11. *Electric Dipole Moment Studies. Part II.* The Dielectric Polarisation of Cyclic Ethers in the Vapour Phase.*

By W. L. G. Gent.

The measurement of the dielectric polarisation of the vapours of ethylene oxide, trimethylene oxide, and tetrahydrofuran at various temperatures is described and the results used to calculate the electric dipole moment and distortion polarisations. The magnitudes of the latter are commented on and the dipole moments compared with those of the substances in solution in non-polar solvents.

In an earlier paper [1] an attempt was made to analyse the dipole moments of dimethyl ether, ethylene oxide, trimethylene oxide, and tetrahydrofuran in terms of models in which the vectorial sum of the primary bond moments was considered to be modified by moments induced in other parts of the molecule. The validity of the conclusions was diminished by uncertainty about the true dipole moments of the cyclic ethers, it being necessary to estimate these quantities from measurements on solutions in non-polar solvents. For this reason, measurements of the dipole moments of the cyclic ethers in the vapour phase have been made.

EXPERIMENTAL

Apparatus.—The dielectric constants of the vapours have been measured by the heterodyne beat method. Since suitable oscillator circuits are now commonplace, no detailed description is necessary. Construction of both oscillators was substantial, to ensure mechanical stability, and of such a kind as to minimise frequency change with temperature. The quartz oscillator (1 Mc./sec.) was controlled by a GT-cut crystal having a temperature variation of 0·0002% per °c. The variable-frequency oscillator was of the negative-transconductance type, with temperature compensation of the tuned circuit, the final variation being 0·0001% per °c. The heptode mixer reduced coupling of the oscillators to a very low level, "locking-in" not occurring until a difference frequency of less than 5 c./sec. The balance frequency was 100 c./sec., displayed on a cathode-ray tube with a 50 c./sec. time base derived from the electric main, as a figure-of-eight.

The standard condenser was similar to that described by Groves,[2] having a capacity increment of 1·862 pF per cm. and of linear behaviour. Groves's design of test-cell was also followed, the nominal capacity being 100 pF. Slow cyclic variations of capacity between 101 and 108 pF were observed and for this reason the cell was air-calibrated before and after every set of measurements. Liquids to give the vapour-bath to the cell were heated electrically; it was advisable to use liquids of low dielectric constant so as to avoid capacity changes of the cell (turbulence at the liquid surface causes a change in the electrode-to-heater capacity).

Ethylene oxide and trimethylene oxide were treated as gases, being introduced into the cell and manometer system from a liquid reservoir, but the vapour pressure of tetrahydrofuran is too small at room temperature to be suitable for accurate measurements in this way. Several arrangements described in the literature were tried for vaporising the liquid but none was found to be very suitable. The device shown in the Figure was efficient and functioned easily enough for all the measurements to be made by one observer. The liquid in the bulb *A* was cooled to −80° and the apparatus evacuated, the tap *B* was closed, and air admitted into the system, forcing liquid up into the electrically heated tube *C*. Boiling was ensured by the platinum point at *P*. When a sufficient pressure of vapour had been established the tap *B* was opened, giving direct communication of vapour and air to ensure that the manometer pressure was also that of the vapour. Pressures were measured on a mercury manometer with mirror scale and eyepiece, corrections being applied for meniscus height, temperature, etc. This is by no means an ideal arrangement for, with the lower-boiling ethers, when the whole

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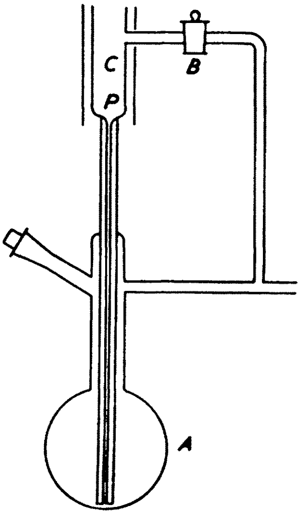
* Part I, *Trans. Faraday Soc.*, 1949, **45**, 1021.

[1] Gent, *Trans. Faraday Soc.*, 1949, **45**, 1021.

[2] Groves, *J.*, 1939, 1144.

apparatus was filled with vapour not only did the contact angle of the mercury alter but there appeared to be some definite reaction. For this reason the results for ethylene and trimethylene oxides were not as accurate as for tetrahydrofuran, in which case only air filled the manometer.



Method.—During most of the experiments a uniform oscillator drift of a few cycles per hour was apparent, due to change in room temperature. The effect of this was overcome by taking all readings on the standard capacitor at noted times, and from the readings when the cell was evacuated, interpolating the actual capacity value at the times when the cell was filled with air or vapour. The cell was filled and emptied ten times at about the same pressure, and the procedure described above then gave a reproducibility of capacity change of ±1 part in 400—700 on air-calibration and about ±1 part in 700—1200 for the vapours of the cyclic ethers, depending on the temperature. 2 Min. were found adequate for thermal equilibration when filling the cell with vapour.

Materials.—Air was passed over a long tube of potassium hydroxide pellets, and water was removed in traps at −80°. Drying with phosphoric oxide was found to introduce traces of impurity which materially increased the polarisation of air.

Ethylene oxide was dried initially over anhydrous calcium sulphate and twice distilled from freshly fused sodium hydroxide; it then had b. p. 10·9°.

Trimethylene oxide was synthesised from trimethylene glycol *via* the chlorohydrin[3] and 3-chloropropyl acetate,[4] ring closure[5] being performed with potassium hydroxide. The product, twice fractionated from fused sodium hydroxide, had b. p. 47°, n_D^{25} 1·3868.

Tetrahydrofuran was kept over sodium hydroxide pellets for one week, to decompose the antioxidant and then twice fractionated from fused sodium hydroxide; it had b. p. 65·6°, n_D^{25} 1·4049.

n-Hexane, of spectroscopic grade, was dried and distilled from sodium, the middle fraction (b. p. 68·7°) being taken.

RESULTS

Results are based on the value for the polarisation of air, $P = 4{\cdot}34_7$ c.c., determined by Coop and Sutton.[6] Dipole moments have been estimated from the quantity B in the Debye equation, $P = A + B/T$, using the relation $\mu = 0{\cdot}001281B^{\frac{1}{2}}$.

The apparent polarisation of a vapour at any temperature may be obtained from the relation :

$$P_{\text{app}} = \frac{\delta c}{p} \cdot \frac{p'}{\delta c'} \cdot P' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which δc is the capacity change on filling the evacuated cell to a pressure p of vapour, the primed quantities referring to air. Because of deviations of the behaviour of vapours from that of an ideal gas the values of P_{app} are greater than the true polarisation at zero pressure, P_0, and must be corrected. If the van der Waals equation is written in the form $(p + a/V'^2)(V' - b) = T/273{\cdot}1$, $V' = \text{volume (c.c.)}/22415$, then for the pressures, temperatures, and probable values of a and b for the substances used $V' - b \approx V'$. It then follows that, within the limits of experimental error of this investigation,

$$P = P_0 + Kp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$K = (273{\cdot}1)^2 aP_0/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Although the change of polarisation with pressure was always in the right direction, its magnitude, as indicated by eq. (3), was always too large by a factor of about 2. Thus, as a check on the method the polarisation of *n*-hexane was measured at 383·9° and found to be

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[3] *Org. Synth.*, 2nd. Edn., Coll. Vol. I, p. 533.

[4] *Ibid.*, 1949, **29**, 33.

[5] *Ibid.*, p. 92.

[6] Coop and Sutton, *J.*, 1938, 1269.

29·5 c.c., in reasonable agreement with that (P_0 29·9 c.c.) found by Kubo,[7] but the polarisation changed by 2·05 c.c./atm., from which $a = 0{\cdot}10$, whereas the critical data for hexane, reported by Edminster,[8] give $a = 0{\cdot}054$. With the cyclic ethers the slopes moved from about 3—1·5 c.c./atm., diminishing with increasing cell temperature, but largely independent of the substance used, although it might be expected that the variation in the case of tetrahydrofuran would be about twice that with ethylene oxide. The reasons for this effect have not been discovered, and give some uncertainty to the absolute magnitude of the polarisations.

Ethylene oxide.

T	P_{app} (c.c.)	p (mm.)	P_0 (c.c.)	T	P_{app} (c.c.)	p (mm.)	P_0 (c.c.)
292·1°	89·7$_8$	132·8	89·0	383·9°	71·5$_0$	171·7	71·2
	90·3$_1$	212·3			71·6$_4$	248·8	
298·7	88·5$_7$	170·7	87·6	409·6	66·5$_3$	199·0	66·4
	88·7$_8$	210·3			66·5$_6$	259·0	
334·6	80·2$_8$	209·3	79·8	449·6	61·4$_9$	219·1	60·9
	80·3$_7$	249·6			61·6$_0$	259·3	

$P_0 = (12{\cdot}9 + 22260/T) \pm 0{\cdot}2$ c.c. $\mu = 1{\cdot}91$ D.

The polarisations at the two higher temperatures do not fit the data for the lower ones, showing a progressive deviation from the expected values. Measurements were made with two different samples of ethylene oxide but with the same result. Stuart's value for the polarisation does not show a similar deflection but this may be due to different experimental arrangements. The effect is probably due to thermal decomposition, which begins to be appreciable, in 2 min. when the oxide is in the cell, at ~370° K.[10] Since this decomposition is of the kind $2C_2H_4O \longrightarrow C_2H_6 + H_2 + 2CO$, there is substitution by non-polar products and an increase of pressure. Both of these effects would tend to lower the polarisation.

The magnitude of the dipole moment is in agreement with earlier value of 1·89 and 1·92 D derived from polarisation data[9, 11] and of 1·88 D from microwave spectroscopy.[13] The distortion polarisation of 12·9 c.c. is larger than that from Stuart's data, $P_{E+A} = 11{\cdot}6$ c.c., the difference being due to the larger polarisations found in the experiments reported here.

There are no recent values of refractive index and density for calculation of the electronic polarisation but reasonable agreement exists between several sets of data to give $P_E = 11{\cdot}0$ c.c. and hence $P_A = 1{\cdot}9$ c.c.

P_E	*Method*	
10·93	*n* and *d* of liquid	(Perkin [13])
11·00	,, ,,	(von Auwers [14])
10·95	*n* of gas	(Ramaswamy [15])
11·06	additive refraction constants	(Vogel [16])

Trimethylene oxide.

T	P_{app} (c.c.)	p (mm.)	P_0 (c.c.)	T	P_{app} (c.c.)	p (mm.)	P_0 (c.c.)
296·8°	95·7$_0$	105·3	95·4	383·9°	78·2$_3$	103·8	77·9
	95·7$_9$	146·1			78·4$_1$	172·5	
353·9	82·6$_0$	106·8	82·4	449·6	69·2$_3$	107·4	69·1
	82·7$_9$	166·0			69·2$_9$	165·1	

$P_0 = (18{\cdot}1 + 22900/T) \pm 0{\cdot}2$ c.c. $\mu = 1{\cdot}94$ D.

The dipole moment is in good agreement with that (1·93 D) found by microwave spectroscopy.[17]

The magnitude of the electronic polarisations appears as $P_E = 15{\cdot}4$ c.c. from refractive index

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[7] Kubo, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **26**, 242.

[8] Edminster, *Ind. Eng. Chem.*, 1938, **30**, 352.

[9] Stuart, *Z. Physik*, 1928, **51**, 490.

[10] Heckert and Mack, *J. Amer. Chem. Soc.*, 1929, **51**, 2706.

[11] Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, **4**, 108.

[12] Cunningham, Boyd, Rogers, Gwinn, and Le Vau, *J. Chem. Phys.*, 1951, **19**, 6760.

[13] Perkin, *J.*, 1893, **63**, 488.

[14] Von Auwers, *Annalen*, 1918, **415**, 145.

[15] Ramaswamy, ref. 12, p. 675.

[16] Vogel, *J.*, 1948, 1833, Table XXII.

[17] Fernandez, Myers, and Gwinn, *J. Chem. Phys.*, 1955, **23**, 788.

and density data[18] and as $P_E = 15{\cdot}7$ c.c. from Vogel's additive refraction constants;[16] use of the experimental value gives the atomic polarisation $P_A = 2{\cdot}7$ c.c.

Tetrahydrofuran.

T	P_{app} (c.c.)	p (mm.)	P_0 (c.c.)	T	P_{app} (c.c.)	p (mm.)	P_0 (c.c.)
340·1°	$72{\cdot}4_7$	168·7	72·0	409·6°	$64{\cdot}5_5$	194·5	64·0
	$72{\cdot}8_0$	295·8			$64{\cdot}9_1$	319·1	
383·9	$67{\cdot}3_4$	175·4	66·9	449·6	$61{\cdot}0_9$	255·5	60·5
	$67{\cdot}6_8$	292·5			$61{\cdot}2_7$	335·2	

$P_0 = (24{\cdot}7 + 16120/T) \pm 0{\cdot}1$ c.c. $\mu = 1{\cdot}63$ D.

The best data on the refractive index and density of the compound seem to be those of Böhme and Schürhoff,[19] which give $P_E = 19{\cdot}9$ c.c., whilst Vogel's additive refraction constants[16] indicate 20·3 c.c.; using the experimental value gives $P_A = 4{\cdot}8$ c.c.

For all three substances the polarisation varied with pressure in about the expected way, but the measurements are not accurate enough for calculation of values for the van der Waals constant *a*. The general impression gained in this work was that a more accurate measure of polarisation could be obtained by working at about 1 atm. pressure and correcting the results by van der Waals equation, unless the pressure could be more accurately measured than with a mercury manometer.

DISCUSSION

The atom polarisations of the three cyclic ethers, ethylene oxide 1·9 c.c., trimethylene oxide 2·8 c.c., tetrahydrofuran 4·7 c.c., show an unusual structure-dependent variation. Whilst the ring of ethylene oxide is inevitably planar this is not necessarily so in the other ethers since the planar configuration is a compromise between the resistance of valency bonds to angular deformation and the torsion applied due to motion of the attached hydrogen atoms. The recent microwave-spectroscopic examination of trimethylene oxide indicates that there is no out-of-plane component of the dipole moment and that, hence, all four atoms are in the same plane. In this respect trimethylene oxide differs from *cyclo*butane which has a non-planar configuration as shown by thermodynamic and spectroscopic data.[20] A similar state of affairs exists also with *cyclo*pentane. It seems probable, therefore, that the tetrahydrofuran ring may be non-planar, although Beach's electron-diffraction investigation[21] was interpreted to indicate a planar arrangement. For five tetrahedral angles there would only be an excess of 7½° over that required for a perfectly planar configuration, so that in this molecule there is evidently much less rigidity than in the other two. Sutton's theory of atom polarisation[6] assumes that the atomic polarisation is due to relative movements of polar bonds and can be accounted for quantitatively in terms of the number of oscillators, the number of angular co-ordinates required to describe the motion, the dipole moments (presumably transition moments), and the force-constants of the bonds concerned. Whilst attempts to find a quantitative relation would be useless in these particular cases because of ignorance of the transition moments and binding force-constants, it may be noted that in the rigid ethylene and trimethylene oxides, where the atom polarisation could be due only to movement of the CH bonds, the values of P_A are $\sim 2 \times 0{\cdot}9$ and $\sim 3 \times 0{\cdot}9$ c.c. respectively. This suggests that each methylene group contributes 0·9 c.c., and the larger increment between trimethylene oxide and tetrahydrofuran may then be assigned to the freeing of the C–O bonds to allow relative movement in the larger molecule. There are no measurements reported in the literature which refer to cyclic molecules containing methylene groups and might be used for comparison.

For a comparison of the electric moments measured in the vapour phase with those in

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[18] Derrick and Bissel, *J. Amer. Chem. Soc.*, 1916, **38**, 2482.

[19] Böhme and Schürhoff, *Chem. Ber.*, 1951, **84**, 41.

[20] Ruthyers, Freeman, Gwinn, and Pitzer, *J. Amer. Chem. Soc.*, 1953, **75**, 5634.

[21] Beach, *J. Chem. Phys.*, 1940, **9**, 54.

solution, it appears that the only reliable measurement of the polarisation of ethylene oxide in benzene is that by Angyal *et al.*[22] With the value of $P_{E+A} = 12{\cdot}9$ c.c. reported here and the total polarisation (ref. 22) $_\infty P_T = 80{\cdot}3$ c.c., we find $\mu = 1{\cdot}82$ D. Allen and Hibbert's data [23] on the polarisation of trimethylene oxide in benzene show an apparent decrease of polarisation with increasing concentration. As some results on other solutions reported by these authors show a similar effect, it seems probable that an instrumental error was involved since the points defined by the dielectric constant of the solutions and mole fraction of solute are collinear and do not extrapolate at $f_2 = 0$ to ε_1, but to a slightly greater value which is much the same for each solute. Accordingly the data for trimethylene oxide have been re-assessed to give $_\infty P_T = 78{\cdot}6$ c.c. from which, by the use of $P_{E+A} = 18{\cdot}1$ c.c., $\mu = 1{\cdot}96$ D. Data for tetrahydrofuran in benzene solution have been reported by Smyth and Walls [24] and by de Vries Robles.[25] Smyth and Walls's data, at both 25° and 50°, show a polarisation rapidly increasing with mole fraction of solute and were extrapolated to zero concentration to give $_\infty P_T = 80{\cdot}7$ c.c. at 25°. The ε_{12}, f_2 points are, however, collinear, with a slope which indicates $_\infty P_T = 96{\cdot}7$ c.c., but the extrapolated value of ε_1 at $f_2 = 0$ is less than the value quoted for benzene. Robles's data, on the other hand, show no abnormal variation of polarisation with concentration and give $_\infty P_T$ 81·2 c.c. at 20°. As the latter is less uncertain and in approximate agreement with that given by Smyth and Walls, it has been used, with $P_{E+A} = 24{\cdot}7$ c.c., to give $\mu = 1{\cdot}65$ D. It is clear that the values of the dipole moments in solution are unreliable and must be accepted with caution.

Comparison of the dipole moments in solution with the vapour-phase values is shown in the annexed Table, together with the data on dimethyl ether quoted by Barclay and Le Fèvre.[26]

	μ gas	μ benzene	$\mu^2_{\text{benzene}}/\mu^2_{\text{gas}}$ obs.	$\mu^2_{\text{benzene}}/\mu^2_{\text{gas}}$ calc.
Dimethyl ether	1·29	1·25	0·938	0·986
Ethylene oxide	1·91	1·82	0·908	0·944
Trimethylene oxide	1·94	1·96	1·021	0·876 *
Tetrahydrofuran	1·63	1·65	1·025	0·863 *

* Calc. for structures quoted earlier.[1]

The fourth column in the Table is calculated from eq. (2) of Angyal, Barclay, and Le Fèvre.[22] Whilst the difference between the observed and calculated values of $\mu^2_{\text{benzene}}/\mu^2_{\text{gas}}$ may be due to error in the dipole moments of the two higher cyclic oxides, such an error would have to be in excess of 0·1 D for either the gas or the benzene solution measurements. Without more reliable estimates of the moments in solutions further comment is not possible.

The electric moments of the cyclic ethers will be considered in detail in a later paper.

The author thanks the Chemical Society for a grant from the Research Fund for the purchase of apparatus, and the Government Chemist, Dr. G. M. Bennett, for encouragement and the loan of some equipment.

BIOCHEMISTRY AND CHEMISTRY DEPT.,
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[*Received, June 11th*, 1956.]

[22] Angyal, Barclay, and Le Fèvre, *J.*, 1950, 3370.
[23] Allen and Hibbert, *J. Amer. Chem. Soc.*, 1934, **56**, 1398.
[24] Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230.
[25] de Vries Robles, *Rec. Trav. chim.*, 1939, **58**, 111.
[26] Barclay and Le Fèvre, *J.*, 1952, 1643.