X-Ray Evidence for Partial Bonding between Sulphur or Selenium and Oxygen in Thio- and Seleno-imines

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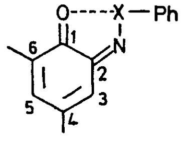
Summary *X*-Ray structural studies of the phenyl thio- and seleno-imines derived from 2,4-xylenol reveal, in both molecules, a *syn* configuration with X · · · O distances of 2·604 Å (X = S) and 2·575 Å (X = Se).

All the recently reported quinone selenoimines[1] and thio-imines[2] show unusually low carbonyl group absorptions in the i.r. spectra compared with, for example, 1,2- or 1,4-benzoquinones. Data for the representative compounds (**1**) and (**2**) are given in Table 1. Thus, regardless of the point of insertion of the imine group, there is significant interaction of the sulphur or selenium with the carbonyl group *via* conjugation. Additionally one might expect through-space interaction between the sulphur or selenium and the oxygen in molecules having the *syn* configuration (**1a**), but not in the inverted *anti* structure (**1b**). The spectra of (**1**) (X = S or Se) were not diagnostic of either configuration, so *X*-ray studies were undertaken. The first showed the sulphur compound to have the *syn* geometry (**1a**) and a S · · · O separation of 2·604(3) Å. Some 15 structures have been reported[4] containing short S · · · O distances ranging from 2·03 to 2·80 Å, most being planar conjugated molecules, and the S · · · O interactions have been discussed in terms of (*p–d*) π orbital overlaps amounting to less than a single bond.[5] In this compound the S · · · O separation should be compared with the sum of van der Waals radii (*ca.* 3·25 Å) and represents a 56% elongation of the single-bond length (*ca.* 1·67 Å).

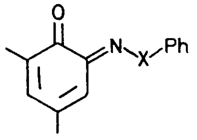
Table 1

	ν(C=O) cm^{-1}		ν(C=O) cm^{-1}
(**1a**) X = S ..	1605	(**2**) X = S	1615
(**1a**) X = Se ..	1605	(**2**) X = Se ..	1613
1,2-Benzoquinone[3]	1667	1,4-Benzoquinone[3]	1664

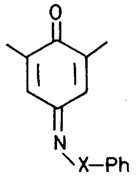
For each compound the spectrum recorded in CCl_4, KBr, and as a Nujol mull was essentially unchanged.



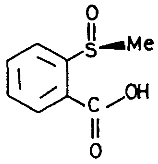
(1a)



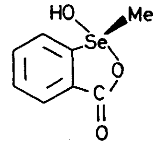
(1b)



(2)



(3)



(4)

The configuration of the selenium compound was difficult to predict owing to lack of a close structural precedent. The larger sum of the van der Waals radii (*ca.* 3·4 Å) and the different space group (*vide infra*) made the *syn* configuration (**1a**) seem at first less likely than it was for the sulphur analogue. However, the *X*-ray study showed that this

TABLE 2

	X = S	X = Se		X = S	X = Se
X · · · O	2·604(3)	2·575(3)	∠N–X–C	99·1(2)	94·2(1)
X–N	1·641(3)	1·805(3)	∠N–X · · · O	78·8(1)	76·6(1)
X–C	1·770(3)	1·924(3)	∠C–O · · · X	96·5(2)	101·0(2)
N=C(2)	1·303(4)	1·308(5)	C(3)=C(4)	1·340(5)	1·322(6)
C(1)=O	1·228(5)	1·240(4)	C(4)–C(5)	1·449(6)	1·453(5)
C(1)–C(2)	1·493(5)	1·486(4)	C(5)=C(6)	1·348(6)	1·341(5)
C(2)–C(3)	1·447(5)	1·443(5)	C(6)–C(1)	1·465(5)	1·443(5)

molecule also contained the *syn* geometry and a Se · · · O separation of 2·575(3) Å, which is significantly shorter than the S · · · O distance. The value represents a 45% extension of the Se–O single-bond length (1·77 Å).

The bond lengths observed elsewhere in the molecules correspond closely (Table 2) and preclude any significant participation of bond patterns other than that shown in (**1a**).

The only previous *X*-ray investigation providing a remote analogy is a comparative study[6] of compounds (**3**) and (**4**) where S · · · O is 2·777 Å and the carboxy-group is twisted 17° out of plane, whereas Se · · · O is 2·374 Å and in that case all atoms except the methyl group are coplanar. These distances, together with ours, indicate that in corresponding molecules selenium seems able to achieve larger overlap integrals with oxygen, thus making a stronger partial bond than sulphur and offering a greater barrier to inversion in the selenium compound. Higher inversion barriers have been reported in other selenoimines compared with the corresponding thioimines.[7]

Crystallographic data: $C_{14}H_{13}NOS$, orthorhombic, $a = 25{\cdot}795$, $b = 11{\cdot}984$, $c = 8{\cdot}064$ Å, space group *Pbca*; $Z = 8$. 1213 reflexions measured on a diffractometer; refined to $R = 3{\cdot}9\%$. $C_{14}H_{13}NOSe$, trigonal, $a = 26{\cdot}774$, $c = 9{\cdot}398$ Å space group $R\bar{3}$, $Z = 18$. 1406 reflexions measured on a diffractometer; refined to $R = 2{\cdot}2\%$.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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