

DIPOLE MOMENT OF INDENE

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ABSTRACT. The dipole moment of indene is determined in three non-polar solvents—cyclohexane, CCl_4 and CS_2 covering a dielectric constant range of about 2.0 to 2.6. The experimental observations are treated in the manner of Guggenheim for obtaining the dipole moment values. The high value of about 0.85 D obtained for the moment of the compound is suggested as probably arising out of the resonance of the molecule between various structures as in the case of the related compounds cyclopentadiene and fluorene.

INTRODUCTION

There are two published reports of dipole moment determinations for indene; (1) by S. Lee (1940) and (2) by Syrkin and Shott Lvova (1944). Both were made in benzene as solvent and the values reported are 0.44 and 0.67 D respectively. Syrkin and Shott Lvova seem to have used the Hedestrand method (1929) for the computation of the moment. On account of the large difference in their values, a redetermination is considered desirable. Hence the present work is undertaken and the dipole moment determined in three non-polar solvents—cyclohexane, carbon tetrachloride and carbon disulphide, covering a dielectric constant range of about 2.0 to 2.6. The results were briefly reported previously (Rao, 1954).

EXPERIMENTAL

The various solutions are made up by weight and the dielectric constants determined by the usual heterodyne beat method, with a crystal oscillator at a frequency of 3.56 Mc/sec. The refractive indices are measured on a Pulfrich refractometer.

The sample of indene obtained from L. Lights and Co. Ltd, is distilled and the fraction condensing in the temperature range 181° — 182°C is collected. This liquid is used in the experiment. The solvents are analytical reagents from E. Merck.

Details of the results are shown in Tables I to IV.

RESULTS

TABLE I

Indene in cyclohexane

Temperature = 31.5°C ;

density of cyclohexane = 0.8052 gm/c.c.

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/w$
—	2.0076	—	—	1.41981	2.01585	—	—
0.00982	2.0172	0.0096	0.978	1.42148	2.02061	0.00476	0.485
0.01786	2.0247	0.0171	0.957	1.42273	2.02416	0.00831	0.465
0.02538	0.0303	0.0227	0.894	1.42390	2.02749	0.01164	0.459
0.03485	2.0379	0.0303	0.869	1.42520	2.03119	0.01534	0.440
0.04590	2.0441	0.0365	0.795	1.42644	2.03472	0.01887	0.411
0.05746	2.0492	0.0416	0.724	1.42800	2.03919	0.02334	0.406

$$\left(\frac{\Delta\epsilon}{w}\right)_{w \rightarrow 0} = 1.025$$

$$\left(\frac{\Delta n^2}{w}\right)_{w \rightarrow 0} = 0.502$$

$$\left(\frac{\Delta}{w}\right)_{w \rightarrow 0} = 0.523 \text{ (graphical)}$$

$$P_0 = 14.08 \text{ c.c.}$$

$$\mu = 0.84 D.$$

TABLE II

Indene in CCl_4

Temperature = 31.5°C ;

density of CCl_4 = 1.5785 gm/c.c.

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n^2_{12}	Δn^2	$\Delta n^2/w$
—	2.2215	—	—	1.45266	2.11022	—	—
0.00361	2.2292	0.0077	2.133	1.45392	2.11388	0.00366	1.014
0.00536	2.2328	0.0113	2.108	1.45445	2.11543	0.00521	0.972
0.00829	2.2377	0.0162	1.954	1.45522	2.11768	0.00746	0.900
0.01164	2.2434	0.0219	1.881	1.45591	2.11967	0.00945	0.812
0.01734	2.2522	0.0307	1.771	1.45683	2.12236	0.01214	0.700
0.02342	2.2572	0.0357	1.524	1.45748	2.12396	0.01374	0.587

$$\left(\frac{\Delta\epsilon}{w}\right)_{w \rightarrow 0} = 2.260$$

$$\left(\frac{\Delta n^2}{w}\right)_{w \rightarrow 0} = 1.088$$

$$\left(\frac{\Delta}{w}\right)_{w \rightarrow 0} = 1.172 \text{ (graphical)}$$

$$P_0 = 14.52 \text{ c.c.}$$

$$\mu = 0.85 D.$$

TABLE III
Indene in CS₂

Temperature = 31.5°C ;

density of CS₂ = 1.2545 gm/c.c.

w	ϵ_{12}	$\Delta\epsilon$	$\Delta\epsilon/w$	n_{12}	n^2_{12}	Δn^2 (-)	$\Delta n^2/w$ (-)
—	2.6212	—	—	1.62173	2.63001	—	—
0.00925	2.6231	0.0019	0.205	1.61917	2.62171	0.00830	0.897
0.01384	2.6250	0.0038	0.275	1.61832	2.61895	0.01106	0.799
0.02074	2.6288	0.0076	0.367	1.61752	2.61638	0.01363	0.657
0.02786	2.6326	0.0114	0.409	1.61745	2.61614	0.01387	0.498
0.03048	2.6357	0.0145	0.476	1.61742	2.61605	0.01396	0.458

$$\begin{array}{ccc}
 (\Delta\epsilon/w) = 0.130 & \begin{array}{c} 2 \\ (\Delta n^2/w) = -1.085 \\ w \rightarrow 0 \end{array} & (\Delta/w) = 1.215 \text{ (graphical)} \\
 & & w \rightarrow 0 \\
 P_0 = 15.79 \text{ e.c.} & & \mu = 0.89 D.
 \end{array}$$

The final values of the dipole moments are given in Table IV.

TABLE IV

Solvent	Dielectric constant of solvent	Orientation polarisation P_0 , e.c.	Dipole moment in Debye units
Cyclohexane	2.0076	14.08 (13.96)	0.84 (0.84)
CCl ₄	2.2215	14.52 (15.41)	0.85 (0.88)
CS ₂	2.6212	15.79 (15.57)	0.89 (0.89)

DISCUSSION

Syrkin and Shott-Lvova claimed that their value (0.67D) is more accurate than the previously published determination by S. Lee (0.44D). The value obtained in the present investigation (approximately 0.85D) is higher than even Syrkin's. Differences in dipole moment values are often attributed to the method of computation, (e.g. different values obtained in nitrobenzene), although, in the present case, the difference is much too large to be accounted for on this ground. The author has used the modified Guggenheim method (1951) while Syrkin's estimate was based on the Hedestrand method. The important differences between the two methods are (1) in the treatment of the atom polarisation, (2), in the use of

linear or a more general parabolic relation between $\epsilon_{12}-w$, ϵ_{12} being the dielectric constant of the solution and w the weight fraction of the solute, and (3) in the use of densities or elimination of density determinations. The Guggenheim method is considered generally to lead to more reliable values of the dipole moments. Further, the consistent values obtained in the three different solvents studied may indicate the correctness of the value obtained by the author.

A more general equation for the computation of the dipole moment is given by Palit (1952) which reduces to that of Guggenheim under some simplified conditions. When the results in the present case are recalculated using the equation of Palit, the values of P_0 and μ given in brackets in Table IV are obtained. The values of β_0 are calculated from refractive measurements alone as indicated by Palit. It will be noted that the neglected term in the Guggenheim equation has no effect on the moment in the case of the solvents cyclohexane and carbon disulphide but is pronounced in the case of carbon tetrachloride.

An approximate estimate of the moment of indene may be derived from general considerations based on the structure of the molecule represented in figure 1.

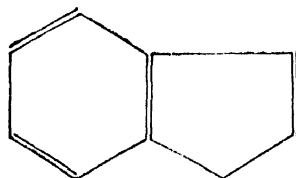


Fig. 1. Structure of indene.

For such an estimate, the methylene group only need be considered. Assuming that two C-H bonds, each of moment $0.40D$, interact at the tetrahedral angle of $109^\circ 28'$, the moment of the methylene group would be $0.46 D$ in fair agreement with the value obtained by Lee. However, such simple considerations are known to give erroneous values. For instance, the moment of diphenyl methane is only $0.23 D$ much below the estimated value. The errors arise from the fact that the moment of a particular bond may vary with the nature of the ring as is observed from a general review of the large amount of data on ring compounds. For indene, if inductive and other influences such, as resonance, are absent, a low value might be anticipated. The observed high value may therefore be explained as due to an inductive or a resonance effect. Judged from the moments of pyrrole and indole ($1.84, 2.02D$), thiophene and thionaphthene ($0.53, 0.68D$) and indene and fluorene (0.85 -author, 0.82 -Le Fevre) inductive effects do not seem to play a very important role in these ring systems. The resonance of the molecule between the various structures may have led to the high value in the case of the related compounds cyclopentadiene and fluorene.

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