

### 61. *The Dielectric Polarisation of Liquid, Dissolved, and Gaseous Paraldehyde.*

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New measurements now recorded show paraldehyde to have a larger apparent moment in the liquid (1.7<sub>3</sub> D.) or dissolved states (light petroleum, 1.7<sub>7</sub>; dioxan, 1.9<sub>0</sub>; carbon tetrachloride, 1.9<sub>3</sub>; benzene, 1.8<sub>7</sub>; chloroform, 2.1<sub>4</sub>) than as a gas (1.44). The last datum follows from the equation:  $\tau P = 44.47 + 12792/T$ . The ratios  $\mu_{\text{liq.}}/\mu_{\text{gas}}$  or  $\mu_{\text{soln.}}/\mu_{\text{gas}}$  are the greatest yet recorded.

These results are discussed in relation to extant theories for the role of the medium in dipole moment measurements.

The atomic polarisation of paraldehyde is approximately one-third of the electronic.

THE present communication extends an earlier one by Le Fèvre and Russell (*J.*, 1936, 496), in which paraldehyde was examined merely because it had a large negative Kerr constant. During the intervening thirteen years, however, its molecular dimensions have been established (Ackerman and Mayer, *J. Chem. Physics*, 1936, 4, 377; Brockway and Carpenter, *J. Amer. Chem. Soc.*, 1936, 58, 1270; Gerding *et al.*, *Rec. Trav. chim.*, 1939, 58, 604, 615; 1941, 60, 258). Its shape allows it credibly to be fitted within an ellipsoid of rotation about the resultant dipole moment as axis (cf. Calderbank and Le Fèvre, *J.*, 1949, 199). Paraldehyde becomes accordingly an attractive "model" upon which to test extant theories for the variation of apparent polarisation and state.

Le Fèvre and Russell (*loc. cit.*) recorded dielectric constant and density figures for the pure liquid and solution of it in nine solvents, but fearing the presence of the equilibrium,  $\text{C}_6\text{H}_{12}\text{O}_3 = 3\text{CH}_3\cdot\text{CHO}$ , refrained from proceeding to a discussion. It is now clear that this anxiety was unjustified, since in ordinary organic media depolymerisation becomes marked only in the presence of acid catalysts (Orton and McKie, *J.*, 1917, 109, 185; Bell, Lidwell, and Vaughan-Jackson, *ibid.*, 1936, 1792). Moreover, in 1936 the necessary polarisation data for the gaseous state were lacking; the provision of these, together with a number of recent or repeated results in various solvents, is the main object of this paper.

The total molecular polarisation of paraldehyde vapour as a function of the absolute temperature has been found to follow the equation:  $P$  (c.c.) =  $44.47 + 12792/T$ , whence  $\mu = 1.44$  D., and the electronic and atomic contributions together (44.47 c.c.) are seen to exceed the  $[R_L]_D$  value (33.1 c.c.) used by Le Fèvre and Russell.

Further, where dissolved paraldehyde is concerned, our additional determination in benzene, light petroleum, and dioxan make it evident that rectilinear relationships do not hold between concentration (as weight fraction,  $w_1$ ) and either the dielectric constants ( $\epsilon_{12}$ ) or the densities ( $d_{12}$ ) of the mixtures (compare Le Fèvre, *Trans. Faraday Soc.*, 1950, 46, 1). With trioxymethylene and trithioformaldehyde, signs of the same phenomenon were found by Calderbank and Le Fèvre (*J.*, 1949, 199). Accordingly both our new measurements in non-polar solvents and those from Le Fèvre and Russell (relating to carbon tetrachloride and chloroform) have been evaluated or recalculated (cf. Le Fèvre, *loc. cit.*) to allow for this effect. The figures so produced are set out in Table I, which includes, for comparison, certain others (under  $\mu^*$ ) previously given in 1936, together with those (under  $\mu_R$ ) obtained by the refractivity method.

TABLE I.

Apparent moment and polarisation of paraldehyde at 25°.

Solvent or state.	Total pn.	Orientn. pn.	$\mu^*$ , D.	$\mu_B$ , D.	$\mu$ , D.
Gas .....	87.40	42.9 <sub>3</sub>	—	1.6 <sub>2</sub>	1.44.
Light petroleum .....	109.0 <sub>2</sub>	64.5 <sub>5</sub>	—	1.9 <sub>2</sub>	1.77
Dioxan .....	119.2 <sub>6</sub>	74.7 <sub>9</sub>	—	2.0 <sub>4</sub>	1.90
Carbon tetrachloride .....	125.7 <sub>3</sub>	81.2 <sub>6</sub>	2.1 <sub>2</sub>	2.1 <sub>3</sub>	1.98
Benzene .....	117.0 <sub>3</sub>	72.5 <sub>6</sub>	2.0 <sub>3</sub>	2.0 <sub>1</sub>	1.87
Chloroform .....	139.4 <sub>6</sub>	94.9 <sub>9</sub>	2.2 <sub>6</sub>	2.2 <sub>7</sub>	2.14
Pure liquid .....	106.6	62.1	1.8 <sub>9</sub>	1.8 <sub>9</sub>	1.73

Le Fèvre and Russell (*loc. cit.*) also list apparent polarisations in six polar solvents, but the significance of these is doubtful (cf. Glasstone, *Ann. Reports*, 1936, **33**, 134). The questions underlying such measurements, and those of Le Fèvre and Le Fèvre (*J.*, 1936, 487), are now being re-examined on a wider basis in this Department. Where paraldehyde is concerned, therefore, we wish, at this stage, to restrict consideration to the data of the above table, chloroform being retained because it has sometimes been thought admissible as a medium for dipole moment work (cf. Le Fèvre and Rayner, *J.*, 1938, 1921; Caldwell and Le Fèvre, *J.*, 1939, 1614; Calderbank and Le Fèvre, *J.*, 1949, 1462; and the Faraday Soc. List of Dipole Moments, 1934).

*Discussion.*—The true moment, as determined for the gaseous phase, is surprisingly lower than the apparent moments shown in solution or the liquid state. Paraldehyde is known to undergo spontaneous depolymerisation on heating (Coffin, *Canad. J. Res.*, 1932, **7**, 75; Dacey and Coffin, *J. Chem. Physics*, 1937, **7**, 315), but from the kinetic study of Burnett and Bell (*Trans. Faraday Soc.*, 1938, **34**, 420) it is evident that even at 261° the time of half-change is *ca.* 31 minutes, while below 210° the pressure changes (used as indexes to reaction rates) were scarcely measurable (Coffin, *loc. cit.*). Accordingly, by confining our experiments to temperatures below 200°, and adhering to the timing already specified (Le Fèvre, Ross, and Smythe, *J.*, 1950, 276), we believe we have not incorrectly attributed the observed polarisations to paraldehyde alone, rather than to a changing system,  $C_6H_{12}O_3 = 3CH_3 \cdot CHO$ .

In terms previously used (Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374; Le Fèvre and Ross, *J.*, 1950, 283) we may summarise the facts thus :

	Light petroleum.	Dioxan.	CCl <sub>4</sub> .	C <sub>6</sub> H <sub>6</sub> .	CHCl <sub>3</sub> .	Liquid.
$\mu_{liq.}^2/\mu_{gas}^2$ .....	1.51	1.74	1.90	1.69	2.22	1.45
$\Delta\mu/\mu_{gas}$ .....	+0.23	+0.32	+0.37	+0.30	+0.49	+0.20

Since the media have been arranged with increasing dielectric constants from left to right, it is obvious that none of the treatments of the "solvent effect" problem in which  $\epsilon$  is the controlling factor can be valid for paraldehyde. On the other hand, those theories which involve the shape of the solute, or the algebraic sign of its Kerr constant, appear—qualitatively at least—to be more successful; indeed the  $\mu_{liq.}/\mu_{gas}$  ratio now found, although higher than any other yet recorded in the literature, can be roughly forecast by applying Higasi's expressions (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284) as though they were intended for polar, as well as non-polar, solvents. Carpenter and Brockway (*loc. cit.*) assign paraldehyde to the first of four models illustrated in their paper. In this, the three oxygen atoms are approximately coplanar with the three methyl-carbon atoms; and these six are 0.47 Å. above a parallel plane containing the remaining carbon atoms; C-O and C-C distances of 1.43 and 1.54 Å. are also given. All intervalency angles are tetrahedral. A scale drawing of the "elevation" of this skeleton (through one of the oxygens and its opposite CH-Me), after adding outlines corresponding to van der Waals radii, shows that rotation about the direction of action of the resultant moment (cf. Calderbank and Le Fèvre, *loc. cit.*) requires a somewhat flat spheroidal cavity. Several may be drawn but the axial ratios  $a : b : c$  are consistently about  $\frac{1}{2} : 1 : 1$ . Following Higasi, therefore,  $k = 2$  in  $B = k^2(k^2 - 1)^{-1}\{1 - (k^2 - 1)^{-\frac{1}{2}} \sin^{-1}(k^2 - 1)^{\frac{1}{2}}/k\} - 1/3$ , whence  $B = 0.195$  and  $\Delta\mu (= 4\pi\alpha n\mu_{gas}B$ , where  $n$  and  $\alpha$  represent the number of molecules of medium per unit volume and their polarisability respectively)  $= 0.20 \times 10^{-18}$  e.s.u. Thus the calculated value of  $(\mu_{liq.}^2/\mu_{gas}^2)$  is 1.30 compared with the 1.45 actually recorded. Further, of course, the fact that  $\mu_{liq.}/\mu_{gas}$  exceeds unity is compatible with  $\theta$  (in expressions derived from the equation of Raman and Krishnan, *Proc. Roy. Soc.*, 1928, *A*, **117**, 589) having a positive sign, *i.e.*, the reverse of that of the Kerr constant. In view, however, of considerations

prompted by the case of sulphur dioxide (*J.*, 1950, 286), this particular aspect will not be pursued.

According to Onsager (*J. Amer. Chem. Soc.*, 1936, **58**, 1486) the true orientation polarisation of a substance should be  $(\epsilon - n^2)(2\epsilon + n^2)V/\epsilon(n^2 + 2)^2$ , where  $V$  = molecular volume and  $n$  is the refractive index for light of infinite wave-length,  $V$  and  $n$  referring to the condensed phase. Frequently (cf. Böttcher, *Physica*, 1939, **6**, 59; Le Fèvre, Smythe, and Roberts, *J.*, 1949, 902) the use of  $n_D$  in place of  $n_\infty$  makes only a small difference. Wilson (*Chem. Reviews*, 1939, **25**, 377) recommends that  $n_{\text{effective}}$ , calculated from the distortion polarisation, be adopted instead. With paraldehyde either route gives an extremely high figure: (a)  $n_D^2 = 1.989$ , from  $[R_L]_D = 33.1$ ,  $(OP)_{\text{calc.}} = 198$  c.c. at 25°; (b)  $n_{\text{eff.}}^2 = 2.499$ , from  $(\Delta P + \epsilon P) = 44.47$ ,  $(OP)_{\text{calc.}} = 151$  c.c. at 25°;  $OP$ , calc. *via*  $\epsilon P = 44.47 + 12792/T$  (cf. p. 290) = 43 c.c. at 25°. Looking over Böttcher's examples, it seems that molecules of the type possessing negative Kerr constants are least satisfactorily handled by the unmodified Onsager formula. (Paraldehyde provides the worst instance to date in our experience.) Onsager, however, was well aware of the limitations imposed by his choice of simplifying and preliminary assumptions (cf. Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43** 391—392). Modifications, giving recognition to the optical anisotropy of the solute, in the manner indicated by Wilson (*loc. cit.*), would certainly improve the situation, but unfortunately neither electric double refraction nor light-scattering studies for gaseous paraldehyde have been made.

With regard to Kirkwood's extension of Onsager's equation (*J. Chem. Physics*, 1939, **7**, 911; *Ann. N.Y. Acad. Sci.*, 1940, **40**, 315), *viz.*,  $M(\epsilon - 1)(2\epsilon + 1)/9\epsilon d = \epsilon P + \Delta P + 4\pi N\mu_g^2/9kT$ , we note (since  $M/d = 133.5$  c.c. and  $\epsilon_{25} = 12.934$ ; Le Fèvre and Russell, *loc. cit.*) that  $g$  is approximately 7.5. This is large (cf. preceding paper for other examples) and would appear to indicate a small value of  $(\cos \gamma)_{\text{average}}$  in  $g = 1 + Z(\cos \gamma)_{\text{av}}$ , where  $Z$  is the number of molecules in the first layer around the one under consideration. If  $Z$  were about six, and all seven molecular resultant dipoles moving about axes not far from parallel, a model is seen in which maximum "contact" of molecular "areas" is tending to occur. It is relevant to mention, however, that cryoscopically (see following paper) there is no evidence that paraldehyde is "associated" in the ordinary sense of the word.

Finally, the theories based on hindered rotation (*e.g.*, those of Debye, or Kincaid and Eyring, see preceding paper) cannot be applied to paraldehyde, for which  $OP_{\text{liq.}}/OP_{\text{gas}}$  is 1.45, since—as was pointed out *a propos* sulphur dioxide—a ratio greater than unity is made impossible by the mathematical forms by which their authors expressed them.

The above paragraphs are chiefly concerned with the liquid-gas relationship. We are indebted to Mr. I. G. Ross for some remarks on paraldehyde as a *solute*: using as axes for the spheroid those quoted before (namely 0.5 : 1.0 : 1.0) the Ross-Sack equation is

$$\mu_{\text{soln.}}/\mu_{\text{gas}} = 3\epsilon[1 + (n_{\text{eff.}}^2 - 1)\xi]/(\epsilon + 2) [\epsilon + (n_{\text{eff.}}^2 - \epsilon)\xi] \dots \dots \dots (1)$$

where in this case  $\xi = (1/e^2) - [(1 - e^2)^{1/2}/e^3] \sin^{-1}e = 0.527$ , and  $e = [1 - (a/b)^2]^{1/2}$ . For comparison, the Higasi equation for solutions may be written as

$$\mu_{\text{soln.}}/\mu_{\text{gas}} = 1 + 3(\xi - 1/3)(\epsilon - 1)/(\epsilon + 2) \dots \dots \dots (2)$$

although it is suggested that the derivation of (2) contains errors and that, with Higasi's approach, the correct form should be

$$\mu_{\text{soln.}}/\mu_{\text{gas}} = 1 + (\xi - 1/3)\epsilon/(\epsilon + 2) \dots \dots \dots (3)$$

The apparent moments in solution, calculated by (1), (2), and (3), are compared below with those actually recorded:

Solvent.	$\mu$ , observed.	$\mu$ , calc. by (1).	$\mu$ , calc. by (2).	$\mu$ , calc. by (3).
Vacuum .....	1.4 <sub>4</sub>	—	—	—
Light petroleum .....	1.7 <sub>7</sub>	1.7 <sub>1</sub>	1.6 <sub>5</sub>	1.5 <sub>8</sub>
Dioxan .....	1.9 <sub>0</sub>	1.7 <sub>2</sub>	1.6 <sub>8</sub>	1.5 <sub>9</sub>
Carbon tetrachloride .....	1.9 <sub>8</sub>	1.7 <sub>2</sub>	1.6 <sub>8</sub>	1.5 <sub>9</sub>
Benzene .....	1.8 <sub>7</sub>	1.7 <sub>2</sub>	1.6 <sub>9</sub>	1.5 <sub>9</sub>

Equation (1) thus gives slightly better results than does that of Higasi, either in its original (2) or its amended (3) form.

*Conclusions.*—Paraldehyde is established as a case where the apparent moment, as ordinarily measured in solution *via* the Debye-Clausius-Mosotti route, is markedly greater than the true moment obtained from the gas. The facts now revealed, while out of harmony

with many of the extant theoretical treatments of the problem, are less so with those in which the anisotropy of molecular shape (or polarisability) is significant.

#### EXPERIMENTAL.

**Materials.**—The paraldehyde was purified by drying it with anhydrous sodium sulphate and then cooling it to 5°, whereafter the frozen material was separated by decantation. This was distilled (the fraction, b. p. 121–124°, being collected), stored over anhydrous sodium sulphate for several days, and redistilled at atmospheric pressure before use as required.

**Polarisation of Gaseous Paraldehyde.**—The method of measurement has been essentially that described previously (*J.*, 1950, 276, apparatus B.M.S.) but with the following improvements. The gas cell was replaced by another of similar construction of 124 instead of 80  $\mu\text{m}^2$  capacity (with air). Its leads were brought through the glass walls and soldered directly to the co-axial cable running to the oscillator. For the oil-thermostat, which had been a source of unsteadiness at higher temperatures (due to surface ripples made by the stirrer as the fluid became hotter and more mobile), an all-metal vapour bath, standing on the floor, was substituted. Its details are given in the figure. It had advantages over the glass apparatus of Groves (*J.*, 1939, 1147) in that it was more robust and formed a complete shield, which could be earthed, around the cell. The whole structure was heavily lagged to minimise heat radiation to the electrical components. By the use of chloroform, carbon tetrachloride, xylene, *n*-butyl alcohol, cyclohexanol, benzyl alcohol, and thymol separately at atmospheric pressure, the temperature of the cell could easily be set to within 0.2° or better. The condensates ran back along a guide to flow down the inside wall of the vessel. The rate of boiling was controlled by adjusting the voltage across the heating coil by means of a "Variac" variable transformer.

The new cell was first calibrated against carbon dioxide (see p. 281). Table II shows the values obtained for  $\delta C/p$ , while the polarisations of paraldehyde follow in Table III.

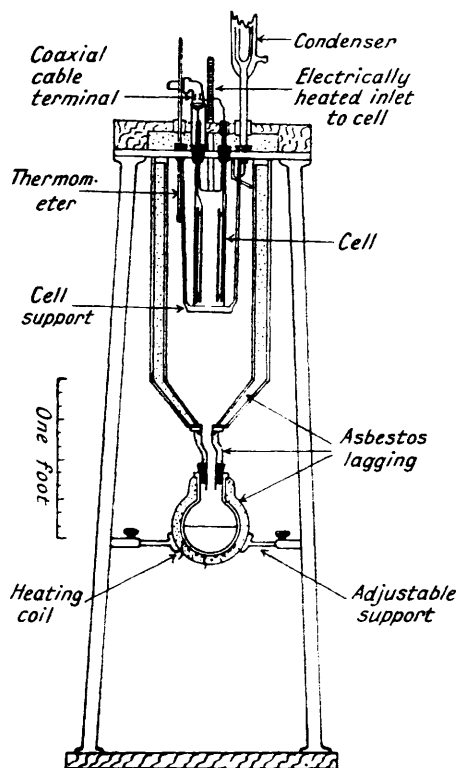


TABLE II.

$\delta C/p$  for carbon dioxide.

$T^\circ, \text{K.}$	$10^6/T.$	$\delta C/p.$	$(\delta C/p)_{\text{calc.}}$	Press. range in cm.	Number of observations.
296.5	3372	7.66	7.662	34–68	10
333.5	2999	6.80	6.800	32–68	13
383.0	2611	5.91	5.905	38–67	13
404.0	2475	5.59	5.592	42–69	11
422.5	2367	5.34	5.342	35–67	12

$$\text{Whence } \alpha' = (2307.0/T) - 0.1185.$$

TABLE III.

Paraldehyde.

$T^\circ, \text{K.}$	$10^6/T.$	$(\delta C/p)_{p=0}$	$P$ (c.c.).	$P$ (calc.).	Press. range in (cm.).	No. of observations.
386	2591	39.0	77.59	77.61	34–53	13
406	2463	36.2	75.71	75.98	29–61	12
437	2288	32.9	74.08	73.74	25–67	12
457	2188	31.0	71.24	72.46	16–52	11
390 *	2564	61.15	77.4	77.27	25–51	7
473 *	2114	46.00	71.54	71.51	23–56	6

$$\text{Whence } P = 44.47 + 12792/T \text{ and } \mu = 1.44 \text{ D.}$$

**Polarisation of Dissolved Paraldehyde.**—Apparatus, techniques, and symbols used have been described before (*J.*, 1948, 1949). The solvents were fractionated (after partial freezing where applicable) and

kept over sodium (except carbon tetrachloride, for which calcium chloride was used). The dielectric constants of light petroleum and of dioxan were determined relatively to benzene (2.2725).

The dielectric constants ( $\epsilon^{25}$ ), densities ( $d_4^{25}$ ), and concentrations ( $w_1 =$  weight fraction) are alone recorded, since the polarisations at infinite dilution do not require the separate evaluation of these quantities for each solution (cf. Le Fèvre, *loc. cit.*):

## (a) Paraldehyde in light petroleum (b. p. 94—99°).

$10^6 w_1$ .....	0	9701	19036	38479	57468	79183
$\epsilon^{25}$ .....	1.9944	2.0158	2.0383	2.0872	2.1376	2.1969
$d_4^{25}$ .....	0.74062	0.74212	0.74367	0.74694	0.75023	0.75399

## (b) Paraldehyde in dioxan.

$10^6 w_1$ .....	0	11221	15414	23323	40590	46453	54439
$\epsilon^{25}$ .....	2.2172	2.2607	2.2770	2.3086	2.3790	2.4017	2.4347
$d_4^{25}$ .....	1.02917	1.02883	1.02863	1.02829	1.02762	1.02744	1.02703

## (c) Paraldehyde in carbon tetrachloride.

$10^6 w_1$ .....	0	11545	19250	49053	72066	108066
$\epsilon^{25}$ .....	2.2270	2.2986	2.3457	2.5331	2.6733	2.8920
$d_4^{25}$ .....	1.58440	1.57338	1.56628	1.53745	1.51644	1.48515

## (d) Paraldehyde in benzene.

$10^5 w_1$ .....	0	493	1029	3424	3482	4522	4765	6467
$\epsilon^{25}$ .....	2.2725	2.2881	2.3044	2.3818	2.3832	2.4159	2.4243	2.4802
$d_4^{25}$ .....	0.87378	0.87410	0.87440	0.87697	0.87750	0.87804	0.87840	0.87996
$10^5 w_1$ .....	7392	8863	9989	10777	12868	16481	20897	
$\epsilon^{25}$ .....	2.5079	2.5674	2.6027	2.6358	2.7159	2.8586	3.0392	
$d_4^{25}$ .....	0.88082	0.88223	0.88342	0.88412	0.88603	0.88962	0.89417	

## (e) Paraldehyde in chloroform.

$10^5 w_1$ .....	0	1098	3028	5389	8870	15528
$\epsilon^{25}$ .....	4.7240	4.8459	5.0617	5.3293	5.7204	6.4533
$d_4^{25}$ .....	1.46814	1.46080	1.44803	1.43258	1.41078	1.36987

From the above measurements the "constants,"  $\alpha\epsilon_2$  and  $\beta d_2$  [i.e.,  $(\epsilon_{12} - \epsilon_2)/w_1$  and  $(d_{12} - d_2)/w_1$ ] show a drift with  $w_1$ . By least squares, the following relationships have been fitted:

Solvent.	No. of solns. and $w_1$ -% range.	$\alpha\epsilon_2$ .	$\beta d_2$ .
Light petroleum .....	5 (1—8%)	$2.204 + 4.76w_1$	$0.1552 + 0.004w_1$
Dioxan .....	6 (1—5.4%)	$3.850 + 2.83w_1$	$0.0316 + 0.147w_1$
Benzene .....	14 (0.5—21%)	$3.067 + 2.78w_1$	$0.0818 + 0.117w_1$
Carbon tetrachloride .....	5 (1—11%)	$6.207 - 0.30w_1$	$0.293w_1 - 0.9582$
Chloroform .....	5 (1—15%)	$11.19 \pm 0.0w_1$	$0.294w_1 - 0.6720$

Using the above data at  $w_1 = 0$ , the polarisations at infinite dilution listed in Table I are calculated as  ${}_{\infty}P_1 = M_1[p_2(1 - \beta) + C\alpha\epsilon_2]$ , the requisite values of  $C$  and  $p_2$  being:

	Light petroleum.	Dioxan.	Carbon tetrachloride.	Benzene.	Chloroform.
$C$ .....	0.25388	0.16390	0.10597	0.18809	0.37724
$p_2$ .....	0.33614	0.28045	0.18321	0.34086	0.04520

*Note on the Atomic Polarisation of Paraldehyde.*—Since the difference between the distortion polarisation (44.5 c.c.) and the molecular refraction (about 33 c.c.) is ca. 11 c.c., paraldehyde must be added to the growing list of cases which disprove the earlier idea that  ${}_A P$  might be taken as approximately 10% of  ${}_E P$ . Coop and Sutton (*J.*, 1938, 1280) and Watson, Kane, and Ramaswamy (*Proc. Roy. Soc.*, 1936, *A*, 156, 130) have provided the most striking instances. The relative position of the present observations can be seen from the following series of  ${}_A P/{}_E P$  ratios:

<i>p</i> -Benzoquinone .....	0.29	(Coop and Sutton, <i>loc. cit.</i> )
<i>p</i> -Dinitrobenzene .....	0.21	" " "
Beryllium acetylacetonate .....	0.42	" " "
Ferric " .....	0.60	" " "
Boron trifluoride .....	0.46	(Watson, Kane, and Ramaswamy, <i>loc. cit.</i> )
Carbon tetrafluoride .....	0.39	" " "
Silicon tetrafluoride .....	0.65	" " "
Cyanogen .....	0.70	" " "
Paraldehyde .....	0.33	(Present work.)

Comparison with data for a number of ethers is interesting :

	Me <sub>2</sub> O.	Et <sub>2</sub> O.	Dioxan.	Trioxan.	Paraldehyde.
$\text{A}P$ .....	2.2	4.0	3.0	ca. 13 *	11.4
$\text{E}P$ .....	12.9	21.9	21.6	19.3	33.1

\* Calculated from the dielectric constant of solid trioxan at 20° (Walker and Carlisle, *Chem. Eng. News*, 1943, 21, 1250), viz.,  $\epsilon = 3.2 - 3.4$  at 1.6 megacycles. The value of  $d^{20}$  is not given ( $d_4^{25} = 1.17$ ), but has been taken as 1.2 since a higher figure would not appreciably affect  $M(\epsilon - 1)/(\epsilon + 2)d = 32$  c.c.

That the three cyclic molecules have similar configurations follows from (a) the structural details for paraldehyde recorded by authors cited at the beginning of this paper, (b) investigations of crystal structure (Moermann, *Rec. Trav. chim.*, 1937, 56, 161), dipole moment (Maryatt and Acree, *J. Res. Nat. Bur. Stand.*, 1944, 33, 71; Calderbank and Le Fèvre, *J.*, 1949, 199), infra-red (Ramsay, *Trans. Faraday Soc.*, 1948, 44, 289) and Raman spectra (Kohlrausch, *Z. physikal. Chem.*, 1937, B, 35, 29) on trioxan, and (c) studies of electron diffraction (Brockway and Sutton, *J. Amer. Chem. Soc.*, 1935, 57, 473) and infra-red and Raman spectra (Ramsay, *Proc. Roy. Soc.*, 1947, 190, 563) on dioxan. Oxygen bond angles and C-O distances, where given, are of the same order throughout (viz.,  $110^\circ \pm 5^\circ$ , and 1.43—1.46 Å.) and closely resemble those for dimethyl ether (Brockway and Sutton, *loc. cit.*).

From Sutton's theory of atom polarisation (see p. 283 for references) it follows that : (1) since this quantity depends on polar groups in a molecule whereas  $\text{E}P$  does not,  $\text{A}P$  cannot be expected to be always the same fraction of  $\text{E}P$ ; (2) if several compounds have essentially common oscillating systems, they have nearly the same  $\text{A}P$ ; and (3) in general  $\text{A}P$  is not additive, but in some circumstances (if  $\mu$  and  $V_O$ , in  $\text{A}P = 4\pi N\mu^2/9V_O$ , are constant) it is roughly proportional to the number of polar bonds, or components.

The figures just quoted illustrate these propositions. The  $\text{A}P/\text{E}P$  fraction for paraldehyde is not that for many other molecules, although the absolute value of its  $\text{A}P$  seems to be of the order of that of trioxan. The angular force constants,  $V_O$ , for bending of C-O-C in dimethyl ether and in dioxan are 0.34—0.46 and  $0.66 \times 10^5$  dynes/cm. respectively (Kohlrausch, *loc. cit.*; Bonner, *J. Chem. Physics*, 1937, 5, 293); since  $\text{A}P = 4\pi Nn\mu^2/9V_O$  (where  $n$  = the number of oscillating components, i.e., 1 for dimethyl ether and 2 for dioxan), the atomic polarisations for these two molecules should be approximately the same, as in fact they are.

The deformation constants of the C-O-C angles in paraldehyde and trioxan have not been determined. However, Ramsay (*Trans. Faraday Soc.*, 1948, 44, 289) attempted to calculate the vibration frequencies of the trioxan ring using the same values for the force constants as for dioxan, but differences between his estimates and those observed are large, and indicate that the force constants in trioxan are appreciably smaller than those in dioxan. Nevertheless, if the bending force constant of C-O-C in trioxan (which as a first approximation should be of the same order as that for paraldehyde, as are the C-O bond distances and the C-O-C angles) is closer to that of dimethyl ether, then we would expect an atomic polarisation approaching three times that of dimethyl ether, or 9 c.c. This is in effect the situation found. These results shown the degree of additivity of  $\text{A}P$  in these compounds. It resembles that which has also been noticed with certain polyhalides and the metal acetylacetonates (Finn and Sutton, *J.*, 1938, 1259; Coop and Sutton, *loc. cit.*).

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