657. *The Dipole Moments of Ethylene Oxide and Carbonyl Chloride in Benzene Solution, and a Note on a Useful Modification of Barclay and Le Fèvre's Equation.*

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In spite of its negative Kerr constant, ethylene oxide shows a *smaller* apparent moment in benzene solution (1·83 D.) than as a gas (1·89 D.). Such behaviour is predicted by several empirical relations, utilising quantities easily deduced from scale drawings, which avoid use of the sometimes inaccessible refractive index required by Barclay and Le Fèvre's original expression. The applicability of the new equations to the examples previously cited (*J.*, 1950, 556), as well as to carbonyl chloride and certain other molecules, is also demonstrated.

RECENT work in Sydney has shown that two substances having *negative* Kerr constants, *viz.*, sulphur dioxide and methylene dichloride, have apparent moments in benzene solution which are *less* than the true values determined in the gaseous state (cf. *J.*, 1950, 283, 556). Such a relationship was unexpected, since all previous discussions utilising the algebraic sign of the Kerr constant had predicted $\mu_{\text{solution}}/\mu_{\text{gas}}$ ratios *greater* than unity in these cases. (A fuller explanation is given in the references just cited, and also in *J.*, 1950, 290.)

In furtherance of the programme outlined earlier (*Trans. Faraday Soc.*, 1947, **43**, 392) we have now examined ethylene oxide and found evidence that it provides a third example of the above type of solvent effect. By contrast, the results for carbonyl chloride now reported display no unorthodox features.

Present Work.—Dry ethylene oxide or carbonyl chloride, purified by distillation, was absorbed in sodium-dried benzene, concentrations being determined by weight. Details of procedure were as recorded by Le Fèvre and Ross (*J.*, 1950, 283) and Barclay and Le Fèvre (*J.*, 1950, 556). The dielectric constants and densities measured are tabulated below under the usual headings (cf. *Trans. Faraday Soc.*, 1950, **46**, 1, wherein methods of calculation are also mentioned).

Ethylene oxide in benzene at 25°.

$w_1 \times 10^5$ ...	0	1073	1155	1355	1722	1777	1878	2069	2174	2680
ε_{12}	2·2725	2·3573	2·3646	2·3792	—	—	2·4198	2·4341	2·4401	—
d_{12}	0·87378	—	—	—	0·87337	0·87353	0·87346	0·87351	0·87350	0·87345

Whence mean $\alpha\varepsilon_2 = 7{\cdot}85$, mean $\beta d_2 = 0{\cdot}015_5$, ${}_{\infty}P_1 = 80{\cdot}3$ c.c.; and, if the distortion polarisation $= 11{\cdot}6$ c.c. (see later), then $\mu = 1{\cdot}83$ D.; by use of the (observed) molecular refraction (11·0 c.c.), μ appears as $1{\cdot}8_4$ D.

Carbonyl chloride in benzene at 25°.

$w_1 \times 10^5$ ...	0	1313	1739	1895	1982	2017	2504	2750
ε_{12}	2·2725	2·2873	2·2929	—	2·2970	—	2·3053	2·3067
d_{12}	0·87378	0·87770	0·87856	0·87954	0·87979	0·87989	0·88194	0·88269

Whence mean $\alpha\varepsilon_2 = 1{\cdot}22$, mean $\beta = 0{\cdot}349$, ${}_{\infty}P_1 = 44{\cdot}6_2$ c.c., and, if the distortion polarisation $= 18{\cdot}3$ c.c. (Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697), then $\mu = 1{\cdot}1_3$ D.

Discussion.—Two determinations of the dipole moment of ethylene oxide as a vapour are in the literature: 1·88 D. (Stuart, *Z. Physik*, 1928, **51**, 490) and 1·91 D. (Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 108). The second figure was obtained from results at two temperatures only, to which a Debye equation $P = 9{\cdot}95 + 22650/T$, was fitted; yet Ramaswamy himself (*ibid.*, p. 675), *via* the Sellmeier dispersion formula and refractive-index measurements on the gas, evaluated the electronic polarisation as 10·91 c.c. In this connection we note that from observations on the liquid (Beilstein, " Handbuch," XVII, 4, and XVII,* 3) the $[R_L]_D$ is 11·0 c.c., while from Vogel's Table XXII of *J.*, 1948, 1833, the constants corresponding to the methylene groups and an " ether " oxygen, without any adjustment for a 3-ring, amount to 11·06 c.c. Ramaswamy's distortion polarisation evidently is too small, and his final μ therefore slightly high. Stuart quotes readings of $(\varepsilon - 1)_{760\text{ mm.}}$ at three temperatures and from these we calculate (using the values for k and N listed by Birge, *Reports Progr. Physics*, 1941, **8**, 126) the relation $P = 11{\cdot}58 + 21680/T$. Since 11·58 is in better accord with the refractivity than is 9·95, we conclude that the moment indicated by $B = 21{,}680$, *viz.*, 1·89 D., is the more correct.

The ratio, $\mu^2_{C_6H_6}/\mu^2_{\text{gas}} = {}_0P_{\text{soln.}}/{}_0P_{\text{gas}}$, found by experiment for ethylene oxide at 25°, is therefore $68{\cdot}7/72{\cdot}7_5 = 0{\cdot}944$, *i.e.*, less than unity, despite a negative Kerr constant ($-10{\cdot}2 \times 10^{-15}$, 760 mm., 19·5°, 5890 A.; Stuart, *Z. Physik*, 1930, **63**, 540).

The structure and dimensions of this molecule are known from electron-diffraction photographs by Ackermann and Mayer (*J. Chem. Physics*, 1946, **4**, 377) and the micro-wave spectroscopic study by Shulman, Dailey, and Townes (*Physical Rev.*, 1948, **74**, 846). Fig. 1 incorporates the interatomic distances and angles cited by these authors, together with the appropriate "Wirkungsradien" (Stuart, *Z. physikal. Chem.*, 1935, *B*, **27**, 350). Following Barclay and Le Fèvre, therefore, A, B, and C are related as 3·90 : 4·46 : 3·64, and exp. x^2 follows as 0·906.

The dipole moment of carbonyl chloride has been determined as $1{\cdot}18_1$ D. in the gaseous state (Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697) and as 1·10 D. dissolved in carbon tetrachloride at 0° (Le Fèvre and Le Fèvre, *J.*, 1935, 1696); when recalculated with modern constants (Birge, *loc. cit.*) these values become 1·19 and 1·11 D., respectively; the present are the first measurements obtained with benzene as a solvent.

FIG. 1.

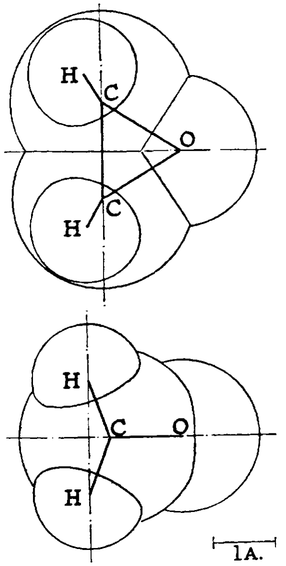
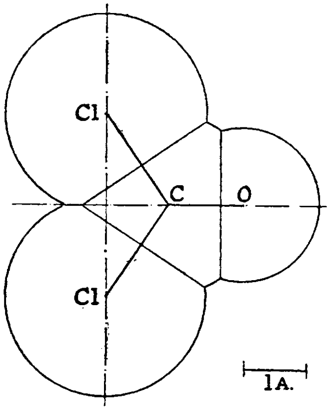


FIG. 2.



The ratio $\mu^2_{C_6H_6}/\mu^2_{gas}$ is therefore 0·902—a figure which, with the positive electric double refraction noted by Hansen (Diss., Karlsruhe, 1912), places carbonyl chloride unexceptionably among the majority of molecules for which the algebraic sign of $\delta\mu (= \mu_{soln.} - \mu_{gas})$ is the reverse of that of the Kerr constant.

In structure, carbonyl chloride is a flat Y for which slightly differing dimensions have been stated in the past. We have adopted the following (from the compilation recently made by Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46) : C–O, 1·18 A., C–Cl, 1·74 A., angle Cl–C–Cl, 112·5°. Fig. 2 shows a sectional plan, from which A, B, and C are 4·95, 6·06, and 3·16, respectively, and exp. x^2 is 0·673.

Alternative Empirical Expressions for $\mu^2_{soln.}/\mu^2_{gas}$.—The cases of ethylene oxide and carbonyl chloride draw attention to a deficiency of Barclay and Le Fèvre's equation as a practically useful means whereby μ_{gas} may be calculated from measurements of $\mu_{soln.}$. In the form proposed, (1), it contained the quotient n^2_2/n^2_1. For those substances which are gases or solids under ordinary conditions the refractive index as a liquid at 25° (our working temperature) is not readily available.

Our search for alternative expressions has been guided by the intuitive guesses (*a*) that the term involving x^2, being concerned essentially with areas, may be a measure of hindrance to rotation, so that exp. x^2 (or perhaps $e^{x^2} - 1$) is reflecting the non-randomness of rotational modes about the greatest and least axes of length of the solute molecule, and (*b*) that a second term is needed whose difference from unity has some relation to the exclusion from spherical distribution of the centres of the molecules surrounding the solute in the directions collinear and perpendicular to its resultant moment, and in consequence to the disturbance from isotropy of its polarisable solvent environment.

Of many tried, we select equations (2), (3), and (4) for especial comparison with (1) :

$$\mu^2_s/\mu^2_g = 1 + (\varepsilon_2 - 1)(\exp.\, x^2 - n^2_2/n^2_1)/(\varepsilon_2 + 2) \tag{1}$$

$$\mu^2_s/\mu^2_g = 1 + (\varepsilon_2 - 1)[\exp.\, x^2 - \exp.(h^2_2 - h^2_1)]/(\varepsilon_2 + 2) \tag{2}$$

$$\mu^2_s/\mu^2_g = 1 + (\varepsilon_2 - 1)\{\exp.\, x^2 - \exp.[(R_1/R_2)(1 - A_1B_1C_1/A_2B_2C_2)]\}/(\varepsilon_2 + 2) \tag{3}$$

$$\mu^2_s/\mu^2_g = 1 + (\varepsilon_2 - 1)\{\exp.\, x^2 - \exp.[(h_1^2/h_2^2)(1 - A_1B_1C_1/A_2B_2C_2)]\}/(\varepsilon_2 + 2) \tag{4}$$

In the above, subscripts 1 and 2 refer to solute and solvent respectively, R and n are molecular refractions and refractive indices, while the quantity h^2 is defined as

$$h^2 = \frac{(A - B)^2 + (B - C)^2 + (C - A)^2}{(A + B + C)^2}$$

where A is fixed as the greatest dimension measured on a scale model drawn as stated by Barclay and Le Fèvre (*loc. cit.*) ; A, B, and C are mutually perpendicular, and of B and C the latter is the lesser. For the factor x^2, however, A is taken along the direction of $\mu_{\text{resultant}}$, etc. (cf. Barclay and Le Fèvre, *loc. cit.*), so that $x^2 = (C^2 - A^2)/(\text{greatest dimension})^2$.

In the following table we apply formulæ (1)—(4) to those substances considered in Table IV of the paper by Barclay and Le Fèvre; for benzene (solvent) h^2_2 = 0·101, $A_2B_2C_2$ = 117·6, and $(\varepsilon_2 - 1)/(\varepsilon_2 + 2)$ = 0·2978 at 25°. It will be observed that each of the four equations modifies $\mu_{C_6H_6}$ in the correct direction. Equations (3) and (4) are particularly successful with paraldehyde, for which the excess of $\mu_{\text{soln.}}$ over μ_{gas} is the greatest on record (cf. *J.*, 1950, 290; the anomalous centrosymmetric molecules studied by Sutton *et al.*, *J.*, 1938, 1254, 1263, 1269, are of course another problem), although they are less satisfactory in other parts of the Table.

							μ_{gas} by :				μ_{gas}
Substance.	*A*.	*B*.	*C*.	h^2_1.	R_1.	$\mu_{C_6H_6}$.†	(1).	(2).	(3).	(4).	(found).†
CH_3Cl *	5·27	3·80	3·80	0·0261	11·5	1·69	1·89	1·82	1·85	1·82	1·86
CH_2Cl_2	4·10	6·10	3·60	0·0551	16·4	1·55	1·59	1·58	1·61	1·61	1·57
$CHCl_3$	4·10	6·50	6·50	0·0394	21·4	1·13	1·02	1·02	0·98	0·99	1·01
$CH_3{\cdot}CN$	5·95	3·80	3·80	0·0504	11·1	3·11—3·51	3·49—3·94	3·37—3·80	3·41—3·85	3·43—3·87	3·94—1·98
$CH_3{\cdot}NO_2$	5·20	4·50	3·80	0·0161	12·5	3·02—3·13	3·30—3·42	3·25—3·37	3·27—3·39	3·22—3·34	3·25—3·37
$COMe_2$	5·15	6·54	3·80	0·0469	$16{\cdot}1_5$	2·74	2·95	2·87	2·82	2·83	2·85—3·02
Paraldehyde	3·80	9·50	9·50	0·1250	33·1	1·87	1·60	1·58	1·45	1·45	1·44
SO_2	3·44	5·00	3·08	0·0472	9·49	1·61	1·70	1·64	1·68	1·71	1·62
NMe_3	3·82	6·55	6·55	0·0521	20·0	0·86	0·78	0·76	0·74	0·74	0·64
C_6H_5Me	8·25	6·05	3·80	0·0910	$31{\cdot}0_6$	0·34	0·37	0·37	0·34	0·35	0·37
C_6H_5Cl	8·08	6·05	3·16	0·1230	$31{\cdot}1_4$	1·59	1·73	1·74	1·66	1·65	1·73
$C_6H_5{\cdot}NO_2$ ‡	8·00	6·05	2·90	0·1380	$32{\cdot}7_4$	3·95	4·29	4·32	4·18	4·17	4·24
$C_6H_5{\cdot}CN$	8·95	6·05	2·90	0·1714	31·4	3·74—3·97	4·09—4·34	4·07—4·32	3·90—4·13	3·83—4·07	4·39

* Table IV of *J.*, 1950, 556 erroneously quotes x^2 as —0·52; it should be —0·48.
† For references, see *J.*, 1950, 556.
‡ The NO_2 group is taken as co-planar with the C_6 ring.

A statistical investigation has been carried out on the material presented in this table. Where ranges of observations exist (as with acetonitrile, nitromethane, etc.), arithmetic means have been struck and used. Application of the "*t*" and "χ^2" tests at the 95% level of significance (cf. Chambers, "Statistical Calculations for Beginners," Cambridge, 1940—46; Whetherburn, "A First Course in Mathematical Statistics," Cambridge, 1946) to the differences between the experimental values and those calculated from equations (1) and (2) shows that there is no significant difference between them—the experimental values could have been drawn from universes represented by either of the equations. However, (1) deals with the data more adequately than does (3) or (4). The tests do not distinguish between equations (2), (3), and (4). The mean differences between observed and calculated values (with standard deviations) are : for (1), 0·071 (0·074); (2), 0·082 (0·105); (3), 0·096 (0·119); (4), 0·104 (0·127).

On the basis of these tests therefore, it appears that equation (1) is to be preferred, but in the absence of data relating to refractive indices, equation (2) may be used to forecast the μ_{gas} without significantly greater error.

In addition to the foregoing considerations we note that (4) fails when the solvent has spherical symmetry.

Applications to Ethylene Oxide and Carbonyl Chloride.—Equations (2), (3), and (4) predict μ_{gas} from $\mu_{C_6H_6}$ as follows :

	$\mu_{C_6H_6}$.	μ_{gas} by : (2).	(3).	(4).	μ_{gas} (found).
Ethylene oxide	1·83	1·88	1·93	1·87	1·89
Carbonyl chloride	1·13	1·20	1·22	1·22	1·19

On the whole, therefore, equation (2) is to be preferred to (3). It is of interest to apply both to the 1935 observations on carbonyl chloride by Le Fèvre and Le Fèvre. If a distortion polarisation of 18·3 c.c. is used (instead of 17·4—to put past and present work on the same basis) in conjunction with modern constants, the apparent moment from the $_{\infty}P_1$ given, *viz.*, 44·7 c.c., becomes 1·09 D. For carbon tetrachloride, h^2_2 is zero, $A_2B_2C_2$ is 166·4, R_2 is 26·5, and $[(\varepsilon_2 - 1)/(\varepsilon_2 + 2)]_0$ is 0·2982. From Vogel's list (*J.*, 1948, 1842) of refraction constants, R_1 is 16·3 c.c. (This figure has been computed deliberately from a general tabular source to illustrate the avoidance of an actual determination of refractive index.) Accordingly, μ_{gas} is calculable by (2) as 1·14 D. and by (3) as 1·21 D.; comparison with the true value (1·19 D.) suggests that the earlier experiments, made under some difficulty in carbon tetrachloride at 0°, were not seriously incorrect.

The authors are grateful to Mr. P. D. Lark for help with the statistical analysis, and to the Commonwealth Research Fund for financial assistance.

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