An Account on the Infrared Absorption of Guanidiniums

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The infrared spectra of several guanidine hydrochlorides have been examined in connection with the structural elucidation of roseonine[1] and roseothricin[2]. Except for a few scattered data[3] it seems that as yet no systematic study has been undertaken on the infrared absorption of guanidines, and accordingly, though the studies are far from comprehensive, results of diagnostic value are reported herein. The spectra are summarised in Fig. 1. The apparent general tendency is that with unsubstituted and symmetrically trisubstituted guanidine hydrochlorides (Nos. 1, 9 and 10) there is only a single strong absorption around 1650 cm^{-1}, whilst with mono- and disubstituted guanidine hydrochlorides (Nos. 2—8) there are two conspicuous bands in the region 1700—1580 cm^{-1}. Furthermore the separation between the two bands is generally wider with disubstituted guanidiniums (ca. 90 cm^{-1}) than with monosubstituted guanidiniums (ca. 20 cm^{-1}). For the sake of convenience we would like to refer to these bands as the guanidinium bands, and in cases when splitting is observed as the guanidinium I (higher frequency) and II (lower frequency) bands. The guanidinium band(s) apparently corresponds to the band around 1660 cm^{-1} of free guanidines which is assigned to the C=N stretching[4]. With guanidine hydrochlorides it would be due to an antisymmetric stretching of the carbon nitrogen bonds in the guanidinium

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[1] K. Nakanishi and M. Ohashi, following paper.

[2] T. Goto, Y. Hirata, S. Hosoya and N. Komatsu, following paper.

[3] H. M. Randall, R. G. Fowler, N. Fuson, J. R. Dangl, "Infrared Determ. of Org. Structures", D. van Nostrand (1949).

[4] E. Lieber, D. R. Levering and L. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

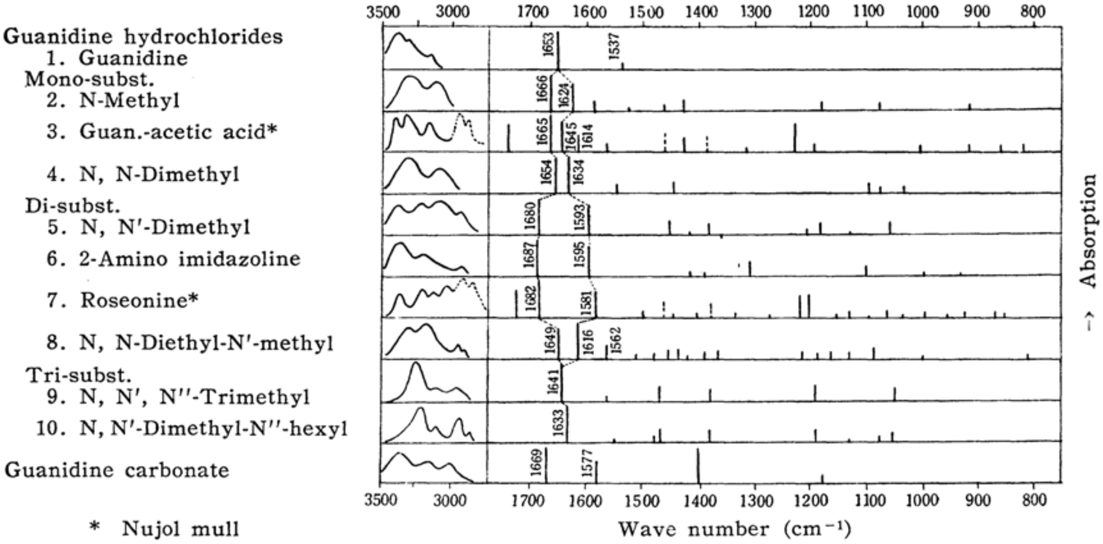

Fig. 1

group, probably coupled to some extent with NH_2^- bending vibrations[5]. A single antisymmetric carbon nitrogen stretching vibration would be expected to be infrared active with unsubstituted and sym. trisubstituted guanidiniums, whilst two such vibrations would be expected with mono- and disubstituted guanidiniums; these expectations are thus in agreement with experimental observations. Since the symmetric carbon nitrogen stretching vibration of guanidiniums reveals itself as a strong absorption around 1000 cm^{-1} in the Raman spectra[6], some of the weak infrared bands around 1000 cm^{-1} could possibly be due to this sort of vibration; however they are of no diagnostic value. The absorption of guanidine carbonate (No. 11) which show bands at 1669 and 1577 cm^{-1} as compared to the single band at 1653 cm^{-1} of guanidine hydrochloride is anomalous. Since the spectra were all recorded in the solid state this is probably due to the influence of the negative ion on the crystal structure, and accordingly the results mentioned in the present paper are valid only for the hydrochlorides.

The relationship between an amino group and a positively charged ammonium group is probably of a continuous nature with no qualitative difference between them. Taking into account the fact that typical ammonium absorptions (N^+H stretching) occur below ca. 3200 cm^{-1} [7], whereas typical amine absorptions (N–H stretching) occur above 3200 cm^{-1}, the following generalisations regarding charge distribution within the guanidinium group may be inferred from the absorption of the guanidiniums in the 3000 cm^{-1} region. Namely, the position of the absorptions in this region (Fig. 1.) corresponds to those of free amines rather than to amine salts, and this suggests that the positive charge resides mainly on the central carbon atom (I) rather than being distributed over the entire guanidinium group (II). This is further supported by the

I II

fact that the absorptions of sym-trisubstituted guanidine hydrochlorides (Nos. 9, 10) which, according to structure I, would mainly possess only —NHR groups, reveal themselves as a more or less single major band, whereas those of other guanidiniums (which sould possess $—NH_2$ groups as well) reveal themselves as a broad band with two or more maxima, a behavior similar to that of free secondary and primary amines, respectively.

Experimental

The guanidines were prepared according to the following methods.

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[6] J. T. Edsall, *J. Phys. Chem.*, **41**, 133 (1937).

[7] K. Nakanishi, T. Goto and M. Ohashi, This Bulletin, **30**, 403 (1957).

N-Methyl guanidine picrate, m. p. 196—198°[8].

N, N-Dimethyl guanidine picrate, m. p. 216—218°[8].

N' N'-Dimethyl guanidine picrate, m. p. 174—175°[9].

2-Aminoimidazoline picrate, m. p. 217°.

N, N-Diethyl-N′-methyl guanidine was prepared by the condensation of methyl isothiocyanate and dimethylamine, followed by treatment with ammonia and mercuric oxide in absolute ethanol solution. This is a new compound. Picrate, yellow plates, m. p. 128—129°.

Anal. Found: C, 40.60, 40.55, H, 4.88, 5.12, N, 23.19, 23.38%. Calcd. for $C_{12}H_{18}O_7N_6$: C, 40.22, H, 5.06. N, 23.46.

N, N′, N″-Trimethyl guanidine picrate, m. p. 210—212°[10].

N, N′-Methyl-N″-*n*-hexyl guanidine was prepared by the treatment of N-methyl-N′-*n*-hexyl thiourea with methylamine and mercuric oxide in absolute ethanol. This is also a new compound but the picrate could not be obtained crystalline, and the crude hydrochloride was submitted directly to infrared measurements.

The picrates were treated with dilute hydrochloric acid, the liberated picric acid was extracted with ether, and the aqueous layer was evaporated to dryness in vacuo to give the respective hydrochlorides.

Infrared absorption measurements. The spectra were recorded on a Hilger H 800 double beam instrument equipped with a sodium chloride prism. Potassium bromide disks were used, and the die and the handpress were those supplied by 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. 0.5 mg.) were ground evenly with 300 mg. of this potassium bromide for 5 minutes.

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