148. *Infrared Absorption of* NMe *and* NMe_2 *Groups in Amines.*

By R. D. Hill and G. D. Meakins.

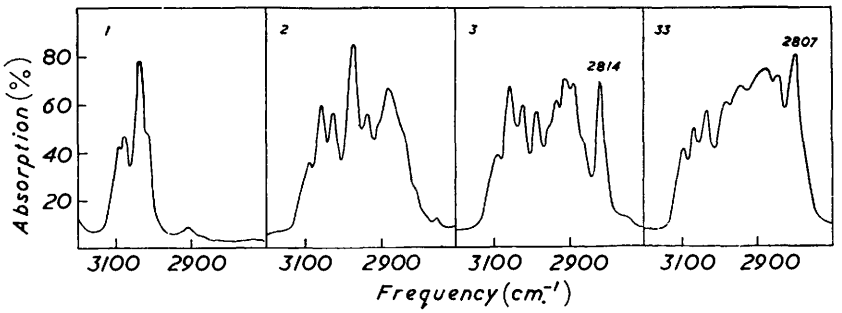
The following correlations have been established for the infrared spectra of amines. An NMe group attached to, or contained in, an aromatic system gives a characteristic band between 2820 and 2810 cm.$^{-1}$. When the group is in an aliphatic, or a non-aromatic heterocyclic, system the band occurs in the 2805—2780 cm.$^{-1}$. range.

The NMe_2 group directly attached to an aromatic system absorbs near 2800 cm.$^{-1}$, while an NMe_2 group not so attached has two specific bands, one between 2825 and 2810 cm.$^{-1}$, and the other between 2775 and 2765 cm.$^{-1}$.

Recently [1] it was shown that the frequencies of the characteristic infrared absorption bands of the methyl group vary according to the nature (carbon or oxygen) of the atom to which the group is attached. This variation led to a method for detecting methoxyl groups in organic compounds by a specific band between 2832 and 2815 cm.$^{-1}$, arising from the symmetric CH stretching vibration of the OCH_3 unit.

The work has now been extended by examining the spectra of a series of amines containing NMe and NMe_2 groups (see Table). This topic has been briefly mentioned by Colthup.[2] With few data available the tentative (erroneous) conclusion reached was that the symmetric CH stretching frequency of the methyl group is increased when the group is attached to nitrogen.

Absorption spectra of 1, *aniline*; *and* 2, N-*ethyl*-; 3, N-*methyl*-; *and* 33, NN-*dimethyl-aniline*.



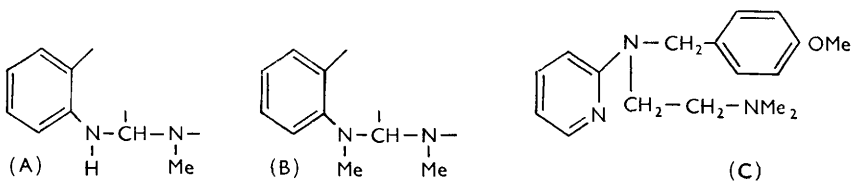
Some amines react with carbon tetrachloride.[3,4] Preliminary work showed that amines (marked * in Table) containing an NH group in aliphatic, or non-aromatic heterocyclic, systems react rapidly at room temperature with the deposition of crystalline

[1] Henbest, Meakins, Nicholls, and Wagland, *J.*, 1957, 1462.
[2] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[3] Russell and Thompson, *J.*, 1955, 483.
[4] Collins, *Chem. and Ind.*, 1957, 704.

material (? amine hydrochlorides). The other compounds in the Table did not react appreciably during the time needed for spectral examination.

The bands in the Table thought to be specifically associated with NMe and NMe_2 groups are in italics, and the amines are divided into four types according to the environment of the basic centre. Inspection of compounds 1 to 19 shows that amines possessing an NMe group attached to, or contained in, an aromatic system [type (I)] are distinguished from the reference compounds by a band occurring between 2820 and 2810 cm.$^{-1}$. The spectra shown in the Figure illustrate the ease with which the NMe group can be detected by the characteristic band on the low-frequency side of the main CH absorption. It is noteworthy that the band is not given by NEt groups [see *N*-ethylaniline (No. 2): note also that the NMe band's intensity in *N*-methylaniline (No. 3) is very close to that in *N*-ethyl-*N*-methylaniline (No. 4)].

With type (II) (Nos. 20—31) the overall distribution of CH bands between the frequency intervals shown in the Table differs from that of type (I). The main change, a higher proportion of bands with frequencies below *ca.* 2950 cm.$^{-1}$, is to be expected on passing from compounds with a high proportion of aromatic hydrogen to the reduced systems of the second type.[5] Despite this increased general absorption in the lower-frequency intervals the NMe group in aliphatic, or non-aromatic heterocyclic, systems can be recognised by a band between 2805 and 2780 cm.$^{-1}$. The alkaloids calycanthine [6] and folicanthine [7] [Nos. 30 and 31, partial structures (A) and (B) respectively] illustrate the possibility of application to natural products.



The intensities of the NMe bands in types (I) and (II) fall into two well-defined groups, and are much higher in the second type. It seems likely that the enhanced intensities of type (II) arise from the increased general absorption below 2950 cm.$^{-1}$ rather than from any appreciable change in the spectral properties of the NMe group. In folicanthine (B), with type (I) and type (II) NMe groups, it is presumably the second type which is mainly responsible for the absorption at 2795 cm.$^{-1}$.

The NMe_2 group directly attached to an aromatic system [type (III)] gives a band near 2800 cm.$^{-1}$, *i.e.*, very close to the position found with the corresponding monomethylamino-group [type (II)]. Thus the main consequence of replacing the hydrogen of an –NHMe group attached to an aromatic system by a second methyl group is to intensify the band ~2800 cm.$^{-1}$ [cf. *NN*-dimethylaniline (No. 33) and *N*-methylaniline (No. 3) in the Table and Figure: this effect supports the assignment of these bands to *N*-methyl vibrations]. Selection of the NMe_2 peak in *NN*-dimethyl-*o*-toluidine (No. 34) is difficult since it possesses two bands, one above and one below the expected frequency. This exceptional behaviour may be connected with substitution *ortho* to the dimethylamino-group.

When the NMe_2 group is not directly attached to an aromatic system [type (IV)] a new pattern emerges. Instead of intensification of the 2805—2780 cm.$^{-1}$ band in the corresponding monomethyl compounds [type (II)], two well-separated bands appear in the 2825—2810 and 2775—2765 cm.$^{-1}$ ranges. The strength of these bands, especially the lower-frequency components, makes detection of this type particularly easy, even in a complex molecule such as the cholesterol derivative (No. 42).

[5] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, pp. 13, 54.
[6] Robinson and Teuber, *Chem. and Ind.*, 1954, 783.
[7] Hodson and Smith, *J.*, 1957, 1877.

CH *stretching bands (cm.$^{-1}$) of* NMe *compounds and, in square brackets, reference amines.*

Most of the compounds were examined in CCl_4 solution: for these molecular extinction coefficients (mole^{-1} l. cm.$^{-1}$) are given in parentheses after the frequency values. Compounds marked * were examined as liquid films and the relative intensities of bands are indicated by s (strong) and m (medium). No intensity values are given for shoulders (sh) on the sides of main bands. All compounds were purified (by fractional distillation or crystallisation) immediately before being examined on a Perkin-Elmer model 21 spectrometer fitted with a calcium fluoride prism. The carbon tetrachloride used as solvent was washed repeatedly with alkali and then water, thoroughly dried and fractionated.

No.		3100	3050	3000	2950	2900	2825	2800	2750	2700
	Type (I). NMe *attached to, or contained in, an aromatic system.*									
[1	Aniline]	3089(15) 3076(17)	3039(40) 3015(17)	—	—	—	—	—	—	
[2	*N*-Ethylaniline]	3089(16) 3057(37)	3023(31)	2972(69)	2930(31)	2879(56)	—	—	—	
3	*N*-Methylaniline	3088(15) 3055(36)	3020(28)	2983(25) 2950(21)	2930(28) 2907(38)	2883(35) 2861 sh	*2814(40)* —	— —	— —	
4	*N*-Ethyl-*N*-methylaniline	3095(23) 3056(30)	3029(23)	2973(>95)	2934(56)	2891(55) 2873(57)	*2817(40)* 2804 sh	—	—	
5	*N*-Methyl-*o*-toluidine	3054(27)	3018(28)	2978(40)	2927(50) 2910(53)	2891(50) 2883 sh	*2816(42)*	—	—	
6	*N*-Methyl-*m*-toluidine	—	3044(35) 3011(29)	2979(39)	2945 sh 2916(53)	2889(44)	*2812(34)*	—	—	
7	*N*-Methyl-*p*-toluidine	—	3046(28) 3028(43)	2980(44)	2921(67)	2877(55)	*2813(41)*	—	—	
[8	Diphenylamine]	3090(27)	3045(53) 3020(34)	—	—	—	—	—	—	
9	*N*-Methyldiphenylamine	3088(31) 3065(42)	3037(45) 3006 sh	—	2942(25)	2881(32)	*2814(28)*	—	—	
[10	*N*-Benzyl-*N*-ethylaniline]	3091(34) 3066(50)	3031(57)	2972(>75)	2930(49)	2896(40) 2875(44)	—	—	—	
11	*N*-Benzyl-*N*-methylaniline	3090(32) 3066(48)	3032(57)	2980(24)	2930(37)	2897(44)	*2818(36)*	—	—	
[12	α-Naphthylamine]	3064(45) 3051 sh	3020(21)	—	—	—	—	—	—	
13	*N*-Ethyl-α-naphthylamine]	3066(50)	3015(21)	2974(67)	2934(29)	2876(42) 2856 sh	—	—	—	
14	*N*-Methyl-α-naphthylamine	3067(52)	3012(22)	2985(27)	2935(28) 2905(34)	2884(35) 2845(19)	*2814(32)*	—	—	
[15	Pyrrole]	No bands with ε>10		—	—	—	—	—	—	
[16	*N*-Ethylpyrrole]	—	—	2978(>50)	2936(32) 2916(16)	2884(20)	—	—	—	
17	*N*-Methylpyrrole	—	—	—	2942(36) 2909(27)	—	*2811(12)*	—	—	
[18	Indole]	3083(20) 3059(28)	3043(24) 3021(11)	—	—	—	—	—	—	
19	*N*-Methylindole	3089 sh 3058(34)	3032(20)	2996(13)	2946(34) 2913(28)	2883(20)	*2817(14)*	—	—	
	Type (II). NMe *in an aliphatic, or a non-aromatic heterocyclic, system.*									
[20	Diethanolamine] *	—	—	—	2926 s	2865 s 2848 s	—	—	—	

No.		3100	3050	3000	2950	2900	2825	2800	2750	2700
	Type (II). NMe *in an aliphatic, or a non-aromatic heterocyclic, system (continued).*									
21	*N*-Methyldiethanolamine	—	—	—	2948(107)	2877(99) 2844(81)	—	*2779(93)*	—	
[22	Pyrrolidine] *	—	—	2955 s	2915 sh	2868 s 2826 sh	—	—	—	
23	*N*-Methylpyrrolidine	—	—	2966(142)	2941(104) 2911(71)	2881(59) 2836(69)	—	*2780(169)*	—	
[24	Piperidine] *	—	—	—	2931 s	2854 s	2805 s	—	2737 m	
[25	*N*-Ethylpiperidine]	—	—	2971(110)	2935(>235)	2886(59) 2856(81)	2802(104)	2767(104) 2755 sh	2731(52) 2703(32)	
26	*N*-Methylpiperidine	—	—	2965(67)	2936(>275)	2888(60) 2856(94)	—	*2782(168)*	2742(69) 2713(53)	
[27	Morpholine] *	—	—	2950 s	2917 s	2850 s	—	2756 m	—	
[28	*N*-Ethylmorpholine]	—	—	2969(150)	2940(98) 2923(87)	2896(76) 2860(116)	2811(133)	2768(80)	2732(27)	
29	*N*-Methylmorpholine	—	—	2967(107)	2940(110) 2916(86)	2897(63) 2861(114)	— —	*2798(160)* 2773(54)	2749(38) 2740(38)	
30	Calycanthine (A)	3079 sh 3052(61)	3022(54)	2964(118)	2929(233) 2907 sh	2857 sh 2843(129)	*2803(140)*	2772(75)	2742 sh 2702(21)	
31	Folicanthine (B)	3069 sh	3049(73)	2962(209)	2935(230) 2910(190)	2866(174) 2851 sh	2807 sh	*2795(190)*	—	
	Type (III). NMe_2 *directly attached to an aromatic system.*									
[32	*NN*-Diethylaniline]	3097(27) 3064(31)	3028(36)	2973(156)	2932(79)	2891 sh 2876(61)	2825 sh	—	—	
33	*NN*-Dimethylaniline	3097(22) 3069(27)	3032(34)	2985(37)	2947(44)	2897 sh 2848(51)	*2807(63)*	—	—	
34	*NN*-Dimethyl-*o*-toluidine	3064(29)	3019(39)	2978(56)	2941(102)	2860(61) *2826(88)*	—	*2785(77)*	—	
35	*NN*-Dimethyl-*m*-toluidine	3079 sh	3043(37)	2975(52)	2943(65) 2917(71)	2883(65) 2851 sh	*2803(65)*	—	—	
36	*NN*-Dimethyl-*p*-toluidine	3098(18) 3071(18)	3007(46)	2975(56)	2942(69) 2917(79)	2871(78)	—	*2797(67)*	—	
	Type (IV). NMe_2 *not directly attached to an aromatic system.*									
37	*iso*Butyldimethylamine	—	—	2952(176)	2910(87)	2871(82) 2856(74)	*2816(104)*	*2767(138)*	2723(42)	
38	1 : 2-Bisdimethylaminoethane	—	—	2970(127)	2944(150)	2860(99)	*2816(179)*	*2769(203)*	2727(45)	
39	Gramine	3083(22) 3059(39)	—	2970(66)	2941(91)	2856(71)	*2813(113)*	*2770(153)*	2720(34)	
40	*N*-Methylgramine	3056(40)	3033(23)	2967(67)	2942(111) 2915(71)	2883(58) 2854(67)	*2815(105)*	*2769(137)*	2728(31)	
41	" Mepyramine base " (C)	3098(20) 3068(29)	3005(65)	2970(99)	2945(125) 2909(88)	2861(77) 2832(94)	*2821(109)*	*2774(125)*	2732(25)	
42	3α-Dimethylaminocholest-5-ene	—	3044(24)	—	2944(>580) 2906 sh	2871(340)	*2812(162)*	*2772(214)*	—	

By reasoning similar to that used with methyl ethers [1] the characteristic bands discussed above can be assigned to the symmetric CH stretching of CH_3 groups attached to nitrogen. Splitting of bands by vibrational coupling, such as that found with the second type of NMe_2 group [type (IV)], occurs frequently when two similar groups are attached to a common atom. It should be stressed that the NMe and NMe_2 correlations are confined at present to amines: preliminary work with substituted amides indicates that they may need modification in different structural types.

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