Studies on the Infrared Spectra of Ephedrine and Related Compounds. II. Infrared Spectra of Diastereoisomeric Ephedrines in 3 Micron Region

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In the preceding paper[1] the present author showed that the infrared spectra of dilute carbon tetrachloride solutions of ephedrines and related compounds in 3 μ region were useful for the discrimination between diastereoisomers. However, there remain some problems unsolved. For example, the questions why there appear always two bands, sharp and broad, and which of OH and NH groups participates in hydrogen bond formation should be answered. Moreover, the reasons why the frequency difference ($\Delta\nu$) between the sharp band and the broad one (150–238 cm.$^{-1}$) is much larger than that found for 2, 3-butanediol[2] (meso-form, 39 cm.$^{-1}$, *d*-form, 45 cm.$^{-1}$) and why $\Delta\nu$'s of pseudo compounds are always larger than those of normal ones also need explanation. In order to obtain information about these problems, the present experiments have been carried out on concentration dependence of ephedrines in carbon tetrachloride solution, solvent effect and the interaction with triethylamine. In connection with these, spectra of ethanolamine and 3-amino-2-butanol and the interaction between benzyl alcohol and triethylamine have been observed.

Experimental

Infrared Measurement.—The spectrophotometer used and its operating conditions were the same as described previously[1]. The spectra were taken with LiF prism at a room temperature adjusted at 25°C±2°. The accuracy of the measurement of wave numbers was ±2 cm^{-1}. Absorption cells of 0.056 cm. (NaCl windows), 0.3, 2.0 cm. (CaF_2 windows), 5 and 10 cm. (silica windows) in length were used. Since the silica cell absorbs 2.75 μ ray by 10–20% in transmission, it is unsuitable for the quantitative measurement of the free OH absorption at 2.76 μ.

Materials and Solvents.—Ephedrine and Ψ-ephedrine were of ther ecemic modification. The spectra of *dl*-ephedrine were quite in agreement with those of *l*-ephedrine. Ethanolamine, diethylamine and triethylamine were carefully distilled through a 40 cm., glass helix-packed column and dried over NaOH. 3-Amino-2-butanol was prepared after the method reported by Vanderbilt et al.[3] The product was liquid and did not crystallize after repeated distillation. Dickey et al.[4] reported that the product obtained by Vanderbilt's method was of erythro series and slightly impure. Benzyl alcohol was washed with sodium hydroxide solution, sodium bisulfite solution and water, dried over potassium carbonate and distilled under a reduced pressure.

Chloroform and carbon tetrachloride were purified as described previously. Benzene was purified by the usual method. Carbon disulfide was shaken with potassium permanganate solution, mercury, mercuric sulfate solution and water, dried over calcium chloride and distilled.

Preparation of Solutions.—On the preparation of solutions care was taken to avoid the contact with atomospheric moisture. It is worth noticing that fine crystallites happen to precipitate gradually in the carbon tetrachloride solution of ephedrines. It was feasible that the precipitation should occur as the concentration increased. Melting points of the precipitates were consistent with hydrochlorides of ephedrines. Although the reason why such precipitation occurred was not clarified, a slow chemical reaction might proceed

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[1] T. Kanzawa, This Bulletin, 29, 398.

[2] L.P. Kuhn, *J. Am. Chem. Soc.*, 74, 2492 (1952).

[3] B.H. Vanderbilt and H.B. Hans, *Ind. Eng. Chem.*, 32, 34 (1940).

[4] F.H. Dickey, W. Fickett and H.J. Lucas, *J. Am. Chem. Soc.*, 74, 944 (1952).

in the carbon tetrachloride solution. The similar precipitation occurred in CS_2 solution of ephedrine already at a concentration of 0.03 M, but the precipitates were not identified. The spectra when precipitation occurred were omitted.

Experimental Results

A. Concentration Dependence of the Spectra in 3 μ Region

Ephedrine.—Concentration dependence of the absorption spectrum of ephedrine in 3 μ region is shown in Fig. 1-a. Over a concentration range from 0.001 to 0.01 M, the spectrum of the carbon tetrachloride solution remains almost unchanged in the relative intensities and positions of bands. On raising the concentration of ephedrine up to 0.21 M it is observed that the intensity of the sharp band component at 3619 cm.$^{-1}$ decreases, that of the broad band component at 3451 cm.$^{-1}$ increases, and besides a new band appears at 3321 cm.$^{-1}$. Such behavior of the concentration dependence will be explained as follows. As long as the concentration remains dilute, the bands due to hydrogen bonding are only from the intramolecular origin. It may be added that from the molecular

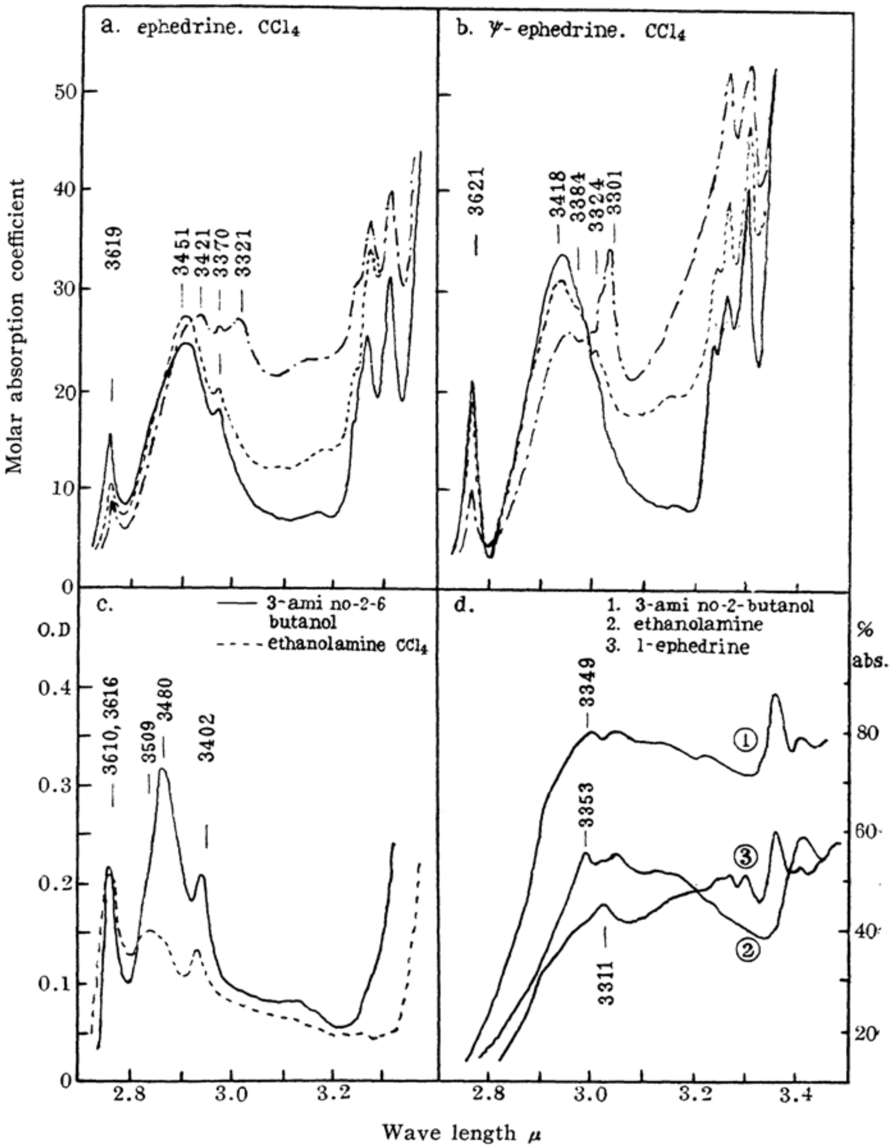

Fig. 1. Spectra of ephedrines, ethanolamine and 3-amino-2-butanol in 3 μ region.

a) ——— 0.0054 M/l. × 2 cm., ---- 0.075 M/l. × 0.3 cm., —-— 0.21 M/l. × 0.056 cm.

b) ——— 0.003 M/l. × 2 cm., ---- 0.05 M/l. × 0.3 cm., —-— 0.11 M/l. × 0.056 cm.

c) ——— ca. 0.005 M/l. d) liquid state. 0.01 mm. thick.

weight determination[5] the formation of ring dimer may be improbable in the dilute solution. However, the change observed at the concentration 0.21 M may be due to the formation of hydrogen bond between molecules.

In the spectra of the solution at lower concentrations the sharp band (3619 cm.$^{-1}$) is clearly due to free OH stretching vibration. The broad band can be ascribed to the intramolecularly hydrogen-bonded OH vibration. Then, a band due to NH vibration may be either covered by the broad band or assigned to a small peak at 3370 cm.$^{-1}$. In this respect the results obtained by Russell and Thompson[6] for carbon tetrachloride solutions of many disubstituted amines will be helpful. According to their results, the absorption of ν (NH) appears in a range 3311–3350 cm.$^{-1}$ for dialkylamines and in 3430–3490 cm.$^{-1}$ for arylalkylamine, diarylamine and heterocyclic compounds. As to the intensity the absorption of dialkylamines is usually very weak compared with that of the other amines. From these results it may be reasonable to assign the band at 3370 cm.$^{-1}$ to free ν (NH), since NH group in ephedrine is very similar in structure to that in dialkylamine. However, whether this ν (NH) band is due to nitrogen atom bridged by a neighboring OH group or not is not certain. Russell and Thompson described that there is some suspicion that the intensity of the NH absorption, so low as almost to disappear, for dialkylamine is connected with a slow chemical reaction of amines with carbon tetrachloride. This description is consistent with the observation in the present experiments that the precipitation of hydrochloride occurs. Therefore the spectra of the alkamine in carbon tetrachloride solution may represent a sort of metastable state of molecule.

At 3.14 μ appears a weak band, which seems to be independent on the change of concentration. The bands at 3.3 μ are due to CH vibration of benzene ring and have no relation with hydrogen bonding.

In connection with the spectra of ephedrines, those of ethanolamine and 3-amino-2-butanol in carbon tetrachloride solution at a concentration of about 0.005 M are recorded and shown in Fig. 1-c., of which the structure is similar to that of ephedrine in 2.7–3.1 μ range. The sharp bands with higher frequency are due to free OH vibration and a band at 3509 or 3490 cm.$^{-1}$ may be due to either free NH vibration or the bonded OH vibration overlapping with free NH vibration. If the bands near 3500 cm^{-1} are due to the intramolecularly hydrogen-bonded OH vibration, the values 101 cm.$^{-1}$ for ethanolamine and 126 cm.$^{-1}$ for 3-amino-2-butanol of the frequency difference between the free and the bonded OH absorption are much less than that for ephedrine (168 cm.$^{-1}$).

The spectrum of the solution at 0.21 M seems to show co-existence of free molecules having intramolecular hydrogen bond and associated molecules. As absorption at a higher concentration than 0.21 M could not be observed because of rapid precipitation of crystallites, a spectrum of *l*-ephedrine in liquid state was taken (Fig. 1-d). It shows a band at 3311 cm.$^{-1}$ with a very weak shoulder near 2.9 μ and continuous absorption over 3.1–3.3 μ. In the previous paper[1], it was reported that in crystalline state *dl*-ephedrine shows only one band at 3300 cm^{-1}, assigned to the perturbed OH vibration. Then, the 3311 cm.$^{-1}$ band for ephedrine in liquid state can be considered to be due to this OH vibration. The weak shoulder near 2.9 μ may be due to the intramolecularly hydrogen-bonded OH absorption still remaining in the liquid state.

From these observations and the assignment of the spectrum at a concentration of 0.0054 M the spectral change accompanied with the changes from dilute solution → concentrated solution → liquid state → solid state may be explained as follows. As the concentration of ephedrine increases from a dilute solution a free molecule having an intramolecular OH···N hydrogen bond (3451 cm.$^{-1}$), gradually associates with a neighboring molecule having free OH group, forming OH···O intermolecular hydrogen bond, which gives rise to a new band at 3321 cm.$^{-1}$*. At the same time the band at 3451 cm.$^{-1}$ shifts to 3421 cm.$^{-1}$ by a reinforcing effect of the intermolecular hydrogen bond formation on the intramolecular one, as is known to occur for the frequency shift during the formation of dimer and polymers of alcohols[2]. In the condensed phase the free OH absorption disappears and only the intense OH absorption (3311 cm.$^{-1}$) relating to the intermolecular hydrogen bond remains.

As to whether NH in the $NHCH_3$ group play a part in hydrogen bond formation, the following fact will be helpful for interpretation; that is, the band at 3370 cm.$^{-1}$ assigned to free NH absorption remains even at a higher concentration (0.21 M), at which the association is appreciable. Thus, it may be concluded that NH group plays almost no rôle in the hydrogen bond formation.

Ψ-Ephedrine.—The spectrum of Ψ-ephedrine in dilute carbon tetrachloride solution is much like that of ephedrine (Fig. 1-b). A sharp band at 3621 cm^{-1} is due to free OH vibration, a broad band at 3418 cm.$^{-1}$ may be due to the intramolecularly hydrogen-bonded OH vibration. However, in this case $\Delta\nu$ (203 cm.$^{-1}$) between the sharp and broad band is larger than that in ephedrine (168 cm.$^{-1}$) and the free NH absorption almost disappears. Although the NH band may be masked by the overlapping of the broad band, a weak band appearing at 3324 cm.$^{-1}$ or a very weak shoulder at 3350 cm.$^{-1}$ may be due to NH vibration.

The spectral change on raising the concentrataion of Ψ-ephedrine proceeds just as in the case of ephedrine; that is, the intensity of the free OH absorption decreases and the broad OH absorption (OH···N) shifts by about 30 cm.$^{-1}$ towarde the lower frequency, accompanied by the appearance of a new band at 3301 cm.$^{-1}$, which is due to intermolecular OH···O hydrogen bonding. As

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[5] E. D. Bergmann, E. Gil-Av and S. Pincas, *J. Am. Chem. Soc.*, **75**, 68 (1953).

[6] R. A. Russell and H. W. Thompson, *J. Chem. Soc.*, **1955**, 483.

* OH absorption for alcohol polymer appears over a range 3338-3384 cm^{-1} [2].

concentration increases, the intensity of the hydrogen-bonded OH absorption (3418 cm.$^{-1}$) rapidly decreases in contrast to the case of ephedrine.

B. Temperature Dependence

In order to observe the temperature dependence of the relative intensities of the free and bonded OH absorption bands, the spectra of ephedrines at about 0.005 M in carbon tetrachloride were taken at about 10° and 55°C. Comparing the spectrum at 10° with that at 25°C, it was found that the intensity of the free OH absorption in the latter increased as usually observed for the intermolecular hydrogen bonding[7]. However, at 55°C the intensities of both free and bonded OH absorptions were lower than those at 25°C for either diastereoisomers. This may be caused by the above-mentioned specific interaction of ephedrines with solvent molecules. A rough estimation of energy of hydrogen bonding for ephedrine and Ψ-ephedrine from the data at 10° and 25°C give the values of about 5 kcal./mol.

C. Solvent Effect

In Fig. 2 are shown the spectra of solutions of ephedrine and Ψ-ephedrine in various solvents, together with that of carbon tetrachloride solutions at a concentration where association is appreciable.

Chloroform.—The free OH absorption shifted slightly towards the lower frequency in chloroform solution (3603 cm.$^{-1}$) more than in carbon tetrachloride solution (3619 cm.$^{-1}$). The bonded OH absorption also shifted by 30–40 cm.$^{-1}$ towards the lower frequency. The band ascribed to ν (NH) in the spectrum of carbon tetrachloride solution appears at almost the same frequency (3360 cm.$^{-1}$) for ephedrine, whereas for Ψ-ephedrine no band corresponding to ν (NH) appears. From the figure it seems that the intermolecular association does not occur at such concentration.

Benzene.—The shift of the free OH absorption towards the lower frequency is large and amounts to 50 cm.$^{-1}$ for both diastereoisomers, compared with that in carbon tetrachloride. The bonded OH absorptions also shift towards the lower frequency. The well-defined band at 3356 cm^{-1} for ephedrine may be due to ν (NH), which remains unchanged on adding triethylamine three times more concentrated as ephedrine, whereas the 3436 cm.$^{-1}$ band shifts to 3401 cm.$^{-1}$. Also a 3311 cm.$^{-1}$ band for Ψ-ephedrine may be due to the NH group. There is no indication that marked association occurs in benzene solution at 0.16 M.

Carbon Disulfide.—The absorption of ephedrines is stronger in carbon disulfide solution, than in other solution. The solution was yellow and unstable, especially for ephedrine.

The free OH absorptions appear at 3597 cm.$^{-1}$ for ephedrine and at 3590 cm.$^{-1}$ for Ψ-ephedrine, which are the frequencies between those in chloroform and benzene solutions. For ephedrine the intensity of the band is greater than for carbon tetrachloride solution of about the same concentration, but for Ψ-ephedrine it is remarkably small and almost zero at 0.16 M.

For ephedrine an intense band appears at 3279 cm.$^{-1}$, which is the lowest value of the bonded

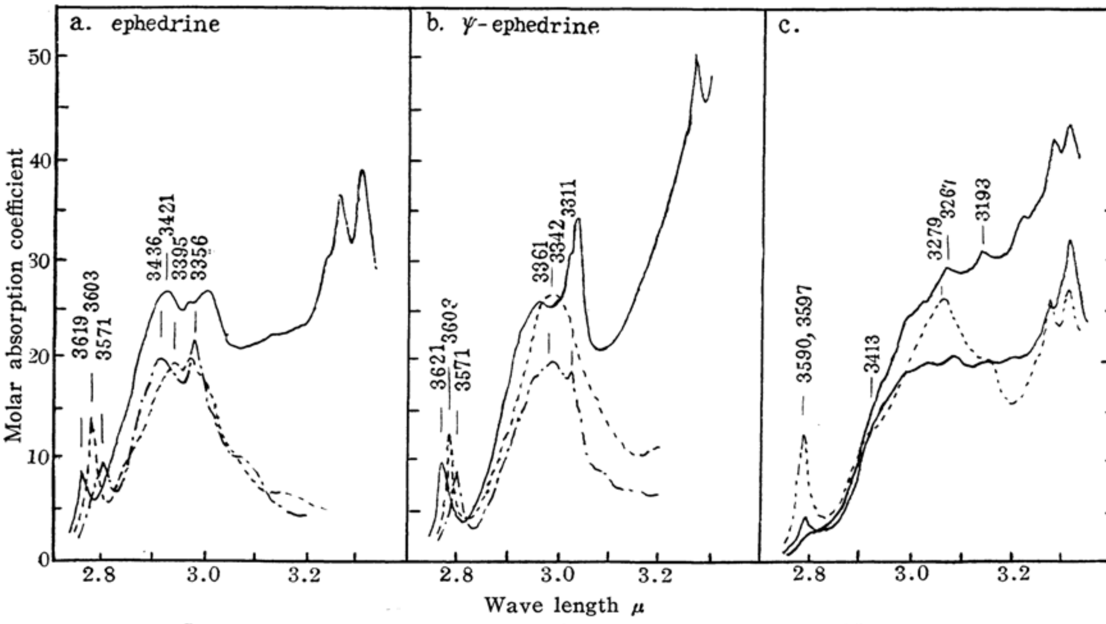

Fig. 2. Solvent effect on spectra of ephedrines. a), b) ——— CCl_4 (ca. 0.1 M/l.), ---- $CHCl_3$ (0.16 M/l.), —·— benzene (0.16 M/l.), cell 0.056 cm. c) CS_2, ---- ephedrine (0.0045 M/l.×2 cm), ——— ψ-ephedrine, 1) 0.0045 M/l.×2 cm., 2) 0.16 M/l. ×0.056 cm.

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[7] e.g. M. Tsuboi, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 76, 376 (1955).

OH vibration observed in the present experiments, if this band be ascribed to the bonded OH vibration. A weak shoulder is observed at about 3410 cm.$^{-1}$, corresponding to the band (3451 cm.$^{-1}$) due to the intramolecularly hydrogen-bonded OH vibration in the carbon tetrachloride solution. It is to be added that the spectrum of ephedrine in carbon disulfide solution is very much like that taken in carbon tetrachloride solution with a small amount of crystalline precipitates, both showing a weak shoulder at 3430 cm.$^{-1}$ and an intense peak at 3280 cm.$^{-1}$. Therefore, such spectra may be due to a metastable state of ephedrine molecule.

It is also remarkable that the absorption of Ψ-ephedrine in such a small concentration as 0.0045 M shows a spectrum like that when an intermolecular interaction occurs.

As is well known a relationship exists between dielectric constant of a solvent and the frequency difference in the OH or NH absorption of a substance in vapor state and in the solution[8]. This relationship is satisfied for the free OH absorption in the present experiments. Thus, the dif-

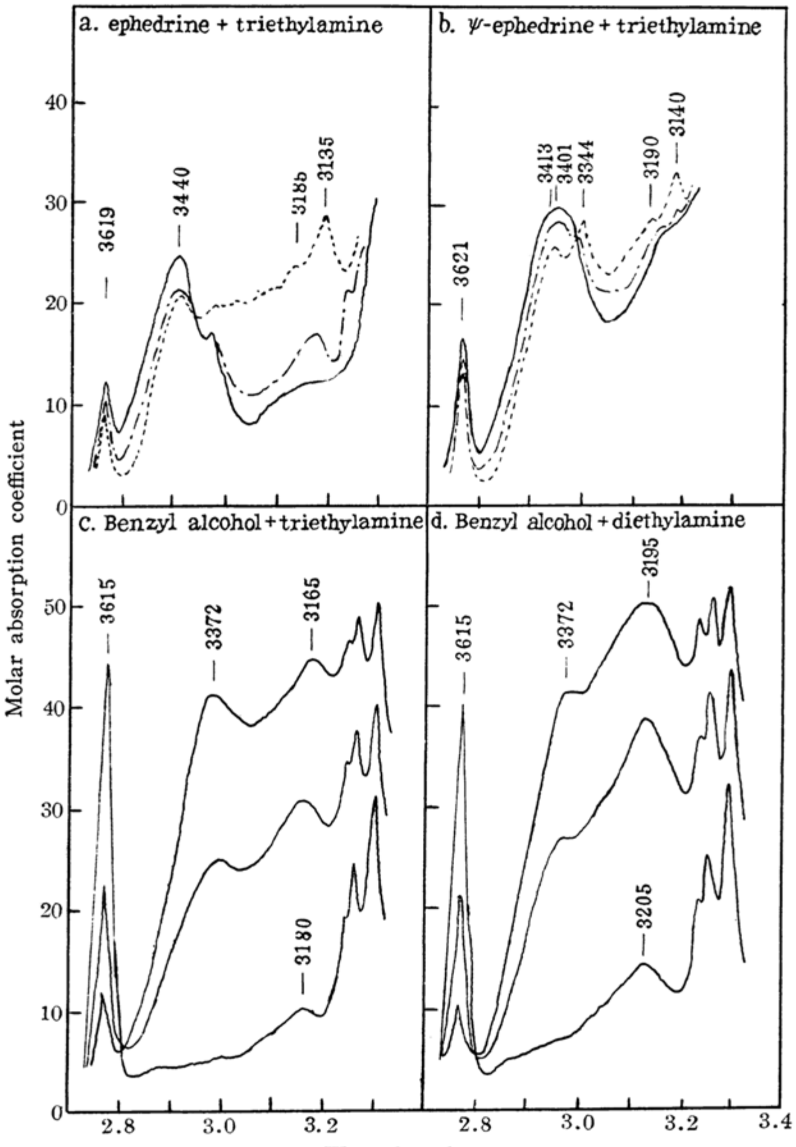

Fig. 3. The interaction of ephedrines and benzyl alcohol with proton acceptor in CCl_4 soln. a), b), ephedrines. 0.03 M/l.+triethylamine, ——— 0.072, —·— 0.27, ---- 0.50 M/l. c), d) 1: 1 mixture in mol. 0.51, 0.179, 0.003 M/l.

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[8] E. Bauer and M. Magat, *J. phys. radium.*, 9, 319 (1938).

ferences in frequency of the free OH absorption in the respective solvents and that of alcohol vapor (3680 cm^{-1}) increases in the order of carbon tetrachloride, chloroform, carbon disulfide and benzene*.

On the other hand, it is also known that the degree of the intermolecular association of phenol in solutions increases in the order of benzene, chloroform and carbon disulfide[9]. From Fig. 2 it will be seen that if the frequency difference in the free and bonded OH absorption means the strength of hydrogen bonding, the above-mentioned relation holds also for the intramolecular hydrogen bonding in the case of ephedrines. In almost the same concentration (about 0.1 M) association seems to occur only in carbon tetrachloride and carbon disulfide solutions, especially strong in the latter.

D. The Interaction with a Proton Acceptor

When a proton acceptor like ethyl ether, ethyl benzoate or pyridine is added to a 0.006 M solution of ephedrine in corbon tetrachloride, no appreciable interaction occurs between ephedrine and the proton acceptor, unless the molar ratio of the latter to the former exceeds 10 : 1. In the case of a molar ratio of 40 : 1 for pyridine to ephedrine new bands due to the intermolecular interaction appear.

In Fig. 3-a and -b are shown the interaction between ephedrines and triethylamine, which is a strong proton acceptor. As seen from the figure the intensity of the free OH band decreases already at the concentration of 0.072 M of triethylamine. As the concentration of triethylamine increases, the intensities of the free and bonded OH vibrations of both isomers decrease, at the same time the bonded OH band shifts towards lower wave number and a new band appears at about 3140 cm.$^{-1}$. Ψ-Ephedrine mixed with higher concentration of triethylamine shows splitting of the band near 3400 cm.$^{-1}$ into two bands at 3413 and 3344 cm.$^{-1}$.

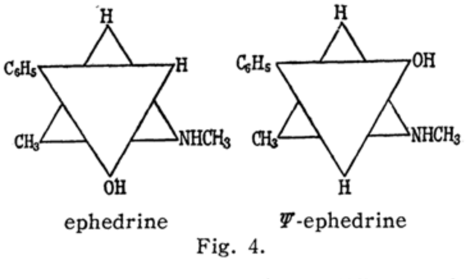
These facts may be explained as follows. At first, a molecule which forms no intramolecular hydrogen bond may interact with triethylamine molecule through either OH or $NHCH_3$ group of the ephedrines. In connection with this assumption, an 1 : 1 mixture in mole of benzyl alcohol and triethylamine or diethylamine was examined. The results are shown in Fig. 3-c and -d. A free OH band of benzyl alcohol at 3615 cm.$^{-1}$ increases its intensity with decreasing concentration of the mixture, while a band at 3372 cm.$^{-1}$ disappears, which seems to be due to the interaction between benzyl alcohol molecules themselves, and the intensity of a band at 3165 cm^{-1} (triethylamine) or 3195 cm.$^{-1}$ (diethylamine) decreases. The band at 3165 or 3195 cm.$^{-1}$, which is due to OH···N intermolecular hydrogen bonding, shifts to 3180 or 3205 cm.$^{-1}$ at a lower concentration.

From these results, it will be evident that the band at 3140 cm.$^{-1}$ observed for ephedrines (Figs. 3-a and -b) can be assigned to OH vibration perturbed by OH···N intermolecular hydrogen bond. Although $NHCH_3$ group may also participate in the hydrogen bond formation of the type NH. . .N, this seems to be rather weak because of the weaker proton donating power of $NHCH_3$ group than OH group[10]. However, the appearance of very weak absorption at 3190 cm.$^{-1}$ and the shift of the bonded OH absorption may suggest that the NH group also takes part in the intermolecular hydrogen bond formation. The splitting of the bonded OH absorption into 3413 and 3344 cm.$^{-1}$ in Ψ-ephedrine may be explained as follows. The lower frequency component is due to OH···N intramolecular hydrogen bond strengthened by the increase of proton accepting power of the N atom because of forming an intermolecular hydrogen bond (NH···N) with triethylamine. A band due to NH···N intermolecular hydrogen bond may be assigned to the absorption at 3185 cm.$^{-1}$, but this assignment is not so conclusive because of the lack of data about the interaction between NH group of amine and N atom of another proton acceptor.

As Ψ-ephedrine shows stronger continuous absorption in 3.0–3.2 μ region than ephedrine at the same concentration, it may be suggested that Ψ-ephedrine interacts more easily with the proton acceptors examined than ephedrine.

Discussion

Although the existence of the intramolecular hydrogen bond in the molecules of both diastereoisomers of ephedrine was verified in various solvents, the appearance of the free OH absorption remained unexplained. This may be accounted for as follows. The conformations of ephedrine and ψ-ephedrine capable of forming the intramolecular hydrogen bond may be illustrated as in Fig. 4.



ephedrine Ψ-ephedrine

Fig. 4.

One of them (ephedrine) is different from that hitherto accepted commonly on the chemical ground[11]. However, the present conformation of ephedrine is in agreement with that suggested recently by Murakami and Fukumoto[12] from consideration of reac-

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* The results of the same kind have been obtained for pyrrole, phenol and methanol (M. Josien and N. Fuson, *J. Chem. Phys.*, 22, 1169 (1954).

9) R.A. Friedel, *J. Am. Chem. Soc.*, 73, 2881 (1951).

10) S. Mizushima, "Structure of molecules and internal rotation." Academic Press Inc. Publishers, New York (1954), p. 133.

11) e.g. W.J. Close, *J. Org. Chem.*, 15, 1131 (1950).

12) M. Murakami and T. Fukumoto, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 76, 270 (1955).

tion mechanism and that found by X-ray crystal analysis for ephedrine hydrochloride[13]. The appearance of the free OH absorption suggests that a part of the molecules have a conformation in which OH and $NHCH_3$ groups are trans. Moreover, it is also possible that in a gauche type molecule the OH group may take an orientation not to form hydrogen bond with $NHCH_3$ group. These two possibilities have actually been observed in the case of ethylene chlorhydrine[14].

The above suggestion that the ephedrine and ψ-ephedrine molecules consist of the mixture of the rotational isomers may be supported by the appearance of one or two more bands in the finger print region spectra in $CHCl_3$ solution than those observed in solid state[1] (970–1190 cm $^{-1}$).

As to whether there are differences in the equilibrium ratio of the rotational isomers between diastereoisomers, only a qualitative discussion may be given. As seen in Fig. 4, it is conceivable that if we assume the repulsion between the phenyl and methyl groups it will give the effects that the OH and $NHCH_3$ groups are more apart for ephedrine than for ψ-ephedrine and thus the hydrogen-bonded conformation of ψ-ephedrine will be relatively more stable, when compared with its trans form, than in the case of ephedrine.

Such a consideration may also explain the difference of $\Delta\nu$ between the present diastereoisomers. In general it is accepted that the magnitude of $\Delta\nu$ is related to the energy of the hydrogen bonding[15] and in solid state related to the distance between a proton donor and an acceptor[16]. Thus, because of the repulsion assumed above, the OH group is to some extent nearer to the $NHCH_3$ group in the gauche type isomer of ψ-ephedrine and the $\Delta\nu$ will be accordingly larger than that for ephedrine. The observed values of $\Delta\nu$ are, as already given, 203 cm.$^{-1}$ for ψ-ephedrine and 168 cm.$^{-1}$ for ephedrine. It is to be remarked that these values are much larger than those found for OH···O intramolecular hydrogen bonds in diols (30–60 cm^{-1})[2]. This may be attributed partly to the difference in the proton affinity of the proton acceptor.

In Table I the values of $\Delta\nu$ of the inter- and intramolecular OH···N hydrogen bonds are summarized. From the Table it is seen that $\Delta\nu$ due to OH···N intermolecular hydrogen bond is very large except that in the case of benzyl alcohol-azobenzene and $\Delta\nu$ due to the intramolecular OH···N hydrogen bond adjucent to a conjugate system like pyridoine is larger than that of intermolecular bond between corresponding pair, phenol-pyridine. It may be said that compared with these $\Delta\nu$ values, those of ephedrines are rather small.

TABLE I

$\Delta\nu$ OF OH. . .N HYDROGEN BOND

Inter-molecular	Phenol-pyridine		770*
	Phenol-N-methylpiperidine		820*
	Benzyl alcohol-azobenzene		170**
	〃	-triethylamine	450
	〃	-diethylamine	420
	Acetaldoxime		470***
Intra-molecular	α-Pyridoin		880*
	Ephedrine		168
	Ψ-Ephedrine		203

* W. Luettke and H. Marsen, *Z. Electrochem.*, 57, 680 (1953).

** M.S.C. Flett, *J. Soc. Dyers and Colourist*, 68, 59 (1952).

*** S. Califano and W. Luettke, *Z. Physik. Chem.*, 5, 240 (1955).

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[13] G.D. Phillips, *Acta Cryst.*, 7, 159 (1954).

[14] S. Mizushima, loc. cit, p. 86.

[15] R.M. Badger, *J. Chem. Phys.*, 8, 288 (1940).

[16] R.C. Lord and R.E. Merrifield, *J. Chem. Phys.*, 21, 166 (1953).