24. *Molecular Polarisability. The Anisotropy of the* H–O *Bond in Normal Alcohols.*

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Measurements of the molar Kerr constants of 14 n-alcohols between methanol and octadecanol are reported. Semi-axes of the polarisability ellipsoids for the first six alcohols are calculated and discussed. From methyl alcohol the longitudinal and transverse polarisabilities of the O–H bond appear as $0{\cdot}09_5$ and $0{\cdot}05 \times 10^{-23}$ c.c. Such values are used to indicate that the preferred conformation of ethyl alcohol is *s-trans*. Approximate constant differences between corresponding semi-axes of adjacent homologues are noted and interpreted as due to a common pattern of configuration throughout the series.

This paper records measurements of the molar Kerr constants $_{\infty}(_{\mathrm{m}}K_2)$ of fourteen normal alcohols at infinite dilution in carbon tetrachloride; it proceeds *inter alia* to an estimate of the semi-axes of the polarisability ellipsoid of the H–O bond, and thence to a consideration of the configurations apparently adopted by the solutes in this medium.

Practical procedures, details regarding calculations, definitions of symbols, etc., follow those of ref. 1. Actual observations of the changes of electric double refraction and refractive index (Na light), caused in carbon tetrachloride by the presence of a weight fraction w_2 of solute, are listed in Table 1, and lead to the coefficients in Table 2. Table 3 gives the values of $_{\infty}(_{\mathrm{m}}K_2)$ derivable with the help of the appropriate dielectric constant and density factors ($\alpha\varepsilon_1$ and β respectively) from Le Fèvre and Williams.[2] The availability[3] of the quantities $_{\infty}\delta_2{}^2$ for the alcohols from methyl to hexyl now makes possible the estimation of " apparent " molecular semi-axes of polarisability for these six substances; " apparent " because, throughout the calculations, the assumption is made that $\mu_{\text{resultant}}$ is always acting parallel to one of the principal axes of the ellipsoid concerned. Results are summaried as Table 4, in which the electronic polarisations $_{\mathrm{E}}P$ are extrapolated from the molecular refractions recorded for the C and G' lines by Vogel,[4] and the dipole moments are from ref. 2.

Previous Electric Double Refraction Data for Alcohols.—The Kerr constants, expressed relatively to B_{CS_2}, of a number of pure alcohols are listed in the International Critical Tables, Vol. VII. Except for ethyl alcohol, they are all markedly negative. Where solutions are concerned, the only earlier work appears to be that by Tsvetkov and Marinen [5] who reported molar Kerr constants for ten of the solutes now studied by us. These authors state that their $_{\mathrm{m}}K$'s were drawn from alcohol–benzene mixtures, but no experimental details were given. The $_{\infty}(_{\mathrm{m}}K_2)$'s of Table 3 vary between being about $\frac{1}{2}$ and $\frac{1}{9}$ of the $_{\mathrm{m}}K$'s claimed by the Russians. The discrepancies are far too great to arise solely from " solvent effects "; their possible origins will be discussed in the following paper. Stuart and Volkmann [6] examined the vapours of methyl and ethyl alcohol in 1933 with indefinite results, quoting $K = B\lambda/n$ (where B = Kerr constant, λ = wavelength *in vacuo* of light used, n = refractive index of field-free medium) at 760 mm. pressure as $\pm 0{\cdot}4 \times 10^{-15}$ and $\pm 0{\cdot}5 \times 10^{-15}$ respectively for temperatures of 98·8° and 102°.

Discussion

Three main points of interest which arise from these results are (*a*) whether or not a reliable estimate of the anistropy of polarisability of the O–H bond can be derived, (*b*)

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[1] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955. **5**, 261; *J.*, 1953, 4041; 1954, 1577.
[2] Le Fèvre and Williams, *J.*, 1960, 108.
[3] Le Fèvre and Rao, *J.*, 1960, 119.
[4] Vogel, *J.*, 1948, 1814.
[5] Tsvetkov and Marinen, *Doklady Akad. Nauk.*, *S.S.S.R.*, 1948, **62**, 67; *Chem. Abs.*, 1949, **48**, 469.
[6] Stuart and Volkmann, *Ann. Phys.*, 1933, **18**, 121.

TABLE 1. *Kerr effects and refractive indexes for solutions of alcohols in carbon tetrachloride at 25°.*

10^5w_2	$10^7\Delta B$	$10^4\Delta n$	10^5w_2	$10^7\Delta B$	$10^4\Delta n$	10^5w_2	$10^7\Delta B$	$10^4\Delta n$	10^5w_2	$10^7\Delta B$	$10^4\Delta n$
	Methyl			*Ethyl*			*Propyl*			*Butyl*	
408	*ca.* 0	−7	297	$-0{\cdot}000_5$	—	245	−0·001	—	929	−0·002	—
456	0·002	—	556	−0·003	−11	463	−0·002	−4	974	−0·001	−13
485	0·001	—	860	−0·004	—	1061	−0·005	—	1368	−0·004	−19
561	0·001	—	920	−0·004	−19	2294	−0·011	—	1653	−0·004	−20
908	0·003	—	1661	−0·005	—	2727	−0·013	—	1725	−0·004	—
1061	0·003	−25	1931	−0·004	−35	2945	−0·018	−42	2288	−0·008	−29
1106	0·003	−28	2349	−0·003	—	3102	−0·018	—	3263	−0·019	−38
1164	0·008	—	2833	−0·003	—	5208	−0·039	−72			
1521	0·010	—	3290	—	−62						
1579	0·010	−35	4296	—	−82						
2053	0·020	—									
2162	0·020	—									
2969	0·032	—									
2888	—	−73									
3534	—	−86									

	Pentyl			*Hexyl*			*Heptyl*	
513	−0·002	—	1822	−0·002	—	879	−0·002	−6
1012	−0·003	−7	1914	−0·002	−12	1412	−0·004	−10
1438	−0·004	−12	2355	−0·005	−16	2372	−0·004	−18
1462	−0·004	—	3538	−0·009	−33	3107	−0·007	−20
2054	−0·008	−24	6518	−0·030	−51	3715	−0·011	−27
2481	−0·009	—	6692	−0·030	−51	5189	−0·015	—
4961	—	−46						

	Octyl			*Nonyl*			*Decyl*	
1378	−0·003	−9	593	−0·002	—	347	*ca.* 0	—
1773	−0·004	−12	898	−0·003	—	474	*ca.* 0	−1
3032	−0·006	−20	1557	−0·006	—	928	−0·002	—
3117	$-0{\cdot}006_5$	−20	1935	−0·006	—	1024	—	−6
3934	−0·008	−25	2699	−0·007	−16	2044	−0·005	—
4647	−0·010	−30	3144	−0·009	−18	2478	−0·005	—
			3285	—	−20	2574	−0·010	−14
			3342	—	−20	4777	−0·020	−22

	Dodecyl			*Tetradecyl*			*Hexadecyl*	
429	−0·001	−1	639	*ca.* 0	−1	199	*ca.* 0	—
2294	−0·003	−9	680	,,	−1	461	,,	—
2566	−0·004	—	1638	,,	−3	1018	,,	−2
2677	−0·004	—	2083	,,	−7	1326	−0·001	−3
4677	−0·007	−17	2860	,,	−8	2755	−0·002	−7
5941	−0·009	—						

	Octadecy			*Cyclopentyl*			*Cyclohexyl*	
375	*ca.* 0	−1	845	−0·001	−1	1003	0·004	*ca.* 0
812	,,	−2	956	−0·001	−1	1156	0·004	,,
900	,,	−2	2208	−0·005	−2	1805	0·004	—
1358	,,	−3	4269	−0·008	−3	2118	0·003	—
			7221	−0·010	−5	2442	0·004	2
						2480	0·003	3
						2995	0·002	5
						5290	−0·004	8
						7510	−0·017	8

TABLE 2. *Coefficients* a *and* b *in equations* $10^7\Delta B = aw_2 + bw_2^2$, *also values of the quotients* $\Sigma\Delta n/\Sigma w_2$.

Solute alcohol	*a*	*b*	$\Sigma\Delta n/\Sigma w_2$	Solute alcohol	*a*	*b*	$\Sigma\Delta n/\Sigma w_2$
Methyl	$-0{\cdot}088_0$	+48·2	−0·240	Nonyl	$-0{\cdot}392_5$	$+3{\cdot}8_5$	−0·059
Ethyl	$-0{\cdot}572_6$ *	+16·0 *	−0·188	Decyl	$-0{\cdot}134_1$	$-6{\cdot}0_2$	$-0{\cdot}047_5$
Propyl	$-0{\cdot}313_4$	$-8{\cdot}3_6$	−0·137	Dodecyl	$-0{\cdot}144_5$	$-0{\cdot}11_4$	$-0{\cdot}036_5$
Butyl	$-0{\cdot}196_1$ †	$-2{\cdot}0_7$ †	−0·125	Tetradecyl	*ca.* 0	—	−0·025
Pentyl	$-0{\cdot}226_6$	$-5{\cdot}9_2$	−0·090	Hexadecyl	$-0{\cdot}014_9$	$-2{\cdot}1_5$	$-0{\cdot}023_5$
Hexyl	$-0{\cdot}017_5$	$-6{\cdot}6_1$	−0·078	Octadecyl	*ca.* 0	—	−0·023
Heptyl	$-0{\cdot}176_4$	$-2{\cdot}2_6$	−0·072	Cyclopentyl ...	$-0{\cdot}230_3$	$+1{\cdot}2_4$	−0·008
Octyl	$-0{\cdot}206_3$	$-0{\cdot}07_6$	−0·065	Cyclohexyl	$+0{\cdot}322_7$	$-7{\cdot}3_7$	$+0{\cdot}012_5$

* Computed from solutions having values of w_2 between 0·01661 and zero.

† Ditto, between 0·02288 and zero.

TABLE 3. *Calculations of molar Kerr constants at infinite dilution in carbon tetrachloride at 25°.*

Solute alcohol	$\alpha\varepsilon_1$	$-\beta$	γ	δ	$_\infty(_{\mathrm{m}}K_2) \times 10^{12}$
Methyl	17·84	1·096	−0·165	−1·26	$-1{\cdot}7_8$
Ethyl	12·54	1·150	−0·129	−8·18	$-4{\cdot}0_8$
Propyl	9·00	1·061	−0·094	−4·48	$-2{\cdot}9_6$
Butyl	7·46	1·025	−0·086	−2·80	$-2{\cdot}2_8$
Pentyl	6·10	0·983	−0·062	−3·24	$-2{\cdot}6_9$
Hexyl	5·55	0·964	$-0{\cdot}053_5$	−0·25	$-0{\cdot}6_6$
Heptyl	4·90	0·981	−0·049	−2·52	$-2{\cdot}4_4$
Octyl	4·28	0·964	−0·045	−2·95	$-2{\cdot}8_9$
Nonyl	$3{\cdot}88_5$	0·959	−0·040	−5·61	$-6{\cdot}0_6$
Decyl	3·64	0·960	−0·033	−1·92	$-1{\cdot}9_5$
Dodecyl	2·97	0·935	−0·025	−2·06	$-2{\cdot}1_0$
Tetradecyl	2·42	0·924	−0·017	*ca.* 0	$+1{\cdot}2_3$
Hexadecyl	2·14	0·896	−0·016	−0·21	$+1{\cdot}2_5$
Octadecyl	2·03	0·920	−0·016	*ca.* 0	$+1{\cdot}9_8$
Cyclopentyl	6·48	0·721	−0·005	−3·29	$-2{\cdot}9_9$
Cyclohexyl	6·56	0·702	+0·009	+4·61	+24·1

TABLE 4. *Derivation of apparent polarisability semi-axes for the normal alcohols* C_1 *to* C_6.

Alcohol	10^{35} $(\theta_1 + \theta_2)$	$_{\mathrm{E}}P$ (c.c.)	10^{23} $(b_1 + b_2 + b_3)$	10^3 $_\infty\delta_2{}^2$	$10^{35}\theta_1$	$10^{35}\theta_2$	μ (D)	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
Methyl	$-0{\cdot}423_3$	8·04	0·956	$12{\cdot}0_5$	$0{\cdot}063_8$	$-0{\cdot}487_1$	1·77	0·315	0·363	0·278
Ethyl...	$-0{\cdot}970_2$	12·62	1·501	$10{\cdot}0_7$	$0{\cdot}131_6$	−1·102	1·79	0·492	0·566	0·444
Propyl	$-0{\cdot}703_9$	17·16	$2{\cdot}040_5$	$9{\cdot}1_6$	$0{\cdot}220_8$	$-0{\cdot}924_7$	$1{\cdot}73_5$	0·672	$0{\cdot}763_5$	0·605
Butyl...	$-0{\cdot}542_2$	21·67	2·577	$8{\cdot}4_7$	$0{\cdot}325_8$	$-0{\cdot}868_0$	1·75	0·852	0·959	0·766
Pentyl	$-0{\cdot}639_7$	26·26	3·123	$7{\cdot}1_9$	$0{\cdot}406_3$	−1·046	$1{\cdot}72_5$	1·032	1·153	0·938
Hexyl	$-0{\cdot}156_9$	30·72	3·653	$6{\cdot}7_6$	$0{\cdot}522_8$	$-0{\cdot}679_7$	1·77	1·212	1·343	1·098

how the values of $_\infty\delta_2{}^2$ now obtained from solutions compare with others recorded earlier in the literature for liquid or gaseous alcohols, and (*c*) what indications, if any, do the present measurements give regarding the configurations adopted by alcohols as solutes. Comments will be made on these questions in the following paragraphs.

(a) *The* O–H *Bond Ellipsoid.*—Unfortunately, from first principles, neither the direction of action of the resultant dipole moment within the reference system provided by the axes of the molecular polarisability ellipsoid, nor the desposition of those axes within the molecular framework, can be forecast with certainty. Possibly with the simplest case, that of methyl alcohol, there is a partial exception to this: the *least* of the polarisability axes may perhaps be identified as that which is perpendicular to the plane defined by the C–O–H chain.

If this is so, then an estimate of $b_{\mathrm{T}}{}^{\mathrm{O-H}}$ can be made straight away, provided $b_{\mathrm{T}}{}^{\mathrm{C-O}}$ and $b_{\mathrm{T}}{}^{\mathrm{C-H}}$ are known; these are thought [7] to be $0{\cdot}039 \times 10^{-23}$ and $0{\cdot}063_5 \times 10^{-23}$ respectively. The desired $b_{\mathrm{T}}{}^{\mathrm{O-H}}$ therefore appears as $(0{\cdot}278 - 3 \times 0{\cdot}063_5 - 0{\cdot}039) \times 10^{-23} = 0{\cdot}049 \times 10^{-23}$. From the refractivity data given by Vogel *et al.*[8] it appears that R_∞ for the O–H link is *ca.* 1·62 c.c., whence $b_{\mathrm{L}}{}^{\mathrm{O-H}} + 2b_{\mathrm{T}}{}^{\mathrm{O-H}} = 0{\cdot}193 \times 10^{-23}$; accordingly $b_{\mathrm{L}}{}^{\mathrm{O-H}}$ is obtained as $(0{\cdot}193 - 0{\cdot}098) \times 10^{-23} = 0{\cdot}095 \times 10^{-23}$. These estimates of the longtitudinal and transverse polarisabilities of the O–H bond are advanced only provisionally. Clearly, they depend *inter alia* very much on the accuracy of the values taken for $b_{\mathrm{T}}{}^{\mathrm{C-H}}$ and $b_{\mathrm{T}}{}^{\mathrm{C-O}}$. A final statement must await completion of work (by other authors) now proceeding on various hydroxyl-containing structures and ethers.

It is noted that Le Fèvre's empirical equation [9] gives, with $r_{\mathrm{O-H}} = 0{\cdot}957$ Å (as in water) and $r_{\mathrm{H}} = 0{\cdot}375$ Å (from $r_{\mathrm{H-H}} = 0{\cdot}75$ Å; these r's are quoted from Tables compiled by Walsh [10]), a forecast that $10^{23}b_{\mathrm{L}}{}^{\mathrm{O-H}}$ is between 0·051 and 0·055, and consequentially that $10^{23}b_{\mathrm{T}}{}^{\mathrm{O-H}}$ should be between 0·071 and 0·069.

The contrast between these " predicted " values and those " found " is marked. The

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[7] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

[8] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

[9] Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.

[10] Walsh, " Progress in Stereochemistry," Ed. Klyne, Vol. 1, Butterworths, London, 1954, Chap. I.

origin of this may well be in Le Fèvre's equation which, to produce $b_L{}^{O-H} = 0{\cdot}095 \times 10^{-23}$, requires r_H to have the unexpected magnitude of 0·77 Å.

Certain indirect evidence may possibly be obtained from the case of the water molecule. It is known [11] that $10^3\delta^2$ is around 34·2 for steam and 9·8 for liquid water (see Tables on pp. 54 and 84 of Bhagavantam [11]). Table 5 shows the values of molecular semi-axes, $10^3\delta^2$, etc., to be expected for H_2O with an H–O–H angle of 105° *provided that this structure may be regarded from the polarisability viewpoint as simply composed of two* O–H *bond ellipsoids.* Attention is naturally attracted to the first line of Table 5 in which is shown a (probably fortuitous) congruence with the recorded Δ^2_{vapour} of steam. It is plain that the O–H link cannot be isotropic, otherwise $\delta^2_{H_2O}$ would be zero. If, however, the ratio $b_L{}^{O-H}/b_T{}^{O-H}$ were *less* than unity a finite $\delta^2_{H_2O}$ should also appear, accompanied by a negativity in $2b_1 - b_2 - b_3$. For instance, with $b_L{}^{O-H} = 0{\cdot}051 \times 10^{-23}$ and $b_T{}^{O-H} = 0{\cdot}071 \times 10^{-23}$, we obtain $\theta_1 = 0{\cdot}005 \times 10^{-35}$ and $\theta_2 = -0{\cdot}21 \times 10^{-35}$ (with $\mu_{H_2O} = 1{\cdot}8$D), so that ${}_mK_{H_2O}$ should be *negative.* Neither the molar Kerr constants of water nor of steam are yet on record, although early observations by Schmidt [12] and Pauthenier [13] suggest that water in bulk displays *positive* electric birefringence. (Owing to the highly associated and hydrogen-bonded state of water, the last fact may be irrelevant.)

TABLE 5. *The molecular anisotropy of* H_2O *expected for different values of* $b_L{}^{OH}$ *and* $b_T{}^{OH}$.

$b_L{}^{O-H}$	$b_T{}^{O-H}$	$b_1{}^{H_2O}$	$b_2{}^{H_2O}$	$b_3{}^{H_2O}$	$10^3\delta_{\text{calc.}}$	$(2b_1 - b_2 - b_3)$
0·095	0·049	0·132	0·156	0·098	34·2	+0·010
$0{\cdot}064_3$	$0{\cdot}064_3$	0·129	0·129	0·129	0	0
0·055	0·069	0·128	0·120	0·138	3·3	−0·002
0·051	0·071	0·127	0·117	0·142	6·4	−0·005
0·041	0·076	0·126	0·108	0·152	19·7	−0·008

(b) *Literature Values of* δ^2 *for Alcohols.*—In the main, the light-scattering data concerned have been provided by Krishnan,[14] Ramakrishna Rao,[15] and Peyrot; [16] the results of, and references to, these and other workers are included in the books of Cabannes [17] and Bhagavantam.[11] Table 6 compares earlier measurements of $10^3\delta^2$, made on the alcohols as liquids and gases, with those now obtained at infinite dilution in carbon tetrachloride. (To put the literature values of δ^2 on the same numerical basis as ${}_\infty\delta_2{}^2$ they have been doubled.)

TABLE 6. *Past and present values of* $10^3\delta^2$ *for the first six n-alcohols.*

State in which measured:	As liquid	As vapour	As liquid	As vapour	At infinite dilution in CCl_4
Alcohol	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
Methyl	7·8	28·6	7·0	29·0	$12{\cdot}0_5$
Ethyl	4·4	15·4	5·2	15·2	10·1
Propyl	3·0	23·0	3·8	20·2	$9{\cdot}1_6$
Butyl	4·2	27·6	3·2	29·0	$8{\cdot}4_7$
Pentyl	4·66	20·2	3·0	22·0	$7{\cdot}1_9$
Hexyl	—	—	—	—	$6{\cdot}7_6$

(Values in columns *a* and *b*, due to Krishnan and R. Rao respectively, are from Cabannes, ref. 17, pp. 252, 253; those in *c* and *d*, due to various authors, are from Bhagavantam, ref. 11, pp. 55 and 84; those in *e* are from ref. 3).

${}_\infty\delta_2{}^2$ diminishes with the addition of each extra CH_2 group, implying that the larger the solute molecule the less its anisotropy. A parallel tendency is displayed, at a generally lower level of anisotropy, among the values for δ^2_{liquid}. Because of the association known

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[11] Bhagavantam, " Scattering of Light and the Raman Effect," Andhra Univ., Waltair, 1940.

[12] Schmidt, Diss., Göttingen, 1901.

[13] Pauthenier, *Compt. rend.*, 1921, **172**, 383.

[14] Krishnan, *Phil. Mag.*, 1925, **50**, 697.

[15] Ramakrishna Rao, *Ind. J. Physics*, 1927, **2**, 61.

[16] Peyrot, *Compt. rend.*, 1936, **203**, 1512.

[17] Cabannes, " La Diffusion Moléculaire de la Lumière," Les Presses Universitaires de France, Paris, 1929.

to occur with pure alcohols, and the large number of possible configurations of hydrogen-bonded " polymeric " species contained in their liquid phases, δ^2_{liquid} is not a property which can easily or usefully be analysed. Yet it is surprising that δ^2_{liquid} should appear more regularly comparable with ${}_{\infty}\delta_2^{\,2}$ than with δ^2_{vapour}, since it is believed that both at infinite dilution and in the gaseous state the individual alcohol molecules are separate. The measurements from which the values of ${}_{\infty}\delta_2^{\,2}$ have been drawn were deliberately made in concentration regions thought (from dielectric polarisation data) to be low enough to avoid the intervention of association effects. In any case, with the techniques available, observations of the Δ's of still more dilute solutions were not possible with any dependable accuracy. It is perhaps a coincidence, but worth mentioning, that ethyl alcohol with the smallest δ^2_{vapour} shows the largest negative molar Kerr constant at infinite dilution; one may suspect therefore that the root of the problem is not the *separateness* of the molecules, but rather their *configurations*, which differ in gas and solution. A study of the values of ${}_{\text{m}}K$ of alcohols as vapours would provide pertinent information.

(c) *The Configurations of Alcohols as Solutes.*—As already stated, the molecular semi-axes of the alcohols named in Table 4 have been computed as though the resultant dipole moments act along one of the principal axial directions. Using the " provisional " values $10^{23}b_{\text{L}}^{\text{OH}} = 0{\cdot}10$ and $10^{23}b_{\text{T}}^{\text{OH}} = 0{\cdot}05$, we can perform the following calculations for methyl alcohol. The oxygen valency angles in H_2O and Me_2O are 105° and 111° respectively,[10] whence component bond moments follow as $\mu_{\text{OH}} = 1{\cdot}5\text{D}$ and $\mu_{\text{C-O}} = 1{\cdot}1\text{D}$. In MeOH these may be taken as interacting at 108°, producing a resultant of 1·77D. This resultant is therefore disposed at just over 60° to the C–O line. Accordingly, the polarisabilities to be expected collinearly with and perpendicularly to $\mu_{\text{resultant}}$ are:

$$10^{23}b_1 = 0{\cdot}192 + 0{\cdot}081\cos^2 60 + 0{\cdot}039\sin^2 60 + 0{\cdot}10\cos^2 48 + 0{\cdot}05\sin^2 48$$

$$10^{23}b_2 = 0{\cdot}192 + 0{\cdot}081\cos^2 30 + 0{\cdot}039\sin^2 30 + 0{\cdot}10\cos^2 42 + 0{\cdot}05\sin^2 42$$

$$10^{23}b_3 = 0{\cdot}192 + 0{\cdot}039 + 0{\cdot}05$$

The results are in reasonable agreement with the magnitudes found:

	Calc.	Found		Calc.	Found		Calc.	Found
$10^{23}b_1$ ...	$0{\cdot}31_4$	$0{\cdot}31_5$	$10^{23}b_2$ ...	$0{\cdot}34_0$	$0{\cdot}36_3$	$10^{23}b_3$ ...	$0{\cdot}28_1$	$0{\cdot}27_8$

With the next homologue, ethyl alcohol, an infinitude of configurations between *s-cis* and *s-trans* is theoretically possible, although (for steric reasons) structures near the *s-cis* extreme would seem less likely than those in which the CH_3 group and the H atom are farther apart. For the *s-trans* extreme form of ethyl alcohol b_3 should be:

$$5b_{\text{i}}^{\text{CH}} + b_{\text{T}}^{\text{C-C}} + b_{\text{T}}^{\text{C-O}} + b_{\text{T}}^{\text{O-H}} = 0{\cdot}436 \times 10^{-23}$$

For the form intermediate between *s-cis* and *s-trans* (in which the triangles defined by CH_3–C–O and H–O–C are in perpendicular planes) b_3 should be:

$$5b_{\text{i}}^{\text{CH}} + b_{\text{T}}^{\text{C-O}} + b_{\text{T}}^{\text{O-H}} + 0{\cdot}0986\cos^2 20 + 0{\cdot}0274\sin^2 20 = 0{\cdot}499 \times 10^{-23}$$

The values observed is $b_3 = 0{\cdot}444 \times 10^{-23}$ with which the first prediction fits better than the second. Estimates of b_1 and b_2 for the *s-trans* configuration are also in fair agreement with experiment:

	Calc.	Found		Calc.	Found		Calc.	Found
$10^{23}b_1$ ...	$0{\cdot}497_5$	0·492	$10^{23}b_2$ ...	0·537	0·566	$10^{23}b_3$ ...	0·436	0·444

Empirical calculations of the potential barriers to internal rotation, made several years ago by Aston *et al.*,[18] showing the *trans*-form to be stabler than the *cis* by *ca.* 1500 cal./mole, are consistent with our conclusion.

Inspection of the semi-axes listed in Table 4 reveals that there is a rough equality in the increase of b_1, b_2, and b_3 per additional CH_2 group. If Δb_{i} is the change from one

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[18] Aston, Isserow, Szasz, and Kennedy, *J. Chem. Phys.*, 1944, **12**, 336; Brickwedde, Moskow, and Aston, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 263; cf. also *J. Chem. Phys.*, 1943, **11**, 532; 1949, **17**, 111.

alcohol to its next, higher homologue, then the "apparent" b_i's (listed before) show differences as follows:

Δb_1	0·177	0·180	0·180	0·180	0·180
Δb_2	0·203	$0{\cdot}197_5$	$0{\cdot}195_5$	0·194	0·190
Δb_3	0·166	0·161	0·161	0·172	0·160

These differences are close to those seen between the calculated values for ethyl and methyl alcohols, *viz.*,

$$0{\cdot}497 - 0{\cdot}314 = 0{\cdot}183;\ 0{\cdot}537 - 0{\cdot}340 = 0{\cdot}197;\ 0{\cdot}436 - 0{\cdot}281 = 0{\cdot}155$$

a fact which suggests a certain repetitive commonness of configuration among the six alcohols under consideration. In particular, it is interesting that in ascending the series stage by stage by the addition of one C–C and two C–H links to each previous alcohol, it appears that the ellipsoid of the entrant C–C link is constantly inclined to the b_1, b_2, and b_3 directions in each previous alcohol. Indeed, it seems that this constant inclination cannot be far from half the tetrahedral angle ($T/2$) or $180° - T/2$, *i.e.*,

$$\Delta b_i = 2b_i^{\mathrm{CH}} + 0{\cdot}0986 \cos^2 (T/2) + 0{\cdot}0274 \sin^2 (T/2) = 0{\cdot}179 \times 10^{-23}$$

This is almost exactly the Δb noted above for the b_1 direction, and is close to the mean of all the Δb's taken together.

Nothing is here disclosed which is out of harmony with the accepted ideas of carbon stereochemistry: the normal alcohols may have their alkyl chains as near-flat zig-zags or arranged along helical paths. That the latter possibility deserves serious consideration is obvious from the arguments of Mumford[19] which, although stated primarily for the homologous n-aliphatic hydrocarbons, are of course easily transferable to any series having C_nH_{2n+1} groups. An extension of the present study (of Kerr effects, depolarisation factors, etc.) to bridge Mumford's C_{16} discontinuity would be worth while.

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[19] Mumford, *J.*, 1952, 4897.