

## Hydrogen—Bonded Complexes of some Ethers with Isomeric Methyl Carbazoles

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The effect of hydrogen bonding on the near U.V. absorption spectra of some Methyl Carbazoles as proton donors with diethyl-ether and tetrahydrofuran as proton acceptors has been studied. The  $\pi \rightarrow \pi^*$  bands of the proton donors shift towards longer wave lengths as a result of such interaction. Using this change in the absorption spectrum, the equilibrium constant in this interaction between the proton donor and the acceptor has been evaluated. It is concluded, from the result, that proton donating power of the Methyl Carbazoles increases in the order 2- Methyl Carbazole > 4- Methyl Carbazole > 3- Methyl Carbazole > 1- Methyl Carbazole, i.e., their base character decreases in the reverse order. The free energy change lies in the range 0.62–1.20 K.Cal/mole.

It has earlier been reported that  $\pi \rightarrow \pi^*$  bands of the conjugated system such as phenols<sup>1</sup> undergo a red shift, and  $n \rightarrow \pi^*$  bands<sup>2,3</sup> in ketones, aldehydes and pyridazine undergo a blue shift as a result of hydrogen bonding. Systematic investigations<sup>4</sup> of the hydrogen bonding effect on the electronic spectra of various secondary amines have been made, but similar study on the absorption bands of 1-methyl-, 2-methyl-, 3-methyl- and 4-methyl carbazoles is still lacking. The purpose of the present investigation is to find the relative order of proton donating capacity of the methyl carbazoles by measuring their absorption spectra. With this object in view the equilibrium constants for hydrogen bond formation between isomeric methyl carbazoles with diethyl ether and tetrahydrofuran are estimated from the  $\pi \rightarrow \pi^*$  red shift phenomenon in the region 275–310 m $\mu$ , the results of which are reported in the present communication.

### EXPERIMENTAL

The isomeric methyl carbazoles were obtained as gifts from Dr. D. P. Chakraborty and coworkers. The G. R. (E. Merck) tetrahydrofuran and B. D. H. reagent diethyl ether were made peroxide free by treatment with ferrous sulphate. They were then refluxed over solid caustic potash and then over calcium hydride and finally distilled over metallic sodium.

The solvent used was G. R. (E. Merck) cyclohexane which was purified by chromatographic adsorption on Al<sub>2</sub>O<sub>3</sub>. The purified solvent showed cut off at 230 m $\mu$ . The spectral measurements were made with Carl Zeiss V. S. U.—1 spectrophotometer using 1 cm. silica cells at 27°. All the solutions were prepared gravimetrically.

1. S. Basu and B. B. Bhowmik, *Trans. Faraday Soc.*, 1963, **59**, 813.
2. G. J. Brealey and M. J. Kasha, *J. Amer. Chem. Soc.*, 1955, **77**, 4462.
3. S. Basu and A. K. Chandra, *Trans. Faraday Soc.*, 1960, **56**, 632.
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## RESULTS

The physico-chemical basis of calculating the equilibrium constant of the hydrogen bonded complex formation reaction has been detailed by Basu and Chandra<sup>3</sup>.

For the equilibrium  $A+B \rightleftharpoons AB$ ,  $K = [AB]/[A][B]$ , it can be deduced that, when  $[A] \gg [B]$ ,

$$\frac{[A]}{(\bar{\epsilon}-\epsilon_0)} = \frac{1}{(\epsilon_1-\epsilon_0)K} + \frac{[A]}{(\epsilon_1-\epsilon_0)} \quad \dots (1)$$

where  $\bar{\epsilon}$  is the formal extinction coefficient,  $\epsilon_0$  and  $\epsilon_1$  are the extinction coefficients of the proton donor B and the hydrogen bonded complex AB respectively. The component A (proton-acceptor) is non-absorbing. K can be evaluated from the slope and intercept of the linear plot of  $[A]/(\bar{\epsilon}-\epsilon_0)$  versus  $[A]$  in equation (1).

On adding increasing amounts of ethers to the cyclohexane solution of the different methyl carbazoles, it is observed that the  $\pi \rightarrow \pi^*$  bands of the latter occurring in the 275–310  $m\mu$  region, shift more progressively to the red and these new peaks at the longer wave length side of the bands of the proton donors may be ascribed to the hydrogen bonded complexes. The ethers do not absorb in the aforesaid region. In Table I are shown the positions of the peaks of the complexed and free solutes observed in the present series of measurements.

TABLE I

*Peak of the  $\pi \rightarrow \pi^*$  absorption band of complexed and non-complexed compounds.*

Compound	$\lambda(m\mu)$		
	Non-Complexed form	Complexed form	
	in Cyclohexane	in Diethyl ether	in Tetrahydro- furan
1—Methyl Carbazole	288	290	291
2—Methyl Carbazole	293	295	295
3—Methyl Carbazole	293	294	295
4—Methyl Carbazole	286	288	288

The equilibrium constant of the hydrogen bonded complexes were determined by absorbance measurements near the peaks of complexes on a series of solutions having the same concentration of the proton donor, mixed with varying amounts of proton acceptor. The plot of  $[A]/(\bar{\epsilon}-\epsilon_0)$  versus  $[A]$  according to equation (1) is found to be linear in all cases, showing the formation of 1 : 1 complexes. In Table II are summarized the relevant experimental data. The K values given in Table II are averaged for several wave lengths.

## DISCUSSION

It is seen from Table II, that for the same proton donor, the equilibrium constant increases in the order tetrahydrofuran > diethyl-ether and for the same proton acceptor

the equilibrium constant increases in the order 2-methyl carbazole > 4-methyl carbazole > 3-methyl carbazole > 1-methyl-carbazole.

TABLE II

Proton donors	Conc. of Proton donor, moles/l	Proton Acceptors	Range of Acceptor conc. (moles/l)	Average Eq. const. l/mole
1. 1-Methyl carbazole	$1.7675 \times 10^{-5}$	Diethyl ether Tetrahydrofuran	0.6667-2.0001 0.7072-2.1216	2.80 4.01
2. 2-Methyl carbazole	$2.1545 \times 10^{-5}$	Diethyl ether Tetrahydrofuran	0.6667-2.0001 0.7072-2.1216	5.00 7.50
3. 3-Methyl carbazole	$1.8785 \times 10^{-5}$	Diethyl ether Tetrahydrofuran	0.6667-2.0001 0.7072-2.1216	3.37 4.30
4. 4-Methyl carbazole	$6.075 \times 10^{-6}$	Diethyl ether Tetrahydrofuran	0.6667-2.0001 0.7072-2.1216	4.00 6.80

Basu and Bhowmik<sup>5</sup> have estimated the hydrogen bonding power of a proton in N-H group of various amines. They found that the equilibrium constant for hydrogen bond formation increases with the decrease in base character, i.e., with an increase in proton donor character of the amines. Following Basu and Bhowmik<sup>5</sup> and on the basis of the equilibrium constant, it can be concluded that the proton donating power has the order 2-methyl- > 4-methyl- > 3-methyl- > 1-methyl carbazole, i.e., their base character decreases in the reverse order.

For all systems the free energy charge, calculated by the relation  $\Delta G = -RT \ln K$  is in the range 0.62-1.20 K.cal/mole, which is a reasonable value for a weak hydrogen bond.

The results may be explained by considering the steric and hyperconjugative effects of the substrate. For example a methyl substituent at 1-position should sterically hinder the formation of these hydrogen bonded complexes with diethyl ether more than with tetrahydrofuran. Because the observed COC bond angles of ethers increases in the order tetrahydrofuran < diethyl ether. Further works on these lines are in progress.

The author is grateful to Dr. D. P. Chakraborty and co-workers, for their kindness in giving the samples of all the isomeric methyl carbaxoles as a gift. The author also expresses his sincere thanks to Professor Sadhan Basu, Palit Professor of Chemistry, University of Calcutta for valuable suggestions and Dr. S. K. Chakraborty for his interest in the work.