

208. NH₂-Stretching Frequencies in Primary Amines.

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Precise frequency values have been obtained for the NH₂ stretching vibrations of a number of primary aliphatic and aromatic amines in solution and in the vapour state.

The greater intensity of the band due to the symmetric NH₂ vibration in aliphatic amines is explained in terms of hybridization changes at the nitrogen atom during vibration.

PRECISE values of N-H stretching frequencies are few since most of the published work has been carried out with the relatively low resolution afforded by a rock-salt prism.

Primary amines give rise to two infrared absorptions, associated respectively with the asymmetric and the symmetric vibration of the NH₂ group, $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$.

The purpose of this study was to obtain precise values for these bands of monomeric primary amines in the vapour state and in carbon tetrachloride solution.

Experimental.—Amines (from British Drug Houses Ltd.) and "AnalaR" carbon tetrachloride used were dried and redistilled several times.

The measurements were made with a Grubb-Parsons G.S.2 double-beam grating spectrometer, the band centres being measured within ± 2 cm.⁻¹.

The vapour studies were carried out in a multiple-reflection cell; ¹ path lengths of 120, 240 cm., etc., were available and the cell could be heated to any desired temperature $\pm 1^\circ$.

The experimental results are tabulated.

NH₂ Bond-stretching frequencies (cm.⁻¹) in primary amines.

	Solution (CCl ₄)		Vapour (path length 120 cm.)		Temp.
	$\nu_a(\text{NH}_2)$	$\nu_s(\text{NH}_2)$	$\nu_a(\text{NH}_2)$	$\nu_s(\text{NH}_2)$	
Methylamine	3398	3344	3425	3360	Room
<i>n</i> -Propylamine	3390	3322	3410	3342	Room
<i>iso</i> Propylamine	3383	3319	3434	3332	32°
<i>n</i> -Butylamine	3387	3324	3412	3348	75
Aniline	3481	3394	3497	3416	150
α -Naphthylamine	3472	3390	3478	3401	200
β -Naphthylamine	3475	3390	3484	3407	200

Discussion.—Except for methylamine, which as the first member of a homologous series is a special case, primary aliphatic amines give rise to two NH absorptions at 3387 ± 5 and 3322 ± 5 cm.⁻¹ in solution; the corresponding vapour values are 3425 ± 15 and 3340 ± 10 cm.⁻¹. For primary aromatic amines, however, they occur at higher frequencies, *viz.*, at 3476 ± 5 and 3391 ± 5 cm.⁻¹ in solution and at 3487 ± 10 and 3408 ± 10 cm.⁻¹ in the vapour state. The average frequency of $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ for aliphatic amines in the vapour state is 3382 cm.⁻¹ and for aromatic amines 3448 cm.⁻¹. This frequency difference can be explained in terms of the configuration of the nitrogen valency bonds.²

In methylamine, and it seems reasonable to suppose in other primary aliphatic amines also, the nitrogen valency bonds are pyramidal.³ In aromatic amines the nitrogen σ -bonds are approximately planar in configuration.⁴ The nitrogen atom is approximately *sp*³-hybridized in aliphatic amines but is close to being *sp*²-hybridized in aromatic amines. This increase in *s*-character of the nitrogen σ -bond-forming orbital in aromatic amines results in shorter and stronger NH bonds, which account for the higher values obtained for the NH₂ stretching frequencies.

Aniline appears to be the only primary aromatic amine previously studied in the vapour phase.^{5,6} Williams, Hofstadter, and Herman,⁶ using a cell of 22 cm. length at 150°, detected one weak absorption at 3573 cm.⁻¹ which they assigned to a NH vibration. In the present study, with a path length of 120 cm. and temperatures of 150–200°, both the $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ absorption bands were recorded for three aromatic amines (Table).

The $\nu_s(\text{NH}_2)$ band of aliphatic amines in the vapour state is much more intense than the $\nu_a(\text{NH}_2)$ band. To a good approximation the only nuclei taking part in the normal vibrations $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ are the nitrogen and the hydrogen atoms, and so the normal co-ordinates, *Q*, can be defined solely in terms of the changes in NH bond lengths during vibration.

The intensity of an absorption band is proportional to the variation of molecular dipole moment, μ , with the normal co-ordinate during vibration, *i.e.*, to $d\mu/dQ$. The electric moment of the NH₂ group can be divided into NH bond moments and the atomic dipole of the lone-pair electrons (Fig. *a*).

A consideration of the form of the $\nu_a(\text{NH}_2)$ vibration shows that the change in dipole moment (symbolized as $+\rightsquigarrow$) as the atoms oscillate is at right-angles to the symmetry axis of the NH₂ group (Fig. *b*); a change of equal magnitude, but along the symmetry axis, will occur for the $\nu_s(\text{NH}_2)$ vibration (Fig. *c*).

¹ White, *J. Opt. Soc. Amer.*, 1942, **32**, 285.

² Orville-Thomas and Parsons, Internat. Meeting European Mol. Spectroscopists, Freiburg i. Br., July, 1957.

³ Nishikawa, Itoh, and Shimoda, *J. Chem. Phys.*, 1955, **23**, 1735.

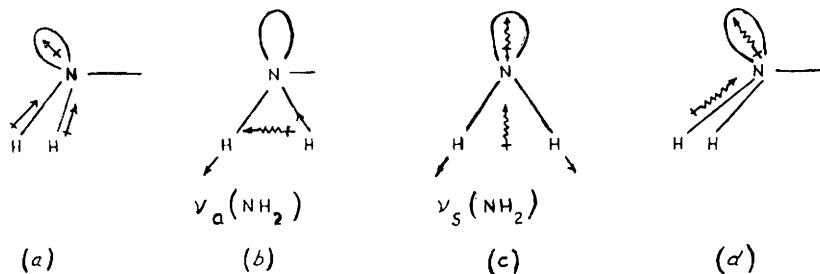
⁴ Coulson, "Valence," Oxford Univ. Press, 1952.

⁵ Kettering and Sleanor, *Physics*, 1933, **4**, 39.

⁶ Williams, Hofstadter, and Herman, *J. Chem. Phys.*, 1939, **7**, 802.

It is now generally accepted that changes of hybridization occur at a central atom as the hybrid bonding orbitals tend to follow the vibrating outer atoms;⁷ evidence has also been adduced for such changes during molecular rotations.⁸ During the $\nu_a(\text{NH}_2)$ vibration the lengthening of one NH bond, which decreases its s -character, is exactly compensated by the gain in s -character of the other NH bond as it contracts. The percentage s -character of the lone-pair orbital remains unchanged and $d\mu/dQ$ depends almost entirely on the polar nature of the NH bond, which is small.⁹ During the $\nu_s(\text{NH}_2)$ vibration there

Variation of electric moment during NH₂ bond-stretching vibrations.



will be a variation in the $s : p$ ratio of the nitrogen orbitals forming bonds to hydrogen. This will be off-set by a compensating change in the s -character of the lone-pair orbital; the atomic dipole will therefore vibrate in phase with the NH bonds. In this case, $d\mu/dQ$ has two components (Figs. *c* and *d*). One component is equal in magnitude to $d\mu/dQ$ for the $\nu_a(\text{NH}_2)$ vibration; the other, much larger contribution arises from the lone-pair electrons forming the atomic dipole. An estimate of the change in dipole moment during the $\nu_s(\text{NH}_2)$ vibration can be obtained by vector addition of the NH₂ bond moments and the atomic dipole when the NH bonds have their maximum and minimum lengths at the extremities of the vibration. This indicates that $d\mu/dQ$ will be greater for the $\nu_s(\text{NH}_2)$ than for the $\nu_a(\text{NH}_2)$ vibration and hence leads to a higher intensity for the $\nu_s(\text{NH}_2)$ band.

In accordance with expectations the same intensity anomaly is found for the vapour-state NH₂ stretching bands in hydroxylamine¹⁰ and in *O*-methylhydroxylamine.¹¹

In the vapour state formamide is planar,¹² the lone-pair electrons contributing to the delocalized π -bonding which embraces the OCN grouping. No atomic dipole is associated with the nitrogen atom and the NH₂ bands are of comparable intensity.¹³ It is interesting to find a similar intensity ratio for the three aromatic amines studied. It seems then that evidence for the considerable sp^2 -hybridized nature of the nitrogen atom in these compounds arises from intensity considerations as well as from the frequency values of the bands.

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⁷ Linnett, *Ann. Reports*, 1953, **50**, 9.

⁸ Orville-Thomas, Cox, and Gordy, *J. Chem. Phys.*, 1954, **22**, 1718; Cox, Gäumann, and Orville-Thomas, *Discuss. Faraday Soc.*, 1955, **19**, 52.

⁹ Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **202**, 548.

¹⁰ Giguère and Liu, *Canad. J. Chem.*, 1952, **30**, 948.

¹¹ Spiers, personal communication.

¹² Kurland, *J. Chem. Phys.*, 1955, **23**, 2202.

¹³ Evans, *ibid.*, 1954, **22**, 1228.