*Molecular Rotations of Polyhydroxycyclohexanes in Relation to their Structures*1)

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Availability of PM-method2) for the case of $[M]^{20}_{\mathrm{D}}(\mathrm{W})$3) of polyhydroxycyclohexanes of C1 conformation was tested here. Names of several substances under discussion, together with the orientation of the unit groups, (OH), in their molecules and their $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ are shown in Table I4). At first, by using the theoretical

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1) Presented at the Symposium on the Structural Chemistry of the Chemical Society of Japan, Sapporo, August 5, 1960.

2) S. Yamana, This Bulletin, **31**, 558 (1958).

3) $[M]^{20}_{\mathrm{D}}(\mathrm{W})$ is a notation which represents the optical molecular rotation of the plane polarized light of wavelength of D-line at 20°C by an aqueous solution of an optically active substance. $[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}$ means a corresponding partial molecular rotation which is caused by the dynamical coupling effect between any two members of unit groups in the molecule.

$$\therefore\quad [M]^{20}_{\mathrm{D}}(\mathrm{W})=\sum[\mu]^{20}_{\mathrm{D}\,\mathrm{obs}}=\sum_{i\neq k}\zeta_i\zeta_k[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}$$

(Ref. Eq. 3 in the previous paper2)). Here, $[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd}}$ is the calculated value by using Kirkwood's theoretical formulae and ζ_i and ζ_k are adjustable parameters.

4) The central group, cyclohexane-ring, does not appear in the calculation.

TABLE I

Name Cyclohexane	Orientation of unit group, (OH)	Obs. $[M]_D^{20}(W)$[5]	Calcd. $\sum[\mu]_{D obs}^{20}$[12]	 Whiffen[9]
(−) 1/2 diol	[(1β), (2α)]	−48.2[6]	−42.7(−42.7)	−45
(+) 3/1,2 triol	[(1α), (2α), (3β)]	92.0[7]	92.2(96.3)	90
(−) 1,2,3/4 tetrol	[(1β), (2β), (3β), (4α)]	−49.2[7]	−49.5(−53.6)	−45
(+) 3/1,2,4 tetrol	[(1α), (2α), (3β), (4α)]	53.9[6]	49.5(53.6)	45
(−) 1,3/2,4 tetrol	[(1β), (2α), (3β), (4α)]	−42.7[7]	−42.7(−42.7)	−45
(+) 3,5/1,2,4 pentitol	[(1α), (2α), (3β), (4α), (5β)]	86.2[8]	85.4(85.4)	90
(+) 1,3,4/2,5 pentitol	[(1β), (2α), (3β), (4β), (5α)]	42[9]	49.5(53.6)	45
(+) 3,5,6/1,2,4 hexitol	[(1α), (2α), (3β), (4α), (5β), (6β)]	117[9]	128.1(128.1)	135

TABLE II. $[\mu]_{D calcd}^{20}\{3/(n^2+2)\}$ AND $[\mu]_{D obs}^{20}$[3], CAUSED BY THE DYNAMICAL COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS IN POLYHYDROXYCYCLOHEXANE OF C1 CONFORMATION

	6β	6α	5β	5α	4β	4α	3β	3α	2β	2α
1α	0	−*A*	−*B*	0	0	0	*B*	0	0	*A*
1β	−*A*	*A*	0	*B*	0	0	0	−*B*	*A*	−*A*
2α	−*B*	0	0	0	*B*	0	*A*	−*A*		
2β	0	*B*	0	0	0	−*B*	−*A*	0		
3α	0	0	*B*	0	0	*A*				
3β	0	0	0	−*B*	*A*	−*A*				
4α	*B*	0	*A*	−*A*						
4β	0	−*B*	−*A*	0						
5α	0	*A*								
5β	*A*	−*A*								

Note:

	$[\mu]_{D calcd}^{20}\{3/(n^2+2)\}$	$[\mu]_{D obs}^{20}$.
A	11.73 (6.50)[12]	42.7 (42.7)
B	1.88 (1.66)	6.8 (10.9)

formulae of Kirkwood[10], all $[\mu]_{D calcd}^{20}\{3/(n^2+2)\}$'s possible in the molecule were calculated[11] and given in Table II. Next, by using these values of $[\mu]_{D calcd}^{20}\{3/(n^2+2)\}$ and an adjustable parameter, ζ_{OH}, the following equation was obtained.

$[M]_D^{20}(W)$ of (−)1,3/2,4 tetrol, −42.7 $\equiv\sum[\mu]_{D obs}^{20}$ of (−)1,3/2,4 tetrol $=(1\beta)\bar{\lambda}(2\alpha)+(1\beta)\bar{\lambda}(3\beta)+(1\beta)\bar{\lambda}(4\alpha)+(2\alpha)\bar{\lambda}(3\beta)+(2\alpha)\bar{\lambda}(4\alpha)+(3\beta)\bar{\lambda}(4\alpha)$[13] $=\{(n^2+2)/3\}\zeta^2_{OH}\{(1\beta)\times(2\alpha)+(1\beta)\times(3\beta)+(1\beta)\times(4\alpha)+(2\alpha)\times(3\beta)+(2\alpha)\times(4\alpha)+(3\beta)\times(4\alpha)\}$[14] $=\{(n^2+2)/3\}\zeta^2_{OH}(-11.73+0+0+11.73+0-11.73)$

$$\therefore\quad \zeta^2_{OH}=3.6402\{3/(n^2+2)\}$$

or

$$\zeta_{OH}=1.9079\{3/(n^2+2)\}^{1/2}$$

The values of *A* and *B* for $[\mu]_{D obs}^{20}$ in Note of table II, can be obtained by multiplying those for $[\mu]_{D calcd}^{20}\{3/(n^2+2)\}$ by $\zeta^2_{OH}\{(n^2+2)/3\}$. By using the values of $[\mu]_{D obs}^{20}$ in Table II, $\sum[\mu]_{obs}$ of all polyhydroxycyclohexanes were calculated and given in the fourth column of Table I. Referring to Table I, it becomes apparent that PM-method is more suitable one to estimate $[M]_D^{20}(W)$ of polyhydroxycyclohexanes than Whiffen's method[9], especially when the optical center is located at the center of mass of a bond.

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[5] From the standpoint that $\partial[M]_D(W)/\partial T$ is small, some values were presumed from $[M]_D(W)$ which had been observed in the neighborhood of 20°C but not exactly at 20°C.

[6] Th. Posternak, D. Reymond and H. Friedli, *Helv. Chim. Acta*, **38**, 205 (1955).

[7] Th. Posternak and D. Reymond, ibid., **38**, 195 (1955).

[8] Th. Posternak, ibid., **33**, 343 (1950).

[9] D. H. Whiffen, *Chemistry and Industry*, **1956**, 964.

[10] S. Yamana, This Bulletin, **30**, 203 (1957).

[11] The molecular model of a cyclohexane derivative and optical data of (OH) are assumed as follows. The length of C-C bond is 1.54Å, and that of C-O bond is 1.42Å. The valency angle of C atom is 109° 28′. Mean polarizability, α, of (OH) is 1.40×10^{-24} (cc.). Anisotropy ratio, β of (OH) is 0.35[10].

[12] The values, calculated by supposing that the optical center of (OH) is located at its O atom, are given in parentheses.

[13] S. Yamana, This Bulletin, **30**, 916 (1957).

[14] Ref. Eq. 32 in the foot-note 32 of the previous paper[2].