Anal.: Calcd. for $C_9H_7O_3Br$: C 44.47; H 2.90. Found: C 44.42; H 3.07%.

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The C—H Stretching Bands of Aliphatic Amines

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The C—H stretching bands of saturated aliphatic hydrocarbons generally observed between 3.38 μ and 3.51 μ.[1] When the alkyl group is attached to oxygen, bands are also found at 3.54–3.55 μ for compounds containing the methoxyl group[2] and at 3.55 μ and 3.68 μ for aldehydes.[3]

Recently, Hill and Meakins[4] and Braunholtz *et al.*[5] have shown that the infrared spectra of compounds containing the NMe or NMe_2 group includes absorption bands of medium to strong intensity between 3.55 μ and 3.62 μ. Absorption is near 3.55–3.57 μ when the group is attached directly to an aromatic system. When the NMe group in in an aliphatic or nonaromatic heterocyclic system the band occurs in the 3.56–3.60 μ range, while the NMe_2 group so attached has two specific bands, one at 3.54–3.56 μ and the other at 3.60–3.62 μ.

We would like to point out that not only methyl and dimethylamines but also a high percentage of other tertiary aliphatic amines and many secondary aliphatic amines have absorption bands in this range when examined as the free bases. For example, an intense band centered around 3.6 μ was observed in the spectra of a series of 2-alkyl derivatives of merimine,[6] 2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine (Fig. 1). This band was absent in merimine derivatives substituted in the 2-position by hydrogen, acetyl, benzoyl, carbethoxy, carbamoyl, or dimethylsulfamoyl.

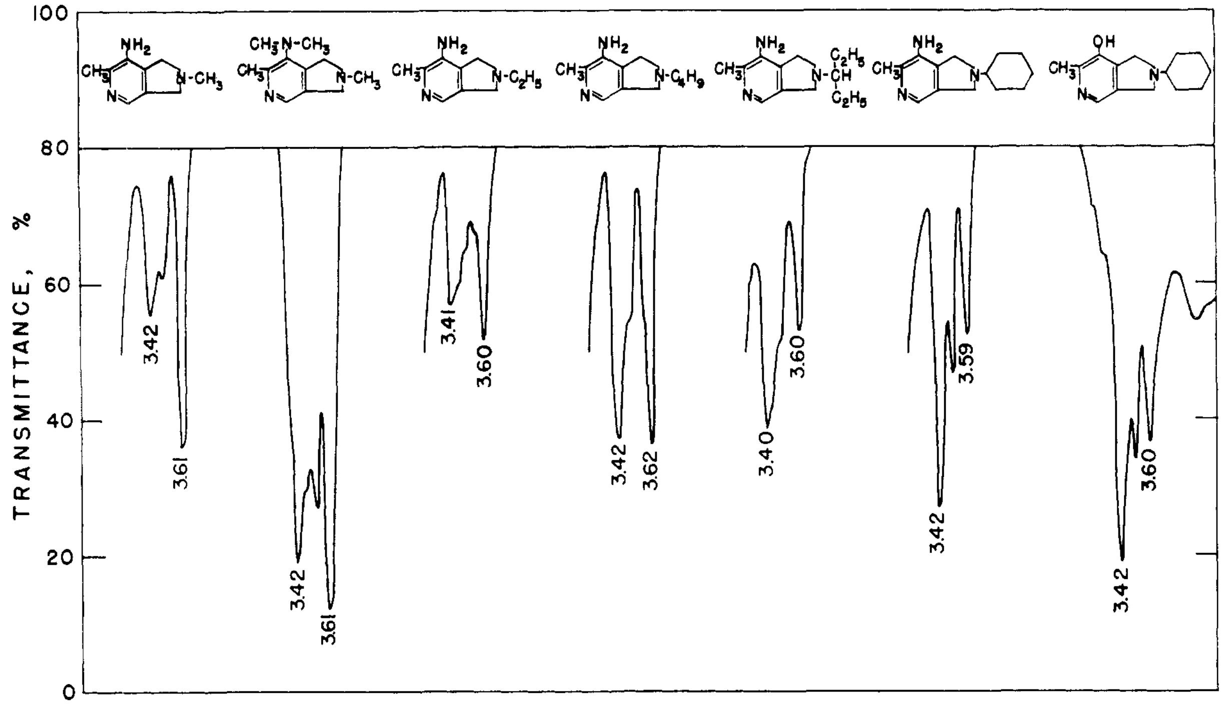

Fig. 1. The C—H stretching bands of 7-substituted-2-alkyl-6-methylmerimines. Spectra were recorded on the Perkin-Elmer Model 21 spectrophotometer. The second sample was a smear. All others were potassium bromide pellets

These observations prompted us to examine the infrared spectra of over one hundred other amines.

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(1) This subject has been reviewed by L. J. Bellamy *The Infra-red Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York, N. Y., 1958.

(2) H. B. Henbest, G. D. Meakins, B. Nicholls, and A. A. Wagland, *J. Chem. Soc.*, 1462 (1957).

(3) A. Pozefsky and N. D. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

(4) R. D. Hill and G. D. Meakins, *J. Chem. Soc.*, 760 (1958).

(5) J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 2780 (1958).

(6) (a) W. B. Wright, Jr., J. S. Webb, and J. M. Smith, Jr., *J. Am. Chem. Soc.*, **79**, 2199 (1957). (b) W. B. Wright, Jr., *J. Org. Chem.*, **24**, 1016 (1959).

A band was present between 3.57 μ and 3.62 μ for all of the tertiary alkylamines. As with the merimines, the relative intensity of the 3.6 μ band compared to the 3.4 μ band was greater when one or more of the alkyl groups was of low molecular weight. This effect may be caused by a lengthening of the 3.4 μ band due to the additional methylene groups in the higher molecular weight compounds. The presence of a benzyl group attached to the nitrogen generally resulted in high relative intensity whereas a branched chain adjacent to the nitrogen resulted in reduced relative intensity.

Thirty-five secondary aliphatic amines were examined. The 3.6 μ band was generally less intense than in the related tertiary alkylamines, was often little more than a shoulder, and was sometimes absent. It also tended to occur at a slightly shorter wave length and was found as low as 3.55 μ. The 3.6 μ band was not observed in primary aliphatic amines or *N*-alkyl substituted amides, anilides, carbamates, carbanilates, or ureas unless a secondary or tertiary aliphatic amine was present elsewhere in the molecule.

TABLE I

THE C—H STRETCHING BANDS OF ALIPHATIC AMINES

	Bands[a,b] Centered at	
Tertiary Aliphatic Amines	3.4μ	3.6μ
N,*N*-Dimethylethylenediamine	3.41	3.61
N,*N*,*N'*,*N'*-Tetramethylethylenediamine	3.41	3.61
4-Hydroxy-1-methylpiperidine	3.42	3.61
Benzyldimethylamine	3.39	3.60
1-Methylpiperazine	3.40	3.60
1-Ethylpiperidine	3.40	3.60
1-Piperidino-2-propanol	3.42	3.60
1-(2-Aminoethyl)pyrrolidine	3.41	3.59
1-(2-Hydroxyethyl)piperidine	3.42	3.59
1-(2-Anilinoethyl)piperidine	3.42	3.59
N-[2-(Benzylmethylamino)propyl]propionanilide	3.39	3.59
N,*N*,*N'*,*N'*-Tetraethylethylenediamine	3.37	3.58
Triethylamine	3.38	3.58
1-Ethylmorpholine	3.39	3.58
α-Diethylaminoacetone	3.40	3.58
N,*N*-Diisopropylethylenediamine	3.39	3.58 (sh)
N-[2-(Piperidino)propyl]propionanilide	3.41	3.58
Benzyldiethylamine	3.37	3.57
1-Benzylpiperazine	3.41	3.57
N-[2-(Ethylphenethylamino)propyl]-propionanilide	3.40	3.57
Secondary Aliphatic Amines		
Hexamethyleneimine	3.41	3.61
Cyclohexylmethylamine	3.42	3.60
N-[2-(Methylamino)propyl]propionanilide	3.40	3.60
Benzylmethylamine	3.41	3.58
Benzylphenethylamine	3.43	3.57
Piperidine	3.40	3.57
Dipropylamine	3.40	3.57
Diamylamine	3.40	3.57 (sh)
Diisopropylamine	3.40	None
Pyrrolidine	3.39	None

[a] All samples measured as smears on the Perkin-Elmer Infracord. [b] Bands in the 3.5μ region are not recorded.

A number of aromatic amines were also examined. In agreement with the earlier investigators,[4,5] the longer wave-length band was observed *only* in those amines containing at least one methyl group attached to the nitrogen.

The absorption bands in the 3.4 μ and 3.6 μ region for a representative group of secondary and tertiary aliphatic amines are reported in Table I.

EXPERIMENTAL

Chemicals. The merimine derivatives were analytically pure. The other compounds were obtained from the compound files and the storeroom shelves. In this study it was felt that the results of a large mass of data outweighed any errors due to small amounts of impurities in the compounds examined

Infrared measurements. The infrared absorption spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer or a Perkin-Elmer Infracord (Model 137). In the former case each sample was calibrated against carbon dioxide at 4.26μ, while in the latter case calibration was against polystyrene film at 3.42μ. Sodium chloride optics were used. The samples were measured as smears or as solids dispersed in potassium bromide pellets.

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2,6-Dicyanopiperidine

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Not unexpectedly the reaction of glutaraldehyde and ammonium cyanide has been found to give substantial amounts of the unreported 2,6-dicyanopiperidine, instead of 1,5-diamino-1,5-dicyanopentane. No effort was made to improve the yield nor to identify any additional products. Hydrolysis in cold concentrated sulfuric acid furnished a diamide, whose melting point corresponded to that for one of the isomeric 2,6-piperidinedicarboxamides reported by Fischer.[1] The *N*-nitroso derivative was also prepared.

The configuration of these compounds was not determined although a single, unsuccessful attempt was made to convert the dinitrile to the known[2] dimethyl 2,6-piperidinedicarboxylate *via* the imino ether hydrochloride. The only pure product isolated and identified was the dicarboxamide; a small amount of a material corresponding to methyl pi-

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(1) E. Fischer, *Ber.*, **34**, 2545 (1912).

(2) R. A. Barnes and H. M. Fales, *J. Am. Chem. Soc.*, **75**, 975 (1953).