A Further Extension of the Linear Relationship Between Molecular Rotation and Bond Refraction in Open-Chain Monosubstituted Alkanes†

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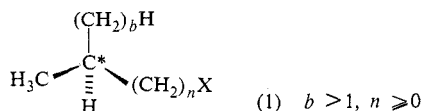Penang, Malaysia.

Abstract

It has been shown that, in the correlations of molecular rotations with bond refractions for open-chain monosubstituted alkanes, $H(CH_2)_b(CH_3)C^*H(CH_2)_nX$ ($b > 1$, $n \geqslant 0$), the compounds with different n and X for a given b can now be grouped into a single series.

Configuration determination of compounds is an important aspect of chemical research. Since optically active compounds have a common physical property, namely molecular rotation, that is easily measurable with a simple and inexpensive instrument, an ideal method for the determination of their configurations is one that can relate directly their molecular rotations to their configurations. We have shown the usefulness of the simple empirical equation[1]

$$[M]_D = m \Sigma R_D + I$$

in correlating the molecular rotations with bond refractions of structurally related series of monosubstituted alkanes[2] and carbohydrates[3] ($[M]_D$ is the molecular rotation, ΣR_D is the sum of bond refractions, and m and I are constants for a given series; the subscript $_D$ denotes the sodium D line).

$$
\begin{array}{c}
(CH_2)_bH \\
| \\
H_3C \diagup \overset{C^*}{\underset{H}{\equiv}} \diagdown (CH_2)_nX
\end{array}
\qquad (1) \quad b > 1, \ n \geqslant 0
$$

In our earlier correlations[2] of open-chain monosubstituted alkanes (1) we were not able to combine the compounds with different n and X for a given b into one single series. For each given b there were n separate series to be correlated.

[1] Davis, D. D., and Jensen, F. R., *J. Org. Chem.*, 1970, **35**, 3410.
[2] Poh, B.-L., *Aust. J. Chem.*, 1980, **33**, 1409.
[3] Poh, B.-L., *Carbohydr. Res.*, 1982, **108**, in press.

Table 1. Molecular rotations of monosubstituted alkanes (1)

b	n	Substituent and $[M]_b$ (neat, $22\pm3°C$)
2	0	OH 10·3,[A] NH_2 5·4,[B] CO_2H 18·0,[A] CO_2Me 27·8,[B] CO_2Et 22·9,[C] Ph 36·6,[C] NO_2 15·6,[B] CN 32·5,[B] Cl 35·3,[B] Br 48·4,[B] I 61·6,[B] HgBr 87·1,[B,D] HgCl 76·2,[B,D] CHO 20·3,[A,E] $CONH_2$ 19,[F,G] OAc 30[H]
2	1	NH_2 −5·1,[I] OH −5·2,[C] CO_2H 10·4,[A] CO_2Et 11·4,[C] F −8·0,[C] Ph 9·2,[C] Br 7·9,[A] COCl 18,[F] I 11,[B] Cl 1·8[B]
2	2	Br 38·8,[A] CO_2H 13·6,[A] NH_2 10·6,[C] OH 9·1,[J] CO_2Et 12·7,[C] CHO 12·0,[A,E] Ph 35·1,[K] COCl 19,[F] $CONH_2$ 19,[F,G] CN 17,[F] I 44[J]
2	3	Br 21·9,[A] CO_2H 11·1,[A] OH 11·9,[L] CO_2Et 13·0,[C] CHO 12·8,[A,E] H 9·9,[L] CN 17,[F] NH_2 12,[I] I 26[J]
2	4	H 11·4,[C] Br 14·9,[A] OH 12·0,[L] NH_2 16,[I] CO_2Et 13·7,[L] CO_2H 12·2[A]
2	5	H 12·5,[C] OH 12·5,[L] Br 14·0[A]
2	6	H 12·5[A]
3	0	OH 12·1,[A] CO_2H 21·4,[A] CO_2Et 27·5,[C] Ph 38,[C] CN 49,[F] Cl 46·5,[B] Br 63,[B] I 92,[B] COCl 14·4,[F] $CONH_2$ 24,[F,G] NH_2 5,[M] OAc 22[H]
3	1	CO_2H −3·6,[A] OH −6·8,[C] CO_2Et −0·7,[C] NH_2 −14,[I] COCl 4·6[F]
3	2	Br 21·0,[A] CO_2H 6·9,[A] NH_2 −0·4,[C] OH −2·1,[C] CO_2Et 5·5,[C] H −9·9,[L] COCl 6·8,[F] CN 2·0[F]
3	3	Br 14·5,[A] CO_2H 3·7,[A] OH 0,[C] NH_2 −0·7,[I] CO_2Et 5·9[C]
3	4	Br 7·8,[A] OH 1·7,[C] H 1·7[C]
3	5	H 2·4[C]
4	0	OH 12·2,[C] NH_2 7·8,[I] CO_2H 24·3,[A] CO_2Et 30·7,[C] Ph 39,[C] CN 51,[F] I 81,[C] COCl 12,[N] $CONH_2$ 18,[F,G] OAc 17[H]
4	1	OH −7·9,[A] CO_2H −6·1,[A] CO_2Et −2·9,[C] CN −6·0,[F] NH_2 −16,[A] COCl 3·5[F]
4	2	Br 16·8,[A] CO_2H 4·1,[A] NH_2 −1·7,[A] OH −4·0,[A] CO_2Et 2·3,[C] H −11·4,[A] CN −1·6[F]
4	3	COCl 3·5,[F] Br 8·3,[A] CO_2H 1·7,[A] H −1·7,[A] OH −0·7,[A] NH_2 −0·8,[A] CO_2Et 2·8,[C] $CONH_2$ 1·6,[F,G] CN 5·3[F]
4	4	Br 5·3,[A] OH 0,[A] NH_2 0·5,[A] CN 2·0[F]
4	5	H 0·8,[A] NH_2 2·4[A]
5	0	COCl 21,[N] CN 43,[N] CO_2H 26,[N] OH 12·5,[C] CO_2Et 32·6,[N] I 90·4,[C] Br 50·0,[C] OAc 13[H]
5	1	CO_2H −8·1,[C] OH −11·1,[N] I 5·4,[N] CO_2Et −4·2,[C] NH_2 −14·5[N]
5	2	Br 14·7,[A] CO_2H 1·9,[C] NH_2 −3·6,[C] H −12·0,[L] OH −6·1,[C] CO_2Et 0·5[C]
5	3	Br 6·2,[A] CO_2H 0·8,[C] OH −2·6,[C] H −2·4,[C] CO_2Et 1·7[C]
5	4	Br 4·0,[A] OH −1·9,[C] H −0·8[C]
6	0	OH 13,[B] NH_2 7,[I] NO_2 30·4,[F] F 16·4,[O] Cl 54,[B] Br 81·1,[B] I 115,[B] CO_2H 27[P]
6	1	CO_2H 26,[A] H −12·5[A]
7	0	CN 40,[O] CO_2H 27,[O] OH 13,[O] CO_2Et 36·5[L]
7	1	OH −11·2,[L] I 2·5,[J] CO_2H −8·1[A]
7	2	CO_2H 1·9[A]
7	3	CO_2H 0·6[A]

[A] Levene, P. A., and Rothen, A., J. Org. Chem., 1937, 1, 76.

[B] Ref. 1.

[C] Marker, R. E., J. Am. Chem. Soc., 1936, 58, 976.

[D] In ethanol.

[E] In heptane.

[F] Levene, P. A., Rothen, A., and Marker, R. E., J. Biol. Chem., 1936, 115, 253.

[G] In 75% alcohol.

[H] Klyne, W., 'Determination of Organic Structure by Physical Methods' pp. 73–130 (Academic Press: New York 1955).

[I] Levene, P. A., and Kuna, M., J. Biol. Chem., 1941, 140, 259.

[J] Levene, P. A., and Rothen, A., J. Biol. Chem., 1936, 115, 415.

[K] Levene, P. A., and Harris, S. A., J. Biol. Chem., 1935, 111, 725.

[L] Levene, P. A., and Marker, R. E., J. Biol. Chem., 1933, 103, 299.

[M] Levene, P. A., Rothen, A., and Marker, R. E., J. Biol. Chem., 1937, 120, 759.

[N] Levene, P. A., and Kuna, M., J. Biol. Chem., 1941, 140, 255.

[O] Filipo, J. S., Jr, and Romano, L. J., J. Org. Chem., 1975, 40, 1514.

[P] Levene, P. A., and Marker, R. E., J. Biol. Chem., 1933, 100, 685.

[Q] Brewster, J. H., J. Am. Chem. Soc., 1959, 81, 5475.

The combination of compounds with different n and X for a given b into the same series is now possible if we use the terms

$$\Sigma R_D(C^*(CH_2)_n X) - \Sigma R_D(C^*(CH_2)_b H)$$

instead of $\Sigma R_D(C^*(CH_2)_n X)$ for the substituents $(CH_2)_n X$ when $n > 0$. For $n = 0$, $\Sigma R_D(C^*X)$ is used as before.[2] When the literature $[M]_D$ values for six different series of monosubstituted alkanes (Table 1) are plotted against ΣR_D values by this approach, satisfactory correlations are obtained (Table 2) (the method of calculating the ΣR_D values has been described;[2] the ΣR_D values for $n \geqslant 2$ are calculated for the more stable antiperiplanar conformer,[2] and they give better correlations). The present extension will enhance the usefulness of the empirical equation in the correlations of molecular rotations of open-chain monosubstituted alkanes.

Table 2. **Correlations of molecular rotations with bond refractions in monosubstituted alkanes (1)**
p, number of points used in correlations; r, correlation coefficient

Series	p	r	Slope (m)	Intercept (I)	Series	p	r	Slope (m)	Intercept (I)
$b = 2$	56	0·978	3·74	6·18	$b = 5$	27	0·950	5·18	1·13
$b = 3$	34	0·925	5·43	0·20	$b = 6$	10	0·967	7·09	8·79
$b = 4$	38	0·910	4·60	1·12	$b = 7$	9	0·952	5·21	5·76

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