Carbohydrate Research, 167 (1987) 19–27
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

^{13}C-N.M.R. SPECTRA OF SOME ACYCLIC PERBENZOYLATED CARBOHYDRATE DERIVATIVES*

NORMA B. D'ACCORSO AND INGE M. E. THIEL†

Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires (Argentina)

(Received August 14th, 1986; accepted for publication in revised form, February 9th, 1987)

ABSTRACT

The ^{13}C-n.m.r. spectra of twelve perbenzoylated alditols, ten perbenzoylated aldononitriles, six 5-(polybenzoyloxyalkyl)tetrazoles, and six 5-(polyhydroxyalkyl)tetrazoles are described and their correlations are discussed.

INTRODUCTION

The ^{13}C-n.m.r. spectra give useful correlations of related structures when the conformation in solution can be ascertained by ^{1}H-n.m.r. spectroscopy for the acetylated derivatives[1–4] or by X-ray crystallography for the free alditols[5]. The conformations of the perbenzoylated alditols[6], aldononitriles, and tetrazole derivatives[7,8] agree frequently with those of the acyclic, hydroxylated or acetylated derivatives[1–4]. The ^{13}C-n.m.r. spectra of free alditols[9–12] and of some acetylated acyclic derivatives[10–13] have been reported, but few references were published on acyclic benzoylated derivatives[14–16].

RESULTS AND DISCUSSION

We describe herein the ^{13}C-n.m.r. spectra of the following compounds: ethylene dibenzoate[17] (**1**), propylene (*R*,*S*)-1,2-dibenzoate[6] (**2**), 1,2,3-tri-*O*-benzoylglycerol[6] (**3**), 1,2,3,4-tetra-*O*-benzoyl-D-erythritol[18] (**4**), 1,2,3,4-tetra-*O*-benzoyl-D,L-threitol[19] (**5**), 1,2,3,4,5-penta-*O*-benzoyl-L-arabinitol[6] (**6**), 1,2,3,4,5-penta-*O*-benzoyl-D-ribitol[20] (**7**), 1,2,3,4,5-penta-*O*-benzoyl-D-xylitol[21] (**8**), 1,2,3,4,5,6-hexa-*O*-benzoyl-D-galactitol[22] (**10**), 1,2,3,4,5,6-hexa-*O*-benzoyl-D-glucitol[23] (**12**), 1,2,3,4,5,6-hexa-*O*-benzoyl-D-mannitol[24] (**14**), 1,2,3,4,5-penta-*O*-benzoyl-6-deoxy-L-mannitol[6] (**16**), 2,3,4,5-tetra-*O*-benzoyl-D-arabinononitrile[25] (**18**), 2,3,4,5-tetra-*O*-benzoyl-D-lyxononitrile (**19**), 2,3,4,5-tetra-*O*-benzoyl-D-xylononitrile[26] (**9**),

---

[*] Part of this work has been presented at the XIIIth International Carbohydrate Symposium, Ithaca, August 10–15, 1986.

[†] To whom correspondence should be addressed.

0008-6215/87/$ 03.50

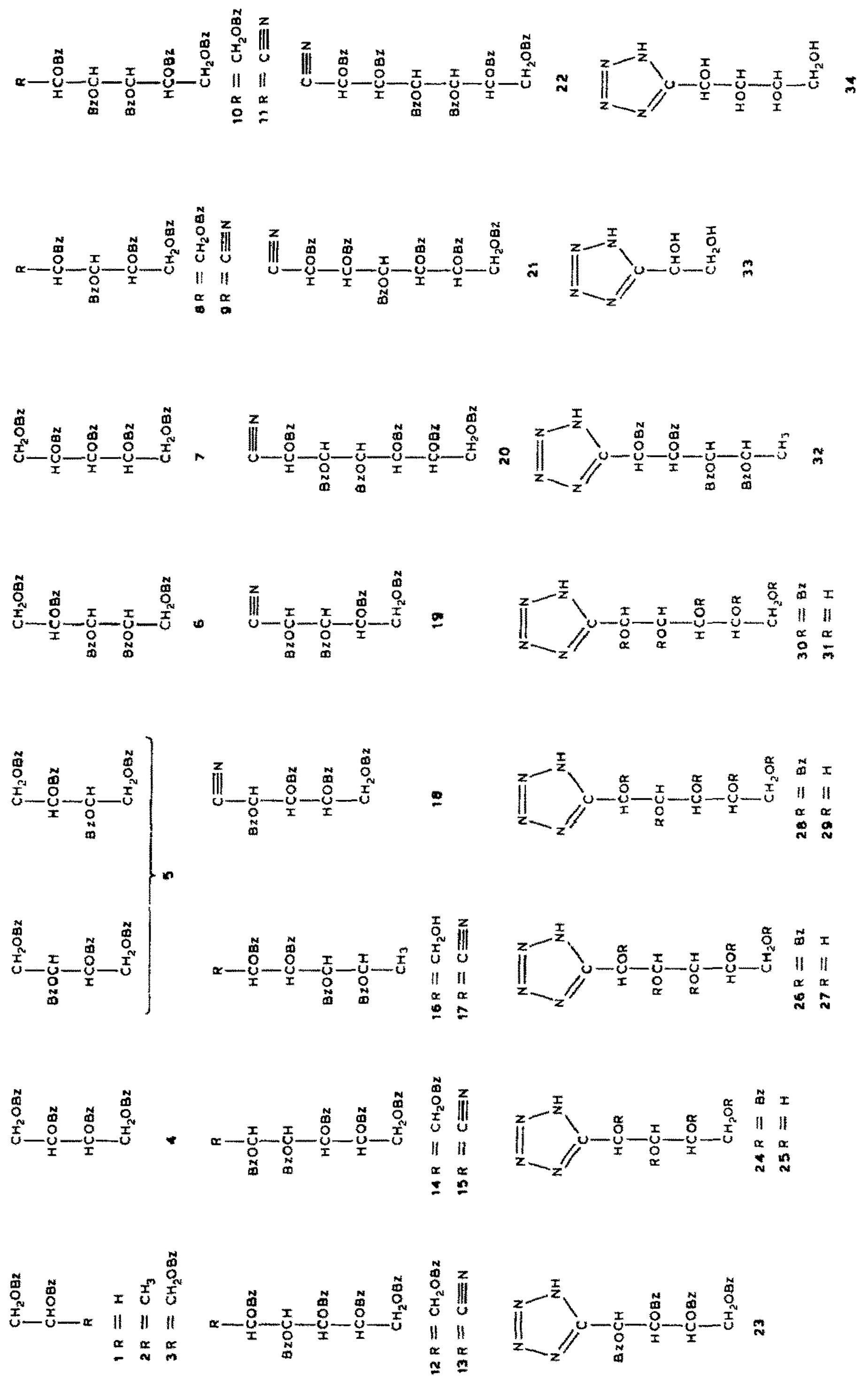
1 R = H
2 R = CH$_3$
3 R = CH$_2$OBz
4
5
6
7
8 R = CH$_2$OBz
9 R = C≡N
10 R = CH$_2$OBz
11 R = C≡N
12 R = CH$_2$OBz
13 R = C≡N
14 R = CH$_2$OBz
15 R = C≡N
16 R = CH$_2$OH
17 R = C≡N
18
19
20
21
22
23
24 R = Bz
25 R = H
26 R = Bz
27 R = H
28 R = Bz
29 R = H
30 R = Bz
31 R = H
32
33
34

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS (δ) OF SOME PERBENZOYLATED ALDITOLS[a]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
1	62.70	62.70				
2	66.71	69.05	16.77			
3	63.10	69.93	63.10			
4	62.63	70.05	70.05	62.63		
5	62.70	70.00	70.00	62.70		
6	62.95	69.25	69.50	69.86	62.52	
7	62.60	70.43	70.43	70.43	62.60	
8	62.52	69.98	69.76	69.98	62.52	
10	63.01	69.30	69.14	69.14	69.30	63.01
12	62.64	70.67	69.04	69.49	69.55	62.44
14	62.59	69.88	69.19	69.19	69.88	61.59
16	62.40	69.93	69.07	71.94	69.35	15.88

[a] Recorded at 25.20 MHz for a solution in (^{2}H)chloroform. The aromatic signals appeared at δ 128.04–133.71 and the carbonyl signals at δ 164.74–165.92.

2,3,4,5,6-penta-*O*-benzoyl-D-galactononitrile[26] (**11**), 2,3,4,5,6-penta-*O*-benzoyl-D-glucononitrile[26] (**13**), 2,3,4,5,6-penta-*O*-benzoyl-D-mannononitrile[26] (**15**), 2,3,4,5-tetra-*O*-benzoyl-6-deoxy-L-mannononitrile[26] (**17**), 2,3,4,5,6,7-hexa-*O*-benzoyl-D-*glycero*-D-*galacto*-heptononitrile[27] (**20**), 2,3,4,5,6,7-hexa-*O*-benzoyl-D-*glycero*-D-*gulo*-heptononitrile[28] (**21**), 2,3,4,5,6,7-hexa-*O*-benzoyl-D-*glycero*-L-*manno*-heptononitrile[28] (**22**), 5-(1,2,3,4-tetra-*O*-benzoyl-D-*arabino*-tetritol-1-yl)tetrazole[25] (**23**), 5-(1,2,3,4-tetra-*O*-benzoyl-D-*xylo*-tetritol-1-yl)tetrazole[25] (**24**), 5-(1,2,3,4,5-penta-*O*-benzoyl-D-*galacto*-pentitol-1-yl)tetrazole[29] (**26**), 5-(1,2,3,4,5-penta-*O*-benzoyl-D-*gluco*-pentitol-1-yl)tetrazole[25] (**28**), 5-(1,2,3,4,5-penta-*O*-benzoyl-D-*manno*-pentitol-1-yl)tetrazole[25] (**30**), 5-(1,2,3,4-tetra-*O*-benzoyl-6-deoxy-L-*manno*-pentitol-1-yl)tetrazole[25] (**32**), 5-[(1*R*,*S*)-1,2-dihydroxyethyl]tetrazole[14] (**33**), 5-(L-*arabino*-tetritol-1-yl)tetrazole[30] (**34**), 5-(D-*xylo*-tetritol-1-yl)tetrazole[25] (**25**), 5-(D-*galacto*-pentitol-1-yl)tetrazole[29] (**27**), 5-(D-*gluco*-pentitol-1-yl)tetrazole[28] (**29**), and 5-(D-*manno*-pentitol-1-yl)tetrazole[25] (**31**).

The ^{1}H-n.m.r. spectra of these compounds[6–8] allowed the determination of their conformations in solution and explained the deviations from the expected chemical shifts in the ^{13}C-n.m.r. correlations. The preferred conformations are as follows: **6**, extended, planar, zig-zag conformation[6]; partial rotation at C-2–C-3 and C-3–C-4 (ref. 6); **8**, partial rotation at C-2–C-3 and C-3–C-4 (ref. 6); **10**, extended, planar, zig-zag conformation[6]; **12**, ${}_2G^-$ (ref. 6); **14**, contribution of a ${}_2G^+$ rotamer[6]; **16**, contribution of a ${}_2G^-$ rotamer[6]; **18**, extended, planar, zig-zag conformation[8]; **9**, ${}_2G^-$ and ${}_3G^+$ contribution[8]; **11**, extended, planar, zig-zag conformation[7]; **13**, ${}_2G^-$ (ref. 7); **15**, ${}_2G^+$ (ref. 7); **14**, contribution of a ${}_2G^-$ rotamer (ref. 6); **20**, extended, planar, zig-zag conformation[8]; **21**, ${}_2G^-$ and ${}_4G^+$ (ref. 8); **22**, ${}_2G^-$ (ref. 8); **23**, extended, planar, zig-zag conformation with some rotameric contribution[8]; **26**, extended, planar, zig-zag conformation[7]; **28**, ${}_1G^-$ (ref. 7); **30**, ${}_1G^+$ (ref. 7); **32**, ${}_1G^-$ (ref. 8); and **29**, ${}_1G^-$ (ref. 7).

TABLE II

^{13}C-N.M.R. CHEMICAL SHIFTS (δ) OF SOME PERBENZOYLATED ALDONONITRILES[a]

Compound	*MHz*[b]	*C≡N*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*Solvent*
A[c]	25.20	114.45	59.88	62.31					$CDCl_3$
18	25.20	114.20	60.59	69.20	69.20	62.18			$CDCl_3$
19	25.20	114.05	61.37	69.95	69.15	62.22			$CDCl_3$
B[d,e]	20.15	114.05	61.80	69.70	70.00	62.27			$CDCl_3$
9	25.20	114.15	59.83	68.66	69.00	62.22			$CDCl_3$
11	15.08	114.08	60.68	68.75	68.93	69.11	62.50		$CDCl_3$
13[f]	100.63	114.82	60.51	68.88	69.12	69.49	62.57		C_6D_6
13	25.20	114.11	59.74	68.32	68.32	69.40	62.42		$CDCl_3$
15	15.08	114.07	62.01	68.08	68.98	69.26	62.33		$CDCl_3$
17	25.20	114.05	61.92	68.66	72.03	69.10	16.41		$CDCl_3$
20[e]	75.52	114.03	60.69	68.27	63.78	68.85	69.44	62.39	$CDCl_3$
21[e]	75.52	113.88	61.58	68.64	69.43	69.72	69.94	62.33	$CDCl_3$
22[e]	75.52	113.90	62.27	68.66	68.96	69.00	69.18	63.03	$CDCl_3$

[a] The aromatic signals appeared at 127.15–134.40 and the carbonyl signals at δ 163.85–165.94. [b] Recorded at. [c] 2,3-Di-*O*-benzoyl-D,L-glyceronitrile[13]. [d] 2,3,4,5-Tetra-*O*-benzoyl-D-ribononitrile[16]. [e] Signals were ascertained by the APT technique. [f] Signals were ascertained by a proton-coupled spectrum.

The ^{13}C-n.m.r. signals of the perbenzoylated alditols **1–8, 10, 12, 14,** and **16** are listed in Table I. The assignments were attributed by comparison with the signals of the acetylated and free compounds having the same structure[9,10], and correlated with structurally related benzoylated acyclic derivatives. The ^{13}C-n.m.r. spectra of the benzoylated aldononitriles **9, 11, 13, 15,** and **17–22** were assigned and are listed in Table II. The chemical shift of the nitrile group agrees with the values given in literature[31].

The assignments of the primary CH_2OBz groups were ascertained by the analysis of the proton-coupled spectrum of **13**. Therefore, the assignments given for 2,3-di-*O*-benzoyl-D,L-glyceronitrile[14] have to be corrected. The assignments for **20–22** were ascertained by the APT technique. In all compounds, the nitrile carbon atom showed a similar shift, δ 114. The signal of the carbon atom of the group vicinal to it was easily assigned to the signal having the lowest chemical shift. The other carbon signals were assigned by correlation with the structurally related benzoylated alditols. This was only possible with good approximation where both types of compounds have the same conformation in solution, which was ascertained by ^{1}H-n.m.r. spectrometry[7,8]. The spectrum of **13** was recorded for solutions in (^{2}H)chloroform and ($^2H_6$)benzene. For the latter solvent, all the signals showed a downfield shift.

In comparing the spectra, it is observed that for compounds having the zigzag extended, planar conformation the signal for C-2 appeared at δ 60.6 ±0.1 (**11, 18,** and **20**). For those compounds having a 120° rotation at C-2–C-3 (2,3,4,5-tetra-*O*-benzoyl-D-ribononitrile, and **15, 17,** and **22**) the signal for C-2 appeared at δ 62.0 ±0.3. Compound **21** showed a $_2G^-$ rotation but, in this case, the value of the signal

TABLE III

^{13}C-N.M.R. CHEMICAL SHIFTS (δ) OF SOME 5-(POLYBENZOYLOXYALKYL)TETRAZOLES[a]

Compound	*C-heter.*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*
A[b,c]	156.07	65.74	64.15			
23[c]	157.55	66.76	71.98	69.99	62.61	
B[d,c]	155.24	66.95	71.22	69.86	62.73	
24[c]	156.77	66.78	71.69	69.73	62.90	
26[c]	156.70	65.93	70.15	69.41	69.01	62.88
28[c]	155.93	66.08	70.30	69.40	69.40	62.50
30[e]	156.75	67.07	71.23	70.39	69.67	62.91
32[c]	155.40	66.03	70.15	71.92	69.46	15.98

[a] Recorded at 25.20 MHz. [b] 5-[1(*R*,*S*)-1,2-Di-*O*-benzoylethyl]tetrazole[13]. [c] For a solution in (^{2}H)chloroform. Aromatic signals appeared at δ 126.87–133.64 and the carbonyl signals at δ 164.58–165.99. [d] 5-(Tetra-*O*-benzoyl-D-*ribo*-tetritol-1-yl)tetrazole[16]. [e] Recorded for a solution in (^{2}H$_5$)pyridine. Aromatic signals appeared at δ 124.55–136.62 and the carbonyl signals at δ 165.23–165.91.

changed as a $_4G^+$ rotation was also present. Compounds having a statistical proportion of similar rotamers, as seen by their coupling constants, gave similar values. As an example, the signal for C-2 of **9** and **13**, C-2 at δ 59.8 ±0.1 and $J_{2,3}$ 6 Hz.

The correlation of the spectra of the benzoylated aldononitriles and alditols having the same structure showed that the change from a primary benzoyloxy to a nitrile group gave a difference of 51–52 p.p.m. The most affected signal is that of the vicinal C-2, and for compounds having the same extended, planar conformation, this difference was of 8.6 p.p.m. A similar rotation in the same direction, for example $_2G^-$ in the D-series, and a similar rotameric contribution gave differences of 10–11 p.p.m. The correlation of the pairs of substances having different rotameric contribution showed unpredictable differences (D-*ribo*, D-*manno*, and L-*manno*).

TABLE IV

^{13}C-N.M.R. CHEMICAL SHIFTS (δ) OF SOME 5-(POLYHYDROXYALKYL)TETRAZOLES[a]

Compound	*C-heter.*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*
33[b]	158.41	66.76	65.07			
34[b]	159.08	65.76	73.50	71.09	63.59	
A[b,c]	157.43	66.92	73.95	71.97	63.49	
25[b]	158.25	66.73	73.37	72.10	63.24	
27[b]	159.82	66.17	73.16	71.02	70.18	64.21
29[d]	160.08	69.19	74.13	73.83	73.16	65.41
31[b]	158.58	65.98	69.26	69.08	68.94	63.98

[a] For a solution in D$_2$O. [b] Recorded at 25.20 MHz. [c] 5-(D-*ribo*-Tetritol-1-yl)tetrazol[16]. [d] Recorded at 100.63 MHz. The signals were ascertained by the proton-coupled spectrum.

The ^{13}C-n.m.r. chemical shifts of 5-[polybenzoyloxyalkyl]tetrazoles (**23, 24, 26, 28, 30,** and **32**) (see Table III) were assigned by correlation with the signals of other acyclic benzoylated compounds of the same conformation, which had been ascertained previously by ^{1}H-n.m.r. spectrometry[7,8]. The signal of the heterocyclic carbon appeared between δ 155 and 160, as expected from previous work[32]. The signal for C-1, next to the tetrazole group and the primary chain carbon, could be assigned easily, and the other carbon signals were determined by correlation with those of the benzoylated alditols and nitriles.

For these benzoylated derivatives, the change from a nitrile to a tetrazole carbon atom corresponded to a difference of 41–43 p.p.m. and from an alditol to a heterocyclic carbon atom to a difference of 93–95 p.p.m. The signal of C-1 of the chain, with respect to that of C-2 of the nitrile, showed a difference of 3.0–4.6 p.p.m. and was the most affected. The rest of the carbon signals showed smaller differences, except in the case where a different rotamer appeared in one of the correlated compounds. The spectrum of the D-*manno* derivative **30** had to be recorded for a solution in pyridine owing to its low solubility in other solvents, in which no good correlation could be observed because of the solvent effect.

The ^{13}C-n.m.r. chemical shifts of some 5-[polyhydroxyalkyl]tetrazoles (**25, 27, 29, 31, 33, 34**) are listed in Table IV. The assignment of the signal for the

TABLE V

^{13}C-N.M.R. CHEMICAL-SHIFT CORRELATIONS

Compounds compared	*ΔCompd.*	*ΔC-1*	*ΔC-2*	*ΔC-3*	*ΔC-4*	*ΔC-5*	*ΔC-6*
A. Perbenzoylated alditols							
A-1	**2** – **3**	3.61	−0.88	−46.33			
A-2	**16** – **14**	−0.19	0.05	0.12	2.75	−0.53	−46.71
A-3	**7** – **6**	−0.35	1.18	0.93	0.57	0.08	
A-4	**7** – **8**	0.08	0.45	0.67	0.45	0.08	
A-5	**12** – **10**	−0.37	1.37	−0.10	0.35	0.25	−0.57
A-6	**12** – **14**	0.05	0.79	−0.15	0.30	0.33	−0.15
B. Perbenzoylated aldononitriles							
B-1	**17** – **15**	−0.02	0.09	0.32	2.95	−0.16	−45.92
B-2	A[a] – **18**	−0.15	1.21	0.50	0.80	0.09	
B-3	**13** – **11**	0.03	−0.94	0.43	0.61	0.29	−0.08
B-4	**13** – **15**	0.04	−2.27	0.66	0.76	0.14	0.09
C. 5-[Polybenzoyloxyalkyl]tetrazoles and 5-[polyhydroxyalkyl]tetrazoles							
C-1	**32** – **30**	−1.04	−1.08	1.53	−0.21	−46.93	
C-2	B[b] – **24**	0.17	−0.47	0.13	−0.17		
C-3	C[c] – **34**	1.16	0.45	0.88	−0.10		
C-4	C[c] – **25**	0.19	0.58	−0.13	0.25		

[a] 2,3,4,5-Tetra-*O*-benzoyl-D-ribononitrile. [b] 5-(1,2,3,4-Tetra-*O*-benzoyl-D-*ribo*-tetritol-1-yl)tetrazole. [c] 5-(D-*ribo*-Tetritol-1-yl)tetrazole.

terminal carbon atom was based on the coupled spectrum of compound **29**. In this case, the assignments were attributed by correlation with the spectra of the free alditols[10] and of the benzoylated tetrazoles having the same configuration. The ^{1}H-n.m.r. coupling constants for **27** (see experimental part) and **29** (ref. 7) showed that the same conformation predominates as in the acyclic acetylated and benzoylated derivatives and, consequently, no significant change in conformation is likely for the other compounds.

The correlation of the spectra of the 5-[polybenzoyloxyalkyl]tetrazoles and the 5-[polyhydroxyalkyl]tetrazoles showed that the acyl groups present shielding effects, specially for the β-carbon atoms, as was also reported for cyclic benzoylated compounds[33]. Comparison of the ^{13}C-n.m.r. shifts of the same type of carbon atoms in related compounds suggests some general conclusions (see Table V). (a) Replacement of a hydrogen atom by a benzoyloxy group on a terminal carbon atom resulted in a difference of 46 p.p.m. for the signal of this carbon atom and important differences for the signal of the β-carbon atom. (A-1, A-2, B-1, and C-1). (b) When the compounds compared showed the same conformation but a different configuration at one carbon atom, the biggest difference was observed for the signal of this carbon atom (A-3, B-2, and C-3, *ribo vs. arabino*; and A-4 and C-2, D-*ribo vs.* D-*xylo*). (c) The comparison of compounds having a configurational change at one carbon atom and an additional conformational change in another part of the

TABLE VI

PREDICTED ^{13}C-CHEMICAL SHIFTS FOR HEXA-*O*-BENZOYLHEPTONONITRILES AND COMPARISON WITH THE OBSERVED VALUES

Compounds		*Chemical shifts (δ)*						
Ref.	*Obs.*[a]	*C≡N*	*C-2*	*C-3*	*C-4 (C-3)*	*C-5 (C-4)*	*C-6 (C-5)*	*C-7 (C-6)*
11		114.08	60.68	68.75	68.93			
14					(69.19)	(69.19)	(69.88)	(62.59)
	20 Predict.	114.08	60.68	68.75	69.06[b]	69.19	69.88	62.59
	Obs.	114.03	60.69	68.27	68.78	68.85	69.45	62.39
	Diff.	0.05	0.01	0.48	0.15	0.34	0.43	0.20
15		114.07	62.01	68.98	69.08			
10					(69.14)	(69.14)	(69.30)	(63.01)
	22 Predict.	114.07	62.01	68.98	69.11[b]	69.14	69.30	63.01
	Obs.	113.90	62.27	68.66	68.96	69.00	69.18	63.03
	Diff.	0.17	0.26	0.32	0.15	0.14	0.12	0.02
19		114.05	61.37	69.95	69.15			
12					69.04	69.49	69.55	62.44
	21 Predict.	114.05	61.37	69.95	(69.10)[b]	(69.49)	(69.55)	(62.44)
	Obs.	113.88	61.58	68.64	69.43	69.72	69.94	62.33
	Diff.	0.17	0.21	1.31	0.33	0.23	0.29	0.11

[a]Compound for which values are predicted and observed. [b]Average between two reference compounds.

molecule showed differences for the signals of both carbon atoms. The conformational change could even compensate the configurational change (A-5 and B-3, D-*gluco vs.* D-*galacto*). (d) When the compounds compared showed a conformational change at the carbon atom having the configurational inversion, the biggest difference was noted for the signal of this carbon atom (A-6 and B-4, D-*gluco vs.* D-*manno*).

Thus, the ^{13}C-n.m.r. spectra of yet unreported benzoylated acyclic compounds may be calculated with approximation, if their conformation is known. The deviations observed with the experimental values may be explained generally by conformational changes. As examples, the predicted signals of 2,3,4,5,6,7-hexa-*O*-benzoylheptononitriles and the observed deviations (which are <1 p.p.m.) are shown in Table VI. The signals for **20** are in good agreement, as the reference compounds show the same conformation. The signals for **22** had to be calculated with a D-*manno* spectrum as reference for an L-configuration, but the agreement is still good owing to the same conformation in these compounds. To calculate the signals for **21**, it was necessary to use the signals of 2,3,4,5-tetra-*O*-benzoyl-D-lyxononitrile (**19**) instead of the spectrum of the L compound which had an unknown conformation. The important difference for the signal of C-3 may be due to the presence of different rotamers, as **21** showed the presence of a $_2G^-$ and a $_4G^+$ rotamer. The values determined may be extended to other compounds and, thus, it is possible to assign the signals for the octa-*O*-benzoylaldobiononitriles on the basis of the values reported by D'Accorso *et al.*[34].

EXPERIMENTAL

General. — The ^{13}C-n.m.r. spectra were recorded with a Varian XL 100 spectrometer at 25.20 MHz (**1–10, 12–14, 16–19, 23–28, 30–34**), with a Bruker WP 60 DS spectrometer at 15.08 MHz (**11** and **15**), with a Bruker WM 400 spectrometer at 100.63 MHz (**13** and **29**), and with a Bruker EM 360 A spectrometer at 75.52 MHz (**20–22**).

*^{1}H-N.m.r. spectrum of 5-[*D-galacto*-pentitol-1-yl]tetrazole* (**27**). — This spectrum was recorded at 400 MHz for a solution in D_2O with Me_4Si as internal standard: δ 5.47 (d, $J_{1,2}$ 1.6 Hz, H-1), 3.95 (dd, $J_{2,3}$ 9.4 Hz, H-2), 3.94 (dd, $J_{4,5}$ 6.4 Hz, H-4), 3.80 (dd, $J_{3,4}$ 1.4 Hz, H-3), and 3.67 (d, H-5).

*^{13}C-N.m.r. data for 2,3,4,5,6-penta-*O*-benzoyl-*D-*gluconononitrile* (**13**). — This spectrum was recorded at 100.63 MHz for a solution in C_6D_6: δ 60.51 (d, $J_{C-2,H-2}$ 150.97 Hz, C-2), 62.57 (t, $J_{C-6,H-6}$ 144.27 Hz, C-6), 68.88 (d, $J_{C-3,H-3}$ 138.31 Hz, C-3), 69.12 (d, $J_{C-4,H-4}$ 149.59 Hz, C-4), and 69.49 (d, $J_{C-5,H-5}$ 137.44 Hz, C-5).

*^{13}C-N.m.r. data for 5-[*D-gluco*-pentitol-1-yl]tetrazole* (**29**). — This spectrum was recorded at 100.63 MHz for a solution in D_2O: δ 65.41 (t, $J_{C-5,H-5}$ 141.69 Hz, C-5), 69.19 (d, $J_{C-1,H-1}$ 148.24 Hz, C-1), 73.16 (d, $J_{C-4,H-4}$ 138.93 Hz, C-4), 73.83 (d, $J_{C-3,H-3}$ 140.62 Hz, C-3), and 74.13 (d, $J_{C-2,H-2}$ 144.64 Hz, C-2).

ACKNOWLEDGMENTS

The authors thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for a fellowship (N. B. D'A.) and acknowledge partial financial support from the Universidad de Buenos Aires and from CONICET. They are indebted to UMYMFOR, (CONICET–FCyN–UBA) (compounds **1–10, 12–14, 16–19, 23,** and **34**); Prof. Dr. M. Fontanille and Dr. D. Adès (Université de Paris-Nord, France) (compounds **11** and **15**); Diplom Chem. A. M. Schüller (Universität Hamburg, West Germany) (compound **13**); Prof. Dr. W. Neumann, Prof. Dr. T. N. Mitchell, and Mr. M. A. Ardjmandian (Universität Dortmund, West Germany) (compounds **20–22**,) for recording the ^{13}C-n.m.r. spectra and thank Prof. Dr. J. O. Deferrari for samples of compounds **19**, and **20–22**.

REFERENCES

1 S. J. Angyal, R. Le Fur, and D. Gagnaire, *Carbohydr. Res.*, 23 (1972) 121–124.
2 W. W. Binkley, D. R. Diehl, and R. W. Binkley, *Carbohydr. Res.*, 18 (1971) 459–465.
3 A. M. Seldes, E. G. Gros, I. M. E. Thiel, and J. O. Deferrari, *Carbohydr. Res.*, 39 (1975) 11–17.
4 L. M. Sweeting, B. Coxon, and R. Varma, *Carbohydr. Res.*, 72 (1979) 43–55.
5 P. L. Durette and D. Horton, *Adv. Carbohydr. Chem.*, 26 (1971) 69–70.
6 N. B. D'Accorso and I. M. E. Thiel, *Rev. Latinoam. Quím.*, 17 (1986) 36–39.
7 I. M. Vazquez, N. B. D'Accorso, I. M. E.. Thiel, and A. M. Schüller, *An. Asoc. Quim. Argent.*, 72 (1984) 583–589.
8 N. B. D'Accorso and I. M. E. Thiel, *Carbohydr. Res.*, 167 (1987) 301–304.
9 W. Voelter, E. Breitmaier, G. Jung, T. Keller, and D. Kiss, *Angew. Chem., Int. Ed. Engl.*, 9 (1970) 803–804.
10 S. J. Angyal and R. Le Fur, *Carbohydr. Res.*, 84 (1980) 201–209.
11 S. J. Angyal and R. Le Fur, *Carbohydr. Res.*, 126 (1984) 15–26.
12 G. W. Schnarr, D. M. Vyas, and W. A. Szarek, *J. Chem. Soc., Perkin Trans 1,* (1979) 496–503.
13 R. H. Furneaux, *Carbohydr. Res.*, 113 (1983) 241–255.
14 N. B. D'Accorso, B. N. Zuazo, and I. M. E. Thiel, *An. Asoc. Quim. Argent.*, 70 (1982) 793–799.
15 R. D. García Lastres, I. M. E. Thiel, and A. M. Schüller, *An. Asoc. Quim. Argent.*, 72 (1984) 247–253.
16 A. M. Martelli, N. B. D'Accorso, and I. M. E. Thiel, *An. Asoc. Quim. Argent.*, in press.
17 J. Houben and W. Fischer, *Ber.*, 64B (1931) 240–247.
18 C. Prevost and R. Lutz, *C.R. Hebd. Seances Acad. Sci.*, 198 (1934) 2264–2266; H. Ohle and G. A. Melkonian, *Ber. Dtsch. Chem. Ges.*, 74 (1941) 291–294.
19 P. W. Kent, K. R. Wood, and V. A. Welch, *J. Chem. Soc.*, (1964) 2493–2497.
20 R. K. Ness, H. W. Diehl, and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, 76 (1954) 763–767.
21 H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, 75 (1953) 2624–2627.
22 J. Wiemann and J. Gardan, *Bull. Soc. Chim. Fr.*, (1958) 433–436.
23 Y. Asahina and H. Shinoda, *J. Pharm. Soc. Jpn.*, 50 (1930) 1–7.
24 T. S. Patterson and A. R. Todd, *J. Chem. Soc.*, (1929) 2876–2889.
25 O. G. Marzoa, J. O. Deferrari, and I. M. E. Thiel, *Carbohydr. Res.*, 73 (1979) 323–326.
26 E. R. de Labriola and V. Deulofeu, *J. Org. Chem.*, 12 (1947) 726–730.
27 P. Brigl, M. Mühlschlegel, and R. Schinle, *Ber. Dtsch. Chem. Ges.*, 64 (1931) 2921–2934.
28 J. O. Deferrari and B. Matsuhiro, *J. Org. Chem.*, 31 (1966) 905–908.
29 J. O. Deferrari, A. M. Seldes, O. G. Marzoa, and I. M. E. Thiel, *Carbohydr. Res.*, 17 (1971) 237–239.
30 A. M. Seldes, J. O. Deferrari, and I. M. E. Thiel, *Carbohydr. Res.*, 39 (1975) 47–51.
31 E. Pretch, T. Clerc, J. Seibl, and W. Simon, *Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden,* Springer-Verlag, 1976, Berlin, p. C-190.
32 J. Golger, J. Světlik, and J. Hrušovský, *Monatsh. Chem.*, 119 (1983) 65–70.
33 N. B. D'Accorso, I. M. E. Thiel, and M. Schüller, *Carbohydr. Res.*, 124 (1983) 177–184.
34 N. B. D'Accorso, B. N. Zuazo, and I. M. E. Thiel, *Carbohydr. Res.*, in press.