An Infrared Study on *N*-Methyloxazolidine-2-thione and -2-selenone

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An infrared investigation on *N*-methyloxazolidine-2-thione and -2-selenone in the range 4000-200 cm^{-1} is reported. The direct comparison of the ir spectra for these compounds allowed us to identify the vibrations related to CS and CSe, and support the previous assignments of the CS modes in the oxazolidine-2-thione; for this compound it has not been possible to synthesize its selenium isologue. On the whole, these experimental assignments are in agreement with those reported for oxazolidine-2-thione. The CS and CSe modes, contributing to the bands falling below 600 cm^{-1}, are compared with those of several similar pentaatomic rings.

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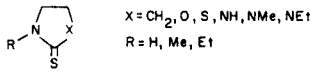
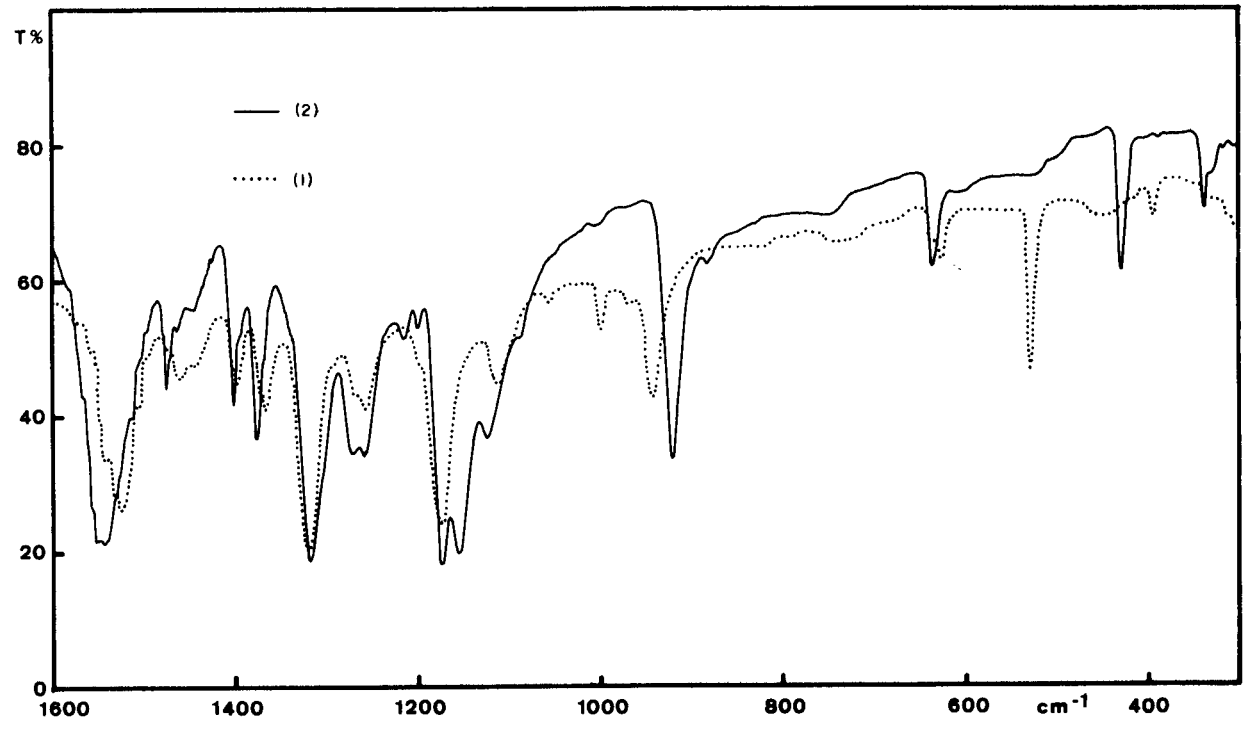
For some time (1-7) we have been interested in the infrared assignments of the vibrations related to the -RN-C(S)-X- group contained in heterocyclic pentaatomic rings of the general formula:



It has been proved that substitution of the thioketone sulphur atom with a selenium atom, which is an "isotopic" substitution (8), is an effective method of locating the C=S vibrations. However, it was not possible to employ selenation to confirm the assignments for oxazolidine-2-thione (X = O), since all attempts to synthesize the corresponding selenium compound were unsuccessful. The difficulty encountered in synthesizing the selenone derivative can probably be attributable to the instability of the oxazolidine ring. In fact, contrary to the result obtained for all other rings which were investigated by us, on reaction with methyl iodide, oxazolidine-2-thione gives a ring opened product, rather then the *S*-methyl derivative (9). Moreover, the ring opening of oxazolidine-2-thione occurs in the presence of some metal ions, which catalyze its polymerization (9-10).

The method outlined by Ettlinger (11) to prepare the oxazolidine-2-thione starting from ethanolamine and carbon disulphide proved unsuccessful with carbon



Superimposed Spectra of **1** (dotted lines) and **2** (full line) in the range 1600-300 cm^{-1} (potassium bromide solid phase)

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Table 1

Assignment of the Oxazolidine-2-thione Bands Around 1000 cm^{-1} (a) (7)

Bands	Assignment (PED % in parentheses) (b)
1107 m	ν C^5O (60), ν C^2S (12)
1029 ms	ν C^4N (51), ω C^4H_2 (19)
965 s	ϱ C^4H_2 (42), ϱ C^5H_2 (28), t C^4H_2 (19)
939 s	ν C^5C^4 (39), ω C^4H_2 (10)
902 s	ν C^5C^4 (37), ν C^5O (19)

(a) Symbols: ν = stretching; ω = wagging; ϱ = rocking; t = twisting; π = out-of-plane bending; δ = in-plane bending. (b) the contributions of less than 10% are excluded.

diselenide; *N*-methyloxazolidine-2-selenone (**2**) was obtained in the reaction between *N*-methylethanolamine and carbon diselenide (see Experimental). For this reason we have prepared *N*-methyloxazolidine-2-thione (**1**) in order to carry out a comparative infrared study and to verify the value of selenation for the oxazolidine ring. Hence, this study will deal with the following two pentaatomic rings.

1

2

Results and Discussion.

The superimposed spectra of **1** and **2** are pictured in the Figure. As can be seen, the spectra are similar except for certain bands around 1000 cm^{-1} and below 600 cm^{-1}. Above 1200 cm^{-1} there are only a few small differences that can be explained in terms of an indirect effect of the selenation. The principal difference is the splitting of the very strong band at 1170 cm^{-1} in **1** into two bands at 1160 vs and 1142 vs cm^{-1}. However, this fact cannot be ascribed to any contribution of ν CS and ν CSe to these bands. In fact, NCT treatment on oxazolidine-2-thione showed that the bands at 1198 s and 1165 vs cm^{-1} arise mainly from twisting of CH_2; in particular the band at 1198 s cm^{-1} was assigned to the CH_2 bonded to the oxygen (85%, PED) and the band at 1165 cm^{-1} was assigned to the one near the nitrogen (73% PED). These two bands seem to blend into one band at 1170 cm^{-1} in **1** whereas they are still separated in **2**, although at lower wavenumbers, *i.e.*, 1160 vs and 1142 vs cm^{-1}. This deduction is supported by the fact that the spectra of oxazolidine-2-thione and **1** are very similar except for the vibrations due to NH and NMe.

The spectra of **1** and **2** differ in some bands below 1000 cm^{-1}. The two bands at 995 m and 939 s cm^{-1} present in the spectrum of **1** have no corresponding bands in **2**. This fact leads us to believe that they can retain some contribution of the ν CS vibration. In this case, the band at 905 s cm^{-1} in **2** could contain a ν CSe contribution. On the other hand, many vibrations (*e.g.*, CH_2 rock, ν CC, ν CO, among others) contribute to determining the absorptions in this region; consequently, the contribution of ν CS and ν CSe to the aforementioned bands is expected to be very low.

Evidence for this hypothesis arises from the assignments carried out on oxazolidine-2-thione reported in Table 1.

In these assignments only the band at 1107 cm^{-1} was recognized to have a small contribution (12%) of ν CS. Since the band at 1107 cm^{-1} in oxazolidine-2-thione is mainly due to the ν C^5O, this justifies the presence of an analogous band at 1110 m cm^{-1} in **2**.

Below 600 cm^{-1}, practically all of the bands are affected by the selenation. In the spectrum of **1** there are three bands at 530 s, 396 m and 267 w cm^{-1}, which, by analogy with oxazolidine-2-thione, can be assigned to the prevailing ν C=S, out-of-plane π C=S and in-plane deformation δ C=S, respectively. These assignments agree well with those previously reported for analogous pentaatomic rings. Table 2 summarizes these results. It is pleasing to

Table 2

A Comparison of the C=S Assignments for Several Five Membered Rings Within 600-200 cm^{-1} (solid phase)

X	Y	ν C=S	π C=S	δ C=S	Literature References
O	NH	513	350	283	(7)
O	NMe	530	396	267	this work
S	NH	585-545	434	292	(6)
S	NMe	595-458	458	347	(4)
S	S	503-454	478	248	(12)
CH_2	NH	497	334	—	(5)
NH	NH	507	—	337	(13)

Table 3

A Comparison of the C=Se Assignments for Several Five Membered Rings Within 600-200 cm^{-1} (solid phase)

X	Y	ν CSe	π CSe	δ CSe	Literature References
O	NMe	420	333	217	this work
S	NH	513-326	280	235	(6)
S	NMe	518-413	286	230	(4)
CH_2	NH	352	280	215	(5)
NH	NH	357	—	—	(2)

note that all of the thionic derivatives show absorptions, arising from a high ν CS contribution, in the range 600-450 cm^{-1}. However, the imidazolidine series differs from all of the other compounds, since in the latter case, the ν CS also contributes to bands found around 1000 cm^{-1}.

As far as the analogous CSe modes in **2** are concerned, there are three bands at 420 ms, 333 m and 217 ms cm^{-1}, which can be attributed to ν CSe, π CSe, respectively. Also in this case, these assignments are in accordance with those found for similar rings reported in Table 3.

EXPERIMENTAL

N-Methyloxazolidine-2-thione (**1**).

Although the literature reports the synthesis of this compound by reacting *N*-methylethanolamine with tributyltin diethylamide (1:2) (14), we have tried to obtain it by Ettlinger's procedure (11) and by the one-step synthesis suggested by Chanon, *et al.* (15), by reacting *N*-methylethanolamine with carbon disulfide. However, both procedures yielded the *N*-methylthiazolidine-2-thione instead of the corresponding oxazolidine.

By analogy with the synthesis of *N*-phenyloxazolidine-2-thione (9), the *N*-methylethanolamine (0.12 moles), dissolved in 90 ml. of dry benzene, was added to a mixture of anhydrous potassium carbonate (0.18 mole) and thiophosgene (0.12 mole) in 200 ml. of dry benzene, over a period of 2 hours and under nitrogen at a temperature of *ca.* 5°. After one night, the solid material was filtered and the solution was evaporated under reduced pressure. A pale yellow oil was obtained, which was shown by gas-chromatography to be a mixture of four compounds; the ir spectrum of this mixture did not exhibit any typical bands of an oxazolidine ring. The same procedure was repeated by diluting 1:10; in this case the final oil was identified as *N*-methyloxazolidine-2-thione (14). This compound was recrystallized from ethyl ether (m.p. 26-27°, lit. m.p. 27-28.5).

N-Methyloxazolidine-2-selenone (**2**).

This compound has been obtained by the procedure outlined by Ettlinger (11). The solvents used in the synthesis were previously deoxygenated by bubbling nitrogen through them and the reaction was carried out under nitrogen.

Potassium hydroxide (1.5×10^{-2} mole) was dissolved in 10 ml. of water and added to *N*-methylethanolamine (1.5×10^{-2} mole). To this solution, cooled to 0°, carbon diselenide (1.5×10^{-2} mole) dissolved in 150 ml. of dioxane was added. The addition was completed in about one hour. Subsequently, solid potassium hydroxide (1.5×10^{-2} mole) and lead nitrate (1.5×10^{-2} mole) in 30 ml. of water were added at room temperature. A yellow solid was formed which in a short time became black. The suspension was digested at ~60° for an hour. The resulting black lead selenide was filtered off and the solution was concentrated to a small volume. From this, after extraction with chloroform, **2** was precipitated by adding petroleum ether (40-60°), m.p. 63-64° dec.

Anal. Calcd. for C_4H_7NOSe: C, 29.3; H, 4.3; N, 8.5. Found: C, 29.3; H, 4.1; N, 8.7.

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