Infrared Study of 1,3-Thiazolidin(e)-2-one, -2-thione, and -2-selone and their 1-Oxa-analogues

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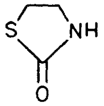
1,3-Thiazolidin(e)-2-one, -2-thione, and -2-selone and their 1-oxa-analogues have been studied by i.r. spectroscopy over the range 4 000—200 cm^{-1}. Spectroscopic evidence shows that in each series the zwitterionic form increases on passing from oxygen to selenium. The ν(C=S) and ν(C=Se) values for 1,3-thiazolidine-2-thione and -2-selone are tentatively located at 1 085 and 968 cm^{-1} respectively. In 1,3-oxazolidine-2-thione ν(C=S) is assigned to the medium intensity band at 1 110 cm^{-1}. Assignments are also made for ν(C–S) and ν(C–O) in the ring and for the out-of-plane and in-plane >C=S and >C=Se deformations.

THE i.r. spectra of pentatomic rings containing oxygen, nitrogen, and sulphur were first investigated by Mecke *et al.*,[1,2] whose assignments were subsequently supported by other authors.[3-6] We have recently synthesized 1,3-thiazolidine-2-selone, which completes the series (1)—(3). Hence we carried out a comparative i.r. investigation to locate the position of the >C=Se vibrations and establish the influence of the exo-heteroatom on the ring properties. For this purpose, the *N*-deuterio and *S*- and *Se*-methyl compound were taken into consideration and use was made of 'selenation'[7,8] to verify all the bands related to the >C=S group in compound (2). The i.r. study was extended to the 1,3-oxazolidines (4) and (5) to clarify the influence of the ring-heteroatom on ring behaviour. A complete study should include compound (6), but attempts to obtain it have not been successful.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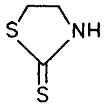
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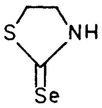
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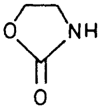
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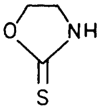
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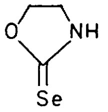
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RESULTS AND DISCUSSION

3 600—2 800 *cm*$^{-1}$: ν(NH) *Vibration*.—Table 1 reports the ν(NH) frequencies for compounds (1)—(5) for saturated CCl_4 solution and for the solid phase (KBr). The NH stretching vibration decreases in the order O, S, Se and the decrease is higher for the solid state and for the associated form in CCl_4 than for the monomeric form. This order may be explained by assuming a

TABLE 1

ν(NH) frequencies (cm^{-1}) for CCl_4 solution and KBr solid phase

	CCl_4 saturated solution			
Compound	Free	Associated	Δν	Solid
(1)	3 430	3 200	230	3 250
(2)	3 418	3 150	268	3 130
(3)	3 410		310[a]	3 100
(4)	3 475	3 240	235	3 230
(5)	3 470	3 195	275	3 210

[a] The low solubility of (3) did not allow us to observe an associated form; hence the Δν value is computed with respect to the solid state.

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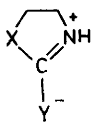
contribution from the resonance structure (A) which increases on passing from O to S and Se, as proved by



(A)

the corresponding increase in $\Delta\nu$ ($= \nu_{\text{free}} - \nu_{\text{ass.}}$). In fact, assuming the formation of a hydrogen bond as being responsible for the decrease in ν(NH) in the associated form, $\Delta\nu$ should change in the opposite way. This trend has been recognized[9-12] for amides, thioamides, and selenoamides.

Inspection of Table 1 shows the influence of the heteroatoms on ν(NH). In the free molecules the exo-heteroatoms produce very small shifts, while the substitution of oxygen for sulphur in the ring changes the ν(NH) mode by *ca.* 50 cm^{-1}. Since this influence can be attributed to electronic and steric effects and the influence of the exo-atom is mostly electronic, it appears that ring strain has the most important effect on the behaviour of ν(NH).

1 800—1 300 cm^{-1}: $\nu(\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{Y})$ *Vibrations.*—Jensen and Nielsen[7] have shown that the antisymmetrical vibration of the N–C=Y group in amides, thioamides, and selenoamides has C=O character in amides and predominantly C=N character in thio- and selenoamides (B band), coupled with the δ(NH) mode. In the first two rows of Table 2 the behaviour of the B band for *N*-deuteriation and *S*- and *Se*-methylation is reported. Decoupling with the δ(NH) deformation for *N*-deuteriation shifts the band towards lower wavenumber. For *S*- or *Se*-methylation the band shifts to higher wavenumber, because of the enhanced π-bond order of $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$.

TABLE 2

Strong bands in the range 1 600—1 000 cm^{-1} for (2) and (3) (KBr solid phase)

Compound	S–C(=Y)–NH	S–C(=Y)–ND	S–C(–YMe)–NH
		$\nu_{\text{max.}}$/cm^{-1}	
(2)	1 510	1 478	1 550
(3)	1 510	1 480	1 542
(2)	1 290	1 300	1 305
(3)	1 295	1 300	1 310
(2)	1 047	1 047	1 054
(3)	1 039	1 037	1 035

On the other hand compounds (1) and (4) exhibit a non-mixed absorption at 1 470m and 1 482ms cm^{-1} respectively (Amide II), due to an NH in-plane deformation and another absorption at 1 350ms and 1 325mw cm^{-1} attributable to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ with smaller π-bond order. A weakening of C–N corresponds to a strengthening of C=O, whose stretching vibration falls at 1 665vs and 1 725vs cm^{-1} in (1) and (4), respectively.

The ν(C=O) frequencies for non-associated molecules in CCl_4 fall at 1 710vs and 1 782vs cm^{-1} for (1) and (4). Since they differ in the ring heteroatom, the variation in ν(C=O) should be attributed either to the difference in electronegativity between S and O or to distortion from planarity of the S–CO–NH group. The ring distortion effect in the thia-series increases the sp^3 hybrid character of the nitrogen, as confirmed by the ν(NH) shifts of 3 475—3 430 and 3 470—3 418 cm^{-1} in (1) and (2) (see Table 1).

1 300—800 cm^{-1}: ν(C=S) *and* ν(C=Se) *Vibrations.*—The superimposed spectra of (2) and (3) differ in the presence of a medium band at 1 085 cm^{-1} in 1,3-thiazolidine-2-thione and in a very strong band at 968 cm^{-1} in the selenium isologue (see Figure 1). The band at 999 cm^{-1}, common to both, has different absorption intensities, stronger in (2) than in (3).

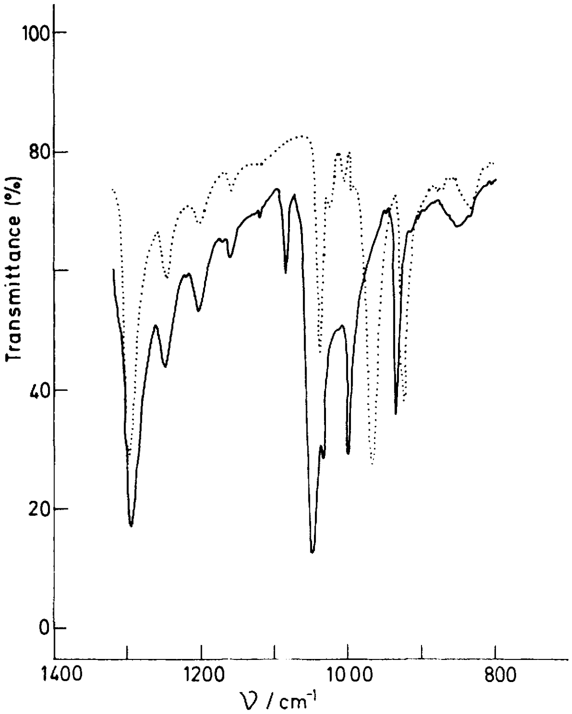


FIGURE 1 Superimposed spectra of 1,3-thiazolidine-2-thione (2) and -2-selone (3) in the range 1 300—800 cm^{-1} (KBr solid phase): ——, (2); · · · ·, (3)

N-Deuteriation leaves all the bands in the range 1 100—950 cm^{-1} practically unchanged, thus excluding any contribution from NH modes. For *S*-methylation the band at 1 085 cm^{-1} disappears and a new peak at 960m cm^{-1} appears. *Se*-Methylation moves the band at 968 to 975 cm^{-1} with a noteworthy reduction in its intensity and with the appearance of a band at 858m cm^{-1}.

Therefore we assign the band at 1 085m cm^{-1} in (2) and that at 968s cm^{-1} in (3) to ν(C=S) and ν(C=Se) respectively; however, the latter cannot be attributed

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to a pure ν(C=Se) but to a mixed vibration. Colthup[13] reports Mecke's assignment of ν(C=S) in 1,3-thiazolidine-2-thione as the strong band at 1 047 cm^{-1}; but this band is also present in (3) and the *S*-methylation leaves it unchanged (see Table 2). Moreover the presence of a similar strong band at 1 062 cm^{-1} in 1,3-thiazolidin-2-one indicates that they all arise from common structural elements, *e.g.* C–C, CH$_2$, or C–N.

The ν(C=S) vibration is reported in the literature as a strong band falling in the region 1 300—1 000 cm^{-1}. Thus the very strong band at 1 290 cm^{-1} in (2) could be attributed to ν(C=S). However its behaviour upon *S*-methylation and selenation clearly excludes any ν(C=S) contribution to the band (see Table 2). A similar band at 1 283 cm^{-1} for (1) seems to confirm that the ring common to all three compounds must be responsible for this absorption.

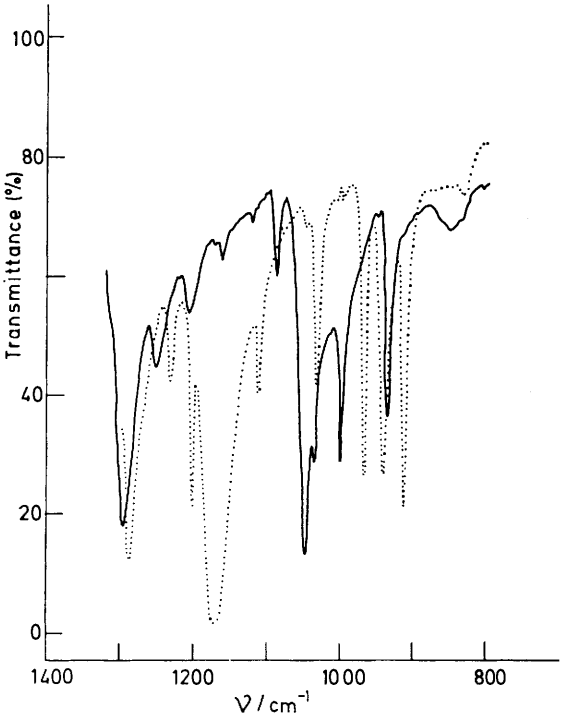

FIGURE 2 Superimposed spectra of 1,3-thiazolidine-2-thione (2) and 1,3-oxazolidin-2-one (5) in the range 1 300—800 cm^{-1} (KBr solid phase): ——, (2); · · · ·, (5)

Mecke assigned ν(C=S) in (5) to the strong band at 1 171 cm^{-1}; the non-availability of (6) and the impossibility of obtaining the *S*-methyl derivative [compound (5) gives ring opening on treatment with MeI[14]] do not allow us to prove his assignment.

However the literature[15] reports ν(C=S) as changing by *ca.* 20—30 cm^{-1} on passing from S to O for an R–X–C=S groups (X = O or S). From this point of view it seems improbable that (5) should have ν(C=S) at 1 171 cm^{-1}, while in (2) the same absorption falls at 1 085 cm^{-1}. However (5) shows a medium peak at 1 110 cm^{-1} (see Figure 2) which could be attributed to ν(C=S) in agreement with the literature data. Experimental proof of the correctness of the assignment was obtained for some metal complexes with (5) bonded through the sulphur atom,[16] where this band disappears.

It is our opinion that the strong band at 1 171 cm^{-1} can be attributed to ν(C–O). This is a very strong band falling in the range 1 100—1 150 cm^{-1} in dialkyl ethers[17] and it is shifted to higher wavenumbers by substitution with groups having conjugative effects, *e.g.* xanthates.[18,19] A similar strong band is present at 1250 cm^{-1} in 1,3-oxazolidin-2-one.

800—200 cm^{-1}: *Out-of-plane* NH *Deformation*, ν(CH$_2$–S) *Ring Vibration, and* δ(C=Y) *and* Δ(C=Y) *Modes.*—The broad band, present in all the compounds at *ca.* 700 cm^{-1}, is due to a pure out-of-plane NH deformation. This assignment is in contrast with that of Singh,[20] who attributed the bands at 697 and 652 cm^{-1} in (2) to symmetric and antisymmetric ν(C–S). On the other hand the ν(CH$_2$–S) vibration must fall in this region; Borch *et al.*[5] assigned the medium band at 674 cm^{-1} in ethylene trithiocarbonate to an almost pure ν_{as}(CH$_2$–S). It is our opinion that only the strong bands at 617, 655, and 656 cm^{-1} in (1)—(3), respectively, can be attributed to the ν(CH$_2$–S) vibration, as the low sensitivity to *N*-deuteriation and the lack of change for *S*- or *Se*-methylation confirm.

Table 3 reports all the bands present in the range 800—200 cm^{-1}. For the thia-series, the bands at 545 and 434 cm^{-1} for (2) and at 513 and 326 cm^{-1} for (3) are undoubtedly due to $>$C=S and $>$C=Se deformation modes, because they are considerably shifted to lower wavenumbers in *S*- and *Se*-methylated compounds.

TABLE 3

Bands present in the range 800—200 cm^{-1}

	ν/cm^{-1}
(1)	697vs, 617s, 584m, 410m, 227w, 213w
(2)	700ms, 655m, 585m, 545m, 434s, 291.5s
(3)	700ms, 656s, 553m, 513s, 326m, 235ms
(4)	766m, 700sbr, 512ms, 204m
(5)	695sbr, 632s, 515s, 433.5w, 350m, 283.5w

EXPERIMENTAL

All compounds were obtained by literature methods[21-24] and recrystallized several times from appropriate solvents.

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The methylthio- and -seleno-derivatives of (2) and (3) were synthesized by refluxing (2) or (3) (10^{-2} mol) with MeI (1.1×10^{-2} mol) in absolute ethanol. By cooling in ice crystalline products were obtained. The methylthio-derivative of (5) could not be obtained even upon treatment with nucleophiles weaker than methyl iodide (such as ethyl bromide and benzyl chloride). The *N*-deuterio-derivatives of (1)—(3) were obtained by recrystallizing the compounds from D_2O. Deuteriation was almost complete for (3), 60% for (2), and 30% for (1). Compounds (4) and (5) underwent little deuteriation on recrystallization from D_2O.

I.r. spectra were recorded with a Perkin-Elmer model 325 instrument over the range 4 000—200 cm^{-1}. Solid samples were recorded as KBr tablets (4 000—400 cm^{-1}) and as mulls in Nujol between CsI discs (450—200 cm^{-1}).

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