An Infrared Spectroscopic Investigation on *N*-Methyl-1,3-thiazolidine-2-thione and -2-selone

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An infrared investigation on *N*-methyl-1,3-thiazolidine-2-thione and -2-selone in the range 4000-200 cm^{-1} is reported. The ν CS and ν CSe vibrations give contributions to the absorptions around 1000 cm^{-1} and below 600 cm^{-1}. The assignments are supported by comparison of their ir spectra with those of *S*- and *Se*-methiodides. The π-bond orders of the thio- and seleno-ketonic links in these compounds are higher than those found for 1,3-imidazolidine-2-thione and -2-selone.

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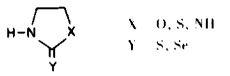
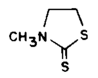
We are interested in the spectroscopic investigation of heterocyclic pentaatomic rings (1-3) having the structure shown. Using the selenation as a diagnostic tool (4-5) to

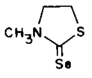


locate the vibrations involving the CY group, we observed that 1,3-imidazolidine-2-thione and -2-selone give rise to CY absorptions below 650 cm^{-1}, since the ir spectrum of the thione compound differs from that of the selone only in this region (2). On the other hand, the infrared spectrum of 1,3-thiazolidine-2-thione (1) differs from its parent selenium compound also around 1000 cm^{-1}, demonstrating that the CS and CSe mode contributions occur in this region.

We shall now present our results on a study of *N*-methyl-1,3-thiazolidine-2-thione and its selenium analogue.



I



II

The superimposed ir spectra of *N*-methyl-1,3-thiazolidine-2-thione and -2-selone are shown in Figure 1.

It is evident that the infrared spectra differ around 1000 cm^{-1}, as found for 1,3-thiazolidine-2-thione and -2-selone (1). In fact, the three strong bands present in I at 1105, 1022 and 981 cm^{-1} are shifted to lower wavenumbers or modified in intensity in II. In order to check the ν CY contribution to these bands, the *S*- and *Se*-methiodides were prepared and their ir spectra compared with those of I and II. All the bands of the *S*- and *Se*-methyl derivatives in the range 1600-200 cm^{-1} are reported in the Table.

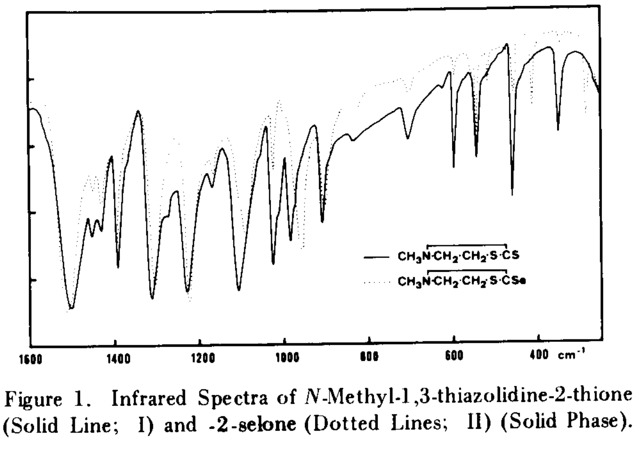


Figure 1. Infrared Spectra of *N*-Methyl-1,3-thiazolidine-2-thione (Solid Line; I) and -2-selone (Dotted Lines; II) (Solid Phase).

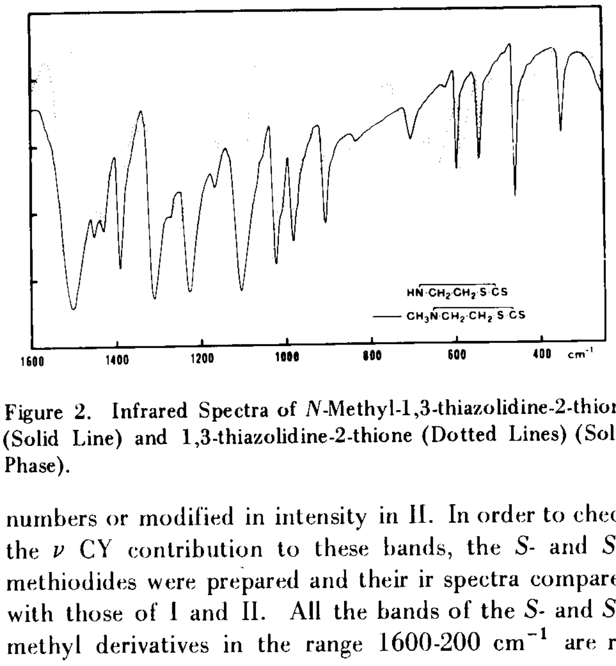


Figure 2. Infrared Spectra of *N*-Methyl-1,3-thiazolidine-2-thione (Solid Line) and 1,3-thiazolidine-2-thione (Dotted Lines) (Solid Phase).

The very strong band at 1105 cm^{-1} in I and the corresponding strong band at 1090 cm^{-1} in II have some ν CY contribution; in fact, both bands decrease in intensities in the Y-methiodides and occur at 1102 s and 1098 m cm^{-1}, respectively.

The strong band at 1022 cm^{-1} in I has in II its corresponding absorption of medium intensity at 1024 cm^{-1}; we believe that this band may be due to a mixed vibration with a little ν C=S. The high value of frequency of ν C=S suggests a π-bond order on C=S higher than that found in 1,3-imidazolidine-2-thione (2) and one would expect a sensitive downward shift when under selenation (5). In this hypothesis, the very strong band at 958 cm^{-1} in II should be considered as due to both ν C=Se and the corresponding absorption at 981 cm^{-1} in I (6). *S*- and *Se*-

methiodides support this point of view. In fact, the band at 958 cm^{-1} in II disappears in *Se*-methiodide with the simultaneous appearance of a new peak at 978 cm^{-1}, corresponding either to the band at 981 in I or to that at 976 cm^{-1} in the *S*-methiodide. In addition, the band at 1022 cm^{-1} in I is split in the *S*-methiodide and two bands at 1031 and 997 cm^{-1} are found, thus denoting its mixed origin.

It is interesting to compare the ir spectrum of I with that of 1,3-thiazolidine-2-thione, previously investigated (1,3). The differences are clearly to be attributed to the change of NH to NCH_3. As shown in Figure 2, the ir spectra considerably differ in the range 600-800 cm^{-1} and 1050-1400 cm^{-1}. In the latter region, the strong bands at 1390, 1228 and 1105 cm^{-1} in I are mainly due to the methyl modes. Hence the band at 1105 cm^{-1} must be attributed to a ν C=S contribution and above all to the methyl rocking modes. Therefore no bands attributable to a pure ν C=S are present in I, in contrast to 1,3-thiazolidine-2-thione, where the medium band at 1085 cm^{-1} was given (1) to a fairly pure ν C=S on the basis of selenation, *N*-deuteriation, *S*-methylation and *S*-coordination to metals.

In the lower frequency region, I has four bands at 595 ms, 542 ms, 458 s and 347 ms cm^{-1}. Excepting the band at 542 cm^{-1}, all the others shift on *S*-methylation, in agreement with some C=S contribution. On the other hand, II shows weak absorptions and some of then occur at the same wavenumbers as those of I (595 w, 457 m, 346 w). This fact was attributed to some suspected impurity of I in II (see Experimental); however, after several recrystallizations of II, its spectrum remained unchanged. Hence the four bands in I must be considered as mixed vibrations, since they split in the selenium isologue. We think that the bands at 518 mw and 413 m cm^{-1} could receive a considerable contribution from ν CSe and δ CSe and that the band at 286 cm^{-1} can reasonably be attributed to the out-of-plane Δ C=Se.

Table

Infrared Frequencies of *S*- and *Se*-Methiodides in Solid Phase between 2000-200 cm^{-1}.

$CH_3N{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}C{\cdot}S{\cdot}CH_3I$	$CH_3N{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CSe{\cdot}CH_3I$
1564 vs	1566 vs
1421 s	1442 w
1408 s	1413 s
1326 s	1405 m
1308 s	1318 s
1268 vw	1265 m
1226 vs	1220 s
1162 mw	1164 mw
1102 s	1098 m
1031 s	1030 vw
997 m	995 w
976 s	978 ms
915 m	930 w
700 m	920 mw
571 mw	900 mw
537 s	698 w
435 w	580 w
367 ms	542 w
254 m	512 m
	414 w
	401 m
	272 m

The comparison of I with 1,3-thiazolidine-2-thione (see Figure 2) shows a correspondence of bands with some displacements below 600 cm^{-1}, whereas in the 600-800 cm^{-1} range 1,3-thiazolidine-2-thione exhibits two strong absorptions and I and II show only one medium band. This fact substantiates our previous assignments (1,3) of 1,3-thiazolidine-2-thione in contrast to the assignment by Singh and Rivest (7) and recently quoted by De Filippo, *et al.* (8), who attribute the bands of 1,3-thiazolidine-2-thione at 700 ms and 655 s cm^{-1} to the symmetric and antisymmetric ν CS in the ring. Obviously, the substitution of the NH hydrogen with a methyl group would not change these vibrations, which would still be present in I and II. The 700 cm^{-1} band in 1,3-thiazolidine-2-thione was attributed (1,3) to the out-of-plane NH deformation on the basis of its disappearance in the *N*-deuterio-derivative and the band at 655 cm^{-1} to the ν CH_2S contribution, because it must fall in this region (9). In I and II the bands present at 703 and 705 cm^{-1} respectively, can be attributed to ν CH_2S.

In conclusion, *N*-methyl-1,3-thiazolidine-2-thione and its selenium isologue differ, not only in the low frequency region, but also around 1000 cm^{-1}, confirming the previous results obtained for 1,3-thiazolidine-2-thione and -2-selone (1). This fact distinguishes the thiazolidines from the imidazolidines, where selenation modifies the infrared spectra below 650 cm^{-1}. In 1,3-imidazolidines the CY bond is an almost single bond (2,10); consequently the CY modes contribute to give absorptions in the low frequency region as also found for thiourea and selenourea (11,12). In 1,3-thiazolidine-2-thione the substitution of the NH hydrogen with methyl shifts the C=S bands towards higher wavenumbers, in agreement with an increase of the π-bond order on C=S (see Figure 2). This could be explained in terms of the hydrogen bondings, which play an important role in the bond order of CS in 1,3-thiazolidine-2-thione, since this link is far from a single bond.

EXPERIMENTAL

N-methyl-1,3-thiazolidine-2-thione (I) was prepared according to the literature (13) and recrystallized several times from ethanol/water mixtures (m.p. 69°; lit. 69.5-70°). *N*-methyl-1,3-thiazolidine-2-selone (II) was prepared using the general procedure outlined by Klayman (14), by reacting a methanolic solution of the *S*-methiodide of I (1 mole) with sodium hydroselenide (2 moles) dissolved in ethanol/water in the presence of sodium bicarbonate (1 mole). After 12 hours, the solution was acidified with acetic acid in order to dispel methyl mercaptan and hydrogen selenide. The solution, concentrated to a small volume, was filtered on paper and cooled on ice bath. Crystalline pale-yellow products were obtained, which were recrystallized from chloroform/petroleum ether (40-60°) m.p. 84° dec.

Anal. Calcd. for C_4H_7NSSe: C, 26.7; H, 3.9; N, 7.8. Found: C, 26.6; H, 4.0; N, 8.0.

The methiodides of I and II were synthesized by refluxing with methyl iodide (1.1 moles) in methanol. On cooling in an ice bath crystalline products were obtained. The methiodide of compound I had m.p. 135° dec.

Anal. Calcd. for $C_5H_{10}INS_2$: C, 21.8; H, 3.7; N, 5.1. Found: C, 21.7; H, 3.8; N, 5.2.

The methiodide of compound II becomes pale yellow at 135-140° and melts with decomposition at 150-155°.

Anal. Calcd. for $C_5H_{10}INSSe$: C, 18.6; H, 3.1; N, 4.4. Found: C, 18.8; H, 3.0; N, 4.4.

The ir spectra of the solid samples were recorded with a Perkin-Elmer 325 instrument in the range 4000-200 cm^{-1} in potassium bromide discs (4000-400 cm^{-1}) and Nujol mulls between cesium iodide discs (450-200 cm^{-1}).

Acknowledgement.

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REFERENCES AND NOTES

(1) F. Cristiani, F. A. Devillanova and G. Verani, *J. Chem. Soc., Perkin Trans. II*, 324 (1977).

(2) F. A. Devillanova and G. Verani, *ibid.*, 1529 (1977).

(3) K. Geetharani and D. N. Sathyanarayana, *Indian J. Chem.*, **14A**, 170 (1976).

(4) K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).

(5) K. A. Jensen, *Ann. N. Y. Acad. Sci.*, **192**, 115 (1972).

(6) A similar band at 968 cm^{-1} in 1,3-thiazolidine-2-selone was attributed by us to a mixed vibration with a high ν CSe contribution.

(7) P. P. Singh and R. Rivest, *Can. J. Chem.*, **46**, 2361 (1968).

(8) D. De Filippo, P. Deplano, A. Diaz and E. F. Trogu, *Rend. Semin. Fac. Sci. Univ. Cagliari*, **46**, 203 (1976).

(9) G. Borch, L. Henriksen, P. H. Nielsen and P. Klaeboe, *Spectrochim. Acta*, **29A**, 1109 (1973).

(10) P. J. Wheatley, *Acta Crystallogr.*, **6**, 369 (1957).

(11) D. Hadži, J. Kidričk, Ž. V. Knezevic and B. Barlič, *Spectrochim. Acta*, **32A**, 693 (1976).

(12) G. B. Aitken, J. L. Duncan and G. P. McQuillan, *J. Chem. Soc. A*, 2695 (1971).

(13) T. C. Owen, *J. Chem. Soc. C*, 1373 (1967).

(14) D. L. Klayman and R. Shine, *J. Org. Chem.*, **34**, 3549 (1963).