

995. *Molecular Polarisability. The Molar Kerr Constants and Dipole Moments of Twelve Alkyl Iodides*

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The molar Kerr constants and dipole moments, measured at infinite dilution in carbon tetrachloride, of methyl, t-butyl, and ethyl iodide, and the n-alkyl iodides up to $C_{11}H_{23}I$, are recorded. Inductive effects in these molecules are briefly discussed. Estimates of the anisotropic polarisability of the C-I bond in aliphatic environments are obtained. A regular increase of anisotropy with increasing chain-branching is apparent. Molar Kerr constants of the n-alkyl iodides fall within the range $+101$ to 141×10^{-12} , and increase gradually, but irregularly, with molecular weight.

THE work described in this Paper was undertaken to extend existing information^{1a} concerning the anisotropic polarisability of the C-I bond in an aliphatic structural environment, and to determine whether trends in molar Kerr constant for the n-alkyl iodide series are similar to those observed in the n-alkyl bromide series.² Molar Kerr constants of methyl and t-butyl iodide at infinite dilution in carbon tetrachloride, previously recorded,^{3a} have been re-examined and complemented by measurements of the molar Kerr constants and dipole moments of ethyl iodide and all the n-alkyl iodides up to $C_{11}H_{23}I$. The results are summarised in Tables 1 and 2.

EXPERIMENTAL

Materials.—Commercial samples of methyl, t-butyl, ethyl, n-propyl, and n-butyl iodide were dried and redistilled immediately before making up solutions; b. p.s (at 760 mm., unless otherwise stated) were: methyl, 42°; t-butyl, 40°/ca. 100 mm.; ethyl, 72°, n-propyl, 102°; n-butyl, 130°. n-Pentyl and n-hexyl iodide, prepared from the purified alcohol and hydriodic acid,⁴ had b. p. 28°/3 mm. and 43°/2.5 mm., respectively. For the remaining members, good quality commercial samples were used without further purification. Carbon tetrachloride, fractionated and dried over calcium chloride, was used as solvent.

Apparatus.—Dielectric constants were determined with apparatus as in ref. 5, associated procedures giving polarisations being standard.^{1b} Kerr effects were recorded photometrically.⁶

Results.—These are listed in usual form in Tables 1 and 2. The symbols have previously been explained.^{1b,3,5,7} For methyl and t-butyl iodide, which had been examined,^{3a} only the Kerr effect was remeasured. Errors quoted in Table 2 were derived from standard deviations in the values of observed quantities.

DISCUSSION *

Previous Measurements.—Agreement between the R_D values of Table 2 and those recorded by Vogel^{4, 8} or estimated by addition of bond refractivity data is satisfactory.

The dipole moments listed in Table 2 are generally lower than literature values.⁹ The difference between the observed results and those of Audsley and Goss¹⁰ (both with carbon

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

¹ R. J. W. Le Fèvre, (a) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (b) "Dipole Moments," Methuen, London, 3rd edn., 1953, ch. 2.

² C. G. Le Fèvre, R. J. W. Le Fèvre, and A. J. Williams, *J.*, 1965, 4188.

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

⁴ A. I. Vogel, *J.*, 1943, 636.

⁵ A. D. Buckingham, J. Y. H. Chau, H. C. Freeman, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao, and J. Tardif, *J.*, 1956, 1405.

⁶ R. J. W. Le Fèvre and G. L. D. Ritchie, *J.*, 1963, 4933.

⁷ R. J. W. Le Fèvre and K. M. S. Sundaram, *J.*, 1962, 1494.

⁸ A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J.*, 1952, 514.

⁹ L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948; A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman, San Francisco, 1963.

¹⁰ A. Audsley and F. R. Goss, *J.*, 1942, 358.

tetrachloride as solvent) is consistently -0.10 ± 0.03 D. Their values, however, had been corrected for solvent effects; when such solvent-effect corrections are neglected, the values are in reasonable accord with those of Table 2.

The only previously determined $\infty(mK_2)$ values are those for methyl and t-butyl iodide, for which $+54.2 \times 10^{-12}$ and $+203 \times 10^{-12}$ are recorded,^{3a} respectively. For the

TABLE 1

Incremental Kerr effects, dielectric constants, etc., for solutions in carbon tetrachloride at 25°

<i>Methyl iodide</i>						<i>t-Butyl iodide</i>							
$10^5 w_2 \dots$	847	1756	2536	2580	3788	5139	392	792	1185	1515	1824	2174	2460
$10^{11} \Delta B$	241	567	788	841	1225	1754	440	860	1287	1690	2033	2426	2691
whence $\Sigma \Delta B / \Sigma w_2 = 3.25 \times 10^{-7}$						whence $\Sigma \Delta B / \Sigma w_2 = 11.0 \times 10^{-7}$							
<i>Ethyl iodide</i>						<i>n-Propyl iodide</i>							
$10^5 w_2 \dots$	463	863	1523	1607	2279	3031	592	981	1624	2415	2797	3251	
$10^4 \Delta \epsilon \dots$	187	343	603	625	891	1191	220	371	609	903	1044	1214	
$10^5 \Delta d \dots$	140	256	442	462	653	867	91	154	242	355	411	476	
$10^4 \Delta n \dots$	2	3	8	9	10	14	—	—	7	11	12	13	
$10^{11} \Delta B \dots$	290	527	914	980	1398	1888	408	663	1071	1610	1884	2309	
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.93$, $\Sigma \Delta d / \Sigma w_2 = 0.289$, $\Sigma \Delta n / \Sigma w_2 = 0.047$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.14$, $\Sigma \Delta B / \Sigma w_2 = 6.14 \times 10^{-7}$						whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.74$, $\Sigma \Delta d / \Sigma w_2 = 0.148$, $\Sigma \Delta n / \Sigma w_2 = 0.043$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.12$, $\Sigma \Delta B / \Sigma w_2 = 6.81 \times 10^{-7}$							
<i>n-Butyl iodide</i>						<i>n-Pentyl iodide</i>							
$10^5 w_2 \dots$	599	953	1090	1258	1539	1570	$10^5 w_2 \dots$	590	995	1691	2140	2465	3080
$10^4 \Delta \epsilon \dots$	211	334	390	452	546	559	$10^4 \Delta \epsilon \dots$	200	330	583	741	835	1080
$10^5 \Delta d \dots$	51	65	69	63	63	71	$-10^5 \Delta d \dots$	54	89	152	181	205	267
$10^4 \Delta n \dots$	2	3	6	7	7	9	$10^4 \Delta n \dots$	3	4	6	9	12	14
$10^{11} \Delta B$	353	568	640	758	930	939	$10^{11} \Delta B$	322	559	966	1231	1430	1799
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.56$, $\Sigma \Delta d / \Sigma w_2 = 0.055$, $\Sigma \Delta n / \Sigma w_2 = 0.048$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.14$, $\Sigma \Delta B / \Sigma w_2 = 5.98 \times 10^{-7}$						whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.44$, $\Sigma \Delta d / \Sigma w_2 = -0.086$, $\Sigma \Delta n / \Sigma w_2 = 0.044$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.13$, $\Sigma \Delta B / \Sigma w_2 = 5.75 \times 10^{-7}$							
<i>n-Hexyl iodide</i>						<i>n-Heptyl iodide</i>							
$10^5 w_2 \dots$	556	1127	1481	1848	2497	3004	649	1115	1679	2315	2439	3045	
$10^4 \Delta \epsilon \dots$	165	336	466	627	860	910	189	325	479	654	690	860	
$-10^5 \Delta d \dots$	102	181	246	313	422	528	149	265	410	566	596	759	
$10^4 \Delta n \dots$	3	5	6	8	12	14	2	4	6	8	10	11	
$10^{11} \Delta B \dots$	322	644	834	1032	1364	1676	389	569	881	1193	1297	1610	
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.20$, $\Sigma \Delta d / \Sigma w_2 = -0.170$, $\Sigma \Delta n / \Sigma w_2 = 0.046$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.13$, $\Sigma \Delta B / \Sigma w_2 = 5.59 \times 10^{-7}$						whence $\Sigma \Delta \epsilon / \Sigma w_2 = 2.84$, $\Sigma \Delta d / \Sigma w_2 = -0.244$, $\Sigma \Delta n / \Sigma w_2 = 0.036$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.11$, $\Sigma \Delta B / \Sigma w_2 = 5.28 \times 10^{-7}$							
<i>n-Octyl iodide</i>						<i>n-Nonyl iodide</i>							
$10^5 w_2 \dots$	485	1032	1422	1836	2112	2351	481	608	1051	1277	1529	1984	
$10^4 \Delta \epsilon \dots$	128	275	379	493	568	627	133	160	276	325	393	511	
$-10^5 \Delta d \dots$	162	342	473	605	702	783	176	219	389	477	566	732	
$10^4 \Delta n \dots$	—	4	5	7	8	9	2	2	3	4	5	7	
$10^{11} \Delta B \dots$	294	559	739	938	1109	1194	203	287	514	645	836	1004	
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 2.67$, $\Sigma \Delta d / \Sigma w_2 = -0.332$, $\Sigma \Delta n / \Sigma w_2 = 0.038$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.11$, $\Sigma \Delta B / \Sigma w_2 = 5.23 \times 10^{-7}$						whence $\Sigma \Delta \epsilon / \Sigma w_2 = 2.59$, $\Sigma \Delta d / \Sigma w_2 = -0.369$, $\Sigma \Delta n / \Sigma w_2 = 0.033$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.10$, $\Sigma \Delta B / \Sigma w_2 = 5.03 \times 10^{-7}$							
<i>n-Decyl iodide</i>						<i>n-Undecyl iodide</i>							
$10^5 w_2 \dots$	727	927	1098	1461	2154	2643	577	833	1264	1582	1962	2350	
$10^4 \Delta \epsilon \dots$	202	250	254	362	529	643	133	196	303	367	484	562	
$-10^5 \Delta d \dots$	316	401	473	628	924	1116	257	382	580	723	913	1090	
$10^4 \Delta n \dots$	3	3	4	5	8	11	2	3	5	6	8	9	
$10^{11} \Delta B \dots$	358	466	538	729	1051	1278	228	331	570	673	821	980	
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 2.48$, $\Sigma \Delta d / \Sigma w_2 = -0.428$, $\Sigma \Delta n / \Sigma w_2 = 0.038$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.11$, $\Sigma \Delta B / \Sigma w_2 = 4.91 \times 10^{-7}$						whence $\Sigma \Delta \epsilon / \Sigma w_2 = 2.38$, $\Sigma \Delta d / \Sigma w_2 = -0.460$, $\Sigma \Delta n / \Sigma w_2 = 0.039$, $\Sigma \Delta n^2 / \Sigma w_2 = 0.11$, $\Sigma \Delta B / \Sigma w_2 = 4.21 \times 10^{-7}$							

remainder of the series, $\infty(mK_2)$ values fall within the range $+101$ to 141×10^{-12} , and increase gradually, but irregularly, with molecular weight. This trend is similar to that observed in the n-alkyl bromide series,² for which the $\infty(mK_2)$ values lie generally within the range $+100$ to 110×10^{-12} .

Magnitude and Direction of Dipole Moments.—For methyl and t-butyl iodide, molecular symmetry is such that dipole moment direction can be assigned unambiguously. However, for the remainder of the series, it is necessary to make assumptions as to the direction of action of the dipole moment. Following a procedure previously employed,¹¹ it has been assumed alternatively (a) that inductive effects may be neglected and the resultant dipole moment, μ_{res} , taken to lie along the C-I axis, or (b) that the observed dipole moment may be regarded as the resultant of the methyl iodide dipole moment (1.48 D ^{3a}), directed along the C-I axis, and an induced moment, μ_{ind} , along the primary C-C bond, as indicated in (I). Treatment (B) yields, for ethyl iodide, $\mu_{ind} = 0.56$ D and $\chi = 17^\circ 24'$, and, for the higher n-alkyl iodides, $\mu_{ind} = 0.65 \pm 0.05$ D and $\chi = 20^\circ \pm 1^\circ$. A similar treatment for t-butyl iodide yields $\mu_{ind} = 0.66$ D. Audsley and Goss,¹⁰ employing a similar approach, obtain $\mu_{ind} = 0.64$ D. Treatment (b) does not take into account the "reversed induced moment" effect postulated¹⁰ for the higher members of the series. Treatments (a) and (b) probably represent opposite extremes of the true picture of molecular dipole moment, and both have therefore been considered in ensuing calculations.

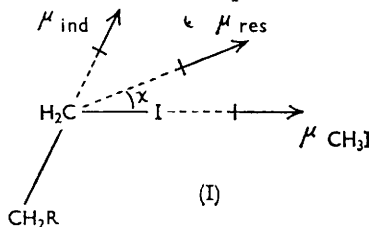


TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants

Solute	α_{E_1}	β	$\gamma'n_1^2$	∞P_2 (c.c.)	R_D (c.c.)	μ (D) *	γ	δ	$10^{12} \infty(mK_2)$
CH ₃ I	3.20 †	0.290 †	—	—	—	1.48 †	0.031 †	46.4	+48.5 ± 3
t-C ₄ H ₉ I	4.77 †	-0.121 †	—	—	—	2.14 †	0.019 †	157	+215 ± 4
C ₂ H ₅ I	3.93	0.182	0.14	88.3	24.3	1.75	0.032	87.7	+101 ± 2
n-C ₃ H ₇ I	3.74	0.148	0.12	95.6	28.9	1.79	0.030	97.3	+123 ± 4
n-C ₄ H ₉ I	3.56	0.035	0.14	102.0	33.4	1.81	0.033	85.4	+117 ± 1
n-C ₅ H ₁₁ I	3.44	-0.054	0.13	110.4	38.8	1.85	0.029	82.1	+121 ± 4
n-C ₆ H ₁₃ I	3.20	-0.107	0.13	114.9	43.5	1.84	0.032	79.9	+126 ± 2
n-C ₇ H ₁₅ I	2.84	-0.154	0.11	115.8	47.6	1.79	0.025	75.4	+127 ± 8
n-C ₈ H ₁₇ I	2.67	-0.210	0.11	121.2	52.9	1.79	0.026	74.7	+134 ± 10
n-C ₉ H ₁₉ I	2.59	-0.369	0.10	127.2	56.7	1.82	0.023	71.9	+137 ± 10
n-C ₁₀ H ₂₁ I	2.48	-0.270	0.11	132.9	61.9	1.82	0.026	70.1	+141 ± 2
n-C ₁₁ H ₂₃ I	2.38	-0.290	0.11	137.8	66.2	1.83	0.027	60.1	+127 ± 5

* It is assumed that $D_P = 1.05R_D$. † From ref. 3a.

C-I Polarisabilities in Methyl and t-Butyl Iodide.—These molecules should, by virtue of their symmetry, possess molecular polarisability ellipsoids of revolution, specifiable by principal components b_1 and $b_2 = b_3$. Since the resultant dipole moments act in directions which correspond to b_1 , the differences ($b_1 - b_2$) can be computed from the $\infty(mK_2)$'s and μ 's of Table 2. The sums ($b_1 + 2b_2$) are drawn from the electronic polarisations, E_P , values for which are given by Audsley and Goss.¹⁰ Molecular principal polarisabilities then emerge as in Table 3.

TABLE 3

Molecular polarisability of methyl and t-butyl iodide *

	E_P (c.c.)	$(b_1 - b_2)$	$(b_1 + 2b_2)$	b_1	$b_2 = b_3$
CH ₃ I	18.5	1.93 (2.15)	22.00 (21.86)	8.62 (8.72)	6.69 (6.57)
t-C ₄ H ₉ I	33.5	4.08 (3.87)	39.83 (39.60)	16.00 (15.78)	11.91 (11.91)

* Values from ref. 3a are shown in parentheses.

The values of b in Table 3, together with the usual bond polarisability values^{1a} for C-C and C-H and a knowledge of molecular geometry, yield estimates of the longitudinal

¹¹ R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J.*, 1965, 2499.

and transverse polarisabilities of the C-I bond, as in Table 4. The CCC bond angle in t-butyl iodide may be taken to be tetrahedral.¹² The b^{CI} values obtained from t-butyl iodide have been adjusted so that $(b_L + 2b_T)$ corresponds to an ${}_E P(\text{C-I})$ of 13.92 c.c.¹³

TABLE 4
C-I Bond polarisability in methyl and t-butyl iodide *

	b_L^{CI}	$(b_T^{\text{CI}} = b_V^{\text{CI}})$	$(b_L + 2b_T)$	$(b_L - b_T)$
CH ₃ I	6.70 (6.81)	4.77 (4.66)	16.24 (16.13)	1.93 (2.15)
t-C ₄ H ₉ I	9.19 (8.82)	3.68 (4.23)	16.55 (17.28)	5.51 (4.59)

* Values from ref. 3a are shown in parentheses.

Polarisability of Ethyl Iodide.—The symmetry of this molecule does not permit the derivation of unambiguous polarisability data. It is possible, however, to estimate the most appropriate C-I bond polarisabilities for the molecule by comparing calculated values, ${}_m K$ (calc.) of the molar Kerr constant with the observed quantity, ${}_m K$ (obs.).

Assuming the CCI bond angle to be tetrahedral, values of b_1 , b_2 , b_3 have been calculated by addition of bond polarisability tensors and diagonalisation of the resulting matrix,

TABLE 5
Evaluation of ${}_m K$ (calc.) for ethyl iodide

Source of b^{CI}	Treatment (a)				Treatment (b)			
	$b_L^{\text{CI}}, b_T^{\text{CI}}, b_V^{\text{CI}}$	b_1, b_2, b_3	μ_1, μ_2, μ_3	$10^{12} {}_m K$ (calc.)	$b_L^{\text{CI}}, b_T^{\text{CI}}, b_V^{\text{CI}}$	b_1, b_2, b_3	μ_1, μ_2, μ_3	$10^{12} {}_m K$ (calc.)
CH ₃ I	6.70	10.30	+1.728	+59.5	6.70	10.30	+1.566	+46.5
	4.77	8.83	+0.280		4.77	8.83	+0.780	
	4.77	8.24	0		4.77	8.24	0	
t-C ₄ H ₉ I ...	9.19	12.76	+1.748	+192.8	9.19	12.76	+1.644	+155.8
	3.68	7.77	+0.081		3.68	7.77	+0.596	
	3.68	7.15	0		3.68	7.15	0	
Inter- polated	7.55	11.13	+1.743	+99.7	8.02	11.60	+1.629	+104.7
	4.50	8.58	+0.159		4.27	8.35	+0.638	
	4.50	7.97	0		4.27	7.74	0	

using standard procedures.^{1a, 14} Such calculations have been carried out with C-I bond polarisabilities obtained (i) from methyl iodide, (ii) from t-butyl iodide, and (iii) by interpolation in the results of (i) and (ii), with the requirements that $(b_L + 2b_T)$ of the C-I bond corresponds to ${}_E P(\text{C-I}) = 13.92$ c.c.¹³ and that ${}_m K$ (calc.) = ${}_m K$ (obs.). These polarisability values, in conjunction with the dipole moment components μ_1 , μ_2 , μ_3 along the axes of b_1 , b_2 , b_3 , respectively, yield values of ${}_m K$ (calc.) which may be compared with the observed data. This procedure has been carried out for both treatments (a) and (b) of the dipole moment direction, as discussed above. The results, as in Table 5, are to be compared with the observed $10^{12} {}_m K$ of $+101 \pm 2$.

TABLE 6
Polarisability of the C-I bond in alkyl iodides

Molecule	b_L^{CI}	$(b_T^{\text{CI}} = b_V^{\text{CI}})$	$(b_L - b_T)$
Methyl iodide	6.70	4.77	1.93
Ethyl iodide	7.6—8.0	4.5—4.3	3.0—3.8
Isopropyl iodide	8.2	4.5	3.7
Cyclohexyl iodide	8.07	4.18	3.89
t-Butyl iodide	9.19	3.68	5.51

Combining the results of Tables 4 and 5 with those for isopropyl¹⁵ and cyclohexyl^{1a} iodide, the polarisability data for a C-I bond in aliphatic structural environments may be

¹² J. O. Williams and W. Gordy, *J. Chem. Phys.*, 1950, **18**, 994.

¹³ R. J. W. Le Fèvre and K. D. Steel, *Chem. and Ind.*, 1961, 670.

¹⁴ J. M. Eckert and R. J. W. Le Fèvre, *J.*, 1962, 1081.

¹⁵ C.-Y. Chen and R. J. W. Le Fèvre, unpublished data.

summarised as in Table 6. The regular trend of increased anisotropy with increased chain-branching is identical with that observed for nitriles¹¹ and for other alkyl halides.^{1a,2}

Polarisability of the n-Alkyl Iodides.—The ability of the n-alkyl iodides to assume more than one conformation complicates the prediction of their molecular polarisability and mK (calc.). A treatment of the problem of internal rotation in n-propyl, n-butyl, n-pentyl, and n-hexyl iodide, together with the corresponding n-alkyl bromides, is described in the Paper which follows. Experimental results for the n-alkyl iodides are therefore presented here without interpretation.

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