811. *Molecular Polarisability: the Dipole Moments, Polarisations, and Molar Kerr Constants of Ten Aliphatic Ketones as Solutes in Carbon Tetrachloride.*

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The properties named in the title are recorded for diethyl, di-n- and di-iso-propyl, di-n- and di-iso-butyl, di-n-pentyl, di-n- and di-iso-hexyl, di-n-heptyl, and di-n-tridecyl ketone in carbon tetrachloride. The apparent conformations of diethyl and di-isopropyl ketone as solutes are inferred from the observed molar Kerr constants to be as in Figs. IG, and between IIA and IIB, respectively. The molar Kerr constants of the higher di-n-alkyl ketones can be satisfactorily forecast from data known for acetone and the related n-alkanes provided the polarisabilities of the attached alkyl groups are represented by ellipsoids of revolution whose long axes are situated at angles to the C=O bond varying from 67° in di-n-pentyl ketone to 63¼° in di-n-tridecyl ketone.

THE molar Kerr constants of the simpler aliphatic ketones as solutes at infinite dilution, $_\infty({}_\mathrm{m}K_2)$, have not hitherto been recorded, except for acetone.[1] From $_\infty({}_\mathrm{m}K_2)_\mathrm{acetone}$, together with light-scattering data,[2] Le Fèvre, Le Fèvre, and Rao [3] deduced the longitudinal, transverse, and "vertical" polarisabilities ($b_\mathrm{L}^\mathrm{C:O}$, $b_\mathrm{T}^\mathrm{C:O}$, and $b_\mathrm{V}^\mathrm{C:O}$ respectively) of the C=O bond as 0·230, 0·140, and 0·046. (Throughout this paper, polarisabilities will be quoted in 10^{-23} c.c.) Observations in ref. 3, and others (unpublished) now accumulating, suggest that these values are of general applicability to structures in which the ketone group is "isolated" (*i.e.*, non-conjugated); accordingly they will be adopted in the analysis of the new $_\infty({}_\mathrm{m}K_2)$ measurements reported in Tables 1 and 2. For none of the

TABLE 1. *Incremental Kerr effects, refractive indexes, dielectric constants, and densities for solutions in carbon tetrachloride at* 25°.

Solute: *Diethyl ketone*

$10^5 w_2$	290	376	641	785	1222	1256	3085	3369	4670
$10^7 \Delta B$	—	—	0·047	0·054	0·091	0·098	0·225	0·247	0·344
$-10^4 \Delta n$	—	—	—	—	—	—	37	40	57
ε^{25}	2·2784	2·2916	2·3394	2·3637	2·4410	2·4465	—	—	—
d_4^{25}	1·57999	1·57899	1·57483	1·57275	1·56612	1·56564	1·53918	1·53512	1·51694

whence $\sum 10^7 \Delta B / \sum w_2 = 7{\cdot}35$; $\sum \Delta n / \sum w_2 = -0{\cdot}120$; $\sum \Delta\varepsilon / \sum w_2 = 17{\cdot}5$; $\sum \Delta d / \sum w_2 = -1{\cdot}50$

Solute: *Di-n-propyl ketone*

$10^5 w_2$	859	929	1253	1392	1648	1757	2528	3006	3858	5255
$10^7 \Delta B$	—	—	—	0·047	0·057	0·061	—	0·106	0·142	0·187
$-10^4 \Delta n$	—	—	—	—	17	—	—	—	39	51
ε^{25}	2·3286	2·3377	2·3765	2·3933	—	2·4357	2·5255	2·5863	—	—
d_4^{25}	—	1·57094	1·56578	1·56421	1·56017	—	—	1·54094	1·52874	1·51031

whence $\sum 10^7 \Delta B / \sum w_2 = 3{\cdot}51$; $\sum \Delta n / \sum w_2 = -0{\cdot}100$; $\sum \Delta\varepsilon / \sum w_2 = 11{\cdot}9$; $\sum \Delta d / \sum w_2 = -1{\cdot}46$

Solute: *Di-isopropyl ketone*

$10^5 w_2$	477	957	1005	1162	1941	2115	3683
$10^7 \Delta B$	—	0·029	0·030	0·035	0·059	0·066	0·118
$-10^4 \Delta n$	—	—	—	—	21	24	41
ε^{25}	2·2896	2·3524	2·3594	2·3785	2·4855	2·5092	—
d_4^{25}	1·57724	1·56996	1·56926	1·56690	1·55510	1·55264	1·52995

whence $\sum 10^7 \Delta B / \sum w_2 = 3{\cdot}07$; $\sum \Delta n / \sum w_2 = -0{\cdot}111$; $\sum \Delta\varepsilon / \sum w_2 = 13{\cdot}2$; $\sum \Delta d / \sum w_2 = -1{\cdot}51$

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[1] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

[2] Le Fèvre and Rao, *J.*, 1957, 3644.

[3] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

TABLE 1. (*Continued*).

Solute: *Di-n-butyl ketone*

$10^5 w_2$	676	1102	1824	2951	3809	5038
$10^7 \Delta B$	0·014	0·024	0·042	0·068	0·085	0·113
$-10^4 \Delta n$	—	—	—	21	27	36
ε^{25}	2·2912	2·3311	—	2·5071	2·5922	2·7091
d_4^{25}	1·57457	1·56826	1·55781	1·54206	1·52926	1·51241

whence $\sum 10^7 \Delta B / \sum w_2 = 2{\cdot}22$; $\sum \Delta n / \sum w_2 = -0{\cdot}071$; $\sum \Delta \varepsilon / \sum w_2 = 9{\cdot}52$; $\sum \Delta d / \sum w_2 = -1{\cdot}46$

Solute: *Di-isobutyl ketone*

$10^5 w_2$	913	929	2009	2262	2500	3432
$10^7 \Delta B$	0·018	0·019	0·038	0·043	0·048	0·064
$-10^4 \Delta n$	—	—	—	21	24	33
ε^{25}	2·3109	2·3127	2·4128	2·4364	2·4586	2·5471
d_4^{25}	1·57043	1·57028	1·55385	1·55012	1·54663	1·53281

whence $\sum 10^7 \Delta B / \sum w_2 = 1{\cdot}93$; $\sum \Delta n / \sum w_2 = -0{\cdot}095$; $\sum \Delta \varepsilon / \sum w_2 = 9{\cdot}25$; $\sum \Delta d / \sum w_2 = -1{\cdot}53$

Solute: *Di-n-pentyl ketone*

$10^5 w_2$	800	1308	1720	2117	2774	3254	3724
$10^7 \Delta B$	—	0·023	0·032	0·039	0·050	0·056	0·067
ε^{25}	2·2901	2·3307	—	2·3942	2·4466	2·4838	2·5211
d_4^{25}	1·57289	1·56553	1·55937	1·55368	1·54432	—	1·53034

whence $\sum 10^7 \Delta B / \sum w_2 = 1{\cdot}80$; $\sum \Delta \varepsilon / \sum w_2 = 7{\cdot}91$; $\sum \Delta d / \sum w_2 = -1{\cdot}46$

$10^5 w_2$	1494	2156	2924
$-10^4 \Delta n$	8	11	16

whence $\sum \Delta n / \sum w_2 = -0{\cdot}053$

Solute: *Di-n-hexyl ketone*

$10^5 w_2$	897	997	1454	1722	2468	2915
$10^7 \Delta B$	0·012	0·013	0·019	0·021	0·032	0·037
$-10^4 \Delta n$	—	—	—	8	11	13

whence $\sum 10^7 \Delta B / \sum w_2 = 1{\cdot}29$; $\sum \Delta n / \sum w_2 = -0{\cdot}045$

$10^5 w_2$	705	940	955	1080	1275	2153
ε^{25}	2·2727	2·2878	2·2890	2·2966	2·3096	2·3651

whence $\sum \Delta \varepsilon / \sum w_2 = 6{\cdot}46$

$10^5 w_2$	720	790	897	997	1454	1722	2915
d_4^{25}	1·57389	1·57291	1·57156	1·57001	1·56346	1·55958	1·54255

whence $\sum \Delta d / \sum w_2 = -1{\cdot}46$

Solute: *Di-isohexyl ketone*

$10^5 w_2$	828	1464	1650	2012	2221	2344
$10^7 \Delta B$	0·010	0·015	0·018	0·023	0·025	0·026
$-10^4 \Delta n$	—	—	—	12	13	14
ε^{25}	2·2794	2·3191	2·3298	2·3536	2·3663	2·3754
d_4^{25}	1·57232	1·56317	1·56035	1·55522	1·55237	1·55043

whence $\sum 10^7 \Delta B / \sum w_2 = 1{\cdot}12$; $\sum \Delta n / \sum w_2 = -0{\cdot}060$; $\sum \Delta \varepsilon / \sum w_2 = 6{\cdot}29$; $\sum \Delta d / \sum w_2 = -1{\cdot}46$

Solute: *Di-n-heptyl ketone*

$10^5 w_2$	236	846	1292	1368	1862	2354	2809	4099
$10^7 \Delta B$	—	—	0·011	0·012	0·016	0·020	0·024	0·035
$-10^4 \Delta n$	—	—	—	—	—	9	11	15
ε^{25}	—	2·2792	2·3057	2·3119	2·3432	2·3715	2·4032	—
d_4^{25}	1·58108	1·57227	1·56601	1·56452	1·55732	1·55050	1·54308	—

whence $\sum 10^7 \Delta B / \sum w_2 = 0{\cdot}858$; $\sum \Delta n / \sum w_2 = -0{\cdot}038$; $\sum \Delta \varepsilon / \sum w_2 = 6{\cdot}19$; $\sum \Delta d / \sum w_2 = -1{\cdot}46$

Solute: *Di-n-tridecyl ketone*

$10^5 w_2$	1121	1144	1581	1649	1675
$10^7 \Delta B$	0·003	0·003	0·004	0·005	0·005
$-10^4 \Delta n$	—	—	3	3	—

whence $\sum 10^7 \Delta B / \sum w_2 = 0{\cdot}277$; $\sum \Delta n / \sum w_2 = -0{\cdot}018$

$10^5 w_2$	468	706	839	1101	1121	1347	1639	1675	1715
ε^{25}	—	2·2446	2·2478	2·2546	2·2550	2·2618	2·2690	—	2·2713
d_4^{25}	1·57782	1·57485	1·57250	1·56961	1·56876	1·56564	—	1·56159	—

whence $\sum \Delta \varepsilon / \sum w_2 = 2{\cdot}53$; $\sum \Delta d / \sum w_2 = -1{\cdot}40$

ten ketones here examined, has any evidence indicating conformation been previously advanced, apart from one reference to diethyl and di-isopropyl ketones.[4,5]

TABLE 2. *Polarisations, dipole moments, and molar Kerr constants (from observations on solutions in carbon tetrachloride at 25°).*

Solute	$\alpha\varepsilon_1$	$-\beta$	$-\gamma$	δ	$_\infty P_2$ (c.c.)	$_\text{D}P$ (c.c.) [a]	μ (D)	$10^{12}{}_\infty({}_\text{m}K_2)$
$(C_2H_5)_2CO$	17·5	0·947	0·082	105	190·2	26·8	2·82	63·7
$(n\text{-}C_3H_7)_2CO$ ...	11·9	0·921	0·069	50·1	183·9	35·7	2·70	39·8
$(iso\text{-}C_3H_7)_2CO$ ...	13·2	0·955	0·076	43·9	200·4	36·2	2·83	33·9
$(n\text{-}C_4H_9)_2CO$ ...	9·52	0·921	0·049	31·7	193·5	45·9	2·69	31·1
$(iso\text{-}C_4H_9)_2CO$ ...	9·25	0·963	0·065	27·6	190·6	45·8	2·66	26·9
$(n\text{-}C_5H_{11})_2CO$ ...	7·91	0·921	0·036	25·7	202·5	55·9	2·68	30·5
$(n\text{-}C_6H_{13})_2CO$ ...	6·46	0·921	0·031	18·4	205·6	65·7	2·61	25·7
$(iso\text{-}C_6H_{13})_2CO$	6·29	0·921	0·041	16·0	202·0	64·8	2·59	22·3
$(n\text{-}C_7H_{15})_2CO$ ...	6·19	0·921	0·026	12·3	228·2	75·9	2·73	19·1
$(n\text{-}C_{13}H_{27})_2CO$ ...	2·53	0·884	0·012	$3{\cdot}9_6$	242·0	131·8	2·32	13·8

[a] *I.e.*, 1·05 R_D.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were purified immediately before use, giving the following ketones: diethyl, b. p. 101—102°, after drying ($MgSO_4$) of the B.D.H. product; di-n-propyl, b. p. 143°; di-n-butyl, b. p. 185—187°; di-n-pentyl, b. p. 222°; di-n-hexyl, b. p. 264°; di-n-heptyl, b. p. 278°; di-n-tridecyl, m. p. 76° (Found: C, 82·2; H, 13·8. Calc. for $C_{27}H_{54}O$: C, 82·15; H, 13·8%); di-isopropyl, b. p. 124—126°; di-isobutyl, b. p. 164—166°; di-isohexyl, b. p. 152°/92 mm. Carbon tetrachloride was from a sulphur-free supply which had been dried ($CaCl_2$), fractionated through a 1-m. column packed with glass helices, then stored with fresh anhydrous calcium chloride. Solutions, containing weight fractions w_2 of solutes, were made up from filtered carbon tetrachloride. Apparatus for the measurement of the dielectric [6] (ε) and Kerr [7] constants (B) of the solutions has been described before. Observations are set out in Table 1, in which Δ implies the difference between solution and solvent, *e.g.*, $\Delta B = B_{12} - B_1$, $\Delta n = n_{12} - n_1$ (refractive-index change), etc. (Subscripts 1, 2, and 12 denote solvent, solute, and solution, in that order.) Calculations relevant to Table 2 are explained in refs. 1, 7, 8, 9. For carbon tetrachloride at 25°, $\varepsilon_1 = 2{\cdot}2270$, $d_1 = 1{\cdot}58454$, $(n_\text{D})_1 = 1{\cdot}4575$, and $B_1 = 0{\cdot}070 \times 10^{-7}$ (Na light).

DISCUSSION

Dipole Moments.—Wesson's list [10] contains no entry for any of these ketones in carbon tetrachloride; acetone in this solvent has [11] $\mu = 2{\cdot}74$ D. Diethyl and di-n- and di-isopropyl ketone as solutes in benzene have [10] $\mu = 2{\cdot}72$, 2·73, and 2·74 D, respectively; the new values in Table 2 are evidently unremarkable (cf. Smyth [12]).

Molar Kerr Constants.—No previous determinations of $_\infty({}_\text{m}K_2)$'s for the ketones of Table 2 exist. An initially rapid, and subsequently more gradual, diminution of molar Kerr constant occurs as the n-alkyl chains are lengthened from acetone,[1] $_\infty({}_\text{m}K_2) = 101 \times 10^{-12}$, to di-n-tridecyl ketone, $_\infty({}_\text{m}K_2) = 13{\cdot}8 \times 10^{-12}$. None of the values is algebraically negative—a fact of interest because Stuart and Volkmann,[4] who recorded

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[4] Stuart and Volkmann, *Ann. Physik*, 1933, **18**, 121.

[5] Stuart, " Die Struktur des Freien Molekuls," Springer Verlag, Berlin, 1952, pp. 456—458.

[6] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

[7] Le Fèvre and Le Fèvre, Chap. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn. Vol. I, p. 2459.

[8] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

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

[10] Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

[11] Le Fèvre and Le Fèvre, *Austral. J. Chem.*, 1954, **7**, 33.

[12] Smyth, " Dielectric Behavior and Structure," McGraw-Hill, New York, 1955, p. 290.

the electric birefringences of, *inter alia*, gaseous diethyl and di-isopropyl ketone at temperatures considerably higher than that used here, give data which, transformed to 25°, correspond to molar Kerr constants of $25{\cdot}0 \times 10^{-12}$ and $-13{\cdot}6 \times 10^{-12}$ respectively. These are strikingly different from the $_{\infty}({}_{m}K_2)$'s now found (Table 2) at infinite dilution, being 39 and 48 units less positive; a similar calculation for acetone from ref. 4, however, yields an $_{m}K$ at 25° of 153×10^{-12}, which is 52 units more positive than the observed[1] $_{\infty}({}_{m}K_2)$ of 101×10^{-12}. Such disagreements seem too great to be due to alterations of molecular conformations by temperature or state; probably their causes lie in practical difficulties in the measurement of Kerr effects with hot vapours.

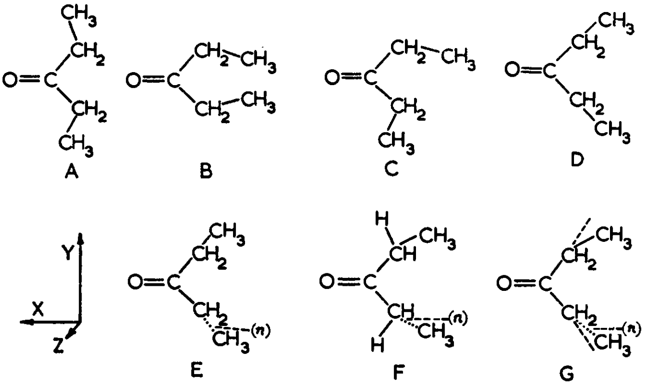
Conformation of Diethyl Ketone.—Le Fèvre and Rao,[2] from data on solutions in carbon tetrachloride, gave the principal polarisabilities of acetone as $b_1 = 0{\cdot}701$, $b_2 = 0{\cdot}684$, and $b_3 = 0{\cdot}482$, where b_1 is measured parallel to the C=O axis, b_2 is perpendicular to b_1 and in the C–C–C plane, and b_3 is normal to this plane. Subtraction of two C–H bond polarisabilities ($b_L^{C-H} = b_T^{C-H} = b_V^{C-H} = 0{\cdot}064$) provides principal polarisabilities for the $(\text{-CH}_2)_2\text{CO}$ unit; from this, in conjunction with longitudinal, transverse, and vertical polarisabilities for the C–C link of $0{\cdot}098_6$, $0{\cdot}027_4$, and $0{\cdot}027_4$, respectively, together with 120° for the C–(CO)–C angle and 109° 28′ for all other C–C–C angles, the results summarised in Table 3 have been calculated by the method outlined in ref. 7, p. 2486. The X axis is chosen to be always along the C=O group, Z to be perpendicular to, and Y to be in, the plane of the paper in diagrams (IA) to (IG). The locations of the principal polarisability directions within the XYZ co-ordinates are defined by the cosines listed.

TABLE 3. *Calculated polarisabilities and molar Kerr constants for seven conformations of diethyl ketone.*

Conformation	b_i (calc.)	Direction cosines with			$10^{12}{}_{m}K$ (calc.)
		X	Y	Z	
IA	$b_1 = 1{\cdot}071$	+1	0	0	123
	$b_2 = 1{\cdot}078$	0	+1	0	
	$b_3 = 0{\cdot}793$	0	0	+1	
IB	$b_1 = 1{\cdot}150$	+1	0	0	228
	$b_2 = 0{\cdot}999$	0	+1	0	
	$b_3 = 0{\cdot}793$	0	0	+1	
IC	$b_1 = 1{\cdot}117$	+0·959	−0·283	0	175
	$b_2 = 1{\cdot}032$	+0·283	+0·989	0	
	$b_3 = 0{\cdot}793$	0	0	+1	
ID	$b_1 = 1{\cdot}021$	+0·976	0	−0·218	47
	$b_2 = 1{\cdot}007$	0	+1	0	
	$b_3 = 0{\cdot}913$	+0·218	0	+0·976	
IE	$b_1 = 1{\cdot}016$	+1	0	0	48
	$b_2 = 1{\cdot}022$	0	+0·934	+0·356	
	$b_3 = 0{\cdot}903$	0	−0·356	+0·934	
IF	$b_1 = 1{\cdot}059$	+1	0	0	104
	$b_2 = 0{\cdot}996$	0	+0·998	+0·066	
	$b_3 = 0{\cdot}887$	0	−0·066	+0·998	
IG	$b_1 = 1{\cdot}026$	+1	0	0	60
	$b_2 = 1{\cdot}010$	0	+0·959	+0·285	
	$b_3 = 0{\cdot}906$	0	−0·285	+0·959	

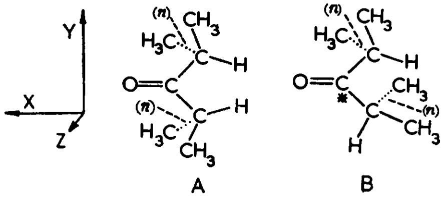
Conformations IA, B, and C are planar and as shown in the diagrams; in D the $\text{C–CH}_2\text{–CH}_3$ triangles are in planes perpendicular to the $\text{CH}_2{\cdot}\text{C}{\cdot}\text{CH}_2$ plane and both methyl groups project up above the latter plane; E is the same as D except that one of the methyl groups (that for which the C–Me bond is indicated by the letter n) projects below the $\text{CH}_2{\cdot}\text{C}{\cdot}\text{CH}_2$ plane; in F the C=O " eclipses " one of the C–H links in each of the methylene groups, *i.e.*, one C–H of each methylene group, and the carbonyl link are in the same plane; for G each $\text{CH}_2\text{–CH}_3$ group of configuration E is rotated inwards about the C–CH_2 bonds, *i.e.*, away from the positive X direction, by 10° from the positions in E.

The observed value of the molar Kerr constant is 63·7 × 10^{-12}, which is much below that calculated for any planar conformation. In E (which sterically is preferable to D) the terminal C–CH_3 groups are out of the CH_2·C·CH_2 plane to the maximum extent and for this the calculated $_{m}K$ is too small. Best agreement is obtained with the intermediate conformation G.



(I)

Conformation of Di-isopropyl Ketone.—Only two conformations of this molecule appear, from Leybold models, to be sterically allowable, namely IIA and B. In IIA the two C–H bonds are coplanar with the C=O and are located as shown in the diagram; in IIB, the two C–H bonds are also coplanar with C=O but one isopropyl group has been rotated through 180° about *C–C from its position in A. Molecular polarisability semiaxes have been computed for the two configurations and, by taking the observed dipole moment as acting along the carbonyl bond axis, the corresponding molar Kerr constants have been estimated.



(II)

TABLE 4. *Calculated polarisabilities and molar Kerr constants for two conformations of di-isopropyl ketone.*

Conformation	b_i (calc.)	Direction cosines with X	Y	Z	10^{12} $_{m}K$ (calc.)
IIA	b_1 = 1·339	+1	0	0	0·3
	b_2 = 1·386	0	+1	0	
	b_3 = 1·292	0	0	+1	
IIB	b_1 = 1·390	+0·886	+0·464	0	52
	b_2 = 1·334	−0·464	+0·886	0	
	b_3 = 1·292	0	0	+1	

The observed value for the molar Kerr constant is 33·9 × 10^{-12}. A mixture of the two forms in the ratio 2(B) : 1(A) would give a resultant $_{m}K$ of *ca.* 35 × 10^{-12} in agreement with that from experiment.

Conformations of Higher Di-n-alkyl Ketones.—From the values of B_{liq} at 20° listed on p. 460 of ref. 5, together with appropriate dielectric constants, densities, and refractive indexes from refs. 13 and 14, molar Kerr constants and anisotropy terms are calculable for the following hydrocarbons as liquids:

	10^7B_{liq}	ε	d	n_D	$10^{12}{}_{\text{m}}K_{\text{liq}}$	$10^{35}\theta_1$
n-Pentane	0·055	1·844	0·6263	1·3577	1·39	$0{\cdot}330_6$
n-Hexane	0·066	1·890	0·6595	1·375	1·70	$0{\cdot}404_3$
n-Heptane	0·076	1·924	0·6837	1·3878	2·14	$0{\cdot}509_0$
n-Dodecane	0·125	2·014	0·7488	$1{\cdot}421_5$	5·08	1·208

By assuming that because of their flexibility these molecules will show anisotropies of polarisability describable by an ellipsoid of rotation, *i.e.*, with $b_1 \neq b_2 = b_3$, the following may be deduced by subtracting from b_1 and b_2 the polarisability known for the C–H bond:

	$(b_1 + b_2 + b_3)$ *	$b_{\text{L}}{}^{\text{alkyl}}$	$(b_{\text{T}} = b_{\text{V}})^{\text{alkyl}}$		$(b_1 + b_2 + b_3)$ *	$b_{\text{L}}{}^{\text{alkyl}}$	$(b_{\text{T}} = b_{\text{V}})^{\text{alkyl}}$
n-Pentane ...	2·916	1·019	0·852	n-Heptane	3·990	1·404	1·197
n-Hexane ...	3·453	1·210	1·026	n-Dodecane	6·675	2·374	2·055

* Calc. from $b_{\text{L}} + b_{\text{T}} + b_{\text{V}} = 0{\cdot}153$ for the C–C bond, and 0·192 for the C–H bond.

These data can now be combined with the three polarisabilities, derived from acetone for the C–CO–C unit. Suppose the alkyl groups to be attached so that their longitudinal polarisability axes lie in the C–CO–C plane and make angles 180° — α° with the C=O bond (*i.e.*, with the direction of action of $\mu_{\text{resultant}}$, along which also the b_1's of the higher ketones are measured); the principal polarisabilities, and hence the ${}_{\text{m}}K$'s which emerge are sensitively dependent on α. Values of α which lead to ${}_{\text{m}}K$'s close to those observed are shown:

Ketone	α	b_1	b_2	b_3	$10^{12}{}_{\text{m}}K$ (calc.)
$(\text{n-C}_5\text{H}_{11})_2\text{CO}$	67	2·072	2·287	1·802	30·7
$(\text{n-C}_6\text{H}_{13})_2\text{CO}$	66·5	2·428	2·661	2·150	26·7
$(\text{n-C}_7\text{H}_{15})_2\text{CO}$	66·5	2·777	3·042	2·492	19·6
$(\text{n-C}_{12}\text{H}_{25})_2\text{CO}$	$63{\cdot}2_5$	4·556	4·919	4·208	14·5

An interesting implication is therefore that the larger the n-alkyl group the more does its maximum polarisability tend towards operation at trigonal angles to the C=O bond (for which limiting situation α should of course be 60°).

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[*Received, March* 13*th*, 1961.]

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[14] Maryott and Smith, " Table of Dielectric Constants of Pure Liquids," Nat. Bur. of Stds. Circular 514, Washington, issued Aug. 10th, 1951.