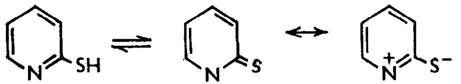
250. *The Infrared Spectra of Some* N-*Heteroaromatic Mercapto-compounds and of Their* N-*Methyl and* S-*Methyl Derivatives.*

By E. Spinner.

The infrared spectra of 2- and 4-mercapto-pyridine, -pyrimidine, and -quinoline, of 2-mercapto-pyrazine and -quinoxaline, of 1-mercaptoisoquinoline, of their *N*-methyl and *S*-methyl derivatives, of 3-mercaptopyridine and 8-mercaptoquinoline, and their *S*-methyl derivatives, have been determined. All the α- and γ-mercapto-aza-compounds are thiocarbonyl compounds. A strong band in the vicinity of 1140 cm.$^{-1}$ can normally be assigned to the thiocarbonyl stretching vibration.



(I) (IIa) (IIb)

The α- and γ-mercapto-derivatives of *N*-heteroaromatic compounds (α- and γ-mercapto-aza-aromatic compounds) are capable of tautomerism, as exemplified by structures (I) and (II) for 2-mercaptopyridine. From an ultraviolet spectral study[1] it was concluded some time ago that 2- and 4-mercapto-pyrimidine (in solution) are present mainly in the thiolactam forms analogous to (II). More recently, 2- and 4-mercaptopyridine,[2,3] and many more complicated α- and γ-mercaptoaza-aromatic compounds,[2,4] have been found

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[1] Boarland and McOmie, *J.*, 1951, 1218.

[2] Albert and Barlin, " Current Trends in Heterocyclic Chemistry," Butterworths, London, 1958, p. 51.

[3] R. A. Jones and Katritzky, *J.*, 1958, 3610.

[4] Albert and Barlin, *J.*, 1959, 2384.

to be present in water principally as thioamides, by a comparison of their ultraviolet spectra and ionization constants with those of their *N*-methyl and *S*-methyl derivatives. Indeed, in aqueous solution, the preponderance of the thioamide form over the mercapto-form * is always even greater [2,4] than is the preponderance of the amide over the hydroxy-form for the corresponding hydroxyaza-compound.[5]

In systems of this type it is not common for a change of medium to change the tautomeric equilibrium position drastically (cf., however, some hydroxyacridines [6a] and hydroxyphenazines [6b]). A study of some α- and γ-mercaptoaza-aromatic compounds in less polar media, by an independent method such as infrared spectroscopy, nevertheless seemed desirable. The infrared spectra obtained do, in fact, show that all the α- and γ-mercaptoaza-derivatives examined in this work are in the thione form, both in the solid state and in solvents of low polarity. Since the infrared spectra of 2- and 4-mercaptopyridine, recently determined (but not described) by Jones and Katritzky,[3] are different from those of 2- and 4-substituted pyridines, these authors concluded that these substances are thiones (cf. also Spinner [7]).

EXPERIMENTAL

Materials.—Most of the substances examined had been prepared in this Department.[4] 2- and 4-Mercaptopyrimidine were kindly supplied by Dr. D. J. Brown; 3-mercaptopyridine was obtained from the *S*-benzoyl derivative,[4] and 2-methylthiopyrimidine from 2-mercaptopyrimidine.[1] In the measurement of the spectra of 3-mercaptopyridine and 8-mercaptoquinoline care was taken to avoid oxidation, to which these substances are prone.

Infrared Spectra.—These † were determined as before.[8]

RESULTS AND DISCUSSION

The structures of the *N*-methyl and *S*-methyl derivatives examined in this work are all known *a priori*, but those of the α- and γ-mercapto-compounds have been established only for aqueous solutions.[4] Three features in the infrared spectrum enable one to differentiate between the mercapto-form and the thioamide form; these are the presence or absence of (1) strong absorption in the range 1600—1630 cm.$^{-1}$, due to a skeletal stretching vibration, (2) a strong thiocarbonyl stretching band near 1140 cm.$^{-1}$, and (3) an N–H stretching band.

The High-frequency Skeletal Stretching Vibrations.—Neither of the two genuine mercapto-compounds examined (3-mercaptopyridine and 8-mercaptoquinoline), and none of the *S*-methyl derivatives examined, shows an intense band in the range 1600—1700 cm.$^{-1}$: for these substances the strongest band observed in this region is a medium-intensity band at 1614 cm.$^{-1}$ in the spectrum of 2-methylthioquinoline. On the other hand, strong or medium-strong bands in the range 1600—1630 cm.$^{-1}$ are shown by all *N*-methylthioamides examined, and by all α- and γ-mercaptoaza-compounds, except 4-mercaptoquinoline, the corresponding strong band for which is at 1578 cm.$^{-1}$ (1587 cm.$^{-1}$ in solution); that for its *N*-methyl derivative is at 1596 cm.$^{-1}$, *i.e.*, at somewhat higher frequencies; however, in the spectrum of 4-methylthioquinoline there is no intense band with a frequency than 1500 cm.$^{-1}$.

These strong bands listed in Tables 1 and 2, at frequencies that are higher than those observed for the aromatic skeletal stretching motions in the methylthio-compounds, are undoubtedly due to stretching vibrations of C=C and C=N bonds which do not form part of an aromatic skeleton. In the corresponding oxygen compounds these bands are usually

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* For convenience, these substances will nevertheless be referred to by their usual names, "mercaptopyridines," etc.

† A complete list of band peaks for all the substances examined is obtainable from the author on request; these spectra are also being recorded in the D.M.S. scheme (Butterworths, London).

[5] Albert and Phillips, *J.*, 1956, 1294.

[6] (*a*) Albert and Short, *J.*, 1945, 760; (*b*) Badger, Pearce, and Pettit, *J.*, 1951, 3204.

[7] Spinner, *J. Org. Chem.*, 1958, **23**, 2037.

[8] Albert and Spinner, *J.*, 1960, 1221.

hidden below the more intense carbonyl stretching bands, or sometimes (*e.g.*, in 4-hydroxypyridine [8]) these vibrations may actually be coupled (mixed) with the carbonyl stretching motion, but in the sulphur compounds studied here these bands appear clearly. On this evidence, all the α- and γ-mercaptoaza-compounds examined are thiones (thiopyridones, thioquinolones, etc.) like their *N*-methyl derivatives, *i.e.*, they are the analogues of (II).

TABLE 1. *The* N–H *stretching, in-plane* N–H *bending,* C=C/C=N *stretching, and* C=S *stretching frequencies in the infrared spectra of some* α- *and* γ-*mercaptoaza-aromatic compounds* (*in cm.*$^{-1}$).

	N–H stret.		N–H bend.		C=S stret.		C=C/C=N stret.	
	Solid	Soln.	Solid	Soln.	Solid	Soln.	Solid	Soln.
2-SH-Pyridine	3162	3356	1573	1590	1136	1143	1611	1620
4-SH-Pyridine	3189		1590		1108	1124	1612	
2-SH-Pyrimidine	3170 *		1567		1186		1607	
4-SH-Pyrimidine	3173		1564		1167		1600	
2-SH-Pyrazine	3180		1575		1161		1607	
2-SH-Quinoline	3164	3362	1584	1581	1104	1104	1620	1620
4-SH-Quinoline	3186	3414	1592		1167	1170	1578	1587
1-SH-Isoquinoline	3189	3376	1570	1570	1176	1169	1630	1627
2-SH-Quinoxaline	3183	3353	1578	1567	1111	1106	1611	1607

* Very weak band.

TABLE 2. *The* C=S *and* C=C/C=N *stretching frequencies in the infrared spectra of some* N-*methylated* α- *and* γ-*mercaptoaza-aromatic compounds* (*in cm.*$^{-1}$).

	C=S stret.		C=C/C=N stret.	
	Solid	Soln.	Solid	Soln.
N-Methyl-2-thiopyridone		1114		1623
N-Methyl-4-thiopyridone	1109	1119	1612	1620
N-Methyl-2-thiopyrimidone			1610	
1-*N*-Methyl-4-thiopyrimidone	1147		1619	
3-*N*-Methyl-4-thiopyrimidone	1141		1604	
N-Methyl-2-thiopyrazone	1146		(1600) *	
N-Methyl-2-thioquinolone		1088		1620
N-Methyl-4-thioquinolone	1160		1596	
N-Methyl-1-thioisoquinolone		1176		1633
N-Methyl-2-thioquinoxalone		1139		1604

* Medium-weak band.

TABLE 3. *Strongest bands in the infrared spectra of some methylthio- and genuine mercapto-aza-aromatic compounds* (*frequencies in cm.*$^{-1}$).

2-MeS-Pyridine	1584ms	1456s	1415s	1126s	753s		
4-MeS-Pyridine	1581s	1481ms	1438ms	1410ms	797s	698ms	
2-MeS-Pyrimidine	1561 + 1545s	1381s	1205s	1185s	767ms	750ms	
4-MeS-Pyrimidine	1567s	1448s	1377s	1284ms	1139ms	980ms	741ms
2-MeS-Pyrazine	1506ms	1472ms	1393ms	1145ms	1130s	1047ms	1004ms
2-MeS-Quinoline	1595ms	1497ms	1135ms	1087s	815s	744ms	
4-MeS-Quinoline	1500ms	1377ms	822s	754s			
1-MeS-Isoquinoline	1551s	1308ms	1298s	992ms	814s	756ms	740ms
2-MeS-Quinoxaline	1147ms	1086s	756s				
3-MeS-Pyridine	1570ms		1471ms	1405ms	1108ms	793ms	707ms
3-SH-Pyridine	1564ms	1515ms	1468ms	1411ms	1110ms	783s	700s
8-MeS-Quinoline	1494ms	988ms	785s	745ms			
8-SH-Quinoline	1492ms	995ms	785s	750m			

For abbreviations, see p. 1223.

The Thiocarbonyl Stretching Frequency.—Until recently the position of this frequency was uncertain [9,10] or controversial; earlier investigators [11,12,13] assigned to it a high

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[9] Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429.

[10] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 293.

[11] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

[12] Thompson, Nicholson, and Short, *Discuss. Faraday Soc.*, 1950, **9**, 222.

[13] Miller, in Gilman " Organic Chemistry," J. Wiley & Sons, 1953, Vol. III, chapter 2.

frequency range (1300—1400 cm.$^{-1}$ or higher), later workers a lower (1170—1265 cm.$^{-1}$)[14] or a wider[15] one (1050—1400 cm.$^{-1}$). Recently, systematic correlation[16,7] of all the data that have become available led to the following conclusions: (1) when unambiguously identifiable [*e.g.*, in $(\text{-CH=CH-})_2\text{C=S}$ and -CS·SR[17] derivatives] the thiocarbonyl stretching frequency is at 1150 ± 70 cm.$^{-1}$; (2) this frequency is hardly susceptible to polar effects; *e.g.*, according to three methods of calculation[18] the C=S stretching frequency in thioformaldehyde should be 1120 ± 40 cm.$^{-1}$, while in thiocarbonyl chloride[19] it is at 1140 cm.$^{-1}$ (by contrast, the carbonyl stretching frequency in carbonyl chloride, 1827 cm.$^{-1}$, is considerably higher than that in formaldehyde, 1744 cm.$^{-1}$); (3) in some molecules, notably primary thioamides and thioureides, there is complete " mixing "[20,21] between the C=S stretching motion and other vibrations of very similar frequencies; in these cases no thiocarbonyl stretching band is observed. Precisely which vibrations will mix with thiocarbonyl stretching is not always certain.

With the exception of *N*-methyl-2-thiopyrimidone, which contains the N·CS·N skeleton, all the *N*-methyl-thiones examined in this work show a strong band in the frequency range 1090—1180 cm.$^{-1}$ (see Table 2); except in *N*-methyl-2-thioisoquinolone, this band is the most intense in the whole spectrum, and it is undoubtedly due to thiocarbonyl stretching (for *N*-methyl-2-thiopyridone and *N*-methyl-4-thiopyridone this was proved by comparison with the infrared spectra of the corresponding oxo-derivatives[7]).

An intense band in the range 1100—1190 cm.$^{-1}$ is observed in the infrared spectra of all the α- and γ-mercaptoaza-compounds studied here (see Table 1); it is the strongest band in the spectrum, except for 2- and 4-mercaptopyrimidine and 1-mercaptoisoquinoline. This is direct evidence for the presence of thiocarbonyl groups in these " mercapto "-compounds. In certain cases this evidence is not absolutely conclusive, because the strongest bands in the spectra of 2-methylthiopyridine (1126 cm.$^{-1}$), 2-methylthiopyrazine (1130 cm.$^{-1}$), and 2-methylthioquinoxaline (1086 cm.$^{-1}$) also fall in this region (nevertheless, the intensity of the 2-methylthiopyridine band at 1126 cm.$^{-1}$, for which $\varepsilon_{\text{max.}}$ is 220, is still considerably lower than that of the 2-mercaptopyridine band at 1144 cm.$^{-1}$, for which $\varepsilon_{\text{max.}}$ is 525).

The N–H *and* S–H *Stretching Bands.*—None of the *S*-methyl or *N*-methyl derivatives examined here shows appreciable absorption in the range 3150—3200 cm.$^{-1}$. In the solid state all the α- and γ-mercaptoaza-compounds examined show a weak band in the range 3160—3190 cm.$^{-1}$. In solution (where solution spectra can be obtained) a weak broad band is shown in the range 3350—3420 cm.$^{-1}$, due, no doubt, to N–H stretching in unassociated molecules (weaker bands also appear at lower frequencies, due to associated molecules). The bands in the range 3160—3190 cm.$^{-1}$ can thus be regarded as evidence for the presence of N–H groups (see Table 1). The two broad and fairly strong bands in the spectrum of 2-mercaptopyrimidine at 2621 and 2526 cm.$^{-1}$ could be due to strongly hydrogen-bonded N–H groups (though they could also be interpreted as S–H stretching bands). The band at 1578 ± 14 cm.$^{-1}$ in the spectra of the α- and γ-mercaptoaza-compounds (see Table 1) is attributed to the in-plane N–H bending vibrations (in the hydroxypyridines and hydroxypyrimidines these vibrations have similar frequencies[8]).

No thioamide form is possible for either 3-mercaptopyridine or 8-mercaptoquinoline; in aqueous solution these are present mostly as zwitterions,[4] but in media of low dielectric constant one would expect them to be present mostly as uncharged molecules, *i.e.*, as

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[14] Marvel, Radzitzky, and Brader, *J. Amer. Chem. Soc.*, 1955, **77**, 5997.

[15] Mecke, Mecke, and Lüttringhaus, *Z. Naturforsch.*, 1955, **10**b, 367; Mecke and Mecke, *Chem. Ber.*, 1956, **89**, 343; Mecke, Mecke, and Lüttringhaus, *ibid.*, 1957, **90**, 975.

[16] J. I. Jones, Kynaston, and Hales, *J.*, 1957, 614.

[17] Bak, Hansen-Nygaard, and Pedersen, *Acta Chem. Scand.*, 1958, **12**, 1451.

[18] Spinner, *Spectrochem. Acta*, 1959, 95.

[19] Thompson, *Trans. Faraday Soc.*, 1941, **37**, 251.

[20] Yamaguchi, Penland, Mizushima, Lane, Curran, and Quagliano, *J. Amer. Chem. Soc.*, **1958**, **80**, 527.

[21] Davies and W. J. Jones, *J.*, 1958, 955.

genuine S–H compounds. The S–H stretching frequency (2575 cm.$^{-1}$ in thiophenol) gives rise to only weak infrared bands. The broad medium-weak band at 2520 cm.$^{-1}$ in the spectrum of 8-mercaptoquinoline (for which there is no counterpart in the spectrum of 8-methylthioquinoline) is attributed to S–H stretching; there is probably some intramolecular hydrogen-bonding between the S–H group and the vicinal nitrogen atom.

3-Mercaptopyridine in solution in carbon tetrachloride shows only a very weak band at 2563 cm.$^{-1}$, which is not necessarily due to S–H stretching; in the solid state there is a broad medium-intensity band at 2400 cm.$^{-1}$ which is presumably an S–H stretching band, the S–H group being hydrogen-bonded (fairly strongly) to a nitrogen atom in a neighbouring molecule.* This band could also, conceivably, be the $^{+}$N–H stretching band of the zwitterion, if there is very strong hydrogen-bonding between the $^{+}$NH group and an S^{-} atom in a neighbouring molecule. However, the infrared spectrum of 3-mercaptopyridine is almost the same in the solid state and in solution (in carbon tetrachloride and carbon disulphide); also, it bears a close resemblance to that of 3-methylthiopyridine; which is expected for uncharged, but not for zwitterionic 3-mercaptopyridine.

N-*Methyl and* S-*Methyl Bands.*—None of these is clearly identifiable, owing to masking by stronger bands.

Resonance with Zwitterion Structures.—For all the thioamides studied here (*i.e.*, the α- and γ-mercaptoaza-compounds and their *N*-methyl derivatives) one can postulate resonance with (fully aromatic) zwitterion structures [like (IIb)], which would confer some single-bond character upon the CS bond and thereby reduce the CS stretching frequency. By comparison, the location of the CO stretching frequencies in 2- and 4-pyridone may be taken to indicate that the CO bond in these substances has about 15% single-bond character.[8] According to the theory of mesomeric effects [22] the C=S bond has a greater tendency to acquire a partial single-bond character than the C=O group (as third-period elements form double bonds less readily than do second-period elements). This should be reflected in correspondingly low C=S stretching frequencies in the thiolactams and thioamides examined in this work.

No experimental infrared spectrum of thioformaldehyde being available, the only standard of comparison is provided by thiocarbonyl chloride, with a C=S stretching frequency of 1140 cm.$^{-1}$. The CS bond order in thiocarbonyl chloride must be at least 2; it could be greater (a partial triple bond character has been postulated for the CO bond in carbonyl chloride, on account of the resonance $\mathrm{Cl_2CO} \longleftrightarrow \mathrm{Cl^{-}Cl{-}C{\equiv}O^{+}}$; similar resonance can be postulated for thiocarbonyl chloride), but it can hardly be less than 2.† A reduction in the CS bond order from 2·0 to 1·9 must lower the CS stretching frequency by at least 40 cm.$^{-1}$. (The C–S stretching frequency [9] is about 695 cm.$^{-1}$.)

The C=S stretching frequency in 2-mercaptopyridine, 1140 cm.$^{-1}$, is no lower than that in thiocarbonyl chloride; that in 4-mercaptopyridine is lowered by 20—30 cm.$^{-1}$. The contributions from the zwitterion structures are certainly no greater in the α- and γ-mercaptoaza-compounds than they are in the α- and γ-hydroxyaza-compounds. In fact, the C=S stretching frequencies listed in Tables 1 and 2 do not suggest that these C=S bonds have any partial single-bond character, *i.e.*, there is no evidence that zwitterion structures, like (IIb), contribute at all in these thiolactams and thioamides. (This, of course, is

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* There is very strong hydrogen bonding in solid 3-hydroxypyridine, the O–H stretching frequency there being 1800 cm.$^{-1}$ + 1860 cm.$^{-1}$ doublet.

† The lowness of the CCl stretching frequencies in thiocarbonyl chloride,[19] 650 cm.$^{-1}$ and 500 cm.$^{-1}$, compared with 845 cm.$^{-1}$ and 750 cm.$^{-1}$ in carbonyl chloride,[19] and 736 cm.$^{-1}$ and 702 cm.$^{-1}$ in methylene dichloride,[23] virtually rules out any partial double-bond character for the CCl bonds in thiocarbonyl chloride, *i.e.*, one can reasonably postulate appreciable contributions from the forms $\mathrm{Cl^{-}\ Cl{-}C{\equiv}S^{+}}$, but not from $\mathrm{^{+}Cl{=}CCl{\cdot}S^{-}}$.

[22] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, p. 77.

[23] Herzberg, "Molecular Spectra and Molecular Structure. Vol. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 317.

implicit in the statement that the thiocarbonyl stretching frequency is insensitive to polar effects.*)

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* In the author's view the bond order of a CO, CS (or any other) double bond is always 2; the C=O stretching frequency, however, is very sensitive to polar effects (inductive, inductomeric, and direct field) while the C=S stretching frequency is not.