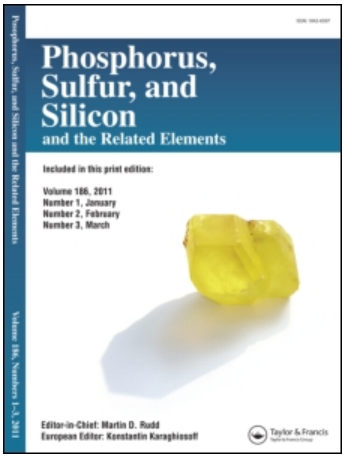

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SYNTHESIS AND VIBRATIONAL PROPERTIES OF SOME BENZAZOLE-2-SELENONES. A COMPARISON WITH THE CORRESPONDING AZOLIDINE DERIVATIVES

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SYNTHESIS AND VIBRATIONAL PROPERTIES OF SOME BENZAZOLE-2-SELENONES. A COMPARISON WITH THE CORRESPONDING AZOLIDINE DERIVATIVES[a]

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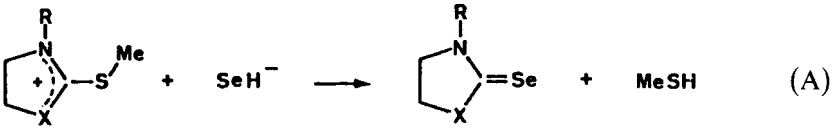
Several benzazole-2-selenone compounds have been prepared and the syntheses are discussed together with those of the corresponding azolidine-2-selenones. The comparisons of the infrared spectra of each selenonic compound with the thionic isologue differ in the low frequency region, while they are very similar in the finger-print region. This similarity can be used as a diagnostic aid in confirming the analogy in structure between sulphur and selenium compounds.

RESULTS AND DISCUSSION

Syntheses

A convenient synthesis of molecules containing the selenoamido entity —NH—CSe— is the method outlined by Klayman and Shine,[1] i.e. a nucleophilic attack of SeH^- on the *S*-methiodide, prepared by reacting the corresponding thionic compound with methyl iodide. In this way, we have synthesized the following selenonic compounds



(A)

where R = H, Me, Et and X = NH, NMe, NEt, S and CH_2.[2-4]

The effectiveness of (A) is dependent on the preparation of the *S*-methyl derivative. In fact, the synthesis of oxazolidines-2-selenone (X = O) fails because the reaction between oxazolidines-2-thione and methyl iodide does not give *S*-methiodide but occurs with ring opening.[5] For this reason, *N*-methyl oxazolidine-2-selenone was prepared by ring closing of *N*-methyl ethanolamine with CSe_2 in presence of $Pb(NO_3)_2$.[6]

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[a]This work was supported by C.N.R. of Rome.
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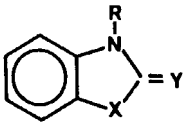
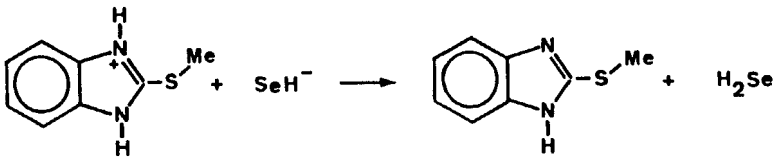
However, although *S*-methiodide is the reagent for (A), sometimes it may not give any nucleophilic substitution with SeH^-. For example, except for VI, none of the following benzazole-2-selenone compounds has been prepared according to (A), although most of their corresponding thionic derivatives yield stable *S*-methiodides.[7-9]



Y = S	X	R	Y = Se
I	NH	H	II
III	NH	Me	IV
V	NMe	Me	VI
VII	O	H	VIII
IX	O	Me	X
XI	S	H	XII
XIII	S	Me	XIV

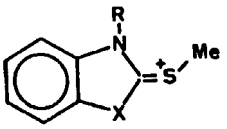
The reaction between the *S*-methiodides of the benzazole series and SeH^- gives different reactions. For example, in order to prepare II in this way, we have obtained a crystalline product identified as *S*-methylbenzimidazole, whose formation can be explained according to the reaction



(B)

where SeH^- acts as base in contrast with its nucleophilic nature. This behaviour of SeH^- can be accounted for by comparing the acidity of the NH hydrogens in benzazole-2-thione derivatives with the corresponding azolidine molecules, which react with SeH^- according to (A). In Table I, the νNH stretching vibrations of the free molecules[10] and the acidity constants (K_A) measured using DMSO as base[11] are reported for some benzazole-2-thione and azolidine-2-thione molecules. As one can see, the benzene ring lowers the νNH frequencies in accordance with an increase of polarity in the NH bond, although this decrease is practically inexistent for the NMe derivatives. However the K_A values are more sensitive to this change since they are about 10 times higher than the corresponding azolidines.

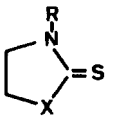
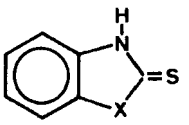
The behaviour of SeH^- as base in (B) could also be ascribed to a decrease in positive charge of the thiocarbonyl carbon in the benzazole-2-thione methiodide, due to the aromaticity of the π system,[12] which favours the delocalization of the charge also on the sulphur atom;



(C)

TABLE I

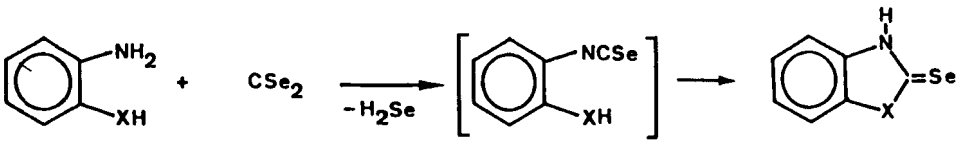
νNH frequencies (cm $^{-1}$) for the free molecules in CCl_4 solutions and acidity constants (K_A; 1 · moles^{-1}) measured towards DMSO

X	 K_A^a	νNH	 K_A^a	νNH
NMe	42	3469	400	3468
O	500	3470	3000	3459
S	200	3418	2000	3410

[a]From Ref. 11.

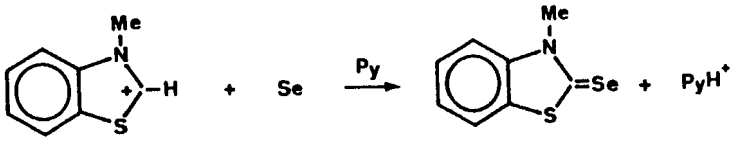
The *S*-methiodide of *N,N'*-dimethylimidazolidine-2-thione, having no hydrogen bonded to the nitrogen, gives the nucleophilic substitution with SeH^- producing VI. However, the *S*-methiodides of *N*-methylbenzoxazole-2-thione and *N*-methylbenzothiazole-2-thione do not react with SeH^- to give X and XIV.

In order to synthesize some benzazole-2-selenone derivatives, we have used the following way suggested by Warner:[13]



(D)

He reacted an *o*-primary amine with CSe_2 in non-polar solvents. (D) occurs via isoselenocyanate, which undergoes a cyclization. In this way, we have prepared II, IV, VIII and XII by starting from the appropriate amine. All attempts to prepare X according to (D) were unsuccessful, thus confirming the mechanism proposed by Warner that (D) occurs through an isoselenocyanate intermediate. X was prepared by the synthesis used for *N*-methyl oxazolidine-2-selenone, i.e. by reacting the *N*-methyl *o*-aminophenol with CSe_2 in presence of $Pb(NO_3)_2$.[6] XIV was obtained by reacting *N*-methylbenzothiazolium iodide with selenium in pyridine,[14] according to the reaction



(E)

Starting from *N*-methyl benzoxazolium iodide, reaction (E) does not give X.

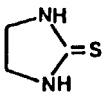
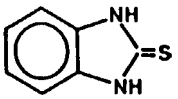
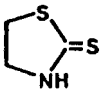
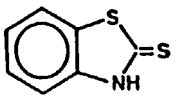
Infrared Spectra

In previous papers[6,15-20] we have used "selenation,[21] i.e. the substitution of the sulphur with the selenium atom, in order to identify the infrared bands which contribute considerably to the >C=S vibrations. In our studies, we have proved that this substitution works very well in assigning the >C=S vibrations.

To summarize the previous studies on the azolidine systems, we have found that the i.r. spectrum of *N*-methyloxazolidine-2-thione differs from that of *N*-methyloxazolidine-2-selenone for some bands falling around 1000 cm^{-1} and below 600 cm^{-1};[6] the same has been found for thiazolidine-2-thione and its *N*-methyl derivative and their corresponding selenonic isologues.[15,18] On the contrary, the imidazolidine-2-thione series[16,17] gives >C=S absorptions mainly below 650 cm^{-1}, since above this frequency both the spectra of each thionic compound and its corresponding selenonic derivative are practically superimpossible. As shown by X-ray structures carried out on some azolidine-2-thione and benzazole-2-thione molecules[22-25] (Table II) condensed benzene strengthens the thiocarbonyl bond. To a shortening of >C=S, a lengthening of the C—N bond corresponds in the benzazole derivatives. In terms of the Abrahams[26] scale, which correlates the double

TABLE II

Bond distances (Å) of the thioamido group in some azolidine- and benzazole-2-thione molecules

	C=S	C—N	Ref.
	1.708	1.322	22
	1.671	1.362	23
 a)	1.68	1.24	24
	1.662	1.353	25

[a] These values are taken from the structure of the thiazolidine-2-thione pentacarbonyltungsten complex; however, as seen for some structures of complexes with substituted imidazolidine-2-thione derivatives, C=S and C—N slightly change under *S*-coordination.

bond character with the length of the carbon–sulphur bond, condensed benzene produces an increase in the double bond character of about 15%. This increase is very effective in the adduct formation of such molecules with molecular iodine. In fact, on passing from azolidines to benzazole compounds, the stability constants for the reaction

$$I_2 + D \rightleftharpoons D \cdot I_2 \qquad (F)$$

(where D is the donor) are about 100 times smaller, thus confirming the higher negative charge present in the sulphur atom in the azolidines.[27]

For all these reasons, we would expect the $\rangle$C=S modes in the i.r. spectra of the benzazole molecules to contribute to bands falling at frequencies higher than those found for the azolidine systems. In Figures 1–4 the i.r. spectra of III, V, IX and XIII are reported (full line) superimposed on those of the corresponding selenium compounds (dotted line) in the 1600–300 cm^{-1} range. Our purpose is to identify the vibrations related to the $\rangle$C=S group on the basis of selenation. An inspection of the figures shows that the spectra of each sulphur compound compared with that of the corresponding selenium derivative are very similar in the finger-print region,[28] since only a few bands are slightly shifted or modified in intensity above 700 cm^{-1}. However, XIII and XIV show significant changes in the two bands at 1097 and 966 cm^{-1} for the thionic compound, which move to 1077 and 945 cm^{-1} in the selenonic

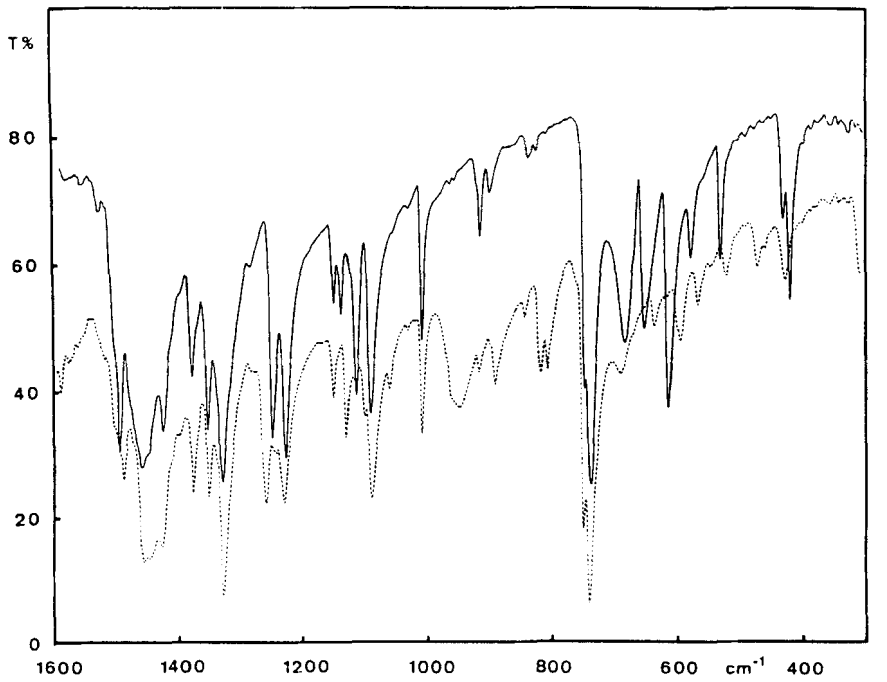


FIGURE 1 Superimposed i.r. spectra of benzoimidazole-2-thione (full line) and benzoimidazole-2-selenone (dotted line) (KBr solid state).

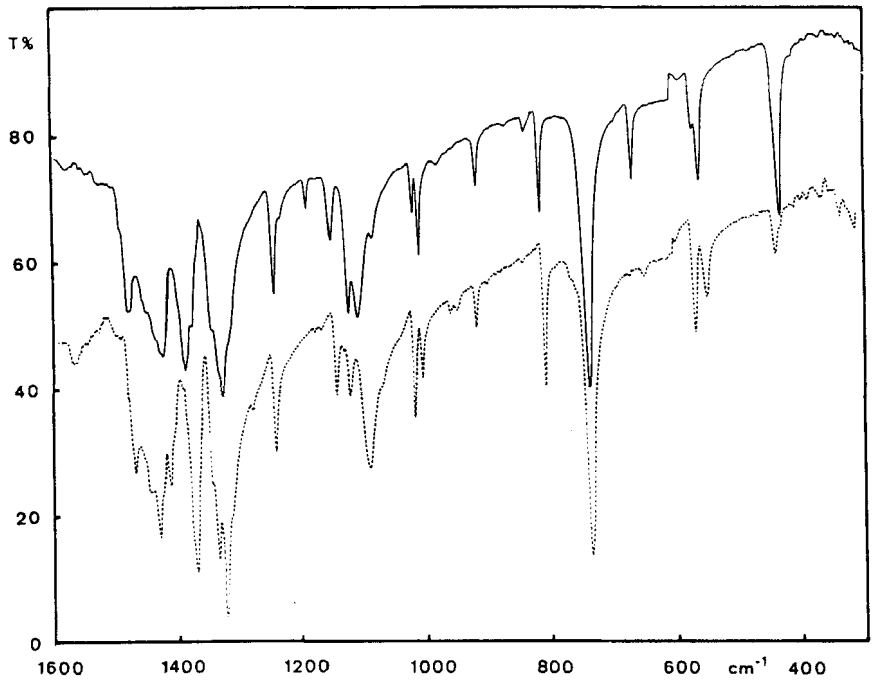


FIGURE 2 Superimposed i.r. spectra of *N,N'*-dimethylbenzoimidazole-2-thione (full line) and *N,N,'*-dimethylbenzoimidazole-2-selenone (dotted line) (KBr solid state).

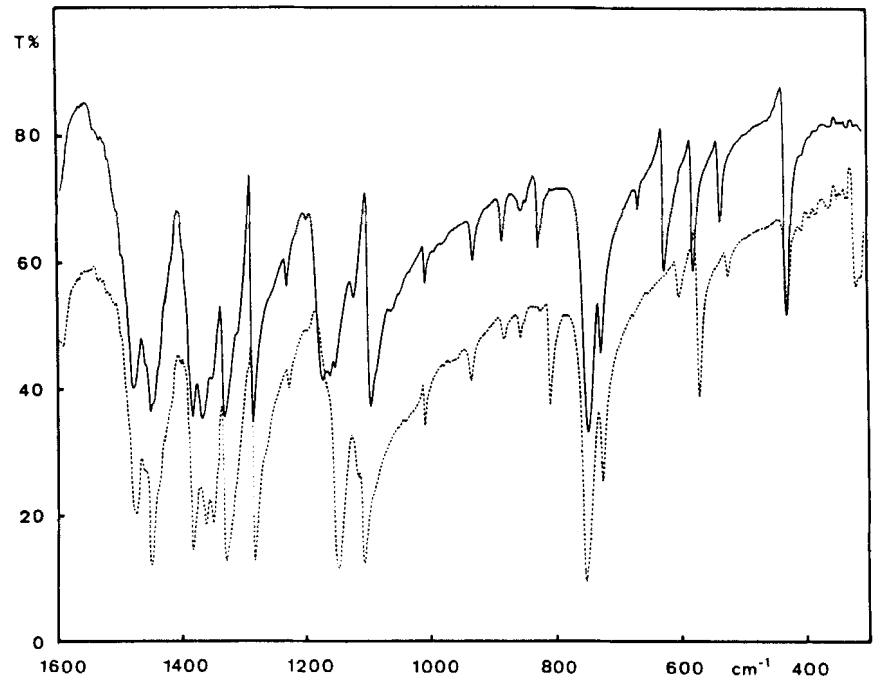


FIGURE 3 Superimposed i.r. spectra of *N*-methylbenzoxazole-2-thione (full line) and *N*-methylbenzoxazole-2-selenone (dotted line) (KBr solid state).

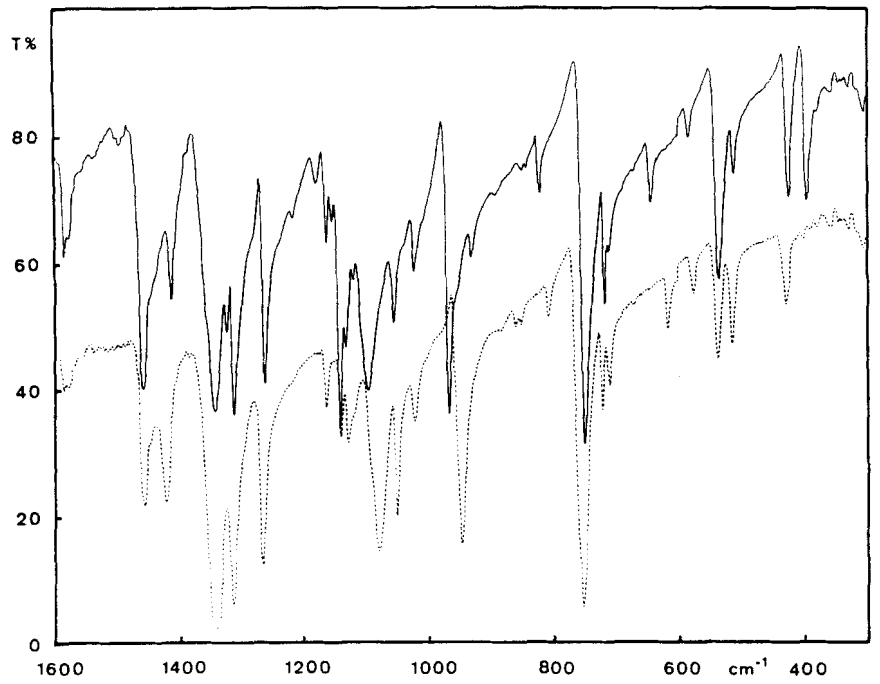


FIGURE 4 Superimposed i.r. spectra of benzothiazole-2-thione (full line) and benzothiazole-2-selenone (dotted line) (KBr solid state).

one (see Figure 4). These shifts indicate that the stretching vibrations of $\rangle C{=}S$ could contribute to these bands. Similar observations were made on the spectra of thiazolidine-2-thione and -2-selenone[15] and they were subsequently corroborated by NCT calculation.[19]

In all the other figures, the low shifts verified for some bands above 700 cm^{-1} could be ascribed only to a secondary selenation effect. The similarity between the spectra of the thionic and its selenonic isologue above 700 cm^{-1} can be used to ascertain the preparation of a selenonic compound.

Below this wavenumber, we recognize the main changes in the i.r. spectra for the sulphur substitution. In Table III, the bands containing contributions of stretching and of deformations of $\rangle C{=}S(Se)$ are reported together with all the other bands falling above 200 cm^{-1}. In accordance to the fact that the stretching and the deformations of $\rangle C{=}S(Se)$ are coupled with other vibrations, several bands are sensitive to selenation and move towards lower frequencies due to substitution of the sulphur with the selenium atom.

EXPERIMENTAL

Benzazole-2-thione derivatives. Benzoxazole-2-thione (VII), benzothiazole-2-thione (XI) and its *N*-methyl derivative (XIII) were purchased from Fluka and recrystallized several times from H_2O/EtOH. Benzimidazole-2-thione (I) was synthesized by reacting *o*-diaminobenzene with potassium ethylxantate in H_2O/EtOH according to literature.[29] *N*-methylbenzimidazole-2-thione (III) was obtained with the same

TABLE III

Infrared absorptions in the low frequency region (cm^{-1})

X	R	Compound	Bands with >C=S(Se) vibration contributions	Other vibrations over 200 cm^{-1}
NH	H	I[a]	656 s, 598 vs, 478 s, 416 vs, 225 s	613 w, 427 ms, 408 sh, 322 vw, 265 s
		II[a]	640 ms, 571 neat, 460 ms, 300 ms, 203 s	612 m, 425 ms, 312 w, 264 m
NMe	H	III	653 s, 615 vs, 421 s, 284 m	580 m, 533 ms, 433 m
		IV	637 mw, 597 m, 474 mw, 310 m, 264 mw	570 m, 524 mw, 430 mw, 283 w
NMe	Me	V	663 m, 423 s, 220 w	556 m, 291 w
		VI	566 m, 327 w, 270 m	547 mw, 432 w
O	H	VII[a]	672 m, 476 s, 427 vs, 266 s	647 sbr, 621 m, 607 s, 597 w, 328 w, 238 m
		VIII[a]	569 ms, 302 m	620 w, 465 w, 424 mw
O	Me	IX	664 w, 622 ms, 273 w, 229 w	576 ms, 534 m, 427 s
		X	600 w, 310 m, 255 w	566 ms, 521 w, 422 m
S	H	XI[a]	601 s, 521 w, 391 s, 298 w	664 s, 566 ms, 499 w, 420 m, 379 m
		XII[a]	579 m, 508 ms, 282 ms	667 vs, 559 ms, 500 w, 418 m, 368 mw
S	Me	XIII	643 mw, 397 m, 227 mw	584 w, 536 s, 511 mw, 425 m, 305 w
		XIV	616 m, 274 m	575 m, 536 s, 514 ms, 428 m, 305 w

[a]Assignments reported in Ref. 9.

procedure from *N*-methyl *o*-diaminobenzene and potassium ethylxantate, m.p. 191°; lit.[30] 191°. *N*-methyl *o*-diaminobenzene was obtained by methylation of *o*-diaminobenzene.[31] *N,N'*-dimethylbenzimidazole-2-thione (V) was prepared by reacting *S*-methyl derivative of I with MeI in MeOH for 48h at 105–110°C in a sealed tube;[30] m.p. 151°; lit. 151°. *S*-methyl derivative of I was obtained from benzimidazole-2-thione and MeI in presence of an equivalent amount of KOH in MeOH as solvent;[30] m.p. 201; lit. 201°. *N*-methylbenzoxazole-2-thione (IX) was synthesized by reacting (VII) with diazomethane in ethyl ether to yield the *S*-methylated isomer;[32] subsequently, this was transformed in IX by reaction with MeI according to literature;[33] m.p. 130°; lit. 130°.

Reaction between S-methylbenzimidazolium iodide and SeH⁻. The *S*-methiodide of I was prepared by refluxing I with MeI in a 1 : 1 molar ratio in MeOH and precipitated by adding ethyl ether. Anal. Calcd. for $C_8H_9IN_2S$: C, 32.9; H, 3.1; N, 9.6. Found: C, 31.3; H, 3.2; N, 9.6.

SeH^- was obtained as suggested by Klayman and Griffin[34] by reducing grey selenium with $NaBH_4$ in absolute ethanol. The $B(OEt)_3$ obtained as byproduct is not separated and the ethanolic solution of SeH^- is used as it stands. To an ethanolic solution (150 ml) containing SeH^- (76 mmoles) prepared as above, *S*-methiodide of I (38 mmoles) dissolved in the smallest amount of absolute ethanol was added. After a night at room temperature, EtOH was distilled until 50 ml of residue and a white crystalline product was obtained, which gave m.p. 201° after recrystallization. Anal. Calcd. for $C_8H_8N_2S$: M.W., 164.2; C, 58.5; H, 3.9; N, 17.1. Found: from a mass spectrum, M.W., 164 a.u.; C, 58.0; H, 4.0; N, 17.2.

The synthesis of an authentic sample[30] confirmed it as the *S*-methylated compound of I.

Benzazole-2-selenone derivatives. Benzimidazole-, benzoxazole- and benzothiazole-2-selenone (II, VIII, XII) were prepared as suggested by Warner.[13] *N*-methylbenzimidazole-2-selenone (IV) was prepared in the same way. CSe_2 (5 mmoles) dissolved in benzene (30 ml) was added slowly to a benzene solution (70 ml) containing *N*-methyl *o*-diaminobenzene (4 mmoles). This solution was refluxed for 24 hours, and concentrated to a volume of ca. 40 ml. On cooling, crude IV was obtained. Further crystallization from $CHCl_3$/petroleum ether 40–60°C gave a pure compound with m.p. 154–158° (dec.). Anal. Calcd. for $C_8H_8N_2Se$: M.W., 211.12; C, 45.5; H, 3.8; N, 13.3. Found: from a mass spectrum, M.W., 212 a.u.; C, 46.0; H, 4.0; N, 13.9. *N,N'*-dimethylbenzimidazole-2-selenone (VI) was obtained by reacting *S*-methiodide of V with SeH^- in absolute EtOH. *S*-methiodide and SeH^- were prepared as above. Anal. Calcd. for: $C_{10}H_{13}IN_2S$: C, 37.5; H, 4.1; N, 8.8. Found: C, 38.1; H, 4.2; N, 8.7.

After reacting *S*-methiodide and SeH^- in the usual way, the ethanolic solution was left to react overnight. The concentration of the residue gave crude VI, which was further recrystallized m.p. 175° (dec.).[35] Anal. Calcd. for $C_9H_{10}N_2Se$: M.W., 225.15; C, 48.0; H, 4.5; N, 12.4. Found: from a mass spectrum, M.W., 226 a.u.; C, 47.7; H, 4.4; N, 12.3. *N*-methylbenzoxazole-2-selenone (X) was obtained in the same way as for the parent *N*-methyloxazolidine-2-selenone.[6] The solvents were previously deoxygenated by bubbling N_2 through them. The reaction itself was carried out in atmosphere of N_2. KOH (15 mmoles) was dissolved in water (10 ml) and added to *N*-methyl *o*-aminophenol (15 mmoles). To this solution at 0°, CSe_2 (15 mmole) in 150 ml of dioxane was added. This operation was completed in ca. 1 hour. At this point, solid KOH (15 mmoles) and $Pb(NO_3)_2$ (15 mmoles) dissolved in water (30 ml) were added. In a short time a black-orange solid was formed. This was digested at ca. 60° for an hour and then the suspension was filtered off to eliminate PbSe. The solution was concentrated to a small volume, and from this a black solid was separated on cooling. This was dissolved in $CHCl_3$ filtered on paper and from the yellow solution, X was precipitated by adding petroleum ether 40–60°, m.p. 160° (dec.). Anal. Calcd. for C_8H_7NOSe: M.W., 212.11; C, 45.3; H, 3.3; N, 6.6. Found: from a mass spectrum, M.W., 213 a.u.; C, 44.9; H, 3.2; N, 6.7. *N*-methyl *o*-aminophenol was prepared by a three steps synthesis:[36] (i) obtaining benzoxazole methiodide from benzoxazole-2-thione and MeI by refluxing for 8 hours at 60°; (ii) inducing a ring opening of the methiodide by alkaline hydrolysis to yield *o*-formylmethylaminophenol; (iii) eliminating the formyl group by acid hydrolysis finally to give *N*-methyl-*o*-aminophenol.

N-methylbenzoxazole-2-selenone (XIV) was synthesized from *N*-methylbenzothiazolium iodide and selenium in pyridine.[14] After crystallization from EtOH, it yielded m.p. 113° (dec.), lit. 113°.

The i.r. spectra were recorded on a Perkin-Elmer mod. 903 spectrophotometer on the solid samples as KBr discs (4000–300 cm^{-1}) and Nujol mulls (450–200 cm^{-1}).

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10. In non polar solvents, these molecules give autoassociation equilibria, and two typical absorptions for νNH, whose relative intensities depend on the concentrations, are present in their i.r. spectra in the 3500–3000 cm^{-1} interval. The neat band at the higher frequency is due to the free molecule, while the other, due to the associated molecules, is broad.
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