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Amino group stretching vibrations in primary aliphatic amines

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Primary aliphatic amines can be characterized by infrared spectroscopy as to the nature and degree of branching of the alkyl chain, using the fundamental antisymmetric and symmetric NH_2 stretching frequencies measured in dilute C_2Cl_4 solution. Where steric and direct conjugation effects are absent both frequencies and the integrated intensity of the antisymmetric band increase linearly with decreasing inductive electron-donating power of the alkyl chain. The integrated intensity of the symmetric band, which is smaller than that for the antisymmetric band in all the 26 compounds studied, is independent of the inductive nature of the alkyl chain as a first approximation. These results indicate that the N-atom lone-pair orbital in RNH_2 plays a negligibly small role in modifying the inductive effect of R on NH_2 frequencies and intensities as long as the N-atom hybridization remains sp^3.

INTRODUCTION

Although the simple amines were among the first compounds to be studied by infrared spectroscopy (1) and to be characterized by absorption bands in the 3 μ region, no detailed high-resolution data which permit the comparison of the fundamental symmetric and antisymmetric stretching vibrations of straight-chain and branched-chain amines appear to be available. In most standard references used in the structural diagnosis of organic compounds these bands are listed as being "near 3 500 and 3 400 cm^{-1}" (2) or "in the region 3 500 – 3 300 cm^{-1}" (3). The results reported here show that frequency, integrated intensity, and bandwidth measurements permit much greater refinement in the structural identification of these compounds, as for the OH stretching vibration in monomeric alcohols (4).

The six possible vibrational modes of the —NH_2 group have been discussed by Califano and Moccia (5) in conjunction with the infrared spectra of substituted anilines, and a limited number of assignments have been made for aliphatic amines in the

fingerprint region of the spectrum. Characteristic shifts in the C—N stretching frequency and in the symmetric and antisymmetric NH_2 bending modes for primary amines with primary, secondary, and tertiary alpha carbon atoms respectively have been reported by Stewart (6), but many of the frequency ranges given overlap badly. Some of these correlations are also based on pure liquid amines, where intermolecular association introduces complications, as Wolff and Schmidt (7) have shown recently. Complete vibrational assignments do not appear to have been made for compounds in this series other than methylamine. This has been reported by Gray and Lord (8).

The 3 μ region is attractive for diagnostic work involving amines because fewer absorptions are found here than in any section of the "fingerprint region", simplifying interpretations. Further, the hydrogenic stretching vibrations are highly localized. Since long path lengths of solvents like tetrachloroethylene can be used, the monomeric amines can be investigated. Detailed work in this region does, however, require a carefully calibrated grating or double-pass lithium or calcium fluoride prism spectrophotometer to achieve the necessary resolution.

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TABLE I

Fundamental NH_2 stretching vibrations in alkyl amines in dilute C_2Cl_4 solution. (Limits on mean values are maximum deviations observed.)

Compound	σ^{*a}	Antisymmetric			Symmetric		
		ν (cm^{-1})	A^b	$\Delta\nu_{1/2}{}^a$ (cm^{-1})	ν (cm^{-1})	A^b	$\Delta\nu_{1/2}{}^a$ (cm^{-1})
RCH_2NH_2 (unbranched or γ-branched)							
Methylamine	0.000	3 401.5	0.51	31	3 341	0.18	51
Ethylamine	−0.100	3 400.5	0.38	31	3 324	0.12	31
n-Propylamine	−0.115	3 393	0.40	26	3 326	0.12	29
n-Butylamine	−0.130	3 391.5	0.41	26	3 325	0.17	34.5
n-Amylamine		3 392	0.41	24.5	3 326	0.16	29
Isoamylamine		3 391	0.38	27^c	3 325	0.16	37^c
n-Hexylamine		3 392	0.37^d	24.5	3 325	0.14^d	27
n-Heptylamine		3 392	0.38	24.5	3 325.5	0.13	27.5
n-Octylamine		3 392	0.41	24	3 325	0.15	23.5
n-Nonylamine		3 392	0.41	23	3 325	0.13	24.5
n-Decylamine		3 392	0.40	23	3 325.5	0.13	24.5
n-Dodecylamine		3 392	0.39	24	3 325.5	0.13	25.5
n-Tetradecylamine		3 392.5	0.42	23	3 325.5	0.13	24
n-Hexadecylamine		3 392	0.47	24.5	3 325.5	0.15	28.5
n-Octadecylamine		3 392	0.41	24.5	3 325.5	0.15	25
Mean values^e		3 392±1	0.41±0.06	24.5	3 325.5±0.5	0.14±0.03	27
$RR'CHNH_2$							
Isopropylamine	−0.190	3 383	0.37	39	3 317.5	0.16	39
s-Butylamine	−0.210	3 386.5	0.38	31.5	3 315	0.14	33
2-Aminohexane		3 384	0.33	36	3 310	0.12	28.5
3-Aminohexane		3 389	0.26	27	3 313.5	0.11	25.5
4-Aminoheptane		3 388	0.29	28	3 314.5	0.15	36
Mean values		3 386±3	0.33±0.07	—	3 314.5±4.5	0.14±0.03	—
$RR'R''CNH_2$							
t-Butylamine	−0.300	3 374^f	0.27	33	3 307	0.18	28
t-Amylamine		3 377	0.30	38.5	3 309.5	0.18	28
Mean values		3 376±2	0.29±0.02	—	3 309±2	0.18	—
$RR'CHCH_2NH_2$							
Isobutylamine	−0.125	3 397.5	0.46	22.5	3 329.5	0.18	35.5
$RR'R''CCH_2NH_2$							
Neopentylamine		3 404.5	0.44	19	3 340	0.18	34
Unsaturated							
Allylamine		3 397	0.79	27	3 330	0.19	36

^{a}From ref. 10.
^{b}Units of integrated intensity are 1×10^6 cm mole^{-1} (log$_e$). These A_{RJ} values can be converted to IUPAC absolute intensity units (cm^2 s^{-1} molecule^{-1}) by multiplying by 4.976×10^{-11}, and to IUPAC practical units (cm^2 l mole^{-1}) by multiplying by 4.343×10^{-1}, as described by Seshadri and Jones (19).
^{c}These abnormally large widths for this γ-branched amine not included in the mean.
^{d}Identical values were obtained in CCl$_4$ solution.
^{e}Methylamine and ethylamine values not included in mean.
^{f}Shoulder on high frequency side of band.

EXPERIMENTAL

Spectral measurements were made with a Beckman IR-7 spectrophotometer with a NaCl foreprism and a 75 lines/mm grating blazed at 12 μ operating in the fourth order. Spectral slit widths were calculated to be about 1.0–1.5 cm^{-1} in this region. The instrument was calibrated as previously described (9), and the accuracy of the frequency measurements is believed to be limited largely by the widths of the absorption bands themselves. All measurements reported are based on duplicate spectra on separate solutions (concentrations below 0.06 M) at ambient temperature. In a few cases weak bands suggesting some intermolecular association were observed (7), but these do not interfere significantly with the analysis presented.

The amines were commercial products purified by fractional distillation or recrystallization until acceptable agreement with physical constants recorded in the literature was obtained. Spectroscopic quality tetrachloroethylene was used as a solvent, since carbon tetrachloride reacts with many amines. A pair of matched 2 cm quartz cells was used. The overlapping wings of the two absorption bands were separated graphically, and areas were determined by numerical integration. Spectrophotometer slit-width effects were negligible because the calculated slit width was only about 5% of the half-intensity bandwidths measured.

RESULTS AND DISCUSSION

Figure 1 shows the fundamental NH$_2$ stretching bands of n-butylamine in comparison with those of aniline and acetamide. The increase in frequency and in the separation between the modes is largely due to a change in hybridization of the N atom from sp^3 in n-butylamine to partial sp^2 character in aniline and to sp^2 hybridization in acetamide. The increase in intensity in the same order reflects increasing N—H bond polarity and an increase in the N lone-pair conjugation with the rest of the molecule (for the symmetric mode).
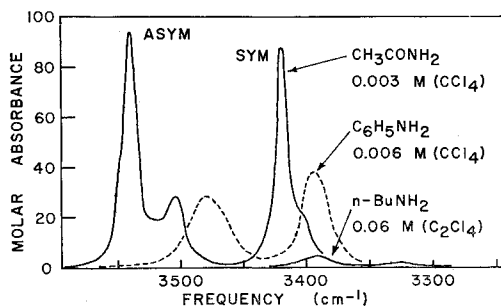

FIG. 1. Fundamental NH$_2$ stretching bands of n-butylamine and those of aniline and acetamide (all in dilute CCl$_4$ or C$_2$Cl$_4$ solution). Concentrations at which the measurements were made are indicated.

The detailed experimental results are summarized in Table I. The data show that aliphatic amines can be classified as straight-chain, singly α-branched, doubly α-branched, singly β-branched, and doubly β-branched compounds on the basis of their NH$_2$ stretching frequencies and integrated intensities. Where a sufficient number of compounds of a given structural type were available average values and maximum deviations observed are included in Table I.

Straight-chain amines (C$_3$ to C$_{18}$, 12 compounds examined) show a remarkable frequency and intensity constancy: ν_{as} = 3 392 $\pm$ 1, ν_s = 3 325.$_5$ $\pm$ 0.$_5$ cm^{-1}; A_{as} = 0.41 $\pm$ 0.06, A_s = 0.14 $\pm$ 0.03 ($\times$ 10^6 cm/mole, log$_e$). Methylamine and ethylamine do not conform to this pattern. The inductive electron-donating effect of an unbranched alkyl chain thus appears to reach its limiting value at about C$_3$. This is confirmed by the fact that branching at the γ-carbon atom as in isoamylamine has no effect on the frequencies or intensities (although the bandwidths are somewhat wider). The wider bandwidths for methylamine and ethylamine may reflect some molecular rotation in solution for these small molecules (11).

Amines of the type RR'CHNH$_2$ are characterized by lower frequencies (ν_{as} = 3 385.$_5$ $\pm$ 3.$_5$, ν_s = 3 414 $\pm$ 4 cm^{-1}, 5 compounds examined) and by a lower average A_{as} value (0.34 $\pm$ 0.08 units), whereas the A_s values do not differ significantly from the corresponding values found in unbranched amines. The greater spread in frequencies and intensities may be related to variations in shielding of the —NH$_2$ group from solvent molecules (12).

The two amines of the type RR'R''CNH$_2$ show a still further reduction in frequency (ν_{as} = 3 376 $\pm$ 2, ν_s = 3 309 $\pm$ 2 cm^{-1}).[2] Only one compound of each of the types RR'CHCH$_2$NH$_2$ and RR'R''CCH$_2$NH$_2$ was available, but the data in Table I would permit the discrimination of these types from the others already discussed on the basis of the combined use of frequencies and intensities.

[2]Undoubtedly all the ν and A ranges quoted for structural types other than the unbranched amines will have to be widened as more compounds are investigated.

With the exception of methylamine and ethylamine, bandwidths for the unbranched amines show considerable regularity, with the symmetric band being slightly wider than the antisymmetric band. For the other amines no apparent bandwidth regularities are observed, possibly because of variations in the shielding of the —NH₂ group from collisions with solvent molecules and other factors such as the presence of several closely spaced and unresolved bands due to rotational isomerism. Rotational isomers have been observed in gaseous n-propylamine in the Raman spectrum (13).

The narrowest bands observed are the antisymmetric bands of the β-branched compounds isobutylamine ($22._5$ cm^{-1}) and neopentylamine (19 cm^{-1}) in which the rotation about Cα—Cβ bond places the —NH₂ group *gauche* with respect to at least one and always to two methyl groups respectively. This is consistent with increased shielding of the —NH₂ group from highly polarizable tetrachloroethylene molecules. There is no indication of intramolecular γ-CH$\cdots$N hydrogen bonding comparable to the γ-CH$\cdots$O interaction which has been detected in n-propanol and other alcohols (14).
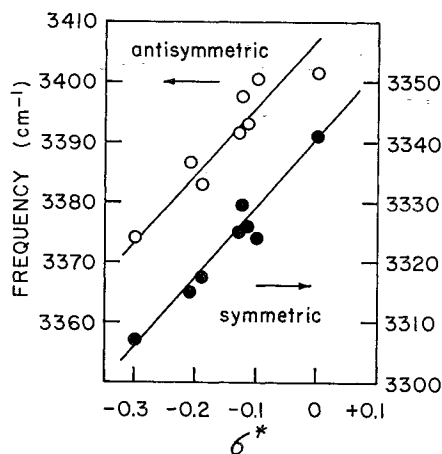

FIG. 2. Linear dependence of the NH₂ stretching frequencies in saturated aliphatic amines on the inductive effect of the alkyl group, as measured by Taft σ^* substituent constants.

To a first approximation both ν_{as} and ν_s are correlated linearly by the Taft inductive

substituent constant σ^* of the alkyl group (10, p. 619) (Fig. 2).

[1] $\qquad \nu_{as}(\text{cm}^{-1}) = 114\sigma^* + 3407$

[2] $\qquad \nu_s(\text{cm}^{-1}) = 114\sigma^* + 3341$

The two slopes are identical, and also equal to the slope of the ν_{as} versus σ_I correlation (10, p. 595) found for aromatic amines, if the appropriate scale adjustment is made, as follows:

[3] $\dfrac{\Delta\sigma^*}{\Delta\sigma_I} = \dfrac{(\sigma^*_{\text{ phenyl}} - \sigma^*_{\text{ methyl}})}{(\sigma_{I\text{ phenyl}} - \sigma_{I\text{ methyl}})}$

$\qquad = \dfrac{(+0.60 - 0.00)}{(+0.10 - (-0.05))} = 4.0.$

Thus the slopes of 19.6 and 29.5 cm^{-1} per σ_I unit found (15) for ν_s and ν_{as} respectively in aromatic amines can be converted into slopes of 78 and 118 cm^{-1} per σ^* unit. This establishes that the antisymmetric frequency (which involves only H-atom movements and no N lone-pair pulsations as a first approximation (16)) shows the same sensitivity to the inductive effect regardless of the N-atom hybridization. On the other hand, the symmetric frequency (which involves H-atom movements plus N lone-pair pulsations) is sensitive to the N-atom hybridization state, or to changes in hybridization which may actually occur during a vibrational cycle because of variation in the lone-pair overlap with the aromatic π-electrons. Expressions [1] and [2] and the same sensitivity of ν_{as} to the inductive effect in anilines suggest that for aliphatic amines the N lone-pair orbital plays a negligible role in modifying the inductive effect on the NH₂ frequencies. Since the deviations from the lines in Fig. 2 are greater than expected on the basis of probable errors in ν and σ^*, these are ascribed to possible mass effects (particularly for methylamine and ethylamine), variations in solvation of the —NH₂ group as the nature of the alkyl group is altered, and possible small changes in the hybridization of the N atom. Calculations of the HNH angle from ν_{as} and ν_s (17) show that hybridization changes with variations in the alkyl group must be slight. For n-alkylamines HNH angle = 107.2° in good agree-

ment with the value of 106.78° for ammonia determined by Herzberg (18).

Although the total electronic effect of m- and p-ring substituents in anilines on ν_{as} and ν_s has been separated into independent inductive and resonance effects (15), this work shows for the first time the inductive effect alone on an —NH$_2$ group which remains in essentially the same hybridization state (sp^3). As the inductive electron-donating power of the alkyl group increases, the apparent electronegativity of the N atom decreases, consequently binding the H atoms less firmly. It is interesting to note that the fundamental monomeric OH stretching frequency in simple saturated alcohols measured in very dilute CCl$_4$ solution shows a linear dependence on σ^* with almost the same slope.
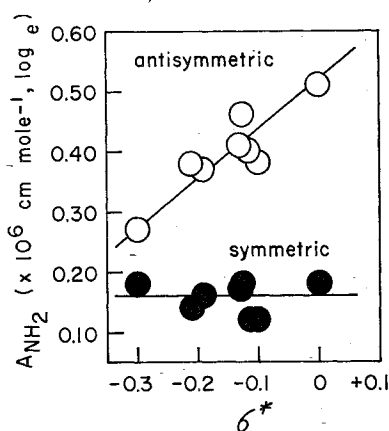

FIG. 3. Dependence of the integrated NH$_2$ band intensities in saturated aliphatic amines on the inductive effect of the alkyl group, as measured by Taft σ^* substituent constants. Measurements in dilute C$_2$Cl$_4$ solution. Units of A are 1×10^6 cm mole^{-1} (log$_e$).

Bearing in mind the uncertainties in band area measurements when broad bands which overlap slightly are involved, A_s is considered to be independent of σ^* (0.16 intensity units) whereas A_{as} increases linearly with increasing σ^* (Fig. 3), leading to the expression

$$[4] \qquad A_{as} = 0.83\sigma^* + 0.52.$$

As the inductive electron-donating power of the alkyl group increases and the apparent electronegativity of the N atom

decreases, the polarity of the NH bonds decreases. Hence A_{as} decreases as it is determined primarily by the NH-bond dipole gradients (16). The increased charge on the N atom would increase the lone-pair dipole change during the symmetric vibration, but this increase is probably offset by the accompanying decrease in the resultant of the NH-bond dipole gradients in the symmetric mode leading to almost constant A_s values. Mason (17) has presented evidence that the "s" character of the N atom in amines and the charge density on it are independent to a certain extent.

Orville-Thomas, Parsons, and Ogden (16) state that A_s is much more intense than A_{as} in the vapor phase spectra of aliphatic amines. In C$_2$Cl$_4$ solution the relative intensities are reversed with $(A_{as}/A_s) \approx 3$ for n-alkylamines. Our attempts to measure quantitatively the integrated band intensities for gaseous methylamine, pressure broadened as required, led to the conclusion that the bands are too badly overlapped to permit the determination of two separate band areas (see for example the published spectrum in ref. 8). No definite conclusion as to whether a radically different solvent effect exists for the two vibrational modes can therefore be reached.

By making the assumption that only the changes of NH-bond moments with bond length contribute to the transition moment, then the NH-bond dipole gradients can be calculated in two independent ways from A_{as} and A_s respectively (12, 17). From the average frequencies and intensities found for n-alkylamines in C$_2$Cl$_4$ solution, the calculated NH bond dipole gradients are 0.26 ± 0.03 D/Å (based on A_{as}) and 0.21 ± 0.03 D/Å (based on A_s). Since the method employed is only strictly applicable to gas phase measurements these values can be considered equal, although in principle the calculation based on A_{as} is more reliable since the antisymmetric mode does not involve any N lone-pair orbital pulsations which can contribute to A_s. Earlier calculations (12) based on an sp^3 amino group with fixed vibrational H amplitudes and fixed charges on N and H atoms show that the resultant dipole moment changes arising

from NH-bond dipole gradients alone in the antisymmetric and symmetric modes respectively should be in the ratio of 1.4:1.0. Since the integrated band intensity is proportional to the square of the transition moment the calculated ratio $(A_{as}/A_s) \approx 2$. The observed ratios range between 2.9 for n-alkylamines to 1.6 for t-alkylamines, and are in good agreement with the crude estimate.

The equivalence of the calculated NH-bond dipole gradients based on A_{as} and A_s in n-alkylamines suggests that the lone-pair contribution to the symmetric mode transition moment is small in these compounds. However, it becomes noticeable in the highly branched amines where the alkyl group is a more powerful electron donor. For t-butylamine the calculated HNH angle is 107.4°, and the calculated NH-bond dipole gradients are 0.21 D/Å (based on A_{as}) and 0.24 D/Å (based on A_s). The latter value is larger in this case because the nitrogen lone-pair contribution to the transition moment of the symmetric mode is not taken into consideration in the calculation.

In N,N-dimethyl-p-phenylenediamine ($A_{as}/A_s = 1.6$, HNH angle = 109.6°) the calculated NH-bond dipole gradients based on A_{as} and A_s respectively are 0.6 and 0.8 D/Å, whereas in p-nitroaniline ($A_{as}/A_s = 0.4$, HNH angle = 113.6°) the corresponding values are 0.8 and 2.0 D/Å (12). The enhanced NH-bond dipole gradients based on the symmetric mode here reflect the lone-pair dipole and π-electron contributions. The small HNH angle in N,N-dimethyl-p-phenylenediamine indicates that there is only very little N lone-pair overlap with the aromatic π-electron.

Besides refining the structural diagnosis of primary aliphatic amines as to chain branching, these measurements may be useful as a reference in the conformational analysis of amines of the type $XCH_2CH_2NH_2$ where $trans$ and $gauche$ isomers are possible, particularly with respect to intramolecular NH$\cdots$X hydrogen bonding in the latter. This is expected to enhance the (A_{as}/A_s) ratio (12) and serves

as a delicate test for such interactions even in cases where frequency shifts are very small. Intramolecular NH$\cdots\pi$-electron bonding is present in allylamine (Table I) since A_{as} is unusually large while A_s remains relatively unchanged from the aliphatic amine value ($A_{as}/A_s = 4.2$ compared with values in the range 1.6–2.9 for saturated amines).

ACKNOWLEDGMENTS

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