SHORT COMMUNICATIONS

THE DIPOLE MOMENT OF ACENAPHTHENE*

By J. Y. H. Chau† and R. J. W. Le Fèvre†

The M.I.T. Tables (Wesson 1948) list the moment of acenaphthene as 1·5–1·6 D, an estimate based upon measurements made by Lumbroso (1947) on solutions in benzene or dioxan and apparently inspired by the theory of Coulson and Rushbrook (1940). However, elementary principles suggest that the polarity of acenaphthene would be about double that of toluene (namely, c. twice 0·37 D, McAlpine and Smyth 1933 ; Baker and Groves 1939). Subsequently the original high figure has been twice reduced, first to 0·97 D (in benzene, Lumbroso 1949) and then to 0·85 D (in benzene, Bergmann, Fischer, and Pullman 1951). No repetition has yet been reported of Lumbroso's determination in dioxan. The present note provides this and also adds new data relating to carbon tetrachloride as solvent.

Experimental

The acenaphthene used had m.p. 96·0 °C (Beilstein's *Handbuch*, V, E II, p. 495, gives 96·2 °C). Dioxan (A.R. grade) was dried over sodium, fractionated (b.p. 100–101 °C), and stored over sodium (cf. Blout and Fields 1948). Carbon tetrachloride was as described by Le Fèvre and Le Fèvre (1954). Observations of dielectric constants ε and densities d are given in Table 1 against concentrations expressed as weight fractions w. Subscripts 12, 1, or 2 indicate solution, solvent, or solute respectively. Experimental techniques and methods of calculation were as noted by Le Fèvre (1953).

The total polarizations, $_{\infty}P_2$, of acenaphthene at infinite dilution emerge via,

$$_{\infty}P_2 = M_2[p_1(1-\beta) + C\alpha\varepsilon_1]$$

(cf. Le Fèvre 1953) as 65·1 c.c. in carbon tetrachloride and 64·5 c.c. in dioxan. The molecular refraction, R_D, for Na-D light follows from the observations of von Auwers and Frühling (1921) on the molten hydrocarbon as 51·93 c.c. Kikina, Schott-'Lvova, and Syrkin (1954) have recently given higher values ranging from 56·1 c.c. for light of $\lambda = 4046·6$ A to 52·03 c.c. for $\lambda = 6439·5$ A. We have not utilized these, however, since the text of the Russian paper has not yet been seen by us. Their effect would be to lower slightly the polarity estimates which follow. In any case, R_D is only an approximation for the distortion polarization. Taking the last-named as 51·9 c.c. we obtain :

$\mu = 0·8_0$ D in carbon tetrachloride,
$\mu = 0·7_9$ D in dioxan.

An attempt has also been made to measure μ_{gas}. Unfortunately an adequate pressure of acenaphthene was only secured at temperatures near the upper limit of usefulness of the apparatus now available (cf. Le Fèvre and Rao 1954,

TABLE 1

OBSERVATIONS ON DIELECTRIC CONSTANTS AND DENSITIES OF ACENAPHTHENE IN CARBON TETRA-CHLORIDE AND DIOXAN AT 25 °C

In carbon tetrachloride					
$10^5 w_2$	0	480	535	780	1243
ε_{12}	2·2270	2·2345	2·2366	2·2399	2·2470
$(d_4^{25})_{12}$	1·5845	1·5814	1·5799	1·5793	1·5775
		1849	1886		
		2·2522	2·2558		
		1·5723	1·5719		

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 1·53_6$, $\quad \Sigma\Delta d/\Sigma w_2 = -0·6600$

In dioxan					
$10^5 w_2$	0	1013	1098	1187	2468
ε_{12}	2·2090	—	2·2253	2·2204	2·2277
$(d_4^{25})_{12}$	1·0280	1·0283	1·0287	1·0286	1·0292
		2597			
		2·2310			
		1·0295			

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0·931$, $\quad \Sigma\Delta d/\Sigma w_2 = 0·051$

1955a, 1955b). The standardizing dielectric was air for which a temperature invariant polarization of 4·34 c.c. (corresponding to $\varepsilon = 1·000582$ at N.T.P.) was adopted. Table 2 shows the polarization observed at 330°, together with

TABLE 2

POLARIZATION OF GASEOUS ACENAPHTHENE

Temperature (°C)	x/x'	No. of Observations	P (obs.)	μD
330	13·50	7	58·6	0·8$_1$

the moment computed as $\mu = 0·012812[(P-R)T]^{\frac{1}{2}}$. Satisfactory agreement with the figures from solutions is displayed, and no abnormal " solvent effect " is indicated.

References

VON AUWERS, K., and FRÜHLING, A. (1921).—*Liebigs Ann.* **422** : 200.
BAKER, J. W., and GROVES, L. G. (1939).—*J. Chem. Soc.* **1939** : 1147.
BERGMANN, E., FISCHER, E., and PULLMAN, B. (1951).—*J. Chim. Phys.* **48** : 356.

BLOUT, E. R., and FIELDS, M. (1948).—*J. Amer. Chem. Soc.* **70** : 189.

COULSON, C. A., and RUSHBROOKE, G. S. (1940).—*Proc. Camb. Phil. Soc.* **36** : 193.

KIKINA, G. G., SCHOTT-'LVOVA, E. A., and SYRKIN, YA. K. (1954).—*Izvest. Akad. Nauk. S.S.S.R. Otdel. Kim. Nauk.* **1954** : 563. (*Chem. Abstr.* **48** : 13316.)

LE FÈVRE, R. J. W. (1953).—" Dipole Moments." 3rd Ed. (Methuen & Co. : London.)

LE FÈVRE, C. G., and LE FÈVRE, R. J. W. (1954).—*J. Chem. Soc.* **1954** : 1577.

LE FÈVRE, R. J. W., and RAO, D. A. A. S. N. (1954).—*Aust. J. Chem.* **7** : 135.

LE FÈVRE, R. J. W., and RAO, D. A. A. S. N. (1955a).—*Aust. J. Chem.* **8** : 39.

LE FÈVRE, R. J. W., and RAO, D. A. A. S. N. (1955b).—*Aust. J. Chem.* **8** : 140.

LUMBROSO, H. (1947).—*C.R. Acad. Sci. Paris* **225** : 1003.

LUMBROSO, H. (1949).—*C.R. Acad. Sci. Paris* **228** : 1425.

McALPINE, K. B., and SMYTH, C. P. (1933).—*J. Amer. Chem. Soc.* **55** : 453.

WESSON, L. G. (1948).—" Tables of Electric Dipole Moments." (The Technology Press : M.I.T. Cambridge, Mass.)