results are obtained if the quinoline fraction is separated from the tars by distillation before the determination.

By-products of the 3-Ethyl-2-propylquinoline Preparation.—The reaction mixture of the Doebner–Miller synthesis, when distilled, gives, besides the water and unchanged reagents (all of which distill below 120° at 15 mm.), two rather well-defined fractions. The first, b. p. 120–200°, consists of N-*n*-butylaniline and 3-ethyl-2-propylquinoline; the second, b. p. over 200° at 15 mm., is made up of tarry materials which may contain tetra- and di-hydro-quinolines (whose homologs have been previously reported as being present in other Doebner–Miller syntheses) and complicated polymerization products. We have confirmed the presence of N-butylaniline (67% of the yield predicted on basis of ethylpropylquinoline formed) as a by-product by the formation of its hydrochloride, m. p. 112–114° (recorded, 114°),[15] and N-butyl-N-phenyl-N′-α-naphthylurea, m. p. 277°. The hydrochloride gave neutral equivalents of 181, 182 and 185, compared with a calculated value of 185. The naphthylurea, a new compound, was prepared by the method of French and Wirtel,[16] and it has the same m. p. as that formed from known N-butylaniline. A mixed melting point showed no depression.

Anal. Calcd. for the N-butyl-N-phenyl-N′-α-naphthylurea, $C_{21}H_{22}N_2O$: N, 8.80. Found: N, 9.03.

In attempting to form the methiodide of 3-ethyl-2-propylquinoline of melting point 172°, described by Kahn,[13] we were able to isolate a material of this melting point. This compound, however, was unstable and gave neutral equivalents on titration with alkali varying from 320 to 381 (theoretical for the hydriodide is 341), showing that it was not a quaternary salt. When we attempted to form the methiodide from highly purified quinoline (through the picrate as above described), the material formed had a m. p. 160–165° and was not titratable with alkali. This is probably the true quaternary methiodide.

Anal. Calcd. for 3-ethyl-2-propylquinoline methiodide, $C_{15}H_{20}NI$: I, 37.28. Calcd. for 3-ethyl-2-propylquinoline hydriodide, $C_{14}H_{18}NI$: I, 38.63. Found (by Fajans' method): I, 37.11.

That the compound described by Kahn was probably the quinoline hydriodide was shown by its formation on passing anhydrous hydrogen iodide through a low-boiling ligroin solution of the pure quinoline. The melting point of this hydriodide was 171–172° and the material was titratable with base. A mixed melting point with the material originally isolated from treatment with methyl iodide was 169–171°.

Summary

1. The condensation of butyraldehyde and aniline in acid and neutral media has been studied.

2. The structure of the dimer of butylidene aniline has been established as well as that of the compound formed from it by the loss of aniline.

3. 3-Ethyl-2-propylquinoline has been prepared in several ways. A mechanism has been suggested for the Doebner–Miller synthesis.

4. The following new compounds have been prepared: the anil of α-ethyl-β-propylacrolein, 1,3-diphenylamino-2-ethylhexane, its diacetyl derivative, α-ethyl-β-propylacrolein-2,4-dinitrophenylhydrazone, N-butyl-N-phenyl-N′-α-naphthylurea, and 3-ethyl-2-propylquinoline hydriodide and methiodide.

CHICAGO, ILLINOIS RECEIVED OCTOBER 16, 1939

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(15) Braun and Murjahn, *Ber.*, **59**, 1202 (1926).

(16) French and Wirtel, THIS JOURNAL, **48**, 1736 (1926).

[CONTRIBUTION FROM THE MENDENHALL LABORATORY OF PHYSICS, OHIO STATE UNIVERSITY]

Spectroscopic Evidence for Hydrogen Bonds: SH, NH and NH_2 Compounds

BY WALTER GORDY[1] AND SPENCER C. STANFORD[2]

Introduction

The hydrogen bond theory,[3] which asserts that under certain conditions a proton may form a bond, or bridge, between two electronegative atoms such as N or O, was proposed by Latimer and Rodebush[4] in 1920. Earlier isolated cases of this type of bonding had been recognized.[5] The wide occurrence of hydrogen bonds, however, has just begun to be realized, largely through measurements of infra-red absorption spectra. The importance of these bridges is evidenced by the fact that chelation, and association between like and unlike molecules, resulting from hydrogen bonds, in turn cause appreciable variations in boiling points, freezing points, viscosities, dielectric constants, heats of mixing and of vaporization, vapor pressures, etc., of many compounds in the liquid and solid states as well as in solution. These bonds also play an important role in the determination of protein structure.[6]

Infrared spectroscopy is particularly well suited

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(3) For a very able discussion of the nature of the hydrogen bond, see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, Chap. IX.

(4) W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(5) T. S. Moore and T. F. Winmill, *J. Chem. Soc.*, **101**, 1635 (1912); P. Pfeiffer, *Ann.*, **398**, 137 (1913).

(6) Mirsky and Pauling, *Proc. Nat. Acad. Sci.*, **22**, 439 (1936).

to the study of hydrogen bonds because it gives direct information about the particular groups of the molecule which participate in the formation of the bonds. For this reason it is generally recognized as superior to methods based on measurements of other physical properties. The usual approach in the spectroscopic method is to observe the effects of the bonding on the group which donates the proton. The bonding weakens the binding force of this group and hence shifts its vibrational band to lower frequencies. The strength of the bond can be estimated from the magnitude of the shift.[7] Also, for hydrogen bonds between unlike molecules it is possible in the same way to compare the intrinsic strengths of organic bases by the effects which these different bases, when used as solvents, will produce on the spectrum of the proton donor group of a suitable solute.[8] In undertaking the present investigation we sought to extend the hydrogen bond theory by discovering other molecules which would donate their proton in hydrogen bond formation. Compounds containing SH, NH or NH_2 were selected because of their importance, especially in biological phenomena, and because they have not been studied extensively by the infrared method.

Instrument.—Although a prism spectrometer was used as a resolving instrument, much better resolution was obtained than is possible with the usual prism instrument. The current was amplified by a Moll thermal relay. Large reflecting mirrors made possible effective use of a 60° rock salt prism, of 7 × 6 cm. face, through which the light was passed twice to increase the dispersion. It was found that with this prism better results could be obtained in the regions studied than with a 60°, 4 × 6 cm., fluorite prism, which was available. The design of the Wadsworth–Littrow type of instrument which was used has been described fully by Strong.[9]

Discussion

SH Compounds.[10]—Numerous instances of hydrogen bonding with the first period elements carbon, nitrogen, oxygen and fluorine have been verified by infrared absorption spectroscopy and other physical methods.[3,11] It was thought for a long time that hydrogen bonding between elements of the second period or between first and second period elements did not exist. For example, Sidgwick[12] has emphasized the improbability of hydrogen bonding with an atom in the second period of elements, saying that as we pass from OH to SH and from hydrogen fluoride to hydrogen chloride the electron acceptor power of the hydrogen practically vanishes. Recently, however, evidence for the association of hydrogen chloride and for the formation of complexes, through hydrogen bonding, between chlorine and an element of the first period has been obtained.[13]

It is known that hydrogen sulfide and the mercaptans are not associated. The molecular weights of some of the mercaptans in benzene solution have been shown to be normal, and in the lower mercaptans the boiling points are less than the corresponding alcohols, in spite of their higher molecular weight. In the present investigation it is shown that spectroscopic methods confirm these conclusions. With regard to the formation of hydrogen bonds between sulfur and elements of the first period, Huggins[11a] states that he knows of no examples of hydrogen bridges joining a sulfur atom with another electronegative atom. He suggests, nevertheless, the possibility of such bridges, saying that they would undoubtedly be very weak. Lassettre[11b] says that molecular weight data show that SH groups do not form hydrogen bonds to any appreciable extent.

The alcohols, with low acidity constants, act as proton donors in complex formation with amines and oxygenated solvents.[14] Although there is a dearth of information on the acidity of the mercaptans, it is usually assumed that they are much more acid than the alcohols.[15] Lucas[16] gives $K_a = 3 \times 10^{-11}$ for ethyl mercaptan as compared with $K_a = 7.3 \times 10^{-20}$ for ethyl alcohol. It

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[7] J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **A162**, 419 (1937); R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

[8] (a) W. Gordy and Spencer C. Stanford, *J. Chem. Phys.*, in press; (b) W. Gordy, *ibid.*, **7**, 93 (1939).

[9] J. Strong, *Rev. Sci. Inst.*, **2**, 585 (1931).

[10] The part of this paper concerned with the mercaptans was given before the American Chemical Society at the Boston Meeting, September, 1939.

[11] (a) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936); (b) E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937); (c) R. Freymann, *J. Phys. Rad.*, **9**, 517 (1938); *ibid.*, **10**, 1 (1939); (d) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337, 2666, 2714 (1938); (e) A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2528 (1938); (f) W. Gordy, *J. Chem. Phys.*, **7**, 163 (1939); THIS JOURNAL, **60**, 605 (1938).

[12] N. V. Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933.

[13] (a) W. Gordy and P. C. Martin, *Phys. Rev.*, **52**, 1075 (1937); *J. Chem. Phys.*, **7**, 99 (1939); (b) B. Vodar, R. Freymann and Y. Ta, *J. Phys. Rad.*, **9**, 282 (1938).

[14] W. Gordy, *J. Chem. Phys.*, **7** 93 (1939).

[15] W. M. Malisoff, E. M. Marks and F. G. Hess, *Chem. Rev.*, **7**, 493 (1930).

[16] H. J. Lucas, "Organic Chemistry," American Book Company, 1935, p. 267.

seemed possible, therefore, that the mercaptans with their larger acidity constants might donate their proton to form complexes such as those formed with the alcohols.

Williams[17] has shown recently that the fundamental vibrational band of the SH group for benzyl, *n*-butyl and *n*-propyl mercaptans lies in the region 3.8–3.9 μ. For comparison we have repeated his results on benzyl and *n*-butyl mercaptans. Curves for these compounds, for thiophenol and for thioacetic acid are given in Fig. 1. The SH band is much more intense for the latter two compounds than for the former.

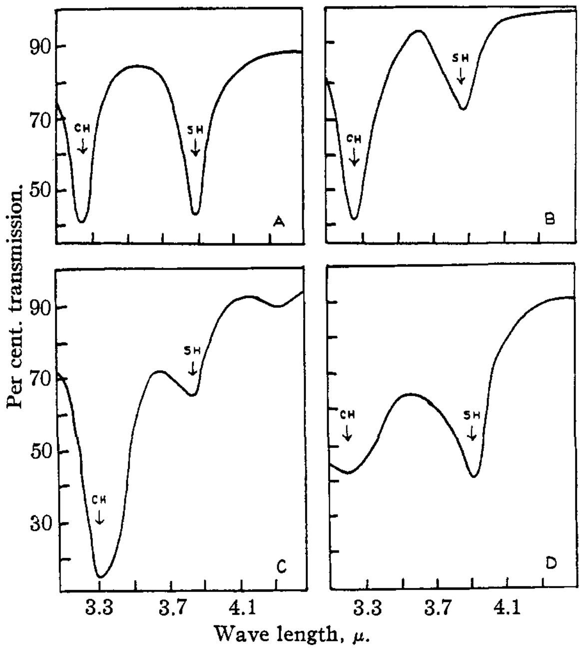

Fig. 1.—Transmission of: A, thiophenol, t = 0.005 cm.; B, benzyl mercaptan, t = 0.005 cm.; C, *n*-butyl mercaptan, t = 0.005 cm.; D, thioacetic acid, t = 0.002 cm.

A comparison of the intensities of the SH bonds of the compounds in Fig. 1 together with a comparison of their acidities leads to the conclusion that if any of these compounds are associated thiophenol would be. To ascertain whether polymerization occurs we measured the absorption of thiophenol in dilute solution in benzene. Figure 2 shows that the SH band does not shift to the shorter wave lengths upon dilution in an inert solvent as does the OH alcohol band,[18] thus confirming the evidence of molecular weights and other physical properties that the mercaptans are not associated in the liquid state.

To test for complex formation we studied, in the region of the SH band, mixtures of some mercaptans with several liquids which previously had been found to form complexes with heavy methyl alcohol through interaction with the OD group.[8b] Transmission curves for the different mixtures were observed and these were compared with theoretical transmission curves computed from Beer's law using the absorption coefficients obtained from the transmission curves of the pure liquids. The results for the thiophenol mixtures are shown in Fig. 3. The broken curves represent the transmission which would be expected of the mixtures if no interaction whatever occurred between the components; the solid

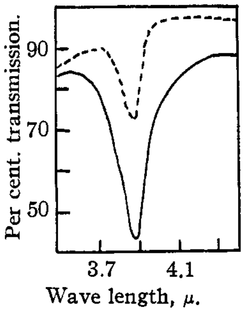

Fig. 2.—Broken line, 0.1 *M* thiophenol in benzene *versus* pure benzene, t = 0.361 cm.; solid line, pure thiophenol, t = 0.005 cm.

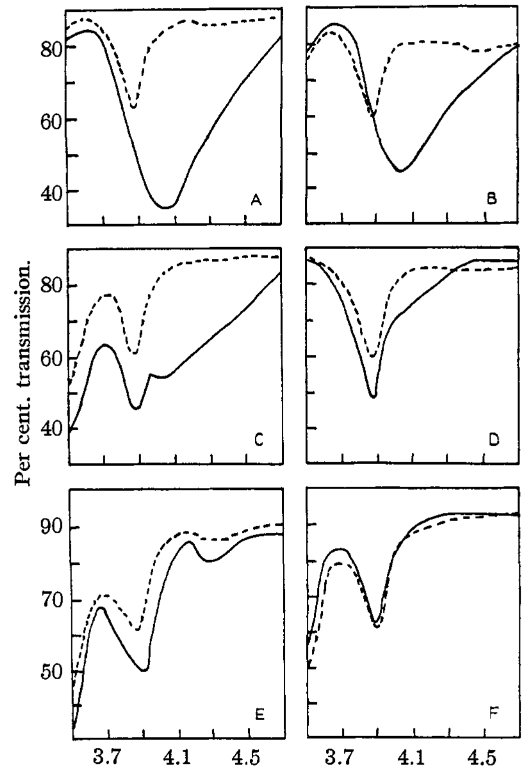

Fig. 3.—Theoretical (broken lines) and observed (solid lines) transmission of mixtures (1:1 vol., t = 0.005 cm.) of thiophenol with: A, pyridine; B, α-picoline; C, dibenzylamine; D, aniline; E, isopropyl ether; F, ethyl-*o*-toluidine.

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(17) D. Williams, *Phys. Rev.*, **54**, 504 (1938).

(18) J. Errera and P. Mollet, *Nature*, **138**, 882 (1936); *Compt. rend.*, **204**, 259 (1937).

curves represent the transmission which was actually observed.

The most pronounced variations observed were for thiophenol with pyridine and with α-picoline. For these mixtures the SH band is shifted to the longer wave lengths by about 0.18 μ or 114 wave numbers, and its intensity is increased several fold. We believe that these results give proof of the formation of SH → N bonds between the thiophenol and the amines.

The results indicate that thiophenol also forms a complex with dibenzylamine, but that the tendency to do so is slightly less than with pyridine or α-picoline. The position of the associational band is 4.04 μ for thiophenol–dibenzylamine as compared with 4.06 μ for thiophenol–pyridine. The rather strong band at 3.88 μ, the position of the SH band of pure thiophenol, indicates that a large percentage of the thiophenol is not linked to the dibenzylamine.

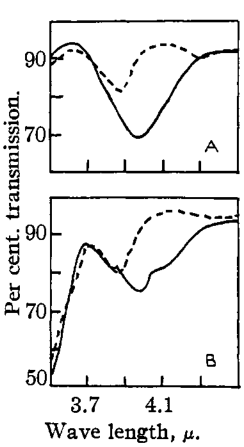

Fig. 4.—Theoretical (broken lines) and observed (solid lines) transmission of mixtures (1:1 vol., t = 0.005 cm.) of benzyl mercaptan with: A, pyridine; B, benzylamine.

Thiophenol tends to form a complex with aniline even less than it does with dibenzylamine. There is no minimum beyond 3.88 μ in the thiophenol–aniline curve although the departure of the experimental from the theoretical curve on the long wave length side of the band probably indicates some interaction. It may be that aniline (K_b = 4.6 × 10^{-10}) is too weakly basic to attract the proton from thiophenol sufficiently to form a hydrogen bridge. The existence of weak hydrogen bonds between the aniline molecules in the liquid state, for which there is evidence,[19] may also be a contributing factor in the non-formation of a complex. Hydrogen bonding between the aniline molecules could of course prevent the aniline nitrogen from accepting a proton from the mercaptan SH. In this connection Zellhoefer, Copley and Marvel[11d] have shown that aniline is a poor solvent for certain haloforms, and they attribute this to the association of the aniline.

Only one oxygenated solvent, isopropyl ether, was investigated for the formation of a complex with thiophenol. In the comparison of the proton-attracting power of liquids previously made,[8b] the ethers were found to form stronger hydrogen bonds with alcohols than did any of the other oxygenated solvents studied. Therefore, it was concluded that if isopropyl ether did not form bonds with the mercaptans, none of the oxygenated solvents would form them. As may be seen from a comparison of the experimental and theoretical curves for thiophenol–isopropyl ether, there is very little interaction. Thus it was not considered worth while to study mixtures of the mercaptans with other oxygenated solvents as there would probably be little complex formation between them.

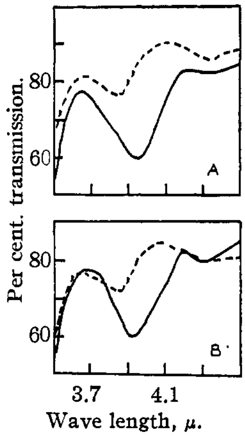

Fig. 5.—Theoretical (broken lines) and observed (solid lines) transmission of mixtures (1:1 vol., t = 0.005 cm.) of n-butyl mercaptan with: A, pyridine; B, α-picoline.

The experimental curve for the ethyl-o-toluidine–thiophenol mixture is almost identical with the theoretical curve computed from Beer's law. This result could be anticipated, for even if the nitrogen of the ethyl-o-toluidine strongly attracted the proton of the SH, steric hindrance would probably prevent association with the thiophenol.

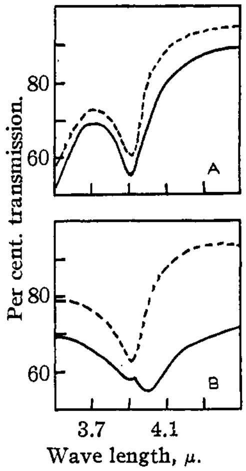

Fig. 6.—Theoretical (broken lines) and observed (solid lines) transmission of mixtures (1:1 vol., t = 0.002 cm.) of thioacetic acid with: A, isopropyl ether; B, pyridine.

Piperidine (K_b = 1.6 × 10^{-3}) formed a white crystalline solid immediately upon being mixed with thiophenol. Similar results were obtained with cyclohexylamine and with triamylamine. Apparently thiophenol forms hydrogen bonds with substances of a rather narrow range of basicities. For substances with basicity constants much lower than that of pyridine, no appreciable interaction occurs. For substances with basicities much higher than that of pyridine, the thiophenol

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(19) W. Gordy, *J. Chem. Phys.*, **7**, 167 (1939).

appears to be completely ionized by the base to form a salt.

Because the aliphatic mercaptans and benzyl mercaptan probably have lower acidity constants than thiophenol, they would be expected to show less tendency to share their proton in hydrogen bond formation. This was found to be true for the cases studied. Figure 4 gives the results obtained for benzyl mercaptan with pyridine and with benzylamine. Both of these liquids form hydrogen bonds with the benzyl mercaptan. The shift in the SH band of benzylamine caused by the pyridine is less than that caused by the pyridine on the SH band of thiophenol. Figure 5 shows the evidence secured for the interaction of *n*-butyl mercaptan with pyridine and α-picoline. A curve was obtained for piperidine which gave a minimum at 4.04 μ, but because of the intense CH absorption of piperidine and the weakness of the mercaptan band, the position of the associational band is probably not very accurate. Evidence was also found for weak hydrogen bonds between pyridine and thioacetic acid, Fig. 6. Isopropyl ether produced no shift in the thioacetic acid band.

TABLE I

THIOPHENOL MIXTURES

Solvent	Position of SH band, μ	Shift, μ	K_b
Pure thiophenol	3.88		
Aniline	3.88	None	4.6×10^{-10}
Pyridine	4.06	0.18	1.2×10^{-9}
α-Picoline	4.06	.16	4.0×10^{-8}
Dibenzylamine[a]	4.04	.16	
Piperidine	White cryst. solid		1.6×10^{-3}
Cyclohexylamine	White cryst. solid		
Triamylamine	White cryst. solid		
Ethyl-*o*-toluidine	3.88	None	
Isopropyl ether	3.91	0.03	
Benzyl Mercaptan Mixtures			
Pure benzyl mercaptan	3.87		
Benzylamine[a]	3.97	0.10	2.4×10^{-5}
Pyridine	3.96	.09	1.2×10^{-9}
Cyclohexylamine	White cryst. solid		
n-Butyl Mercaptan Mixtures			
Pure *n*-butyl mercaptan	3.86		
Pyridine	3.95	0.09	1.2×10^{-9}
Piperidine	4.00	.14	1.6×10^{-3}
α-Picoline	3.94	.08	4.0×10^{-8}
Cyclohexylamine	White cryst. solid		
Thioacetic Acid Mixtures			
Pure thioacetic acid	3.91		
Isopropyl ether	3.91	None	
Pyridine[a]	3.99	0.08	1.2×10^{-9}

[a] In each of these cases a weak band due to unmodified SH appeared.

The results for all the SH compounds are summarized in Table I.

NH and NH_2 Compounds.—Hydrogen bridges formed through an amine hydrogen probably play a significant role in the determination of protein structure.[6,11a,20] Attempts have been made to study directly hydrogen bonds in protein molecules.[21] Nevertheless the complexity of the protein molecules with their overlapping OH and NH_2 absorption makes the method difficult and the interpretation of the data somewhat uncertain. Thus it seems well to obtain all the data possible on the simpler NH and NH_2 compounds. This should be valuable in predicting behavior in the more complex cases.

Buswell, Rodebush and Roy[22] have made a significant contribution in their work on the acid amides. Although they succeeded in showing that association is present they could not tell whether it was due to NH → N or NH → O bonds, as both are possible. Even though there is some evidence for the very weak association of liquid ammonia,[3] physical data indicate that the aliphatic amines are not generally associated.[23] That the lack of association is not due to the weaker proton acceptor power of the amine nitrogen is evidenced by the marked perturbation produced by the amine nitrogen on the OD band of heavy alcohol[8] and is also evidenced by the basicity constants of these compounds.

Certain aromatic amines, nevertheless, are sufficiently acidic to share their proton to form hydrogen bridges. One of us has already shown that aniline is associated through NH → N bonds and that it will form complexes through NH → O bonds to certain oxygenated solvents.[19] The bonds are very weak, the shifts obtained being about one-fourth that found for methyl alcohol. Although Buswell, Rodebush and Roy[24] failed to find spectroscopic evidence for the association of aniline, their failure to observe the small shift may have been due to the low resolving power of their instrument, as other physical data[11d] agree

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(20) L. Pauling and C. Niemann, THIS JOURNAL, **61** 1860 (1939).

(21) J. W. Ellis and J. Bath, *J. Chem. Phys.*, **6**, 723 (1938).

(22) A. M. Buswell, W. H. Rodebush and M. F. Roy, THIS JOURNAL, **60**, 2444 (1938).

(23) W. D. Kumler, *ibid.*, **60**, 2239 (1938).

(24) (a) A. M. Buswell, W. H. Rodebush and M. F. Roy, THIS JOURNAL, **60**, 2239 (1938). (b) As this paper goes to press A. M. Buswell, J. R. Downing and W. H. Rodebush (THIS JOURNAL **61**, 3252 (1939)) publish two curves for aniline in CCl_4: one 0.64 *M* and the other 0.01 *M*, showing the NH_2 absorption at the same position in both of these solutions. They offer these curves as evidence that aniline does not associate in the liquid state. That they did not detect the weak association of aniline was obviously due to their failure to study a sufficiently concentrated solution or the pure liquid.

with the interpretation that it is weakly associated. The work which has just appeared by Yeou Ta[25] on the third harmonic of the xylidines shows that they are associated except in the cases where steric hindrance prevents.

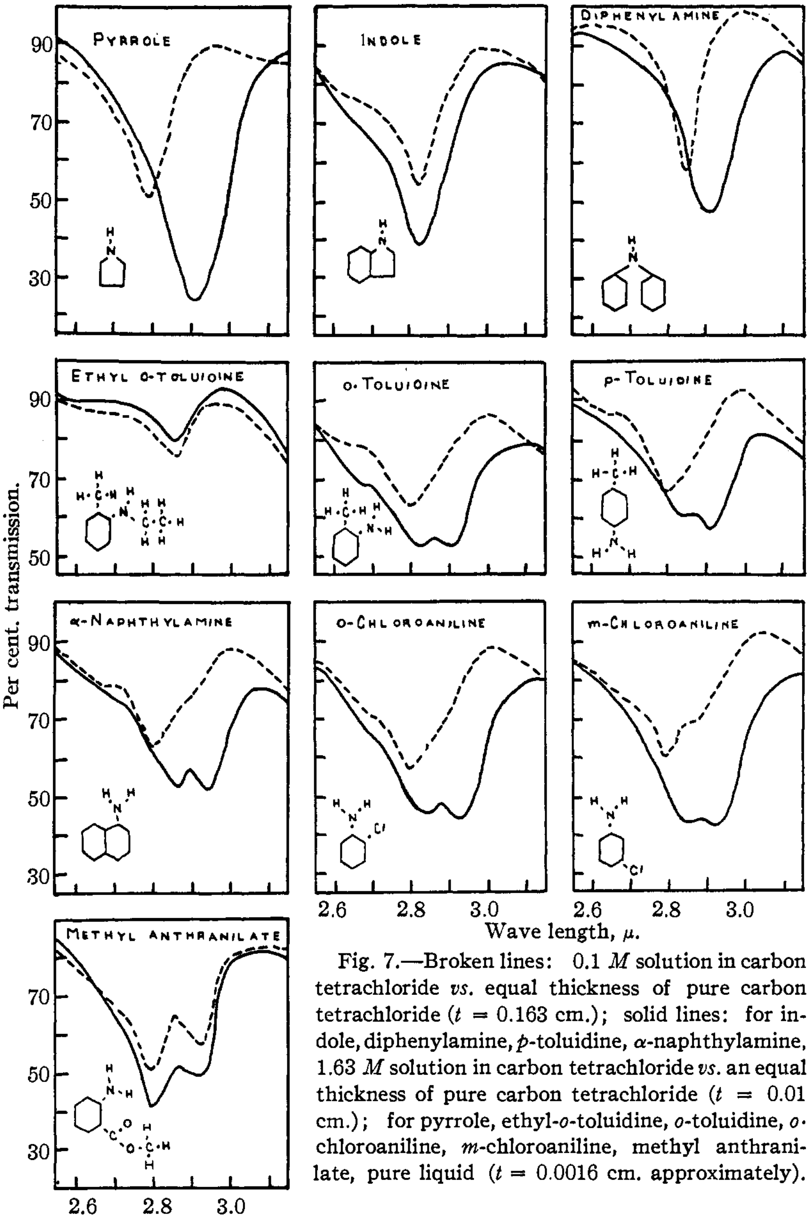

Fig. 7.—Broken lines: 0.1 *M* solution in carbon tetrachloride *vs.* equal thickness of pure carbon tetrachloride (t = 0.163 cm.); solid lines: for indole, diphenylamine, *p*-toluidine, α-naphthylamine, 1.63 *M* solution in carbon tetrachloride *vs.* an equal thickness of pure carbon tetrachloride (t = 0.01 cm.); for pyrrole, ethyl-*o*-toluidine, *o*-toluidine, *o*-chloroaniline, *m*-chloroaniline, methyl anthranilate, pure liquid (t = 0.0016 cm. approximately).

Pyrrole is more acidic than the aliphatic amines, and there are reasons to believe that it is associated.[26] Freymann[27] has shown that the third harmonic shifts to the longer wave lengths and is broadened appreciably as the pyrrole is changed from the vapor to the liquid state.

Wulf and Liddel[28] studied a number of amines by the infrared method. Their measurements were made in the region of the second harmonic of the NH band. As they made observations of only very dilute solutions in carbon tetrachloride, they could not study intermolecular association. They found that whenever a C=O group is adjacent to the NH_2 group, as in benzamide or methyl anthranilate, the NH band is appreciably perturbed. Hendricks, Wulf, Hilbert and Liddel[29] made similar studies of numerous compounds in which chelation was found to occur through OH → N bridges.

The present investigation included a number of amines having lower basicity constants than that of aniline, previously found to be weakly associated through hydrogen bonds. We obtained the absorption spectrum characteristic of the NH or NH_2 group of the unassociated amine in dilute solution of carbon tetrachloride and compared this with the absorption of the same group in the pure liquid or in concentrated solution when the compound was a solid. We also ran each of these compounds in an oxygenated solvent, *n*-butyl ether, in order to detect complex formation through NH → O bonds with the ether. In each case the cell thickness and concentration were arranged so that the different curves for the same substance represent approximately the same number of absorbers. Thus it is possible to observe the effects of association upon the intensity of the band as well as upon its position.

Figure 7 shows the study of the association of the pure substance. The dotted lines represent

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(25) Y. Ta, *Compt. rend.*, **208**, 1993 (1939).

(26) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936).

(27) M. Freymann, *Compt. rend.*, **205**, 852 (1937).

(28) O. R. Wulf and U. Liddel, THIS JOURNAL, **57**, 1464 (1935).

(29) S. B. Hendricks, O. R. Wulf, G. E. Hilbert and U. Liddel, *ibid.*, **58**, 1991 (1936).

the absorption of the dilute solution, 0.1 molar, and the solid lines represent that of the pure liquid or concentrated solution. The solution curves represent the ratio of the transmission of the solution to that of an equal thickness of the pure solvent. For the pure liquid the curves represent the ratio of the transmission of the cell containing the liquid to that of the empty cell. Because, for the reason discussed above, the associational bonds here are likely weaker than those for alcohol, we think that we are safe in assuming that the band which appears in the 0.1 molar solution is that of the monomeric form. The departure of the curve for the concentrated solution from that for the dilute solution may therefore be taken as a measure of the interaction which occurs.

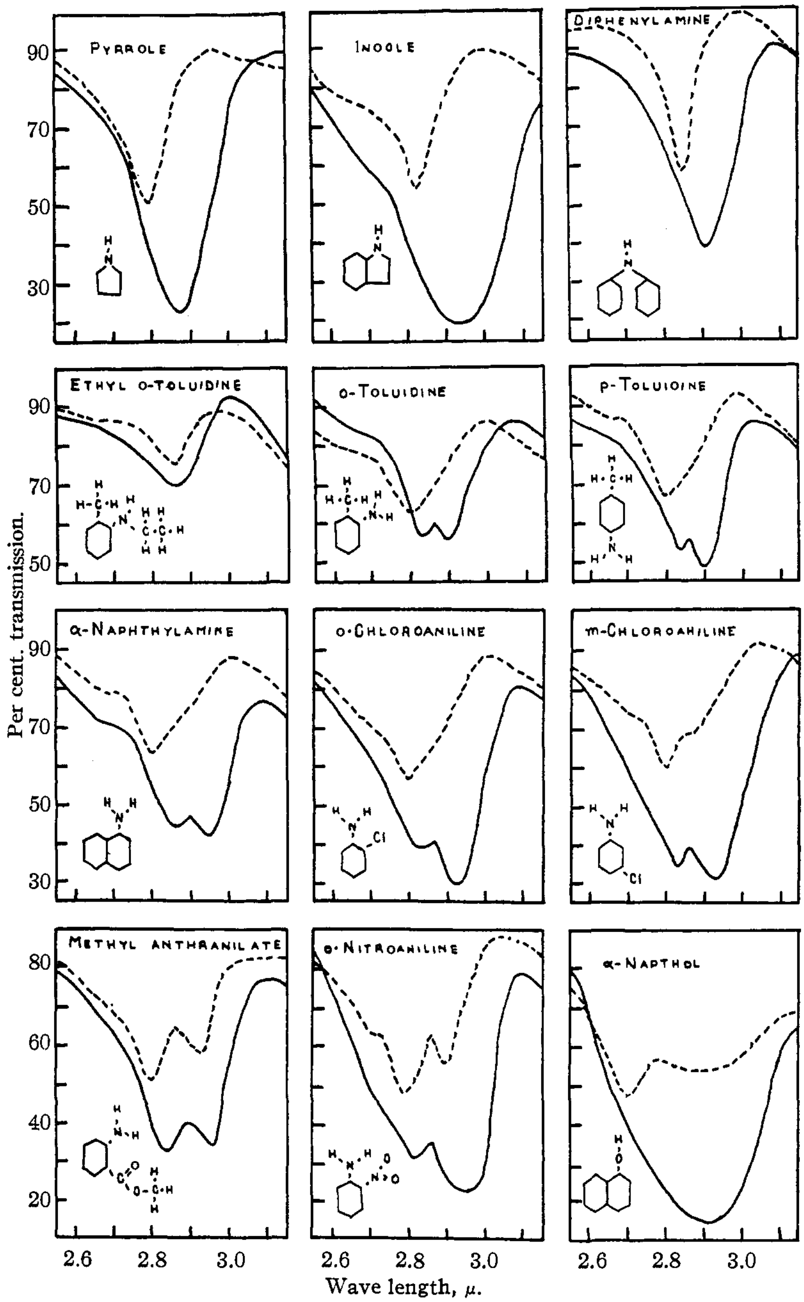

Fig. 8.—Broken lines: 0.1 *M* solution in carbon tetrachloride *vs.* an equal thickness of pure carbon tetrachloride (t = 0.16 cm.); solid lines: 0.1 *M* solution in *n*-butyl ether *vs.* an equal thickness of *n*-butyl ether (t = 0.163 cm.).

For pyrrole, diphenylamine, *o*- and *p*-toluidine, α-naphthylamine, *o*- and *m*-chloroaniline, the shifts to the longer wave lengths and the increase of intensity in the band are evidence that hydrogen bonding occurs in the pure liquid or the concentrated solution. It is interesting to note that for indole, ethyl-*o*-toluidine and methyl anthranilate no shift nor marked intensity change occurs, an indication that these substances do not polymerize. From a consideration of the structural formula for ethyl-*o*-toluidine, which is given in the figure, it is rather obvious that steric hindrance may prevent polymerization of this compound. Intermolecular hydrogen bonds between the methyl anthranilate molecules are no doubt prevented by the formation of intramolecular bonds to the C=O group. That intramolecular bonds exist here is clear from a comparison of the curve for the dilute solution with those for the other NH_2 compounds given in the figure. This chelation is also evident from the experiments of Wulf and Liddel.[28] In view of the association of the similar compound, pyrrole, the failure of indole to polymerize is not so obvious. That it is not due to the fact that indole holds its proton too firmly to share it is shown by its donating it to form a complex with *n*-butyl ether. We are inclined toward the interpretation that steric hin-

TABLE II

Substance	Minima in transmission curves, μ: 0.1 mol. sol. in CCl_4	1.63 mol. sol. in CCl_4	Pure liquid	0.1 mol. sol. in *n*-butyl ether	K_b
Pyrrole	2.79		2.90	2.87	
Indole	2.82	2.83		2.93	
Diphenylamine	2.85	1.91		1.91	
Ethyl-*o*-toluidine	2.86		2.86	2.86	
o-Toluidine	2.80		2.83 2.91	2.83 2.90	3.5×10^{-10}
p-Toluidine	2.80	2.84 2.91		2.83 2.90	2.1×10^{-10}
α-Naphthylamine	2.80	2.86 2.94		2.86 2.94	1.0×10^{-13}
o-Chloroaniline	2.80		2.84 2.93	2.83 2.93	9.2×10^{-12}
m-Chloroaniline	2.80		2.84 2.93	2.83 2.93	3.4×10^{-11}
Methyl anthranilate	2.80 2.93		2.80 2.93	2.83 2.96	
o-Nitroaniline	2.79 2.89			2.82 2.95	1.5×10^{-14}
α-Naphthol	2.70 2.91			2.91	1.0×10^{-8}

drance prevents this polymerization. On the other hand, it may seem a little strange, though not impossible, that steric hindrance would prevent association between indole molecules and yet not prevent association between indole and ether.

The bands for the NH compounds are rather symmetrical and sharp. For the NH_2 compounds the association splits the band into a doublet with one component only slightly shifted from the position of maximum absorption of the monomeric band. This splitting may arise from the possibility that only one of the protons of the NH_2 group is involved in hydrogen bond formation. Even for the monomeric form of these compounds the bands are broader and more complex than those for the NH compounds. Wulf and Liddel[28] pointed out that in the region of the second harmonic the NH_2 absorption is complex as compared with that of NH and OH. Our curves, however, do not resemble closely those of these researchers. It is not to be expected that bands in the fundamental region should be similar to those of the second harmonic, as no simple relation exists between them.

Figure 8 shows a study of complex formation between *n*-butyl ether and the above-mentioned compounds. In addition, one other NH_2 compound, *o*-nitroaniline, is included, also an OH compound, α-naphthol. The curves for 0.1 molar solution in carbon tetrachloride are repeated here for comparison. All the curves given in this figure are for 0.1 molar solutions of the same thickness, 0.163 cm. Therefore any appreciable departure of the curves for the *n*-butyl ether solutions from those of the same substances in carbon tetrachloride is evidence for the interaction of the solute with *n*-butyl ether.

The same substances which were found to be polymerized through hydrogen bonds were also found to form complexes with the *n*-butyl ether. Yet indole, which, as was mentioned above, apparently does not polymerize, interacts strongly with the ether. The results indicate that ethyl-*o*-toluidine does not form a complex with the *n*-butyl ether. The curve for the methyl anthranilate in the *n*-butyl ether solution is somewhat more intense than the curve for the carbon tetrachloride solution of the same concentration, but the minima are only slightly shifted from the position of those for the carbon tetrachloride solution. Since the intermolecular bonds with the ether, if they are formed, would probably be of the same order of strength as the intramolecular bonds, which are already formed and which would probably be broken if a complex is formed, it is not possible to predict whether there is much interaction between the *n*-butyl ether and the methyl anthranilate. For *o*-nitroaniline the departure of the curve for the *n*-butyl ether solution from that for the solution in carbon tetrachloride is much more pronounced, an indication that the intramolecular hydrogen bonds to the NO_2 group do not prevent interaction with the ether. From previous measurements it is known that an ether oxygen attracts the proton of an hydroxyl group more strongly than does an oxygen of the nitro group of nitrobenzene or nitrotoluene.

The curves which are included for α-naphthol make possible a comparison of the strength of the bonds formed through an NH_2 group with those through an OH group. It is obvious that the effects of *n*-butyl ether on the OH band of the α-naphthol are much more pronounced than the effects of this solvent upon the absorption of the NH_2 group of the α-naphthylamine. The curve for the 0.1 molar solution of α-naphthol in carbon tetrachloride shows that the polymerization of the α-naphthol is not completely broken down at this concentration, as there is still absorption in the region of 2.9 μ. The band appearing at 2.7 μ is the monomolecular band.

The positions of minima in the transmission curves for the pure liquids and different solutions are given in Table II.

In other reports[8] there is a comparison of the proton-attracting power of many different solvents, including *n*-butyl ether. By use of the data given there with the shifts in the NH or NH_2 bands caused by the *n*-butyl ether, it is possible to predict the interaction of these other solvents with the amines studied here.

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Summary

The association of the mercaptans with certain electron donor solvents has been investigated by means of infrared spectroscopy. The study included 1:1 volume mixtures of thiophenol with isopropyl ether, ethyl-*o*-toluidine, aniline, pyridine, α-picoline and dibenzylamine. For the ethyl-*o*-toluidine mixture the SH band of the thiophenol was virtually unaffected. For the mixtures with isopropyl ether, and with aniline, only a slight perturbation of the band occurred. For the mixtures with pyridine, α-picoline and dibenzylamine there was a shift of approximately 0.18 μ to the longer wave lengths, together with a broadening and a marked increase in intensity. These effects, we believe, indicate hydrogen bonding between the latter solvents and the thiophenol, with the SH group donating the proton. Similar but less pronounced effects were observed for *n*-butyl mercaptan, benzyl mercaptan and thioacetic acid with some of these solvents. A 0.1 *M* solution of thiophenol in benzene was studied, and the SH band was found to appear at the same position for the solution as for the pure liquid. This failure of the SH band to shift to shorter wave lengths upon dilution in an inert solvent is evidence that thiophenol is not polymerized in the liquid state.

The study included a number of amines having basicity constants about the same as or lower than that of aniline. All were found to be associated through hydrogen bonds except those for which steric hindrance would be expected to prevent the association. The absorption spectrum of the NH or NH_2 group of the unassociated amine in dilute solution in carbon tetrachloride was obtained and compared with the absorption of the same group of the pure liquid or of a concentrated solution when the compound was a solid. Each of the compounds was studied in an oxygenated solvent, *n*-butyl ether, in order to detect complex formation through NH $\rightarrow$ O bonds with the ether. The following compounds were found to be polymerized in the pure state, also to form complexes with the ether: pyrrole, diphenylamine, *o*- and *p*-toluidine, α-naphthylamine, *o*- and *m*-chloroaniline. Although the results indicate that indole does not polymerize, it appears to form a complex with *n*-butyl ether. Ethyl-*o*-toluidine apparently neither polymerizes nor forms complexes. Its lack of association can be ascribed to steric hindrance. Evidence was found for chelation in methyl anthranilate and *o*-nitroaniline. This chelation likely prevents appreciable polymerization or complex formation with these compounds. α-Naphthol, the one OH compound included, was found to be more strongly associated than the NH or NH_2 compounds of similar structure.

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