Micro-wave Absorption in Benzene Solution of Cyclohexane-1, 4-dione

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(Received October 13, 1962)

With an aim of checking the polarity of cyclohexane-1, 4-dione molecule, dielectric absorption of this substance in micro-wave region (0.446 molar benzene solution) has been measured with use of a resonant cavity which was originally designed by Dr. Hatori of this Institute. The results obtained at a frequency of 9.4 Gc/sec. (3.2 cm.) are shown in the following table:

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TABLE I. DIELECTRIC LOSS AND DIELECTRIC CONSTANT AT 3.2 cm. (20°C)

Substance	$\tan\delta \cdot 10^4$	ε'
Benzene	5.8	2.282
Cyclohexane-1, 4-dione in benzene	22.3	2.383
Chlorobenzene in benzene	28.6	2.286

For the sake of comparison, the results obtained with the solution of chlorobenzene in benzene (0.049 molar) are also shown in Table I.

Considering the fact that a fairly large value of the dipole moment has been reported so far for cyclohexane-1, 4-dione (1.2~1.5 Debye)[1-5], the $\tan\delta$ value for this compound as listed in Table I is unexpectedly small, being less than that of chlorobenzene solution, the concentration of which is almost one tenth of the former, while the increment of dielectric constant with the former is much more appreciable. This seems to indicate that either the actual dipole moment of this compound should be much smaller than those so far obtained by other investigators or that we must seek for the mechanism of dielectric absorption which differs from that of usual Debye absorption.

If we assume the magnitude of relaxation time for cyclohexane-1, 4-dione as 7×10^{-12} sec.[6], we can calculate an apparent dipole moment of the compound with use of the following equation:

$$\mu^2 = 6750\,\varepsilon' \boldsymbol{k}T(1+\omega^2\tau^2)\tan\delta/(\varepsilon'+2)^2\pi c\boldsymbol{N}\omega\tau$$

where ε', $\boldsymbol{k}$, T, c, $\boldsymbol{N}$, ω, and τ are the dielectric constant of the solution, Boltzmann's constant, absolute temperature, molar concentration, Avogadro's number, angular frequency, and the relaxation time of the molecule, respectively. The value of dipole moment thus calculated is 0.43 Debye, suggesting that the molecule of cyclohexane-1, 4-dione exists almost in a non-polar conformation.

We may conclude, therefore, that 1) the larger values of dipole moment so far reported for this compound by a number of investigators are due to their underestimation of atom polarization or "vibration polarization" in calculating μ value from the observed molar polarization, and 2) the "libration" of two carbonyl groups attached at the opposite ends of flexible ring, or "puckering" should be responsible for such a high value of atom polarization (Chiba's estimation is ~33 cc.)[5], and 3) consequently, cyclohexane-1, 4-dione exists predominantly in the flexible form with two carbonyl groups directed almost in opposite sense: libration of the groups may give rise to a small apparent dipole moment.

Details will be published later in this Bulletin.

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6) τ values for chlorobenzene and cyclohexanone are 8×10^{-12} sec. and 6×10^{-12} sec., respectively.