¹H-NMR SPECTRA AND THE CONFORMATION OF 1,6 : 2,3-
AND 1,6 : 3,4-DIANHYDRO-β-D-HEXOPYRANOSES
AND THEIR DERIVATIVES

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The ¹H-NMR spectra of 1,6 : 2,3- and 1,6 : 3,4-dianhydro-β-D-hexopyranoses and their acetyl-, trichloroacetylcarbamoyl- and 2- or 4-deoxy derivatives were measured in hexadeuteriodimethyl sulfoxide or deuteriochloroform. In these solvents dianhydro derivatives assume the half-chair conformations $^5H_0$ or $^1H_0$ which are not distinctly affected by the presence of substituents. The effects of substituents on the chemical shifts and the adjusted relation for the dependence of the vicinal coupling constants on the torsion angle are discussed from the point of view of conformation and the interactions of the oxirane ring with the oxygen $O_{(5)}$ and $O_{(6)}$ of the 1,6-anhydropyranose skeleton. Intramolecular hydrogen bonds in free dianhydrohexopyranoses were measured and identified in tetrachloromethane solution.

In our preceding paper[1] we discussed the ¹H-NMR spectra of 1,6-anhydro-β-D-hexopyranoses and their conformations in dependence on the configurations of the substituents in positions $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$. The oxirane ring in 1,6 : 2,3- and 1,6 : 3,4-dianhydro-β-D-hexopyranoses *I—VIII* leads to an almost complete restriction of the flexibility of the 6,8-dioxabicyclo [3.2.1]-octane system and to a planarization of the pyranose ring of these compounds. The fixation of four carbon atoms in a plane ($C_{(1)}$ to $C_{(4)}$ in 1,6 : 2,3-dianhydro- and $C_{(2)}$ to $C_{(5)}$ in 1,6 : 3,4-dianhydro derivatives) enforces flattened half-chair conformations of the type $^5H_0$ or $^1H_0$, respectively, or also (as suggested by the models) the envelope conformation E_0.

The ¹H-NMR data of several dianhydrohexopyranoses and their deoxy derivatives can be found in the literature[2⁻⁷], but these substances have not yet been surveyed exhaustively; as regards the ¹³C-NMR spectra, see ref.[8]. In this paper we want to discuss the ¹H-NMR parameters of the complete series of these substances in detail from the point of view of the effect of the position and the orientation of the substituents on the chemical shifts of protons, and to obtain, as far as possible, detailed information on their conformation.

The ¹H-NMR spectra of 1,6 : 2,3- and 1,6 : 3,4-dianhydro-β-D-hexopyranoses *Ia—VIIIa*, their acetates *Ib—VIIIb*, trichloroacetylcarbamoyl derivatives *Ic—VIIIc*

and 2- and 4-deoxy derivatives $IX - XII$ were measured in deuteriochloroform, and their parameters are given in Table I−IV. Free dianhydro-β-D-hexopyranoses Ia to $VIIIa$ were also measured in hexadeuteriodimethyl sulfoxide (Table V).

Chemical Shifts

The proton H-1 appearing always at the lowest field $(\delta = 5\cdot20 - 5\cdot76)$ can be easily assigned in the whole series of the dianhydro derivatives $I - VIII$ studied. In hydroxy derivatives $Ia - VIIIa$ and 2- or 4-deoxy derivatives the proton H-5 follows in a somewhat higher field $(\delta = 4\cdot40 - 4\cdot81)$. In the case of acetates $Ib - VIIIb$ and trichloroace-
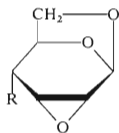
TABLE I

^{1}H-NMR Parameters of 1,6 : 2,3-Dianhydro- and 1,6 : 3,4-Dianhydro-β-D-hexapyranoses in Deuteriochloroform

Compound	Chemical shifts, δ							
	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	OH[b]
Ia	5·60	3·13	3·39	3·62[a]	4·40	3·66	3·89	3·02
IIa	5·59	3·06[a]	3·06[a]	4·26[a]	4·41	4·19	3·80	2·49
$IIIa$	5·69	3·45	3·14	3·91	4·42	3·78	3·74	2·55
IVa	5·65	3·61[a]	3·34	4·24	4·41	4·01	3·60[a]	2·41
Va	5·20	3·59	3·34	3·22	4·69	3·96	3·78	2·59
VIa	5·32	3·83[a]	3·00	3·13	4·73	4·05	3·87[a]	2·18
$VIIa$	5·23	3·79	3·13	3·60[a]	4·81	4·01	3·53[a]	2·41
$VIIIa$	5·28	3·77[a]	3·32	3·77[a]	4·79	3·95	3·53	2·41

	Coupling constants, Hz						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6en}$	$J_{5,6ex}$	$J_{6en,6ex}$
Ia	1·3	4·1	4·7	0·8	2·3	6·8	−8·3
IIa	1·0[c]	4·0[c]	0·0[c]	5·3	1·9	6·4	−8·4
$IIIa$	3·1	3·8	0·8	1·2	2·3	7·0	−7·4
IVa	2·9	4·1	3·1	6·4	1·5	5·9	−7·7
Va	0·7	4·5	4·1	1·7	0·6	4·6	−7·5
VIa	3·1	0·0	4·0	1·6	0·6	4·7	−7·5
$VIIa$	0·7	0·3	4·0	4·8	0·6	5·0	−6·8
$VIIIa$	3·6	3·6	4·3	4·5	0·6	4·8	−6·8

[a] Partial overlapping of the signals; [b] broadened singlet; $J_{OH,H}$ was not observed. [c] J values were obtained after addition of Eu(FOD)$_3$.

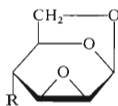tylcarbamoyl derivatives $Ic - VIIIc$ this proton is preceded by the proton on the carbon atom carrying the O-acetyl group $(\delta = 4 \cdot 64 - 5 \cdot 36)$. The signals follow of the H-6en proton $(\delta = 3 \cdot 66 - 4 \cdot 19)$ which appear — with the exception of derivative I — always in a lower field than the signals of H-6en proton of the same compound $(\delta = 3 \cdot 53 - 3 \cdot 98)$. In hydroxy derivatives $Ia - VIIIa$ the proton on the carbon atom carrying the hydroxy group also appears in this region $(\delta = 3 \cdot 59 - 4 \cdot 26)$. In the case of dianhydro derivatives the protons of the oxirane ring appear in the highest field usually $(\delta = 3 \cdot 00 - 3 \cdot 85)$, with the exception of derivatives VII and $VIII$, where at higher field the H-6ex proton absorbs, as well as in the case of deoxy derivatives $IX - XII$ where, of course, the signals of both protons of the ---CH$_2$--- group lie at a substantially higher field $(\delta = 1 \cdot 71 - 2 \cdot 46)$.
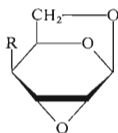
ᴅ-*allo*	ᴅ-*gulo*	ᴅ-*manno*	ᴅ-*talo*
Ia, R = OH	IIa, R = OH	$IIIa$, R = OH	IVa, R = OH
Ib, R = OAc	IIb, R = OAc	$IIIb$, R = OAc	IVb, R = OAc
Ic, R = OTAC	IIc, R = OTAC	$IIIc$, R = OTAC	IVc, R = OTAC
IX; R = H		X, R = H	

ᴅ-*allo*	ᴅ-*altro*	ᴅ-*galacto*	ᴅ-*talo*
Va, R = OH	VIa, R = OH	$VIIa$, R = OH	$VIIIa$, R = OH
Vb, R = OAc	VIb, R = OAc	$VIIb$, R = OAc	$VIIIb$, R = OAc
Vc, R = OTAC	VIc, R = OTAC	$VIIc$, R = OTAC	$VIIIc$, R = OTAC
XI, R = H		XII, R = H	
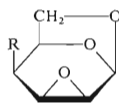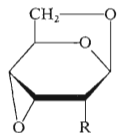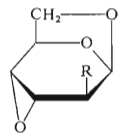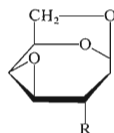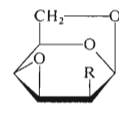
TAC = trichloroacetylcarbamoyl.

   The comparison of the chemical shifts of the protons of hydroxy derivatives $Ia - VIIIa$, acetates $Ib - VIIIb$ and trichloroacetylcarbamoyl derivatives $Ic - VIIIc$ with corresponding 2- and 4-deoxy derivatives $IX - XII$ permits the expression of

the effect of the substituents in the positions 2 and 4 on the chemical shifts of individual protons of the tricyclic skeleton. The average values of these effects are given in Table VI. The distinct deshielding effect $(0.16-0.37$ ppm) of the substituents in the positions 2 and/or 4 on both protons of the neighbouring oxirane ring is interesting, if it is *cis*-oriented with respect to the substituent OR. The distinct transfer of the effect of the substituent up to the position $C_{(\gamma)}$ is evidently a consequence of the easy polarizability of the C—C bond of the oxirane ring due to its interaction with the neighbouring *cis*-oriented OR substituent, similarly as in the case of C=C bonds. When the orientation of the OR substituent is *trans* with respect to the oxirane ring, the affecting of the oxirane protons is small $(0.09$ to 0.06 ppm). The deshielding

TABLE II

^{1}H-NMR Parameters of Acetates of 1,6 : 2,3-Dianhydro- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses in Deuteriochloroform

Compound	Chemical shifts, δ							
	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	OAc
Ib	5·65	3·10	3·45	4·71	4·46	3·77	3·91	2·20
IIb	5·60	3·05[a]	3·05[a]	5·15	4·53	4·07	3·80	2·12
IIIb	5·72	3·47	3·13	4·96	4·44	3·80	3·74	2·17
IVb	5·67	3·58[a]	3·39	5·23	4·48	4·04	3·62[a]	2·15
Vb	5·27	4·64	3·42	3·20	4·75	4·00	3·80	2·18
VIb	5·44	4·84	3·01	3·14	4·74	4·12	3·88	2·15
VIIb	5·22	4·82[a]	3·10	3·63	4·86[a]	4·02	3·53	2·15
VIIIb	5·41	4·92	3·41	3·76	4·82	4·08	3·59	2·20

Compound	Coupling constants, Hz						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6en}$	$J_{5,6ex}$	$J_{6en,6ex}$
Ib	1·3	4·1	4·8	0·8	2·0	7·0	−8·4
IIb	0·7[b]	3·7[b]	0·0[b]	5·2	1·9	6·5	−8·4
IIIb	3·2	3·8	0·7	1·1	1·6	7·3	−7·8
IVb	2·9	4·1	3·1	6·2	1·6	6·2	−7·6
Vb	0·8	4·5	4·1	1·7	0·5	4·6	−7·5
VIb	2·9	0·0	4·0	1·4	0·6	4·5	−7·6
VIIb	0·7	0·4	4·1	5·0	0·6	5·0	−6·9
VIIIb	3·5	3·6	4·5	4·5	0·3	4·8	−6·9

[a] Partial overlapping of the signals; [b] J values were determined from the spectrum after addition of Eu(FOD)$_3$.

effect of the 4β-OR substituents* on H-6en (0·34–0·40 ppm) is also characteristic. Evidently the van der Waals contribution participates decisively in this effect.

The investigated series of isomeric dianhydro derivatives also permit the expression of the effect of the change in orientation of the substituent in a given position as a difference in the shifts of protons in derivatives differing merely by the configuration of the given substituent. The average values of these effects for OH, OCOCH$_3$, OCONHCOCCl$_3$ and epoxy groups are listed in Table VII. The values for the effect

TABLE III
^{1}H-NMR Parameters of Trichloroacetylcarbamoyl Derivatives of 1,6 : 2,3-Dianhydro- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses in Deuteriochloroform

Compound	Chemical shifts, δ							
	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	NH[b]
Ic	5·70	3·18	3·54	4·86	4·58	3·84	3·98	9·00
IIc	5·63	3·08	3·18	5·26	4·63	4·16	3·87	8·62
IIIc	5·76	3·53	3·24	5·06	4·58	3·85	3·79	8·75
IVc	5·72	3·67	3·48	5·36	4·62	4·07	3·69[a]	8·70
Vc	5·36	4·77[a]	3·49	3·28	4·82[a]	4·04	3·82	8·88
VIc	5·53	4·93	3·10	3·20	4·79	4·14	3·90	8·63
VIIc	5·34	4·90[a]	3·23	3·69	4·91[a]	4·04	3·57	8·75
VIIIc	5·50	5·03	3·49	3·84	4·89	4·05	3·63	8·88

	Coupling constants, Hz						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6en}$	$J_{5,6ex}$	$J_{6en,6ex}$
Ic	1·2	4·0	4·8	0·7	2·1	6·9	−8·6
IIc	1·1	3·9	0·0	5·2	1·9	6·4	−8·7
IIIc	3·1	3·8	0·8	1·2	1·4	7·5	−7·8
IVc	2·8	4·1	3·0	6·2	1·5	5·9	−7·7
Vc	0·8	4·5	4·1	1·7	0·5	4·6	−7·6
VIc	2·8	0·0	4·0	1·6	0·6	4·7	−7·5
VIIc	0·7	0·3	4·0	4·8	0·6	5·0	−6·8
VIIIc	3·5	3·6	4·5	4·5	0·3	4·8	−6·9

[a] Partial overlapping of the signals; [b] broadened singlet.

* For the indication of the configuration in positions 2, 3 and 4 we use in this paper the symbols α and β: the symbol β for the substituent in the *endo* position (*cis* with respect to the 1,6-anhydro bridge) and the symbol α for the substituent in the position *exo* (*trans* to 1,6-anhydro bridge).

TABLE IV

1H-NMR Parameters of 4-Deoxy-1,6 : 2,3-Dianhydro- and 2-Deoxy-1,6 : 3,4-Dianhydro-β-D-hexopyranoses in Deuteriochloroform

Compound	Chemical shifts, δ								
	H-1	H-2α	H-2β	H-3	H-4α	H-4β	H-5	H-6en	H-6ex
IX	5·58	—	2·98	3·16	2·46	1·71	4·41	3·76	3·91
X	5·68	3·36	—	3·13	2·22	1·98	4·43	3·67[a]	3·67[a]
XI	5·40	2·18	1·88	3·09[a]	—	3·09[a]	4·68	4·07	3·79
XII	5·41	1·91	2·06	3·14	3·57[a]	—	4·81	4·04	3·52[a]

Compound	Coupling constants, Hz												
	$J_{1,2\alpha}$	$J_{1,2\beta}$	$J_{2\alpha,3}$	$J_{2\beta,3}$	$J_{3,4\alpha}$	$J_{3,4\beta}$	$J_{4\alpha,5}$	$J_{4\beta,5}$	$J_{5,6en}$	$J_{5,6ex}$	$J_{2,2}$	$J_{4,4}$	$J_{6,6}$
IX	—	1·2	—	4·1	0·3	5·1	4·9	0·7	1·8	6·0	—	−15·3	−7·4
X	3·1	—	3·9	—	3·0	0·8	5·4	1·0	b	b	—	−15·1	b
XI	2·8	0·8	0·6	b	—	b	—	1·7	0·5	4·4	−15·3	—	−7·2
XII	3·2	0·5	3·2	0·8	4·2	—	4·9	—	0·5	4·9	−15·3	—	−6·4

[a] Partial overlapping; [b] J values were not determined.

of the orientation of the epoxy-group also depend on the presence and the configuration of the neighbouring OR group.

Acylation with Trichloroacetyl Isocyanate

Primary, secondary and the majority of tertiary alcohols react with trichloroacetyl isocyanate (TAI) at room temperature within several minutes under formation of trichloroacetylcarbamoyl derivatives (TAC), affording a signal of the NH proton $(\delta = 8 - 10)$ easily detectable in the ^{1}H-NMR spectra and inducing characteristic acylation downfield shifts of protons on $C_{(\alpha)}$ (prim-alcohols 0·5 − 0·9 ppm, sec-alcohols 0·9 − 1·5 ppm)[9]. For a survey see[10].

TABLE V

^{1}H-NMR Parameters of 1,6 : 2,3-Dianhydro- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses in Hexadeuteriodimethyl Sulfoxide

Compound	Chemical shifts, δ							
	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	OH
Ia	5·54	3·03	3·25	3·61^a	4·24	3·61^a	3·72	5·08
IIa	5·51	2·95^a	2·92^a	3·98^a	4·29	4·03^a	3·63	5·57
IIIa	5·65	3·41	2·96	3·76	4·29	3·43^a	3·43^a	5·49
IVa	5·63	3·52	3·17	4·01	4·24	3·87	3·39	5·40
Va	5·03	3·43	3·16^a	3·23^a	4·69	3·89	3·58	4·98
VIa	5·15	3·59	2·82	3·17	4·67	3·99	3·69	5·23
VIIa	5·04	3·51	2·96	3·60	4·86	4·03	3·34	5·42
VIIIa	5·13	3·65^a	3·09	3·73^a	4·84	3·79^a	3·39	4·83

Compound	Coupling constants, Hz							
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6en}$	$J_{5,6ex}$	$J_{6en,6ex}$	$J_{OH,H}$
Ia	1·3	4·0	4·6	0·7	2·4	6·8	−7·8	6·5
IIa	0·9	3·9	0·0	4·8	1·9	6·4	−7·7	4·7
IIIa	3·2	3·8	0·6	1·1	^{b}	^{b}	^{b}	5·5
IVa	2·9	4·0	3·0	6·0	1·6	5·9	−6·9	5·5
Va	0·8	4·2	4·1	1·1	0·6	4·4	−7·2	5·5
VIa	2·8	0·0	4·0	1·5	0·7	4·3	−7·3	7·1
VIIa	0·7	0·3	4·1	4·8	0·6	4·9	−6·4	3·5
VIIIa	3·6	3·3	4·4	4·5	0·4	4·8	−6·3	8·5

^{a} Partial overlapping of the signals; ^{b} The J value could not be determined.

The studied series of isomeric dianhydro-β-D-hexopyranoses $Ia — VIIIa$ represents a group of rigid monohydroxy derivatives with well defined spacial arrangement, suitable for a detailed study of the effect of TAI acylations. The ^{1}H-NMR data of acetates $Ib — VIIIb$ also permit a comparison of the effect of acetylation and TAI-acylation. The acetylation shifts of the protons of eight isomeric dianhydro-β-D-hexo-pyranoses, defined as the difference of the shift of a given proton in the acetate and in the hydroxy derivative, are listed in Table VIII. The acetylation downfield shift of $C_{(\alpha)}$—H attains the values 0·89 up to 1·15 ppm, while for the protons on more remote carbons these values are much lower, non-characteristic, and occasionally also weakly negative (0·13 to −0·12 ppm). The highest negative value (−0·12 ppm) was found for H-6en in *gulo*-derivative II and it is evidently caused by the decrease of the van der Waals deshielding effect due to 4β-acylation (distance $O_{(4)}\cdots$H-en on a model is 0·22 nm).

TABLE VI

Effects of Substituents in Positions 2 and 4 on the Chemical Shifts of Protons in 1,6 : 2,3- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses in Deuteriochloroform

Defined as the difference of chemical shifts in the substituted compound (R = OH, OAc, OTAC) and the corresponding deoxy derivative (R = H). The values given in the Table are the arithmetical mean of two (in the case of H-1, H-5, H-6en, H-6ex) or four (in the case of H-2, H-3, H-4) values of the differences defined in this manner.

Substituent R	H-1	H-2, H-3, H-4 R—CH—CH—CH \\O/			H-5	H-6en	H-6ex
2α-OH	−0·19	—	—	—	0·00	−0·07	0·00
2β-OH	−0·10	1·87^a	0·19^a	0·18^a	0·01	−0·05	0·04
4α-OH	0·01	1·78^b	−0·05^b	0·06^b	−0·01	−0·10	0·02
4β-OH	−0·01	—	—	—	−0·01	0·38	−0·09
2α-OAc	−0·16	—	—	—	0·06	−0·04	0·01
2β-OAc	0·02	2·94^a	0·29^a	0·16^a	0·03	0·04	0·08
4α-OAc	0·05	2·77^b	−0·06^b	0·07^b	0·03	0·07	0·03
4β-OAc	0·00	—	—	—	0·08	0·34	−0·08
2α-OTAC	−0·05	—	—	—	0·12	−0·01	0·04
2β-OTAC	0·11	3·07^a	0·37^a	0·24^a	0·09	0·04	0·11
4α-OTAC	0·10	2·87^b	0·06^b	0·09^b	0·16	0·13	0·09
4β-OTAC	0·04	—	—	—	0·20	0·40	−0·01

^{a} For the epoxide *cis*-oriented to the substituent R, without regard to whether it is in position 2 or 4; ^{b} for the epoxide *trans*-oriented to the substituent R, without regard to whether it is in position 2 or 4.

TAI-Acylations of dianhydro-β-D-hexopyranoses $Ia - VIIIa$ take place easily and under the conditions used (see Experimental) they are terminated before the ^{1}H-NMR spectrum can be recorded. The ^{1}H-NMR parameters of trichloroacetylcarbamoyl derivatives $Ic - VIIIc$ are given in Table III and the TAI-acylation shifts, defined as the difference of the shift of a given proton in trichloroacetylcarbamoyl derivative and in hydroxy derivative, are listed in Table IX. The shifts induced by TAI are largest for $C_{(\alpha)}$—H (within the 1·00 to 1·24 ppm range), much smaller for $C_{(\beta)}$—H (0·10 to 0·22 ppm), and still smaller for other protons $C_{(\gamma)}$ and $C_{(\delta)}$—H (≤ 0.09 ppm). The only case of a weak upfield shift (-0.03 ppm) was again observed for H-6en

TABLE VII

Effect of Orientation of the Substituents R in Positions 2, 3 and 4 on the Chemical Shifts of Protons in 1,6 : 2,3- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses

Defined as the difference of chemical shifts in derivatives with a β-oriented substituent and an α-oriented substituent. In the Table arithmetical means of the values determined in this manner are given.

Substituent	H-1	H-2, H-3, H-4 R—CH—CH—CH \O/		H-5	H-6en	H-6ex
2-OH	0·08	a	−0·34^b −0·08^b	0·01	0·01	0·04
4-OH	−0·02	a	0·20^c 0·16^c	0·00	0·38	−0·11
2-OAc	0·18	a	−0·40^b −0·05^b	−0·02	0·09	0·07
4-OAc	−0·05	a	0·28^c 0·12^c	0·05	0·27	−0·11
2-OTAC	0·16	a	−0·37^b −0·09^b	−0·02	0·05	0·07
4-OTAC	−0·05	a	0·25^c 0·14^c	0·04	0·27	−0·10
2,3-epoxy^d	0·07	0·25	a a	0·00	0·05	−0·17
2,3-epoxy^e	0·07	0·05	a a	−0·02	−0·10	−0·19
2,3-epoxy^f	0·10	0·27(β) −0·24(α)	a a	0·02	−0·09	−0·14
3,4-epoxy^d	−0·01	0·17	a a	0·11	0·02	−0·26
3,4-epoxy^e	−0·03	0·04	a a	0·08	−0·08	−0·30
3,4-epoxy^f	0·01	0·18(β) −0·27(α)	a a	0·13	−0·03	−0·28

^{a} When the orientation of the substituent is changed, the orientation (configuration) of these protons also changes and therefore the effect of the substituent cannot be expressed for them in this manner; ^{b} the values for 2α,3α-epoxy- and 3α,4α-epoxy derivatives, without regard to the position of R (2 or 4); ^{c} the values for 2β,3β-epoxy and 3β,4β-epoxy derivatives, without regard to the position of R (2 or 4); ^{d} the values for 4α-R or 2α-R derivatives (R = OH, OAc, OTAC); ^{e} the values for 4β-R or 2β-R derivatives (R = OH, OAc, OTAC); ^{f} the values for 4-deoxy or 2-deoxy derivatives (R = H); the configurations of the protons $C_{(4)}$—H$_2$ or $C_{(2)}$—H$_2$ are given in brackets.

in *gulo*-derivative *II*. A comparison of the acetylation and the TAI-acylation shifts of all 56 protons of dianhydro derivatives *Ia* — *VIIIa* leads to the conclusion that the TAI-acylation shifts are generally higher (more positive), actually averagely by 0·11 ppm for $C_{(\alpha)}$—H, 0·10 ppm for $C_{(\beta)}$—H and 0·05 ppm for $C_{(\gamma)}$ and $C_{(\delta)}$—H. This is evidently due to the stronger inductive effect of the trichloroacetylcarbamoyl group. Hence, the *in situ* acylation with TAI permits an easy obtaining of acylation effects which are more distinct and more characteristic than in classical acetylation.

TABLE VIII

Acylation Shifts in Acetates of 1,6 : 2,3-Dianhydro- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses

Defined as the difference of chemical shifts of protons in the acetate and the hydroxy derivative; measured in deuteriochloroform.

Compounds	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex
Ib — Ia	0·05	−0·03	0·06	1·09	0·06	0·11	0·02
IIb — IIa	0·01	−0·01	−0·01	0·89	0·12	−0·12	0·00
IIIb — IIIa	0·03	0·02	−0·01	1·05	0·02	0·02	0·00
IVb — IVa	0·02	−0·03	0·05	0·99	0·07	0·03	0·02
Vb — Va	0·07	1·05	0·08	−0·02	0·07	0·04	0·02
VIb — VIa	0·12	1·01	0·01	0·01	0·01	0·07	0·01
VIIb — VIIa	−0·01	1·03	−0·03	0·03	0·05	0·01	0·00
VIIIb — VIIIa	0·13	1·15	0·09	−0·01	0·03	0·13	0·06

TABLE IX

Acylation Shifts of Protons in Trichloroacetylcarbamoyl Derivatives of 1,6 : 2,3- and 1,6 : 3,4--Dianhydro-β-D-hexopyranoses

Defined as the difference in chemical shifts after addition of trichloroacetyl isocyanate and before it; measured in deuteriochloroform.

Compounds	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex
Ic — Ia	0·10	0·05	0·15	1·24	0·18	0·18	0·09
IIc — IIa	0·04	0·02	0·12	1·00	0·22	−0·03	0·07
IIIc — IIIa	0·07	0·08	0·10	1·15	0·16	0·07	0·05
IVc — IVa	0·07	0·06	0·14	1·12	0·21	0·06	0·09
Vc — Va	0·16	1·18	0·15	0·06	0·13	0·08	0·04
VIc — VIa	0·21	1·10	0·10	0·07	0·06	0·09	0·03
VIIc — VIIa	0·11	1·11	0·10	0·09	0·10	0·03	0·04
VIIIc — VIIIa	0·22	1·26	0·17	0·07	0·10	0·10	0·10

Vicinal Coupling Constants

Dianhydro derivatives $I-XII$ form a tricyclic system which should be considerably rigid according to models. The fixation of four carbon atoms in plane (two oxirane carbons and two carbons vicinal to them) has a considerable flattening of the tetra-hydropyran ring as a consequence. This ring should assume the half-chair confor-mation of the type $^5H_0$ in 1,6 : 2,3-dianhydro derivatives $I-IV$, IX, X or $^1H_0$ in 1,6 : 3,4-dianhydro derivatives $V-VIII$, XI, XII or an envelope conformation E_0. The torsion angles of the protons H—C—C—H for dianhydro derivatives $I-XII$, obtained with Dreiding models, are given in Table X. The X-ray diffraction analysis of the crystalline *gulo*-derivative IIa demonstrated[11] the existence of two types of molecules with a slightly different geometry. The calculation of the torsion angles of protons $\theta_{i,j}$ from these X-ray data leads to the following values: $\theta_{1,2} = 56·1$ and $59·4°$, $\theta_{2,3} = 5·6$ and $14·3°$, $\theta_{3,4} = 92·3$ and $98·3°$, $\theta_{4,5} = 52·7$ and $51·8°$, $\theta_{5,6en} = 107·0$ and $106·4°$, $\theta_{5,6ex} = 19·8$ and $13·6°$. Their comparison with the average values obtained from models (Table X) shows deviations lower than $10°$, with the exception of the value of the $\theta_{2,3}$ protons of the oxirane ring, where in the second type of the molecules a deviation of $14·3°$ from the idealized eclipsed geometry is observed. Hence, it seems that the models represent the average spacial arrangement of the molecules of dianhydrohexopyranoses satisfactorily, with the exception of possible deformations on the oxirane ring.

Tᴀʙʟᴇ X

Torsion Angles H—C—C—H in the Series of 1,6 : 2,3- and 1,6 : 3,4-Dianhydro-β-ᴅ-hexopyra-noses and Their 2- and 4-Deoxy Derivatives, Obtained from Dreiding Models (rounded up to 5°)

The symbols ↑ and ↓ mean the expectable increase or decrease of the torsion angles, caused by repulsion interactions of the oxirane ring and the ethereal oxygen.

Compound	H-1/H-2	H-2/H-3	H-3/H-4	H-4/H-5	H-5/H-6en	H-5/H-6ex
I	50↑	0	30↓	70↓	105↑	20↓
II	50↑	0	90↑	50↑	105↑	20↓
III	5↑	0	80↓	75↑	105↓	20↑
IV	5↑	0	40↓	45↓	105↓	20↑
V	75↓	30↓	0	45↑	95↓	30↑
VI	45↑	90↑	0	45↑	95↓	30↑
VII	75↑	85↑	0	10↑	95↓	30↑
VIII	45↓	35↓	0	10↑	95↓	30↓
IX	50↑	0	30↓ 90↑	70↓ 50↑	105↑	20↓
X	5↑	0	80↑ 40↓	75↓ 45↓	105↓	20↑
XI	75↓ 45↑	30↓ 90↑	0	45↑	95↓	30↑
XII	75↑ 45↓	85↑ 35↓	0	10↑	95↑	30↓

Information on the conformational behaviour of dianhydrohexopyranoses in solutions is relatively most easily attainable from vicinal interaction constants, $^3J_{H,H}$. Experimental values of $^3J_{H,H}$ in the series of hydroxy derivatives, acetates, trichloroacetylcarbamoyl derivatives and deoxydianhydrohexoses are given in Table I−V. In our preceding paper[1] we adjusted the values of the coefficients A, B, C and D in the relation $^3J_{H,H} = A + B \cos \theta + C \cos 2\theta + D \cos 3\theta$ (A = 5·95, B = −1·35, C = 5·45, D = −0·45) for the tetrahydropyranose system, and used them after appropriate corrections for the electronegativity of the substituents for conformational study of 1,6-anhydro-β-D-hexopyranoses. In doing this we started from the assumption that the position of the minimum of $^3J_{H,H}$ is at $\theta = 90°$ (cf.[12,13]). The relationship used gives for $\theta = 90°$ and $\theta = 0°$ or $180°$ the values $^3J_{H,H} = 0·5$ and 9·6 or

TABLE XI

Torsion Angles H—C—C—H Obtained from Experimental $^3J_{H,H}$ Values on Using the Relationship $^3J_{H,H} = f(\phi)$ (see the text) and Rounded up to 5°, for 1,6 : 2,3- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses and Their 2- and 4-Deoxy Derivatives.

The deviations from the values of the angles determined on Dreiding models (Table X) are given in brackets.

Compound	Torsion angles between protons					
	H-1/H-2	H-2/H-3	H-3/H-4	H-4/H-5	H-5/H-6en	H-5/H-6ex
I	65 (+15)	a	25 (−5)	75 (+5)	115 (+10)	15 (−5)
II	70 (+20)	a	90^b (0)	35 (−15)	115 (+10)	20 (0)
III	40 (+35)	a	75 (−5)	70 (−5)	115 (+10)	0 (−20)
IV	45 (+40)	a	45 (+5)	20 (−25)	110 (+5)	25 (+5)
V	75 (0)	30 (0)	a	60 (+15)	85^e (−10)	40 (+10)
VI	50 (+5)	90^b (0)	a	60 (+15)	80^f (−15)	40.(+10)
VII	75 (0)	85 (0)	a	25 (+15)	100^g (+5)	35 (+5)
VIII	45 (0)	40 (+5)	a	30 (+20)	95^g (0)	40 (+10)
IX	65 (+15)	a	30 (0)	80 (+10)	115 (+10)	25 (+5)
			90 (0)	40 (−10)		
X	40 (+35)	a	75 (−5)	75 (0)	c	c
			50 (+10)	40 (−5)		
XI	75 (0)	c	a	60 (+15)	85^e (−10)	40 (+10)
	55 (+10)	100 (+10)^d				
XII	80 (+5)	75 (−10)	a	20 (+10)	95^g (0)	35 (+5)
	50 (+5)	50 (+15)				

^{a} For $^3J_{H,H}$ between the oxirane protons the relation $^3J_{H,H} = f(\theta)$ was not adjusted. The torsion angle should be close to 0°; ^{b} the experimental value $^3J_{H,H} = 0·0$ Hz is lower than the lowest theoretical value of $^3J_{H,H}$ for 90°; ^{c} the $^3J_{H,H}$ values were not determined; ^{d} alternative value 80 (−10); ^{e} alternative value 95 (0); ^{f} alternative value 100 (+5); ^{g} alternative value 85 (−10).

13·2 Hz, respectively, which is in good agreement with the experimental values $J_{ax,eq}$ and $J_{eq,eq}$ in cyclohexane[14]. Dianhydro-β-D-hexopyranoses $I-XII$ afford important experimental material for the checking of the validity of the assumption used. From models it follows that the torsion angle of protons H-3 and H-4 in *gulo*-derivative II and the torsion angle of protons H-2 and H-3 in *allo*-derivative VI should be practically equal to 90°. This value is supported by the results of X-ray diffraction analysis of a crystal of compound II, where[11] for the two types of molecules present the angles $\theta_{3,4} = 92\cdot3$ and 98·3° were found. Experimentally found values of $^3J_{H,H}$ are in both derivatives mentioned equal to zero — as the only ones in the whole series. In cases when the models show torsion angles 5 to 10° smaller or larger than 90° the non-zero values of $^3J_{H,H}$ were found within the 0·3 to 0·8 Hz range. These observations confirm the justification of the assumption of the minimum of $^3J_{H,H}$ for $\theta = 90°$ experimentally. The same is true of the utilizability of the adjusted relation $^3J_{H,H} = f(\theta)$ which — after correction for electronegativities, gives for $\theta = 90°$ theoretical values of about 0·3 Hz for $^3J_{3,4}$ in II and for $^3J_{2,3}$ in IV.

The presence of the oxirane ring in dianhydro derivatives $I-XII$ leads to an increase in valence angles C—C—H of oxirane protons, or also to changes in bond lengths in the fragment C—CH—CH—C. The stereochemical interpretation of $^3J_{H,H}$ protons in the fragment CH—CH—C by means of the relation $^3J_{H,H} = f(\theta)$ thus requires a correction for the presence of the oxirane ring. As the easiest we chose the empirical method of correction based on the comparison of the averaged $^3J_{H,H}$ values of the methyl protons in 1,2-epoxypropane and in propane. Literature gives the values $^3J_{CH_3,CH}$ equal to 5·0 Hz (ref.[15]) or 7·4 Hz (ref.[16]) for these compounds. Their ratio leads then to the correction factor 0·676 for the oxirane ring, which was used in the relation $^3J_{H,H} = f(\theta)$ for $^3J_{H,H}$ in the fragment CH—CH—C.
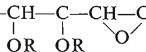
The coupling constant $^3J_{H,H}$ between both oxirane protons varies in compounds $I-VIII$ between 3·7 to 4·5 Hz, while the average value is 4·05 Hz. (For comparison in oxirane[17,18] and 1,2-epoxypropane[15,16] the value 4·5 Hz was found between the *cis* oriented oxirane protons). While the models represent an idealized state with a 0° torsion angle between the protons, the X-ray diffraction data[11] for the *gulo*-derivative IIa show deviations from the eclipsed arrangement of the oxirane protons (5·6 or 14·3°, resp. in the two types of molecules) which evidently can exist even in solution, and this also in further dianhydro derivatives. In principle the decrease of the value of $^3J_{H,H}$ should express the increase of the deviation from the eclipsed arrangement, but the possibility of the effect of other factors and the inaccessibility of geometrical data do not permit the reliable interpretation of the experimental values of $^3J_{H,H}$ of oxirane protons in this sense. For other $^3J_{H,H}$ the relationship

$^3J_{H,H} = f(\theta)$ corrected for the electronegativities of substituents was used in the same manner as in our preceding paper[1].

The values of individual vicinal coupling constants for hydroxy derivative, acetate, trichloroacetylcarbamoyl derivative and for deoxy derivative of a given configuration show a striking similarity, which can also be seen in the values of the determined torsion angles, which in an absolute majority of cases do not exceed the 5° range. Therefore we give in Table XI only average values of torsion angles (rounded up to 5°) for each configurational type determined from the relation $^3J_{H,H} = f(\theta)$, and in brackets the deviations from the torsion angles obtained from models (Table X). In the majority of the cases the deviations are smaller than 15°, in agreement with the expected rigidity of the system. Larger deviations $(20° - 40°)$ were found merely for $\theta_{1,2}$ in derivatives *II*, *III* and *IV*, and for $\theta_{4,5}$ in derivatives *IV* and *VIII*. These deviations from idealized conformations, represented by the models, also could be caused by non-bonding repulsive interactions between the oxirane oxygen and the oxygen $O_{(5)}$ in derivatives *I*, *II*, *V* and *VI* with an α-oriented oxirane ring or the oxygen $O_{(6)}$ (in derivatives *III*, *IV*, *VII* and *VIII* with a β-oriented oxirane ring). The trends in the changes of the torsion angles, which could cause these repulsion interactions, can be estimated from models. The expected trends of the changes of the torsion angles are represented symbolically in Table X. The experimentally determined deviations are mostly in agreement with the trends thus expected, or they are zero, and only in a few cases the deviations have an opposite sign (compare Tables X and XI) and values lower than 10°.

Long-Range Couplings

In dianhydro derivatives *I − XII* eight various types of long-range couplings occur, extending over four bonds $(^4J_{H,H})$. From the comparison of the data for hydroxy derivatives, acetates and trichloroacetylcarbamoyl derivatives it follows that the nature of the substituents has little effect on their values (the differences do not exceed 0·2 Hz), which is in agreement with the conformational conclusion obtained from $^3J_{H,H}$. Therefore we present in Table XII representative values of $^4J_{H,H}$ only for the series of the acetates *Ib − VIIIb*. The signs of the constants $^4J_{H,H}$ were not determined, and the given values are absolute. The highest absolute values of $^4J_{H,H}$ (1·0 to 2·3 Hz) were observed in the fragment —CH—C—CH—C—, *i.e.* between the protons H-3
and H-5 in derivatives *I − IV*, and between the protons H-1 and H-3 in derivatives *V − VIII*, while the protons in the transoid arrangement (one with α- and the other with β-configuration) have higher values (1·8 to 2·3 Hz) than in the *cisoid* arrangement (1·0 to 1·6 Hz). In the fragments CH—C——CH the values $^4J_{H,H}$ are generally
lower: in the *transoid* arrangement 0·5 to 0·9 Hz $(^4J_{1,3}$ in derivatives *I*, *II*, $^4J_{2,4}$ in

derivatives *II, III, VI* and *VII* and $^4J_{3,5}$ in derivatives *V* and *VI*) and in the *cisoid* arrangement they are zero ($^4J_{1,3}$ in derivatives *III* and *IV*, $^4J_{2,4}$ in derivatives *I, IV, V* and *VIII* and $^4J_{3,5}$ in derivatives *VII* and *VIII*). The coupling constants between the protons H-4 and H-6en or H-6ex have non-zero values only in derivatives with a 4β-OR substituent (*II* and *IV*), while the value $^4J_{4,6ex}$ is higher than $^4J_{4,6en}$ according to expectation. In all other cases the values $^4J_{4,6}$ are practically zero. The interaction path of other $^4J_{H,H}$ (between H-1 and H-5, H-6en or H-6ex) leads *via* the oxygen atom and it is not directly affected by the position and the orientation of the substituents. Their values are generally small and practically constant within the 0·2 to 0·5 Hz range. The non-zero interactions over five bonds were observed in derivatives *I* and *III* only, between the protons H-1 and H-4 (0·3 or 0·6 Hz respectively), again in the *transoid* arrangement of the interacting protons. In view of the low values, uncertainty of the signs and the complexity of the relationship to geometrical parameters the constants ^4J were not interpreted in the conformational sense.

Geminal Couplings

In dianhydrohexopyranoses *I—VIII* a sole geminal interaction is observed, *i.e.* between the protons H-6en and H-6ex. In deoxy derivatives *IX—XII* there is also $^2J_{H,H}$ between the protons H-4 (in *IX* and *X*) or H-2 (in *XI* and *XII*). The values of $^2J_{H,H}$ in deoxy derivatives lie within the narrow range $-15\cdot1$ to $-15\cdot3$ Hz without

Table XII

Long-range Coupling Constants of Protons in Acetates of 1,6:2,3- and 1,6:3,4-Dianhydro-β-D-hexopyranoses in Deuteriochloroform

Compound	Long-range coupling constants (^4J)[a]							
	$J_{1,3}$	$J_{2,4}$	$J_{3,5}$	$J_{4,6en}$	$J_{4,6ex}$	$J_{1,5}$	$J_{1,6en}$	$J_{1,6ex}$
Ib	0·7	∼0	2·0	∼0	∼0	∼0·3[b]	0·4	0·4
IIb	0·5[c]	0·7	1·8	0·2[b]	0·8	∼0·3[b]	0·5	0·4
IIIb	∼0	0·9	1·6	∼0	∼0	∼0·3[b]	0·5	0·4
IVb	∼0	∼0	1·0	∼0·2[b]	0·4	∼0·3[b]	0·5	0·4
Vb	2·1	∼0	0·7	∼0	∼0	∼0·3[b]	∼0·3[b]	∼0·2[b]
VIb	2·3	0·8	0·6	∼0	∼0	∼0·3[b]	∼0·2[b]	∼0·2[b]
VIIb	1·6	0·6	∼0	∼0	∼0	∼0·3[b]	0·4	0·4
VIIIb	1·0	∼0	∼0	∼0	∼0	∼0·3[b]	∼0·3[b]	∼0·3[b]

[a] Given in absolute values (the signs were not determined); [b] the values were determined from the changes in the half-widths of the signals during the decoupling experiment (no splitting of the lines was observed); [c] the value was determined from the spectrum after addition of Eu(FOD)$_3$.

any evident effect of the position and the configuration of neighbouring oxirane ring. In contrast to this the range of the observed values of $^2J_{6en,6ex}$ is relatively broad $(-6\cdot3$ to $-8\cdot7$ Hz$)$. In hydroxy derivatives $Ia - VIIIa$ we observed the effect of solvent on $^2J_{6,6}$: in dimethyl sulfoxide the absolute value of $^2J_{6,6}$ of each of the hydroxy derivatives is averagely by $0\cdot5$ Hz lower than in deuteriochloroform, evidently in consequence of the different dielectric constant of both solvents. The nature of the substituent R $(R = OH, OCOCH_3, OCONHCOCCl_3)$ has a negligible effect on the value of $^2J_{6,6}$. However, in deoxy derivatives with R = H the observed absolute values are $0\cdot5$ to 1 Hz lower. In the series of hydroxy derivatives, acetates and trichloroacetylcarbamoyl derivatives we observed the same effect of the position and the orientation of the oxirane ring on $^2J_{6,6}$. If the oxirane ring is in positions $2\alpha, 3\alpha$ the observed values are within the $-8\cdot3$ to $-8\cdot7$ Hz limits, if it is in positions $2\beta, 3\beta$ or $3\alpha, 4\alpha$ the values of $^2J_{6,6}$ are between $-7\cdot4$ to $-7\cdot8$ Hz, and finally, if it is in position $3\beta, 4\beta$ the $^2J_{6,6}$ values are $-6\cdot8$ to $-6\cdot9$ Hz. Hence, the absolute value of $^2J_{6,6}$ practically decreases with the decreasing distance between the $C_{(6)}$—H_2 group and the oxirane oxygen.

Intramolecular Hydrogen Bonds

In connection with the study of the conformation of dianhydro derivatives $I - VIII$ we also studied spacial orientation of their OH groups and the existence of intramolecular hydrogen bonds in hydroxy derivatives $Ia - VIIIa$. The hydroxyl group of these substances can form five-membered intramolecular hydrogen bonds of three types, differing in their proton acceptor which can be (A) the oxirane oxygen, (B) the oxygen $O_{(5)}$ of the tetrahydropyrane ring, or (C) the oxygen $O_{(6)}$ of the 1,6-anhydride bond. The frequencies of the absorption bands of the hydroxyl groups and the lengths of the potential intramolecular hydrogen bonds (determined from models and defined as the distance l between the oxygen atoms of the donor and the acceptor group[19], are given in Table XIII. Of all dianhydro compounds only the *gulo*-epoxide IIa cannot form intramolecular hydrogen bond because the distance l is greater than $0\cdot35$ nm; hence, only the band of the OH group is present in the spectrum at 3628 cm^{-1}. Compounds $IIIa$ and $VIIa$ form intramolecular hydrogen bonds of the type b), to which the band of the bound OH group at 3582 and 3585 cm^{-1} corresponds. The *altro*-epoxide VIa forms a hydrogen bond of type c) $(l = 0\cdot27$ nm$)$ with an absorption band at 3565 cm^{-1}. The situation is more complex in *talo*-epoxide $VIIIa$ where hydrogen bonds of type a) and c) are possible, the strength of which cannot be determined in view of the small difference in frequencies. In *allo*-epoxide Ia and Va the intramolecular hydrogen bonds of type a) and b) can be formed theoretically, but the absorption bands at 3570 cm^{-1} or 3569 cm^{-1} indicate the type a). The *talo*-epoxide IVa is to a certain extent an exception in this series, since the position of the absorption band at 3592 cm^{-1} does not correlate with the distance

TABLE XIII

IR Absorption Bands of OH Groups in 1,6 : 2,3- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses in Tetrachloromethane ($c = 1 . 10^{-3}$ M)

| Compound | Free OH[a] | | | | Intramolecularly bonded OH[a] | | | | | | | | | | | | | | |
| | | | | | (A) O—H···O△ | | | | | (B) O—H···O$<^{C(1)}_{C(5)}$ | | | | | (C) O—H···O$<^{C(11)}_{C(6)}$ | | | | |
	%	ν(OH)	$\Delta\nu_{1/2}$	A	%	ν(OH)	$\Delta\nu_{1/2}$	A	l	%	ν(OH)	$\Delta\nu_{1/2}$	A	l	%	ν(OH)	$\Delta\nu_{1/2}$	A	l
Ia	—	—	—	—	100	3 570	10·0	129	2·8	—	—	—	—	3·0	—	—	—	—	4·5
IIa	100	3 628	9·5	127	—	—	—	—	3·7	—	—	—	—	3·6	—	—	—	—	3·9
IIIa	13	3 622	9·5	17	—	—	—	—	3·7	87	3 582	10	114	2·8	—	—	—	—	4·5
IVa	24	3 621	10·0	32	76	3 592	10·0	100	2·8	—	—	—	—	3·6	—	—	—	—	3·9
Va	—	—	—	—	100	3 569	9·5	129	2·8	—	—	—	—	3·0	—	—	—	—	3·7
VIa	—	—	—	—	—	—	—	—	3·7	—	—	—	—	3·6	100	3 565	12	107	2·7
VIIa	25	3 626	9·5	32	—	—	—	—	3·7	75	3 585	10	97	3·0	—	—	—	—	3·7
VIIIa	—	—	—	—	—	—	—	—	2·8	—	—	—	—	2·7	b	3 569	9·5	133	2·7

[a] % Percentage of the given form, calculated from A; ν(OH) frequency of the OH band; $\nu_{1/2}$ half-width of the OH band; l distance between the oxygens of the donor and the acceptor group. [b] No definite decision can be made between the types (A) and (C).

$l = 0.28$ nm measured on a model. In comparison with compounds *Ia* and *Va* the band is shifted to higher frequencies, which indicates a greater distance between the oxygen atoms of the donor and the acceptor group. This is in agreement with the values of $^3J_{H,H}$ of *talo*-epoxide *IV*, from which it follows that this compound has the most deformed conformation compared with the idealized conformation represented by the model (Table XI).

EXPERIMENTAL

1,6 : 2,3- and 1,6 : 3,4-Dianhydro-β-D-hexopyranoses *Ia—VIIIa* were synthetized using methods described earlier[20—25]. Their acetates *Ib—VIIIb* were prepared on acetylation with acetic anhydride in pyridine[26]. Trichloroacetylcarbamoyl derivatives *Ic—VIIIc* were obtained from dianhydrohexopyranoses *Ia—VIIIa* by *in situ* acylation with trichloroacetyl isocyanate (TAI) in the measuring cell: To a solution of the hydroxy compound in deuteriochloroform (about 20 mg in 0·4 ml) 3 drops of TAI were added and the trichloroacetylcarbamoyl derivatives *Ic—VIIIc* formed were measured immediately. 4-Deoxy-1,6 : 2,3-dianhydro- and 2-deoxy-1,6 : 3,4-dianhydro-β-D-hexopyranoses *IX*, *X*, *XI* and *XII* were prepared according to literature[27—29].

The ^{1}H-NMR spectra were measured on a Varian HA-100 spectrometer (at 100 MHz frequency) with about 20 mg of substance in 0·4 ml of deuteriochloroform (using tetramethylsilane as internal reference) at about 30°C. Hydroxy derivatives *Ia—VIIIa* were also measured in hexadeuteriodimethyl sulfoxide with hexamethyldisiloxane as internal reference, and their chemical shifts are corrected with reference to tetramethylsilane, taking $\delta_{HMDS} = 0.06$. The majority of the investigated substances affords pseudo first-order spectra at 100 MHz frequency (with mild distortions of the intensities of the lines), and therefore the chemical shifts were obtained by first order analysis with the exception of the protons of the methylene groups $C_{(6)}$—H₂ (which were analysed as the AB-parts of the ABX spectra, where X = $C_{(5)}$—H, under elimination of long-range couplings by decoupling) and the protons of the methylene groups $C_{(2)}$—H₂ or $C_{(4)}$—H₂ in 2-deoxy- or 4-deoxy derivatives *IX—XII* (which were analysed as AB spectra under elimination of their other interactions by decoupling). The chemical shifts were determined with 0·01 ppm accuracy. The signals were assigned on the basis of expected chemical shift values and the observed multiplicity, and the assignment was confirmed by decoupling experiments. The signal of each proton was expanded on a 50 Hz scale and the coupling constant values were read from it (confirmed by gradual elimination of all remaining protons of the molecule). The error of J values should be smaller than 0·1 Hz. In 1,6 : 2,3-dianhydro-β-D-gulopyranoside (*IIa*) and its acetate *IIb*, where a complete overlapping of the signals of protons H-2 and H-3 took place, the shift reagent, tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) europium (III) (Eu(FOD)₃) was used for their separation. The IR spectra of dianhydro derivatives *Ia—VIIIa* (Table XIII) were measured on a UR-20 Zeiss-Jena spectrometer in tetrachloromethane at $1 . 10^{-3}$M concentration, when intermolecular association no longer took place.

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