

for hydroxyl; despite the presence of an ester function, the substance failed to give a positive hydroxamic acid-ferric chloride test.

Anal. Calcd for $C_{38}H_{48}NO_7$ (625.77): C, 72.94; H, 6.93; N, 2.24. Found: C, 72.85; H, 6.79; N, 2.22.

5-O-Acetyl-2,3,4,6-tetra-O-benzyl-N,N-dimethyl-L-idonamide (5).—Crystalline 2,3,4,6-tetra-O-benzyl-N,N-dimethyl-L-idonamide³ (4, 600 mg) was acetylated as described above for the preparation of 2 to give syrupy 5 (530 mg, 82%) which was purified by chromatography on a column of silica gel (50 g) using benzene-ether (7:4): $[\alpha]^{20D} -0.5^\circ$ (*c* 2.03, chloroform); ir absorption (neat) at 1740 cm^{-1} (ester CO) but none for a hydroxyl group; like 2, 5 failed to give a positive hydroxylamine-ferric chloride test.

Anal. Calcd for $C_{38}H_{48}NO_7$ (625.77): C, 72.99; H, 6.93; N, 2.24. Found: C, 73.57; H, 6.63; N, 2.15.

Registry No.—2, 16134-26-2; 3, 16134-27-3; 5, 16134-28-4; 6, 16134-29-5; 7, 16134-30-8; 8, 16134-31-9; 10 (2-benzyl-2-phenylhydrazone), 16134-32-0.

Acknowledgments.—We thank Dr. Norman E. Sharpless for X-ray diffraction measurements, and Dr. Louis A. Cohen for helpful discussions regarding mechanisms. We are indebted to the staff of the Section on Analytical Services and Instrumentation of this institute for elemental analyses and spectra.

Molecular Rotations of Poly-O-acetyl Carbohydrates in Relation to Their Structures.

III.¹ $[M]^{20D}$ Change Caused by the Group Change at the Carbon-6 Atom in D-Glucopyranose Derivative

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The molecular rotation, $[M]^{20D}$, of the 6-Y-6-deoxy-D-glucopyranose derivatives (RY) are plotted against the *S* value of the Y group which attaches to the C-6 atom. These $[M]^{20D}$ -*S* (at C-6) plots can be divided into two moieties at a certain *S* value and the slopes (or shapes) of these moieties can be interpreted from the standpoint of the stereochemistry.

In the previous paper,¹ the present author elucidated that every atom (or radical only under a special condition) has its own new optical property *S*² and that it is an effective method of interpreting the molecular rotation, $[M]^{20D}$ of carbohydrates to plot it against *S* value of an atom (or radical) which attaches to C-1 atom.^{3,4}

In this article, the author applies this method to the C-6 atom of the D-glucopyranose derivatives.⁵ The substances and their molecular rotations, under discussion in this article are given in Tables I and II.⁶

Next, these $[M]^{20D}$ values are plotted against the *S* value of the atom (or radical) Y which attaches to the C-6 atom, but the values of *S* used in this article are as follows: *S* of H atom is -1.8; *S* of F atom is 0.8; *S* of Cl atom is 5.8; *S* of Br atom is 8.7; *S* of I atom is 14.0; *S* of (OH) radical is 1.2; *S* of (OAc) radical is 2.5; *S* of (OMe) radical is 3.2.^{1,7} The results are shown in Figure 2 (2,3,4-tri-O-acetyl-6-Y-6-deoxy-β-D-glucopyranosyl compounds), Figure 3 (methyl 6-Y-6-deoxy-β-D-glucopyranoside derivatives), Figure 4 (6-Y-6-deoxy-α-D-

glucopyranoside derivatives), and Figure 5 (6-Y-6-deoxy-α-D-glucopyranosyl halide derivatives).^{8,9,10}

It is apparent in Figure 2 that the $[M]^{20D}$ -*S* (at C-6) plot of 1,2,3,4-tetra-O-acetyl 6-Y-6-deoxy-β-D-glucopyranose, 9' has a discontinuity between the abscissal values of (OAc) and (OMe). In other words, the plot of 9' in Figure 2 is composed of two moieties [the one is that between the abscissal values of F and (OAc) (*i.e.*, the left-hand moiety) and the other is between the abscissal values of (OMe) and I (*i.e.*, the right-hand moiety)]. The plot of 10' in Figure 2 should also be divided into two moieties [the one is between the abscissal values of H and OAc (*i.e.*, the left-hand moiety) and the other is between the abscissal values of OMe and I (*i.e.*, the right-hand moiety)], as the right-hand moiety of the plot of 10' is, no doubt, symmetrical with that of the plot of 9', with regard to the axis of abscissa. The similar phenomenon is seen for the plots of 8' in Figure 3. The left-hand moiety of the plot of 8' is, however, between the abscissal values of H and OMe (and not OAc) and the right-hand moiety is between the abscissal values of Cl and I. It is clear that the left-hand moiety of the plot of 8' is symmetrical with that of the plot of 10' and the right-hand moiety of the plot of 8' is parallel to that of the plot of 10'.¹¹ Such a discontinuity in a plot can be seen not only in β-D series (Figures 2 and 3), but also in α-D series (Figures 4 and 5), where it is somewhat strange that the abscissa of OH belongs to the right-hand moieties of the plots of 6 and 8.

(1) Part II: S. Yamana, *J. Org. Chem.*, **32**, 185 (1967).

(2) The value of *S* can be just equal to the atomic refraction, R_D only for halogen.¹

(3) The C-1 atom is a ring carbon atom which is combined directly with the ring oxygen atom, O*. The C-6 atom is, however, not a ring carbon atom.⁴

(4) See Figure 1.

(5) The reason why only D-glucopyranose derivatives are used in this article is that only their $[M]^{20D}$ data are abundant.

(6) Compound numbers are as follows: (1), 6-Y-6-deoxy-α-D-glucopyranosyl fluoride; (1'), 6-Y-6-deoxy-β-D-glucopyranosyl fluoride; (2), 2,3,4-tri-O-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl fluoride; (2'), 2,3,4-tri-O-acetyl-6-Y-6-deoxy-β-D-glucopyranosyl fluoride; (3), 2,3,4-tri-O-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl chloride; (4), 2,3,4-tri-O-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl bromide; (5), 2,3,4-tri-O-acetyl-6-Y-6-deoxy-α-D-glucopyranosyl iodide; (6), 6-Y-6-deoxy-α-D-glucopyranose; (7'), 2,3,4-tri-O-acetyl-6-Y-6-deoxy-β-D-glucopyranose; (8), methyl-6-Y-6-deoxy-α-D-glucopyranoside; (8'), methyl-6-Y-6-deoxy-β-D-glucopyranoside; (9), 1,2,3,4-tetra-O-acetyl-6-Y-6-deoxy-α-D-glucopyranose; (9'), 1,2,3,4-tetra-O-acetyl-6-Y-6-deoxy-β-D-glucopyranose; (10), methyl-2,3,4-tri-O-acetyl-6-Y-6-deoxy-α-D-glucopyranoside; (10'), methyl-2,3,4-tri-O-acetyl-6-Y-6-deoxy-β-D-glucopyranoside; (11'), 1,2,3,4-tetra-O-methyl-6-Y-6-deoxy-β-D-glucopyranose.

(7) S. Yamana, *ibid.*, **31**, 3698 (1966).

(8) In order to see the influences of the X-1 group⁹ on the shape of $[M]^{20D}$ -*S* (at C-6) plots, Figure 2 is drawn. All the substances in Figure 2 have (OAc)-4, but the kind of X-1 group present is not definite.

(9) The designation X-1 group means the X group which attaches to C-1 atom, and so on.

(10) In order to see the influences of Z-4 group on the shape of $[M]^{20D}$ -*S* (at C-6) plots, Figure 3 is drawn. All the substances in Figure 3 have a (OMe)-1 group, but the kind of Z-4 group present is not definite.

(11) The plot of 11' seems to have no discontinuity on it. This problem can not be discussed now, however, for lack of $[M]^{20D}$ datum of the hydride.

TABLE I
 [M]²⁰D OF α-D-GLUCOPYRANOSE DERIVATIVES (SEE FIGURE 1)

Compd	X at C-1	Z at C-2-4	[M] ²⁰ D for Y at C-6							
			H	F	Cl	Br	I	OH	OAc	OMe
1	F	OH	ee	ee	178.1 ^{a,w}	200.9 ^{b,w}	ee	176.1 ^{d,w,ff}	ee	ee
2	F	OAc	ee	ee	349.4 ^{a,c}	386.0 ^{b,c}	ee	ee	315.5 ^{c,e}	ee
3	Cl	OAc	629.8 ^{c,f}	ee	675.3 ^{a,c}	ee	ee	614.4 ^{c,g,ff}	615.6 ^{c,h}	ee
4	Br	OAc	870.9 ^{c,i,ff}	868.5 ^{c,i,ff}	810.1 ^{a,c}	817.5 ^{c,k}	857.0 ^{c,l,ff}	802.6 ^{c,g,ff}	813.4 ^{c,m}	ee
5	I	OAc	ee	ee	ee	ee	1083.2 ^{c,l,ff}	ee	1087.8 ^{c,m}	ee
6	OH	OH	163.7 ^{n,w}	156.3 ^{i,w,ff}	183.7 ^{o,w}	211.2 ^{q,w,ff}	ee	198.4 ^{r,w}	ee	213.6 ^{s,w,ff}
8	OMe	OH	272.1 ^{t,w}	84.4 ^{u,w,ff}	297.0 ^{v,w,ff}	276.1 ^{v,w,ff}	308.6 ^{x,w,ff}	301.0 ^{y,w,ff}	ee	266.3 ^{v,w,ff}
9	OAc	OAc	ee	ee	409.3 ^{a,z}	454.8 ^{c,z,ff}	467.4 ^{c,z,ff}	ee	396.6 ^{c,aa}	405.1 ^{c,bb,ff}
10	OMe	OAc	484.4 ^{c,v}	ee	554.9 ^{p,v,ff}	502.4 ^{p,v,ff}	499.5 ^{c,z,ff}	476.6 ^{c,dd}	472.8 ^{c,aa}	ee

^a B. Helferich and H. Bredereck, *Ber.*, **60**, 1995 (1927). ^b F. Micheel, A. Klemer, M. Nolte, H. Nordiek, L. Tork, and H. Westermann, *Chem. Ber.*, **90**, 1612 (1957). ^c In chloroform. ^d B. Helferich, K. Bäuerlein, and F. Wiegand, *Ann. Chem.*, **447**, 27 (1926). ^e D. H. Brauns, *J. Amer. Chem. Soc.*, **45**, 833 (1923). ^f E. Hardegger and R. M. Montavon, *Helv. Chim. Acta*, **30**, 632 (1947). ^g G. Zemplén and A. Gerecs, *Ber.*, **64**, 1545 (1931). ^h E. Pacsu, *ibid.*, **61**, 1508 (1928). ⁱ J. Compton, *J. Amer. Chem. Soc.*, **60**, 395 (1938). ^j B. Helferich and A. Gnüchtel, *Ber.*, **74**, 1035 (1941). ^k P. Karrer and A. P. Smirnoff, *Helv. Chim. Acta*, **5**, 124 (1922). ^l B. Helferich and H. Collatz, *Ber.*, **61**, 1640 (1928). ^m D. H. Brauns, *J. Amer. Chem. Soc.*, **47**, 1280 (1925). ⁿ E. Zissis, N. K. Richtmyer, and C. S. Hudson, *ibid.*, **73**, 4714 (1951). ^o D. C. C. Smith, *J. Chem. Soc.*, 1244 (1956). ^p In pyridine. ^q K. Freudenberg, H. Toepffer, and C. C. Andersen, *Ber.*, **61**, 1750 (1928). ^r C. N. Riiber, *ibid.*, **56**, 2185 (1923). ^s D. J. Bell, *J. Chem. Soc.*, 859 (1936). ^t W. D. Maclay, R. M. Hann, and C. S. Hudson, *J. Amer. Chem. Soc.*, **61**, 1660 (1939). ^u N. F. Taylor and P. W. Kent, *J. Chem. Soc.*, 872 (1958). ^v B. Helferich, W. Klein, and W. Schäfer, *Ber.*, **59**, 79 (1926). ^w In water. ^x A. L. Raymond and E. F. Schroeder, *J. Amer. Chem. Soc.*, **70**, 2785 (1948). ^y W. J. Heddle and E. G. Percival, *J. Chem. Soc.*, 1690 (1938). ^z B. Helferich and E. Himmen, *Ber.*, **61**, 1825 (1928). ^{aa} C. S. Hudson and J. K. Dale, *J. Amer. Chem. Soc.*, **37**, 1264 (1915). ^{bb} B. Helferich and E. Günther, *Ber.*, **64B**, 1276 (1931). ^{cc} B. Helferich and A. Schneidmüller, *ibid.*, **60**, 2002 (1927). ^{dd} B. Helferich, H. Bredereck, and A. Schneidmüller, *Ann. Chem.*, **458**, 111 (1927). ^{ee} Unknown. ^{ff} This was assumed from the [M]_D, which had been observed in the neighborhood of 20°.

TABLE II

[M]²⁰D OF β-D-GLUCOPYRANOSE DERIVATIVES (SEE FIGURE 1)

Compd	X at C-1	Z at C-2-4	[M] ²⁰ D for Y at C-6							
			H	F	Cl	Br	I	(OH)	(OAc)	(OMe)
1'	F	OH	aa	aa	aa	85.8 ^{b,w}	aa	aa	aa	aa
2'	F	OAc	aa	aa	aa	133.6 ^{b,c}	aa	aa	70.1 ^{b,c}	aa
7'	OH	OAc	aa	aa	58.8 ^{c,d,bb}	86.0 ^{a,f}	130.1 ^{c,g,bb}	aa	7.6 ^{e,h}	aa
9'	OAc	OAc	aa	70.4 ^{i,p,bb}	64.5 ^{c,d,bb}	49.9 ^{i,t,bb}	41.8 ^{c,g,bb}	42.1 ^{c,k}	14.8 ^{c,l}	75.7 ^{c,m,bb}
8'	OMe	OH	-97.3 ^{n,w}	aa	-103.6 ^{c,w,bb}	-89.7 ^{i,w,bb}	-51.7 ^{q,w,bb}	-66.4 ^{r,w}	aa	-55.0 ^{m,w,bb}
10'	OMe	OAc	-37.4 ^{c,x}	aa	-33.2 ^{c,p,bb}	-5.4 ^{c,u}	10.3 ^{c,e}	-60.2 ^{c,v,bb}	-65.9 ^{c,l}	-48.5 ^{c,x}
11'	OMe	OMe	aa	aa	aa	-10.5 ^{c,u}	29.8 ^{c,u}	-47.7 ^{c,v}	aa	-43.4 ^{s,w}

^a In acetone. ^b See footnote b in Table I. ^c In chloroform. ^d See footnote a in Table I. ^e In ethanol. ^f E. Fischer and K. Zach, *Ber.*, **45**, 456 (1912). ^g See footnote l in Table I. ^h E. Fischer and K. Delbrück, *Ber.*, **42**, 2776 (1909). ⁱ See footnote j in Table I. ^j E. Fischer, B. Helferich, and P. Ostmann, *Ber.*, **53**, 873 (1920). ^k B. Helferich and W. Klein, *Ann. Chem.*, **450**, 219 (1926). ^l See footnote aa in Table I. ^m See footnote bb in Table I. ⁿ See footnote t in Table I. ^o See footnote cc in Table I. ^p In pyridine. ^q See footnote x in Table I. ^r C. N. Riiber, *Ber.*, **57**, 1797 (1924). ^s See footnote i in Table I. ^t In tetrachloroethane. ^u J. C. Irvine and J. W. H. Oldham, *J. Chem. Soc.*, **127**, 2729 (1925). ^v See footnote dd in Table I. ^w In water. ^x B. Helferich and E. Himmen, *Ber.*, **62B**, 2136 (1929). ^y J. W. Oldham, *J. Amer. Chem. Soc.*, **56**, 1360 (1934). ^z F. Micheel and O. Littmann, *Ann. Chem.*, **466**, 115 (1928). ^{aa} Unknown. ^{bb} This was assumed from the [M]_D, which had been observed in the neighborhood of 20°.

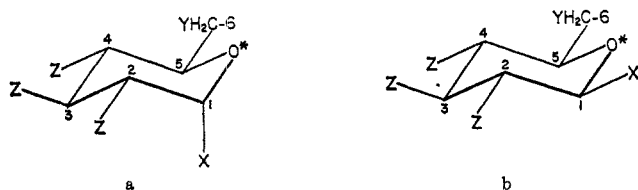


Figure 1.—(a) 6-Y-6-deoxy-α-D-glucopyranose derivative of C1 conformation; (b) 6-Y-6-deoxy-β-D-glucopyranose derivative of C1 conformation.

Thus, four following empirical rules are obtained, concerning [M]²⁰D change caused by the group change at the C-6 atom.

Rules 1-4 have already been presented in the previous paper,⁷ concerning [M]²⁰D change caused by the group change at the C-1 atom.

Rule 5.—[M]²⁰D-S (at C-6) plot (which is obtained by plotting the molecular rotation, [M]²⁰D, of 6-Y-6-deoxy-D-glucopyranose derivative (RY) against the S value of the

Y group) can generally be divided into two moieties at a certain abscissal value.

Rule 6.—The shape of a moiety of a [M]²⁰D-S (at C-6) plot of a kind of 6-Y-6-deoxy-D-glucopyranose derivative is, approximately parallel to (or symmetrical with) those of the other kinds of 6-Y-6-deoxy-D-glucopyranose derivative.

Rule 6'.—The shape of the right-hand moiety of the [M]²⁰D-S (at C-6) plot which is given by the substance having the OMe-1 group is always symmetrical with that of the substance having the OAc-1 group.

Rule 7.—The sign of the slope (or shape) of the left-hand moiety (which corresponds to the small value of S) is greatly influenced by the kind of Z-4 group and the sign of the slope (or shape) of the right-hand moiety (which corresponds to the large value of S) is greatly influenced by the kind of X-1 group.

Interpretation of Empirical Rules.—In order to interpret these empirical rules reasonably, the stereochemical view point is useful, which is suggested by the following two phenomena. (1) The position of a dis-

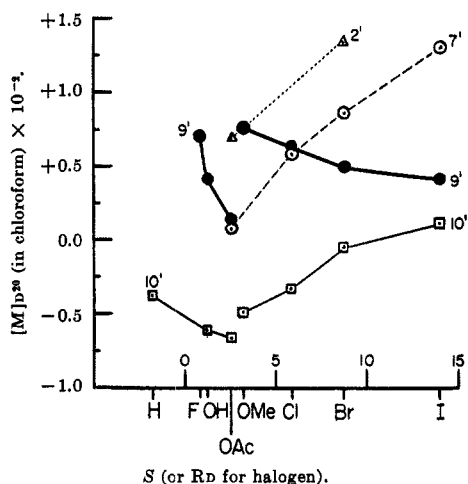


Figure 2.⁶—Molecular rotation of 2,3,4-tri-*O*-acetyl-6-*Y*-6-deoxy- β -*D*-glucopyranosyl compound as a function of *S* value of the group *Y* which attaches to the C-6 atom.

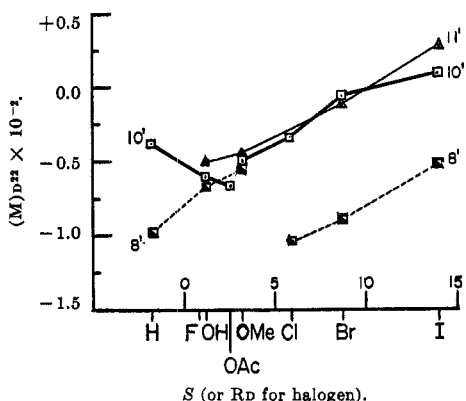


Figure 3.⁶—Molecular rotation of methyl-6-*Y*-6-deoxy- β -*D*-glucopyranoside derivative as a function of *S* value of the group *Y* which attaches to the C-6 atom.

continuity on the plot is apparently concerned with *S* value of the *Y*-6 group and the *S* value of a group seems to be concerned with the volume of this group.¹² (2) In the previous paper,¹ the symmetry of $[M]^{20D}-S$ (at C-1) plots of some substances can well be interpreted by the (matter and mirror image) relation in the molecules. The symmetry of $[M]^{20D}-S$ (at C-6) plots in this article, may also be interpreted by the (matter and mirror image) relation.

On the other hand, referring to the structure of the 6-*Y*-6-deoxy-*D*-glucopyranose derivative, the *Y*-6 group is considered to be free to rotate about the axis of the C-6-C-5 bond and the position which has minimal potential and makes the *Y*-6 group rest, will be decided principally by steric repulsions and secondarily by electric forces and hydrogen bonding forces between the atoms in the molecule (especially between the *Y*-6 group itself and the *Z*-4 or *X*-1 groups). Moreover, it has already been presumed that there are three kinds of stable positions of the *Y*-6 group (*i.e.*, *trans*-, *gauche* I, and *gauche* II positions)¹³ (see Figure 6).

Referring to Figure 6, we can anticipate the following: (1) The *t* position (*i.e.*, *trans* position) is the nearest to the *Z*-4 group and the farthest from the *O** atom (ac-

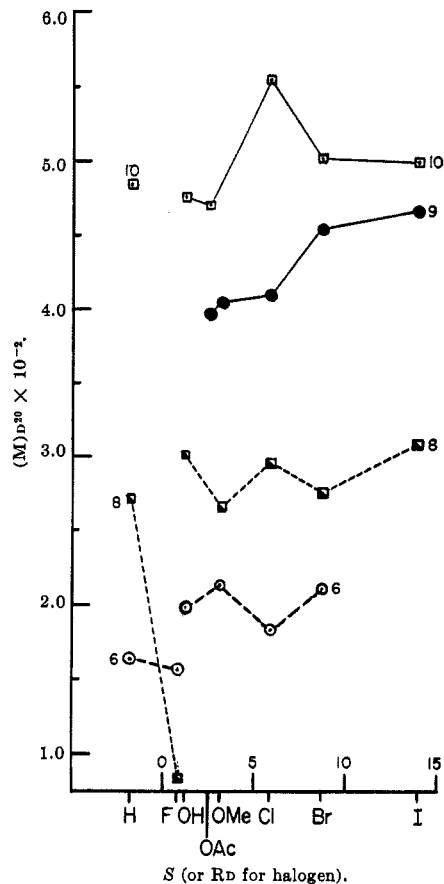


Figure 4.⁶—Molecular rotation of 6-*Y*-6-deoxy- α -*D*-glucopyranoside derivative as a function of *S* value of the group *Y* which attaches to the C-6 atom.

cordingly, it is very far from *X*-1 group). The partial molecular rotation, $[M]^{20D}_{\text{obsd}}$,¹⁴ caused by the dynamic coupling effect of *Y*-6 group (at the *t* position) is, therefore, expected to be greatly influenced by the kind of *Z*-4 group, but it may be almost indifferent to the kind of *X*-1 group. (2) The *g*I and *g*II positions (*i.e.*, *gauche* I and *gauche* II positions) are near to the *O** atom (accordingly, also to the *X*-1 group), but they are far from the *Z*-4 group. The partial molecular rotation, $[M]^{20D}_{\text{obsd}}$, caused by the dynamic coupling effect of the *Y*-6 group (at the *g*I or *g*II position) is, therefore, expected to be greatly influenced by the kind of *X*-1 group, but it may be almost indifferent to the kind of *Z*-4 group.

On the other hand, in the molecules of the substances discussed in this article, only *X*, *Y*, and *Z* can change. Accordingly, the most stable position at which the *Y*-6 group can stay should be determined by the volumes of these three kinds of groups. The fundamental idea for it may be as follows. (a) When the sum of the radii of the *Y*-6 and *Z*-4 groups is small, the *Y*-6 group can stay at *t* position (without being rejected by *Z*-4 group). (b) If the sum of the radii of the *Y*-6 and *Z*-4 groups is fairly large, the *Y*-6 group is rejected by the *Z*-4 group and is forced to stay at positions other than the *t* position (probably, mostly at the *g*I position).^{15,16}

Of course, if the stay position of the *Y*-6 group changes (for example, from the *t* position to the *g*I position), the internal conformation of the C-6-*Y*-6 bond

(12) The term "volume" in this case does not mean the whole volume of a group but it means the effective volume which influences the neighboring atoms.

(13) S. Yamana, *Bull. Chem. Soc. Jap.*, **30**, 920 (1957).

(14) S. Yamana, *ibid.*, **31**, 558 (1958).

(15) The H-4 atom may repulse a group at the *g*II position.

(16) See Figure 6.

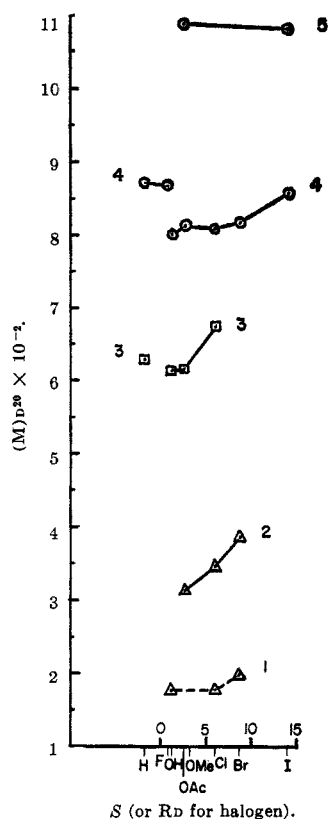


Figure 5.⁶—Molecular rotation of 6-Y-6-deoxy- α -D-glucopyranosyl halide derivative as a function of S value of the group Y which attaches to the C-6 atom.

changes and accordingly the partial molecular rotation, $[M]^{20}_{\text{Dobsd}}$, caused by the C-6-Y-6 bond (or by Y-6 group) changes.¹⁷

If the kind of Z-4 group is definite, this internal conformation changes suddenly when the volume of the Y-6 group rises to some extent. This may be the principal reason for the discontinuity on the $[M]^{20}_{\text{D}}-S$ (at C-6) plot and moreover for the symmetry of some moieties of the $[M]^{20}_{\text{D}}-S$ (at C-6) plot. These fundamental ideas are applicable for the concrete examples in the figures as follows. All the substances in Figure 2 (*i.e.*, 2', 7', 9', and 10') have the OAc-4 group and the arrangements of the atoms near the *t* position in these substances are

(17) According to Whiffen's (or Brewster's) method, the conformational unit, (Y-6 (at the *t* position)-C-6-C-5-C-4) should cause partial negative molecular rotation. The other unit, (Y-6 (at the *gI* position)-C-6-C-5-O*) should cause partial positive molecular rotation.^{18,19} The conformational unit which is concerned with Y-6 (at the *gII* position) may cause partial molecular rotation of very small magnitude.^{18,19}

(18) D. H. Whiffen, *Chem. Ind.* (London), 964 (1956).

(19) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959); *Tetrahedron*, **13**, 106 (1961).

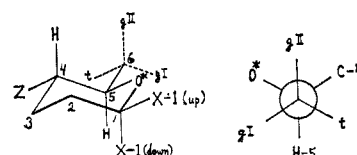


Figure 6.—Stable internal conformations of C-6-Y-6 bond along the C-6-C-5 bond: *t*, *trans* position; *gI*, *gauche I* position; *gII*, *gauche II* position.

similar to each other. When the kind of Y-6 group is the one which is smaller than OAc (*i.e.*, H, F, OH, and OAc), it can stay at the *t* position, which causes partial negative molecular rotation.¹⁶ In this case, the slope of the $[M]^{20}_{\text{D}}-S$ (at C-6) plot (*i.e.*, the left-hand moiety) is also negative in sign,¹⁶ but, when the kind of Y is one which is larger than OMe (*i.e.*, OMe, Cl, Br, or I), the Y-6 group can not stay at the *t* position and is forced to the *gI* or *gII* position which is so near to the X-1 group that it may be the principal reason for the fact that the slopes of the right-hand moieties of the $[M]^{20}_{\text{D}}-S$ (at C-6) plots of 2', 7', and 10' are all positive in sign.^{17,20}

All the substances in Figure 3 (*i.e.*, 8', 10', and 11') have the OMe-1 group and the manner of arrangements of atoms near the *gI* position is common to all these substances. The parallelism and the positive sign of the slopes of the right-hand moieties of the plots of 8', 10', and 11' may suggest that, in these three methyl β -D-glucopyranosides, the Y-6 group is situated at the *gI* position owing to the repulsion by the Z-4 group. It is strange, however, that the left-hand moiety of the plot of 8' in which the Z-4 group is OH (which has a small volume and is expected to permit the Y-6 group to stay at the *t* position) is symmetrical with that of the plot of 10' in which the Z-4 group is OAc. The elucidation of this phenomenon is also left for the future.

The slopes of the right-hand moieties of the plots in Figure 4 are not straight but zigzag, which may be due to the following fact. In the α -D-glucopyranose derivatives, the X-1 group is under the pyranose ring.⁴ In this case, the Y-6 group is not shielded by the O* atom from the steric influences of the X-1 group and the internal conformation changes concerning both of these two groups (*i.e.*, Y-6 and X-1) should be considered. The detailed study of this complicated case is left for the future.

Acknowledgment.—The author wishes to express his many thanks to Mr. Makoto Yamashiro for his assistance in calculating the molecular rotations.

(20) The study of the reason for the phenomenon that the slope of the right-hand moiety of the plot of 9' is negative in sign (rule 6') is left for the future.