769. *Molecular Polarisability. The Molar Kerr Constants of n-Alkyl Bromides*

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The molar Kerr constants, at infinite dilution in carbon tetrachloride, of ethyl and higher n-alkyl bromides up to $C_{18}H_{37}Br$ appear almost independent of molecular size and weight. Using $b_L^{C-Br} = 5.30$ and $b_T^{C-Br} = 2.70$ with a C–C–Br angle of 109°, the $_mK$ calculated for ethyl bromide is 100.1×10^{-12} *versus* 100.6×10^{-12} by experiment. Numerically satisfactory predictions of the $_mK$'s for bromides with five or more carbon atoms can be based on either planar, zig-zag, or helical arrangement of the C_nH_{2n+1} groups.

THIS Paper adds measurements of the molar Kerr constants $_\infty(_mK_2)$ of the n-alkyl bromides of the previous Paper at infinite dilution in carbon tetrachloride at 25°; it proceeds *inter alia* to examine whether these $_\infty(_mK_2)$'s can be calculated *a priori* from a knowledge of the longitudinal, b_L^{C-Br}, and transverse, b_T^{C-Br}, polarisabilities of the C–Br link, together with other information drawn from electric birefringence data on the related n-hydrocarbons.

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TABLE 1

Electric double refractions and refractive indices of solutions of n-bromides in carbon tetrachloride

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Ethyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
611	0·050	−1
887	0·076	−2
1096	0·085	−2
1130	0·096	−2
2090	0·164	−6
5560	0·342	−13

n-Propyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
714	0·060	−2
1380	0·104	−2
1443	0·109	−2
1461	0·111	−3
2131	0·162	−4
2143	0·162	−4

n-Butyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
590	0·046	−1
999	0·074	−3
1942	0·137	−4
2263	0·168	—
2824	—	−6
3318	—	−6
4009	0·275	—
4173	0·276	—
4661	—	−7
4852	0·347	—

n-Pentyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
384	0·023	ca. 0
809	0·054	,, 0
1371	0·092	−2
1698	0·119	−3
1725	0·105	−2
1967	0·134	−2
2626	0·180	−4
2684	0·179	−3
2771	0·180	−3
3816	0·257	−5

n-Hexyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
224	0·015	ca. 0
392	0·022	,, 0
809	0·043	−1
980	0·058	−1
1024	0·060	−1
3317	0·186	−2

n-Heptyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
276	0·015	ca. 0
921	0·051	,, 0
1162	0·067	,, 0
1817	0·103	−1
3296	0·183	−3
3892	0·216	−4

n-Octyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
158	0·006	ca. 0
812	0·042	,, 0
1550	0·076	,, 0
1609	0·082	,, 0
2710	0·133	,, 0
3665	0·187	−2
3857	0·195	−2
6977	0·334	−4

n-Nonyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
241	0·003	ca. 0
462	0·018	,, 0
551	0·023	,, 0
571	0·029	,, 0
650	0·028	,, 0
767	0·032	−1
1021	0·041	−1
1036	0·045	−1
1526	0·068	—
2248	0·097	—
2879	—	−2
3049	—	−3

n-Decyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
556	0·034	ca. 0
1162	0·049	,, 0
1178	0·051	,, 0
1667	0·066	,, 0
3439	0·146	,, 0
6669	0·284	−2

n-Dodecyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
841	0·031	ca. 0
2228	0·082	,, 0
2679	0·099	,, 0
2876	0·106	−1
2956	0·108	−1
3104	0·113	−2

n-Hexadecyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
512	0·018	ca. 0
901	0·029	,, 0
1716	0·055	,, 0
1735	0·056	,, 0
3072	0·090	,, 0
3543	0·104	,, 0

n-Octadecyl bromide

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$
967	0·016	ca. 0
909	0·025	,, 0
1137	0·039	−1
1150	0·037	−1
1178	0·035	—
1872	0·058	−1
2040	0·065	−1
2190	0·064	—
2591	0·081	−2
2553	—	−2
2771	0·086	—
2782	0·081	−2

Practical procedures, definitions of symbols, details of calculation methods, etc., follow those described by Le Fèvre and Le Fèvre.[1] The changes in the Kerr constant and refractive index caused in carbon tetrachloride by a weight fraction w_2 of solute bromide are listed in Table 1 under ΔB and Δn, respectively. Since, in general, graphs of ΔB *versus* w_2 are curved while those of Δn *versus* w_2 are rectilinear, the ΔB's are fitted by least squares to equations of the form $(\Delta B)_{w_2} = P w_2 + Q w_2^2$, and the Δn's are averaged as $S = \Sigma \Delta n / \Sigma w_2$. Table 2 shows values of P, Q, and S for the various bromides. As explained in ref. 1, it is assumed that at high dilutions, approaching $w_2 = 0$, both properties are rectilinear with w_2, *i.e.*,

$$B_{12} = B_1(1 + w_2 \delta), \text{ and } n_{12} = n_1(1 + w_2 \gamma),$$

so that the desired coefficients δ and γ, appropriate to infinite dilution, are given by $P = B_1 \delta$ and $S = n_1 \gamma$ (cf. Table 3); then:

$$_\infty(_mK_2) = M_2[_sK_1(1 - \beta + \gamma + \delta - H\gamma - J\alpha\varepsilon_1)].$$

The required density and dielectric constant factors (β and $\alpha\varepsilon_1$) are in the preceding Paper;

[1] C. G. Fèvre and R. J. W. Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (b) *J.*, 1953, 4041; (c) *J.*, 1954, 1577; (d) ch. XXXV in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York, London, 3rd edn., vol. I, p. 2459; (e) *J.*, 1956, 3549.

other data needed for carbon tetrachloride at 25° and with sodium D-light are: $B_1 = 0.070 \times 10^{-7}$, $n_1 = 1.4575$, $H = 2.060$, $J = 0.4731$, $_sK_1 = 0.749 \times 10^{-14}$. (Subscripts 1, 2, and 12 denote, respectively, solvent, solute, and solution.)

TABLE 2

Coefficients P and Q in equations fitted by least squares to observations in Table 1; also values of $S = \Sigma\Delta n/\Sigma w_2$

n-Bromide	P	Q	$-10^4 S$	n-Bromide	P	Q	$-10^4 S$
Ethyl	8·767	$-4·7_0$	229	Octyl	$5·21_2$	$-5·8_7$	47
Propyl	$6·90_8$	$-16·9$	183	Nonyl	$4·19_2$	$+7·1_8$	60
Butyl	$7·25_2$	$-7·12$	188	Decyl	$4·26_3$	$+0·2_4$	10
Amyl	$6·57_6$	$+3·8_7$	80	Dodecyl	$3·75_7$	$-3·2_1$	27
Hexyl	$5·80_5$	$-5·8_9$	82	Hexadecyl	$3·45_3$	$-15·4$	*ca.* 0
Heptyl	$5·72_4$	$-4·6_6$	89	Octadecyl	$3·15_5$	$-4·2_8$	40

TABLE 3

Calculations of $_\infty(_mK_2)$ for n-alkyl bromides *

Solute	$\alpha\varepsilon_1$	$-\beta$	$-\gamma$	δ	$_\infty(_mK_2) \times 10^{12}$
CH_3Br	5·72	$-0·051$	0·028	74·3	51·6
C_2H_5Br	6·44	0·084	0·016	125·2	100·6
C_3H_7Br	5·87	0·175	0·013	113·0	102·6
C_4H_9Br	5·23	0·249	0·013	103·6	105·1
$C_5H_{11}Br$	4·76	0·297	0·006	93·94	105·2
$C_6H_{13}Br$	4·37	0·351	0·006	82·92	101·7
$C_7H_{15}Br$	3·99	0·394	0·006	81·77	109·0
$C_8H_{17}Br$	3·68	$0·412_5$	0·003	74·46	107·2
$C_9H_{19}Br$	3·33	0·448	0·004	59·89	92·8
$C_{10}H_{21}Br$	3·07	0·489	0·001	60·90	100·9
$C_{12}H_{25}Br$	2·82	0·533	0·002	53·67	100·6
$C_{16}H_{33}Br$	2·26	0·597	*ca.* 0	49·33	114·0
$C_{18}H_{37}Br$	2·07	0·601	0·003	45·07	114·1

* Data for CH_3Br from ref. 1 (1954); values of $\alpha\varepsilon_1$ and β from preceding Paper.

DISCUSSION †

The $_\infty(_mK_2)$'s of ethyl and subsequent bromides in Table 3 fall between the limits $92·8 \times 10^{-12}$ for $C_9H_{19}Br$ and $114·1 \times 10^{-12}$ for $C_{18}H_{37}Br$; their mean value is 104×10^{-12}. They appear nearly independent of molecular size or weight, and this together with the near-constancy of the dipole moments throughout the series implies that the $_mK$'s of higher bromides might be calculable *a priori* provided the polarisability ellipsoid for ethyl bromide can be established.

The Molar Kerr Constant and Principal Polarisabilities of Ethyl Bromide.—In this molecule the C–C–Br angle [2] is reputed to be $109° \pm 2°$; in what follows we take it as tetrahedral and proceed to calculate [3,4] b_1, b_2, and b_3 for ethyl bromide from the longitudinal and transverse polarisabilities of the C–H, C–C, and C–Br bonds, with the resultant moment directed along the C–Br link. For C–H, $b_L = b_T = b_V = 0·64$, and for C–C, $b_L = 0·99$, $b_T = 0·27$ (cf. ref. 1a). There is some doubt concerning the proper values for C–Br in the structural environment of ethyl bromide. Table 4 shows the results of using data from (a) methyl bromide,[1c] (b) *t*-butyl bromide,[1a] and (c) cyclopentyl bromide; [1e] of these, set (c) yields an $_mK$ calc. (100×10^{-12}) in satisfactory agreement with the $_mK$ found (101×10^{-12}). The total, $b_1 + b_2 + b_3 = 21·83$, corresponds to an electronic polarisation of 18·36 c.c., so that $_EP/R_D$ is $0·96_3$, *i.e.*, well within the range for such quotients. Complete certainty regarding $_EP$ is never possible. The molecular refractions listed for ethyl bromide by Vogel [5] are not quite rectilinear if plotted against $1/\lambda^2$ and give $_EP = R_\infty$ as 18·52 c.c. from R_C and R_G, or 18·48 c.c. from R_D and R_F; the mean R_∞ is 18·50 c.c. whence $b_1 + b_2 + b_3 =$

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

[2] *Chem. Soc. Special Publ.* No. 11, ed. Sutton, London, 1958, M 133.
[3] Ref. 1d, p. 2486.
[4] J. M. Eckert and R. J. W. Le Fèvre, *J.*, 1962, 1081.
[5] A. I. Vogel, *J.*, 1943, 636.

22·00. From Le Fèvre and Steel's table [6] of bond electronic polarisations, $_{\rm E}P$ and $\Sigma b_{\rm i}$ are 18·54 and 22·04 $\times$ 10^{-24} c.c., respectively.

TABLE 4

Calculations of b_1, b_2, b_3, and $_{\rm m}K$ for ethyl bromide * using C–Br polarisabilities
from three different environments

Source †	$b_{\rm L}^{\rm C-Br}$	$b_{\rm T}^{\rm C-Br} = b_{\rm V}^{\rm C-Br}$	b_1	b_2	b_3	$10^{12}{}_{\rm m}K_2$ (calc.)	$\theta°$
a	4·65	3·10	8·25	7·16	6·57	55·2	12
b	5·98	2·58	9·55	6·67	6·05	133	4·5
c	5·30	2·70	8·87$_5$	6·78$_5$	6·17	100·1	6·3

* $\theta°$ is the angle between the C–Br link and the polarisability semi-axis b_1. † See text.

If the small angle between b_1 and C–Br be ignored and the assumption be allowed that $\mu_{\rm resultant}$ acts parallel to the b_1 axis, estimates of $b_1^{\rm EtBr}$, $b_2^{\rm EtBr}$, and $b_3^{\rm EtBr}$ can be extracted [7] from the observed $_\infty({}_{\rm m}K_2)$ and the electronic polarisation, the dipole moment, the depolarisation factor for light scattered transversely by ethyl bromide, and the isothermal compressibility of this substance. Data for the last two properties have been recorded by Krishnan [8] (cf. also ref. 9 for equations and definitions). Proceeding as in ref. 7, slightly different values of the semi-axes are produced (Table 5) according to the $_{\rm E}P$ used to give the total $b_1 + b_2 + b_3$; however, the $b_{\rm i}$'s forecast in Table 4 (source c) from bond polarisabilities are seen to be close to those in Table 5, a fact which encourages belief that the longitudinal and transverse polarisabilities of the C–Br bond in ethyl bromide have been correctly chosen, and that the deviation of $\mu_{\rm resultant}$ from the b_1 direction is small. In all calculations below involving n-alkyl bromides we have accordingly used $b_{\rm L}^{\rm C-Br} = 5·30$ and $b_{\rm T}^{\rm C-Br} = b_{\rm V}^{\rm C-Br} = 2·70$.

TABLE 5

Polarisability semi-axes for ethyl bromide estimated from $_\infty({}_{\rm m}K_2)$, $_{\rm E}P$, and
light-scattering data

$_{\rm E}P$ (c.c.)	18·36	18·50	18·54	b_2	6·79	6·89	6·92
$b_1 + b_2 + b_3$ ...	21·83	22·00	22·04	b_3	6·18	6·19	6·19
b_1	8·86	8·92	8·93				

Conformation and Polarisability Semi-axes of n-propyl Bromide.—Table 6 gives details of some of the computations made for this molecule in the following conformations: A, a planar *trans* zig-zag; B, the *cis* form of A; and C, various rotational isomers generated from A by turning the plane containing the CH_2–CH_3 bond about the CH_2–CH_2 axis by $\alpha°$.

The $_{\rm m}K$'s predicted for A and B are seen to exceed the observed value; when the angles between b_1 and the resultant moment are treated as zero the calculated $_{\rm m}K$'s become only slightly higher (138·7 $\times$ 10^{-12} and 117·6 $\times$ 10^{-12}, respectively). The $_{\rm m}K$'s for conformations of type C fall from 134·6 $\times$ 10^{-12} when $\alpha = 15°$ to 103·7 $\times$ 10^{-12} when $\alpha = 60°$; the $_{\rm m}K$ from experiment is 102·7 $\times$ 10^{-12}.

Prediction of $_{\rm m}K$'s of Higher Members of the n-Alkyl Bromide Series.—Given the above information for ethyl bromide, the $_{\rm m}K$'s of higher homologues are calculable with fair success by distributing the polarisability increments appropriate for the additional C–C and C–H links equally over $b_1^{\rm EtBr}$, $b_2^{\rm EtBr}$, and $b_3^{\rm EtBr}$; this is equivalent to supposing that each entrant C–C bond is introduced at the half-tetrahedral angle to the principal axes in the molecule being expanded. Numerical results are shown in Table 7. The calculated and observed $_{\rm m}K$'s diverge with the C_9, C_{16}, and C_{18} members, but among the remaining eight the disagreements do not exceed the uncertainties often experienced with direct measurements.

[6] R. J. W. Le Fèvre and K. D. Steel, *Chem. and Ind.*, 1961, 670.
[7] Ref. 1d, p. 2491, where the equation given for b_2 should be amended to contain the term $\pm(6D-3C^2)^{0·5}/6$.
[8] Krishnan, *Phil. Mag.*, 1925, **50**, 697.
[9] R. J. W. Le Fèvre and B. Purnachandra Rao, *J.*, 1957, 3644.

TABLE 6

Polarisability semi-axes, moment components, and molar Kerr constants calculated
for the conformations A, B, and C of n-propyl bromide

| Conformation | Principal semi-axes | Direction cosines with | | | Moment components | $10^{12}{}_m K$ (calc.) |
		X	Y	Z		
A	$b_1 = 11.15$	-0.4184	$+0.9083$	0	$\mu_1 = -1.964$	
	$b_2 = 8.34$	$+0.9083$	$+0.4184$	0	$\mu_2 = -0.133$	137.9
	$b_3 = 7.72$	0	0	1	$\mu_3 = 0$	
B	$b_1 = 10.84$	-0.2861	$+0.9582$	0	$\mu_1 = -1.966$	
	$b_2 = 8.65$	$+0.9582$	$+0.2861$	0	$\mu_2 = -0.123$	117.1
	$b_3 = 7.72$	0	0	1	$\mu_3 = 0$	
C †	$b_1 = 10.72$	$+0.4544$	$+0.8827$	$+0.1199$	$\mu_1 = -1.940$	
	$b_2 = 8.35$	$+0.8896$	-0.4426	-0.1130	$\mu_2 = +0.220$	103.7
	$b_3 = 8.16$	$+0.0467$	-0.1579	$+0.9863$	$\mu_3 = +0.261$	

* The X and Y axes are in the Br–C–C plane with X parallel to the CH_2–CH_2 bond.   † With $\alpha = 60°$.

TABLE 7

Molar Kerr constants predicted by assuming isotropic additions of C–CH_2 units to
b_1, b_2, and b_3 of ethyl bromide

n-Bromide	b_1	b_2	b_3	$10_m{}^{12}K$ (calc.)	$10^{12}{}_m K$ (obs.)
C_2H_5	8.88	6.79	6.17	101.7	100.6
C_3H_7	10.67	8.58	7.96	105.9	102.6
C_4H_9	12.46	10.37	9.75	104.8	105.1
C_5H_{11}	14.25	12.16	11.54	104.8	105.2
C_6H_{13}	16.04	13.95	13.33	105.9	101.7
C_7H_{15}	17.83	15.74	15.12	105.9	109.0
C_8H_{17}	19.62	17.53	16.91	104.8	107.2
C_9H_{19}	21.41	19.32	18.70	102.8	92.8
$C_{10}H_{21}$	23.20	21.11	20.49	101.7	100.9
$C_{12}H_{25}$	26.78	24.69	24.07	103.8	100.6
$C_{16}H_{33}$	33.94	31.85	31.23	104.8	114.0
$C_{18}H_{37}$	37.52	35.43	34.81	103.8	114.1

TABLE 8

Anisotropic polarisabilities of *n*-alkyl groups deduced from data on n-paraffins

	$10^7 B^{20}$	$n_D{}^{20}$	$d_4{}^{20}$	ε^{20}	$10^{12}{}_m K_{liq}$	b_L^{alkyl}	b_T^{alky}
Pentane	0.055	1.358	0.6263	1.844	1.39	10.19	8.52
Hexane	0.066	1.375	0.6595	1.890	1.70	12.10	10.26
Heptane	0.076	1.388	0.6837	1.924	2.14	14.04	11.97
Octane	0.087	1.397	0.7028	1.948	2.66	15.98	13.69
Nonane	0.094	1.405	0.7174	1.972	3.10	17.88	15.42
Decane	0.103	1.412	0.7300	1.991	3.66	19.82	17.14
Dodecane	0.125	1.421_5	0.7488	2.014	5.08	23.74	20.55

Alternative Calculations using Anisotropies of Alkyl Groups.—A less empirical approach
to the problem could start from the n-paraffins, the Kerr constants B for which as liquids
have been recorded for n-pentane and above by Stuart.[10] Together with appropriate
refractive indices, densities, and dielectric constants from the literature,[11] these yield the
molar quantities in the sixth column of Table 8. Assuming that the polarisability ellipsoids
of n-hydrocarbons have two equal semi-axes, and using data already quoted for the C–C
and C–H bonds, the apparent longitudinal and transverse polarisabilities of the alkyl
groups emerge as in columns 7 and 8 of Table 8.

The smooth increases per C–C link [*ca.* 2 for b_L^{alkyl} and 1.7 for b_T^{alkyl}], thus revealed,
strongly suggest a regularity of conformation throughout the series. Two attempts to
recognise this regularity have been made. The first supposes that these alkyl groups adopt
flat all-*trans* arrangements, with every C–C–C angle at the tetrahedral value; then each
C–C bond should contribute 0.75 to b_L^{alkyl} and 0.39 to b_T^{alkyl}, and each C–H bond 0.64 to

[10] H. A. Stuart, " Die Struktur des Freienmoleküls," Springer, Berlin, Göttingen, Heidelberg, 1952,
p. 460.
[11] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam,
1950.

both the longitudinal and transverse directions. Semi-axes as in Table 9 are thus obtained.

TABLE 9

Anisotropic polarisabilities predicted for zig-zag alkyl groups C_nH_{2n+1}

n:	5	6	7	8	9	10	12	16	18
b_L^{alkyl}	10·04	12·07	14·10	16·13	18·16	20·19	24·25	32·37	36·43
b_T^{alkyl}	8·60	10·27	11·94	13·61	15·28	16·95	20·29	26·97	30·31

Values for the C_5, C_6, and C_7 members in Table 9 are close to those deduced from observations (Table 8); however, with the longer alkyl radicals an excessive anisotropy is forecast. The second attempt is more successful with the higher alkyls; we consider the preceding zig-zag twisted into a helix which repeats itself after eight C–C links. According to Mumford [12] each C–C bond adds 1·20 Å to the length of a n-alkane; therefore in the present problem all the C–C links are taken as inclined towards the central axis of the helix at an angle of 38·8°, *i.e.*, $\cos^{-1}(1·20/1·54)$. One C–C should thus contribute 0·707 to b_L^{alkyl} and 0·411 to b_T^{alkyl}; Table 10 shows predictions on this basis (after additions of values for the C–H bonds).

TABLE 10

Anisotropic polarisabilities predicted for helical n-alkyl groups

n:	5	6	7	8	9	10	12	16	18
b_L^{alkyl} ...	9·8$_7$	11·8$_6$	13·8$_4$	15·8$_3$	17·8$_2$	19·8$_1$	23·7$_8$	(31·7$_3$)	(35·7$_0$)
b_T^{alkyl} ...	8·6$_8$	10·3$_8$	12·0$_7$	13·7$_6$	15·4$_5$	17·1$_4$	20·5$_3$	(27·2$_9$)	(30·6$_7$)

Agreement between the polarisabilities in Table 10 with those from experiment in Table 8 improves with the size of the alkyl group. Through the absence of dielectric constant data for $C_{16}H_{34}$ and $C_{18}H_{38}$, polarisabilities for the n-cetyl and n-octadecyl groups are omitted from Table 8; the bracketed values in Table 10 are obtained by calculation and cannot be compared with observations directly on the hydrocarbons.

TABLE 11

Calculated $_mK$'s assuming planar *trans*-conformations of n-alkyl groups

	10^{12} K (calc.)			
n in $C_nH_{2n+1}Br$	$\beta = 0°$	$\beta = 40°$	$\beta = 45°$	10^{12} K (obs.)
5	159·4	115·3	100·5	105·2
6	151·2	106·7	89·5	101·7
7	184·6	116·5	94·4	109·0
8	173·6	104·1	82·2	107·2
9	203·3	113·8	85·6	92·8
10	—	102·0	74·2	100·9
12	—	105·9	70·5	100·6
16	—	112·3	—	114·0
18	—	115·1	59·6	114·1

Principal polarisabilities, and hence molar Kerr constants, can be computed from the data of Tables 9 and 10 by tensorially adding the semi-axes adopted above for the C–Br bond. Table 11 refers to the attachment of C–Br to the flat all-*trans* alkyl groups of Table 9; the angle β denotes the rotations of the Br–$C_{(1)}$–$C_{(2)}$ plane about the $C_{(1)}$–$C_{(2)}$ line (so that $\beta = 0$ for a wholly planar zig-zag molecule). Calculations using the methods of ref. 4 have been carried through with $\beta = 0$, 10, 30, 35, 40, 45, and 60°, but for brevity the results of only three of these are shown. In all cases values of β which make $_mK$(calc.) $= _mK$(obs.) exist within the range 40° $\pm$ 5°; models having $\beta = 0°$ produce $_mK$'s which are too large, and the excess becomes greater as the series is ascended.

In Table 12 we utilise the alkyl-group polarisabilities of Table 10. The angles α between the C–Br links and the helical axes may lie, because of rotations about the $C_{(1)}$–$C_{(2)}$ bond, between roughly 30 and 110°; calculations have therefore been made for various α's within this range.

[12] S. A. Mumford, *J.*, 1952, 4897.

TABLE 12

Calculated $_mK$'s assuming helical conformations of n-alkyl groups

n in $C_nH_{2n+1}Br$	Angle $\alpha°$							α *
	62	60	57	54	50	45	39	
5	93·6	101·0	102·4	102·5	105·3	113·9	——	50
6	——	91·1	98·8	104·5	112·1	119·0	135·2	55
7	93·4	106·6	107·3	109·2	116·0	——	——	55
8	78·6	——	——	91·9	98·8	113·1	——	47
9	96·7	104·7	113·0	114·3	126·8	——	——	65
10	——	93·9	100·7	103·7	113·5	——	——	56
12	96·5	105·1	114·6	123·7	137·9	——	——	59
16	——	86·3	94·1	102·5	118·8	——	——	51
18	——	94·8	106·1	117·2	139·9	——	——	56

* Values of α giving best agreement between $_mK$(obs.) and $_mK$(calc.)