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Note

Conformation of some benzoylated aldononitriles and 5-(polybenzoyloxyalkyl)tetrazoles as determined by their ^{1}H-n.m.r. spectra*

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For the correct interpretation of the ^{13}C-n.m.r. spectra of benzoylated acyclic carbohydrate derivatives, it was necessary to know their conformation, which could be assigned by analysis of the ^{1}H-n.m.r. spectra[1,2]. Coupling constants of 7.4–10.7 Hz corresponded to *trans*-diaxial vicinal protons, and of 3.0–4.4 Hz to vicinal-*gauche* protons[1]. We present herein some spectra of benzoylated aldononitriles and 5-(polybenzoyloxyalkyl)tetrazoles.

The conformations of 2,3,4,5-tetra-*O*-benzoyl-D-arabinononitrile[3] (**1**), 2,3,4,5-tetra-*O*-benzoyl-D-xylononitrile[4] (**2**), 2,3,4,5-tetra-*O*-benzoyl-6-deoxy-L-mannononitrile[4] (**3**), 2,3,4,5,6,7-hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile[5] (**4**), 2,3,4,5,6,7-hexa-*O*-benzoyl-D-*glycero*-D-*gulo*-heptononitrile[6] (**5**), 2,3,4,5,6,7-hexa-*O*-benzoyl-D-*glycero*-L-*manno*-heptononitrile[6] (**6**), 5-(1,2,3,4-tetra-*O*-benzoyl-D-*arabino*-tetritol-1-yl)tetrazole[3] (**7**), and 5-(1,2,3,4-tetrabenzoyl-5-deoxy-L-*manno*-pentitol-1-yl)tetrazole[3] (**8**) were determined by ^{1}H-n.m.r. spectroscopy, the spectra being amenable to first-order analysis. The assignments and coupling constants are listed in Tables I and II.

The reference conformation for acyclic carbohydrate derivatives is the extended, planar, zig-zag conformation. Not always the same conformation is observed for the free and the acetylated acyclic derivatives[7]. When the 1,3 interaction between bulky groups was apparent, a 120° rotation is proposed and named as proposed earlier. Frequently, no complete rotation was observed and the participation of several rotamers had to be postulated[2].

The acetylated acyclic derivatives having an *arabino* or *galacto* configuration were reported in the extended, planar, zig-zag conformation[8–10], the same as that for some benzoylated derivatives[1,2]. The same conformation was observed for **1**,

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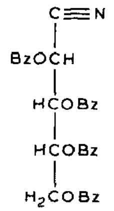

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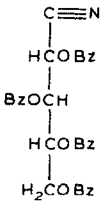

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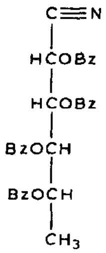

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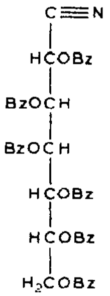

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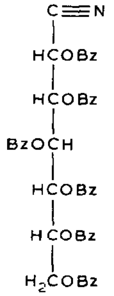

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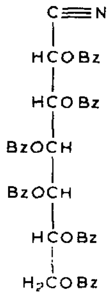

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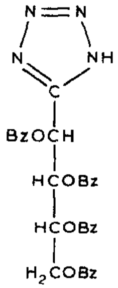

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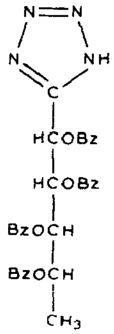

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TABLE I

N.M.R. DATA OF PERBENZOYLATED ALDONONITRILES **1–6**[a]

Compound	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5a ($J_{4,5b}$)	H-5 ($J_{5,6}$)	H-5b ($J_{5a,5b}$)	H-6 ($J_{6,7a}$)	H-7a ($J_{6,7b}$)	H-7b ($J_{7a,7b}$)
1[b]	6.09 d (4.4)	6.23 dd (7.3)	5.98 ddd (3.6)[c]	4.93 dd (5.1)		4.61 dd (12.4)			
2[b]	6.14 d (6.5)	6.09 dd (3.3)	6.16 ddd (5.5)[c]	4.74 dd (5.9)		4.67 dd (11.9)			
3[b]	5.99 d (5.0)	6.20 dd (2.9)	5.90 dd (6.8)		5.53 m (6.4)		1.48 d		
4[d]	5.87 d (4.1)	6.05 dd (7.9)	6.11 dd (2.1)		6.20 dd (7.9)		5.72 m (3.5)	4.76 dd (5.4)	4.37 dd (12.4)
5[d]	6.11 d (4.4)	6.08 dd (4.0)	6.11 dd (8.3)		6.06 dd (7.5)		5.74 m (3.4)	4.78 dd (4.9)	4.42 dd (12.4)
6[d]	5.86 d (4.3)	6.06 dd (2.0)	6.09 dd (8.0)		5.98 dd (3.3)		5.84 m (4.6)	4.53 dd (7.2)	4.39 dd (11.8)

[a]For solutions in (^{2}H)chloroform, δ values, J values in Hz. [b]At 200 MHz. [c]$J_{4,5a}$. [d]At 300 MHz.

TABLE II

N.M.R. DATA OF 5-(POLYBENZOYLOXYALKYL)TETRAZOLES **7** AND **8**[a]

Compound	*H-1* ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4a}$)	*H-4a* ($J_{3,4b}$)	*H-4b* ($J_{4a,4b}$)
7	6.94 d (5.1)	6.46 dd (6.9)	5.94 ddd (3.2)	4.83 dd (5.7)	4.55 dd (12.4)
8	6.83 d (5.6)	6.39 dd (3.7)	5.94 dd (5.5)	5.53 dt (6.4)	1.49 d

[a] For solutions in (^{2}H)chloroform, at 200 MHz.

but the structurally related tetrazole derivative **7** showed $J_{1,2}$ 5.1 Hz; this indicates a deviation from this conformation which could be attributed to the presence of more than one rotamer at C-1–C-2. An extended, planar, zig-zag conformation was observed for **4**.

For the compounds having the *ribo* or *xylo* configuration, 1,3 interactions were deduced from molecular models and have been reported for acetylated[8–10] and benzoylated[2,11] derivatives, These 1,3 interactions produced deviations from the expexted ^1J value (7–10 Hz) for the extended, planar, zig-zag conformation. Compound **2** showed $J_{2,3}$ 6.5 and $J_{3,4}$ 5.9 Hz, which indicated the presence of rotamers with an important contribution of $_2G^-$ and $_3G^+$. Similar observations were reported previously[2,7].

Compounds having the *manno* configuration do not show 1,3 interactions and consequently both free and acetylated derivatives exist in the planar, zig-zag conformation[7,8]. All the benzoylated acyclic derivatives so far reported showed a rotation at the C-2–C-3 linkage[1,2]. For compound **3**, the expected antirelationship of H-2 and H-3 gave a reduced value of $J_{2,3}$ 5.0 Hz, which can be attributed nearly to a *gauche* relationship. The rotation proposed for C-2–C-3 gives rise, in both cases, to 1,3 interactions. The $_2G^+$ rotation gives an interaction between two benzoyl groups, whereas the $_2G^-$ rotation gives an interaction between the small nitrile and a benzoyl group and is, therefore, preferred. A similar situation obtains for compound **8**, but $J_{1,2}$ 5.8 Hz shows that, in addition to the $_1G^-$ rotation, other rotamers are present.

For compound **6**, the $_2G^-$ rotamer is predominant and the rest of the chain is extended, and for compound **5**, the $_2G^-$ rotation is present together with an additional $_4G^+$ rotation which avoid an interaction between the benzoyl groups at C-3 and C-5.

EXPERIMENTAL

The compounds studied were prepared by methods previously described[3–6].

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