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Hydrogen Bonding between Phenols and Carbon Disulphide[*1]

A. B. Sannigrahi[*2] and A. K. Chandra

Chemistry Department, University College of Science & Technology, Calcutta-9, India

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The effect of hydrogen bonding on the near ultraviolet absorption spectra of some phenols was studied with carbon disulfide as a base. The results show that the $\pi \rightarrow \pi^*$ bands of phenols move toward longer wavelength and the $n \rightarrow \pi^*$ band of carbon disulphide moves toward shorter wavelength. From the optical density measurements in the wavelength regions where both the bands occur the stability constants of the hydrogen bonded complexes were measured. From the result it was concluded that proton donating power of the phenols increases in the order *p*-cresol$<$phenol$<$$\beta$-naphthol$<$$\alpha$-naphthol which is exactly the relative order of their acidities. These results also support the electrostatic theory of hydrogen bonding.

The hydrogen bond formation involving sulphur atom is not so well known as that involving oxygen and nitrogen atoms. In fact, there are a few articles in the literature suggesting that thiols do not form hydrogen bonds. Plant, Tarbell and Whiteman1) found that infrared spectra of a series of amino thiols gave no indication of hydrogen bonding. However, Gordy and Stanford2) reported distinct infrared evidence that mercaptans formed hydrogen bonds with strong nitrogen bases such as pyridine and picolines. The UV absorption of cysteine3) suggests hydrogen bonding of the S-H group with carbonyl or amino compounds. Evidence that sulphur atom can act as a base in the hydrogen bonding interaction is still less. Direct evidence of the sulphur atom acting as a base has been offered for ethylene-thio urea,4) thio amides,5) disulfides,6) and 2-thiopyridone.7) In order to further the development of a better understanding of the hydrogen bonding properties of sulphur atom acting as a base, the present investigation was undertaken with phenol-carbon disulphide systems.

Since the effect of hydrogen bonding on the electronic spectra of organic molecules was unambiguously detected and explained, the ultraviolet and visible spectroscopy has been applied by a number of authors to the study of hydrogen bond in solution. The effect of hydrogen bonding on the electronic spectra depends on the nature of the electronic transition in the molecule. The $\pi \rightarrow \pi^*$ bands of molecules with conjugated system such as phenols shift towards longer wavelength and the $n \rightarrow \pi^*$ bands in ketones, aldehydes, pyridazine, *etc.*, move towards shorter wavelength as the result of hydrogen bonding. Furthermore, it was shown by several authors8,9) that these phenomena are applicable to the determination of the free energy change for the equilibrium between various proton donors and acceptors. Such a study is useful not only to determine the mechanism of hydrogen bonding but also to find a relation between the nature of the electronic transition in the resonating molecules and their behaviour in the hydrogen bond formation.

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[*2] Present address: Department of Applied Chemistry, Indian Institute of Technology, Kharagpur, India.

1) D. Plant, D. S. Tarbell and C. Whiteman, *J. Amr. Chem. Soc.*, **77**, 1572 (1955).

2) W. Gordy and S. C. Stanford, *ibid.*, **62**, 497 (1940).

3) R. H. DeDeken *et al.*, *Biochem. et Biophysics Acta*, **19**, 45 (1956).

4) P. J. Wheatly, *Acta Cryst.*, **6**, 369 (1953).

5) M. St. C. Flett, *J. Chem. Soc.*, **1953**, 347.

6) R. Cecil, *Biochem. J.*, **49**, 183 (1951).

7) B. R. Penfold, *Acta Cryst.*, **6**, 707 (1953).

8) S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

9) A. B. Sannigrahi and A. K. Chandra, *J. Phys. Chem.*, **67**, 1106 (1963).

In all the previous experiments the physico-chemical basis underlying the method of calculating the equilibrium constants was the Benesi and Hildebrand equation(10) or its modification(11). These methods, however, have a common failing, namely, they cannot be applied to the cases where both the donor and acceptor have comparable absorption in the wavelength region of interest Chandra and Banerjee(12) have developed a simple method which treats the spectral data specifically in the region where both the components, donor and acceptor, and the complex have appreciable absorption and permit a direct evaluation of equilibrium constant with minimum computation. Since in the present investigation both carbon disulfide and phenols have their characteristic absorption bands in the almost same wavelength region, Chandra and Banerjee's method has been employed here to determine the stability constants of the hydrogen bonding equilibria.

Method of Calculation

The physico-chemical basis of Chandra and Banerjee's expression is discussed in details elsewhere.(12) Let the equilibrium be represented by

$$A + B \leftrightharpoons AB \quad K = \frac{C}{([A]-C)([B]-C)} \qquad (1)$$

where [A] and [B] represent the initial concentrations of the two components, and C, the equilibrium concentration of hydrogen bonded complex.

The optical density (O. D.) per cm of the path of a solution containing the molecular species of (1) is given by

$$\text{O. D.} = \varepsilon_c C + \varepsilon_1([A]-C) + \varepsilon_2([B]-C) \qquad (2)$$

where ε_c, ε_1 and ε_2 are the molar extinction coefficients of AB, A and B respectively.

Supposing $[B] = m[A]$

$$\text{O. D.} = (\varepsilon_c - \varepsilon_1 - \varepsilon_2)C + (\varepsilon_1 + m\varepsilon_2)[A] \qquad (3)$$

Let us write

$$D = \text{O. D.} - (\varepsilon_1 + m\varepsilon_2)[A] = \bar{\varepsilon}C \qquad (4)$$

where $\bar{\varepsilon} = \varepsilon_c - \varepsilon_1 - \varepsilon_2$

From Eqs. (1), (3) and (4) and neglecting C^2 one gets

$$\frac{m[A]}{D(1+m)} = \frac{1}{\bar{\varepsilon}} + \frac{1}{K\bar{\varepsilon}} \cdot \frac{1}{(1+m)[A]} \qquad (5)$$

The relation (5) shows that plot of $m[A]/D(1+m)$ against $1/(1+m)[A]$ should be linear if 1 : 1 complex formation occurs. From the intercept and slope of the line the equilibrium constant and molar extinction coefficient of the complex may be calculated. This method has been followed in the present investigation to obtain the equilibrium constants of the complexes of the phenols with carbon disulphide and to evaluate the molar extinction coefficients of the complexes.

Experimental

In the present study, phenol, *p*-cresol, α- and β-naphthols have been used as the proton donors. Phenols and *p*-cresol were purified by distillation under reduced pressure. E. Merck's α-naphthol and β-naphthol were recrystallised before use. The commercial carbon disulphide was purified first by shaking with dilute solution of $KMnO_4$, then with Hg and finally with mercurous sulphate. It was dried over anhydrous $CaCl_2$ and then fractionated from water bath at 55—65°C. The fraction boiling between 46—47°C was collected.

Solvent employed was B. D. H. *n*-heptane which was purified by chromatographic adsorption on Al_2O_3. The purified solvent showed cut off at 220 mμ. Spectral measurements were made in Beckman Model DU Spectrophotometer using 1 cm silica cells at 27°C. All the solutions were prepared gravimetrically.

Results and Discussions

The $\pi \rightarrow \pi^*$ band of phenol is known to undergo a red shift whenever the phenol interacts with

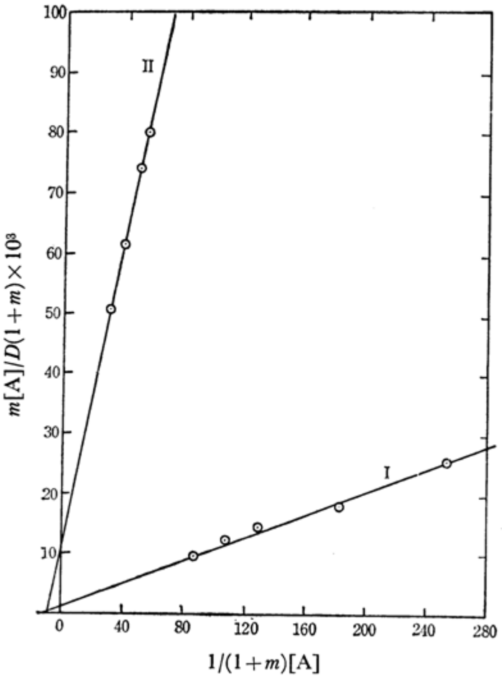

Fig. 1. The plot of Eq. (5) for 1 : 1 hydrogen bonded complexes of carbon disulphide with (I) β-naphthol (292 mμ) and (II) phenol (288 mμ). The concentration of carbon disulphide was varied and the spectral measurements were made at the wavelengths indicated with the inparenthesis.

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10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **70**, 2832 (1948).

11) a) L. T. Andrews, *Chem. Revs.*, **54**, 713 (1954). b) J. Landoller and H. McConnell, *J. Am. Chem. Soc.*, **74**, 1221 (1952).

12) A. K. Chandra and S. Banerijee, *J. Phys. Chem.*, **66**, 952 (1962).

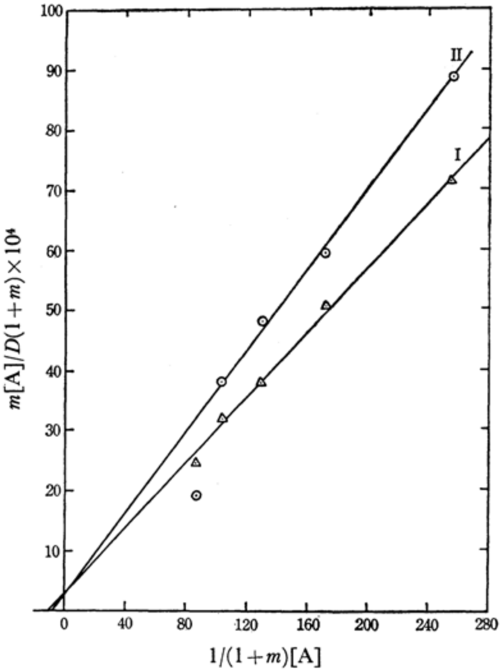

Fig. 2. The plot of Eq. (5) for 1 : 1 hydrogen bonded complexes of carbon disulphide with (I) α-naphthol (330 mμ) and (II) p-cresol (292 mμ). The concentration of carbondisulphde was varied and the spectral measurements were made at the wavelengths indicated within the parenthesis.

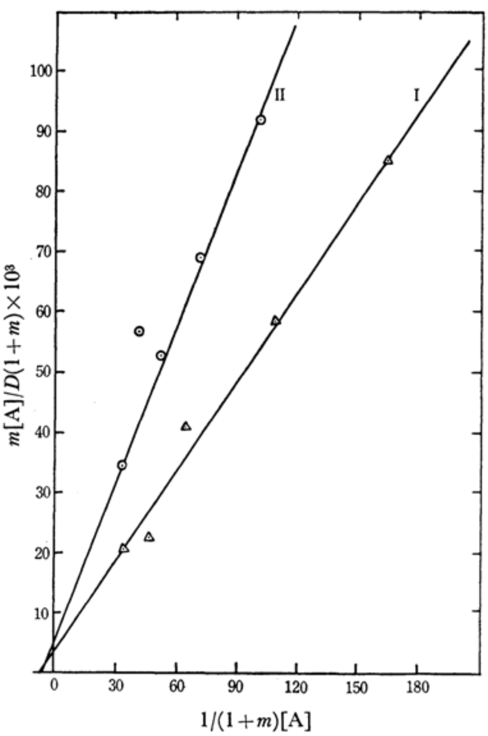

Fig. 3. The plot of Eq. (5) for 1 : 1 hydrogen bonded complexes of carbon disulphide with (I) phenol (296 mμ) and (II) p-cresol (296 mμ). The concentration of the phenols was varied and the spectral measurements were made at the wavelengths indicated within the parenthesis.

solvent through the formation of a hydrogen bond. The magnitude of the shift in the band is generally about 30—40 Å, as a result of this effect. It is expected, therefore, that if to a n-heptane solution of phenol increasing amount of carbon disulphide is added, the $\pi\rightarrow\pi^*$ band of the phenol should move to the red if phenol forms hydrogen bond with carbon disulphide. On the other hand, $n\rightarrow\pi^*$ band of a π-electron system having a hetero-atom is known to undergo a blue shift as a result of hydrogen bonding interaction with a proton donor. So if carbon disulphide forms hydrogen bond with phenol it is expected that its $n\rightarrow\pi^*$ band which appears at 318 mμ should move to the blue on increasing addition of phenol. But in view of the strong superposition of $\pi\rightarrow\pi^*$ band of phenol and $n\rightarrow\pi^*$ band of carbon disulphide, the position of the new peak due to the complex cannot be located in the absorption spectra of phenol-carbon disulphide mixture. Since it is established from the infrared measurement[13] that phenol forms hydrogen bond with carbon disulphide where it was shown that O–H stretching vibration of phenol broadened and moved to lower frequency on interaction with carbon disulphide, it is presumed that the new peak due to complex should appear at longer wavelength side of the phenol band and shorter wavelength side of the carbon disulphide band. With this presumption, the O. D. measurements were made on mixtures of phenol and carbon disulphide at several wavelengths in the range of 284—310 mμ and in some cases in the range of 326—330 mμ in two series of experiments. In one series of experiments, the O. D. measurements were made on mixtures having constant concentration of a proton donor (such as phenol) with varying concentration of proton acceptor. In the second series of experiments the mixtures having constant concentration of a proton acceptor and different concentrations of proton donor were used. The plots of $m[A]/D(1+m)$ against $1/(1+m)[A]$ were always found to be linear in both series of experiment, where $m[A]$ represents the variable concentration and [A], the constant concentration of the proton donor or acceptor as the case might be. The linear plots indicate the formation of 1 : 1 hydrogen bonded complex in both series of experiments. From the slope and intercept of these straight lines the equilibrium constants of the hydrogen bonded complexes were calculated using Eq. (5). No appreciable difference in K values was noted for a given system in

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[13] R. Mecke, *Discussions Faraday Soc.*, **9**, 161 (1950).

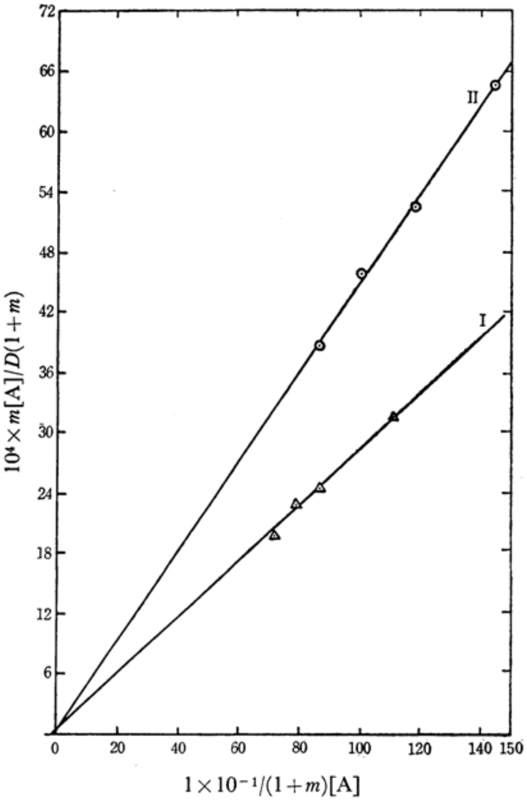

Fig. 4. The plot of Eq. (5) for 1 : 1 hydrogen bonded complexes of carbon disulphide with (I) α-naphthol (308 mμ) and (II) β-naphthol (310 mμ). The concentrations of the naphthols was varied and the spectral measurements were made at the wavelengths indicated within the parenthesis.

both series of experiments and also for measurements at different wavelengths. Figures 1—4 show the plots at the wavelengths indicated therein. In Table 1 are given the values of equilibrium constants of the complexes measured at several wavelengths in two sets of experiments and also the mean values of the equilibrium constants for the four different systems studied in this investigation. In Fig. 5 is shown the plot of pK_a of phenols against the logarithm of the mean value of the stability constants. This plot is also linear as expected.

The calculated absorption curves of the complexes shown in Figs. 6—9 are obtained using the optical density data of phenol - carbon disulphide mixtures of particular concentrations of phenols and carbon disulphide in the wavelength region from 270 mμ to 340 mμ, which covers the absorption regions of both phenols and carbon disulphide and knowing the equilibrium constant. Since the errors involved in determining the molar extinction coefficients of the complexes might be notoriously large, their extinction coefficients are, therefore, not reported. The spectral patterns remain generally unchanged on hydrogen bond formation.

The occurrence of many peaks within the calculated absorption curves of the complexes cannot

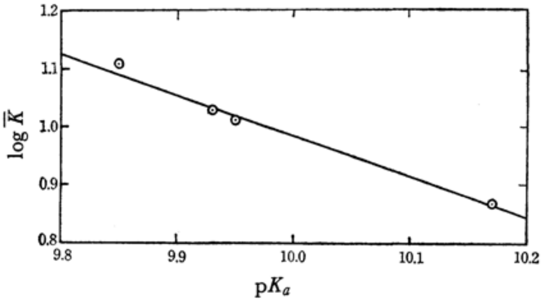

Fig. 5. Plot of log K vs. pK_a of the phenols.

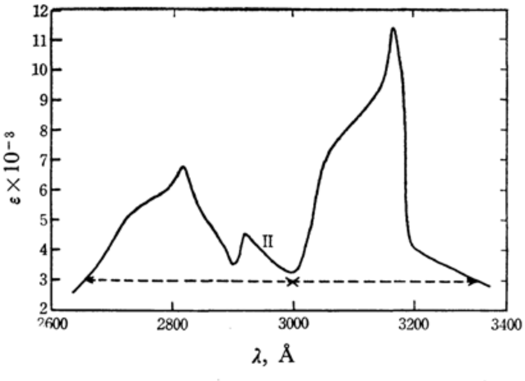

Fig. 6. The calculated absorption spectra of p-cresol - carbon disulphide complex.

TABLE 1. AVERAGE VALUES OF THE EQUILIBRIUM CONSTANTS OF THE HYDROGEN BONDED COMPLEXES AND pK_a VALUES OF THE PHENOLS

	Complexes of	Values of the equilibrium constants measured at several wavelengths indicated in the parenthesis in mμ in both sets of experiments	Mean values of K	log K	pK_a of phenols
1	p-Cresol+carbon disulphide	6.4 (296), 8.0 (300), 8.0 (297), 7.2 (284)	7.4	0.8696	10.17
2	Phenol+carbon disulphide	9.0 (288), 10.0 (296), 10.0 (292), 12.0 (296)	10.25	1.0107	9.95
3	β-Naphthol+carbon disulphide	10.0 (292), 11.0 (310), 12.0 (310), 10.0 (305)	10.75	1.0314	9.93
4	α-Naphthol+carbon disulphide	14.0 (308), 12.0 (330), 12.0 (326), 14.0 (310)	13.0	1.1139	9.85

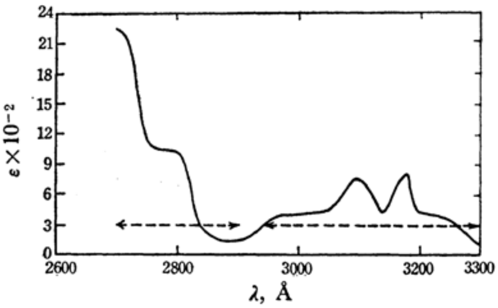

Fig. 7. The calculated absorption spectra of phenol - carbon disulphide complex.

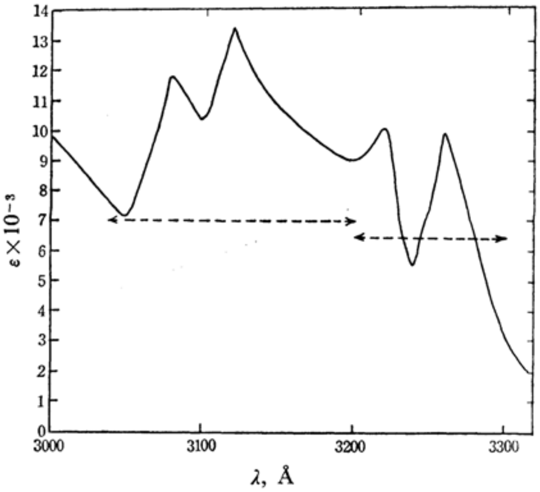

Fig. 8. The calculated absorption spectra of α-naphthol - carbon disulphide complex.

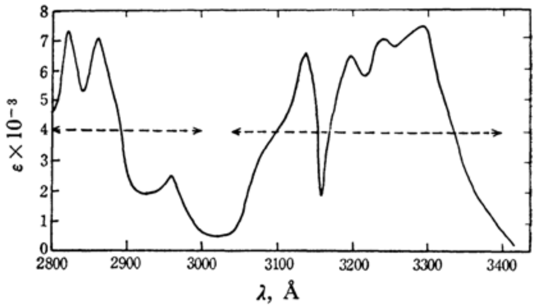

Fig. 9. The calculated absorption spectra of β-naphthol - carbon disulphide complex.

be accounted for at the moment. So the centers of the bands were calculated by the following formula

$$\bar{\lambda}=\frac{\sum_i \lambda_i \varepsilon_i}{\sum_i \varepsilon_i}$$

where the summation was carried out over the wavelength regions indicated by the arrow heads in the Figs. 6—9. Such a selection of the summation range was made because at the two ends of the arrow the absorption curves of the corresponding complex showed distinct minima. In Table 2 are reported the centres of the bands of the complexes along with the bands of the corresponding phenols. For both phenol and *p*-cresol complex, the $\pi\rightarrow\pi^*$ band of the phenols undergoes a red shift and the $n\rightarrow\pi^*$ band of carbon disulphide undergoes a blue shift as a result of hydrogen bonding. For α- and β-naphthols the complication arises because the $\pi\rightarrow\pi^*$ bands of phenols appear in

TABLE 2. ELECTRONIC ABSORPTION BANDS OF PHENOLS AND THEIR HYDROGEN BONDED COMPLEXES WITH CARBON DISULPHIDE

$n\rightarrow\pi^*$ band of carbon disulphide, Å	$\pi\rightarrow\pi^*$ bands of phenols		Centres of the bands of the complexes with carbon disulphide, Å	
	Phenols	λ_{max}, Å		
3180	*p*-Cresol	2800	2820	3132
	Phenol	2720, 2780	2754	3113
	β-Naphthol	2850, 3140, 3280	2970	3223
	α-Naphthol	3080, 3220	3122	3234

TABLE 3. EQUILIBRIUM CONSTANTS OF PHENOLS WITH SOME PROTON ACCEPTORS

Proton donors	Proton acceptors			
	Carbon disulphide (27°C)	Ether[a)] (25°C)	Dioxane[b)] (20°C)	Trimethyl amine[a)] (25°C)
p-Cresol	7.8	—	—	65
Phenol	10.3	10.8	16.4	86
β-Naphthol	10.8	14.5	18.3	230
α-Naphthol	13.0	15.7	20.9	110

a) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co. (1960).
b) H. Baba and S. Suzuki, *J. Chem. Phys.*, **35**, 1118 (1961).

the same region where the $n \rightarrow \pi^*$ band of carbon disulphide occurs. In the absorption curves, however, there are peaks at the longer wavelength side of the longest wavelength $\pi \rightarrow \pi^*$ band of α- and β-naphthols. In view of this the calculated shifts of the $\pi \rightarrow \pi^*$ bands of α- and β-naphthol due to hydrogen bonding have little significance. However, in spite of the limitations in the accuracy of the present graphical method, we may conclude that the calculated shift and the anomaly in the spectra of phenol and carbon disulphide mixtures is mainly due to the hydrogen bonding effect.

From the Table 1 it is seen that carbon disulphide forms weak hydrogen bonded complex with phenols and on the basis of equilibrium constant measurements it can be concluded that the proton donating power of the phenols has the order *p*-cresol < phenol < β-naphthol < α-naphthol which is exactly the relative order of their acidities. In the following table (Table 3) are reproduced the reported values of equilibrium constants of the hydrogen bonded complexes of the same series of phenols with other proton acceptors. They are obtained from the literature indicated in the table.

On the basis of these reported values of the stability constants it may be concluded that proton accepting power of the four different acceptors increases in the order carbon disulphide < ether < dioxane < trimethylamine. In other words the strengths of the H-bond increases in the order S···H-O < O···H-O < N···H-O. This is also supported by the results of infrared measurements13) on phenol dissolved in carbon disulphide and diethyl ether. Both the O–H stretching frequency shift, *i. e.*, $\Delta\nu_s$ and $\nu_{1/2}$ which is a measure of the bandwidth are reported to be (55, 160)cm^{-1} and (640, 700)cm^{-1} for carbon disulphide and ether respectively.

All these results support the electrostatic theory of hydrogen bond. The extent of electrostatic interaction depends on the dipole moment of the proton acceptor or the electron donor molecule. Since carbon disulphide has no net dipole moment while all the other proton acceptors of the Table 3 have, one might wonder whether the hydrogen bond involving carbon disulphide as a base is at all electrostatic. We have emphasised in our previous communication9) that it is the lone pair dipole moment and not the net dipole moment of the electron donor molecule, which is important in the electrostatic interaction involved in the hydrogen bond formation. The sulphur atom in carbon disulphide has two lone pair ortibals and since they are approximately in sp^2 hybridised state, the lone pair orbitals must have dipole moment which contributes to the electrostatic interaction.