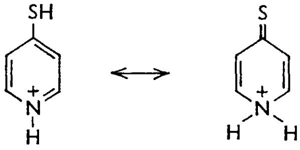
604. *The Infrared Spectra and Structures of the Hydrochlorides of 4-Mercaptopyridine and 4-Mercaptoquinoline.*

By E. Spinner.

An examination of the infrared spectra of the hydrochlorides of 4-methylthio- and 4-mercapto-pyridine and -quinoline has shown the latter to have cations that are protonated at the sulphur atom.

2- and 4-Mercaptopyridine and related compounds are known to be thiones and not genuine mercapto-compounds.[1-3] Protonation of a thione (thioamide) might occur preferentially at the sulphur atom, giving a cation such as (I), or at the nitrogen atom, to give one of the type of (II). There is no agreement concerning the preferred site of protonation in open-chain thioamides. The thiourea cation shows no appreciable Raman band in the region 2000—2600 cm.$^{-1}$ where SH compounds normally have a strong Raman band, and was therefore taken to be *N*-protonated.[4] However, the infrared [4-6] and ultraviolet [6-8] spectra of cations of thioureas and thioamides have been variously interpreted in terms of both *N*- [4,8] and *S*-protonation [5,6] and further work is required to settle this problem.



(I) (II)

The electronic spectra of pyridinethione and quinolinethione cations [1] are not strikingly like those of the cations of the corresponding methylthio-compounds [*e.g.*, ion (I; SMe in place of SH)]; however, the band displacements observed there are normally smaller than the shift, of 22 mμ, found [9] between *p*-nitrothiophenol and *p*-nitrothioanisole, and the electronic spectra seem compatible with either type of cation structure. Infrared spectra, on the other hand, can be expected to decide clearly between the two alternatives in favourable circumstances, because 2- and 4-pyridinethiones, quinolinethiones, etc., show very intense absorption in the range 1090—1190 cm.$^{-1}$ which, in most cases,[2] can be unambiguously assigned to C=S stretching (this assignment has been accepted by Jones and Katritzky [3b]).

2-Methylthio-pyridine and -quinoline, unfortunately, show fairly intense absorption near 1100 cm.$^{-1}$ in spite of not being thiocarbonyl compounds; also, they are quite weak bases (pK_a —1·07 and —1·44, respectively); after dissolution in hot concentrated hydrochloric acid, the latter crystallized as the neutral species, and the former evolved hydrogen sulphide. The study of the cations of α-mercaptoaza-aromatic compounds was therefore not pursued. On the other hand, 4-mercaptopyridine and 4-mercaptoquinoline, two typical γ-mercaptoaza-aromatic compounds, formed stable hydrochlorides. Such infrared bands as these substances show near 1100 cm.$^{-1}$ are too weak to be assignable to thiocarbonyl stretching, which is good evidence for the absence of a thiocarbonyl group. Moreover, the infrared spectra of these compounds resemble those of the hydrochlorides

[1] Albert and Barlin, *J.*, 1959, 2384.
[2] Spinner, *J. Org. Chem.*, 1958, **23**, 2037; *J.*, 1960, 1237.
[3] Jones and Katritzky, *J.*, (*a*) 1958, 3610; (*b*) 1960, 2947.
[4] Spinner, *Spectrochim. Acta*, 1959, **15**, 95.
[5] Kutzelnigg and Mecke, *Spectrochim. Acta*, 1961, **17**, 530.
[6] Janssen, *Spectrochim. Acta*, 1961, **17**, 530.
[7] Rosenthal and Taylor, *J. Amer. Chem. Soc.*, 1957, **79**, 2684.
[8] Hosaya, Tanaka, and Nagakura, *Bull. Chem. Soc. Japan*, 1960, **33**, 850.
[9] Burawoy, Critchley, and Thompson, *Tetrahedron*, 1958, **4**, 403.

of 4-methylthiopyridine and 4-methylthioquinoline, respectively, very closely, as is to be expected if the former ions have structures of type (I). (The replacement of SH by SMe should have only a slight effect on most of the infrared spectrum.)

One prominent difference between the spectra of the mercapto- and the thiomethyl compound cation is the band near 2250 cm.$^{-1}$ shown only by the former, which is undoubtedly due to S–H stretching. Its location, to be compared with 2570 cm.$^{-1}$ for ordinary thiophenols in the liquid phase, shows that the SH bonds are involved considerably in hydrogen-bonding. However, the bonds principally involved in hydrogen-bonding are the $^+$N–H bonds (stretching frequency, 2700 ± 80 cm.$^{-1}$), as is to be expected for ions of this type. A band in the spectra of mercapto-compound cation at 1097 ± 6, for which the cations of the methylthio-compounds seem to show no counterpart, is tentatively assigned to S–H in-plane bending. Assignments are made (see below) for most of the main bands in the pyridinium-ion spectra, but for the quinolinium ions this cannot be done at present.

Experimental and Results.—The compounds, kindly provided by Drs. G. B. Barlin and W. L. F. Armarego, were purified as the neutral species and converted into the hydrochlorides by means of either concentrated hydrochloric acid or hydrogen chloride in methanol. Infrared spectra were taken as before.[10] In the following list of band peaks, wave numbers are given in cm.$^{-1}$, followed by intensities (in parentheses) with the same significance as before,[10] and by band assignments (in bold type); aromatic vibrations are numbered according to the scheme used by Lord and his co-workers.[11] Very weak bands are, in general, not given.

4-*Mercaptopyridine hydrochloride:* 3047 (0·2), **C–H st**; 2970 (0·3), **C–H st**; 2900 (0·1); 2805 (0·4), 2774 (0·65), **$^+$N–H st**; 2725 (0·1), 2612 (0·1); 2270 (0·5), **S–H st**; 1941, (0·25); 1829 (0·1); 1625 (1·0), **8a**; 1598 (0·7), **8b**; 1498 (0·4), **19a**; 1479 (1·1), **19b**; 1371 (0·3); 1303 (0·1); 1248 (0·4); 1197 (0·5), **9a?**; 1132 (0·2); 1108 (0·5); 1092 (0·4), **–S–H i.p. be**; 1020 (0·1); 1009 (0·15), **1**; 975 (0·1); 794 (1·0), **11**; 715 (0·2).

4-*Methylthiopyridine hydrochloride:* 3035 (0·1), **C–H st**; 2981 + 2975 (0·2), **C–H st**; 2767 (0·3), 2725 (0·8), **$^+$N–H st**. 2690 (0·2), 2672 (0·4), 2629 (0·4); 1930 (0·1); 1832 (0·1); 1625 (1·0), **8a**; 1600 (0·8), **8b**; 1505 (0·3), **19a**; 1485 (0·6), **19b**; 1435 (0·3) **Me be**; 1383 (0·3) **Me be + ?**; 1302 (0·03); 1242 (0·02); 1219 (0·15); 1192 (0·05), **9a?**; 1131 (0·15); 1113 (0·7); 1015 (0·03); 984 (0·1), **1**; 803 (1·0), 11; 731 (0·1), **C–S–C antisym. st ?**.

4-*Mercaptoquinoline hydrochloride:* 3068 + 3061 (0·3), **C–H st**; 2750 (0·4), 2708 (0·9), **$^+$N–H st**; 2658 (0·2); 2225 (0·5), **S–H st**; 1985 (0·2); 1953 (0·1); 1827 (0·1); 1624 (0·4); 1610 (0·1); 1585 (1·1); 1537 (0·2); 1487 (0·3); 1408 (0·6); 1388 (0·4); 1370 (0·2); 1277 (0·6); 1261 (0·3); 1224 (0·35); 1205 (0·25); 1163 (0·2); 1149 (0·1); 1103 (0·2), **–S–H i.p. be**; 1028 (0·3); 1007 (0·1); 975 (0·3); 916 (0·1); 837 (0·1); 826 (0·1); 813 (0·6), **C–H o.p. be**; 748 (0·4); 669 (0·1).

4-*Methylthioquinoline hydrochloride:* 2985 (0·2), **C–H st (Me)**; 2672 + 2644 (0·7) **$^+$N–H st**; 1813 (0·05); 1628 (0·3); 1616 (0·2); 1586 (0·8); 1540 (0·1); 1479 (0·5); 1409 (0·6); 1390 (0·35); 1367 (0·05); 1283 (0·4); 1253 (0·05); 1232 (0·1); 1198 (0·5); 1143 (0·1); 1032 (0·15); 988 (0·3); 942 (0·1); 915 (0·1); 821 (0·7), **C–H o.p. be**; 804 (0·3); 775 (0·15); 760, (0·4); 671 (0·1).

DEPARTMENT OF MEDICAL CHEMISTRY, INSTITUTE OF ADVANCED STUDIES,
THE AUSTRALIAN NATIONAL UNIVERSITY,
CANBERRA, AUSTRALIA.

[*Received, December 28th,* 1961.]

---

[10] Spinner, preceding paper.

[11] Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, **21**, 1170; Lord, Marston, and Miller, *Spectrochim. Acta*, 1957, **9**, 113.