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Electric Dipole Moment of 4-Chloro-2,3-tetra-, penta-, and hexamethylene Quinoline

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Electric dipole moments of 4-chloro-2,3-tetra-, penta-, and hexamethylene quinolines[1–3] have been determined in benzene solution at a frequency of 1 MHz by Guggenheim method.[4] The reported results indicate that these compounds are non-planar and the dipole moment increases with the increase in the size of substituted methylene ring.

Recently a series of useful antidepressant and biologically active compounds like, 4-chloro-2,3-tetra-, penta- and hexamethylene quinolines have been prepared and their physical properties have been reported.[1–3] It has been found[6–8] that the dipole moment measurements of substituted quinolines and naphthalenes provide valuable information regarding the mode of interaction and the distribution of π-electrons to assign the structural configuration of these compounds. From this point of view the present series of organic compounds has been selected for the measurement of electric dipole moment and thereby to examine the influence of the size of the substituted methylene ring on the π-electron distribution of 4-chloroquinoline.

Experimental

The dielectric constant measurements were carried out at 25 °C at a radio frequency of 1 MHz with the help of a "Toshniwal" Dipole Meter type RLO9 supplied by Scientific and Industrial Instrument Co., India. The instrument works on a well known principle of heterodyne beat method. The resulting beat frequency is projected on the screen of a cathode ray tube with a 50 cycles per second. A Lissajous figure is obtained on the screen. The readings were recorded at the resonance point indicated on the CRT screen by the formation of a single loop pattern, *i.e.*, an ellipse or a circle.

Refractive indices of the solvent and solutions were determined at 25 °C with the help of "ASCO" Abbe-Refractometer (made in India). The range of this instrument is 1.3000 to 1.7000, the maximum precision attainable being 0.0002. Sodium D-line was used as a source of light and the refractometer was standardized with the help of a glass slab of known refractive index. The instrument directly gives the value of refractive index which is measured with the reading telescope.

The compounds 4-chloro-2,3-tetra-, penta-, and hexamethylene quinolines obtained from Central Drug Research Institute, Lucknow, India were recrystallized from benzene, dried and kept in a vacuum desiccator.

The dipole moment has been calculated by Guggenheim method,[4] *i.e.* by plotting** a quantity Δ against the concentration C, in moles of polar solute per cm^3 given by the relation:

$$\Delta = (\varepsilon_{12}-n_{12}^2) - (\varepsilon_1-n_1^2) \tag{1}$$

where ε_1, n_1 and ε_{12}, n_{12} represent the dielectric constant and refractive index of pure solvent and solution respectively.

The slope $(\Delta/C)_0$ of the curve at $C=0$ is then used to calculate the dipole moment by means of the equation[9] given below:

$$\mu^2 = \frac{9kT}{4\pi N}\,\frac{3}{(\varepsilon_1+2)(n_1^2+2)}\left(\frac{\Delta}{C}\right)_0 \tag{2}$$

The dipole moment, μ, has also been calculated from Eq. (2) by determining the slope (Δ/C), using the mathematical relation based on least squares method,[5] namely

$$\left(\frac{\Delta}{C}\right) = \frac{\sum\Delta\sum C - n\sum(\Delta C)}{(\sum C)^2 - n\sum(C^2)} \tag{3}$$

where Δ and C represent their usual meaning and that n is the number of observations recorded.

In order to make an estimate of the precision of equipments (Dipole Meter & Refractometer), the dipole moments of some of the liquids like, methanol, pyridine, acetone, and nitrobenzene are determined in benzene solution and are given in Table 1 along with their reported values for the sake of comparison. The experimental and literature values are found to be within the maximum deviation of ±3%.

TABLE 1. DIPOLE MOMENT (μ) OF METHANOL, PYRIDINE, ACETONE, AND NITROBENZENE IN BENZENE SOLUTION AT 25 °C

Substance	$\mu\times10^{18}$ e.s.u.	
	Experimental	Literature[a]
Methanol	1.73	1.68
Pyridine	2.22	2.20
Acetone	2.84	2.76[b]
Nitrobenzene	3.86	3.98

a) G.C. Pimentel and A.L. McClellan, "The Hydrogen Bond," Reinhold Publishing Co., New York, N.Y. (1960), p. 15. b) C.P. Smyth, "Dielectric Behaviour and Structure," McGraw Hill Book Co., New York (1955), p. 48.

Results

The refractive index, n_{12}, and dielectric constant, ε_{12}, of 4-chloro-2,3-tetra-, penta-, and hexamethylene quinolines are determined in benzene solution at different concentrations at 25 °C and are recorded in Table 2. The Δ values calculated from Eq. (1) are also given in Table 2. These Δ values are plotted against C as shown in Fig. 1. The slopes (Δ/C), evaluated from these linear plots as well as from least-squares relation[5] have been used to determine dipole moment μ, by Guggenheim method.[4] The obtained (Δ/C) and μ values are summarized in Table 3.

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** The slope is directly obtained from the plot of $(\varepsilon_{12}-n_{12}^2)$ against C as the second term on the right hand side in Eq. (1) is constant.

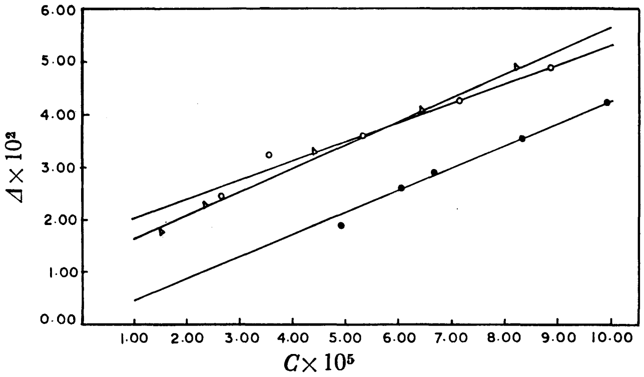


Fig. 1. Plot of Δ *vs.* C for tetra, penta, and hexa salts in benzene solutions at 25 °C.
△: 4-Chloro-2,3-hexamethylene quinoline, ○: 4-chloro-2,3-tetramethylene quinoline, ●: 4-chloro-2,3-pentamethylene quinoline.

Table 2. Refractive index (n_{12}), dielectric constant (ε_{12}), and Δ values of 4-chloro-2,3-tetra-, penta-, and hexamethylene quinolines in benzene at different concentrations (25 °C)

Concn $C \times 10^5$	Refractive index n_{12}	Dielectric constant ε_{12}	$\Delta \times 10^2$ $[\Delta = (\varepsilon_{12} - n_{12}^2)]$
4-Chloro-2,3-tetramethylene quinoline			
0.00	1.5026	2.274	—
2.65	1.5032	2.284	2.44
3.56	1.5036	2.293	3.22
5.34	1.5040	2.298	3.60
7.16	1.5049	2.307	4.23
8.87	1.5054	2.315	4.88
4-Chloro-2,3-pentamethylene quinoline			
4.94	1.5037	2.280	1.89
6.06	1.5040	2.288	2.60
6.67	1.5047	2.293	2.89
8.38	1.5052	2.301	3.54
9.94	1.5056	2.309	4.22
4-Chloro-2,3-hexamethylene quinoline			
1.56	1.5032	2.277	1.74
2.39	1.5034	2.283	2.28
4.47	1.5038	2.294	3.26
6.49	1.5041	2.303	4.07
8.26	1.5044	2.312	4.88

Table 3. (Δ/C) and dipole moment (μ) of tetra-, penta-, and hexa salts in benzene solution at 25 °C

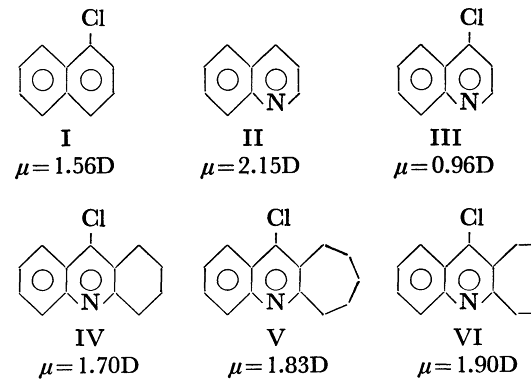
Salt	Graphical method Least squares method $(\Delta/C) \times 10^{-3}$	$\mu \times 10^{18}$ e.s.u.	
Tetra	0.365 0.365[a]	1.70 1.70[a]	1.70
Penta	0.425 0.415[a]	1.84 1.82[a]	1.83
Hexa	0.445 0.460[a]	1.88 1.92[a]	1.90

a) Slope (Δ/C), evaluated from least-squares method (Ref. 5).

Discussion

It may be observed from Table 3 that the dipole moments of 4-chloro-2,3-tetra-, penta-, and hexamethylene quinolines in benzene solution determined by using (Δ/C) values obtained from graphical and least squares[5] methods are found to be in an excellent agreement and are within the maximum deviation of 2%. It may also be noted that the dipole moment of these compounds increases in the increasing order of the size of substituted methylene ring, *i.e.*, μ tetra$<\mu$ penta$<\mu$ hexa as 4-chloroquinoline being the common constituent to all the above investigated polar compounds.

The geometrical structures and dipole moments[6-8] of 1-chloronaphthalene, quinoline, 4-chloroquinoline, and 4-chloro-2,3-tetra-, penta-, and hexamethylene quinolines are represented in Fig. 2 (see I, II, III, IV, V, and VI respectively).



I $\mu = 1.56$D
II $\mu = 2.15$D
III $\mu = 0.96$D
IV $\mu = 1.70$D
V $\mu = 1.83$D
VI $\mu = 1.90$D

Fig. 2.

It is clear from Fig. 2 (see III) that the 4-chloroquinoline has two dipoles of similar magnitudes that of quinoline itself (2.15D) and the other associated with the C–Cl bond (1.56D). The Cl-substituent increases the electronegativity of the carbon atom to which it is attached and this consequently modifies the π-electron distribution of the quinoline ring. The p-electrons of chlorine atom interacts with the π-electrons of quinoline ring which reduced the net dipole moment of the 4-chloroquinoline (0.96D).

The dipole moments of 4-chloro-2,3-tetra-, penta-, and hexamethylene quinoline are not only in the regular increasing order but are almost twice that of 4-chloroquinoline, which establishes that the substitution of methylene ring is definitely on the different plane to that of the quinoline ring. The dipole moment of these compounds can be considered as the sum of the moments of 4-chloroquinoline and substituent methylene ring, which interact with one another thereby resulting in an increase of the net magnitude of dipole moment.

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