302. *The Effect of Dissolution in Benzene on the Apparent Dipole Moment of* 1 : 8-*Cineole.*

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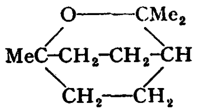
New determinations show $\mu_{gas} = 1{\cdot}58$ D and $\mu_{C_6H_6} = 1{\cdot}57$ D. These values are in agreement with predictions based on two of the empirical formulæ given previously (*J.*, 1950, 3370).

DURING the preceding measurements, pure specimens of 1 : 8-cineole (I) were being prepared for other work. The constitution of (I) rests on Perkin's synthesis of α-terpineol, and hence of *cis*-terpin from which some cineole may be obtained by dehydration. As constituting a cyclic ether, the component atoms in (I) *must* be mutually "locked," in contradistinction to those in such open-chain (and therefore flexible) species as (II). Accordingly, the molecular shape of (I) seemed predictable with fair certainty from known interatomic distances and valency angles.

(I)



(II)

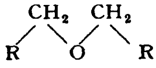


FIG. 1. *Side-view of* 1 : 8-*cineole. Dipole axis assumed to bisect oxygen bond angle.*

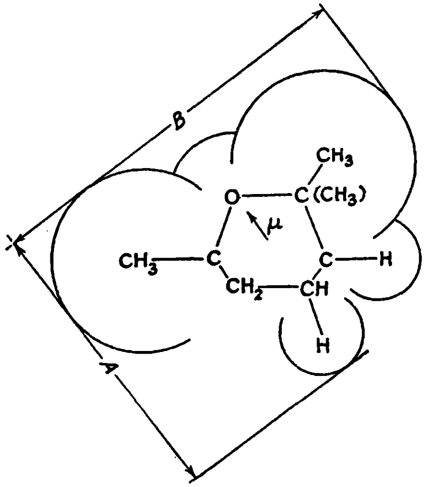
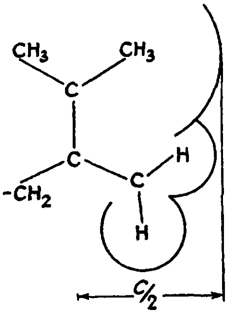


FIG. 2. 1 : 8-*Cineole seen from right-hand end of Fig.* 1, i.e., *along direction of* H–C *and* C–O *bonds.*



Figs. 1 and 2 show different aspects of cineole, drawn (using Stuart's "Wirkungsradien") as described before (*J.*, 1950, 556, 3370). From these we find the dimensions *A*, *B*, and *C* to be related as 6·48 : 8·35 : 6·36, whence $x^2 = -0{\cdot}022$ and $h_1^2 = 0{\cdot}017$. Since (see Experimental section) $(n_1^2)_D^{25}$ is 2·1176 and $[R_L]_D^{\text{Cineole}}$ is 45·5 c.c., we can forecast the ratios between the apparent dipole moment, $\mu_{C_6H_6}$, in benzene (appropriate constants for which are in the preceding paper) and the corresponding true value, μ_{gas}, as follow :

By equation (*a*) (p. 1646) $\mu^2_{C_6H_6}/\mu^2_{gas} = 0{\cdot}976$
" " (*b*) " $= 0{\cdot}968$
" " (*c*) " $= 1{\cdot}281$

Examination of ten solutions (from *ca.* 1 to 6%) yielded a total polarisation of 95·8 c.c. and—*via* the $[R_L]_D$ just quoted—the figure 1·57 D for $\mu_{C_6H_6}$. From this, μ_{gas} should be, by (*a*) 1·59 D, by (*b*) $1{\cdot}59_5$ D, and by (*c*) 1·39 D.

The direct measurement of μ_{gas} was therefore next undertaken, polarisations being read at seven temperatures between 200° and 300°. The resulting Debye equation, $P = 39{\cdot}5 + 15131/T$, however, displayed an " A " term (39·5 c.c.) which was less than the molecular refraction (45·5 c.c.) of cineole. Distortion polarisations are notoriously difficult to fix precisely. Fortunately this error need not seriously impair the correctness of the moment obtainable from B (= 15131) since μ_{gas} is determined not by the *height* of the P versus $1/T$ line above the $1/T$ axis but only by its slope.

We therefore calculate μ_{gas} as $0{\cdot}01281 \times 15131^{\frac{1}{2}} = 1{\cdot}58$ D—a result which again (cf. previous papers) justifies a preference for equations (*a*) and (*b*) over (*c*).

Two other points may be mentioned briefly : (*a*) The moment now recorded for cineole is some 0·4 D higher than those found for the simple aliphatic ethers. This is reconcilable with the structure (I) since, where comparisons are available, cyclic ethers seem to be more polar than their nearest open-chain relatives :

Substance	Moment	Reference
Ethylene oxide ...	1·89 (gas) ; 1·83 (C_6H_6)	Angyal, Barclay, and Le Fèvre, *J.*, 1950, 3370.
Dimethyl ether ...	1·29 (gas) ; 1·25 (C_6H_6)	Previous paper.
Tetrahydrofuran...	1·71—1·83 (C_6H_6–dioxan)	Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230.
Diethyl ether	1·17 (gas) ; 1·26 (C_6H_6)	Previous paper.

For the closest analogue to 1 : 8-cineole, *viz.*, diethyl ether, a moment of 1·87 D has been recorded, without experimental details, by Hibbert and Allen (*J. Amer. Chem. Soc.*, 1932, **54**, 4115).

(*b*) We find the dielectric constant of 1 : 8-cineole at 25° to be 4·480 relatively to that of chloroform (for which $\varepsilon = 4{\cdot}724$; cf. Ball, *J.*, 1930, 570). The corresponding density and refractive index (D line) are 0·9209 and 1·4552 respectively. By using these data, the orientation polarisation calculable *via* the Clausius–Mosotti–Debye or the Onsager relation (cf. *J. Amer. Chem. Soc.*, 1936, **58**, 1486) is shown to be

$$_{\text{O}}P = 3M(\varepsilon - n^2)/(\varepsilon + 2)(n^2 + 2)d$$

or

$$_{\text{O}}P = M(\varepsilon - n^2)(2\varepsilon + n^2)/(n^2 + 2)^2\varepsilon d$$

From the former, μ becomes 1·53 D, and from the latter 1·77 D ; μ_{gas} (found) is 1·58 D. It is perhaps relevant that Böttcher (*Physica*, 1939, **6**, 59) included two ethers in his wide survey of the applicability of the Onsager equation and that the moments estimated for these were both *ca.* 0·3 D higher than those from direct measurement.

EXPERIMENTAL

1 : 8-Cineole was purified *via* its crystalline *o*-cresol complex; after final distillation (b. p. 173·5°/758 mm.) the material showed $n_{\text{D}}^{18\cdot2}$ 1·4590, $d_{\text{D}}^{18\cdot2}$ 0·9272, whence $[R_L]_{\text{D}} = 45{\cdot}4_8$ c.c. This stock was kept over bright sodium wire until required.

Polarisation Data for Solutions in Benzene.—These are listed in Table 1, under the usual headings (cf. *Trans. Faraday Soc.*, 1950, **46**, 1).

TABLE 1. 1 : 8-*Cineole in benzene at* 25°.

10^5w_1	ε^{25}	d_4^{25}	$\alpha\varepsilon_2$	βd_2	10^5w_1	ε^{25}	d_4^{25}	$\alpha\varepsilon_2$	βd_2
866	2·2866	0·87444	1·63	0·076	3272	2·3304	0·87484	1·77	0·032
901	2·2871	0·87447	1·62	0·077	3330	2·3295	0·87610	1·71	0·070
1127	2·2932	0·87461	1·75	0·074	4429	2·3522	0·87634	1·80	0·058
1521	2·2987	0·87462	1·72	0·075	5239	2·3646	0·87668	1·76	0·055
1731	2·3023	0·87471	1·72	0·054	6318	2·3881	0·87694	1·83	0·050

whence $(\alpha\varepsilon_2)_{w_1} = 1{\cdot}65 + 2{\cdot}7w_1$
$(\beta d_2)_{w_1} = 0{\cdot}075 - 0{\cdot}46w_1$
and $({}_{\text{T}}P)^{25}_{w_1=0} = 95{\cdot}8$ c.c.

Polarisation Data for Cineole as a Vapour.—Essentially the circuits and ancillary equipment depicted in Figs. 1 and 2 of *J.*, 1950, 276 have been used. The b. p. of cineole, however, necessitated new arrangements for heating the replaceable capacity and for observing the pressure of its contents. The former requirement has been adequately met by building a thermostatically controlled oven, the latter less satisfactorily by the insertion of a glass-diaphragm gauge between the cell and an ordinary barometer. Details concerning these items will be given in a subsequent communication describing the work for which they were particularly developed.

The procedures of measurement and calculation have been set out previously (*Trans. Faraday Soc.*, 1947, **43**, 374). In Table 2, *P* is the total polarisation at the stated temperature computed relatively to the standardising gas used, namely sulphur dioxide (cf. *J.*, 1950, 276), *i.e.*

$$P^{\text{cineole}} = xP^{\text{SO}_2}/x' = (\delta C/p)^{\text{cineole}}_{p=0}.(10{\cdot}9 + 16160/T)/(\delta C/p)^{\text{SO}_2}_{p=0}$$

TABLE 2.

T (A)	No. of observations	Range (cm. Hg)	*x*/*x*′	*P* (c.c.)	*P* (calc.)	*T* (A)	No. of observations	Range (cm. Hg)	*x*/*x*′	*P* (c.c.)	*P* (calc.)
474·0°	20	19—62	$1{\cdot}59_1$	$71{\cdot}5_8$	$71{\cdot}4_1$	519·1°	13	17—53	$1{\cdot}63_1$	$68{\cdot}5_5$	$68{\cdot}6_4$
490·0	17	18—61	$1{\cdot}60_3$	$70{\cdot}3_4$	$70{\cdot}3_7$	538	19	18—63	$1{\cdot}66_3$	$68{\cdot}0_8$	$67{\cdot}6_1$
493·1	15	20—56	$1{\cdot}60_6$	$70{\cdot}1_3$	$70{\cdot}1_8$	587	16	16—62	$1{\cdot}68_9$	$64{\cdot}9_1$	$65{\cdot}2_7$
509·2	16	20—58	$1{\cdot}63_2$	$69{\cdot}5_9$	$69{\cdot}2_0$						

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