563. *Molecular Polarisability. The Dipole Moments, Molar Kerr Constants, and Conformations of Eight Di-n-alkyl Ethers as Solutes in Carbon Tetrachloride.*

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Measurements on dimethyl ether provide information on the anisotropy of polarisability of the unit CH_2–O–CH_2, and from this the molar Kerr constants are calculated for various conformations of the next two higher ethers. Diethyl ether appears as represented by Fig. 3, and di-n-propyl ether as described in the text relevant to structures 4d and 4e. The other ethers cannot be allotted single apparent conformations owing to the large number of possible rotational isomers. If decyl groups have polarisability ellipsoids of revolution, then calculated and observed values of ${}_{\mathrm{m}}K$ agree when the longitudinal polarisability axes of the decyl groups in $(C_{10}H_{21})_2O$ lie in the C–O–C plane and make angles of 65° to the direction of $\mu_{\mathrm{resultant}}$.

The present work was started with two objectives, first, to measure the anisotropy of polarisability of dimethyl ether and, secondly, to use the information so obtained, in conjunction with already known polarisabilities of C–C and C–H bonds, to investigate the average or apparent conformations adopted by higher di-n-alkyl ethers when dissolved in carbon tetrachloride at ordinary temperatures. Eight ethers have been considered. Requisite experimental data (dielectric constants, electric birefringences, etc.), providing dipole moments, molar Kerr constants, etc., are summarised and discussed below.

Experimental

Materials, Apparatus, etc.—Dimethyl ether, prepared from methyl alcohol, then passed through potassium hydroxide solution and two columns of potassium hydroxide pellets, was slowly bubbled *via* a fine capillary tube into weighed amounts of cold carbon tetrachloride. The higher ethers were prepared and/or purified[1] to give: diethyl ether (b. p. 33·5—34·5°), dipropyl ether (b. p. 89—90°), dibutyl ether (b. p. 140—142°), dipentyl ether (b. p. 185—188°), di-isopentyl ether (b. p. 171—173°), didecyl ether (b. p. 175—180°/3—4 mm.), and dihexadecyl

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[1] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1951, 2nd edn., p. 308.

TABLE 1.

Incremental Kerr effects, refractive indices, dielectric constants, and densities for solutions in carbon tetrachloride at 25°.

Solute: *Dimethyl ether*

10^5w_2	2908	3032	3399	3533	4440
$10^7\Delta B$	−0·020	−0·021	−0·025	−0·028	−0·035

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}745$

10^5w_2	782	1178	1267	1812	2908
$-10^4\Delta n$	23	33	—	54	—
ε^{25}	2·2781	2·3013	2·3139	2·3448	2·3996
d_4^{25}	1·56830	1·56085	1·55814	1·54639	1·52882

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}291$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 6{\cdot}43$; $\Sigma\Delta d/\Sigma w_2 = -2{\cdot}04$

Solute: *Diethyl ether*

10^5w_2	2826	2934	3016	3812	3894	3975	5161	6551
$10^7\Delta B$	—	−0·024	−0·025	−0·032	−0·031	−0·033	−0·038	−0·048
$-10^4\Delta n$	56	56	69	—	—	—	—	120
d_4^{25}	1·53246	1·53170	—	—	—	—	—	1·47074

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}787$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}200$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}79$

Solute: *Dipropyl ether*

10^5w_2	1128	1892	2187	2811	2969	3792
$10^7\Delta B$	−0·007	−0·013	−0·014	−0·018	−0·019	−0·024
$-10^4\Delta n$	18	—	34	45	—	60
ε^{25}	2·2562	2·2752	2·2854	2·3063	2·3106	2·3319
d_4^{25}	—	1·5527	—	1·5367	1·5350	1·5218

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}643$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}158$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}73$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}67_3$

Solute: *Dibutyl ether*

10^5w_2	1438	3718	5663	7742	10,826	12,329	15,219	16,529
$10^7\Delta B$	−0·005	−0·015	−0·025	−0·036	−0·055	−0·062	−0·073	−0·076
$-10^4\Delta n$	—	—	—	87	—	137	164	—
ε^{25}	2·2530	2·2923	2·3260	2·3607	2·4074	2·4342	2·4776	—
d_4^{25}	1·5609	1·5243	1·4944	1·4654	1·4209	1·4007	1·3631	—

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}472$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}110$;
$\Delta\varepsilon = 1{\cdot}79w_2 - 0{\cdot}982w_2^2$; $\Delta d = -1{\cdot}66w_2 + 1{\cdot}32w_2^2$

Solute: *Dipentyl ether*

10^5w_2	3404	4418	5698	11,240
$10^7\Delta B$	−0·013	−0·017	−0·022	−0·044
$-10^4\Delta n$	—	37	48	87

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}388$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}083$

10^5w_2	554	1158	1717	2020	2842	3404
ε^{25}	2·2348	2·2426	2·2521	2·2587	2·2673	2·2768
d_4^{25}	1·57531	1·56594	1·55698	1·55215	1·53954	1·53041

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}45$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}60$.

Solute: *Di-isopentyl ether*

10^5w_2	4262	9001	14,042	15,299	16,799	17,470	18,725	24,442
$10^7\Delta B$	−0·013	−0·029	−0·045	−0·050	−0·056	−0·057	−0·063	—
$-10^4\Delta n$	—	—	—	135	—	—	162	201
ε^{25}	2·2839	2·3426	2·4003	2·4141	—	2·4372	2·4505	2·5079
d_4^{25}	1·5177	1·4490	1·3824	1·3682	—	1·3396	1·3249	1·2607

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}327$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}086$;
$\Delta\varepsilon = 1{\cdot}35w_2 - 0{\cdot}844w_2^2$; $\Delta d = -1{\cdot}59w_2 + 1{\cdot}11w_2^2$

Solute: *Didecyl ether*

10^5w_2	2471	4220	4875	5674	7253	7826
$10^7\Delta B$	−0·005	−0·009	−0·011	−0·014	−0·016	−0·018
$-10^4\Delta n$	—	16	—	23	—	30
ε^{25}	2·2430	2·2522	2·2553	2·2594	2·2672	2·2695
d_4^{25}	1·54737	1·52194	1·51196	1·50164	1·48152	1·47239

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}223$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}039$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}61$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}49$

TABLE 1. (*Continued.*)

Solute: *Dihexadecyl ether*

10^5w_2	1290	2477	3124	6588	8230	8824
$10^7\Delta B$	—	—	—	$-0{\cdot}008$	$-0{\cdot}011$	$-0{\cdot}011$
$-10^4\Delta n$	—	—	—	8	11	—
ε^{25}	—	2·2304	2·2390	2·2455	2·2499	—
d_4^{25}	1·56554	1·54992	1·53970	1·49134	—	—

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -0{\cdot}126$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}013$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}28$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}43$

TABLE 2.

Polarisation, dipole moments, and molar Kerr constants (from observations on solutions in carbon tetrachloride at 25°).

Solute	$\alpha\varepsilon_1$	$-\beta$	$-\gamma$	$-\delta$	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ(D)*	$_\infty({}_mK_2) \times 10^{12}$
Me_2O	6·43	1·29	0·200	$10{\cdot}6_4$	50·2	13·6	1·32	−3·9
Et_2O	3·87 †	$1{\cdot}13_2$	0·137	$11{\cdot}2_4$	59·3	22·1	1·32	−6·0
$Pr^n{}_2O$	2·73 ‡	$1{\cdot}05_6$ ‡	0·108	9·19	68·1	30·9	1·32	−6·4
$Bu^n{}_2O$	1·79 ‡	$1{\cdot}04_8$ ‡	0·075	6·74	73·5	41·2	1·21	−5·3
$(n\text{-}C_5H_{11})_2O$	1·45	$1{\cdot}01_0$	0·057	5·54	82·3	50·2	1·20	−4·9
$(\text{iso-}C_5H_{11})_2O$	1·35 ‡	$1{\cdot}00_3$ ‡	0·059	4·67	80·9	50·3	1·17	−3·8
$(n\text{-}C_{10}H_{21})_2O$	0·61	$0{\cdot}94_0$	0·027	3·18	125·2	95·7	1·10	−3·4
$(\text{n-}C_{16}H_{33})_2O$	0·28	$0{\cdot}90_3$	0·009	1·79	176·3	150·5	0·95	$+0{\cdot}0_3$

* Calculated by assuming $_DP = 1{\cdot}05\ R_D$. Alternatively, the use of $_DP$'s as estimated by Barclay and Le Fèvre [4] leads to dipole moment values D of: 1·31 (Me_2O), $1{\cdot}30_5$ (Et_2O), 1·28 (n-Pr_2O), and 1·21 (n-Bu_2O).

If for $(C_{16}H_{33})_2O$ the distortion polarisation is assumed to be equal to R_D, then $\mu = 1{\cdot}12$ D.

† Calculated from data in ref. 3.

‡ Measurements made in 1957 by M. R. Smith.

ether (m. p. 56°, after recrystallisation from diethyl ether). Infrared spectra of the purified products indicated in each case an absence of O–H bonds. Carbon tetrachloride, as solvent, was from a sulphur-free bulk supply which had been dried ($CaCl_2$), fractionated through a 1-m. column packed with glass helices, and then stored with fresh anhydrous calcium chloride. Symbols, methods of calculation, and headings used in the following Tables are explained in ref. 2, pp. 280—283; for convenience these have been recently summarised by Le Fèvre and Sundaram (*J.*, 1962, 1494). For carbon tetrachloride at 25°, $\varepsilon_1 = 2{\cdot}2270$, $d_1 = 1{\cdot}5845_4$, $(n_D)_1 = 1{\cdot}4575$, and $B_1 = 0{\cdot}070 \times 10^{-7}$ (sodium light).

Previous Measurements.—Dipole-moment determinations made before 1948 are listed by Wesson [3] in the M.I.T. Tables which do not contain values for didecyl and dihexadecyl ether. Since 1948 the following dipole moments (in Debye units) have been recorded (solvent or state, and reference, given in brackets; B = benzene; G = gaseous state; it should be noted that not all the μ's which follow, or those quoted by Wesson, are deduced by assuming $_DP = R_D$): dimethyl ether, 1·25 (B; 4), 1·29 (G; 4); diethyl ether, 1·26 (B; 4), 1·17 (G; 4), 1·21 (5), 1·18 (B; 6), 1·27 (in CCl_4; 7), 1·14 (in CS_2; 7), 1·14 (G; 8), 1·28 (B; 9); di-n-propyl ether, 1·13 (B; 4), 1·18 (G; 4), 1·31 (B; 9); di-n-butyl ether, 1·09 (B; 4), 1·17 (G; 4), 1·26 (B; 9), 1·17 (in kerosene; 10), 1·22 (B; 10), 1·13 (in toluene; 10). Stuart and Volkmann,[11] and Stuart [12] have recorded the Kerr constants K of the following ethers as gases ($10^{-15}\ K$ for $\lambda = 5400°$ A and 760 mm. pressure): dimethyl ether [11] −5 (at 18°), diethyl ether [11] −3·9 (at 62·7°), di-n-propyl ether [11] −2·3 (at 123·9°), and di-n-butyl ether [12] −0·7 (at 184°). The International Critical Tables [13] cite the Kerr constant B for liquid diethyl ether as −0·205

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[2] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[3] Wesson, " Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.

[4] Barclay and Le Fèvre, *J.*, 1952, 1643.

[5] Jatkar and Deshpande, *J. Univ. Poona Sci. and Technol.*, 1954, 48.

[6] Sobczyk and Sykin, *Roczniki Chem.*, 1957, **31**, 1245.

[7] Kapustin, *J. Exp. Theor. Phys.* (*U.S.S.R.*), 1947, **17**, 30.

[8] Moore and Hobbs, *J. Amer. Chem. Soc.*, 1949, **71**, 411.

[9] Spurr and Zeitlin, *J. Amer. Chem. Soc.*, 1950, **72**, 4832.

[10] Li and Terry, *J. Amer. Chem. Soc.*, 1948, **70**, 344.

[11] Stuart and Volkmann, *Ann. Phys.*, 1933, **18**, 121.

[12] Stuart, " Die Struktur des freien Moleküls," Springer, Berlin, 1952.

[13] International Critical Tables, 1930, Vol. VII, 1st edn., pp. 110—112.

relative to $B(CS_2)$ as unity; The Le Fèvres [14a] give B as $= -0{\cdot}614 \times 10^{-7}$ (at 25° for sodium light, whence ${}_{\mathrm{m}}K_{\mathrm{liquid}} = -5{\cdot}3 \times 10^{-12}$), and ${}_{\infty}({}_{\mathrm{m}}K_2)$ as $-7{\cdot}5 \times 10^{-12}$ and $-8{\cdot}5 \times 10^{-12}$, respectively, in carbon tetrachloride and benzene at 20°.

DISCUSSION

Dimethyl Ether.—Molecular symmetry is such that the principal axes can be located as shown in Fig. 1a, with b_1 and b_2 in the plane of C–O–C, b_1 bisecting the angle COC; b_3 is normal to this plane. Le Fèvre and Le Fèvre [14b] have specified the polarisability ellipsoid for the C–O bond in paraldehyde by the semi-axes: $b_{\mathrm{L}}^{\mathrm{C-O}} = 0{\cdot}081$, $b_{\mathrm{T}}^{\mathrm{C-O}} = b_{\mathrm{V}}^{\mathrm{C-O}} = 0{\cdot}039$ (all $\times 10^{-23}$ c.c.) * on the assumption that the " lone-pair " electronic polarisability contributions can be included in the " effective " semi-axes for the C–O links and that the bond ellipsoids thus described are axially symmetric about the inter-centre line. These values, used in conjunction with a C–O–C bond angle [15] of 111° ± 4° and the permanent dipole moment of 1·32 D acting along b_1, yield a calculated ${}_{\mathrm{m}}K$ of $(-0{\cdot}2 \pm 0{\cdot}8) \times 10^{-12}$ against the observed ${}_{\infty}({}_{\mathrm{m}}K_2)$ of $-3{\cdot}9 \times 10^{-12}$. For each C–H link $b_{\mathrm{L}}^{\mathrm{C-H}} = b_{\mathrm{T}}^{\mathrm{C-H}} = b_{\mathrm{V}}^{\mathrm{C-H}} = 0{\cdot}064$ (ref. 16). The experimental errors when handling this gaseous solute are relatively great, estimated at *ca.* $\pm 1{\cdot}0 \times 10^{-12}$, but not sufficient to explain the discrepancy. A direct evaluation of the C–O bond semi-axes has also been attempted: the assumptions outlined above being retained, ${}_{\infty}({}_{\mathrm{m}}K_2)$ and ${}_{\mathrm{E}}P$ (= 12·84 c.c. from addition of bond electronic polarisations listed in ref. 17) can be expressed in terms of the two unknowns $b_{\mathrm{L}}^{\mathrm{C-O}}$ and $b_{\mathrm{T}}^{\mathrm{C-O}}$; however, equations thus derived cannot be solved.

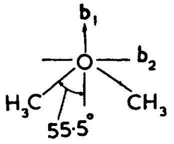

FIG. 1a.

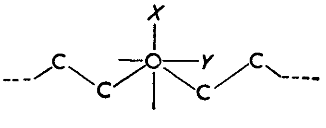

FIG. 1b.

Stuart and Volkmann [11] have recorded Δ, the depolarisation factor of transversely scattered light, for gaseous dimethyl ether as 0·016 from which a third equation in b_i is available, namely,

$$\frac{10\Delta}{6 - 7\Delta} = [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/(b_1 + b_2 + b_3)^2.$$

The other two equations are:

$$b_1 + b_2 + b_3 = 1{\cdot}527$$

and

$${}_{\infty}({}_{\mathrm{m}}K_2) = (2\pi N/9)(\theta_1 + \theta_2),$$

where

$$\theta_1 = (1/45kT)({}_{\mathrm{D}}P/{}_{\mathrm{E}}P)[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]$$

and

$$\theta_2 = (1/45k^2T^2)\,\mu^2[2b_1 - b_2 - b_3]$$

Results emerge as:

	From present work	From Stuart and Volkmann [11]
b_1	0·490	0·486
b_2	0·620 or 0·417	0·630 or 0·431
b_3	0·417 or 0·620	0·431 or 0·630
Σb	1·527	1·547

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* Bond and molecular polarisabilities are quoted throughout in 10^{-23} c.c. units.

[14] Le Fèvre and Le Fèvre, (*a*) *J.*, 1953, 4041; (*b*) *J.*, 1956, 3549.

[15] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958, M 138.

[16] Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1955, 1121.

[17] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

The ambiguity in b_2 and b_3 is caused by there being alternative solutions for the quadratic equation giving b_2 or b_3. By subtracting two C–H bond contributions from the present set of values, we derive for the polarisability semi-axes of the structural group $H_2C–O–CH_2$: $b_1' = 0{\cdot}362$, $b_2' = 0{\cdot}492$ or $0{\cdot}289$, $b_3' = 0{\cdot}289$ or $0{\cdot}492$. These are used in subsequent calculations.

Higher Ethers as Planar Zig-zags.—For the geometrical specifications of the alkyl groups, the angles $\widehat{COC}$ have been taken as 108°, and the angles $\widehat{CCO}$ and $\widehat{CCC}$ as 110° (see ref. 15; M 174). For the C–C bonds we assume[14b] the values $b_L^{C-C} = 0{\cdot}099$, $b_T^{C-C} = b_V^{C-C} = 0{\cdot}027$. Initially we examined the " planar " (*i.e.*, with all the carbon atoms and the oxygen of a particular structure lying in the one plane) zig-zag conformations for the ethers $(C_nH_{2n+1})_2O$, where n = 2, 3, 4, 5, 10, and 16. Calculated values of the molecular semi-axes and molar Kerr constants are listed in Table 3; in all cases the principal axes b_1, b_2, and b_3 coincide with the directions X, Y, and Z, respectively, of Fig. 1b.

TABLE 3.

	3A *				3B †				
n	b_1	b_2	b_3	$10^{12}{}_{m}K$ (calc.)	b_1	b_2	b_3	$10^{12}{}_{m}K$ (calc.)	$_{\infty}({}_{m}K_2) \times 10^{12}$
2	0·845	1·029	0·727	−2·9	0·845	0·826	0·930	−5·9	−6·0
3	1·204	1·434	1·037	−0·1	1·204	1·231	1·240	−6·0	−6·4
4	1·559	1·843	1·347	+3·5	1·559	1·640	1·550	−5·4	−5·3
5	1·918	2·248	1·657	+7·7	1·918	2·045	1·860	−4·2	−4·9
10	3·701	4·285	3·207	+37·6	3·701	4·082	3·410	+11·0	−3·4
16	5·843	6·727	5·067	+98·1	5·843	6·524	5·270	+53·8	+0·03

* b_2' for the $H_2C–O–CH_2$ group is 0·492.
† b_2' ,, ,, ,, 0·289.

The values of $_{m}K$(calc.) in Table 3B are in good agreement with experiment for n = 2, 3, 4, and 5, whence the inference could be drawn that, at infinite dilution in carbon tetrachloride, these solute molecules exist as the " planar " extended structures, and that for the higher homologues, n = 10 and 16, the zig-zag arrangement is destroyed. Such is true only if, for the $H_2C–O–CH_2$ group, b_3' (which coincides with the Z direction) is greater than b_2'. Stuart (ref. 18, p. 544) has discounted this assumption as being incompatible with Silberstein's theory; Barclay and Le Fèvre[4] have shown that the ratios $\mu_{\text{sol.}}^2/\mu_{\text{gas}}^2$ found by experiment do not agree with those calculated for extended zig-zag structures of diethyl, di-n-propyl, and di-n-butyl ether. Volkmann[19] came to a similar conclusion from comparison of the molecular anisotropies (derived from the depolarisation factors for transversely scattered light) of dimethyl, diethyl, and di-n-propyl ether as gases. Molecular anisotropy factors, calculated from the semi-axes of Table 3B, compared with values of δ_{gas}^2 derived from data in refs. 11, 18, and 19 are:

n	δ_{gas}^2	δ^2 calc. *ex* 3B	n	δ_{gas}^2	δ^2 calc. *ex* 3B
2	0·043—0·044	0·003	3	0·024	0·0002

The evidence summarised above suggests that the apparent agreement between the $_{m}K$'s of Table 3B and those derived from experiment is fortuitous. Accordingly we reassessed the problem, accepting the values of b_2' and b_3' alternative to those used in Table 3B. It follows, of course, that diethyl ether and the higher di-n-alkyl ethers do not adopt " planar " extended configurations in the experimental medium.

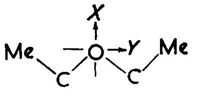

FIG. 2a.

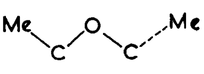

FIG. 2b.

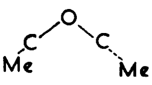

FIG. 2c.

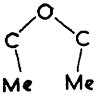

FIG. 2d.

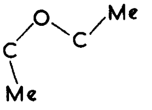

FIG. 2e.

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[18] Stuart, *Z. Phys.*, 1930, **63**, 533.
[19] Volkmann, *Angew. Chem.*, 1949, **61**, 201.

Diethyl Ether.—Figs. 2a—e represent hypothetical conformations of diethyl ether; 2a, 2d, and 2e are planar, if we disregard the hydrogen atoms, while 2c is achieved by rotating the methyl groups about the adjacent C–O bonds as axes, until they are 90° from their respective positions shown in 2a (*i.e.*, so that they are on opposite sides of the C–O–C plane). Form 2b represents structures intermediate between 2a and 2c. Stuart [20] has shown from steric considerations that the methyl groups of diethyl ether can have rotation opportunities of about 70° around the energetically most stable form 2a, and that conformations intermediate between 2c (which is sterically improbable) and 2d (which is sterically impossible), *i.e.*, having rotations α° greater than ± 90° from 2a, need not be seriously considered. Table 4 summarises the polarisability semi-axes and molar Kerr constants calculated for structures 2a—e. Only for forms 2a and 2d do the principal axes coincide with the directions X, Y, and Z.

TABLE 4.

Structure	α (°)	b_1	b_2	b_3	$10^{12}{}_{\mathrm{m}}K$ (calc.)
2a	0	0·845	1·029	0·727	−2·9
2b	20	0·838	1·026	0·737	−5·1
,,	24	0·835	1·025	0·741	−6·1
,,	30	0·830	1·022	0·749	−7·7
2c	90	0·806	0·983	0·812	−16·1
2d	180	0·933	0·941	0·727	+21·3
2e		0·887	0·987	0·727	+9·0

The observed $_\infty({}_{\mathrm{m}}K_2)$ is $-6{\cdot}0 \times 10^{-12}$, indicating that the effective conformation of diethyl ether in carbon tetrachloride is one in which the methyl groups are rotated *ca.* 24° from the "planar" zig-zag structure so that they are "*trans*" with respect to the C–O–C plane (Fig. 3).

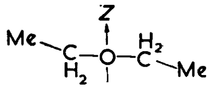

FIG. 3.

Di-n-propyl Ether.—From the polarisability parameters of the structure described above for diethyl ether can be derived, by subtraction of two C–H bond contributions, the matrix elements defining the polarisability tensor (in terms of the axes X, Y, and Z) of the group $H_2C{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$. Addition of two terminal methyl groups gives rise to an infinitude of possible conformations (see Fig. 4a). In 4b and 4c the Me–C–C planes are normal to the C–O–C plane, the methyl groups being located as shown. Scale models indicate that rotations of the methyl groups from the 4b and 4c positions towards the positive X direction are unlikely on steric grounds (see particularly ref. 21 regarding volume requirements of a lone electron pair; 4d represents an intermediate in which the methyl groups have been rotated in the negative X direction from 4b or 4c so that they each become parallel with the closest C–O bond. Molecular semi-axes and molar Kerr constants calculable for structures 4b—d are listed in Table 5.

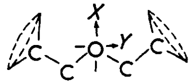

FIG. 4a.

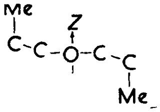

FIG. 4b.

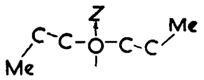

FIG. 4c.

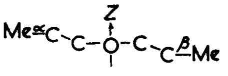

FIG. 4d.

TABLE 5.

Structure	b_1	b_2	b_3	$10^{12}{}_{\mathrm{m}}K$ (calc.)
4b	1·145	1·338	1·192	−21·6
4c	1·164	1·376	1·135	−15·0
4d	1·195	1·427	1·053	−3·3
4e	1·187	1·413	1·075	−6·5

Structure 4e, which gives excellent agreement with the observed $_\infty({}_{\mathrm{m}}K_2)$ of $-6{\cdot}4 \times 10^{-12}$, is generated by a 20° rotation of the α-methyl group (in Fig. 4d) in the negative Z direction and of the β-methyl group in the positive Z direction.

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[20] Stuart, *Phys. Rev.*, 1931, **38**, 1372.

[21] Aroney and Le Fèvre, *Proc. Chem. Soc.*, 1958, 82; *J.*, 1958, 3002.

Volkmann,[19] when observing that the molecular anisotropy factor for di-n-propyl ether vapour was distinctly lower than for dimethyl and diethyl ether (which, following Stuart,[20] he assumed to be planar), concluded that di-n-propyl ether must be more isotropic and therefore non-planar. If the calculated b's of the structures now suggested for diethyl and dipropyl ether are converted into δ^2(calc.) they yield 0·019 and 0·013, respectively. As a result of the ambiguity in locating b_2 and b_3 within the $H_2C{-}O{-}CH_2$ group, each of these molecules can have two possible conformations (one planar and one non-planar) indistinguishable by their electric moments and molar Kerr constants but differing greatly in their molecular anisotropies. For the non-planar forms, 2b and 4e, the values of δ^2(calc.) agree not unreasonably with those already quoted for $\delta_{gas}{}^2$ (not unreasonably, remembering the uncertainties of Δ_{gas} values; ref. 18 for example lists two possible values of Δ for dimethyl ether leading to $\delta_{gas}{}^2$ of 0·027 and 0·045, of which the former was used in deriving the molecular semi-axes of dimethyl ether) while the planar structures yield δ^2(calc.) values of a different order of magnitude.

Ethers of Formulæ (n-$C_nH_{2n+1})_2O$, *where* n = 4, 5, 10, *and* 16.—If one C–H link from each terminal carbon of structure 4e is replaced by a methyl group, thus giving di-n-butyl ether, the distance between the oxygen atom and each methyl group is now too great for any steric interaction, and a number of rotational isomers can be found for which ${}_mK$(calc.) equals ${}_mK$(obs.). This lack of specificity is common to all ethers with $n > 3$. Le Fèvre and Williams[22] have calculated, from experimental data for pure liquid decane, the polarisability semi-axes of this hydrocarbon, assuming that its ellipsoid is one of rotation, *i.e.*, having $b_1 \neq b_2 = b_3$; b_1 and b_2 appear as 2·046 and 1·778, respectively. Subtraction of three C–H bond contributions from each of these yields polarisability parameters for the group $C_{10}H_{19}$ which can now be combined with the semi-axes of the group $H_2C{-}O{-}CH_2$. If in di-n-decyl ether $b_L^{C_{10}H_{19}}$ lies in the C–O–C plane and makes an angle of $180° - \theta°$ with the positive X direction (parallel to $\mu_{resultant}$) then the calculated molar Kerr constant will be of the order of ${}_\infty({}_mK_2)$ observed when $\theta = 65°$ (cf. ref. 23, p. 4153).

Compound	θ°	b_1	b_2	b_3	$10^{12}{}_mK$ (calc.)	$10^{12}{}_\infty({}_mK_2)$
$(n\text{-}C_{10}H_{21})_2O$	65	3·63	4·10	3·46	−3·7	−3·4

The semi-axes b_1, b_2, and b_3 lie along the X, Y, and Z co-ordinates, respectively.

An analogous calculation for di-n-hexadecyl ether cannot be made because not all the properties required to give ${}_mK$ for $C_{16}H_{34}$ are on record. If the cetyl radical is more " crumpled " than its lower homologues its anisotropy will be less; if it were completely isotropic then ${}_mK$(calc.) for $(C_{16}H_{33})_2O$ would be $-1{\cdot}3 \times 10^{-12}$. If, by analogy with di-n-decyl ether, each $b_L^{C_{16}H_{31}}$ lies in the C–O–C plane and has $\theta = 65°$ (cf. also ref. 23, p. 4153) then agreement with experiment is achieved only if the ratio $b_L^{C_{16}H_{31}}/b_T^{C_{16}H_{31}} = b_L^{C_{16}H_{31}}/b_V^{C_{16}H_{31}}$ is 1·085.

Compound	θ°	b_1	b_2	b_3	$10^{12}{}_mK$ (calc.)	$10^{12}{}_\infty({}_mK_2)$
$(n\text{-}C_{16}H_{33})_2O$	65	5·79	6·21	5·64	+0·06	+0·03

The semi-axes b_1, b_2, and b_3 lie along X, Y, and Z, respectively.

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[22] Le Fèvre and Williams, unpublished work.

[23] Aroney, Izsak, and Le Fèvre, *J.*, 1961, 4148.