996. *Molecular Polarisability. Internal Rotation in n-Alkyl Bromides and Iodides*

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A theory is presented whereby expectation values for the anisotropic molecular polarisability tensor, and thence of the molar Kerr constant (averaged over allowed configurations), of n-alkyl halide molecules can be calculated. Only staggered configurations of the n-alkyl halide chain are allowed, and tetrahedral bond angles are assumed. Configurations are weighted according to *gauche/trans* energy differences and excluded volume considerations. The treatment is applied to n-propyl, n-butyl, n-pentyl, and n-hexyl bromides and iodides, satisfactory agreement between theory and experiment being obtained. For n-propyl bromide and iodide, *gauche/trans* energy differences (in kcal./mole) are $-0{\cdot}2_6 \pm 0{\cdot}5$ and $+1{\cdot}3_1 \pm 0{\cdot}5$, respectively.

This Paper deals with the calculation of expectation values for the anisotropic molecular polarisability tensor of n-alkyl halides. Such calculations are complicated by the problem of internal rotation in these molecules, since, unlike the molecular dipole moment, the molecular polarisability is sensitive to the configuration of the n-alkyl halide chain. These complications, however, suggest an approach which might be expected to give information concerning internal rotation in n-alkyl halides where methods involving dipole moments fail.

The general method here presented involves the calculation, by way of estimates of molecular polarisability, of expectation values for molar Kerr constants, and comparison of these values with observed molar Kerr constants, in order to test the adequacy of the molecular model chosen. The n-alkyl bromide series has already been treated [1] in this way, assuming rigid planar "zig-zag" or helical models of the n-alkyl chain and postulating an "equivalent" conformation of the C–Br bond to obtain agreement between observed and calculated results. The present treatment employs a dynamic model, averaged over all staggered configurations, in preference to the rigid models previously employed.[1] Similar dynamic models have been described for other systems.[2,3a,4] The n-alkane series has been treated in like manner,[5,6a,7] expectation values of the depolarisation ratio being

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[1] C. G. Le Fèvre, R. J. W. Le Fèvre, and A. J. Williams, *J.*, 1965, 4188.
[2] M. Aroney, D. Izsak, and R. J. W. Le Fèvre, *J.*, 1962, 1407.
[3] R. J. W. Le Fèvre and B. J. Orr, (*a*) *Austral. J. Chem.*, 1964, **17**, 1098; (*b*) preceding Paper.
[4] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J.*, 1965, 3619.
[5] R. S. Stein, *J. Chem. Phys.*, 1953, **21**, 1193.
[6] R. P. Smith and E. M. Mortensen, *J. Chem. Phys.*, (*a*) 1961, **35**, 714; (*b*) 1960, **32**, 502.
[7] C. Clément and P. Bothorel, *J. Chim. phys.*, 1964, 1262.

calculated. In this Paper, results have been calculated for n-propyl, n-butyl, n-pentyl, and n-hexyl bromides and iodides, for which experimental results are available.[1,3b]

THEORY

A Molecular Model.—Our treatment, which is analogous to that used for the n-alkane series,[6a] assumes that all bond angles are tetrahedral, and restricts allowed conformations to *gauche* (G), *trans* (T), and *gauche'* (G') types only. Such a model for aliphatic chains has been employed extensively.[8] It follows that, in all such staggered configurations, the bond direction vectors of the n-alkyl halide chain coincide with those of a diamond lattice. Choosing reference axes X, Y, Z to coincide with the co-ordinate system of the diamond lattice, and giving each bond-direction vector a magnitude of $\sqrt{3}$ units, it follows that every vector projects on every axis as 1 or -1 (written as $\bar{1}$ for convenience). The bond-direction vectors, numerically labelled, are: 0, 111; 1,$\bar{1}11$; 2, $1\bar{1}1$; 3, $11\bar{1}$; 4, $\bar{1}\bar{1}\bar{1}$; 5, $1\bar{1}\bar{1}$; 6, $\bar{1}1\bar{1}$; 7, $\bar{1}\bar{1}1$.

Calculation of the Molecular Polarisability Tensor.—The problem of estimating the polarisability tensor of a molecule by addition of band polarisability tensors has been treated in several ways.[5-7,9-11] A treatment based on the methods of Smith and Mortensen,[6] and specifically applicable to the n-alkyl halides, is here presented.

For any bond, the polarisability tensor, referred to the longitudinal, transverse, and vertical bond axes (L, T, V, respectively), is

$$\alpha = \begin{bmatrix} b_L & 0 & 0 \\ 0 & b_T & 0 \\ 0 & 0 & b_V \end{bmatrix}.$$

This tensor may be referred to an arbitrary set of axes, X, Y, Z, by means of the orthogonal transformation:

$$\alpha' = \begin{bmatrix} b_{XX} & b_{XY} & b_{XZ} \\ b_{YX} & b_{YY} & b_{YZ} \\ b_{ZX} & b_{ZY} & b_{ZZ} \end{bmatrix} = \lambda \, . \, \alpha \, . \, \lambda' \qquad (1)$$

where

$$\lambda = \begin{bmatrix} l_X & t_X & v_X \\ l_Y & t_Y & v_Y \\ l_Z & t_Z & v_Z \end{bmatrix}$$

is the orthogonal transformation matrix relating the principal axes L, T, V of the bond to the axes X, Y, Z, and its elements (l_X, t_X, v_X, etc.) are the corresponding direction cosines. λ' is the transpose of λ.

If the polarisability tensors of all the bonds in a molecule of given geometry are referred to the same set of arbitrary axes, X, Y, Z, then the components of the molecular polarisability tensor $\mathbf{A}'$, referred to axes X, Y, Z, can be obtained simply by summation of the corresponding bond tensor components, giving

$$\mathbf{A}' = \begin{bmatrix} B_{XX} & B_{XY} & B_{XZ} \\ B_{YX} & B_{YY} & B_{YZ} \\ B_{ZX} & B_{ZY} & B_{ZZ} \end{bmatrix} = \sum_{i=1}^{n} \alpha'(i) \qquad (2)$$

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[8] S. Mizuschima, "Structure of Molecules and Internal Rotation," Academic Press, New York, 1954.

[9] C. G. Le Fèvre and R. J. W. Le Fèvre, (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*b*) ch. XXXVI "Physical Methods of Organic Chemistry," ed. A. Weissberger, Interscience, New York, 3rd edn., vol. I, p. 2459.

[10] R. J. W. Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

[11] J. M. Eckert and R. J. W. Le Fèvre, *J.*, 1962, 1081.

Here, the symbol B represents components of molecular polarisability, the symbol b being reserved for bond polarisability components. Similarly, the symbols $\mathbf{A}$ and $\mathbf{A}'$ represent molecular polarisability tensors, referred, respectively, to principal and arbitrary axes, whilst α and α' are reserved for bond polarisability tensors; $b(i)$ represents components of the bond polarisability tensor $\alpha'(i)$ of the ith bond, and n is the number of bonds in the molecule.

Employing the factorisation procedure of Smith and Mortensen,[6b] equation (1) becomes

$$\alpha'(i) = \lambda(i) \,.\, \alpha(i) \,.\, \lambda'(i) = \bar{\alpha}(i)\mathbf{I} + \tfrac{1}{3}\gamma(i)\mathbf{F}(i) + \delta(i)\mathbf{G}(i), \tag{3}$$

where $\bar{\alpha}(i) = \tfrac{1}{3}[b_{\mathrm{L}}(i) + b_{\mathrm{T}}(i) + b_{\mathrm{V}}(i)]$, $\gamma(i) = b_{\mathrm{L}}(i) - \tfrac{1}{2}[b_{\mathrm{T}}(i) + b_{\mathrm{V}}(i)]$,

$\delta(i) = \tfrac{1}{2}[b_{\mathrm{T}}(i) - b_{\mathrm{V}}(i)]$, $\mathbf{I}$ is the unit matrix,

$$\mathbf{F}(i) = \lambda(i) \,.\, \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \,.\, \lambda'(i), \text{ and } \mathbf{G}(i) = \lambda(i) \,.\, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \,.\, \lambda'(i).$$

Summation of the $\alpha'(i)$ gives, by equation (2),

$$\mathbf{A}' = \sum_{i=1}^{n} \alpha'(i) = \mathbf{I}\sum_{i=1}^{n} \bar{\alpha}(i) + \tfrac{1}{3}\sum_{i=1}^{n} \gamma(i)\mathbf{F}(i) + \sum_{i=1}^{n} \delta(i)\mathbf{G}(i) \tag{4}$$

The factor $\sum_{i=1}^{n} \bar{\alpha}(i)$ may be recognised as the mean molecular electronic polarisability, α_{E}. Equation (4) gives an expression for the molecular polarisability tensor, $\mathbf{A}'$, in which components of bond polarisability appear as scalar coefficients of matrices which are functions only of molecular geometry.

For n-alkyl halides, in which it may be assumed that all bond angles are tetrahedral and all bonds axially symmetric, equation (4) reduces [6b] to

$$\mathbf{A}' = \mathbf{I}\alpha_{\mathrm{E}} + \tfrac{1}{3}\Gamma_{\mathrm{CX}}\mathbf{F}(i) + \tfrac{1}{3}\Gamma_{\mathrm{CC}}\sum_{\mathrm{CC}}\mathbf{F}(i), \tag{5}$$

where $\Gamma_{\mathrm{CX}} = (\gamma_{\mathrm{CX}} - \gamma_{\mathrm{CH}})$, $\Gamma_{\mathrm{CC}} = (\gamma_{\mathrm{CC}} - 2\gamma_{\mathrm{CH}})$, and X = halogen. The summation is taken over C–C bonds only.

With the additional assumption that n-alkyl halide chains assume only staggered configurations, and choosing the axes X, Y, Z to coincide with the axes of the diamond lattice unit-cell, it may be shown, by analogy with the n-alkene series,[6a] that the components of $\mathbf{A}'$ are given by

$$\begin{aligned} B_{\mathrm{XX}} &= B_{\mathrm{YY}} = B_{\mathrm{ZZ}} = \alpha_{\mathrm{E}}, \\ B_{\mathrm{XY}} &= B_{\mathrm{YX}} = \tfrac{1}{3}[\Gamma_{\mathrm{CX}} + \Gamma_{\mathrm{CC}}(n_0 - n_1 - n_2 + n_3)], \\ B_{\mathrm{XZ}} &= B_{\mathrm{ZX}} = \tfrac{1}{3}[\Gamma_{\mathrm{CX}} + \Gamma_{\mathrm{CC}}(n_0 - n_1 + n_2 - n_3)], \\ B_{\mathrm{YZ}} &= B_{\mathrm{ZY}} = \tfrac{1}{3}[\Gamma_{\mathrm{CX}} + \Gamma_{\mathrm{CC}}(n_0 + n_1 - n_2 - n_3)], \end{aligned} \tag{6}$$

where the C–X bond is taken always to lie along direction 0, and n_0, n_1, n_2, n_3 are the numbers of C–C bonds lying along directions 0 or 4, 1 or 5, 2 or 6, 3 or 7, respectively. Hence, with the molecular model described above, the evaluation of $\mathbf{A}'$ for a particular configuration is reduced to a determination of n_0, n_1, n_2, and n_3, provided that the polarisability parameters α_{E}, Γ_{CX}, and Γ_{CC} are known.

In order to evaluate molar Kerr constants for each configuration of the n-alkyl halide chain, it is necessary to obtain the molecular polarisability tensor in its diagonalised form:[10,11]

$$\mathbf{A} = \begin{bmatrix} B_1 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & B_3 \end{bmatrix}.$$

In the present work, this process has been performed by the Sydney University digital computers SILLIAC and KDF9. The principal molecular polarisabilities, B_1, B_2, B_3, together with the principal components, μ_1, μ_2, μ_3, of dipole moment, may then be used to calculate the molar Kerr constant in the usual way.[9-11]

Identification of Configurations.—As a matter of convenience in determining configurational stability, each configuration of the n-alkyl halide chain is labelled according to the sequence of conformations of each set of three consecutive C–X or C–C bonds, commencing with the C–X bond and proceeding bond by bond along the chain. For example, the nine staggered configurations of n-butyl halides are labelled in this scheme as GG, GT, GG', TG, TT, TG', $G'G$, $G'T$, and $G'G'$. The first letter of each label indicates whether the second C–C bond of the chain is *gauche*, *trans*, or *gauche'* with respect to the C–X bond and the first C–C bond. The second letter of each label indicates the conformation of the third C–C bond with respect to the first and second C–C bonds. The labelling convention can readily be extended to longer n-alkyl halide chains.

Evaluation of n_0, n_1, n_2, n_3.—Assuming that the polarisability data, α_E, Γ_{CX}, and Γ_{CC}, are known, all that remains in determining the molecular polarisability tensor **A**′ of a particular configuration is to relate the configuration label to the quantities n_0, n_1, n_2, n_3. This can be achieved by means of Table 1, in which the direction of the ith bond is expressed as a function of the directions of bonds $(i - 1)$ and $(i - 2)$, and of its conformation (G, T, or G') with respect to those bonds. In the present work, the C–X bond and first C–C bond have been chosen by convention to lie along directions 0 and 3, respectively. The values of n_0, n_1, n_2, and n_3 for the various staggered configurations of n-propyl, n-butyl, n-pentyl, and n-hexyl halides have been estimated on the basis of this scheme, and have been used in calculating molecular polarisability.

TABLE 1

Configurational code for staggered n-alkyl halide chains

Conformation of bond i	Bond direction			Conformation of bond i	Bond direction			Conformation of bond i	Bond direction		
	$(i - 2)$	$(i - 1)$	i		$(i - 2)$	$(i - 1)$	i		$(i - 2)$	$(i - 1)$	i
G			7	G			1	G			4
T	0	1	0	T	4	7	4	T	3	5	3
G'			6	G'			2	G'			2
G			5	G			7	G			1
T	0	2	0	T	6	4	6	T	3	6	3
G'			7	G'			5	G'			4
G			6	G			0	G			6
T	0	3	0	T	6	1	6	T	5	4	5
G'			5	G'			7	G'			7
G			1	G			5	G			7
T	2	0	2	T	6	3	6	T	5	2	5
G'			3	G'			0	G'			0
G			3	G			3	G			0
T	2	5	2	T	1	0	1	T	5	3	5
G'			4	G'			2	G'			6
G			4	G			4	G			5
T	2	7	2	T	1	6	1	T	7	4	7
G'			1	G'			3	G'			6
G			2	G			2	G			6
T	4	5	4	T	1	7	1	T	7	1	7
G'			3	G'			4	G'			0
G			3	G			2	G			0
T	4	6	4	T	3	0	3	T	7	2	7
G'			1	G'			1	G'			5

Configurational Stability of an n-Alkyl Halide Chain.—Evaluation of the expectation value, $\langle {}_{\mathrm{m}}K \rangle$, of the molar Kerr constant requires a knowledge of the relative stability of each of the possible configurations. This can be achieved by assigning a statistical configurational weight, X_j, to the jth configuration, and applying the relationship:

$$\langle {}_{m}K \rangle = \sum_{j=1}^{n} {}_{m}K_j \, . \, X_j \tag{7}$$

where ${}_{m}K_j$ is the molar Kerr constant calculated for the jth configuration, and summation is carried over all n configurations. No allowance has been made in the present treatment for the effects of differing partition functions of the various configurations. Such effects, however, have been shown [6a, 7, 8] to be negligibly small in similar systems.

The configurational weight, X_j, can be evaluated from the relationship:

$$X_j = \exp\,(-U_j/\boldsymbol{k}T) / \sum_{j=1}^{n} \exp\,(-U_j/\boldsymbol{k}T) \tag{8}$$

where U_j is the internal potential energy of the jth configuration. U_j (referred to $U = 0$ for the completely *trans* configuration) can be estimated by summation of the energetic contributions of each *gauche* or *gauche'* conformation in the chain. Hence, each time G or G' appears in the configuration label, a contribution ΔE, corresponding to the energy difference between *gauche* and *trans* conformations of the particular sequence of three bonds, is made to U_j. If G or G' appears as the first letter in the configurational label, ΔE is the *gauche/trans* energy difference estimated for the corresponding n-propyl halide. In all other cases, ΔE may be taken as $+0{\cdot}8$ kcal./mole, which is the *gauche/trans* energy difference found in hydrocarbon chains.[7, 12]

It is also necessary to make allowance for the so-called " excluded volume " effect, which arises from large steric interactions resulting when two atoms tend to occupy the same site. Configurations in which such an effect arises are disallowed, and may be excluded from calculations of the expectation value, $\langle {}_{m}K \rangle$. Examination of molecular models of n-alkyl bromides and iodides indicates that it is possible to employ a criterion for exclusion identical with that in the n-alkane series.[6a] Hence, for n-alkyl bromides and iodides with nine or fewer carbon atoms, the disallowed isomers are those in which the sequence GG' (or $G'G$) occurs in the configuration label. Longer chains with this sequence are also disallowed, but in addition certain other isomers are disallowed.

RESULTS AND DISCUSSION

Direction of Resultant Dipole Moment.—In order to calculate ${}_{m}K_j$, it is necessary to know the direction of action of the resultant dipole moment, μ_{res}, with respect to the axes X, Y, Z. Following the treatment of this problem employed in the preceding Paper,[3b] we assume alternatively that (a) μ_{res} may be taken to lie along the C–X axis, or (b) μ_{res} acts at an angle χ to the C–X axis, as the resultant of the methyl halide dipole moment along the C–X bond and an induced moment, μ_{res}, along the primary C–C bond. It has therefore been assumed that, for the n-alkyl halides, χ is negligibly affected by changes in molecular configuration, since induced moment effects in the hydrocarbon chain beyond the primary C–C bond should be small. For the n-alkyl iodides, treatment (b) yielded [3b] $\mu_{ind} = 0{\cdot}65 \pm 0{\cdot}05$ D and $\chi = 20° \pm 1°$. For the n-alkyl bromides,[1] $\mu_{res} = 1{\cdot}95 \pm 0{\cdot}02$ D and $\mu_{CH_3Br} = 1{\cdot}73$ D, whence treatment (b) yields $\mu_{res} = 0{\cdot}49 \pm 0{\cdot}04$ D and $\chi = 14° \pm 3°$. Values of μ_{ind} employed in calculating ${}_{m}K_j$ are as determined experimentally.[1, 3b] As Table 3 indicates, the difference between the results calculated with treatments (a) and (b) is small, except for n-pentyl and n-hexyl iodide.

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[12] S. Mizushima, p. 98 of ref. 7; N. P. Borisova and M. W. Wolkenstein, *Zhur. strukt. Khim.*, 1961, **2**, 469; K. Nagai and T. Ishikawa, *J. Chem. Phys.*, 1962, **37**, 496; L. S. Bartell and D. A. Kohl, *ibid.*, 1963, **39**, 3097.

*Bond Polarisability Data.**—Polarisability data for the C–X bond in n-alkyl halides can be evaluated from the corresponding ethyl halide. Such data were calculated in the preceding Paper [3b] for ethyl iodide, employing both treatments (a) and (b) of dipole moment direction. Similar calculations for ethyl bromide yield corresponding data for the C–Br bond. These results, together with the usual polarisabilities for C–C and C–H bonds,[10] allow tabulation of the following data:

TABLE 2

Values of ${}_mK_j$ and X_j for n-alkyl halides

Allowed configurations	X_j	$10^{12}{}_mK_j$ (a)	$10^{12}{}_mK_j$ (b)	X_j	$10^{12}{}_mK_j$ (a)	$10^{12}{}_mK_j$ (b)
		n-Propyl bromide			*n-Propyl iodide*	
G,G′	0·378	+93·8	+89·8	0·089	+95·0	+99·5
T	0·244	+137·4	+133·8	0·821	+132·1	+128·7
		n-Butyl bromide			*n-Butyl iodide*	
GG, G′G′	0·074	+82·0	+74·9	0·016	+87·4	+94·9
GT, G′T	0·286	+82·7	+87·5	0·061	+88·2	+86·9
TG, TG′	0·048	+125·2	+118·6	0·145	+124·8	+124·0
TT	0·185	+125·9	+131·2	0·558	+125·6	+115·9
		n-Pentyl bromide			*n-Pentyl iodide*	
GGG, G′G′G′	0·013	+114·1	+104·4	0·003	+120·4	+124·0
GGT, G′G′T	0·051	+71·6	+61·5	0·011	+82·0	+85·8
GTG, G′TG′	0·051	+71·6	+73·4	0·011	+82·0	+108·2
GTT, G′TT	0·197	+72·3	+74·1	0·042	+82·2	+143·6
GTG′, G′TG	0·051	+114·8	+117·0	0·011	+121·1	+139·9
TGG, TG′G′	0·008	+114·1	+104·4	0·026	+120·4	+124·0
TGT, TG′T	0·033	+158·1	+148·7	0·101	+160·0	+163·3
TTG, TTG′	0·033	+114·8	+117·0	0·101	+121·1	+139·9
TTT	0·127	+158·8	+161·3	0·389	+160·9	+179·7
		n-Hexyl bromide			*n-Hexyl iodide*	
GGGG, G′G′G′G′	0·002	+104·6	+103·7	0·001	+109·5	+125·1
GGGT, G′G′G′T	0·009	+104·6	+91·7	0·002	+109·5	+109·6
GGTG, G′G′TG′	0·009	+104·6	+91·7	0·002	+109·5	+109·6
GGTT, G′G′TT	0·035	+61·7	+48·3	0·008	+71·3	+71·8
GGTG′, G′G′TG	0·009	+61·7	+60·4	0·002	+71·3	+87·2
GTGG, G′TG′G′	0·009	+104·6	+103·7	0·002	+109·5	+125·1
GTGT, G′TG′T	0·035	+62·3	+73·1	0·008	+72·2	+103·1
GTTG, G′TTG′	0·035	+61·7	+60·4	0·008	+71·3	+87·2
GTTT, G′TTT	0·137	+63·0	+73·8	0·030	+73·1	+103·9
GTTG′, G′TTG	0·035	+105·3	+104·4	0·008	+110·3	+125·6
GTG′T, G′TGT	0·035	+106·0	+117·1	0·008	+110·9	+141·7
GTG′G′, G′TGG	0·009	+104·6	+103·7	0·002	+109·5	+125·1
TGGG, TG′G′G′	0·002	+104·6	+103·7	0·005	+109·5	+125·1
TGGT, TG′G′T	0·006	+104·6	+91·7	0·018	+109·5	+109·6
TGTG, TG′TG′	0·006	+148·3	+135·7	0·018	+148·5	+144·2
TGTT, TG′TT	0·023	+149·0	+136·4	0·070	+148·9	+148·1
TGTG′, TG′TG	0·006	+149·0	+148·5	0·018	+148·9	+163·4
TTGG, TTG′G′	0·006	+104·6	+103·7	0·018	+109·5	+125·1
TTGT, TTG′T	0·023	+106·0	+117·1	0·070	+110·9	+141·7
TTTG, TTTG′	0·023	+149·0	+148·5	0·070	+148·9	+163·4
TTTT	0·088	+150·3	+161·9	0·271	+150·1	+180·6

	Γ_{CC}	Γ_{CBr}	Γ_{CI}	$\bar{\alpha}_{CC}$	$\bar{\alpha}_{CH}$	$\bar{\alpha}_{CBr}$	$\bar{\alpha}_{CI}$
Treatment (a)	0·72	$2{\cdot}6_0$	$3{\cdot}0_5$	0·51	0·64	3·57	5·52
Treatment (b)	0·72	$2{\cdot}6_0$	$3{\cdot}7_5$	0·51	0·64	3·57	5·52

It is to be noted that change of dipole moment direction has a negligible effect on Γ_{CBr}, as extracted from ethyl bromide, in contrast to Γ_{CI} in ethyl iodide. The mean molecular electronic polarisability, α_E, can readily be evaluated by summation of the $\bar{\alpha}$'s over all

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* Molecular and bond polarisabilities are throughout expressed in 10^{-24} c.c. units.

bonds in the molecule, as in equation (4). This provides all the information necessary to calculate ${}_{\mathrm{m}}K_{\mathrm{j}}$, values of which appear in Table 2.

TABLE 3

Observed and calculated molar Kerr constants for n-alkyl halides

		$10^{12}\langle{}_{\mathrm{m}}K\rangle$				$10^{12}\langle{}_{\mathrm{m}}K\rangle$	
Bromide	$10^{12}{}_{\mathrm{m}}K$ (obs.)	(a)	(b)	Iodide	$10^{12}{}_{\mathrm{m}}K$ (obs.)	(a)	(b)
n-Propyl	$+103 \pm 5$	$+104$	$+100$	n-Propyl	$+123 \pm 4$	$+125$	$+123$
n-Butyl	$+105 \pm 6$	$+95$	$+97$	n-Butyl	$+117 \pm 1$	$+120$	$+114$
n-Pentyl	$+105 \pm 5$	$+98$	$+97$	n-Pentyl	$+121 \pm 4$	$+140$	$+158$
n-Hexyl	$+102 \pm 8$	$+92$	$+96$	n-Hexyl	$+126 \pm 2$	$+130$	$+150$

Evaluation of ΔE *for n-Propyl Halides.*—Values of the *gauche*/*trans* energy difference, ΔE, for n-propyl bromide and iodide have been chosen to obtain optimum agreement between calculated and observed molar Kerr constants. For n-propyl bromide, $\Delta E = -0{\cdot}2_6 \pm 0{\cdot}5$ kcal./mole; for n-propyl iodide, $\Delta E = +1{\cdot}3_1 \pm 0{\cdot}5$ kcal./mole. Errors quoted have been estimated from standard deviations in observed molar Kerr constants. Spectroscopic determinations [13,14] give ΔE's for n-propyl bromide ranging from 0·0 to −0·4 kcal./mole, in good agreement with our results. No previous determination of ΔE for n-propyl iodide has been recorded. Whereas ΔE for n-propyl bromide is of the same order as that for n-propyl chloride [13,15] and fluoride,[16] ΔE for n-propyl iodide is considerably greater, the *gauche*-isomers being much less stable than the *trans*-isomer. This effect is apparently due to the increased steric repulsion associated with *gauche* conformations of the bulky iodine atom. With the above values of ΔE, it is possible to calculate the configurational weights, X_{j}, as in Table 2.

Evaluation of $\langle{}_{\mathrm{m}}K\rangle$ *for n-Propyl Halides.*—Values of $\langle{}_{\mathrm{m}}K\rangle$, calculated from the data of Table 2 by means of equation (7), are compared with experimental results, ${}_{\mathrm{m}}K$(obs.), in Table 3. It is estimated that the uncertainty associated with each value of $10^{12}\langle{}_{\mathrm{m}}K\rangle$ is *ca.* ±10. Hence, agreement is satisfactory in all cases but that of n-pentyl iodide, for which $\langle{}_{\mathrm{m}}K\rangle$ is appreciably higher than ${}_{\mathrm{m}}K$(obs.). Agreement is particularly good for the n-alkyl bromide series, and for n-butyl iodide. The close agreement of the n-propyl halides is, of course, achieved by appropriately choosing ΔE.

Conclusions.—In view of the results presented above, it can be concluded that the molecular model examined is consistent with experiment, and that molar Kerr constants in the n-alkyl bromide and iodide series can be satisfactorily predicted in terms of a limited number of polarisability and energy parameters. The present model is preferable to that previously employed [1] for the n-alkyl bromides, in that it is more consistent with accepted treatments of internal rotation in aliphatic systems [8] and does not involve empirical determination of " equivalent " conformations. The fact, that ΔE for n-propyl bromide as determined above agrees well with the results of other methods [13,14] encourages confidence in the value of ΔE calculated for n-propyl iodide ($+1{\cdot}3_1 \pm 0{\cdot}5$ kcal./mole), for which no previous determination is recorded.

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