167. *The Electric Dipole Moments of Nickel Carbonyl, Di-iodoacetylene, Diethyl Sulphide, Diethylsulphone, and Decalin.*

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THE moments of nickel carbonyl and di-iodoacetylene were determined in connexion with the problem of the constitution of bivalent carbon compounds; the former (already briefly communicated; Sutton and Bentley, *Nature*, 1932, **130**, 314) in order to provide a further test of the Lewis–Langmuir structure for carbon monoxide, the latter in order to see whether or no the existence of an *iso*-form could be detected.

The moment of diethylsulphone was determined in order to ascertain whether the empirical rule given by one of us (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668), relating the moments and orienting powers of groups, applied to sulphones, and since diethyl sulphide had to be prepared incidentally its moment was redetermined.

Finally, needing a non-polar solvent for use at temperatures up to 150°, we checked the observations on decalin (decahydronaphthalene) made by Bretscher, who had already used it for this purpose (*Physikal. Z.*, 1931, **32**, 767).

EXPERIMENTAL.

Preparation and Purification of Materials.—Benzene. A. R. Benzene was purified as described previously (Sutton, *loc. cit.*).

Carbon tetrachloride. Messrs. Albright and Wilson's liquid for medicinal purposes was refluxed, and then distilled, over P_2O_5 in a stream of dry air.

Decalin. A specimen obtained from Messrs. Hopkin and Williams was stirred with a mixture of conc. H_2SO_4 and oleum for about 2 hr. and, after removal of the acid layer, for a further 2 hr. with acid $KMnO_4$ soln. The decalin was then separated, washed with alkali and with H_2O, dried over $CaCl_2$, and fractionated with two five-bulb Young–Thomas columns in series. The fraction of b. p. 190—192°/749·5 mm. was shaken with P_2O_5, distilled off, and used for the measurements. From the data of Hückel (*Annalen*, 1925, **441**, 42), this is mainly the *cis*-isomeride (*cis*-, b. p. 192°; *trans*-, b. p. 185°); for reasons which will appear in the discussion, no attempts were made to obtain one form pure.

Di-iodoacetylene. This was prepared according to Biltz (*Ber.*, 1904, **37**, 4415) and recrystallised from ligroin (b. p. 60—80°), the solution being made up at 40—50° and then cooled to − 15° in order to avoid decomp.; m. p. 77—78° (Biltz, *Ber.*, 1897, **30**, 1204, 78°; Baeyer, *Ber.*, 1885, **18**, 2274, 78°; Nef, *Annalen*, 1897, **298**, 344, 81°; de Chalmont, *Amer. Chem. J.*, 1897, **19**, 877, 82°) (Found: C, 8·64; H, 0. Calc. for C_2I_2: C, 8·64%). Three specimens, A, B, and C were made.

Nickel carbonyl. A specimen supplied by the Mond Nickel Co., and obtained through the kindness of Mr. A. C. G. Egerton, F.R.S., was used without further purification.

Diethyl sulphide. This was prepared by the method of Klason (*Ber.*, 1887, **20**, 3413) from $EtHSO_4$ and K_2S. It was freed from EtSH by washing with conc. KOH aq., washed, dried with $CaCl_2$, and twice distilled, the fraction of b. p. 92·3—92·4°/775 mm. being used (Nasini, *Ber.*, 1882, **15**, 2882, 92·2—93°/754 mm.; Beckmann, *J. pr. Chem.*, 1878, **17**, 451, 91·9°/754·7 mm.; Carrara and Coppadoro, *Gazzetta*, 1894, **33**, i, 343, 92°/758·5 mm.).

Diethylsulphoxide and diethylsulphone. The former was prepared from Et_2S by Pummerer's method (*Ber.*, 1910, **43**, 1407). As much H_2O and AcOH as possible were removed by heating to 50° in vac.: the solid which separated when the residue was cooled in a freezing mixture was filtered off and had m. p. 7—12° (Pummerer, *loc. cit.*, 4—6°). This substance appeared to undergo concurrent oxidation and reduction, to sulphone and sulphide respectively, on being heated, and purification by distillation was therefore impracticable. Moreover, its low m. p. and hygroscopic nature made recrystn. difficult, and attempts to purify it were therefore unsatisfactory. Consequently, it was not used for measurements but was converted by Pummerer's method (*loc. cit.*) into the sulphone, which was recrystallised twice from ligroin (b. p. 60—80°); m. p. 69·5—71·0° (Pummerer, 73—74°).

Dipole-moment Determinations.—Dielectric-constant measurements. These were made with the heterodyne apparatus already described (Sutton, *loc. cit.*). Most of the determinations in C_6H_6 solution at 25° were made with the dilution condenser therein described: some of these, and all those in CCl_4 at 0°, were made with a condenser of the Sayce–Briscoe type (see Ball, J., 1930, 570). Another condenser, similar to the latter, but modified so that it could be completely immersed in the bath liquid, was used for the measurements at high temps. It was made of Pyrex glass and its capacity was assumed to be independent of temp.; the probable change would be equal to the linear expansion, *i.e.*, about 0·05% per 100°.

Densities. Those at 0° and 25° were made in Sprengel–Ostwald type pyknometers. Those of decalin at the higher temps. were also made in one of this type, but it had four graduations which were under the bath-liquid surface and were illuminated and observed by periscopes. The tip projected a short distance above the surface and the adjustment was made by applying a slight pressure to expel the contents through it until the meniscus was level with one of the graduations (the calibrations for which were known), after which it was capped, allowed to cool, and weighed as usual. This pyknometer was first " aged " as recommended by Bretscher (*Physikal. Z.*, 1931, **32**, 768) and then calibrated with H_2O at three temps., the coeff. of cubical expansion of the glass being so found (29×10^{-6} c.c./c.c./°C.).

The high-temperature thermostat was a brass cylinder holding 6½ l. of dibutyl phthalate, heated by an external main heater and an internal subsidiary heater, which was controlled by a mercury-filled thermoregulator. Further details of the high-temperature technique will be given later.

Refractive indices. These were measured at 25° for the Hg green line (5461) as before described.

In the following tables f_2 = molar fraction of solute; d = density, from the mean d–f_2 line; ε^T = dielectric constant at $T°$; n = refractive index at 25° (λ 5461); P_2, ${}_{E}P_2$, and ${}_{A+O}P_2$ = total, electron, and atom + orientation polarisations, respectively, of solute.

The following consts. were determined and used throughout the calculations:

	d.	ϵ.	P_1.	$n_{5461}^{25°}$.	${}_{E}P_1$.
C_6H_6 at 25°	0·8740	2·2727*	26·600	1·5020	26·366
CCl_4 at 0°	1·6317	2·2748	28·116	—	—
25°	1·5846	2·2244	28·142	1·46046	26·604

* From Hartshorn and Oliver (*Proc. Roy. Soc.*, 1929, *A*, **123**, 664).

Nickel Carbonyl in Carbon Tetrachloride at 0°.

	$d_{4°}$.					
f_2.	0°.	25°.	$\epsilon^{0°}$.	$n_{5461}^{25°}$.	P_2.	${}_{E}P_2$.
0·03060	1·6208	1·5726	2·2787	1·46057	39·38	37·38
0·01578	1·6258	—	2·2767	—	39·52	—

Mean P_2 = 39·45 ± 0·1 c.c.; ${}_{E}P_2$ = 37·4 ± 0·1 c.c. (value calc. for Tl line 535, from data in Landolt–Börnstein, = 35·5 c.c.).

$$P_2 - {}_{E}P_2 = P_{A+O}P_2 = 2 \text{ c.c.};\ \mu = (0{\cdot}3) \times 10^{-18} \text{ e.s.u.}$$

Di-iodoacetylene in Carbon Tetrachloride at 0°.

A (1)	0·03070	1·6775	1·6289	2·3039	1·46671	39·6	34·8
(2)	0·01890	1·65985	1·61145	2·3029	1·46410	48·0	35·2
(3)	0·00883	1·64485	1·5968	2·2996	1·46202	68·2	37·1
B (1)	0·01270	1·6505	1·60225	2·2836	1·46285	35·9	36·05
(2)	0·01168	1·6490	1·6008	2·2880	1·46254	42·7	35·8
(3)	0·01069	1·6477	1·59975	2·2873	1·46239	43·1	35·6
(4)	0·01323	1·6512	1·6030	2·2835	—	35·15	—
C (1)	0·00894	1·64490	—	2·2828	—	39·1	—

Remarks. A (1) measured 3 days after prepn.; (2) as (1), recryst.; (3) as (2), left one day more. B (1) measured 1 day after prepn.; (2) as (1); (3) measured 2 days after prepn.; (4) measured 10 days after prepn. C (1) measured immediately after prepn.

P_2 at inf. diln. = 39·2 c.c.; ${}_{E}P_2$ at inf. diln. = 36·3 c.c.;
$P_2 - {}_{E}P_2 = {}_{A+O}P_2 = 2{\cdot}9$ c.c.; $\mu = (0{\cdot}33) \times 10^{-18}$ e.s.u.

Diethyl Sulphide, in Benzene at 25°.

f_2.	d.	$\epsilon^{25°}$.	$n^{25°}_{5461}$.	P_2.	${}_{E}P_2$.
0·04108	0·8719	2·4100	1·4991	80·1	28·5
0·03442	0·8722	2·3890	1·4995	80·9	28·4
0·02347	0·8728	2·3519	1·5003	81·1	28·0
0·01491	0·8732	2·3223	—	80·6	—

P_2 at inf. diln. = 81·5 c.c.; ${}_{E}P_2$ at inf. diln. = 27·8 c.c.;
$P_2 - {}_{E}P_2 = {}_{A+O}P_2 = 53{\cdot}7$ c.c.; $\mu = 1{\cdot}61 \times 10^{-18}$ e.s.u.

Diethylsulphone, in Benzene at 25°.

0·02882	0·8835	3·0875	1·5007	381·0	28·8
0·02236	0·8814	2·8985	—	390·2	—
0·01354	0·8785	2·6487	1·5014	405·6	28·1
0·00938	0·8771	2·5326	1·5016	414·1	27·5

P_2 at inf. diln. = 429·5 c.c.; ${}_{E}P_2$ at inf. diln. = 27·5 c.c.;
$P_2 - {}_{E}P_2 = {}_{A+O}P_2 = 402$ c.c.; $\mu = 4{\cdot}41 \times 10^{-18}$ e.s.u.

Decalin, 25°—142·4°.

T.	$d^T_{4°}$.	ϵ^T.	P.	T.	$d^T_{4°}$.	ϵ^T.	P.
25·0°	0·8787	2·1542	43·68	101·4°	0·8208	2·0622	44·01
41·5	0·8663	2·1342	43·75	131·8	0·7972	2·0238	44·09
45·9	0·8630	2·1284	43·75	142·4	0·7881	2·0079	44·08
75·6	0·8406	2·0928	43·88				

$\mu = 0{\cdot}0 \times 10^{-18}$ e.s.u.

DISCUSSION OF RESULTS.

All electric dipole moment values herein quoted are given in Debye units, *i.e.*, 1×10^{-18} e.s.u.

Nickel Carbonyl.—The apparent orientation polarisation of this substance, 2 c.c., is so small that the moment is indistinguishable from zero by the method used. Consequently, as was previously argued (Sutton and Bentley, *loc. cit.*), the most probable structure is  $\begin{matrix} O{\equiv}C\searrow & & \swarrow C{\equiv}O \\ & Ni & \\ O{\equiv}C\nearrow & & \nwarrow C{\equiv}O \end{matrix}$, with the groups arranged tetrahedrally. The structure  $\begin{matrix} C{\equiv}O\searrow & & \swarrow O{\equiv}C \\ & Ni & \\ C{\equiv}O\nearrow & & \nwarrow O{\equiv}C \end{matrix}$ is also possible, but is rather less probable.

Two points in the argument may be amplified. First, the objection to the structure  $\begin{matrix} C{=}O\searrow & & \swarrow O{=}C \\ & Ni & \\ C{=}O\nearrow & & \nwarrow O{=}C \end{matrix}$, that, like the methyl and ethyl orthocarbonic esters, it would have an appreciable moment, is not weakened by the fact that certain other CX_4 compounds, *e.g.*, pentaerythrityl tetra-chloride or -bromide, have no appreciable moment (Ebert, Eisenschitz, and von Hartel, *Z. physikal. Chem.*, 1928, *B*, **1**, 94), because the latter differ in an important respect: the atoms next the central atom have not merely one further atom or group attached to each of them, as have the oxygen atoms in the orthocarbonic esters or in the second nickel carbonyl formula, but have three, and therefore the interlocking of the groups which might rotate is more complete (Eucken and Meyer, *Physikal. Z.*, 1929, **30**, 402). Although two out of the three attached atoms in each rotatable group are hydrogen, there is increasing evidence (Sidgwick, *Ann. Reports*, 1932, **29**, 67 *et seq.*) that, so far as steric effects are concerned, their effective radius, and therefore their relative importance, is greater than was previously thought.

Secondly, although the angle between the oxygen valencies in the second structure is unknown, it would probably be equal to that between the double and single bonds of a nitrogen atom and hence would cause an appreciable asymmetry, as shown by the moment of 1·87 found for carbodianil, NPh:C:NPh, by Bergmann and Schütz (*Z. physikal. Chem.*, 1933, *B*, **19**, 389; see also Sidgwick, Sutton, and Thomas, this vol., p. 406).

Another possible structure is  $\begin{matrix}O{=}C\searrow & & \swarrow C{=}O\\ & Ni & \\ O{=}C\nearrow & & \nwarrow C{=}O\end{matrix}$; the carbon atoms, having only sextets of electrons in their valency groups, are analogous to boron in its trichloride, and since in the latter the three bonds are coplanar (Ulich and Nespital, *Z. Elektrochem.*, 1931, **37**, 559; Bergmann and Engel, *Physikal. Z.*, 1931, **32**, 507), it is probable that in the former the single and double bonds would be collinear, giving the molecule a symmetrical, non-polar structure. That carbon atoms in such a state would act as donor atoms seems, however, very improbable, there being no known examples of such behaviour, and hence it is unlikely that the substance would exist solely in this form.

We therefore conclude that the first structure is the most probable, though a resonance state between it and the last one is possible, and this is further, strong evidence that the free carbon monoxide molecule itself has the co-ordinate triple-link structure, either entirely (Hammick, New, Sidgwick, and Sutton, J., 1930, 1876) or, at least, predominantly in a resonance with the double-bonded one (Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 1000).

Iron pentacarbonyl is reported to have a small moment of 0·64 (Bergmann and Engel, *Z. physikal. Chem.*, 1931, *B*, **13**, 232), but since the moment of each CO radical with the co-ordinate link joining it to the central atom would be large (about 3—5, see Ulich and Nespital, *loc. cit.*, for analogous cases), this total moment, if real, indicates only a slight departure from a symmetrical arrangement.

Di-iodoacetylene.—As recorded on p. 653, eight measurements of total polarisation were made upon three separately prepared specimens. Six of the eight values of P_2 were between 35·2 and 43·2 c.c., giving a mean value of 39·2 c.c., which corresponds to an apparent orientation polarisation of 3 c.c. and an apparent moment of 0·33. Since the atom polarisations of several di-iodo-compounds appear to be about 3 c.c. (Smyth, "Dielectric Constant and Molecular Structure," New York, 1931, pp. 164, 166), it is clear that this moment is indistinguishable from zero by the method used, and consequently that the molecule is symmetrical. The first sample, A, gave two values of P_2 greater than 43 c.c., but neither of the later specimens did, even on standing for 10 days before measurement. We therefore concluded that the high values did not indicate a change of di-iodoacetylene itself into a polar form, but the accidental presence of some polar impurity, either introduced, or else produced by partial decomposition, during one recrystallisation. It is a fair conclusion that the purest specimens which we obtained had no appreciable moment.

Acetylene itself is non-polar (Smyth and Zahn, *J. Amer. Chem. Soc.*, 1925, **47**, 2501) and the finite value for the moment of diphenylacetylene reported by Smyth and Dornte (*ibid.*, 1931, **53**, 1296) has subsequently been shown to be incorrect by Schütz (footnote, Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 117) and by Weissberger and Sängewald (*ibid.*, 1933, *B*, **20**, 145), who find no moment. Thus the electric dipole moment measurements provide no evidence of the existence of the *iso*- (*i.e.*, acetylidene) structure which was suggested by Nef (*Annalen*, 1897, **298**, 202), supported by Lawrie (*Amer. Chem. J.*, 1906, **36**, 487), criticised by Biltz (*Ber.*, 1913, **46**, 143), and again supported by Mrs. Ingold (J., 1924, **125**, 1528), since in all probability this would be polar.

In the definite, so-called bivalent carbon compounds—carbon monoxide, the *iso*-cyanides, and the fulminates—the sextet of valency electrons on the bivalent carbon atom is made up to an octet by the formation of a co-ordinate link from the neighbouring atom (see Hammick, New, Sidgwick, Sutton, *loc. cit.*; New and Sutton, J., 1932, 1415, and above) and since this is impossible in the suggested acetylidene form, because the neighbouring atom already has a fully shared octet, the analogy used by Nef breaks down, and there is no reason, *a priori*, to expect this form to exist.

Diethyl Sulphide and Diethylsulphone.—The value found for the moment of the sulphide, 1·61, agrees well with that of 1·57 previously reported by Hunter and Partington (J., 1931, 2062). In diphenyl sulphide the C–S link moment is clearly in the same sense as that of the C–Cl link, *i.e.*, negative, having the negative pole nearer the sulphur atom, because the moment of the *pp'*-dichloro-derivative is numerically less than that of the parent substance (Bergmann and Tschudnowsky, *loc. cit.*, p. 107). If, now, we make the plausible assumption that the moment of the aliphatic C–S link, in diethyl sulphide, is in the same sense, the algebraic difference of moment between the aromatic and the aliphatic compound, $\mu_{\mathrm{Ph_2S}} - \mu_{\mathrm{Et_2S}}$, is $-1{\cdot}47 + 1{\cdot}61 = +0{\cdot}14$. The intercovalency angle in each compound being taken as 140° (Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, *B*, **10**, 397; Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230), the algebraic change along each C–S valency is $+0{\cdot}14/2 \times \cos 70° = +0{\cdot}2$.

Similarly, from the moments of diphenylsulphone, 5·10 (de Vries and Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888, 5·05; Bergmann and Tschudnowsky, *Ber.*, 1932, **65**, 457, 5·14) and *p*-chlorodiphenylsulphone, 4·42 (Bergmann and Tschudnowsky, *loc. cit.*), the sulphone group moment is obviously negative in aromatic compounds, and if this is true also in aliphatic compounds, the algebraic difference $\mu_{\mathrm{Ph_2SO_2}} - \mu_{\mathrm{Et_2SO}}$ is $-5{\cdot}1 + 4{\cdot}4 = -0{\cdot}7$.

It was previously pointed out (Sutton, *loc. cit.*) that if the moments of pairs of aromatic and aliphatic compounds are so compared, the *tert.*-alkyl derivatives being taken for comparison whenever possible in order to make a rough allowance for the greater polarisability of the phenyl group, then the differences are positive when the attached group is *op*-directing and negative when it is *m*-directing. It was further shown that they indicate relative movements of electric charges and are related to the " electromeric " effects postulated by Robinson in theories of organic reaction (*Rapp. Inst. Intern. Chim. Solvay*, 1931, p. 423). The present data for sulphides and sulphones provide further support for these generalisations : the positive difference for the former agrees with the *op*-directing power of the sulphur atom in thio-ethers, as shown in the halogenation and the sulphonation of diphenyl sulphide (Fries and Vogt, *Annalen*, 1911, **381**, 341; Bourgeois and Abraham, *Rec. trav. chim.*, 1911, **30**, 418; Bou, *Ber.*, 1895, **28**, 2321; Boeseken and Waterman, *Rec. trav. chim.*, 1910, **29**, 327; Bourgeois and Peterman, *ibid.*, 1903, **22**, 350), while the negative difference for the latter agrees with the *m*-nitration of diphenylsulphone (Martinet and Haehl, *Compt. rend.*, 1921, **173**, 775; cf. Twist and Smiles, J., 1925, **127**, 1248).

According to the view of Baldwin and Robinson (J., 1932, 1445), the sulphone group, unlike the carbonyl group, does not act by partaking in an electromeric effect with the benzene ring to which it is attached, but by setting up electromeric effects within the benzene ring by virtue of its great polarising power. It seems probable that the field acting on an unsaturated system would have to exceed a certain minimum strength before this kind of abnormal polarisation, which is not a simple deformation, could occur, and hence that, although an aliphatic and an aromatic group might have the same polarisabilities as measured by their refractivities, when very small field strengths are applied, yet they would be different in the big field near a highly polar group.

Decalin.—The polarisation of decalin was found to increase by 1% between 25° and 142·4°, and since this behaviour is the opposite to that of a polar substance, our observations confirm the conclusions of Bretscher (*Physikal. Z.*, 1931, **32**, 767) and Lautsch (*Z. physikal. Chem.*, 1928, *B*, **1**, 115) that this substance is non-polar. The increase is too great to be due to expansion of the condenser (see p. 653) and is of the same order as that found by Dornte and Smyth (*J. Amer. Chem. Soc.*, 1930, **52**, 3546) for open-chain paraffins, and for benzene and carbon tetrachloride by Meyer (*Z. physikal. Chem.*, 1930, *B*, **8**, 43), who stated that it was a real change in deformation polarisation.

Our decalin was a mixture of the two stereoisomerides (see p. 652), and it therefore follows that both are non-polar. The densities and refractivities of the isomerides differ appreciably (Hückel, *loc. cit.*), however, and hence, in using the substance as a non-polar solvent, it is necessary to know the constants of the batch taken. *cyclo*Hexane and methyl*cyclo*hexane are also non-polar (Weissberger and Sängewald, *Physikal. Z.*, 1929, **30**, 268; Williams, *J. Amer. Chem. Soc.*, 1930, **52**, 1831) and it can be demonstrated that, in general, since open-chain paraffins are non-polar (Dornte and Smyth, *loc. cit.*), all strainless cyclic paraffins should be so too. The former class is non-polar because the moments of the C–H links balance, owing to their tetrahedral arrangement, and because the C–C link moment is zero (Debye, "Polare Molekeln," Leipzig, 1929, p. 59). Now suppose that from such a molecule two hydrogen atoms are removed, one from each of two carbon atoms which are subsequently to be joined to give a strainless ring, then there are left two unbalanced, equal moments acting along the directions of the former C–H links. From the conditions, the molecule can be oriented strainlessly so that these moments balance, making the whole non-polar again, and so that the atoms are in the correct positions for ring closure to be made. This latter is now effected by allowing the unshared electrons on the two carbon atoms to form a covalency, and since it is a symmetrical process the cyclic paraffin so made is non-polar. This conclusion is perfectly general, since it applies to any strainless configuration of any cyclic compound formed from any suitable open-chain paraffin, no matter how long or complex, by any number of ring closures.

As a corollary, the moment of any monosubstitution product should be equal to that of a corresponding open-chain compound (cf. Sutton, *loc. cit.*). Williams's measurements on some *cyclo*hexane derivatives (*J. Amer. Chem. Soc.*, 1930, **52**, 1831) did not support this view, but most of the later ones made by Hassel and Naeshagen do so (*Z. physikal. Chem.*, 1932, *B*, **15**, 373; *ibid.*, *B*, **19**, 434) as do also those of Donle and Wolf (*ibid.*, 1930, *B*, **8**, 55) on *l*-menthol, *l*-borneol, and their esters, if comparisons are made between moments calculated similarly (*i.e.*, both corrected, or both uncorrected, for atom polarisation, P_A), as shown below :

Cyclic substance.			Open-chain substance.		
*cyclo*Hexanol	1·9	*a*			
	1·69	*b*			
2-Methyl*cyclo*hexanol	1·95	*a*	*iso*Propyl alcohol	1·72	*d*
3- ,,	1·9	*a*			
4- ,,	1·9	*a*	2-Heptanol	1·7	*j*
	1·71	*b*			
l-Menthol	1·68	*c*			
l-Borneol	1·66	*c*			
1 : 3 : 5-Trimethyl*cyclo*hexanol	1·86	*b*	*tert.*-Butyl alcohol	1·65	*f*
				1·71	*d*
1 : 2 : 4 : 5-Tetramethyl*cyclo*hexanol	1·94	*b*	*tert.*-Amyl alcohol	1·66	*b*
				1·83	*g*
*cyclo*Hexyl acetate	1·90	*b*			
l-Menthyl acetate	1·94	*c*	*iso*Propyl acetate	1·89	*d*
l-Bornyl acetate	1·97	*c*			
Chloro*cyclo*hexane	2·3	*a*	*sec.*-Butyl chloride	2·09	*h*
	2·07	*e*			
Bromo- ,,	2·3	*a*	*sec.*-Butyl bromide	2·12	*h*
	2·11	*e*			
Iodo- ,,	1·98	*e*	*sec.*-Butyl iodide	2·04	*h*

(*a*) Williams, *loc. cit.* (*b*) Hassel and Naeshagen, *Z. physikal. Chem.*, 1932, *B*, **19**, 434. (*c*) Donle and Wolf, *loc. cit.*, uncorr. for P_A. (*d*) Donle, *Z. physikal. Chem.*, 1931, *B*, **14**, 326, uncorr. for P_A. (*e*) Hassel and Naeshagen, *ibid.*, 1932, *B*, **15**, 373. (*f*) Smyth and Dornte, *J. Amer. Chem. Soc.*, 1931, **53**, 545. (*g*) Lange, *Z. Physik*, 1925, **33**, 169. (*h*) Parts, *Z. physikal. Chem.*, 1930, *B*, **7**, 327. (*j*) Errera and Sherrill, *Leipziger Vorträge*, 1929, p. 41.

A similar concordance would be anticipated between the moments of the aliphatic and the strainless cyclic mono-ketones, and it has been found by Wolf (*Z. physikal. Chem.*, 1929, *B*, **3**, 128, 139), Williams (*loc. cit.*), Donle and Volkert (*Z. physikal. Chem.*, 1930, *B*, **8**, 60), and Hassel and Naeshagen (*ibid.*, 1932, *B*, **19**, 434). The last authors report some exceptions, but do not yet regard them as established beyond doubt.

The simple strained cyclic paraffins should, from their symmetry, be non-polar, but those which are fused to strainless rings, or have alkyl groups attached to them, might be polar. In unsaturated compounds a new type of link is introduced, and they are polar unless symmetrical. Slight ring strain appears to have no effect on the moments of mono-substitution products (*e.g.*, borneol) but has been found to affect those of the ketones (Wolf, *loc. cit.*; *Physikal. Z.*, 1930, **31**, 227; Donle and Volkert, *loc. cit.*).

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