

Studies in Spectroscopy. Part VIII. The N-H Vibration in Secondary Amines.*

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The infrared spectra of dimethylamine, diethylamine, and their trifluoro-derivatives have been measured, and the N-H stretching and deformation bands have been assigned.

PRIMARY alkylamines show two absorption bands in the NH stretching region ($3\ \mu$) arising from the symmetric and asymmetric vibrations, and an NH_2 deformation absorption near $6.2\ \mu$. Secondary alkylamines show only a single NH stretching vibration near $3\ \mu$ and the NH deformation absorption expected at $6.2\text{--}6.5\ \mu$ is apparently absent or is too weak to be of use diagnostically. These correlations have been obtained from spectra of liquid amines, their solutions, or of mulls of solid amines. In connection with a study of bisperfluoroalkylamines (*J.*, 1955, 2532), the infrared spectra of the secondary amines dimethylamine, diethylamine, bis-2 : 2 : 2-trifluoromethylamine, and bistrifluoromethylamine have been recorded, since these compounds enable the effect of progressive increase in negativity of the alkyl groups on the NH stretching and deformation vibrations to be studied. Russell and Thompson (*J.*, 1955, 483) have recently studied the spectra of a number of unsubstituted amines and have noted the marked change in strength of the NH band with structure of the amine.

The NH stretching vibration at $2.99\ \mu$ for dimethylamine vapour is extremely weak ($\epsilon\ 0.7$) and would be missed unless high pressures were used (see Fig.). Diethylamine vapour similarly shows only a very weak NH stretching vibration at $3.00\ \mu$ ($\epsilon\ 0.3$, see Fig. and Table). Neither amine has a band in the $6\text{--}7\text{-}\mu$ region which can immediately be assigned to the NH deformation vibration, although it is possible that this vibration might be masked by the CH deformation band centred on $6.8\ \mu$ which shows several small side bands and inflections (see Fig.). The CH_2 and CH_3 stretching vibrations appear as a doublet at $3.37, 3.55\ \mu$.

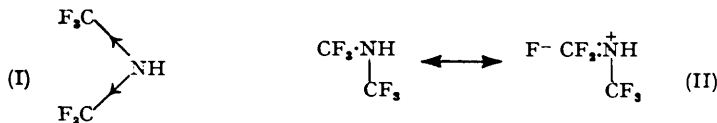
The spectrum of bis-2 : 2 : 2-trifluoroethylamine vapour shows a well-defined NH stretching vibration at $2.92\ \mu$, *i.e.*, at a wavelength distinctly shorter than that for the unsubstituted dialkylamines; the intensity is also markedly increased ($\epsilon\ 5.3$; see Fig.). The CH_2 stretching vibration is at $3.40\ \mu$ and the CH_2 deformation vibration can be assigned either to the strong band at $6.67\ \mu$ ($\epsilon\ 28.0$) or to one or more of the weaker bands which immediately follow it (see Fig.). The $6.67\text{-}\mu$ band is probably the NH deformation vibration, however, [cf. $(\text{CF}_3)_2\text{NH}$, p. 4170], and strong support for this assignment is given by the spectra of *N*-nitro-bis-2 : 2 : 2-trifluoroethylamine and *N*-nitrosobis-2 : 2 : 2-trifluoroethylamine (C.S. No. 233). In these compounds the N-H bond is absent, and the $6.67\text{-}\mu$ band disappears from the spectra, whereas the pattern and position of the weaker bands near $7\ \mu$ remain virtually unchanged (see Fig.); one or more of these weaker bands can thus be assigned to the CH_2 deformation vibration.

The NH stretching vibration for liquid diethylamine and bis-2 : 2 : 2-trifluoroethylamine is at a longer wavelength (3.05 and $2.95\ \mu$ respectively) than in the vapour spectra, revealing the effect of hydrogen bonding possible in the liquid. The intensity of the NH vibration is almost the same for the two liquids (see Table).

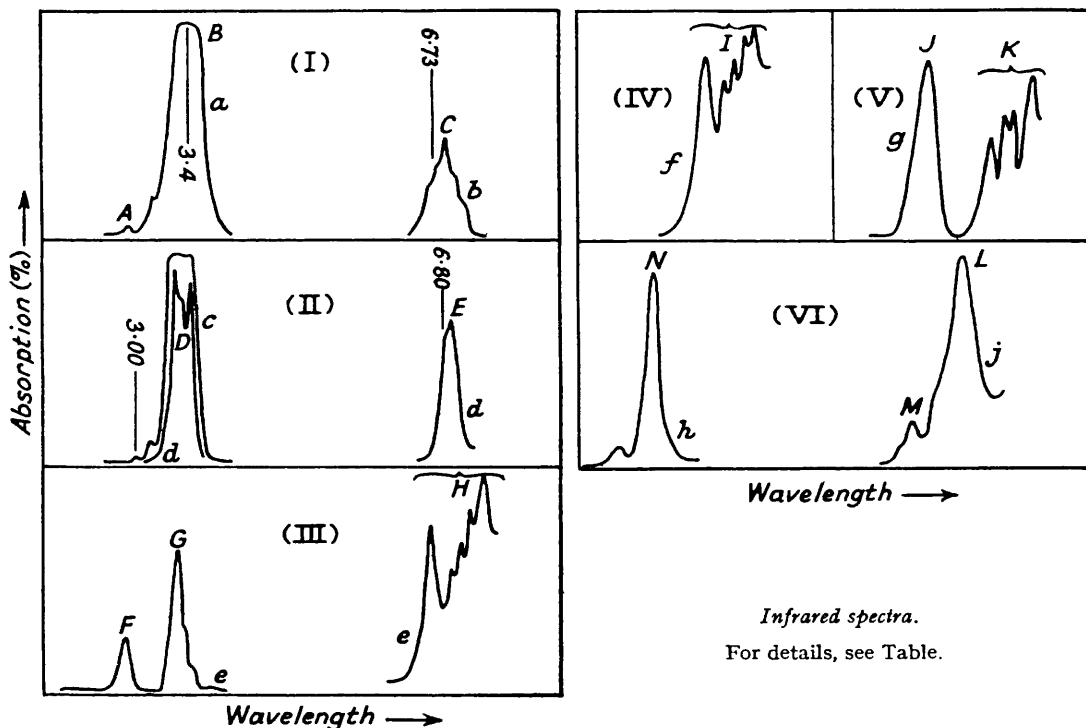
The infrared spectrum of bistrifluoromethylamine is most interesting. The NH stretching vibration appears at $2.89\ \mu$ thus continuing the shift to shorter wavelength with increase in negativity of the alkyl group of the secondary amine; this increase in negativity also causes a large increase in intensity ($\epsilon\ 43$) associated with the positive character of the hydrogen atom (see Fig.). The inductive effect of the trifluoromethyl groups (I) and the hyperconjugation effect of fluorine (II) (*J.*, 1952, 3490; 1953, 992) act in the same direction.

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There are two bands in the 6–7- μ region which require explanation (see Fig.). The weak band at 6.19 μ (ϵ 11) could be assigned to the NH deformation vibration of bis-trifluoromethylamine. This would mean that this vibration is increased in intensity relative



to that in dimethylamine or diethylamine which do not show a band in this region of the spectrum; support for this would be given by the fact that the intensity of an NH deformation band is enhanced by attachment of other electron-attracting groups to nitrogen, *e.g.*, as in *N*-alkylamides which show a band at 6.4–6.6 μ : $-\text{C}(\text{O})\text{NH}- \longleftrightarrow -\text{C}(\text{O}^-)\text{NH}^-$.



The possibility of assigning the 6.65- μ band to the NH deformation vibration must also be considered. In favour of this assignment is first the difficulty of assigning it to anything else, since a band of such intensity (ϵ 310) cannot be ignored; it is not one of the C–F stretching vibrations which lie in the usual region *ca.* 8 μ (7.39, 7.92, 8.33, 8.73 μ). Secondly, there is no possibility of confusion with CH_2 deformation vibrations. Thirdly, the band is at the same position as the 6.67- μ band of bis-2 : 2 : 2-trifluoroethylamine, which is plausibly assigned to the NH deformation vibration. The main argument against this assignment of the 6.65- μ band is its extremely high extinction coefficient (ϵ 310). The increase in intensity parallels that of the NH stretching band (2.89 μ) relative to the corresponding band in bis-2 : 2 : 2-trifluoroethylamine, however, and the evidence thus favours the 6.65- μ band as the NH deformation vibration.

If these assignments for the fluoroalkylamines are correct, then it becomes possible that the corresponding vibration in dimethylamine and diethylamine is masked by the CH_2

deformation vibration at 6.8μ ; examination of the last band does reveal a side peak or inflection at 6.73μ for dimethylamine and 6.80μ for diethylamine; the intensities of these bands are similar to that of the $6.67\text{-}\mu$ band in bis-2 : 2 : 2-trifluoroethylamine. These bands are tentatively assigned to the NH deformation vibration, and a detailed investigation of other dialkylamines in the $6.6\text{--}6.9\text{-}\mu$ region of the spectrum is clearly merited.

EXPERIMENTAL

Spectra were recorded by a Perkin-Elmer Model 21 double beam spectrometer with sodium chloride optics. A 10-cm. gas cell was used for vapour spectra, and the extinction coefficient, ϵ , was calculated from the expression $\epsilon = (D \times 760 \times 22.4 \times 290) / 10 \times p \times 273$ where D = optical density, and p is the pressure in mm. The percentage absorption at a particular wavelength was measured from a base-line drawn through the background (points of zero absorption) of the spectrum; since a balancing absorption cell was not used, this background was usually at 25–30% of the full scale deflection. The extinction coefficients are thus not absolute values, but since the same cell was used for all the vapour spectra, under precisely the same conditions, and with the same base line and slit programme, the ϵ values can be compared with each other. Russell and Thompson (*loc. cit.*) have discussed the dangers of using extinction coefficients, and have employed integrated band areas as a more precise method of comparison of the fundamental NH vibration of various secondary amines, but extinction coefficients have been used for the present comparisons since one is considering 10-fold changes in ϵ , and the errors involved by changes in the apparent half band widths are relatively small. The comparisons are clearly only semi-quantitative, however, particularly since a rock-salt prism, which has poor resolving power in the $3\text{-}\mu$ region, was used. The following slit widths were used :

Wavelength (μ)	2.89	2.95	3.00	3.05	6.15	6.19	6.65
Slit (μ)	37	38	39	39	70	71	75

Sealed cells (nominally 0.025 and 0.050 mm.) and capillary films were used to obtain spectra of the liquids. The results are summarised in the annexed Table.

Compound	C.S. Graph no.	State *	3- μ band ‡			6-7- μ band ‡			CH ₂ vibrations ‡		
			p † (mm.)	λ	Abs. (%)	ϵ	λ	Abs. (%)	ϵ	Stretching (λ)	Deformation (λ)
Me ₂ NH	(I)	249 V	38 <i>a</i>	2.99 <i>A</i>	4.0	0.8	Not certain	—	—	3.39 <i>B</i>	—
			660	2.99	38.0	0.6					
			15 <i>b</i>	—	—	—	—	—	—	{ 6.73 (infl., ϵ 20), 6.82 <i>C</i> ,	
Et ₂ NH	(II)	248 V	95 <i>c</i>	3.00	3.0	0.2	Not certain	—	—	—	6.80, 6.87 <i>E</i> ,
			14 <i>d</i>	—	—	—					
(CF ₃ -CH ₂) ₂ NH...	(III)	246 V	39 <i>e</i>	2.92 <i>F</i>	23.0	5.3	6.67	75.0	28	3.40 <i>G</i>	6.67 <i>H</i> , 6.87 <i>H</i> , 6.97 <i>H</i> , 7.07 <i>H</i> , 7.21 <i>H</i>
(CF ₃ -CH ₂) ₂ NH...	(IV)	245 L	0.25 <i>f</i>	2.95	50.0	—	6.67	83.0	—	3.42	6.67 <i>I</i> , 6.87 <i>I</i> , 6.97 <i>I</i> , 7.07 <i>I</i> , 7.20 <i>I</i>
(CF ₃ -CH ₂) ₂ N-NO ₂	(V)	243 C	<i>g</i>	—	—	—	6.32 <i>J</i>	—	—	—	6.95 <i>K</i> , 7.07 <i>K</i> , 7.16 <i>K</i> , 7.40 <i>K</i> ,
(CF ₃) ₂ NH	(VI)	244 V	2	—	—	—	6.65	54.5	310	None	None
			2	—	—	—	6.19	—	—		
			5	2.89	76.5	42	6.65	86.0	310		
			5	—	—	—	6.15	—	—		
			15 <i>j</i>	2.89	56.0	43	6.65 <i>L</i>	—	—		
			15 <i>j</i>	—	—	—	6.19 <i>M</i>	19.0	11		
150 <i>h</i>	2.89 <i>N</i>	—	—	—	6.65	—	—				
150	—	—	—	—	6.19	86.0	10				
Et ₂ NH	—	247 L	0.025	3.05	51.5	—	Not certain	—	—	3.37, 6.73 (infl., 75% absorption), 3.46, 6.87, 7.25	

* V, vapour; L, liquid; C, capillary film.

† Pressure (gas) or thickness (liquid). Letters define relevant curve in Figure.

‡ Capital italic letters define regions of curves in the Figure in which the maxima occur.

Dimethylamine (Found : *M*, 46.0. Calc. for C_2H_7N : *M*, 45.0) and diethylamine (Found : *M*, 72.0. Calc. for $C_4H_{11}N$: *M*, 73.0) were commercial samples, dried and fractionated *in vacuo*.

Bis-2 : 2 : 2-trifluoroethylamine, b. p. 82° , was dried and redistilled immediately before use (Found : *M*, 181. Calc. for $C_4H_5NF_6$: *M*, 181).

N-Nitrobis-2 : 2 : 2-trifluoroethylamine shows bands at 6.95, 7.07, and 7.16 μ closely similar to those of bis-2 : 2 : 2-trifluoroethylamine. The asymmetric stretching vibration of the NO_2 group at 6.32 μ does not overlap the region under consideration.

N-Nitrosobis-2 : 2 : 2-trifluoroethylamine was prepared by B. J. H. Mattinson; the region between the $N:O$ stretching vibration (6.5 μ) and the bands at 7.02 and 7.05 μ is devoid of even weak peaks. The spectrum is discussed further in the following paper.

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