566. *An Infrared Absorption Band of the* N-*Methyl Group in the Region of* 2800 *cm.*$^{-1}$.*

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The infrared spectra of a variety of organic bases containing the >NMe group include an absorption band of medium to strong intensity between 2760 and 2820 cm.$^{-1}$, which provides a valuable diagnostic test for this group. Structural modifications which involve the lone pair of nitrogen electrons, such as salt formation, or co-ordination of the nitrogen atom to a metal, cause the disappearance of this absorption band; the disappearance is, however, partly masked in the spectra of certain salts by overlapping bands due to >NH$^+$.

It has recently been shown [1] that the infrared spectra of compounds containing the methoxyl group include absorption bands of medium strength between 2832 and 2815 cm.$^{-1}$, on the low-frequency side of the alkyl C–H stretching bands. We now draw attention

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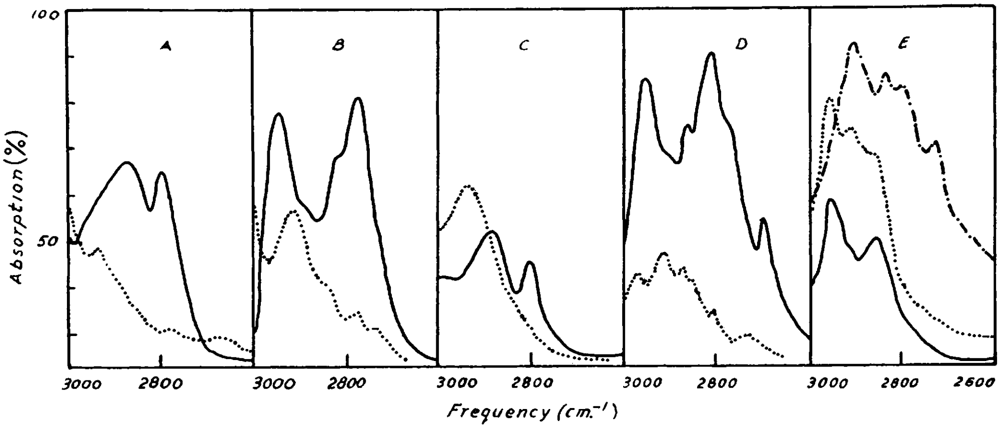
* After the submission of this communication, a paper entitled " Infrared Absorption of NMe and NMe$_2$ groups in Amines," by Hill and Meakins appeared (*J.*, 1958, 760), in which this characteristic band of the :NMe group when attached to, or contained in, an aromatic, aliphatic, or a non-aromatic heterocyclic system is discussed, without reference however to derivatives in which the lone pair of electrons on the nitrogen atom has become occupied in bond formation.

[1] Henbest, Meakins, Nicholls, and Wagland, *J.*, 1957, 1462.

to similar features originally observed in recent investigations[2,3] of organic bases containing the $\gt$NMe group; their spectra, also, exhibit medium to strong absorption bands, between 2760 and 2820 cm.$^{-1}$, which we believe to be characteristic of the $\gt$NMe group, provided that the nitrogen atom retains its lone pair of electrons. The disappearance of this band in the circumstances described below adds to the potential usefulness of the correlation.

Certain typical examples of the *N*-methyl absorption are illustrated in the Figure (*A*—*D*); the Table shows the presence (and, where possible, exact position) or absence of this band in a number of spectra studied by us or recorded elsewhere. We find that the absorption spectrum in the 2800 cm.$^{-1}$ region is sometimes more complex when the nitrogen atom carries an alkyl group other than methyl (Fig. *E*); such cases are not included in the present correlation, although absorption bands very close to 2800 cm.$^{-1}$ have been recorded in the spectra of, for example, diethylamine and triethylamine (Nakanishi *et al.*[4]). However, we consider that the absence of a band of moderate strength in the region of 2800 cm.$^{-1}$ is a reliable criterion for the absence of an $\gt$NMe group with a free lone pair of electrons.

Infrared spectra of organic bases and their derivatives in the region 2600—3000 *cm.*$^{-1}$; *substances in liquid film, or in hexachlorobutadiene mull* (*marked* *), *or in vapour phase* (*marked* †).



A, *Dimethylaniline* (——) *and its methiodide* (. . . .).*
B, *Trimethylamine* (——) † *and tetramethylammonium iodide* (. . . .).*
C, *Monomethylaniline* (——) *and* N-*methylacetanilide* (. . . .).*
D, 1 : 4-*Dimethylpiperazine* (——) *and dibromo*-1 : 4-*dimethylpiperazinepalladium* (. . . .).*
E, *Ethylaniline* (——), NN-*diethyl*-p-*toluidine* (. . . .), *and piperidine* (— · — · —).

Because of the different physical states of the various samples, the relative intensities of the spectra are not comparable.

There is little doubt regarding the nature of the vibration giving rise to these bands. In the infrared spectrum of monomethylamine vapour, the band at 2820 cm.$^{-1}$ has a parallel-type contour and has accordingly been assigned to the symmetrical C–H stretching frequency of the $\gt$NMe group.[5] An earlier assignment of Raman data[6] has suggested that the analogous frequency (2815 cm.$^{-1}$ in the liquid state), and another polarised Raman line at 2880 cm.$^{-1}$, constituted a Fermi-resonance doublet involving the C–H stretching fundamental and the overtone of the symmetrical methyl deformation frequency at 1430 cm.$^{-1}$. This assignment seems slightly preferable, if less specific, but in any case there is no doubt that the intensity of the infrared band is derived principally from the C–H

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[2] Mann and Watson, preceding paper.
[3] Braunholtz and Mann, in the press.
[4] Nakanishi, Goto, and Ohashi, *Bull. Chem. Soc. Japan*, 1957, **30**, 403.
[5] Gray and Lord, *J. Chem. Phys.*, 1957, **26**, 690.
[6] Kohlrausch, " Ramanspektren," Becker and Erler, Leipzig, 1943, p. 216.

stretching vibration of the $>$NMe group. Waldron's infrared data [7] on the methylammonium ion and its *N*-deutero-derivative show that on salt formation the corresponding fundamental C–H stretching vibration has the considerably higher frequency of 2917 cm.$^{-1}$, where it is probably too far removed from the overtone of the CH_3 deformation frequency (2×1428 cm.$^{-1}$) to interact with it strongly by Fermi resonance. Thus the shift of the $>$NMe fundamental is the cause of the disappearance of the strong characteristic band on salt formation. Weak overtone bands may still persist in the 2800 cm.$^{-1}$ region.

The occurrence of a prominent absorption band in the region of 2800 *cm.*$^{-1}$ *in compounds containing* $>$NMe *groups.* (*Samples in liquid film unless otherwise stated.*)

Compound	Band *	Position †	Phase
Aliphatic amines			
$Me{\cdot}NH_2$ [5]	+	2820	(a)
Me_2NH [a]	+		(a)
Me_3N	+	2760, 2810	(a)
$Me{\cdot}NH{\cdot}NH_2$ [a]	+		(a)
$Me_2N{\cdot}NH_2$ [a]	+		(a)
$Me{\cdot}NH{\cdot}NHMe$ [a]	+		(a)
$Me_2N{\cdot}NHMe$ [a]	+		(a)
$Me_2N{\cdot}NMe_2$ [a]	+		(a)
$Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$ [2]	+	2800 (2850, 2750)	(a)
1 : 4-Dimethylpiperazine [2]	+	2810	
1 : 2 : 2 : 4 : 5 : 5-Hexamethylpiperazine	+	2800	
$Ph{\cdot}CH_2{\cdot}NHMe$	+	2780	
Aromatic amines			
$Ph{\cdot}NHMe$	+	2807	
$Ph{\cdot}NMe_2$	+	2795	
p-$Me{\cdot}C_6H_4{\cdot}NMe_2$	+	2790	
m-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$	+	2815	(c)
p-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$	—		(c)
1 : 2-Dihydro-1-methylquinolino (3′ : 2′-3 : 4)quinoline	+	2790	(c)
Salts			
$Me{\cdot}NH_3^+$ [7]	— ‡		(d)
$Me_2NH_2^+$ [b]	— ‡		(c)
Me_3NH^+ [b]	— ‡		(c)
Me_4N^+ [b]	—	see Fig. (B)	(c)
Salts			
$Me_2(n\text{-}C_6H_{13})NH^+$ [4]	—		(b)
$Ph{\cdot}CH_2{\cdot}NHMe_2^+$ [4]	—		(b)
$Ph{\cdot}NMe_3^+$	—		(c)
Co-ordination compounds			
Dibromotetramethylethylenediaminepalladium [2]	—		(c)
Dibromo-1 : 4-dimethylpiperazinepalladium [2]	—		(c)
trans-$(C_2H_4)PtCl_2{\cdot}NMe_3$ [c]	—		(c)
Me_3N,BCl_3 [d]	—		(b)
Me_3N,BF_3 [d]	—		(b)
Miscellaneous §			
$Me{\cdot}NO_2$	+	2790	
$Me{\cdot}NH{\cdot}CO{\cdot}CH_3$ [e]	—		(e)
$Ph{\cdot}NMe{\cdot}CO{\cdot}CH_3$	—		(c)
NN′-Dimethyloxamide [e]	—		(c)
Echinopsine (III)	—		(c)
N-Methylacridone (II)	+	2840	(c)
1 : 2 : 3 : 4-Tetrahydro-1-methyl-4-oxoquinoline (I)	+	2835	
$Me_2N{\cdot}N{=}N{\cdot}NMe_2$ [a]	+		(a)
$Me_2N{\cdot}N{=}CH_2$ [a]	+		(a)
$Me_2N{\cdot}BCl_2$ [f]	+	2800	(a)
$(Me{\cdot}SiH_2)_2NMe$ [f]	+	2802	(a)
$Me{\cdot}SiH_2{\cdot}NMe_2$ [f]	+	2801	(a)
$Me_3Si{\cdot}NMe_2$ [f]	+	2800	(a)
1-Methylpyrrole [g]	+	2812	

* + denotes band present, — band absent.

† Where no position is quoted, the presence of the band was deduced from a published curve or line drawing (*e.g.*, refs. 4 and *a*).

‡ The 2800 cm.$^{-1}$ band is partly overlapped in these spectra by absorption due to $\geqslant NH^+$ groups, but it is nevertheless clear that no prominent bands are present. This is confirmed by the spectra of the $\geqslant ND^+$ derivatives.

§ This section of the Table includes those compounds in which the lone pair may be only partially involved in bond formation.

(a) Gas or vapour.
(b) KBr disc.
(c) Hexachlorobutadiene mull.
(d) Single crystal.
(e) CCl_4 solution.

[a] Pierson, Fletcher, and Gantz, *Analyt. Chem.*, 1956, **28**, 1218. [b] Ebsworth and Sheppard, unpublished work. [c] D. B. Powell, personal communication. [d] Peterson and Bauer, personal communication. [e] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **24**, 408. [f] Ebsworth, unpublished work. [g] Mirone and Drusiani, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1954, **16**, 69.

It is especially noteworthy that medium to strong absorption in the 2800 cm.$^{-1}$ region does not normally occur for molecules in which the nitrogen lone pair of electrons is no longer present as such, *i.e.*, when it is fully involved in bond formation. Thus (see Figure and Table), the absorption band is consistently absent in the spectra of salts (the observations are particularly clear-cut in the case of quaternary compounds: Figs. *A* and *B*),

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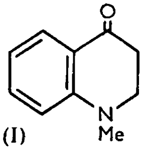
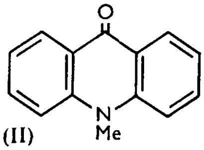
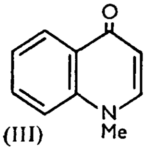
[7] Waldron, *J. Chem. Phys.*, 1953, **21**, 734.

and when co-ordination of the nitrogen atom to a metal occurs [2] (Fig. *D*). It is also absent (as a prominent band) from the spectra of all the amides studied.


(I)


(II)


(III)

The apparently close correlation between the occurrence or absence of significant >NMe absorption and the degree of commitment of the lone pair is shown by the observations on compounds (I), (II), and (III), which are related to the amides. The band is present at 2835 cm.$^{-1}$ in the normal ketone 1 : 2 : 3 : 4-tetrahydro-1-methyl-4-oxoquinoline (I); it is weak (at 2840 cm.$^{-1}$) in *N*-methylacridone (II), and absent in the non-ketonic echinopsine (III). There is also an interesting contrast between the compound $Me_2N{\cdot}BCl_2$ (band present) and the closely related compound Me_3N,BCl_3 (band absent). The occurrence of the band in the Si–N–Me derivatives suggests that, although the basic properties of the nitrogen are reduced by the adjacent silicon atom, there remains some degree of localisation of the lone pair on the nitrogen. Hedberg [8] has proposed that in trisilylamine, $(SiH_3)_3N$, coplanar bonding around the nitrogen atom occurs with about 50% delocalisation of the odd electron pair.

Further, the band is present at 2815 cm.$^{-1}$ in the spectrum of *NN*-dimethyl-*m*-nitroaniline, but absent from that of the *p*-isomer, confirming the marked contribution, in the resonance hybrid of the latter compound, of the quinonoid form having the NMe_2^+ group.

From the data at present available, it appears that the *N*-methyl correlation is rather widely applicable. It has, for example, been found useful in structural studies of salt formation in bases such as 1 : 2-dihydro-1-methylquinolino(3′ : 2′-3 : 4)quinoline.[9]

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[8] Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.
[9] Braunholtz and Mann, *J.*, 1955, 381; cf. ref. 3.