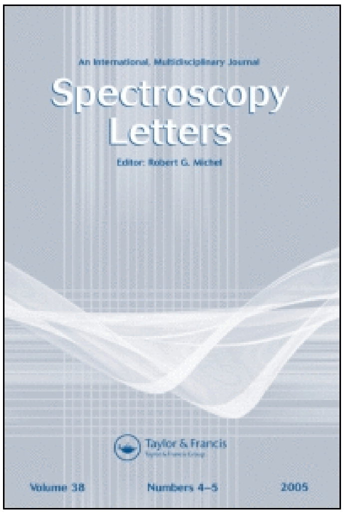

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Conformational Analysis of Some 1,2-0-IsoproIpylidene-α-D-glucogfuranose Derivatives by PMR Spectroscopy[1]

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CONFORMATIONAL ANALYSIS OF SOME I,2-O-ISOPROPYLIDENE-α-D-GLUCOFURANOSE DERIVATIVES BY PMR SPECTROSCOPY[I].

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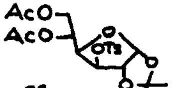
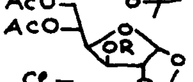
This paper deals with the conformational analysis of some I,2-O-isopropylidene-α-D-glucofuranose derivatives[2], viz. 3-O-toluene-p-sulphonyl-5,6-di-O-acetyl-(I), 3-O-toluene-p-sulphonyl-5-O-acetyl-6-chloro-6-deoxy-(2), 3,5,6-tri-O-acetyl-(3), 3,5-di-O-acetyl-6-chloro-6-deoxy-(4), 3-O-(N-phenyl) carbamoyl-5,6-di-O-acetyl-(5), 3-O-(N-phenyl)carbamoyl-5-O--acetyl-6-chloro-6-deoxy-(6), 3-O-(N-phenyl)carbamoyl-6-O-acetyl-(7) and 6-O-acetyl, 3,5-O-phenyl boronate (8), that are of considerable interest from the point of view of their synthetic utilization as well as the possibility of establishing relationship between PMR parameters, conformation and reactivity of the mentioned class of compounds. Table I shows PMR parameters for compounds I-8 which we have studied, for protons at C-6 and C-5, which were obtained by means of NMR spectrum computation program (the program was developed by one of us A.S.Fridman), and the values of corresponding dihedral and

TABLE I

Calculated Characteristics of Protons at C-5 and C-6 of I,2-O-Isopropylidene-α-D-Glucofuranose Derivatives

	Compound	Chemical Shifts, δ ppm H-6	H'-6	H-5	Coupling Constants, Hz $J_{6,6'}$	$J_{6,5}$	$J_{6',5}$	Dihedral Angles $\varnothing_I(6,5)$	$\varnothing_2(6',5)$	Projected Angles, θ
I		4.075	4.585	5.067	-I2.32	4.27	2.05	55	66	I2I
2		3.724	3.873	4.923	-I2.38	2.77	2.98	62	6I	I23
3		3.964	4.422	5.029	-I2.20	5.79	2.II	52	67	II9
4		3.7I9	3.8I9	5.I59	-I2.66	4.95	2.7I	55	64	II9
5		4.I04	4.698	5.263	-II.88	5.77	2.36	52	66	II8
6		3.720	3.850	5.254	-I2.3I	4.93	2.66	55	65	I20
7		4.I66	4.484	3.998	-II.70	7.I0	2.35	47	66	II3
8		4.III	4.277	4.485	-II.84	3.40	4.I9	6I	58	II9

R = -CONHPh

projected angles. Table 2 furnishes PMR data on compounds *I*-*8* for the protons at C-I, C-2, C-3 and C-4 found from among appropriate spectra of the first order[3].

Conformation of Substituets at C_5- C_6. On the basis of the data in Table I one can see that the most populated conformation of proton H-5 with respect to protons H-6 and H'-6 (H-6 is the methylene proton at higher field; H'-6 is that at lower field; the signals of protons H-6 and H'-6 cannot be assigned individually) in compounds *I*-*6*, is the *gauche*-*gauche* conformation (Fig.I); therefore, the sum of dihedral angles ϕ_I and ϕ_2 must be ~I20°; i.e. it must be equal to projected angle θ. However, the sum of dihedral angles obtained from the Karplus equation[4] for compounds *I* and *2* and *3*-*6* noticeably differ from I20°, being II2 to II5° and I02 to I04°,respectively. An unexpected fact should be emphasized here that projected angle θ of compounds *I* and *2* considerably differs from that of compounds *3*-*6*, which is most likely to be explained by an additional factor at 3-*O*-toluene-p-sulphonyl group that makes a material contribution to constant *A* of Karplus equation[4] than by a greater population of the *gauche*-*gauche* conformation of these derivatives. We have elaborated a kind of Karplus equation (similar to the information of Slessor and Tracey[5]) that can be used for compounds *I* and *2* ($J = \underline{A}\cos^2\phi$ - $- 0.28$; $0 \leqslant \phi \leqslant 90°$; $J = \underline{B}\cos^2\phi - 0.28$; $90° \leqslant \phi \leqslant I80°$; $\underline{A} = I3.9$; $\underline{A} = 0.9\underline{B}$) and compounds *3*-*6* (A = I6.0).The values of ϕ and θ are given in Table I.

Compound *7* has been chosen as a model,wherein along with the *gauche*-*gauche* conformation of protons at C-5 and C-6 one could expect the *gauche*-*anti* conformation to be populated owing to a fluctuating intramolecular hydrogen bond of the C_5-OH group with the C_6-OAc grouping (Fig.2). The IR spectrum analysis[6] of compound 7 (its data are given in Table 3) has shown two bands at 3470 and 3350 cm^{-I} that correspond to νOH combined with a hydrogen bond. Alonside with this the νC=O band of the second group is shifted till I735 cm^{-I},which testifies to that this group participates in the origination of an intramolecular hydrogen bond. Analogous shift, to a lesser degree though, reveals the νC=O band of the carbonylate group. Thus, we can assume that there exist two types of intramolecular hydrogen bond; (i) between OH and acetyl groups (νOH 3350 cm^{-I}) and (ii) between OH group and 3-O-carbamoyl (N-phenyl) group at C-3 (νOH 3470 cm^{-I}), the former hydrogen bond can give rise to the population of both *gauche*-*gauche* and *gauche*-*anti* conformations. In fact, the value of projected angle θ, found from compound 7, noticeably differs from I20°,which testifies to a certain population of the *gauche*-*anti* conformation.

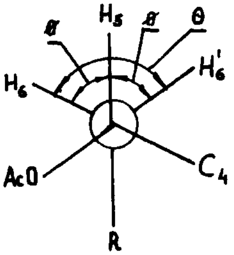


Fig.I

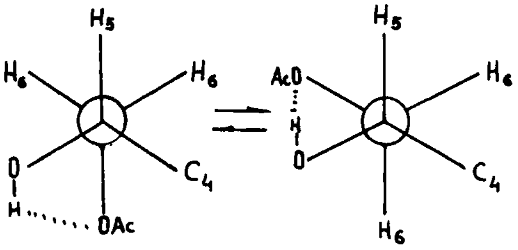


Fig.2

Compound 8 has also been chosen as a model. The value of the projected angle, found with the help of the aforementioned formulas (A=I6.0), perfectly coincides with the presumable I20°.

6-*O*-acetyl group in all 5,6-di-*O*-acetyl derivatives exerts a non-equivalent influence (See also[7]) on the protons at C-6, the difference ratio between the values of chemical shifts, as compared with 6-chloro-6deoxy derivatives, being within the following range

$$\frac{(H\text{-}6_{OAc} - H\text{-}6_{Cl})}{(H'\text{-}6_{OAc} - H'\text{-}6_{Cl})} = 0.4I \div 0.49$$

Conformation of Substituents at C_4-C_5. The data analysis of Table 2 ($J_{4,5}$) reveals that the *anti* conformation is the most populated conformation of protons at C-4 - C-5 for compounds *I*-*7*. Considerable variations of values $J_{4,5}$ noticed in compounds with the 3-*O*-(N-phenyl)carbamoyl group perfectly match the IR spectroscopy data (See Table 3): (i) the intensive νN-H band at 3370 cm^{-I} points to a possible existence of intramolecular hydrogen bond with the acetyl group at C-5, which accords with the bend at I740 cm^{-I} on the carbonyl groups band. It is probable that this intramolecular hydrogen bond causes changes in the side chain conformation and, as a result, decreases the coupling constant; (ii) in the case of 6-chloro-6-deoxy of compound *6*, the IR spectrum shows only weak H-bonded νN-H band though there are no obvious reasons for this phenomenon; absence of an intramolecular hydrogen bond leads to conformation H-5 - H-4 *anti* that in most respects is similar to compouns *2* and *4* or a change in the furanose ring conformation makes origination of the intramolecular hydrogen bond less possible to occur and results in the same effect; (iii) in the case of compound *7*, the IR spectrum shows only a νN-H band not combined with a hydrogen bond, whereas there are two OH bands and the one at 3470 cm^{-I} may correspond to the band combined through a hydrogen bond with the oxygen functions of 3-O-(N-phenyl)carbamoyl group (I758-I745 cm^{-I}) which leads to an effect similar to compound 5.

Table 2

Characteristics of Protons at C-I, C-2, C-3 and C-4 of I,2-O--Isopropylidene-α-D-Glucofuranose Derivatives[3].

Compound	Chemical Shift,		ppm		Coupling Constant,			Hz
	H-I	H-2	H-3	H-4	$J_{I,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
1	5.88	4.74	5.0I	4.46	3.5	<0.4	2.5	9.5
2	5.78	4.64	4.98	4.50	3.6	<0.4	2.9	9.25
3	5.78	4.35	5.23	4.23	3.5	<0.4	2.5	9.5
4	5.85	4.44	5.29	4.42	3.5	<0.4	3.0	9.25
5	5.92	4.65	5.26	4.46	4.0	<0.4	2.75	8.0
6	5.89	4.66	5.24	4.50	3.5	0.75	3.0	9.75
7	5.97	4.68	5.37	4.28	4.0	<0.4	2.75	8.75
8	5.78	4.63	4.45	4.30	3.75	0.75	2.5	0.75

Table 3

IR Spectroscopy Data[6] on Compounds 5, 6 and 7.

Compound	Adsorption Bands, cm^{-I}			Ph	Intensity Ratio
	νC=O	νO-H	νN-H		
5	I758 (shoulder at I740)		3450 (sharp, free) 3370 (sharp, H-bonded)	I605	$\frac{NH_{free}}{NH_{bond}} = \frac{I}{3}$
6	I758		3450 (sharp) 3370 (sharp)	I605	$\frac{NH_{free}}{NH_{bond}} = \frac{3}{I}$
7	I735(Ac) I745 (CO-NH)	3470 (broad) 3350 (broad)	3450 (sharp)	I605	$\frac{OH_{3470}}{OH_{3350}} = \frac{I}{I}$

Conformation of the Furanose Ring. Data on the coupling constants of protons at C-I, C-2, C-3 and C-4 (see Table 2) give every proof that conformations $_4V \leftrightarrow {}^3T_4 \leftrightarrow {}^3V \leftrightarrow {}^3T_2$ of the pseudorotational scheme[8] are obviously populated for the furanose ring; they show that the furanose ring, when fused with the I,2-O-isopropylidene group, is of considerable mobility. It does not as yet seem possible, however, to make more definite conclusions where specific shares of each separate conformation are concerned. It is most likely that considerable results in the conformational analysis of carbohydrate furanose derivatives will be attained through compputer analysis of PMR parameters[9], so as to find the most populated segment of the cycle of pseudorotation for each separate compound or group of compounds conformationally alike and calculate the specific share of each conformation of this segment in the time-averaged result observed as PMR spectrum.

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REFERENCES

I. Preliminary results of the present work were reported at the 3rd ALL-Union Conference on Dynamyc Stereochemistry and Conformational Analysis held in Odessa, June I973.

2. Compounds 2,4 and 6 have been synthsized by means of the detected by us new reaction of acetylsalicyloyl chloride with diols (A.A.Akhrem, V.V.Zharkov, G.V.Zaitseva and I.A.Mikhailopulo, Tetrahedron Letters, I973, I475). The results (A.A.Akhrem, G.V.Zaitseva,and I.A.Mikhailopulo, Carbohydrate Res. in press) as well as the synthesis and

structure proof of the compounds **I**,**3**,**5**,**7** and **8** will be reported on in a separate paper.

3. PMR spectra for I5% solutions of compounds in $CDCl_3$ have been recorded on the Varian HA-IOO Spectrometer; HMDS has been used as internal standard.
4. M.Karplus, *J.Chem.Phys.* **I30**, II (I959).
5. K.N.Slessor and A.S.Tracey, *Can.J.Chem.* **49**, 2874 (I97I).
6. IR spectra have been recorded on the UR-20 spectrophotometer (Carl Zeiss, DDR) in diluted solutions of CCl_4 and $CHCl_3$ free of alcohol.
7. B.Coxon, *Carbohydrate Res.* **8**, I25 (I968).
8. L.D.Hall, P.R.Steiner and C.Pedersen, *Can.J.Chem.* **48**, II55 (I970).
9. L.D.Hall, S.A.Black, K.N.Slessor and A.S.Tracey, *Can.J.Chem.* **50**, I9I2 (I972).

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