Note

Conformation of the D-pentononitrile tetraacetates

WENDELL W. BINKLEY
New York Sugar Trade Laboratory, 37 Warren Street, New York, N. Y. 10007 (U. S. A.)

DONALD R. DIEHL AND ROGER W. BINKLEY
Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115 (U. S. A.)

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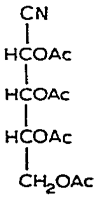
Numerous investigations of the conformations of acyclic monosaccharide derivatives have been undertaken recently through the use of n.m.r. spectroscopy[1]. The greatest portion of the knowledge in this area results from studies by Horton and coworkers[1a–e], who have demonstrated that a planar, zigzag arrangement of carbon atoms is favored, except in those cases where such an arrangement leads to destabilizing, eclipsed 1,3-interactions of pairs of substituents along the chain. Whenever such 1,3-interactions would occur, the molecules appear to favor a bent or "sickle" conformation arising by rotation about one of the carbon–carbon bonds of the planar, zigzag form.

In the course of investigations of the photochemistry of sugar oximes[2], we have prepared the tetraacetates of all four D-pentononitriles. Since these compounds provide a complete set of acyclic pentose derivatives, for which conformational assignments based on n.m.r. spectroscopy have not been made, we have measured the n.m.r. spectra of the four: D-ribononitrile tetraacetate (**1**), D-arabinononitrile tetraacetate (**2**), D-xylononitrile tetraacetate (**3**), and D-lyxononitrile tetraacetate (**4**). As a result of these measurements, we now suggest a favored conformation for each.



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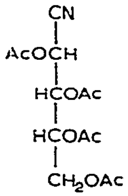

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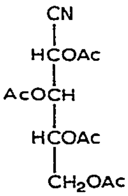

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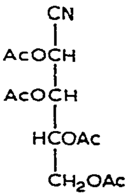

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The 60-MHz n.m.r. spectrum of each acetylated nitrile (**1–4**) was obtained at 35° in chloroform-d, acetone-d_6, and dimethyl sulfoxide-d_6; 2% (v/v) tetramethylsilane was employed as an internal standard. In general, the spectra measured in dimethyl sulfoxide-d_6 were the most informative (see Fig. 1) and, in fact, were the only ones that permitted essentially first-order analyses[3].

TABLE I

CHEMICAL-SHIFT DATA AND COUPLING CONSTANTS FOR D-PENTONONITRILE TETRAACETATES AT 60 MHz

Tetraacetate of	*Chemical shifts (p.p.m.) in dimethyl sulfoxide*-d$_6$										
	H-2	($J_{2,3}$)	*H-3*	($J_{3,4}$)	*H-4*	($J_{4,5}$)	*H-5*	($J_{4,5'}$)	*H-5'*	($J_{5,5'}$)	*Acetyl groups*
D-Ribononitrile (1)	5.83	(2.8)	5.39[a]	(6.7)[a]	5.20[a]	(3.4)[a]	4.26	(3.3)	4.17	(12.4)[b]	2.02, 2.08, 2.13(2)
D-Arabinononitrile (2)	5.78	(2.8)	5.50	(7.5)	5.16	(3.8)	4.21	(3.7)	4.15	(12.4)[b]	1.96(2), 2.07(2)
D-Xylononitrile (3)	5.74	(3.8)	5.50	(8.0)	5.28	(4.5)	4.21	(5.7)	3.98	(11.2)	2.00, 2.07, 2.15(2)
D-Lyxononitrile (4)	5.79	(4.1)	5.59[a]	(3.3)[a]	5.36[a]	(3.7)[a]	4.22	(5.1)	4.04	(11.5)	2.03, 2.08, 2.12, 2.19

[a] Determined from 100-MHz spectra. [b] In acetone-d_6.

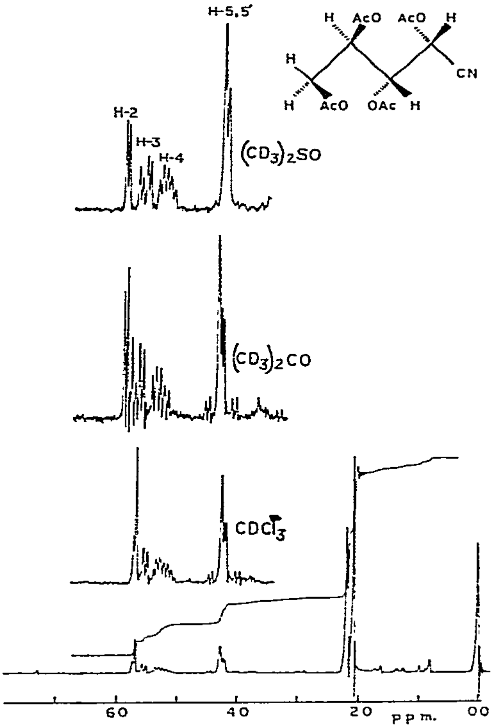


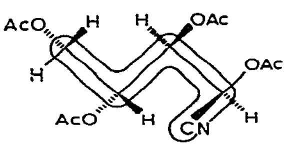
Fig. 1. N.m.r. spectra at 60 MHz of D-arabinononitrile tetraacetate (**2**) in chloroform-*d*, acetone-d_6, and dimethyl sulfoxide-d_6.

For two compounds (**1** and **4**) spin-decoupling was necessary for definite assignment of all signals in the spectra; consequently, 100-MHz spectra were required for these two to permit first-order analyses. Assignments for compounds **2** and **3** were made easily from the 60-MHz spectra, and were confirmed by spin-decoupling. The chemical shifts and the coupling constants measured are given in Table I.

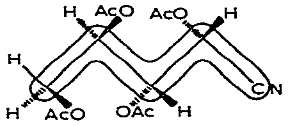
The n.m.r. spectra of each of the four nitrile tetraacetates studied showed essentially the same pattern of chemical shifts, with four signals outside the acetyl region. The resonance at lowest field was a doublet assigned to H-2. This doublet was followed at higher field by a doublet of doublets, attributed to H-3. This pattern was easily observed in the spectrum of D-arabinononitrile tetraacetate (**2**), where it is clearly separated from the H-4 signal, whose absorption lies further upfield. In D-xylononitrile tetraacetate (**3**) the separation between H-3 and H-4 was not as great as in **2**, although it was sufficient for assignments to be made. In the case of the other two nitrile tetraacetates (**1** and **4**), there was sufficient overlap between the H-3 and H-4 signals to necessitate spin-decoupling to identify for each molecule the signals associated with these two protons. At 100-MHz, the separation between the H-3 and H-4 signals in D-ribononitrile tetraacetate (**1**) and D-lyxononitrile tetraacetate (**4**) increased sufficiently to allow each of the coupling-constants to be determined. The remaining absorption outside the acetate region was a signal further upfield from the

H-4 signal. This absorption, attributed to H-5 and H-5′, gave the anticipated eight-line patterns.

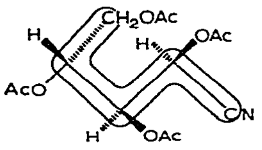
By utilizing the Karplus equation[4], the favored conformation for each nitrile tetraacetate (**1**–**4**) was predicted. This procedure has been used extensively in related systems[1]. For the coupling-constant–dihedral angle relationship, it was assumed



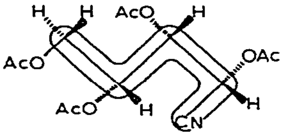
1a



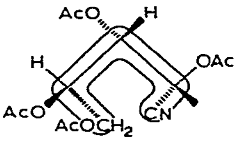
2a



3a,b



4a



4b

that a value of 8–9 Hz corresponds to an antiparallel arrangement of hydrogen atoms whereas values of 2–3 Hz indicate a gauche disposition of two vicinal protons. On this basis, the following conformational assignments have been made for compounds **1**–**4**.

D-*Arabinononitrile tetraacetate** (**2**). — The coupling-constants determined for this compound indicates that its favored conformation (**2a**) has the same type of planar, zigzag backbone composed of carbon atoms 1–5 that has been found characteristic of other acetylated acyclic derivatives of arabinose. The value of 2.8 Hz for $J_{2,3}$ indicates a gauche arrangement between H-2 and H-3, whereas the value of 7.5 Hz for $J_{3,4}$ suggests that H-3 and H-4 are essentially antiparallel in the favored conformer. Of the two gauche arrangements possible between H-2 and H-3, only the one selected does not lead to a 1,3-interaction between acetoxyl groups on C-2 and C-4. The value of 7.5 Hz for $J_{3,4}$ is slightly less than that expected for a completely antiparallel disposition of H-3 and H-4; this may result from distortion away from the perfectly antiparallel arrangement, or from a significant population of other conformers whose $J_{3,4}$ values are smaller than 8–9 Hz. Since conformers that involve a rotation about the C-3–C-4 bond away from the position depicted in **2a** would, presumably, be of considerably higher energy, they are unlikely to be significantly populated. A slight rotation about the C-3–C-4 bond in the favored conformer appears to be the best explanation for the low $J_{3,4}$ value observed. The small, and essentially equal, values of $J_{4,5}$ and $J_{4,5'}$ (3.8 and 3.7 Hz) imply a gauche arrangement between H-4 and H-5 and also between H-4 and H-5′. The staggered arrangement

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*The n.m.r. spectrum of D-arabinononitrile tetraacetate has been reported (Ref. 1*h*) and a conformation assigned. Our results agree with those reported in Ref. 1*h*.

that is proposed (**2a**) is the only one that would allow equal values for $J_{4,5}$ and $J_{4,5'}$. Conformation **2a** corresponds to the best situation for relief of steric strain in D-arabinononitrile tetraacetate (**2**).

D-*Xylononitrile tetraacetate* (**3**). — A consideration of the coupling-constants recorded for D-xylononitrile tetraacetate (**3**) indicates that the favored conformation for **3** is the "sickle" arrangement of the carbon skeleton (**3a** or **3b**). The values of $J_{2,3}$ (3.8 Hz) and $J_{3,4}$ (8.0 Hz) indicate that H-2 and H-3 are gauche with respect to each other, whereas H-3 and H-4 are antiparallel. Of the two possible gauche arrangements of H-2 and H-3, only the one depicted (**3a** and **3b**) does not involve a 1,3-interaction. The values of 4.5 Hz and 5.7 Hz for $J_{4,5}$ and $J_{4,5'}$ suggest that more than one conformational state may be populated. The conformers appearing to have similar energies and, thus, the most likely to be populated, are **3a** (where H-5 and H-5′ both are gauche with respect to H-4) and **3b** (where H-5′ is antiparallel to H-4 and H-5 and H-4 are gauche). The conformation having H-5 antiparallel to H-4, and H-5′ and H-4 gauche, would experience a destabilizing 1,3-interaction.

D-*Ribononitrile tetraacetate* (**1**). — The conformation of D-ribononitrile tetraacetate (**1**) indicated by the spin-coupling data is a somewhat distorted "sickle" arrangement (**1a**). The value of 2.8 Hz for the $J_{2,3}$ coupling-constant is consistent with one of two possible gauche arrangements of H-2 and H-3. Between these, only that shown (**1a**) does not involve a destabilizing 1,3-interaction between the nitrile group and the acetate group on C-4. The coupling constant of 6.7 Hz for $J_{3,4}$ is noticeably smaller than that expected for an antiparallel arrangement of H-3 and H-4. The possibility that this value results from population of several different conformers arising from rotation about the C-3 to C-4 bond is remote, since such rotamers would experience considerable destabilizing interaction. The observed value of 6.7 Hz appears to result, as with **2**, from an essentially antiparallel arrangement of H-3 and H-4 that has been rotated slightly to relieve strain. As with **2**, the small, and effectively equal, values of $J_{4,5}$ and $J_{4,5'}$ (3.4 and 3.5 Hz) imply a gauche arrangement between H-4 and H-5 and between H-4 and H-5′.

D-*Lyxononitrile tetraacetate* (**4**). — The determination of the conformation of D-lyxononitrile tetraacetate (**4**) from the coupling constants was more difficult than for the other three nitrile tetraacetates (**1**–**3**). The results from n.m.r. analysis of **4** are consistent with either a "sickle" (**4a**) or a "U" shaped (**4b**) conformation. The value of 4.1 Hz for $J_{2,3}$, and of 3.3 Hz for $J_{3,4}$, suggest a gauche arrangement between H-2 and H-3 and also between H-3 and H-4. Although 1,3-interactions favor one of the two possible, gauche arrangements for H-2 and H-3, the staggered arrangements for H-3 and H-4 appear similar in energy and may both be populated; hence, both the "sickle" (**4a**) and the "U" (**4b**) conformations of the carbon chain are reasonable. The $J_{4,5}$ and $J_{4,5'}$ values (3.7 and 5.1 Hz) are similar to those observed in **3**, and their significance is, presumably, the same; however, the arrangement of groups arround the C-4–C-5 bond shown in **4a** (and implied in **4b**) appears to be the least strained.

Conclusion. — The results from this study are in agreement with those obtained in earlier studies[1] with respect to the importance of 1,3-interactions in determining the conformation of acyclic sugar derivatives. One noteworthy feature of these compounds is that rotation occurs primarily about the C-3–C-4 bond of D-xylononitrile tetraacetate (**3**), but about the C-2–C-3 bond of the *ribo* (**1**) and *lyxo* (**4**) analogues*.

EXPERIMENTAL

General. — N.m.r. spectra were measured at 60 MHz with a Varian T-60 spectrometer and at 100 MHz with a JEOLCO spectrometer; in each case with tetramethylsilane (2%) as an internal standard. I.r. spectra were recorded with a Beckman IR-8 spectrometer.

Materials. — *A.* D-*Xylononitrile tetraacetate* (**3**). A mixture of acetic anhydride (10 ml) and fused sodium acetate (1 g) was heated to 105–110° and D-xylose oxime (1 g) was added at such a rate as to keep the reaction at this temperature; heating was continued for 1 h at 80–90°. Partial removal of the solvent was achieved under diminished pressure at the same temperature, chloroform (15 ml) was added to the residue, and the mixture was washed with saturated, aqueous sodium hydrogen carbonate at 10° until all of the acetic anhydride had been removed. The chloroform solution was dried (sodium sulfate) and evaporated to give crystals; yield 1.07 g (51%); m.p. 78–79° (twice recrystallized from 95% ethanol) (lit.[5] m.p. 81–82°).

B. D-*Arabinononitrile tetraacetate* (**2**). D-Arabinose oxime (1 g) was converted into **2** by the procedure used in the preparation of **3**. The yield of crystalline product was 1.2 g (59%); m.p. 118–119° (twice recrystallized from 95% ethanol) (lit.[6] m.p. 120–121°).

C. D-*Ribononitrile tetraacetate* (**1**). D-Ribose oxime (1 g) was converted into **1** by the procedure used for preparation of **3**. The yield of crystalline product was 610 mg (29%); m.p. 69–70° (thrice recrystallized from 95% ethanol) (lit.[7] m.p. 71–72°).

D. D-*Lyxononitrile tetraacetate* (**4**). D-Lyxose oxime (1 g) was allowed to react with acetic anhydride and sodium acetate as described in part *A*. The product(s) was a syrup; yield, 1.52 g. To ensure the highest degree of homogeneity, the product was purified by column chromatography, with subsequent distillation at 0.2 torr to give a light-yellow syrup; $[\alpha]_D^{20}$ $-2.2°$ (*c* 3.0, chloroform), $\lambda_{max}^{CHCl_3}$ 5.68, 7.37, 8.18 (acetate), 9.48 μm.

Anal. Calc. for $C_{13}H_{17}NO_8$: C, 49.52; H, 5.44; N, 4.44. Found: C, 50.23; H, 5.56; N, 4.37.

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