Tetrahedron, 1965, Vol. 21, pp. 709 to 715. Pergamon Press Ltd. Printed in Northern Ireland

RE-EXAMINATION OF THE PM-METHOD

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(*Received* 26 *October* 1964; *in revised form* 6 *December* 1964)

Abstract—The application of the PM-method[1] has been tested and some cases where it does not apply are discussed.

ACCORDING to the quantum-mechanical theory of dispersion,[2] the molecular rotation, $[M]_\lambda$ is given by:

$$[M]_\lambda = \{288\,\pi^2 N/\lambda^2\}\{(n_\lambda^2 + 2)/3\}g_\lambda \tag{1}$$

Here, the various physical constants have their usual meaning. Kirkwood concluded[3] that the total gyration parameter, g_λ is given by:

$$g_\lambda = g_\lambda^{(0)} + g_\lambda^{(1)} + \sum_i g_\lambda^{(i)} \tag{2}$$

where[4] the first term $g_\lambda^{(0)}$ represents the dynamic coupling effect which originates from the electronic correlative interactions between different groups. The second term $g_\lambda^{(1)}$ has not been studied in detail and is usually neglected; $g_\lambda^{(i)}$ the third term represents the one-electron effect, i.e., the intrinsic rotation of each group due to the motion of an electron in the asymmetric Hartree field.

By assuming

$$g_\lambda \fallingdotseq g_\lambda^{(0)} \tag{3}$$

and combining Eq. 3 with Eq. 1, Kirkwood proposed:

$$[M]_\lambda = \{288\,\pi^2 N/\lambda^2\}\{(n_\lambda^2 + 2)/3\}g_\lambda^{(0)}. \tag{4}$$

In the previous paper,[1] this Eq. 4 for the wave-length of Na D-line was applied with some modification of symbols as

$$[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd(XY)}} = \{288\pi^2 N/\lambda^2\}\{(n^2 + 2)/3\}g_{\mathrm{XY}}. \tag{5}$$

As the neglect of two terms,

$$g^{(1)} \quad \text{and} \quad \sum_i g^{(i)},$$

as well as other factors may cause a discrepancy between the computed and the observed optical rotations, a new adjustable parameter κ has been introduced as in:

$$\kappa_{\mathrm{XY}}[\mu]^{20}_{\mathrm{D}\,\mathrm{calcd(XY)}} = [\mu]^{20}_{\mathrm{D}\,\mathrm{obs(XY)}} \tag{6}$$ [5]

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[1] S. Yamana, *J. Amer. Chem. Soc.* **86**, 1606 (1964).
[2] J. G. Kirkwood, *J. Chem. Phys.* **5**, 479 (1937).
[3] J. G. Kirkwood, *J. Chem. Phys.* **7**, 139 (1939).
[4] H. Murakami, *J. Chem. Phys.* **27**, 1231 (1957).
[5] S. Yamana, *Bull. Chem. Soc. Japan* **31**, 558 (1958).

and further, for simplification, κ was factorized as

$$\kappa_{XY} = \zeta_X \zeta_Y. \tag{7}$$[5]

Thus, from Eqs. 6 and 7,

$$\zeta_X \zeta_Y [\mu]^{20}_{D\,\mathrm{calcd}(XY)} = [\mu]^{20}_{D\,\mathrm{obs}(XY)} \tag{8}$$[1]

Equation 8 is the fundamental formula in the PM-method which relates the Kirkwood's term, $[\mu]^{20}_{D\,\mathrm{calcd}(XY)}$ to the partial molecular rotation, $[\mu]^{20}_{D\,\mathrm{obs}(XY)}$ and it has been shown that Eq. 8 is applicable in a number of cases.[1] It is probable, however, that in spite of introduction of κ- or ζ-coefficients the result of neglecting $g_\lambda^{(1)} + \sum_i g_\lambda^{(i)}$ cannot be overcome completely and, in some cases, causes a discrepancy between the computed and the observed optical rotations. Consequently, the PM-method has been re-examined (especially Eqs. 6 and 7). The compounds and their observed molecular rotations are listed in Tables 1, 2 and 3.

TABLE 1

Cyclohexane derivative	Unit group	$[M]^{20}_D$ [6]	Ref.
(−)-*trans*-1,2-Cyclohexanediol	$[(OH)^{1\beta}, (OH)^{2\alpha}]$	−54·0°	7
(−)-*trans*-2-Aminocyclohexanol	$[(OH)^{1\beta}, (NH_2)^{2\alpha}]$	−46·3°	8
(−)-*trans*-2-Chlorocyclohexanol	$[(OH^{1\beta}, Cl^{2\alpha}]$	ca. −53·8°	9
(−)-*trans*-2-Methylcyclohexanol	$[(OH)^{1\beta}, (CH_3)^{2\alpha}]$	−43·9°	10
(−)-*trans*-2-Chloro-1-aminocyclohexane	$[(NH_2)^{1\beta}, Cl^{2\alpha}]$	−59·3° [11]	12
(−)-*trans*-2-Methyl-1-aminocyclohexane	$[(NH_2)^{1\beta}, (CH_3)^{2\alpha}]$	$-29{\cdot}1^\circ_{\mathrm{al}}$[11]	12
(+)-*cis*-3-Methylcyclohexanol	$[(OH)^{1\beta}, (CH_3)^{3\beta}]$	2·2°	13
(+)-1,3-Dimethylcyclohexane	$[(CH_3)^{1\beta}, (CH_3)^{3\alpha}]$[14]	1·4°	15

al: alcoholic solution.

TABLE 2

Cyclopentane derivative	Unit group	$[M]^{20}_D$ [6]	Ref.
(−)-*trans*-1,2-Cyclopentanediol	$[(OH)^{1\beta}, (OH)^{2\alpha}]$	$-34{\cdot}3^\circ_{\mathrm{w}}$[11]	16
(+)-*trans*-2-Aminocyclopentanol	$[(OH)^{1\alpha}, (NH_2)^{2\beta}]$	38·6°	17
(−)-*trans*-3-Methylcyclopentanol	$[(OH)^{1\beta}, (CH_3)^{3\alpha}]$	−6·5°	18
(+)-*trans*-1,3-Dimethylcyclopentane	$[(CH_3)^{1\beta}, (CH_3)^{3\alpha}]$	2·3°	19

w: water solution.

[6] Some of $[M]^{20}_D$ values were assumed from $[M]_D$ which had been observed in the neighbourhood of 20°.

[7] N. A. B. Wilson and J. Read, *J. Chem. Soc.* 1269 (1935).

[8] R. M. Godchot and M. Mousseron, *C.R. Acad. Sci., Paris* **194**, 981 (1932).

[9] F. J. Zeelen, M. E. Kronenberg and E. Havinga, *Rec. Trav. Chim.* **77**, 674 (1958).

[10] G. A. C. Gough, H. Hunter and J. Kenyon, *J. Chem. Soc.* 2052 (1926).

[11] For lack of data, $[\alpha]_D$ is computed by applying the data of $[\alpha]_{546}$ and $[\alpha]_{579}$ to Drude's single term Eq., $[\alpha]_\lambda = A/(\lambda^2 - \lambda_0^2)$

[12] M. Mousseron and P. Froger, *Bull. Soc. Chim. Fr.* **14**, 843 (1947).

[13] D. S. Noyce and D. B. Denny, *J. Amer. Chem. Soc.* **74**, 5912 (1952).

[14] The author expresses his great thanks to Prof. James H. Brewster (Purdue University) for his experiments to re-confirm the absolute configuration of (+)-*trans*-1,3-dimethylcyclohexane.

[15] M. Mousseron, *Bull. Soc. Chim. Fr.* 218 (1946).

[16] M. Mousseron and R. Richaud, *Bull. Soc. Chim. Fr.* 643 (1946).

[17] M. Mousseron and R. Granger, *Bull. Soc. Chim. Fr.* 850 (1947).

[18] M. Godchot, G. Cauquil and M. R. Calas, *Bull. Soc. Chim. Fr.* **6**, 1358 (1939).

[19] S. F. Birch and R. A. Dean, *J. Chem. Soc.* 2477 (1953).

TABLE 3

Menthol-like compound	Unit group	$[M]_D$	Ref.
(+)-Neomenthylamine	$[(CH_3)^{1\beta}, (NH_2)^{3\alpha}, (\text{iso-}C_3H_7)^{4\alpha}, \text{ch.R}]^{20}$	23·5°	21

In order to simplify computations, molecular models are assumed as follows; The cyclohexane-ring exists only in C1 conformation (i.e. the number of equatorial groups becomes as many as possible in Tables 1, 2 and 3) and the cyclopentane-ring plane is a flat regular pentagon and the length of its side is 1·54 Å. The angle, 109°28′, between the two bonds which project up and down the cyclopentane-ring from the same ring carbon atom is bisected by the cyclopentane-ring plane.[23] The characteristics used in this article are as below:

Bond length: C—C bond is 1·54 Å; C—O bond is 1·42 Å; C—N bond is 1·47 Å; C—Cl bond is 1·78 Å. Mean polarizability, α^{25}: α of OH group is $1{\cdot}04 \times 10^{-24}$ cc; α of NH_2 group is $1{\cdot}79 \times 10^{-24}$ cc; α of Cl atom is $2{\cdot}36 \times 10^{-24}$ cc; α of CH_3 group is $2{\cdot}27 \times 10^{-24}$ cc. Anisotropy ratio, β^{26}: β of OH group is 0·35; β of NH_2 group is 0·10; β of Cl atom is 0·33; β of CH_3 group is 0·35. Refractive index, n:n of cyclohexane derivative is n_1; n of cyclopentane derivative is n_2; n of carbohydrate is n_3; n of menthol-like compound is n_4.

The $[\mu]^{20}_{D\ \text{calcd(XY)}}\{3/(n^2 + 2)\}$ values are calculated by Eq. 5.[1] These computed values are given in Tables 4, 5 and 6.

TABLE 4. $[\mu]^{20}_{D\ \text{calcd(XY)}}\{3/(n_1{}^2 + 2)\}$, (= (X) × (Y)), CAUSED BY THE DYNAMIC COUPLING EFFECT BETWEEN TWO UNIT GROUPS, X AND Y, IN CYCLOHEXANE DERIVATIVE

	C1 Conformation					
	$Y^{4\beta}$	$Y^{4\alpha}$	$Y^{3\beta}$	$Y^{3\alpha}$	$Y^{2\beta}$	$Y^{2\alpha}$
$X^{1\alpha}$	0	0	G	0	0	E
$X^{1\beta}$	0	0	0	$-F$	E	$-E$

X	Y	E^{27}	F^{27}	G^{27}
OH	OH	11·73 (6·50)	1·88 (1·66)	1·88 (1·66)
OH	NH_2	5·75 (3·03)	0·93 (0·79)	0·92 (0·80)
OH	Cl	17·50 (11·29)	5·38 (3·70)	2·87 (2·79)
OH	CH_3	25·30 (13·35)	4·20 (3·70)	4·04 (3·34)
NH_2	Cl	8·60 (5·48)	2·63 (1·76)	1·42 (1·38)
NH_2	CH_3	12·39 (6·43)	2·06 (1·76)	2·00 (1·66)
Cl	CH_3	38·15 (23·81)	6·38 (6·22)	11·53 (7·44)
CH_3	CH_3	54·54 (27·64)	9·02 (7·45)	9·02 (7·45)

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[20] Owing to the steric repulsion of $(NH_2)^{3\alpha}$, the symmetrical type is only one possible type of the internal conformation of the isopropyl group. In this case, the following simplification may be introduced,

$$(\text{iso-}C_3H_7)^{4\alpha} \fallingdotseq (CH_3)^{4\alpha} + (CH_3)^{\alpha 8\cdot d} + (CH_3)^{\alpha 8\cdot e} \quad \text{(cf. 22).}$$

[21] J. Read and R. G. Johnston, *J. Chem. Soc.* 226 (1934).

[22] S. Yamana, *Bull. Chem. Soc. Japan* **34**, 1414 (1961).

[23] Strictly speaking, the cyclopentane-ring is not a perfectly flat plane (ref. 24).

[24] K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.* **81**, 3213 (1959).

[25] Landolt Börnstein, *Physikalisch-Chemische Tabellen* Hw. II. p. 985.

[26] Landolt Börnstein, *Physikalisch-Chemische Tabellen* 5th Ed., Eg. II, p. 90, 91; Eg. III, p. 1205.

[27] Given in parentheses are the values computed by assuming the position of the optical centre of unit groups as follows: O-atom (in OH group), N-atom (in NH_2 group), Cl-atom, C-atom (in CH_3 group).

TABLE 5. $[\mu]^{20}_{D\,calcd(XY)}\{3/(n_2^2+2)\}$, $(=(X)\times(Y))$, CAUSED BY THE DYNAMIC COUPLING EFFECT BETWEEN TWO UNIT GROUPS, X AND Y, IN CYCLOPENTANE DERIVATIVE

	$Y^{3\beta}$	$Y^{3\alpha}$	$Y^{2\beta}$	$Y^{2\alpha}$
$X^{1\alpha}$	Q	0	P	0
$X^{1\beta}$	0	$-Q$	0	$-P$

X	Y	P^{27}	Q^{27}
OH	OH	8·35 (4·43)	1·68 (1·09)
OH	NH_2	4·09 (2·12)	0·82 (0·52)
OH	Cl	13·58 (7·69)	3·04 (2·00)
OH	CH_3	18·03 (9·02)	3·63 (2·26)
CH_3	CH_3	38·90 (18·42)	7·87 (4·69)

TABLE 6. $[\mu]^{20}_{D\,calcd(XY)}\{3/(n_4^2+2)\}$, $(=(X)\times(Y))$, CAUSED BY THE DYNAMIC COUPLING EFFECT BETWEEN ANY TWO MEMBERS OF UNIT GROUPS IN (+)-NEOMENTHYLAMINE[22]

	$(CH_3)^{\alpha 8\cdot f}$	$(CH_3)^{\alpha 8\cdot e}$	$(CH_3)^{\alpha 8\cdot d}$	$(CH_3)^{4\alpha}$	$(NH_2)^{3\alpha}$	$(CH_3)^{1\beta}$
ch.R	0	$-D$	D	0	0	0
$(CH_3)^{1\beta}$	0	4·41	−4·41	0	−2·00	
$(NH_2)^{3\alpha}$	0	−2·00	1·55	12·39		
$(CH_3)^{4\alpha}$	0	0	0			
$(CH_3)^{\alpha 8\cdot d}$	0	0				
$(CH_3)^{\alpha 8\cdot e}$	0		0			
$(CH_3)^{\alpha 8\cdot f}$		0	0			

By using Table 4, the value of $\kappa_{OH,OH}$ in the cyclohexane derivative is computed as follows: $[M]^{20}_{D}$ of (−)-*trans*-1,2-cyclohexanediol, $-54{\cdot}0° \equiv \sum_{X,Y} [\mu]^{20}_{D\,obs(XY)}$ of (−)-*trans*-1,2-cyclohexanediol $= (OH)^{1\beta}\Lambda(OH)^{2\alpha} = (OH)^{1\beta} \times (OH)^{2\alpha}\kappa_{OH,OH}\{(n_1^2 + 2)/3\} = -11{\cdot}73\ \kappa_{OH,OH}\{(n_1^2+2)/3\}$

$$\therefore\ \kappa_{OH,OH} = 4{\cdot}6036\{3/(n_1^2+2)\}. \tag{9}$$

Similarly, by using Tables 4, 5 and 6, the values of all κ's are computed and given in Table 7.

It is apparent from Table 7, that the value of κ_{XY} of Eq. 6 is independent of the compound and is almost constant in a pair of definite groups, X and Y. Thus, it can be said that, in addition to the bond length, the dipole moment of a bond, etc., the value of κ_{XY} is useful in the determination of organic structure (i.e. orientation or conformation).

TABLE 7. $\kappa_{XY}\{(n^2 + 2)/3\}$

κ_{XY}	Cyclohexane derivative	Cyclopentane derivative	Pyranose	Menthol-like compound
$\kappa_{OH,OH}$	4·6036	$4{\cdot}1078_w$	4·5183[28]	4·2796[22]
κ_{OH,NH_2}	8·0522	9·4377		
$\kappa_{OH,Cl}$	ca. 3·0743			
κ_{OH,CH_3}	1·7352	1·7906	1·5440[29]	1·5066[22]
$\kappa_{NH_2,Cl}$	6·8953			
κ_{NH_2,CH_3}	$2{\cdot}3487_{al}$			2·3642[30]
κ_{CH_3,CH_3}	−0·1552	−0·2922		

w: water solution, al: alcoholic solution.

Next, if Eq. 7 is correct, the values in the first column of Table 7 can be related to the ζ-coefficients as follows:

$$4{\cdot}6036\{3/(n_1^2 + 2)\} = \zeta_{OH}^2 \tag{10}$$

$$8{\cdot}0522\{3/(n_1^2 + 2)\} = \zeta_{OH}\zeta_{NH_2} \tag{11}$$

$$\text{ca. } 3{\cdot}0743\{3/(n_1^2 + 2)\} = \zeta_{OH}\zeta_{Cl} \tag{12}$$

$$1{\cdot}7352\{3/(n_1^2 + 2)\} = \zeta_{OH}\zeta_{CH_3} \tag{13}$$

$$6{\cdot}8953\{3/(n_1^2 + 2)\} = \zeta_{NH_2}\zeta_{Cl} \tag{14}$$

$$2{\cdot}3487\{3/(n_1^2 + 2)\} = \zeta_{NH_2}\zeta_{CH_3} \tag{15}$$

$$-0{\cdot}1552\{3/(n_1^2 + 2)\} = \zeta_{CH_3}^2. \tag{16}$$

From Eq. 10,

$$\zeta_{OH} = 2{\cdot}1456\{3/(n_1^2 + 2)\}^{1/2} \tag{10'}$$

By substituting Eq. 10′ in Eqs. 11, 12 and 13, respectively,

$$\zeta_{NH_2} = 3{\cdot}7529\{3/(n_1^2 + 2)\}^{1/2} \tag{11'}$$

$$\zeta_{Cl} = \text{ca. } 1{\cdot}4328\{3/(n_1^2 + 2)\}^{1/2} \tag{12'}$$

$$\zeta_{CH_3} = 0{\cdot}8087\{3/(n_1^2 + 2)\}^{1/2}. \tag{13'}$$

From Eqs. 11′ and 12′,

$$\zeta_{NH_2}\zeta_{Cl} = \text{ca. } 5{\cdot}3772\{3/(n_1^2 + 2)\}.$$

This value is of the same order in Eq. 14, $6{\cdot}8953\{3/(n_1^2 + 2)\}$. Moreover, from Eqs. 11′ and 13′, the value of $\zeta_{NH_2}\zeta_{CH_3}$ is computed as $3{\cdot}0350\{3/(n_1^2 + 2)\}$ which is of the

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[28] S. Yamana, *Bull. Chem. Soc. Japan* **35**, 1421 (1962).

[29] S. Yamana, *Bull. Chem. Soc. Japan* **35**, 1269 (1962).

[30] By using Tables 3 and 6 and Ref. 20, $[M]_D^{20}$ of (+)-neomenthylamine, $23{\cdot}5 \equiv \sum_{X.Y} [\mu]^{20}_{D\,obs(XY)}$ of (+)-neomenthylamine $\simeq (CH_3)^{1\beta}\lambda(NH_2)^{3\alpha} + (CH_3)^{1\beta}\lambda(CH_3)^{4\alpha} + (CH_3)^{1\beta}\lambda(CH_3)^{\alpha8.d} + (CH_3)^{1\beta}\lambda(CH_3)^{\alpha8.e} + (CH_3)^{1\beta}\lambda ch.R + (NH_2)^{3\alpha}\lambda(CH_3)^{4\alpha} + (NH_2)^{3\alpha}\lambda(CH_3)^{\alpha8.d} + (NH_2)^{3\alpha}\lambda(CH_3)^{\alpha8.e} + (NH_2)^{3\alpha}\lambda ch.R + (CH_3)^{4\alpha}\lambda(CH_3)^{\alpha8.d} + (CH_3)^{4\alpha}\lambda(CH_3)^{\alpha8.e} + (CH_3)^{4\alpha}\lambda ch.R + (CH_3)^{\alpha8.d}\lambda(CH_3)^{8\alpha.e} + (CH_3)^{\alpha8.d}\lambda ch.R + (CH_3)^{\alpha8.e}\lambda ch.R = -2{\cdot}00\{(n_4^2 + 2)/3\}\kappa_{NH_2,CH_3} + 0 - 4{\cdot}41\{(n_4^2 + 2)/3\}\kappa_{CH_3,CH_3} + 4{\cdot}41\{(n_4^2 + 2)/3\}\kappa_{CH_3,CH_3} + 0 + 12{\cdot}39\{(n_4^2 + 2)/3\}\kappa_{NH_2,CH_3} + 1{\cdot}55\{(n_4^2 + 2)/3\}\kappa_{NH_2,CH_3} - 2{\cdot}00\{(n_4^2 + 2)/3\}\kappa_{NH_2,CH_3} + 0 + 0 + 0 + 0 + 0 + D - D = 9{\cdot}94\{(n_4^2 + 2)/3\}\kappa_{NH_2,CH_3}$

$$\therefore\ \kappa_{NH_2,CH_3} \simeq 2{\cdot}3642\{3/(n_4^2 + 2)\}$$

same order as that in Eq. 15, $2{\cdot}3487\{3/(n_1^2+2)\}$. These facts indicate that Eq. 7 may be applied and accordingly should be rewritten as

$$\kappa_{XY} \fallingdotseq \zeta_X\zeta_Y. \tag{7'}$$

The values of ζ_i may, of course, vary according to the type of compounds containing the unit group i. One explanation for the value of κ_{XY} being nearly but not exactly equal to the value of $\zeta_X\zeta_Y$ may be due to the incorrect assumption that all the compounds exist in only the C1 conformation. At any rate, the rightness of Eqs. 6 and 7′ indicate the availability of the PM-method. On the other hand, from Eq. 13′,

$$\zeta^2_{CH_3} = [0{\cdot}8087\{3/(n_1^2+2)\}^{1/2}]^2 = 0{\cdot}6540\{3/(n_1^2+2)\}. \tag{17}$$

This value differs from that given in Eq. 16, $-0{\cdot}1552\{3/(n_1^2+2)\}$, and therefore:

$$\kappa_{CH_3,CH_3} \neq \zeta^2_{CH_3}. \tag{18}$$

It is, therefore, apparent that the PM-method is not generally applicable.

The case where the PM-method does not apply

(+)-*cis*-3-methylcyclohexanol has no plane or centre of symmetry and accordingly it is optically active. ($[M]_D = 2{\cdot}2°$[31]). Both of its $\sum_{X,Y}[\mu]^{20}_{D\,calcd(XY)}$ and $\sum_{X,Y}[\mu]^{20}_{D\,obs(XY)}$ are, however, computed as zero. This discrepancy between the observed and the computed values may be due to the neglect of $\{g^{(1)}+\sum_i g^{(i)}\}$ in Eq. 2. But the case of Eq. 18 is somewhat different.

Being apparent in Table 1, $\sum_{X,Y}[\mu]^{20}_{D\,obs(XY)}$ of (+)-*trans*-1,3-dimethylcyclohexane,

$$I = (CH_3)^{1\beta}\lambda(CH_3)^{3\alpha}\,{}^{31} = (CH_3)^{1\beta}\times(CH_3)^{3\alpha}\{(n_1^2+2)/3\} = -9{\cdot}02\{(n_1^2+2)/3\}\zeta^2_{CH_3}\,{}^{32} \tag{19}$$

When using Eq. 17, the value of

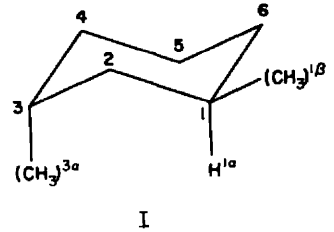
$$\sum_{X,Y}[\mu]^{20}_{D\,obs(XY)}$$

of (+)-*trans*-1,3-dimethylcyclohexane in Eq. 19 becomes −5·9 which is quite different from the observed value of $[M]^{20}_D$, 1·4.[31] This discrepancy between the computed and the observed values is too large to be explained by the neglect of

$$\{g^{(1)}+\sum_i g^{(i)}\}$$

in Eq. 2, and accordingly the following explanation should be considered.

The CH_3 group has no hydrogen bonding force and moreover its volume is fairly large. In (+)-*trans*-1,3-dimethylcyclohexane, therefore, each one of the two CH_3



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[31] cf. Table 1.

[32] Table 4 is used.

groups repulses the other H atoms in the molecule. Particularly, the axial CH_3 group (i.e. $(CH_3)^{3\alpha}$) repulses the $H^{1\alpha}$-atom fairly strongly which is under the butressing effect of the $(CH_3)^{1\beta}$ and this repulsion may cause some degree of distortion of the ring.[33] In this case, the cyclane ring is not symmetrical as regards to one or both of the two CH_3 groups and the partial rotation, $[\mu]_{D\ obs}^{20}$ due to the dynamic coupling effect between the distorted ring and CH_3 group may have a plus value. This can be the principal reason for the reversion of the sign of optical rotation as is also the case with (+)-*trans*-1,3-dimethylcyclopentane.

[33] R. Bentley, *J. Amer. Chem. Soc.* **82**, 2811 (1960).