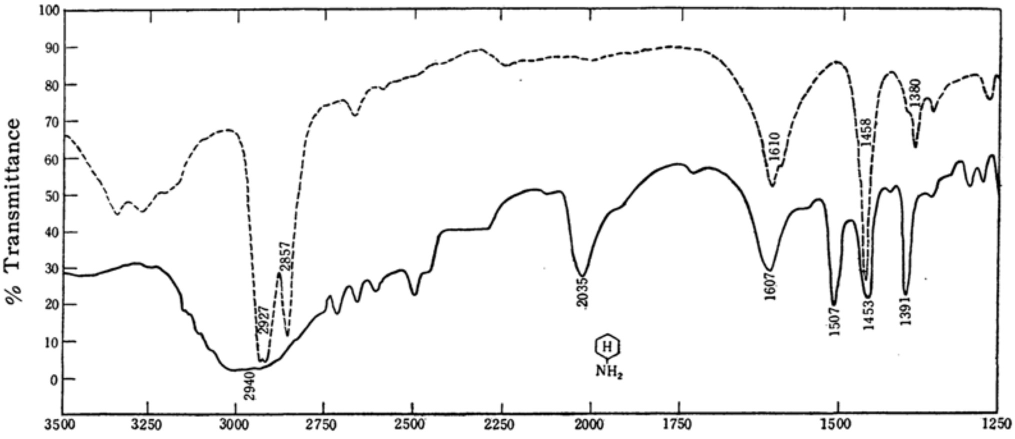
Infrared Spectra of Organic Ammonium Compounds

By Koji NAKANISHI, Toshio GOTO and Mamoru OHASHI

(Received January 7, 1957)

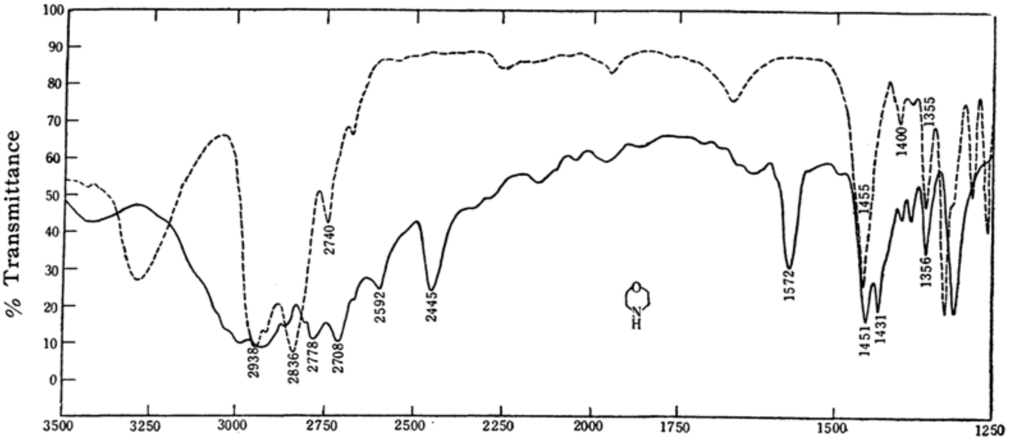
In connection with the structural elucidation of the natural product, roseonine[1] and roseothricin[2], the infrared spectra of about one hundred authentic amines have been compared with the spectra of their hydrochlorides[3] (potassium bromide disk). Representative results are shown in Table I, Figs. 1-4, and are summarised in Table II.



Wave number (cm^{-1})

Fig. 1. Primary amine

Cyclohexylamine (No. 8, 8a): ---- free, —— hydrochloride



Wave number (cm^{-1})

Fig. 2. Secondary amine

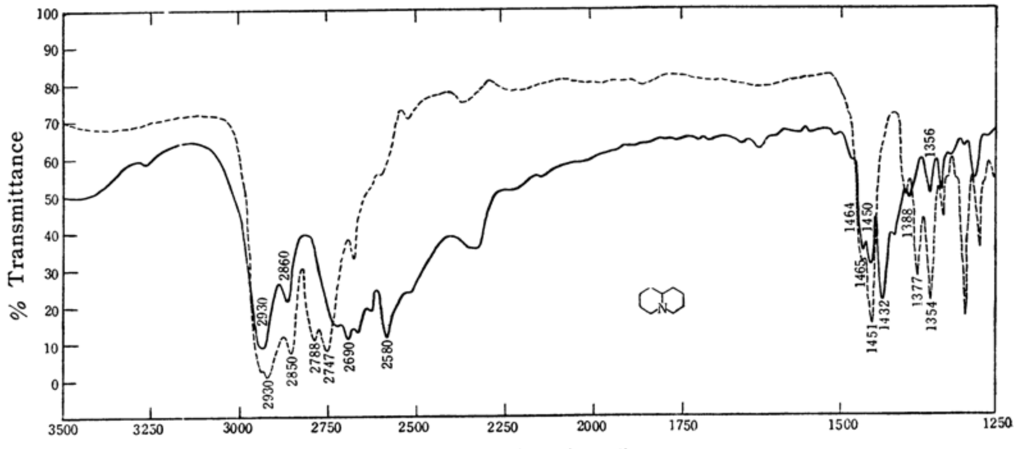
Morpholine (No. 18, 18a): ---- free, —— hydrochloride

---

[1] K. Nakanishi, T. Ito, M. Ohashi, I. Morimoto and Y. Hirata, This Bulletin, **27**, 539 (1954).
K. Nakanishi, T. Ito and Y. Hirata, *J. Am. Chem. Soc.*, **76**, 2845 (1954); K. Nakanishi and M. Ohashi, This Bulletin, (in press).

[2] T. Goto, Y. Hirata, S. Hosoya and N. Komatsu, ibid., **30**, 304 (1957).

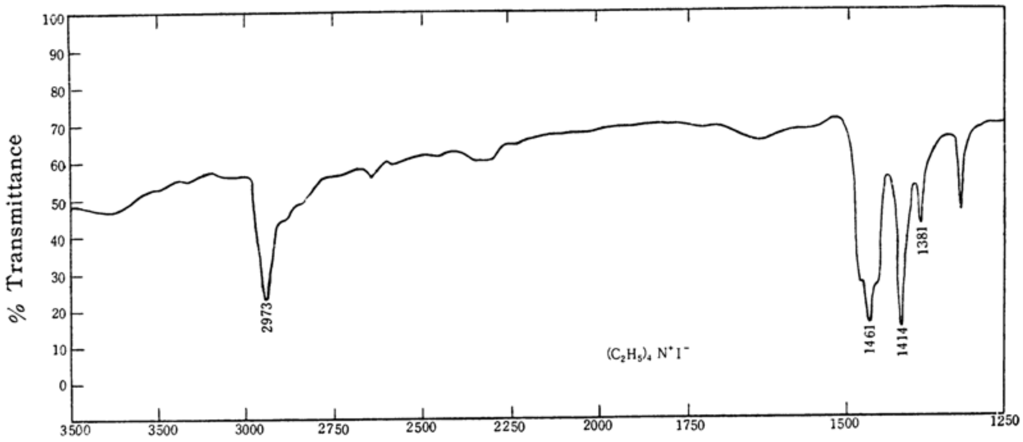
[3] For summaries of existing data on the ammonium group see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen (1954), p. 202, and R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," Interscience (1956), p. 514, 520.



Wave number (cm^{-1})

Fig. 3. Tertiary amine

Quinolizidine (No. 31, 31a): ---- free, —— hydrochloride



Wave number (cm^{-1})

Fig. 4. Quaternary ammonium salt

Tetraethylammonium iodide (No. 50)

Thus primary, secondary, and tertiary amine hydrochlorides, and quaternary ammonium salts can be differentiated fairly accurately from the results of Table II. The characteristic shape and position of the prominent group of absorptions lying at the highest frequency usually suffice to identify primary and tertiary amine hydrochlorides. The corresponding absorption of secondary amine hydrochlorides is less characteristic and in this case absorption in the 1600–1550 cm^{-1} region also has to be taken into account. Open or cyclic azomethines containing the grouping $>$C=N— were not included in the studies. Hydrochlorides of these compounds possess one to several absorptions in the region of 2200–1800 cm^{-1} ("immonium band") in addition to the ammonium band at 2500–2300 cm^{-1}; furthermore the C=N stretching band is shifted 30–40 cm^{-1} toward higher frequency upon attachment of a proton to the nitrogen⁴⁾. Incidentally the region of the ammonium band of azomethine hydrochlorides is roughly similar to that of tertiary amines and seem also to be easily differentiated from normal C—H stretching absorptions (see figures in reference 4). The α, β- and the β, γ-unsaturated tertiary amines and their salts⁵⁾ are not included in the present paper, either

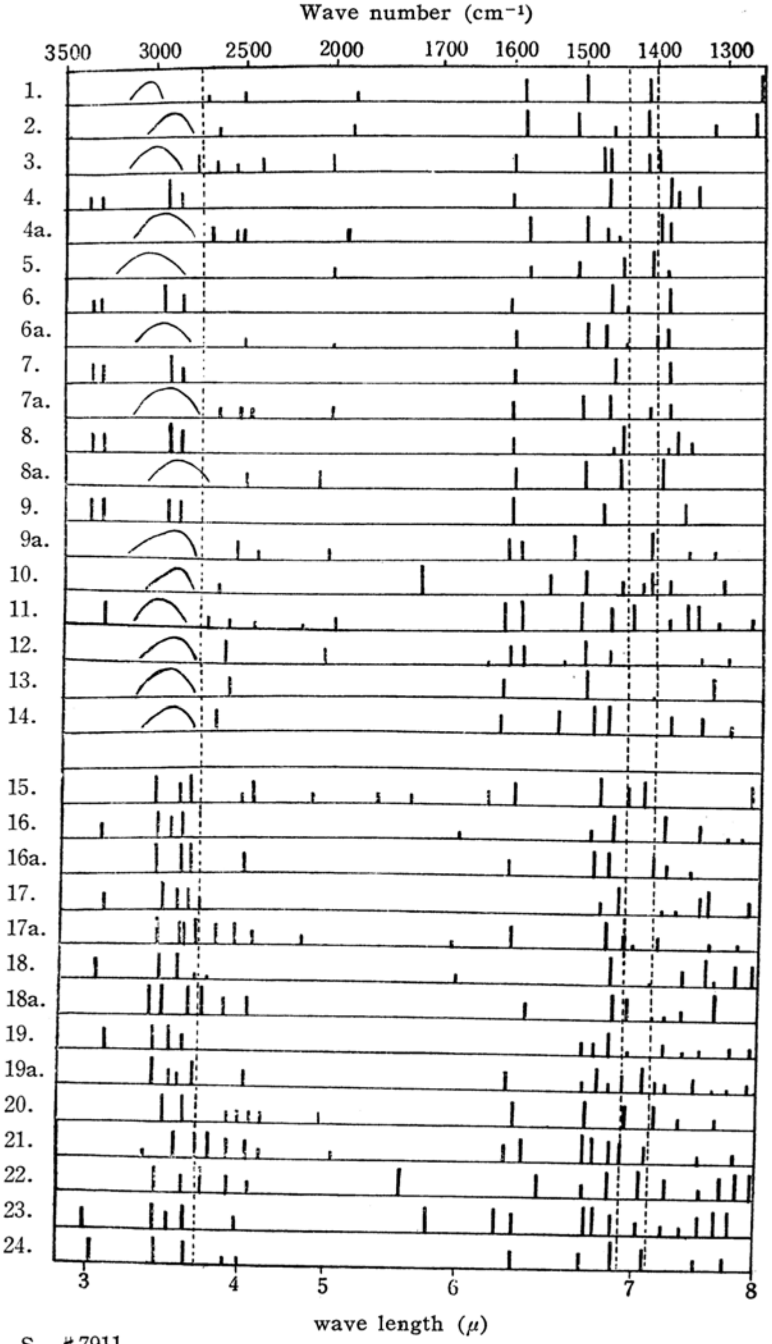
---

4) a. B. Witkop, *Experientia*, **10**, 420 (1954)
b. *idem.*, *J. Am. Chem. Soc.*, **76**, 5597 (1954).

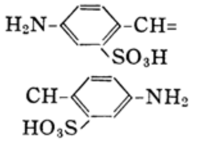
5) N. J. Leonard and V. W. Gash, ibid., **76**, 2681 (1954).

TABLE I

INFRARED ABSORPTION OF AMINES AND AMINE HYDROCHLORIDES

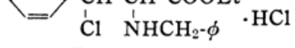


1. Methylamine HCl
S. ♯6369
2. CF$_3$CH$_2$NH$_2$·HCl
S. ♯7339
3. Ethylamine HCl
4. Isopropylamine
4a. Isopropylamine HCl
5. *n*-Propylamine HCl
6. *n*-Butylamine
6a. *n*-Butylamine HCl
7. *n*-Hexylamine
7a. *n*-Hexylamine HCl
8. Cyclohexylamine
8a. Cyclohexylamine HCl
9. Ethylenediamine
S. ♯5319
9a. Ethylenediamine HCl
S. ♯8183
10. Ethyl glycinate HCl
S. ♯6702
11. Indolethylamine HCl
12. Aniline HCl
13. Benzidine 2HCl
S. ♯6621
14.



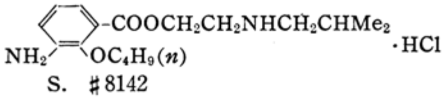
nujol S. ♯5825
15. Dimethylamine HCl
16. Diethylamine
16a. Diethylamine HCl
17. Piperidine
17a. Piperidine HCl
18. Morpholine
18a. Morpholine HCl
19. *dl*-Ephedrine
19a. *dl*-Ephedrine HCl
20. 2-Me-piperidine HCl
S. ♯8774
21. N-Benzylaniline HCl
S. ♯8620

22.



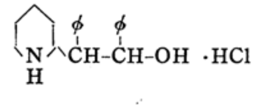
S. ♯7911

23.



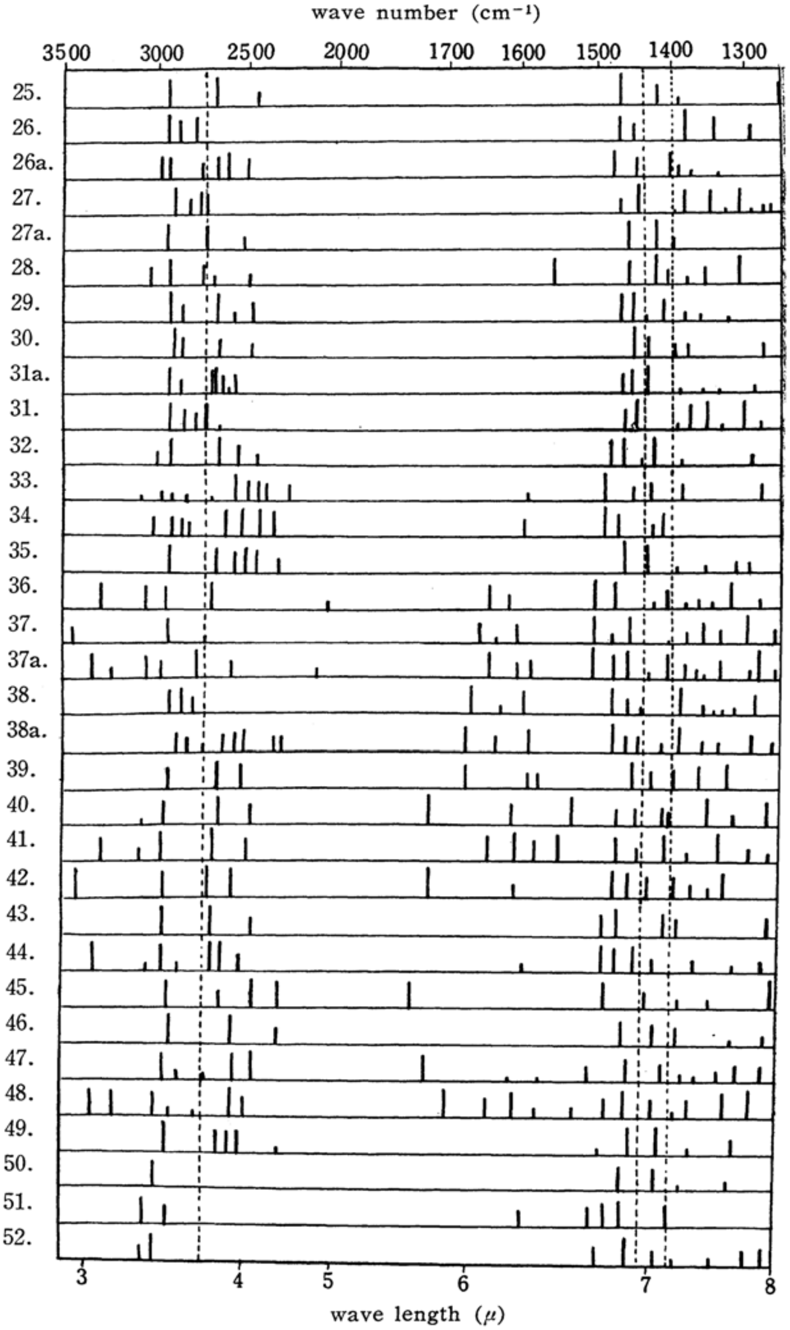
S. ♯8142

24.

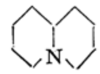


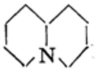
S. ♯6687

TABLE I (continued)

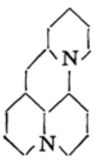


25. Trimethylamine HCl
S. ♯6377
26. Triethylamine
26a. Triethylamine HCl
27. N-Ethylpiperidine
CCl$_4$ soln.
27a. N-Ethylpiperidine HI
28. N-Ethylmorpholine HI
29. Dimethylhexylamine HCl
30. Diethylhexylamine HCl

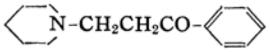
31a.

·HCl

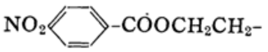
31.


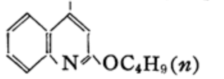
32. Dimethylbenzylamine HCl
33. Dimethylaniline HCl
34. Diethylaniline HCl

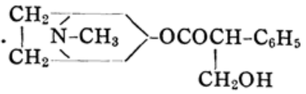
35.

·2HCl

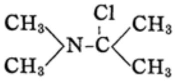
36. Morphine HCl
37. Ethylmorphine
37a. Ethylmorphine HCl
38. Strychnine
38a. Strychnine HCl

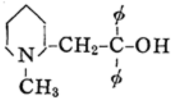
39.

·HCl S. ♯8772

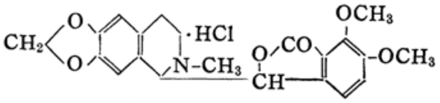
40.

NEt$_2$·HCl S. ♯8419

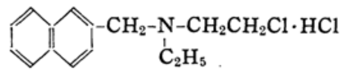
41.

·HCl
S. ♯7502

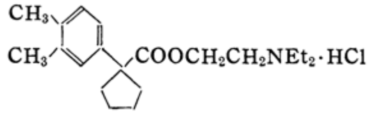
42.

·HCl S. ♯7533

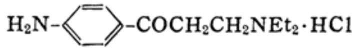
43.

$(CH_3)_2N\text{-}\overset{Cl}{C}(CH_3)_2$
·HCl
S. ♯7388

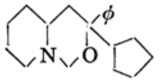
44.

·HCl S. ♯6688

45.

S. ♯7163

46.

S. ♯7444

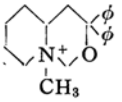
47.


48.


49.  ·HCl S. ♯6678

50. $(C_2H_5)_4N^+ I^-$

51.  $\overset{+}{N}(CH_3)_3 I^-$ S. ♯7333

52.  Br^- S. ♯6679

Dotted line at 2750 cm^{-1} marks approximate differentiating line between amines and hydrochlorides.

Dotted line covering the region 1440-1400 cm^{-1} shows the range of the —CH_2—N^+— band. All data were obtained with KBr disks except when specified. Data taken from the Sadtler Catalog (S. P. Sadtler and Son, Inc., 2100 Arch St., Philadelphia 3, Pa., U. S. A.) are marked with S followed by the number of the spectrum card.

TABLE II

CHARACTERISTIC ABSORPTIONS OF AMINE SALTS

Figures in parentheses show number of samples examined, samples which conformed to the generalisation (+), and samples of which differentiation by means of infrared spectroscopy was somewhat dubious (±), respectively.

Primary amine-HCl (19, +17, ±2)

3200-2800:	s and br, overlaps with C—H stretching bands.
2800-2400:	several weak bands.
2100-1900:	w, absent in some cases.
1610-1550 : 1510-1480	m, obscured in aromatic compounds by the 1600, 1580, and 1500 bands; the second band is usually the stronger.

Secondary amine-HCl (18, +16, ±2)

2800-2400:	s or m, several bands; the overlap with the C—H stretching band is midway between that of primary and tertiary amine hydrochlorides.
2100-1900:	w, absent in some cases.
1600-1550:	m, obscured in aromatic compounds by the 1600, 1580, and 1500 bands.

Tertiary amine-HCl (51, +46, ±5)

2750-2300:	s, several bands; may be clearly differentiated from C—H stretching bands.

The intensity of the NH^+ bending band is too weak to be of any practical value.

Quaternary ammonium salt (4 samples) showed no absorption in the regions specified.

The shift to lower frequencies of the NH^+-stretching band of tertiary amine hydrochlorides has been attributed to a strong hydrogen bond of the type $N^+—H\cdots Cl$[6]; in connection with this, it has been found that the tetraphenyl borates of mono-, di-, and tri-methylamine, in which the hydrogen bond $N^+—H\cdots(C_6H_5)_4B^-$ is sterically hindered, all absorb around 3100 cm^{-1} [7].

A peculiarity, observed in the spectra of many free secondary and tertiary amines, was the appearance of a set of medium to strong bands around 2800–2700 cm^{-1}, i. e., on the lower frequency side of the C—H stretching band*. For example, these are apparent in the spectra of diethylamine (Table I, No. 16), triethylamine (No. 26), piperidine (No. 17), quinolizidine (No. 31), N-dimethylbenzylamine etc. These bands, however, do not interfere with the characterization of amine types, since they disappear upon conversion into the hydrochloride. The same relation seems also to hold for solution spectra; compare the spectra of nicotine and nicotine monohydrochloride (carbon tetrachloride solution) in Fig. 1B of reference 4a, and it is seen that the band at 2809 cm^{-1} in the former compound is absent in the latter.

It has also been noted that a methylene group adjacent to an ammonium nitrogen absorbed in the region 1440–1400 cm^{-1} instead of the normal range around 1470 cm^{-1} (Fig. 5). This is a sort of behavior similar to the well-known displacement to lower frequencies of the bands of methylene and methyl groups alpha to a carbonyl group[8]. Provided that direct comparisons of spectra of amines with their respective hydrochlorides are possible, or that absorption in the 1440–1400 cm^{-1} region by other groups may safely be disregarded, the band would enable one to characterize

---

6) R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953).

7) Personal communication from Dr. K. Nakamoto, Osaka University. See also, *Kagaku-no-Ryoiki*, Extra Number, **23**, 84 (1956).

* Three communications dealing with these bands have recently been published. However, the origin is as yet not clear.
E. Wenkert, D. K. Roychaudhuri, *J. Am. Chem. Soc.*, **78**, 6417 (1965); **79** 1519 (1957).
S. Oseko, *J. Pharm. Soc. Japan*, **77**, 118 (1957).

8) S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).
R. N. Jones and A. R. H. Cole, *J. Am. Chem. Soc.*, **74**, 5648 (1952).
R. N. Jones, A. R. H. Cole and B. Nolin, ibid., 5662.

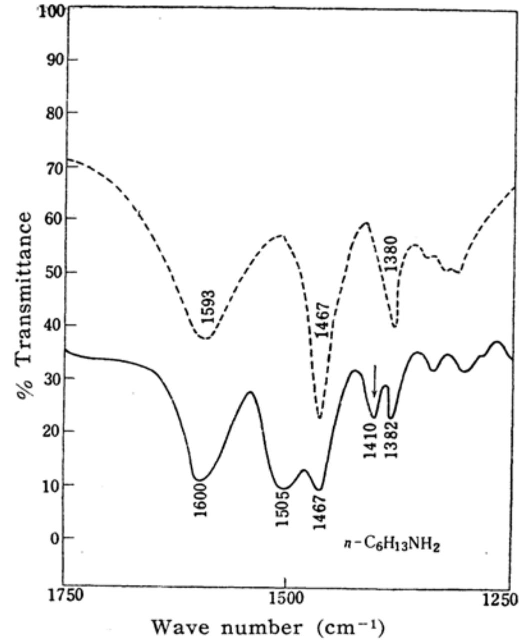


Fig. 5. —CH_2—N^+— band
n-Hexylamine: ---- free, —— hydrochloride

the grouping —CH_2—N^+—. Thus the spectra of isopropylamine hydrochloride and cyclohexylamine hydrochloride (Fig. 1) which lack the adjacent methylene group show no (additional) band in this region. Amongst 74 ammonium salts devoid of groupings which could absorb around 1420 cm^{-1}, e. g., —COOH, —OH, —$CONH_2$, —$COOCH_3$, —CH_2CO—, 62 gave positive results, 5 gave somewhat dubious results, and 7 gave negative results. With amines containing the above-mentioned groups, characterization of the —CH_2N— group was equally possible in most cases by comparing the spectra of the free amine and its hydrochloride.

Infrared Absorption Measurements.—The spectra were recorded on a Hilger H 800 double beam instrument equipped with sodium chloride optics; whenever necessary the region 1300-1750 cm^{-1} was measured with a calcium fluoride prism. Potassium bromide disks were used, and the die and handpress were those supplied by the Hilger and Watts Co. Analytical grade potassium bromide was ground to pass a 200 mesh sieve and dried at 150°C for 24 hours. The samples (ca. 1 mg.) were ground evenly with 300 mg. of this potassium bromide for 5 min.

The authors wish to express their gratitude to Professor Yoshimasa Hirata for his guidance and interest in this research, to Drs. Junji Koizumi, Nihon Shinyaku Co., Shigeo Oseko, Dainihon Pharmaceutical Co., Akira Fujino and Masao Yamaguchi, Osaka City University, for the gifts of valuable amines, and to Dr. Hideo Kamio, Takeda Pharmaceutical Co. for giving them access to the Sadtler Catalog. They are also grateful for a grant from the Ministry of Education for the purchase of the spectrophotometer.

Chemical Institute, Nagoya University
Chikusa, Nagoya