Conformational Studies of D-Glycals by ^{1}H Nuclear Magnetic Resonance Spectroscopy

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The preferred half-chair conformations of the fully *O*-acetylated D-glycals (and related compounds), as indicated by ^{1}H n.m.r. spectroscopy, show that the coupling constant $^4J_{2,4}$ is the most sensitive to conformational change. All six fully *O*-acetylated-D-glycals favour the $^4H_5$(D) conformation in solution, except di-*O*-acetyl-D-xylal which adopts the alternative $^5H_4$(D) conformation. These conformational preferences can be rationalised by considering the interactions between the substituents at C(3), C(4), and C(5) and the ' allylic effect '. With the introduction of a substituent at C(2) in glucals and galactals, ring-flattening or inversion to the $^5H_4$ conformation can take place to relieve strain.

NUCLEAR magnetic resonance spectroscopy is the most powerful and direct technique available for the investigation of the conformational aspects of monosaccharide derivatives in solution.[1] It was used [2] for the first conformational assignment of an unsaturated carbohydrate derivative, *viz.* the glycal 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol (tri-*O*-acetyl-D-glucal) (8). Chemical transformations based on the glycals are of extreme importance and it is well known that their conformational and configurational properties play a major part in determining the course of reaction.[3] During work [4] on the preparation of 2-*C*-cyano-glycals anomalies were observed in the n.m.r. spectral data given [5] for 3,4-di-*O*-acetyl-1,5-anhydro-2-deoxy-L-*erythro*-pent-1-enitol (di-*O*-acetyl-L-arabinal) and -D-*threo*-pent-1-enitol (di-*O*-acetyl-D-xylal) (12) and it was therefore decided to carry out a comprehensive conformational study of the D-glycals by using ^{1}H n.m.r. spectroscopy.

The compounds investigated were the five fully *O*-acetylated-D-glycals: 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*ribo*-hex-1-enitol (tri-*O*-acetyl-D-allal) (2), the corresponding D-*xylo*- and D-*lyxo*-isomers [tri-*O*-acetyl-D-gulal (1) [6] and tri-*O*-acetyl-D-galactal (5),[7a] respectively], 3,4-di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*erythro*-pent-1-enitol (di-*O*-acetyl-D-arabinal) (3) [7b] and the corresponding D-*threo*-isomer (di-*O*-acetyl-D-xylal) (12);[7c] the 2-*C*-cyano-derivatives of the foregoing D-galactal and D-arabinal (6) [4] and (4),[4] respectively, and 4,6-di-*O*-acetyl-1,5-anhydro-3-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (4,6-di-*O*-acetyl-3-*O*-benzyl-D-glucal) (9) [4] and its 2-*C*-cyano-derivative (11).[4]

ANALYSES AND SPECTRA

Full analyses were made of proton chemical shifts (Table 1) and coupling constants (Tables 2 and 3) for compounds (2)—(6) and (12) including, where present, the ABX spin systems of the C(6) methylene protons with the H-5 proton. This system in the gulal (1) could not be analysed because the three protons have the same chemical shift. The 5-, 6-, or 7-spin systems of these compounds were finally simulated to check agreement with the observed spectra. Spectra of the glucals (9) and (11) were analysed on a first-order basis for coupling constants important to the conformational discussion.

[1] (*a*) P. L. Durette and D. Horton, *Adv. Carbohydrate Chem.*, 1971, **26**, 49; (*b*) B. Coxon, *Methods Carbohydrate Chem.*, 1972, **6**, 513.

[2] (*a*) L. D. Hall and L. F. Johnson, *Tetrahedron*, 1964, **20**, 883; (*b*) L. D. Hall and J. F. Manville, *Carbohydrate Res.*, 1968, **8**, 295; (*c*) A.C.S. Advances in Chemistry Series, 1968, No. 74, p. 228.

[3] R. J. Ferrier, *Adv. Carbohydrate Chem.*, 1969, **24**, 199.

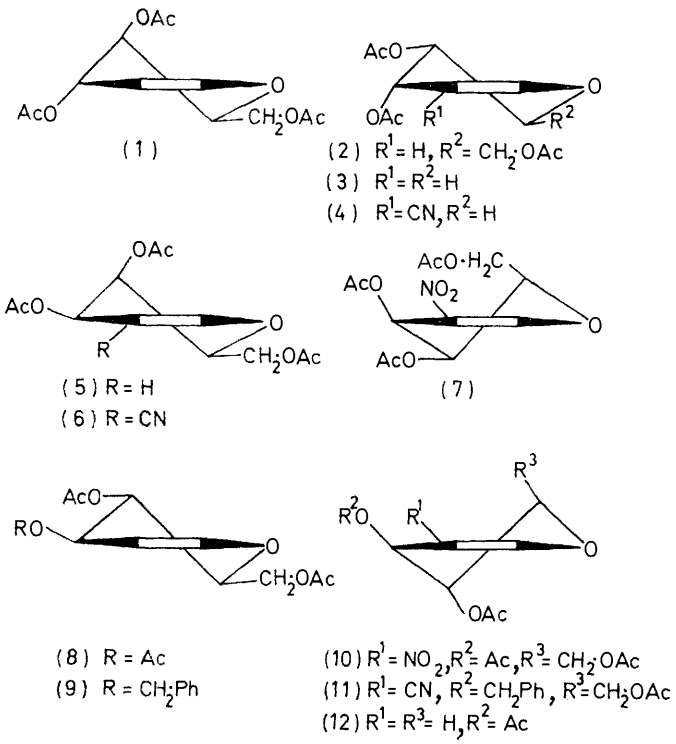
[4] R. H. Hall and A. Jordaan, *J.C.S. Perkin I*, 1973, 1059.

[5] M. Fuertes, G. Garcia-Muñoz, R. Mandroñero, M. Stud, and M. Rico, *Tetrahedron*, 1970, **26**, 4823.

[6] D. M. Climent and R. J. Ferrier, *J. Chem. Soc.* (*C*), 1966, 441.

[7] See *Methods Carbohydrate Chem.*, (*a*) 1963, **2**, 457; (*b*) 1962, **1**, 84; (*c*) 1962, **1**, 184.

Assignments were made on the basis of equal splittings in different multiplets and independently by extensive use of spin-decoupling starting at the easily assigned H-1 resonance and progressing through the spectrum. Particular attention was given to long-range couplings and of the sixteen that were well resolved the signs of twelve were determined by ^1H–$\{^1H\}$ INDOR. The INDOR experiments confirmed the assignments. Data given in the Tables are for 0·3M-solutions in the solvent indicated in Table 1. In spectra obtained with these and other solvents ([$^2H_5$]pyridine and [$^2H_6$]acetone) no solvent dependence was observed for the directly measurable couplings.



The glycals are shown in their preferred conformations

In the spectra of the arabinals (3) and (4) the presence of a large coupling ($J_{4,5}$) in the lower field H-5 resonance allowed this to be assigned to H-5*ax*.

In the spectrum of the xylal (12) the H-2, H-3, and H-4 signals are too close together for spin decoupling. Assignment of these multiplets can be made from the lack of intensity distortion of the H-2 lines. Also, the addition of the shift reagent Eu(fod)$_3$ produced a simple spectrum on which spin decoupling and INDOR experiments were performed. The signals of the protons at the acetoxy-bearing positions C(3) and C(4) were shifted downfield more than those of all other protons so that only a very small quantity of shift reagent was required. Line broadening was so slight that the smallest coupling to H-3 was still resolved. The addition of shift reagent caused no significant change in coupling constants extracted from the simple splittings, *viz.* $J_{4,5ax}$ and $J_{4,5eq}$. Satisfactory agreement between the observed unshifted spectrum and the calculated spectrum was obtained with coupling constants from the shifted spectrum by adjustment of the chemical shifts. Assignment of H-5*ax* and H-5*eq* cannot be made from the $J_{4,5}$ values and the lower field H-5 octet which shows the larger $J_{3,5}$ value was assigned to H-5*eq*. The chemical shifts and coupling constants of the xylal (12) and the arabinal (3) are at variance with those reported [5] for compound (12) and the enantiomeric L-arabinal.

The spectra of the galactals (5) and (6) are difficult to analyse directly because of a small coupling ($J_{1,5}$) which broadens the H-5 signal. With H-1 decoupled, H-5 gave a sharply defined multiplet from which starting estimates of $J_{4,5}$, $J_{5,6}$, $J_{5,6'}$, and $J_{3,5}$ were obtained for use in the second-order analyses. Excellent agreement was obtained with the five coupling constants previously reported [8] for the galactal (5).

The spectrum of the allal (2) is simple since it shows no long-range couplings, while in the spectrum of the gulal (1) the H-4 multiplet is not well resolved since it arises from three rather small couplings. The important $J_{4,5}$ could not be obtained from H-5 which is degenerate with H-6 and H-6′, but an estimate of its magnitude was made by subtraction of the known values of $J_{2,4}$ and $J_{3,4}$ from the multiplet. Addition of Eu(fod)$_3$ was ineffective in removing the degeneracy. Spectra of the glucal (9) at various temperatures showed no change in the coupling constants between 37 and −40 °C.

The signs of coupling constants were determined by the ^1H–$\{^1H\}$ INDOR [9] method. In all cases both the highest- and lowest-field lines of the multiplet were monitored separately to give a check on the results.

TABLE 1

Chemical shifts (δ) for the glycals

Compound	Solvent	H-1	H-2	H-3	H-4	H-5*ax*	H-5*eq*	H-6	H-6′
(1)	C_6D_6	6·18	5·04	5·16	5·26	4·18 [b]		4·18	4·18
(2)	C_6D_6	6·22	4·68	5·60	5·16	4·28 [b]		4·48	4·24
(3)	C_6D_6	6·33	4·66	5·50	5·16	3·85	3·71		
(4)	C_6D_6	6·39		5·44	4·91	3·48	3·35		
(5)	C_6D_6	6·16	4·54	5·48	5·38	3·93		4·22	4·14
(6)	C_6D_6	6·59		5·52	5·36	3·75		3·99	3·95
(8) [a]	$CDCl_3$	6·53	4·81	5·34	5·20	4·19		4·09	4·29
(9)	$CDCl_3$	6·45	4·93	4·00	5·27	4·32 [b]		*c*	*c*
(11)	$CDCl_3$	7·20		3·97	5·21	4·54 [b]		*c*	*c*
(12)	C_6D_6	6·36	4·93	5·08	4·95	3·68	4·01		

[a] Ref. 2. [b] The resonance was located by decoupling. [c] Not analysed. Acetoxy- and benzyloxy-resonances are not shown.

[8] I. Lundt and C. Pedersen, *Acta Chem. Scand.*, 1971, **25**, 2749.
[9] E. B. Baker, *J. Chem. Phys.*, 1962, **37**, 911.

This procedure was essential for the sign of $J_{3,5ax}$ in the galactals (5) and (6) where the broadness of the H-5 resonance (in the absence of triple resonance at H-1) made it impossible to assign INDOR deflections to individual H-5 lines, but the shift of the INDOR deflections accompanying change of the monitor line gave the sign. No attempt was made to obtain the signs of coupling constants less than or equal to 0·5 Hz in magnitude but the signs of all long-range couplings greater than this were obtained with the exception of $J_{3,5eq}$ in the glucal (11) and $J_{1,3}$ in the 2-*C*-cyano-arabinal (4). In the latter compound H-1 and H-3 have no common coupling to another proton whereas in the ation as the galactal (5) is strongly suggested by the similarity of the coupling constants. The values of $J_{4,5ax}$, $J_{4,5eq}$, and $J_{5ax,5eq}$ are significantly different in the arabinal (4) and the arabinal (3), and since the three-bond couplings are smaller in compound (4) this could indicate that C(5) is further out of the O–C(1)–C(2)–C(3) plane. The increase in $|J_{5ax,5eq}|$ for compound (4) also suggests a distortion making the oxygen lone pairs less eclipsed with the coupled protons.[11]

Hall and Johnson have commented [2a] on the flattening of the ring in the glucal (8) shown by the value of $J_{4,5ax}$, which is smaller than the accepted range (8—12 Hz) for *ax,ax* couplings. In compounds (1)—(3),

TABLE 2

Values of ^2J and ^3J (Hz) for the glycals

	Conformation	$J_{1,2}$	$J_{2,3}$ [a]	$J_{3,4}$ [a]	$J_{4,5ax}$ [a]	$J_{4,5eq}$ [a]	$J_{5ax,5eq}$ [c]	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$ [d]
(1)	$^4H_5$	5·8	5·2, *v,eq'* (*v,ax'*)	2·5, *eq',eq* (*ax',ax*)	1·5, *eq,ax*	(*ax,eq*)		*e*	*e*	*e*
(2)	$^4H_5$	6·0	5·9, *v,eq'*, (*v,ax'*)	3·9, *eq'ax* (*ax',eq*)	10·1, *ax,ax*	(*eq,eq*)		4·9	2·4	−12·5
(3)	$^4H_5$	6·0	4·9, *v,eq'* (*v,ax'*)	4·2, *eq',ax* (*ax',eq*)	9·3, *ax,ax* (*eq,ax*)	3·7, *ax,eq* (*eq,eq*)	−10·6			
(4)	$^4H_5$			4·0, *eq',ax* (*ax'eq*)	7·0, *ax,ax* (*eq,ax*)	2·8, *ax,eq* (*eq,eq*)	−12·0			
(5)	$^4H_5$	6·3	2·5, *v,ax'* (*v,eq'*)	4·6, *ax',eq* (*eq',ax*)	1·8, *eq,ax*	(*ax,eq*)		7·1	5·0	−11·5
(6)	$^4H_5$			4·4, *ax',eq* (*eq',ax*)	1·4, *eq,ax*	(*ax,eq*)		7·3	5·5	−11·6
(8) [b]	$^4H_5$	6·4	3·2, *v,ax'* (*v,eq'*)	6·4, *ax',ax* (*eq',eq*)	6·8, *ax,ax*	(*eq,eq*)		6·3	2·4	−14·5
(9)		6·3	3·7	4·5		5·0		*e*	*e*	*e*
(11)	$^5H_4$			3·0, *eq',eq* (*ax',ax*)	3·0, *eq,ax*	(*ax,eq*)		*e*	*e*	*e*
(12)	$^5H_4$	6·2	4·6, *v,eq'* (*v,ax'*)	2·7, *eq',eq* (*ax',ax*)	2·2, *eq,ax* (*ax,ax*)	3·2, *eq,eq* (*ax,eq*)	− 12·2			

[a] *v* (vinyl), *ax'*, *eq'*, *ax*, *eq*: orientations of coupled protons in the preferred and (in parentheses) alternative half-chair conformation. [b] Ref. 2. [c] Sign determined by INDOR. [d] Where given, the sign was indicated by second-order analysis. [e] Not analysed.

analogous galactal (6) there is a well-resolved $^5J_{1,4}$. All signs were determined relative to a three-bond coupling and since these are positive the absolute signs of four-bond couplings are readily obtained. In compounds (3), (4), and (12) the experiment to determine the sign of $J_{3,5eq}$ also gives the sign of $J_{5ax,5eq}$.

CONFORMATIONAL ANALYSES

The preferred conformations of the glycals are shown in Table 2 as $^4H_5$ and $^5H_4$ [the (D) notation has been omitted]. The two- and three-bond coupling constants are also shown together with the orientations of the coupled protons in the two alternative conformations. The distinction between conformations $^4H_5$ and $^5H_4$ can be made unequivocally on the basis of $J_{3,4}$ and $J_{4,5}$ in all cases except those of the galactals (5) and (6) and the glucal (9), which is clearly in an intermediate conformation. The preferred conformation of the galactal (5) can be inferred primarily from the vinyl-allylic coupling $J_{2,3}$. Such couplings depend on the torsion angle the allylic proton makes with the olefin plane [10] and are smallest when the angle is 90°, so that the smaller values of $J_{2,3}$ indicate a *pseudo*-axial (*ax'*) orientation for H-3. The preference of the galactal (6) for the same conform-

[10] R. J. Abraham, H. Gottschalck, H. Paulsen, and W. A. Thomas, *J. Chem. Soc.*, 1965, 6268.

(11), and (12) $J_{3,4}$ and $J_{4,5}$ are either large (9·3—10·1 Hz) where the protons are *ax',ax* or *ax,ax* in preferred conformation, or small (2·2—3·2 Hz) where the protons *would be ax',ax* or *ax,ax* in the *alternative* conformation. A high degree of conformational purity can therefore be ascribed to these compounds and also probably to the galactal (5) because of the small $J_{2,3}$ value.

TABLE 3

Values of ^4J (Hz) for the glycals

Compound	$J_{1,5}$	$J_{1,3}$	$J_{2,4}$	$J_{3,5ax}$		$J_{3,5eq}$
(1)	*a*		+1·6			
(2)						
(3)		−0·9				+1·3
(4)		−1·6				
(5)	*a*	−1·8	+1·7	+1·1		
(6) [b]	*a*	|1·1|		+1·1		
(8) [c]		−1·3	|0·5|	|0·7|		
(9)		−1·2	+0·9		|1·2|	
(11)		*a*				|1·3|
(12)		*a*	+1·7	|0·5|		+1·7

[a] Small coupling indicated by decoupling. [b] A $^5J_{1,4}$ of 0·4 Hz is observed in this compound. [c] Ref. 2.

The determined signs of the four-bond coupling constants (Table 3) are all positive except in the case of $J_{1,3}$ where a negative π-contribution is known [12] to

[11] M. Anteunis, *Bull. Soc. chim. belges*, 1966, **75**, 413.
[12] M. Barfield, *J. Chem. Phys.*, 1968, **48**, 4463.

dominate. There is qualitative agreement between the observed values of $J_{1,3}$ and the angle dependence expressed by the Garbisch equation [13] in that where $J_{2,3}$ is large $|J_{1,3}|$ is small, but in compound (3) $|J_{1,3}|$ is rather large. Large values of $J_{3,5}$ are confined to *eq',eq* and *ax',ax* orientations of the protons and although on average the *eq',eq* arrangement gives the larger values the difference is not pronounced. The $J_{2,4}$ value is large where H-4 is equatorial and not observed where H-4 is axial, except in the case of the glucal (8) where a small $|J_{2,4}|$ has been reported.[2c] This is extra evidence for the flattening of the ring in this compound and shows that $J_{2,4}$ is a sensitive indicator of conformational change. All three four-bond couplings in the glucal (9) show that it is deformed towards the $^5H_4$ conformation.

DISCUSSION

Ferrier and Sankey [14] rationalised the conformational preferences of 2,3-unsaturated pyranose derivatives by considering the various interactions involved and a similar method can be employed for the D-glycals. The 'allylic effect' will again exert control over the conformational features and in the *O*-acetyl-D-glycals the allylic acetoxy-group will favour the *quasi*-axial configuration by 0·8 kcal mol^{-1} (A). The non-allylic interactions in glycals are a 1,2-*quasi*-equatorial–equatorial interaction between substituents at C(3) and C(4), a 1,2-diequatorial interaction between substituents at C(4) and C(5) and a 1,3-*quasi*-axial–axial interaction between substituents at C(3) and C(5) (B^1, B^2, and C, respectively) and approximate energetic differences (ΔE) for the various interactions can be assessed as shown in Table 4. Also, where there is a substituent at C(2), the

TABLE 4

Non-allylic interactions in *O*-acetyl-D-glycals

Interaction	Substituents	ΔE/kcal mol^{-1}
B^1 and B^2	H,H	0
	H,OAc (CH_2·OAc)	0·1 [a,b]
	OAc,OAc (CH_2·OAc)	0·4 [b,c]
C	H,H	0
	H,OAc (CH_2·OAc)	0·4 [b,d]
	OAc,CH_2·OAc	2·2 [c]

[a] E. Eliel, N. L. Allinger, S. J. Angyal, and G. L. Morrison, 'Conformational Analysis,' Wiley, New York, 1965, p. 357. [b] ΔE will not be affected appreciably by interchanging acetoxy- and acetoxymethyl groups. [c] See ref. 14 and references therein. [d] See ref. *a*, p. 44. Only one interaction is involved, so the free energy difference will be considerably lower than that given in the reference (0·4—1·5 kcal mol^{-1}).

interaction between it and substituents at C(3) (the $A^{1,2}$ effect) [15] must be taken into account. By employing these values the energy gain of the $^4H_5$ conformation over the $^5H_4$ conformation for the *O*-acetyl-D-glycals can be estimated.

Thus with the glucal (8) the unfavourable allylic effect and the unfavourable B^1 and B^2 interactions destabilise the $^4H_5$ conformation, but inversion would introduce a large C interaction and the overall energy gain (ΔG) over the $^5H_4$ conformation is $-0{\cdot}8(A) - 0{\cdot}4(B^1) - 0{\cdot}4(B^2) + 2{\cdot}2(C) = 0{\cdot}6$ kcal mol^{-1}. Similar analysis of the other *O*-acetyl-D-glycals (Table 5) shows

TABLE 5

Conformation preferences of the *O*-acetyl-D-glycals

	Conformation preference		
Compound	Experimental	$^4H_5$ / $^5H_4$	ΔG/kcal mol^{-1}
(1)	$^4H_5$		1·2
(2)	$^4H_5$		0·4
(3)	$^4H_5$		0·4
(5)	$^4H_5$		1·4
(8)	$^4H_5$		0·6
(12)	$^5H_4$		−0·8

that, in agreement with experimental results, only the xylal (12) favours the $^5H_4$ conformation. Examination of the n.m.r. data in the literature shows that all xylals [14,16,17] adopt this conformation, and with the exception of the 2-*C*-nitro-D-galactal (7) [16a] and -D-glucal (10) [16a] (see below) all gulals,[18] allals,[19] arabinals,[16b,20] galactals,[8,21] and glucals [2,19,22] adopt the alternative $^4H_5$ conformation.

With gulals, allals, arabinals, and xylals the introduction of a substituent at C(2) would further stabilise these adopted conformations as the C(3)-substituent in each case is *quasi*-axial. However, with the galactal (5) and the glucal (8) this $A^{1,2}$ effect is destabilising. For the former, inversion will take place with the introduction of an energy factor in excess of 1·4 kcal mol^{-1}; only 0·6 kcal mol^{-1} is required to have a similar effect on the glucal. That the 2-*C*-cyano-D-galactal (6) retains the $^4H_5$ conformation whereas the 2-*C*-nitro-D-galactal (7) adopts the $^5H_4$ conformation indicates that the destabilising energy factor introduced by the C(2)–CN group must be less than 1·4 kcal mol^{-1}, whereas that of the C(2)–NO_2 group is more.

The introduction at C(2) of tri-*O*-acetyl-D-glucal (8) of such substituents as OAc,[23] SCN,[24] and Cl [25] cause further flattening of the ring, as shown by the smaller $J_{3,4}$ and $J_{4,5}$ values. The analogous 2-*C*-cyano-D-glucal cannot be prepared by the method described for other glycals.[4] However, comparison of the data for the glucals (8) and (9) reveals that in (9) a further ring flattening occurs (the 'allylic effect' must therefore

[13] E. W. Garbisch, *J. Amer. Chem. Soc.*, 1964, **86**, 5561.
[14] R. J. Ferrier and G. H. Sankey, *J. Chem. Soc.* (*C*), 1966, 2345.
[15] F. Johnson, *Chem. Rev.*, 1968, **68**, 375.
[16] (*a*) R. U. Lemieux, T. L. Nagabhushan, and I. K. O'Neill, *Canad. J. Chem.*, 1968, **46**, 413; (*b*) K. Bock, I. Lundt, and C. Pedersen, *Acta Chem. Scand.*, 1969, **23**, 2083.
[17] M. Katsuhara, S. Wakahara, and K. Takuyama, *Bull. Chem. Soc. Japan*, 1968, **41**, 1208.
[18] R. U. Lemieux, E. Fraga, and K. A. Watanabe, *Canad. J. Chem.*, 1968, **46**, 91.
[19] (*a*) M. Sharma and R. K. Brown, *Canad. J. Chem.*, 1966, **44**, 2825; (*b*) B. Fraser-Reid, B. J. Carthy, and B. Radatus, *Tetrahedron*, 1972, **28**, 2741; (*c*) R. J. Ferrier and M. M. Ponpipom, *J. Chem. Soc.* (*C*), 1971, 553; (*d*) E. E. Leutzinger, T. Meguro, L. B. Townsend, D. A. Shuman, M. P. Schweizer, C. M. Stewart, and R. K. Robins, *J. Org. Chem.*, 1972, **37**, 3695.
[20] (*a*) N. A. Hughes, *Carbohydrate Res.*, 1972, **25**, 242; (*b*) E. L. Albano, R. L. Tolman, and R. K. Robins, *ibid.*, 1971, **19**, 63.
[21] N. Pravdić and H. G. Fletcher, *Croat. Chem. Acta*, 1969, **41**, 125.
[22] I. Lundt and C. Pedersen, *Acta Chem. Scand.*, 1971, **25**, 2320.
[23] R. J. Ferrier, W. G. Overend, and G. H. Sankey, *J. Chem. Soc.*, 1965, 2830.
[24] K. Igarashi and T. Honma, *J. Org. Chem.*, 1967, **32**, 2521.
[25] J. Adamson and A. B. Foster, *Carbohydrate Res.*, 1969, **10**, 517.

apply to benzyloxy-groups). The 2-*C*-cyano-D-glucal (11), however, inverts to the $^5H_4$ conformation showing that the $A^{1,2}$ strain introduced by the CN group must be approaching 0·6 kcal mol^{-1}.

EXPERIMENTAL

N.m.r. spectra were recorded on Varian HA-100 and XL-100 spectrometers. Iterative computations were performed on an I.B.M. 360 computer using the program UEAITR,[26] and simulated spectra were produced with the XL-100 system using the program SIMEQ (C. W. F. Kort). M.p.s were determined on a hot-stage apparatus. I.r. spectra were measured with a Perkin-Elmer 257 spectrophotometer and mass spectra with an A.E.I. MS9 spectrometer by use of the direct insertion technique.

Except for the two compounds described below all the derivatives investigated in this paper were prepared by standard procedures.[4,7]

[26] R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Magnetic Resonance*, 1970, **3**, 84.

3,4,6-*Tri*-O-*acetyl*-1,5-*anhydro*-2-*deoxy*-D-xylo-*hex*-1-*enitol* (*Tri*-O-*acetyl*-D-*gulal*) (1).—Compound (1) was prepared from D-idose [27] by a modification of Fischer and Zach's method. Work-up as described [4] for similar compounds gave an oil which slowly crystallised. Recrystallisation from ethanol (96%) gave the glycal (1) as needles, m.p. 97—98° (lit.,[6] 97—98°).

3,4,6-*Tri*-O-*acetyl*-1,5-*anhydro*-2-*deoxy*-D-ribo-*hex*-1-*enitol* (*Tri*-O-*acetyl*-D-*allal*) (2).—Compound (2) was prepared from D-allose [28] by a modification of Fischer and Zach's method. Work-up [4] gave an oil which slowly crystallised. Recrystallisation from ether–hexane gave the *glycal* (2) as crystals, m.p. 83—84°, $\nu_{max.}$ ($CHCl_3$) 1750 (CO) and 1645 cm^{-1} (conj. C=C), *m/e* 213 ($M^+ - CH_3{\cdot}CO_2$) (Found: C, 53·2; H, 5·8. $C_{12}H_{16}O_7$ requires C, 52·9; H, 5·9%).

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[27] W. M. zu Reckendorf, *Methods Carbohydrate Chem.*, 1972, **6**, 129.

[28] J. D. Stevens, *Methods Carbohydrate Chem.*, 1972, **6**, 123.