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

Tertiary Aliphatic Amines	Bands[a,b] Centered at 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-

(1) E. Fischer, *Ber.*, **34**, 2545 (1912).
(2) R. A. Barnes and H. M. Fales, *J. Am. Chem. Soc.*, **75**, 975 (1953).

peridine-2-carboxamide-6-carboxylate was also recovered.

EXPERIMENTAL[3]

2,6-Dicyanopiperidine. A solution consisting of 12.0 g. of sodium cyanide (0.24 mole) and 13.0 g. of ammonium chloride (0.24 mole) in 50 ml. of water was cooled to 0°. To this was added with stirring 50 ml. of 20% aqueous glutaraldehyde (0.1 mole) during 60 min.; the temperature was kept below 5°. After another 6.0 g. of sodium cyanide and 6.5 g. of ammonium chloride had been added, the solution was allowed to stand at 5° for 10 days. The dark-colored, crystalline solid which had separated was removed by filtration and dried. This solid was then extracted several times with hot benzene and the combined benzene solutions evaporated to leave 3.8 g. of yellow needles, m.p. 110–115°. A small quantity (0.3 g.) was also recovered by extracting the aqueous mother liquors with four 100-ml. portions of ether and two 100-ml. portions of benzene, combining, drying, and evaporating. The total recovery corresponded to a 30% yield.

Recrystallization from benzene after decolorization gave long, flat, white needles, m.p. 114–115°.

Anal. Calcd. for $C_7H_9N_3$: C, 62.20; H, 6.71; N, 31.09. Found: C, 62.41; H, 6.71; N, 30.90.

The *hydrochloride* was prepared by dissolving some of the compound in benzene and saturating the solution with dry hydrogen chloride. The product turns dark and shrinks between 235–250° but does not melt up to 250°; it is very poorly soluble in 2-propanol and absolute ethanol, fairly soluble in 95% ethanol, and readily soluble in water. Hot solutions in 90% ethanol exhibit a strong hydrogen cyanide odor.

Anal. Calcd. for $C_7H_{10}N_3Cl$: N, 24.48. Found: N, 24.03.

The *N-nitroso* derivative was obtained as pale yellow, felted needles after recrystallization from benzene-heptane (2:1); m.p. 143.5–144.5°.

Anal. Calcd. for $C_7H_8N_4O$: C, 51.21; H, 4.91; N, 34.13. Found: C, 51.04; H, 4.83; N, 34.08.

Piperidine-2,6-dicarboxamide. Recrystallized dicyano compound (0.5 g.) was added in small portions to 5 g. of 95% sulfuric acid chilled in an ice-water bath. Each increment was allowed to dissolve before adding the next because too rapid addition caused a fume-off. The yellow colored solution was allowed to stand overnight at room temperature, poured over ice, neutralized to the bromophenol blue end point with aqueous sodium hydroxide, and cooled to 5°. The solid was removed and washed with cold water; 0.45 g., m.p. 228–230°. Recrystallization from water did not change the melting point. Fischer[1] reported 228–229° for the diamide from the low-melting isomer of 2,6-piperidine dicarboxylic acid.

Anal. Calcd. for $C_7H_{13}N_3O_2$: C, 49.11; H, 7.65; N, 24.55. Found: C, 49.32; H, 7.80; N, 24.66.

2,6-Dicyanopiperidine (*ca.* 1 g.) was dissolved in 25 ml. of absolute methanol; the solution was cooled to 5° and saturated with hydrogen chloride. Initially the hydrochloride separated, but it dissolved in the excess hydrogen chloride. During the 5 days that the solution stood at 5° a fine white powder separated; the latter was removed by filtration and retained (A). The methanolic filtrate was evaporated to dryness, the solid residue dissolved in 5 ml. of water, and neutralized with sodium bicarbonate. Evaporation of this aqueous solution on the steam bath left a residue which was first extracted several times with chloroform (B) and then with absolute ethanol (C); the remaining residue was sodium chloride. Extract B was evaporated and the solid residue twice recrystallized from carbon tetrachloride, white needles, m.p. 110.5–111.5°. The analyses are consistent with those required for *methyl piperidine-2-carboxamide-6-carboxylate.*

Anal. Calcd. for $C_8H_{14}N_2O_3$: C, 51.59; H, 7.58; N, 15.05. Found: C, 51.65; H, 7.79; N, 14.82.

(3) All melting points are uncorrected.

The solid, m.p. 210–215°, recovered by evaporating extract C, was once recrystallized from methyl ethyl ketone plus ethanol and once from water, coarse prisms, m.p. 227–229° (dec.). Admixture with the piperidine-2,6-dicarboxamide prepared above did not depress the melting point.

Fraction A was dissolved in methanol-water, neutralized with bicarbonate, and worked up as before. A chloroform-soluble fraction melting at 75–80° was obtained but was not successfully purified.

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Participation of 3-Picoline in Aldol-Type Condensations[1,2]

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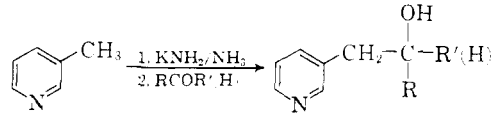
In 1951 Brown and Murphey[3] elegantly demonstrated that the methyl group of 3-picoline shows prototropic activity, when they found that the reaction of 3-picoline, methyl chloride, and sodium amide in liquid ammonia solution gave a mixture of 3-ethyl-, 3-isopropyl- and 3-*t*-butylpyridine. More recently we reported that 3-picolylpotassium, prepared from the tar base and potassium amide in liquid ammonia, can be acylated[4] with aromatic and heterocyclic esters to give a series of 3-picolylketones, $3\text{-}C_5H_4NCH_2COR$, (R = aryl and heterocyclic) and alkylated[5] with a series of alkyl halides to give a number of 3-alkylpyridines, $3\text{-}C_5H_4NCH_2R$ (R = alkyl).

We have now found that 3-picolylpotassium will undergo aldol-type condensations with aldehydes and ketones to give a series of carbinols containing the 3-picolyl radical.



In order to arrive at the best reaction conditions, a study was made of the reaction of benzophenone with 3-picolylpotassium. It was found that the interaction of a 1:1:1 molar ratio of 3-picoline:potassium amide:ketone, using two hours to prepare the anion of the tar base and stirring the reaction mixture for one or two hours after the ketone

(1) This work was performed under Contract No. At(30-1)-670 between the U. S. Atomic Energy Commission and the University of Pittsburgh.

(2) Based on part of the thesis presented by A.D.M. to the Graduate Faculty of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree.

(3) H. C. Brown and W. A. Murphey, *J. Am. Chem. Soc.*, **73**, 3308 (1951).

(4) A. D. Miller, C. Osuch, N. N. Goldberg, and R. Levine, *J. Am. Chem. Soc.*, **78**, 674 (1956).

(5) A. D. Miller and R. Levine, *J. Org. Chem.*, **22**, 168 (1957).