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Intramolecular Hydrogen Bonds. XV.[1] Intramolecular Interaction in *N*-Alkylaminoalkanonitriles

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The ν_{NH} values of monomeric alkylmethylamines in carbon tetrachloride solutions are associated with the rotational isomerism about the N–C bond. In the series of *N*-alkylaminoalkanonitriles, the intramolecular hydrogen-bonding interaction of the NH group with the π-electrons of the CN group was deduced on the basis of the ν_{NH} values and a model examination; in the α-series, the NH group probably interacts exclusively, and in the β-series it partially interacts, but in the γ-series it shows no interaction.

There have been many reports on the intramolecular hydrogen bondings in which a hydroxyl group participates;[2] this subject has, indeed, hitherto been dealt with in this series of studies. The results have prompted us to investigate the intramolecular hydrogen bonding in which an amino group parcipitates, since the situation should be very similar in the two series of compounds.

The literature contains scant information on the intramolecular hydrogen bonding involving a secondary amino group. Several reports have, however, recently been published on the rotational isomerism around the N–C bond in *N*-alkylanilines[3] and on the intramolecular interaction between the NH group and the π-electrons in ω-secondary amino-alkylbenzenes;[3,4] the results are essentially omparable with those of the corresponding hydroxyl compounds.

The present paper will report on the rotational isomerism in alkylmethylamines and the intramolecular interaction between the NH group and the π-electrons of the CN group in *N*-alkylaminoalkanonitriles, and the results will be compared with those of the corresponding ω-hydroxyalkanonitriles previously reported on.[5]

Experimental

Samples. The dimethylamine was liberated from commercial aqueous dimethylamine, and the other alkylmethylamines were obtained by the reported method.[6] The α-*N*-alkylaminoalkanonitriles were prepared from the corresponding cyanohydrines by treating them with monoalkylamines in methanol.[7] The β-*N*-alkylaminopropionitriles were synthesized by the reaction of acryronitrile with alkylamines in methanol.[8] The γ-*N*-methylaminobutyronitrile was obtained by the reaction of γ-bromobutyronitrile with methylamine.[9] All the samples were purified through fractional distillation in an atmosphere of nitrogen; their physical constants agreed with those reported in the literature, and their purity was further proved by their gas chromatograms and/or NMR spectra. Compounds **7**, **8**, **9**, **10**, and **15** have not been reported previously; their analytical data are summarized in Table 2.

The carbon tetrachloride was fractionally distilled over phosphorus pentoxide.

Infrared Measurement. This was carried out at *ca.* 20°C, unless otherwise noted, in the same manner as has previously been described,[1] using a grating infrared spectrometer, Model DS-403G, of the Japan Spectroscopic Co.; the spectrometer was equipped with cells with a path-length of 5.0 cm. Each amine was weighed and dissolved in carbon tetrachloride in a concentration of 0.005 mol/*l* or less immediately before the measurement. The NMR examination of some amine solutions at a higher concentration indicated that no significant reaction of the amines with the solvent occurred during the period required for the infrared measurement.

Results and Discussion

The NH stretching absorption spectra of four alkylmethylamines are shown in Fig. 1A. The spectrum of ethylmethylamine is unsymmetric, with a widely-broadened part being centered at 3347

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[4] M. Ōki and K. Mutai, *ibid.*, **38**, 387 (1965); **39**, 809 (1966); **38**, 393 (1965).

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[7] A. H. Cooke and S. F. Cox, *J. Chem. Soc.*, **1949**, 2334.

[8] D. S. Tarbell, N. Shakespeare, C. J. Claus and J. F. Bunnett, *J. Amer. Chem. Soc.*, **68**, 1217 (1946).

[9] W. Keil, *Hoppe-Seyler's Z. Physiol. Chem.*, **171**, 245 (1927).

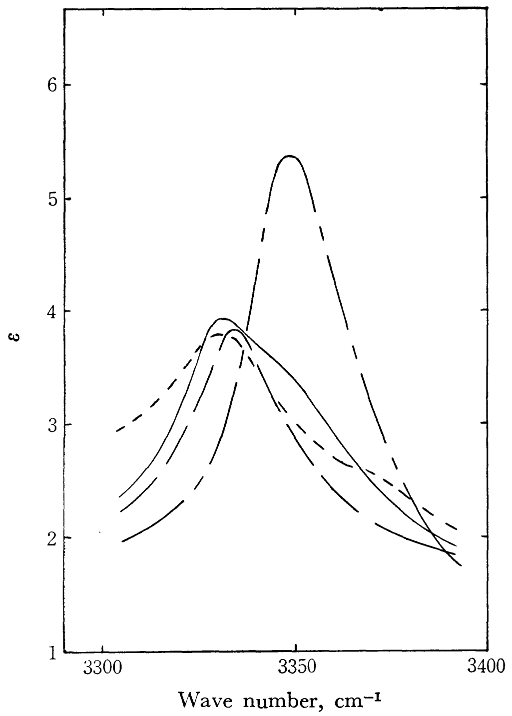

Fig. 1(A). NH spectra of alkylmethylamines.
Alkyl: methyl (— — —), ethyl (———), isopropyl (— —) and *t*-butyl (- - - - -)

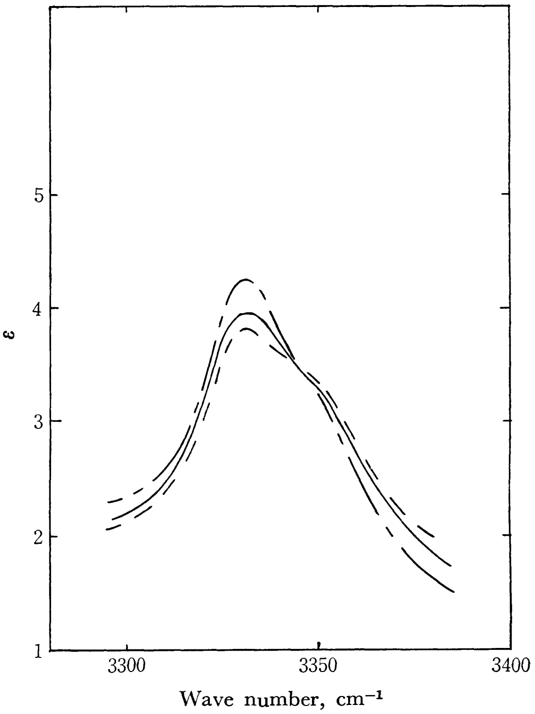

Fig. 1(B). Temperature dependence of the NH spectrum of ethylmethylamine.
10°C: — — — 20°C: ——— 36°C: - - - - -

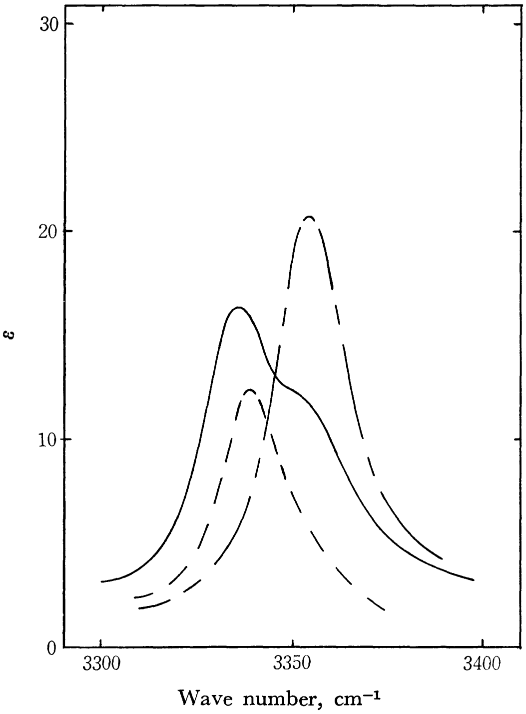

Fig. 1(C). NH spectra of α-(*N*-alkylamino)-acetonitriles.
Alkyl: methyl (— — —), ethyl (———) and isopropyl (- - - - -).

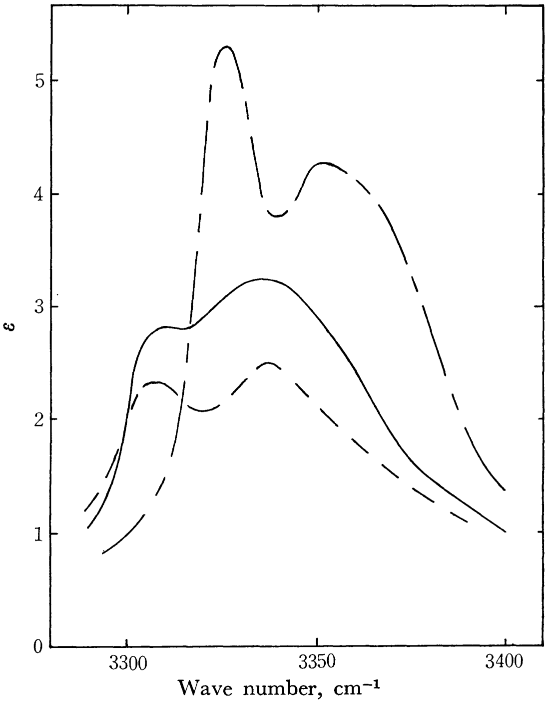

Fig. 1(D). NH spectra of β-(*N*-alkylamino)-propionitriles.
Alkyl: methyl (— — —), ethyl (———) and isopropyl (- - - - -).

cm^{-1}, while those of dimethylamine and isopropylmethylamine are almost symmetrical. *t*-Butylmethylamine shows a broad adsorption.

A more detailed inspection of the band-shape was not performed because of the very low ε values. Moreover, even if it were made, it would not permit a confident discussion of the results. Accordingly, we will mainly discuss the peak frequencies, insofar as there is no intense shoulder or broadening. The apparent spectral data are summarized in Table 1.

TABLE 1. THE SPECTRAL PROPERTIES OF ν_{NH} OF ALKYLMETHYLAMINES, $R-NH-CH_3$

No.	R	ν^a_{max}, cm^{-1}	ε^a
1	CH_3	3348	5.4
2	C_2H_5	3347* 3331	3.9
3	$(CH_3)_2CH$	3334	3.8
4	$(CH_3)_3C$	3330	3.8

* Value at the center of the broadened part.

The unsymmetry of the spectrum of ethylmethylamine can not be caused by any molecular association, since no association explains the symmetry of the spectra of the other amines examined under the same conditions. The peak frequencies and the shapes of the spectra vary with the type of alkyl substituent (R); hence, the concept of the rotational isomerism about the C-N axis may be valid in explaining these facts, as has been made for a similar phenomenon observed in aliphatic alcohols[10] and in *N*-alkylanilines.[3]

According to the projection along the C_R-N bond (C_R is the carbon atom of an alkyl group, R, attached to the nitrogen atom), there are three possible types of steric environment around the N-H group, one or two of which can be taken by each amine depending on the type of R and on the rotational position to be favored. Fig. 2 shows the so-called Newman projection along the C_R-N bond, in which the nitrogen atom is described on the upper side, the circle denoted the C_R atom, and C is the methyl group.

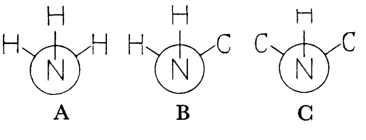

Fig. 2. Three types of steric environment around the NH group in alkylmethylamines.

In this model examination, the following three assumptions were made; (1) the tricovalently-bound nitrogen atom has a tetrahedron-like structure, with the N atom at the center of the tetrahedron and with the four electron orbitals pointing towards the vertices, since such a structure is generally seen in most aliphatic, sterically-uncrowded amines; (2) the steric size of the lone pair of electrons on the nitrogen atom is expected to be much smaller than that of any alkyl group, and almost equal to that of the hydrogen atom, on the basis of the conformational analysis of piperidine compounds,[11] and (3) the molecule takes a skew form, but not an eclipsed one. Hence, the hydrogen atom of the NH group in dimethylamine and also in *t*-butylmethylamine must be in the same steric environment, A or C respectively, because it always exists between two of the three hydrogen atoms or methyl groups on C_R, no matter in what rotational position it exists.

When the R group is ethyl, on the other hand, there are two possible steric environments, A and B. Similarly, two environments, B and C, are possible for the NH group of isopropylmethylamine. The spectral data seem to indicate that the NH group of ethylmethylamine exists in the environment B in a major proportion. This can probably be attributed to the steric effect of the methyl group for the following reasons: in Fig. 3, which shows the Newman projection along the N–C_R bond in each amine, dimethyl- and *t*-butylmethylamine can take only one conformation, I or IV respectively. Ethylmethylamine can exist in three conformations, IIa—c; IIa corresponds to the environment B and may be sterically preferable, while IIb and IIc may be less preferable. This interpretation can be suppoted by measuring the temperature dependence of the relative intensity of the two observed band-components. As Fig. 1B shows, the intensity of the maximum absorption relative to the broadened part decreases with an increase in the temperature. This phenomenon agrees with the thermodynamical generalization that the proportion of a stable conformation becomes higher at a lower temerature. On the other hand, isopropylmethylamine can exist in three conformations, IIIa—c. The two of them,

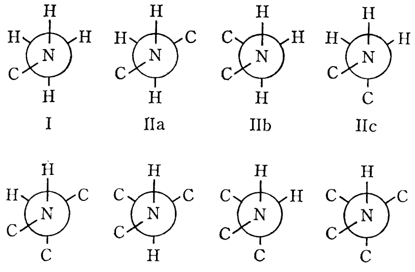

Fig. 3. Conformations about the N–C_R bond in alkylmethylamines.

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[10] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

[11] N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 1277 (1965); N. L. Allinger, J. G. D. Carpenter and F. M. Karkowski, *ibid.*, **87**, 1232 (1965); J. B. Lambert and R. G. Keske, *ibid.*, **88**, 620 (1966); J. B. Lambert, R. G. Keske, R. E. Carhart and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967).

TABLE 2. PHYSICAL PROPERTIES, NITROGEN-ANALYTICAL DATA AND NH-SPECTRAL DATA OF *N*-ALKYLAMINOALKANONITRILES

No.	RNH-CR$_1$R$_2$-CN R	R$_1$	R$_2$	Bp, °C/mmHg	n_D^{18}	N % Found (Calcd)	ν_{NH}^a, cm^{-1}	$\Delta\nu_{1/2}^a$, cm^{-1}	ε^a
5	CH$_3$	H	H	60/18	1.4221		3355	26	21
6	C$_2$H$_5$	H	H	69/19	1.4260		3355* 3336	49	17
7	(CH$_3$)$_2$CH	H	H	74/20	1.4264	29.05 (28.55)	3338	29	13
8	CH$_3$	CH$_3$	H	61/28.5	1.4193	33.52 (33.30)	3353* 3343	32	13
9	C$_2$H$_5$	CH$_3$	H	68/24	1.4224	28.90 (28.55)	3343* 3328	37	10
10	(CH$_3$)$_2$CH	CH$_3$	H	64/19	1.4229	25.11 (24.98)	3329	30	10
11	CH$_3$	CH$_3$	CH$_3$	59/24	1.4186		3347	30	7
12	C$_2$H$_5$	CH$_3$	CH$_3$	60/19	1.4217		3324	28	7
	RNH-(CH$_2$)$_n$-CN R		n						
13	CH$_3$		2	79/20	1.4328		3356 3326		4.3 5.3
14	C$_2$H$_5$		2	81/19	1.4336		3336 3307		3.2 2.8
15	(CH$_3$)$_2$CH		2	88/20	1.4325	24.86 (24.98)	3337 3307		2.5 2.3
16	CH$_3$		3	97—98/60			3371	52	5.1

* Value at the center of the broadened part.

IIIa and IIIb, may be indistinguishable in steric preference from each other and correspond to the environments, B and C respectively. Therefore, the observed single NH bond seems to be due to the NH species in both environments, rather than in either of them. In fact, the band has been essentially identical with those observed at 10 and 40°C.

α-(*N*-Alkylamino)-alkanonitriles. Some NH spectra are shown in Fig. 1C, and the apparent spectral data are summarized in Table 2. The spectra of *N*-alkylaminoacetonitriles (**5**—**7**) are similar in general shape to, but are somewhat different in peak frequency from, those of the alkylmethylamines. When the alkyl group, R, is methyl or isopropyl, they show a single, almost symmetrical NH spectrum. When R is ethyl, the spectrum is widely broadened on the higher-frequency side. This may be explained in terms of the same alkyl effect as has been suggested as the origin of a similar phenomenon observed in alkylmethylamines, since the rotational isomerism about the C_R–N bond can be illustrated by Fig. 3, in which N–CH$_3$ is replaced by N–CH$_2$CN. On the other hand, in the projection along the C_α–N bond, all the acetonitriles predominantly prefer the same conformation, V, containing R and CN in a *trans* relationship, as is shown in Fig. 4. This conformer would involve an additional stabilization, one which should result from an attractive interaction which is probable between the NH group and the π-electrons of the CN group. As for the presence of the interaction, no evidence can be obtained from the spectral data of ν_{NH} and ε, and it can not, of course, be ascertained whether the interaction is of the usual charge-transfer type or of the electrostatic-attraction type. The observed ε values, much higher than those of alkylmethylamines, can not provide decisive evidence for the presence of the interaction, because both types of interaction and also the electron-attractive CN group would serve to increase the N–H bond moment and, thereby, to increase the ε value. The presence of the interaction is yet suggested in view of a situation similar to that in α-cyanohydrines, in which the interaction between the OH and the CN group results in no significant lowering of the OH stretching frequency.[5]

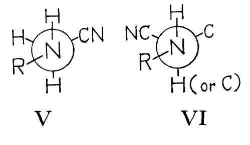
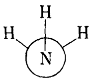
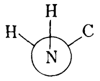
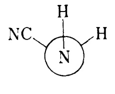
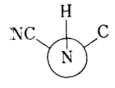


Fig. 4. Projection along the C_α–N bond in α-*N*-alkylaminoalkanonitirles.

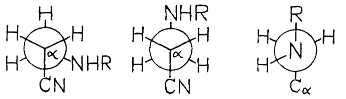
In α-(*N*-alkylamino)-propionitriles (**8**—**10**) and -isobutyronitriles (**11** and **12**), the peak frequencies are lower by *ca.* 10 cm^{-1}, irrespective of the number of α-methyl groups, than those of the corresponding alkylaminoacetonitriles. This lowering seems to be attributable to the steric effect of the α-methyl groups, and its independence of the number of methyl groups seems to suggest that both series of nitriles involve an essentially equal steric environment around the N–H group when they contain the same R. These suggestions can be supported by an examination of their models; in the rotation around the C_R–N bond, the steric environment around the NH group is again as is shown in Fig. 2. On the other hand, the conformation, VI, about the C_α–N bond, which is shown in Fig. 4, may be preferable for both nitriles, if it is assumed that; (1) the CN group is much smaller in steric size than the methyl,[12] and that, hence, CH_3 and R are preferably *trans*, and (2) the interaction between the NH group and the π-electrons of the CN group is possible. This conformation contains one more methyl group skew to the NH group than does the conformation V of the alkylaminoacetonitriles. If the presence of this methyl group is responsible for the lowering of *ca.* 10 cm^{-1} in the NH frequency, the conformation VI may contribute to a major component of the band. Consequently, the above assignments can be summarized as in Table 3; the combination of the forms A and D, for example, gives the ν_{NH} of 3355 cm^{-1}.

TABLE 3. RELATIONSHIP BETWEEN THE NH FREQUENCIES AND THE STERIC AND/OR INTERACTING CONDITIONS

Projection along the N–C_R Bond Projection along the N–C_α Bond		 A	 B
	D	3355	3336
	E	3345	3328

β-(*N*-Alkylamino)-propionitriles (13—15) and γ-(*N*-Methylamino)-butyronitrile (16).

The NH spectra of the former contain apparently two resolved bands with a spacing of *ca.* 30 cm^{-1}, independent of the type of alkyl, as Fig. 1D shows; the lower and the higher frequency bands may be due to the interacted and the free NH species respectively. In the projection along the C_α—C_β bond, the CN and the NH group can be in a skew (VII) or *trans* relationship (VIII), as is shown in Fig. 5. In the skew form VII, the NH group can interact with the CN group, while most of the free NH species should exist in the sterically preferable *trans* form VIII.



VII VIII IX

Fig. 5. Projection along the C_α–C_β bond (forms VII and VIII) and along the N–C_β bond (form IX).

On the other hand, the projection along the N–C_β bond shows that the both interacted and free NH groups must be located in a position skew to the C_α atom in Form IX, which is sterically preferable. Accordingly, the difference in frequency among the alkylaminopropionitriles depends mainly on the type of R and may again be explained in terms of the same steric effect of R as that which has been mentioned above in the case of the α-alkylaminonitriles.

Finally, the γ-methylamino group does not interact with the nitrile group, probably because of the thermodynamically more difficult formation of a largering through interaction. The same phenomenon was observed in γ-hydroxybutyronitrile.[5]

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[12] N. L. Allinger and W. Szkryblo, *J. Org. Chem.*, **27**, 460 (1962); B. Rickborn and F. R. Jensen, *ibid.*, **27**, 4606 (1962).