely first order and shows that the *C1* chair conformation, having the acetoxymethyl group equatorial and the four acetoxy groups axial, is the favored conformation. In addition to the normal spin couplings of vicinal protons, long-range ^4J couplings are observed between the equatorial protons H-1 and H-3, and similarly between H-2 and H-4. A ^5J coupling between H-1 and H-4 is also observed. The alternative chair (*1C*) conformation, having all groups equatorial except the acetoxymethyl group, is considerably less stable than the *C1* form.

Conformational analysis of polysubstituted chains and ring systems may be studied conveniently by use of various types of carbohydrate derivative. Such compounds offer the advantage that several stereoisomers, and frequently complete sets of stereoisomers, are available in a given system. A program in this laboratory has been concerned with determination of favored conformation and conformational populations at equilibrium, in highly substituted tetrahydropyran ring systems, as provided by pyranoid sugar derivatives,[1] and in the open-chain structures of acyclic derivatives of sugars.[6]

Polysubstituted tetrahydropyran derivatives may be formulated in two energetically nonequivalent chairlike conformations and in a flexible cycle of skew forms interconvertible through the boat forms.[7,8] Conformers in the flexible cycle are generally considered to be of higher energy than the favored chairlike conformer, except perhaps for certain fused-ring derivatives.[9] A rationale for predicting the favored chair conformation for pyranose sugars and their derivatives

(1) This paper is part of a series "Application of 220-MHz Nmr to the Solution of Stereochemical Problems." For previous papers from this laboratory concerned with conformations of pyranoid sugar derivatives, see (a) D. Horton and W. N. Turner, *J. Org. Chem.*, **30**, 3387 (1965); (b) C. V. Holland, D. Horton, and J. S. Jewell, *ibid.*, **32**, 1818 (1967); (c) N. S. Bhacca and D. Horton, *Chem. Commun.*, 867 (1967); (d) C. V. Holland, D. Horton, M. J. Miller, and N. S. Bhacca, *J. Org. Chem.*, **32**, 3077 (1967); (e) N. S. Bhacca and D. Horton, *J. Amer. Chem. Soc.*, **89**, 5993 (1967).

(2) A preliminary report of part of this work has been given: P. L. Durette, D. Horton, and N. S. Bhacca, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p C22.

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(6) D. Horton and Martha J. Miller, *J. Org. Chem.*, **30**, 2457 (1965); H. S. El Khadem, D. Horton, and T. F. Page, Jr., *ibid.*, **33**, 734 (1968).

(7) D. Horton in "Handbook of Biochemistry and Biophysics," H. C. Damm, Ed., World Publishing Co., Cleveland, Ohio, 1966, pp 128–131.

(8) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 6.

(9) C. Cone and L. Hough, *Carbohyd. Res.*, **1**, 1 (1965).

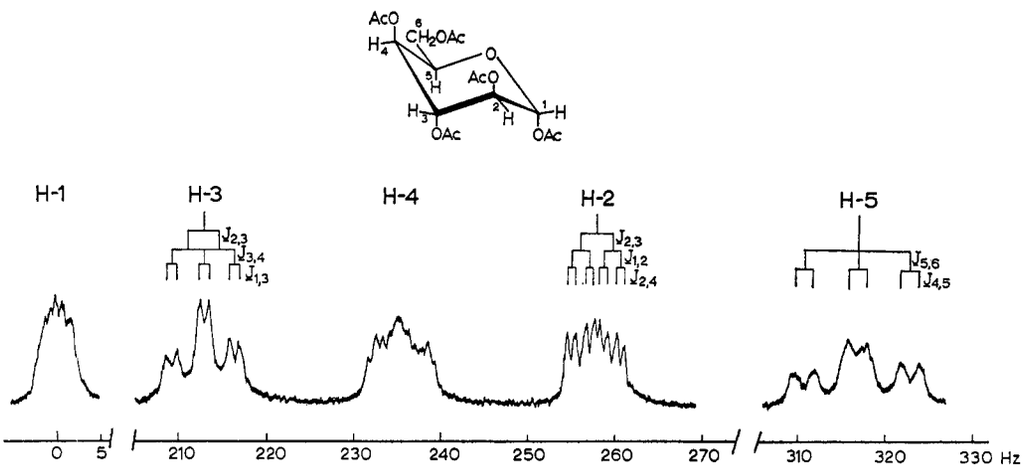


Figure 1.—The low-field portion of the 220-MHz nmr spectrum of α-D-idopyranose pentaacetate (1) in acetone-d_6 at 15°. The scale divisions give chemical shifts in hertz upfield from the H-1 signal. The H-6 signal (not shown) appears as a two-proton doublet, width 6.0 Hz, at 402 Hz upfield from the H-1 signal.

was put forward by Reeves,[10] based on summation of a set of conformational "instability factors." The conformational assignments upon which Reeves' correlations were based were made from data on the formation or nonformation of cuprammonium–diol complexes. The fact that the cuprammonium reagent may itself influence the conformation of a sugar introduces complications in the interpretation of such data. The advent of nmr techniques for the study of conformations in solution has removed this objection from conformational assignments, and it is usually possible to make a clear-cut assignment of one chair conformer or the other, based on the values of vicinal proton–proton spin couplings.[1,11,12]

In certain cases spin-coupling data suggest that the less-favored chair conformer is present in substantial proportion in equilibrium with the favored form, and such a conformational equilibrium has recently been demonstrated directly, for β-D-ribopyranose tetraacetate, by low-temperature nmr spectroscopy at 220 MHz.[1e]

One of the most significant factors to emerge from conformational studies on pyranose sugars and their derivatives is the observation that the favored conformation is not necessarily that chairlike conformer having the greater number of bulky substituents oriented equatorially. An extreme case is tri-*O*-acetyl-β-D-xylopyranosyl chloride (2). This tetrasubstituted, pyranose sugar derivative has, in various solvents, all four substituents axial in the favored conformation;[1b,13] the energy difference between this form and the all-equatorial form is sufficient that the proportion of the latter form statistically present is too small to be observed by conventional low-temperature nmr spectroscopy.[2] There appears to be a strong driving force (anomeric effect)[1a,14,15] for a polar group at C-1 of an aldopyranose derivative to adopt the axial orientation.

Based on the principle that various conformational elements in a polysubstituted, six-membered ring system give rise to additive elements of conformational destabilization, relative to a hypothetical system having no interacitons between substituents, values have been estimated for the conformational free energies of substituent groups in various environments in substituted, pyranose sugars dissolved in organic solvents[15] and in free sugars in aqueous solution.[8] These values, which include a term for the anomeric effect, permit calculation of a predicted, relative free energy for each chair conformer of a given pyranose sugar or its peracetate. The predicted $\Delta G°$ value for one chair conformer is generally considerably less than that of the other chair conformer. Direct observation of the favored conformation by nmr spectroscopy has provided, in many instances, experimental verification of the conformations predicted.

α-D-Idopyranose is a key compound in conformational studies on the six-carbon, pyranose sugars because the favored chair conformation of this sugar and its pentaacetate can be supposed, based on algebraic summation of estimated values for conformational free energies of the ring substituents,[8,10,15] to be the reverse of that chair conformer shown to be the stable form in the common D-hexopyranoses and their pentaacetates. Of the two possible chairlike conformations of α-D-idopyranose, the *C1* (D) conformer (*CA* in the Isbell–Tipson[16] system of conformational nomenclature[17]) has the hydroxymethyl group oriented equatorially and the four hydroxyl groups oriented axially. The alternative *1C* (D) conformer has the four hydroxyl groups equatorial and the hydroxymethyl group axial. By the "instability factors" of Reeves,[10] or by the conformational free-energy values of Angyal,[8] the *1C* (D) conformation is predicted to be favored strongly over the

(10) R. E. Reeves, *Advan. Carbohyd. Chem.*, **6**, 108 (1951).

(11) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958). R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **43**, 2059 (1965); **44**, 249 (1966).

(12) L. D. Hall, *Advan. Carbohyd. Chem.*, **19**, 51 (1964).

(13) H. Paulsen, F. Garrido Espinosa, W. P. Trautwein, and K. Heyns, *Ber.*, **101**, 179 (1968); *cf.* L. D. Hall and J. F. Manville, *Carbohyd. Res.*, **4**, 512 (1967).

(14) J. T. Edward, *Chem. Ind.* (London), 1102 (1955).

(15) R. U. Lemieux in "Molecular Rearrangements," part 2, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 735–743.

(16) H. S. Isbell, *J. Res. Natl. Bur. Stand.*, **57**, 171 (1956). H. S. Isbell and R. S. Tipson, *Science*, **130**, 793 (1959); *J. Res. Nat. Bur. Stand., Sect. A*, **64**, 171 (1960).

(17) The considerations given in this discussion for α-D-idopyranose pentaacetate (1) apply equally for the L enantiomorph. The form shown herein to be the stable chair conformer of **1**, having the acetoxymethyl group equatorial and the four acetoxy groups axial, is *C1* by the Reeves nomenclature; the stable conformer of the L enantiomorph would be named *1C*. By the Isbell–Tipson system[16] the stable conformer is named α-D- (or L-) idopyranose-*CA* pentaacetate. The nonfavored conformer is the *1C* (D) or *C1* (L) form [α-D- (or L-) idopyranose-*CE* pentaacetate, by the Isbell–Tipson system].

TABLE I

CHEMICAL-SHIFT DATA FOR α-D-IDOPYRANOSE PENTAACETATE (1) IN ACETONE-d_6 AT 20° AND 220 MHZ

Solvent	Scale	Chemical shifts of protons H-1	H-2	H-3	H-4	H-5	H-6[a]	CHOAc	CH_2OAc
$(CD_3)_2CO$	Hz upfield from H-1	0	257	213	235	317	402		
	Ppm upfield from H-1	0	1.17	0.97	1.07	1.45	1.83		
	τ scale	4.02	5.19	4.99	5.09	5.47	5.85	7.87,[b] 7.89[b]	8.00[c]
$CDCl_3$	Hz upfield from H-1	0	260	218	248	350	412		
	Ppm upfield from H-1	0	1.18	0.99	1.13	1.59	1.87		
	τ scale	3.93	5.11	4.92	5.06	5.52	5.80	7.89,[d] 7.90[c]	7.94[c]

[a] Doublet, lower-field peak approximately twice the intensity of the higher-field peak. [b] Integral, six protons. [c] Integral, three protons. [d] Integral, nine protons.

C1 (D) conformation, in aqueous solution. For the corresponding pentaacetate, in chloroform solution, the estimated conformational free energies[15] would also indicate that the *1C* (D) conformation is the stable form, if it can be assumed that an axial acetoxymethyl group exerts a steric effect at least as great as that of an acetoxy group.

The pentaacetate (1) of α-D-idopyranose has been characterized on a crystalline basis,[18] and the present report describes conformational assignments from nmr spectroscopic data measured at 220 MHz. The results indicate that substance **1**, in acetone-d_6 or chloroform-*d*, adopts the *C1* (D) conformation, having four axial substituents and one equatorial substituent, as the favored form. This result is the opposite of that predicted by summation of conformational free-energy values.

Spectral Interpretations.—The pmr spectrum (Figure 1) of α-D-idopyranose pentaacetate (**1**), at 220 MHz in acetone-d_6, is completely first-order. Chemical-shift data are listed in Table I; Table II gives coupling constants. Each of the methine protons gives rise to a multiplet that is well separated from neighboring signals, so that no significant virtual coupling[19] is possible, and the couplings derived by first-order analysis should be close to the absolute $|J|$ values. The methylene group gives rise to a two-proton signal that appears as a doublet, indicating that the two C-6 protons are equivalent. The spacing of this doublet gives the $J_{5,6}$ coupling constant. The highest field, methine proton signal, that of H-5, appears as a triplet of narrow doublets, through coupling with H-6 and with H-4, and the small splitting gives the $J_{4,5}$ coupling constant. Another triplet of doublets, observed at next to lowest field, is assigned to H-3; the triplet structure arises through equal coupling of H-3 with H-2 and H-4, and the additional splitting arises by long-range coupling with H-1 (W arrangement[20,21] of H-1 and H-3). The eight-peak multiplet to lower field of the H-5 signal is assigned to H-2, and the multiplicity arises by unequal coupling of H-2 with three other protons. The largest splitting is caused by the $J_{2,3}$ coupling, and a smaller splitting gives $J_{1,2}$; the smallest splitting is attributable to long-range coupling of H-2 with H-4 (W arrangement[20,21]).

TABLE II

PROTON–PROTON COUPLING CONSTANTS FOR α-D-IDOPYRANOSE PENTAACETATE (1) IN ACETONE-d_6

Vicinal couplings, Hz					Long-range couplings, Hz		
$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{1,3}$	$J_{1,4}$	$J_{2,4}$
2.1	3.6	3.5	2.1	6.0	1.0	0.6	0.9

Of the two remaining methine proton signals, that at lowest field can be assigned to H-1, and the multiplet between the H-3 and H-2 signals must, therefore, be that of H-4. On the basis of the couplings already assigned, the H-1 signal should appear as a quartet of width 3.1 Hz and the H-4 signal should appear as an octet of width 5.6 Hz. The observed signals, however, indicate that there is a small, additional coupling of about 0.6 Hz between H-1 and H-4. On this basis the H-1 signal should appear as an octet and the H-4 signal as a 16-line multiplet; the small difference in magnitude between the long-range splittings prevented each of these multiplets from being resolved completely.

The acetyl-group signals appear as a high-field singlet, assigned to the primary acetoxy group, and a partially resolved group of signals at lower field that was assigned to the four acetoxy groups attached axially to the ring; the latter were not assigned individually.

Addition of a few drops of benzene-d_6 to the prepared sample caused the C-6 protons to become slightly nonequivalent, as observed in a doubling of the higher field peak of the H-6 signal and concomitant increase in complexity of the H-5 signal.

The nmr spectrum in chloroform-*d* is similar to that observed in acetone-d_6 and the H-6 protons are still equivalent in this solvent. Some differences in chemical shifts are observed (Table I); notably the separation of the H-2 and H-4 signals is smaller.

The advantages of measurements at 220 MHz is well illustrated by the separation of the H-3, H-4, and H-2 signals shown in Figure 1. Although the separation of the H-3 and H-2 signals is a mere 0.20 ppm, the three signals are completely separated and there is hardly any buildup in intensity of the inner portions of the H-3 and H-2 signals. In contrast, a comparable spectrum measured at 100 MHz (Varian HA-100 spectrometer) showed the three multiplets almost contiguous, with strong intensity buildup of the inner portions of the H-3 and H-2 signals.

Discussion

The small magnitudes (2.1–3.6 Hz) of the vicinal couplings observed for **1** in acetone-d_6 clearly exclude the *1C* (D) conformation which, with the axial arrangement of H-1, H-2, H-3, and H-4, would have given a series of large (8–10 Hz) vicinal couplings. The couplings observed are fully consistent with the *C1* (D) conformation

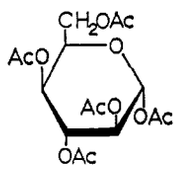
(18) H. Paulsen, W. P. Trautwein, F. Garrido Espinosa, and K. Heyns, *Ber.*, **100**, 2822 (1967).

(19) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1961).

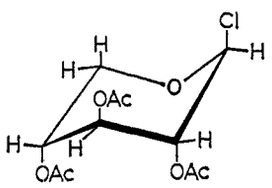
(20) L. D. Hall and L. Hough, *Proc. Chem. Soc.* (London), 382 (1962); K. Heyns, J. Weyer, and H. Paulsen, *Ber.*, **98**, 327 (1965).

(21) D. Horton and J. S. Jewell, *Carbohyd. Res.*, **5**, 149 (1967).

having H-1, H-2, H-3, and H-4 equatorial.[22] The data are not in accord with formulation of **1** in a skew conformation because such a structure would be expected to give rise to one or more large, vicinal couplings.[23]

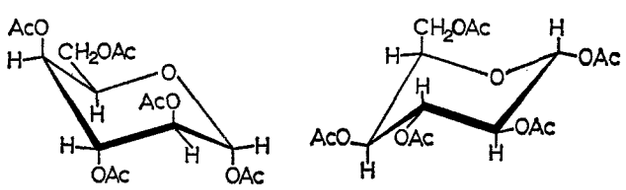


1



2

In view of the fact that the molecule of α-D-idopyranose pentaacetate in the favored *C1* (D) conformation



C1 (D) favored

1C (D) not favored

has the supposedly strong destabilizing influence of two pairs of *syn*-diaxial acetoxy groups, it is difficult to reconcile the observed behavior with the predictions based on current theory.[24] It does not appear probable that the anomeric effect is alone responsible for controlling the conformation of **1**. It has been observed[1b] that a related example, tri-*O*-acetyl-β-D-xylopyranosyl chloride (**2**), favors the all-axial *1C* (D) conformation even in rather polar solvents such as acetone and acetonitrile, although the anomeric effect is considered[8,15] to be diminished on passing from solvents of low polarity to solvents of high polarity. It may be noted that the *C1* (D) conformation is also favored in the case of the penta-*O*-benzoyl analog[25] of **1** and also with 1,2,3,6-tetra-*O*-acetyl-α-D-idopyranose.[18]

Possibly there are attractive interactions between axial acetoxy groups and other groups in the molecule, or repulsive interactions between vicinal, equatorial groups, that should be considered in any model for predicting favored conformation. Detailed speculation on this point is not warranted until data on conformational and configurational equilibria in a series of related compounds become available.

Extensive long-range couplings through the W arrangement of bonds are commonly observable in bridged ring systems,[20,21] and ^5J couplings have also been observed in some bridged ring systems.[26] The present example is unusual, however, in that such couplings are here exhibited by a pyranoid ring-system that is not bridged. This observation suggests that the molecule of **1** may be conformationally quite rigid, with libration about the shape corresponding to the minimum energy being energetically unfavorable.

Experimental Section

Nmr spectra were measured at 220 MHz with a Varian spectrometer equipped with a superconducting solenoid.[27] The sample of α-D-idopyranose pentaacetate (**1**) had mp 94–95° and $[\alpha]^{20}D$ +55.2° (*c* 0.8, chloroform), in good agreement with literature values.[18] The concentration of sample was ~10% and tetramethylsilane (τ 10.00) was used as the internal standard for spectra measured in chloroform-*d*. Spectra were measured at 15–20°, and coupling constants (Table II) were measured directly from spectra recorded at 100-Hz sweep width. Data on chemical shifts are given in Table I.

Registry No.—1, 16299-15-5.

(22) A small proportion of the *1C* (D) conformer undoubtedly exists in equilibrium with the favored *C1* (D) form, but the proportion of the nonfavored form can be expected to be not more than 10% and it may be considerably less than this.

(23) A nonchair conformation has been proposed [R. Bentley, *J. Amer. Chem. Soc.*, **82**, 2811 (1960)], based on cuprammonium-complexing data, for methyl β-D-idopyranoside in aqueous solution, and the α-D anomer was considered to adopt the *1C* conformation.

(24) Since this manuscript was submitted for publication a paper has appeared by P. R. Sundarajan and V. S. R. Rao [*Tetrahedron*, **24**, 289 (1968)] that describes potential energy calculations for the aldohexopyranoses and aldopentopyranoses. If polar interactions are ignored completely, and Kitaigorodsky-type functions are used to determine the nonbonded interaction energies, it can be calculated that the lowest energy conformer for all D-aldohexopyranoses would be the *C1* (D) chair form. However, since there is abundant evidence[1,8,15] that polar factors are significant in influencing conformation, a complete theoretical model for predicting favored conformation would have to include terms for polar interactions. The quantitative significance of polar factors, in relation to steric factors, is difficult to assess.

(25) N. S. Bhacca, D. Horton, and H. Paulsen, unpublished data.

(26) L. D. Hall, J. F. Manville, and A. Tracey, *Carbohyd. Res.*, **4**, 514 (1967); J. C. Jochims, G. Laigel, and W. Meyer zu Reckendorf, *Tetrahedron Lett.*, 3227 (1967).

(27) F. A. Nelson and H. E. Weaver, "High-Resolution Superconducting Spectrometer," presented at the International Conference on Magnetic Resonance and Relaxation, XIVth Colloque Ampère, Ljubljana, Yugoslavia, Sept 1966.