pressure lower than that which would be necessary to squeeze out the soluble constituent. The phenomena are more complicated when the two associated substances are liable to give several complexes, for example, 1–1 and 1–2. Suppose the 1–2 complex is formed ; and then we try to obtain by compression the 1–1 complex. Very often, the squeezing out of one molecule of the soluble substance from the 1–2 complex requires a pressure at which the 1–1 complex is no longer stable ; hence it is impossible with the isotherm method to determine the molecular area relative to the second complex, this remaining unobserved.

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Electric Induction in Molecules and the Polarity of the C—H Bond

FOR non-mesomeric molecules the molecular electric moment may be formally divided into the vector sums of the group moments and of the induced moments. Calculation of these latter has been attempted by Smallwood and Herzfeld[1], Smyth[2] and Groves and Sugden[3] ; but the number of examples of any one molecular type considered has been too small to substantiate the methods. The calculations of the last-named authors, based on a method suggested by Frank[4], appear to be the most valid.

The known or determinable geometry of ethylene oxide and its homologues, and the analogous sulphides and imines, makes these compounds particularly suitable for calculating electric induction within molecules. The dipole moments of the cyclic ethers are known with a fair degree of accuracy and are shown in the accompanying table. These values have been used in the preliminary calculations outlined below.

The original Groves–Sugden model is over-simplified in that methyl and methylene groups are treated as carbon atoms with the polarizability proper to the groups. This implies a polarization symmetry which the group does not possess, and accordingly the induced moment has now been computed separately for every atom in a molecule (Model 1). Equations are obtained relating the molecular moment, the group moments $\mu(CH_2 - O)$, $\mu(H - C)$ and the induced moment. Mutual solutions of these equations give simultaneous values of the group moments which average : $\mu(CH_2 - O) = 2.05$ D., $\mu(H - C) = -0.46$ D. Substitution of the latter value in the equations yields the individual values of $\mu(CH_2 - O)$ shown in the table.

Variation of polarizability with type of bond implies that the quantity depends chiefly on the bonding electrons. The Groves–Sugden model assumes that these electrons are symmetrically distributed over a spherical surface defined by the atomic covalent radius. The fact of directed valence indicates a localization of polarizable material. Accordingly a new model (Model II) has been used in which the bonding electron pair between two atoms is concentrated at the 'point of contact' of spheres with the appropriate covalent radii. Bond polarizabilities[3] are now employed, allowance being made in the case of the $CH_2 - O$ group for the unbonded electrons. Equations similar to those derived from Model I lead to average values of the group moments : $\mu(CH_2 - O) = 1.83$ D., $\mu(H - C) = -0.41$ D. Individual values of $\mu(CH_2 - O)$, obtained as before, are shown in the table.

In reality, there is neither a spherically symmetrical nor a point distribution of valency electrons. These are extremes, somewhere between which is the most probable configuration. For the ethylene oxide molecule, in which the two group moments are most closely juxtaposed, there is clearly under-compensation for the induced moment by Model I and over-compensation by Model II. For these two reasons the mean values of the group moments (see table) are taken to be approximately correct. The average of these gives $\mu(CH_2 - O) = 1.93$ D., and correspondingly $\mu(H - C) = -0.43$ D.

	Molecular moment μ	Group moment $\mu(CH_2 - O)$		
		Model I	Model II	Mean
		Debye units		
Ethylene oxide	1.88[5]	1.58	2.02	1.80
Trimethylene oxide	2.01[6]	2.15	1.72	1.94
Tetramethylene oxide	1.71[7]	2.20	1.74	1.97
Dimethyl ether	1.28[3]	2.20	1.80	2.00

The magnitude of the moment of the C – H bond was determined by Timm and Mecke[9] as ~ 0.3 D. and by Rollefson and Havens[10] as 0.31 D. from measurements of refractive indices in the infra-red region. It has been calculated by Coulson[11] to be 0.4 D. The result of the present investigation is, therefore, in fair agreement.

The sign of the moment has caused some controversy. Smyth[1] supports the view that the polarity is $\overset{-}{C} - \overset{+}{H}$, chiefly on the grounds that the parallelism of electronegativity difference and bond moment demands such a relation. A calculation by Hirschfelder reported by Smyth appeared to substantiate the position, but Coulson[11] has shown that the treatment is incorrect and that, in fact, application of the method of molecular orbitals to methane leads to the polarity $\overset{+}{C} - \overset{-}{H}$. The calculations reported here also indicate this charge distribution.

An attempt is being made to formulate a more adequate model than either of those used, and the measurement of the dipole moments of the cyclic oxides, sulphides and imines in the vapour phase is in progress. Details of the calculations outlined above will be published elsewhere in due course.

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The Three Coefficients of Viscosity of Anisotropic Liquids

BEFORE and during the War, investigations were reported on the viscosity of anisotropic liquids[1,2,3,4]. As is well known, the flow of an anisotropic liquid influences the orientation of the molecules. On the other hand, the value of the viscosity coefficient depends on this orientation. Therefore this coefficient is a function of the velocity-gradient, and the usual definition of the viscosity coefficient for these liquids loses its significance. If under the influence of any factor the molecules of the liquid should be orientated in one direction and the motion is unable to change this orientation, then we have the viscosity coefficient in the ordinary sense. But in this case we have to deal with the anisotropy of the viscosity, and in case of a liquid of the type of p-azoxyanisol we have three principal viscosity coefficients belonging to the three directions of orientation ; these are : (1) direction of the flow ; (2) direction of the velocity gradient ; (3) perpendicular to both these directions. Having given the molecules an orientation by means of a magnetic field in such circumstances that the flow did not change this orientation, I obtained the following values for the three principal viscosity coefficients for p-azoxyanisol and p-azoxyphenetol[2].

Substance and temperature	Molecules parallel to the direction of the flow, η_1	Molecules parallel to the gradient of velocity, η_2	Molecules perpendicular to the direction of flow and to the velocity gradient, η_3
p-Azoxyanisol 122° C.	0.024 ± 0.0005	0.092 ± 0.004	0.034 ± 0.003
p-Azoxyphenetol 144·4° C.	0.013 ± 0.0005	0.083 ± 0.004	0.025 ± 0.003

These results throw light on those obtained by the other investigators. The results of the older investigators (Eichwald[5] and Dickenschied[6]) obtained by the method of flow through capillary tubes are in agreement with my results. Evidently, in both cases we were dealing with the orientation of molecules parallel to the direction of flow. Zwetkoff and Michajlow[3], using the method of flow through a tube with rectangular cross-section, by application of the strongest available magnetic field and with the smallest possible velocity of flow, obtained values about 80 per cent of my value, η_2. From the dependence of the results on the intensity of the magnetic field, it is clear that these investigators did not reach the state of constant orientation of molecules, and that the flow of the liquid changed this orientation. The results obtained by these authors for the different values of velocity and for different intensities of magnetic field lie between η_1 (orientation parallel to the flow) and η_2 (parallel to the velocity gradient) $\eta_1 \leqq \eta_{Zwetkoff} < \eta_2$.

The measurements recently published by Becherer and Kast[4] were not carried out with constant orientation of the molecules. They were, however, orientated (at least in the layers where the phenomenon of viscosity chiefly takes place) in the planes of friction, but without a definite angle in this plane. The value obtained by these investigators is therefore not one of the three principal coefficients in the sense given by me. Clearly, $\eta_1 < \eta_{Kast} < \eta_3$, because in my measurements of η_1 and η_3 we have also an orientation parallel to the plane of friction, but once parallel and then perpendicular to the direction of the flow.

Hence the coefficient η_1 was measured by other workers as well as by me. The method of flow through capillaries gives usually the result corresponding to an orientation of molecules in the direction of flow ; the other values given by different investigators do not correspond to constant orientation of molecules.

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