Tetrahedron, 1966, Vol. 22, pp. 1597 to 1600. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRIC DIPOLE MOMENT OF NAPHTHALENE TETRACHLORIDE, DI-n-AMYLAMINE, TRI-n-AMYLAMINE AND DI-ALLYLAMINE

B. KRISHNA, B. B. L. SAXENA and S. C. SRIVASTAVA
University of Allahabad, Allahabad, INDIA

(*Received* 11 *August* 1965; *in revised form* 25 *November* 1965)

Abstract—Electric dipole moments of naphthalene tetrachloride, di-n-amylamine, tri-n-amylamine and di-allylamine have been determined in benzene solution at 1 Mc/s. The results have been discussed in the light of molecular structure of these compounds.

THE apparatus employed has been described earlier.[1,2] The exact resonance point was obtained by means of a cathode ray tube which was used to observe Lissajous figures produced by beat frequency and 50 c/s main frequency. The last traces of moisture in di-n-amylamine, tri-n-amylamine and di-allylamine (Fluka AG, Buchs SG) were removed by distillation and the fractions boiling at 194–196°; 245–249° and 109–110° respectively, were collected and employed for measurement. Benzene (A.R., B.D.H. grade) was distilled in a quick fit apparatus and fraction boiling at 78·5–79·5° was collected. Naphthalene tetrachloride (A.R., B.D.H. grade) was used without any further purification.

The polarization at infinite dilution was calculated by employing the Halverstadt and Kumler[3] equation in the form:

$$P_{2\infty} = \frac{M_1 3\alpha v_1}{(\varepsilon_1 + 2)^2}(M_1\beta + M_2 v_1)\frac{(\varepsilon_1 - 1)}{(\varepsilon_1 + 2)} \tag{1}$$

where M_1 and M_2 are the mol. wt. of solvent and solute respectively; α and β are defined by the expression:

$$\varepsilon_{12} = \varepsilon_1 + \alpha f_2 \tag{2}$$

and

$$v_{12} = v_1 + \beta f_2 \tag{3}$$

where f_2 represents the mole fraction of the solute; ε_1 and ε_{12} are the dielectric constants of the pure solvent and the solution respectively; v_1 and v_{12} represent the specific volumes of the pure solvent and the solution respectively. The values of the various quantities measured are given in Tables 1–4. The values of α, β, v_1 and ε_1 were calculated by the method of least squares.[4]

[1] B. Krishna and K. K. Srivastava, *J. Chem. Phys.* **27**, 835 (1957).
[2] B. Krishna and K. K. Srivastava, *J. Chem. Phys.* **32**, 663 (1960).
[3] I. F. Halverstadt and W. T. Kumler, *J. Amer. Chem. Soc.* **64**, 2988 (1942).
[4] J. W. Mellor, *Higher Mathematics for students of Chemistry and Physics* p. 326. Dover Publications, New York (1954).

TABLE 1. NAPHTHALENE TETRACHLORIDE IN BENZENE (TEMP 25°)

S. No.	f_2	ε_{12}	ν_{12}
1	0·00087	2·3157	1·1440
2	0·00173	2·3278	1·1424
3	0·00269	2.3471	1.1407
4	0·00355	2·3607	1·1394
5	0·00443	2·3710	1·1381
6	0·00526	2·3843	1·1368
7	0·00679	2·4053	1·1330

$\alpha = 15{\cdot}8597$ $M_1 = 78{\cdot}19$
$\beta = -1{\cdot}7758$ $M_2 = 269{\cdot}84$
$\varepsilon_1 = 2{\cdot}3021$ $P_e = 63{\cdot}02$
$\nu_1 = 1{\cdot}1461$ $P_{2\infty} = 282{\cdot}1183$
$\mu = 3{\cdot}27 \times 10^{-18}$ e.s.u.

TABLE 2. DI-n-AMYLAMINE IN BENZENE (TEMP 25°)

S. No.	f_2	ε_{12}	ν_{12}
1	0·00465	2·2812	1·1494
2	0·00618	2·2864	1·1502
3	0·00648	2·2880	1·1508
4	0·01114	2·2909	1·1515
5	0·01674	2·2998	1·1519
6	0·02234	2·3098	1·1538
7	0·02872	2·3229	1·1556

$\alpha = 1{\cdot}5228$ $M_1 = 78{\cdot}19$
$\beta = 0{\cdot}2199$ $M_2 = 157{\cdot}00$
$\varepsilon_1 = 2{\cdot}2758$ $P_e = 51{\cdot}99$
$\nu_1 = 1{\cdot}1477$ $P_{2\infty} = 81{\cdot}24$
$\mu = 1{\cdot}20 \times 10^{-18}$ e.s.u.

TABLE 3. TRI-n-AMYLAMINE IN BENZENE (TEMP 25°)

S. No.	f_2	ε_{12}	ν_{12}
1	0·00158	2·2815	1·1475
2	0·00315	2·2869	1·1482
3	0·00469	2·2892	1·1483
4	0·00861	2·2903	1·1498
5	0·01091	2·2916	1·1506
6	0·01402	2·2950	1·1516
7	0·01912	2·2960	1·1532

$\alpha = 0{\cdot}7168$ $M_1 = 78{\cdot}19$
$\beta = 0{\cdot}3584$ $M_2 = 227{\cdot}00$
$\varepsilon_1 = 1{\cdot}1469$ $P_e = 75{\cdot}31$
$\nu_1 = 2{\cdot}2837$ $P_{2\infty} = 96{\cdot}8870$
$\mu = 1{\cdot}03 \times 10^{-18}$ e.s.u.

TABLE 4. DI-ALLYLAMINE IN BENZENE (TEMP 25°)

S. No.	f_2	ε_{12}	ν_{12}
1	0·00359	2·2959	1·1487
2	0·00719	2·3038	1·1492
3	0·01071	2·3069	1·1498
4	0·01436	2·3156	1·1504
5	0·01950	2·3315	1·1514
6	0·02652	2·3356	1·1524
7	0·03487	2·3484	1·1539

$\alpha = 1{\cdot}7073$ $M_1 = 78{\cdot}19$
$\beta = 0{\cdot}1664$ $M_2 = 97{\cdot}00$
$\varepsilon_1 = 2{\cdot}2764$ $P_e = 32{\cdot}51$
$\nu_1 = 1{\cdot}1404$ $P_{2\infty} = 61{\cdot}87$
$\mu = 1{\cdot}20 \times 10^{-18}$ e.s.u.

The values of dipole moments obtained for amines are of the expected order of magnitude and will not be discussed. As regards naphthalene tetrachloride, the following considerations will show that a value of 3·27 D for the dipole moment is reasonable.

Naphthalene tetrachloride (Fig. 1) is a derivative of tetralin formed by replacement of one hydrogen atom at each of 1, 2, 3 and 4 carbon atoms. The X-ray analysis by Lasheen[5] shows that the hexane ring has a half-chair structure. Further, the C—Cl bonds in 1 and 4 positions are axial and in 2 and 3 positions are equatorial and they correspond to C_2 symmetry. The C—Cl bonds at 1 and 4 positions are oppositely directed. Consequently, as an approximation the moment due to the C—Cl bonds in 1 and 4 positions may be regarded as cancelled and the resultant moment of naphthalene tetrachloride should be equal to that of 2,3-dichlorotetralin.

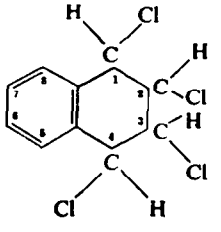

FIG. 1

The work of Fujita[6] shows that dichlorotetralin can occur in various conformations: *cis*-ae, *cis*-ea, *trans*-aa, and *trans*-ee, He observed a dipole moment value for 2,3-dichlorotetralin at room temperature of 1·6 D. From this he concluded that 2,3-dichlorotetralin has a *trans* configuration and the apparent observed moment should vary with the abundance ratio of two conformations (i.e. *trans*-aa, and *trans*-ee) at a given temperature unless the energy difference, ΔE, between them is too large.

[5] M. A. Lasheen, *Acta Cryst.* **5**, 593 (1952).
[6] T. Fujita, *J. Amer. Chem. Soc.* **79**, 2471 (1957).

This abundance ratio is such that 2,3-dichlorotetralin moment should be equal to 1·6 D at room temperature.

However in naphthalene tetrachloride the C—Cl bonds are equatorial[5] and hence the observed dipole moment of naphthalene tetrachloride should be equal to that of 2,3-dichlorotetralin in the *trans*-ee conformation. The calculations of Fujite[6] indicate that the dipole moment of 2,3-dichlorotetralin in *trans*-ee conformation should be equal to 3·1 D. Consequently, the observed value of 3·27 D for naphthalene tetrachloride closely agrees with the theoretical value.