The Crystal Structure of the 2-Oxo-2-phenylethyl Esters of Thiocyanic and Selenocyanic Acid (Phenacyl Thiocyanate and Phenacyl Selenocyanate)

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The structures of the title compounds, $PhC(O)CH_2XCN$, X=S, I, and X=Se, II, have been determined by X-ray methods. The compounds are monoclinic with space group $P2_1/c$ and are isomorphous.
The non-hydrogen atoms of the compounds are virtually coplanar. The $C(CH_2)$-X bond is *syn*-periplanar (*"cis"*) to the C=O bond and fairly strong X–O intramolecular contacts are present, 2.684 Å (I), 2.722 Å (II). The compounds may be considered as three-coordinated sulfur and selenium complexes with the X–O interaction *trans* to the cyano group. The XCN group is strictly *anti*-periplanar to the $C(CH_2)$–C(C=O) bond.
IR spectra of the compounds in solution imply that, in noncoordinating solvents, this conformation is predominant, while in coordinating solvents the *syn*-clinal (*gauche*) conformation is contributing to the spectra.

The crystal structures of the 4-nitrobenzyl pseudohalides, $4\text{-}NO_2\text{–}PhCH_2XCN$, X being Te, Se and S, and of $PhCH_2SeCN$ have been reported.[1] In $4\text{-}NO_2\text{–}PhCH_2XCN$, the heteroatoms form fairly strong intermolecular contacts to oxygen atoms of neighbouring nitro groups, and in $PhCH_2SeCN$ to nitrogen atoms of neighbouring selenocyanate groups. We therefore suggested that these compounds be considered as distorted square planar Te(II), Se(II) and S(II) complexes. The lengths of the various intermolecular contacts implied the following bond orders: (i) *trans*-O(N)----X–CN ≫ *trans*-O(N)----X-benzyl; (ii) Te----O > Se----O > S----O and (iii) Se----O > Se----N. Regardless of the strength of the intramolecular contacts, the pseudohalide group, XCN, was observed to be *syn*-clinal (*gauche*) to the $C(CH_2)$–C(Ar) bond. This conformation appears to be quite general for organic pseudohalides, RXCN, in the solid state. Presumably this conformation is retained in solution and in gas phase (*cf.* Refs. 1 and 2).

In an attempt to further examine the conformational preference of organic pseudohalides, we have turned to structural studies of compounds containing oxygen atoms suitably positioned for intramolecular contacts with the heteroatoms. The extensive studies by Piette and coworkers[3–5] on compounds of the type 2–X–PhC(O)Y (X=SCN, SeCN, SeSPh, SeCl, SeBr, TeBr and Y=Me, H, OEt) give convincing evidence for intramolecular contacts between the heteroatom and the carbonyl oxygen atom, particularly in the case of ketones and aldehydes. Characteristic of this interaction is the shift toward lower frequencies of the carbonyl stretching band at ~1700 cm^{-1}. The ester group is less susceptible to interactions with *ortho*-substituted heteroatoms; the tellurium atom, however, does interact with this group.[6]

In the 2-oxo-2-phenylethyl esters of thiocyanic acid and selenocyanic acid, $PhC(O)CH_2SCN$,

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(phenacyl thioacyanate), I, and $PhC(O)CH_2SeCN$, (phenacyl selenocyanate), II, the absorption due to the carbonyl group (KBr) appears as single bands at 1678 and 1668 cm^{-1}, respectively. These wave numbers are significantly lower than in the parent unsubstituted ketone, acetophenone, 1691 cm^{-1} (CCl_4),[7] in the phenacyl halides, $PhC(O)CH_2X$ (X=F, Cl, Br and I)[7-10] and in $PhC(O)CH_2NO_2$.[11,12] The low wave numbers in I and II point up the possible presence of intramolecular S−O and Se−O interactions. This study reports on the structures of these compounds. Contrary to the observation of only one carbonyl stretching band in solid samples of I and II, the compounds displayed a doublet in most solvents, 13–17 cm^{-1} apart in I and 6–8 cm^{-1} apart in II. The results from a study on the carbonyl stretching bands in several solvents are also reported and the conformation of the two compounds in solution is discussed.

Experimental

Materials. The compounds were prepared and purified as previously described.[13] Suitable crystals for the single crystal X-ray analyses were grown from concentrated diethyl ether solutions. The solvents used for the IR study were of highest purity available and were further purified by standard methods.

X-ray data and structure determinations. An Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo$K\alpha$ radiation was used for the determination of the cell parameters and the recording of intensity data. All work was done at room temperature, ≃19 °C. The cell parameters were determined by least square fits to 25 independent reflections with $\lambda K\alpha_1$ = 0.70926 and $\lambda K\alpha_2$ = 0.71354 Å.[14] For the recording of intensity data ($0° \leq \Theta \leq 28°$), the ω-scan technique with variable scan speed, 0.8-4 °min^{-1}, was used in both cases. The minimum scan width was 1.5° including 2×0.25° background scans. At intervals of 100 recordings, the orientation of the crystals was checked and reorientated if the reference reciprocal vectors varied more than 0.05° from the present values. The intensity of 3 standard reflections were measured every hour and the intensity data later corrected by linear interpolation according to their variations. The correction factors varied between 0.97 and 1.06 for I and between 0.98 and 1.05 for II. The intensity data were corrected for Lorentz polarization and absorption effects, the latter being based upon crystal faces and dimensions.

The crystals of the compounds are isomorphous with the space group $P2_1/c$ (no. 14). Their structures were solved by interpretation of Patterson and Fourier density maps. The procedure of refinements and inclusions of non-hydrogen atoms followed the same pattern as in Ref. 1. All computer programs used belong to the Enraf-Nonius Structure Determination Pack, version SDP-plus 1.0 (1981).

Table 1 summarizes the crystal data and other relevant information. Fractional atomic coordinates and thermal parameters are listed in Table 2. The hydrogen atoms were placed geometrically (C−H = 0.95 Å) and refined. These data have been made available to the Crystallographic Data Center at Cambridge (U.K.). Tables of observed and calculated structure factors are available from the authors.

IR measurements. 0.040 M solutions of the compounds in some selected solvents were studied in the 1650–1750 cm^{-1} region. Cells with NaCl win-

Table 1. Crystal data and structural parameters.

	I	II
a (Å)	10.852(2)	10.725(2)
b	5.565(1)	5.708(1)
c	15.110(3)	15.312(2)
β°	105.54 (2)	106.02 (1)
V (Å^3)	879.2	900.95
M	177.23	224.12
Z	4	4
F (000)	368	440
D_c gcm^{-3}	1.339	1.652
Abs. coeff. (cm^{-1})	3.†	44.3
Cryst.dim. (mm)	0.3×0.3×0.4	0.13×0.2×0.4
Tr.coeff. min.-max.	0.907−0.915	0.416−0.608
Fudge factor, p	0.03	0.02
Scale factor	0.127	0.286
No. of refl.	2129	2174
No. of refl. $I > 2\sigma(I)$, N	1541	1235
$R = \Sigma \lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.039	0.035
R_w[a]	0.051	0.032
$S = [\Sigma w(\Delta F)^2/N-n]^{1/2}$	1.908	1.409
Diff. four. max. eÅ^{-3}	0.235	0.261

[a] $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$, $w^{-1} = \sigma^2(I)/4Lp \cdot I$, $\sigma^2(I) = \sigma^2(I)_{count} + (pI)^2$

Table 2. Fractional atomic coordinates and their e.s.d. (anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $B = 4/3\ [a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab\cos\gamma\ B(1.2) + ac\cos\beta\ B(1,3) + bc\cos\alpha\ B(2,3)]$; starred atoms were refined isotropically)

Ato	x	y	z	B(Å²)	Ato	x	y	z	B(Å²)
S	0.32592(6)	0.34454(9)	0.13354(3)	6.35(1)	SE	0.32588(4)	0.33496(8)	0.14004(2)	5.79(1)
C1	0.4263(2)	0.5658(3)	0.1225(1)	5.15(4)	C1	0.4327(3)	0.5739(7)	0.1232(2)	4.68(9)
N	0.4915(2)	0.7228(3)	0.1177(1)	6.61(4)	N	0.4942(3)	0.7272(6)	0.1146(2)	6.21(9)
C2	0.3145(2)	0.1940(3)	0.0255(1)	4.40(4)	C2	0.3115(3)	0.1866(6)	0.0234(2)	4.19(8)
C3	0.2163(2)	−0.0004(3)	0.0177(1)	4.18(3)	C3	0.2159(3)	−0.0087(6)	0.1070(2)	3.82(8)
O	0.1624(1)	−0.0214(3)	0.07787(8)	5.97(3)	O	0.1642(2)	−0.0332(5)	0.0782(1)	5.52(6)
C4	0.1885(1)	−0.1631(3)	−0.0628(1)	3.84(3)	C4	0.1858(3)	−0.1656(6)	−0.0627(2)	3.58(7)
C5	0.2598(2)	−0.1614(3)	−0.1267(1)	4.58(4)	C5	0.2558(3)	−0.1625(7)	−0.1270(2)	4.35(8)
C6	0.2320(2)	−0.3238(3)	−0.1983(1)	5.31(4)	C6	0.2261(3)	−0.3185(7)	−0.1983(2)	5.03(9)
C7	0.1341(2)	−0.4855(4)	−0.2076(1)	5.37(4)	C7	0.1283(4)	−0.4773(7)	−0.2065(2)	5.02(9)
C8	0.0623(2)	−0.4870(4)	−0.1447(1)	5.38(4)	C8	0.0582(3)	−0.4815(7)	−0.1436(3)	5.08(9)
C9	0.0899(2)	−0.3264(3)	−0.0729(1)	4.79(4)	C9	0.0865(3)	−0.3260(7)	−0.0725(2)	4.50(8)
H21	0.399(2)	0.131(3)	0.029(1)	6.4(5)*	H21	0.393(3)	0.136(6)	0.020(2)	6.0(9)*
H22	0.287(1)	0.301(3)	−0.023(1)	6.0(4)*	H22	0.280(3)	0.301(6)	−0.024(2)	5.6(8)*
H5	0.327(1)	−0.056(3)	−0.119(1)	4.8(4)*	H5	0.326(2)	−0.058(5)	−0.119(2)	3.9(7)*
H6	0.285(2)	−0.325(3)	−0.241(1)	7.1(5)*	H6	0.284(3)	−0.316(5)	−0.239(2)	5.3(8)*
H7	0.114(1)	−0.598(3)	−0.259(1)	6.1(4)*	H7	0.110(3)	−0.582(6)	−0.257(2)	4.9(8)*
H8	−0.002(2)	−0.606(3)	−0.149(1)	6.5(5)*	H8	−0.010(3)	−0.588(6)	−0.149(2)	5.0(8)*
H9	0.047(1)	−0.314(3)	−0.032(1)	5.1(4)*	H9	0.042(3)	−0.319(6)	−0.026(2)	5.7(8)*

dows with a path length of 0.05 cm were used. Owing to the small separation between the two bands in the case of the selenocyanate, II, the majority of the measurements were performed on the thiocyanate, I. All measurements were performed at 23(2) °C using a Perkin Elmer 399B Infrared Spectrophotometer.

Results

An ORTEP drawing of I, $PhC(O)CH_2SCN$, is shown in Fig. 1. Since the compounds I and II are isomorphous and structurally most similar, Fig. 1 is representative also for II and the sulfur atom is termed X. This atom, X, the cyano carbon atom, C1, and the methylene carbon atom, C2, are in the plane of the paper. The distances of the various atoms from this plane, i.e., C1–X–C2, together with bond lengths and bond angles are listed in Table 3.

Considering the non-hydrogen atoms, the molecules are virtually planar. The small torsional angles are qualitatively equal in the I and II; the angles between the terminal planes, C1–X–C2 and phenyl ring, are 13.4° (I) and 14.7° (II); the torsional angles C2C3(O)C4/phenyl ring are 6.6° (I) and 8.5° (II).

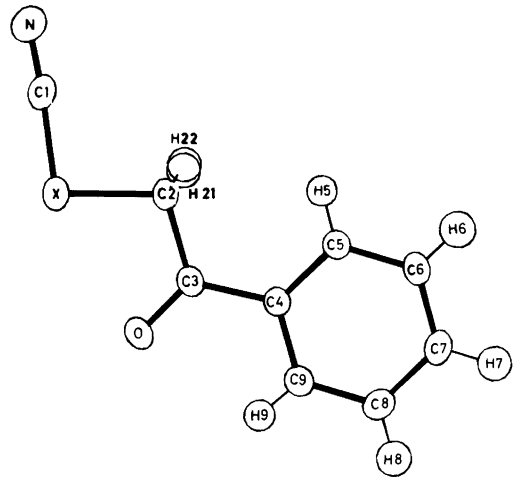

Fig. 1. ORTEP drawing of I. The sulfur atom, X, the cyano carbon atom, C1, and the methylene carbon atom, C2, are in the plane of the paper.

Table 3. Distances of the various atoms in I from the C1–S–C2 plane and in II from the C1–Se–C2 plane as shown in Fig. 1 together with bond lengths and bond angles

	I(X=S)	II(X=Se)
Distance from the C1–X–C2-plane (Å)		
N	0.034(2)	0.048(3)
C3	0.138(2)	0.127(3)
O	0.253(1)	0.252(2)
C4	0.120(2)	0.104(3)
C5	−0.171(2)	−0.220(4)
C6	−0.222(2)	−0.270(4)
C7	−0.026(2)	−0.004(4)
C8	0.325(2)	0.323(4)
C9	0.370(2)	0.382(4)
H21	−0.83(2)	−0.78(3)
H22	0.74(2)	0.76(2)
Bond lengths (Å)		
N–C1	1.138(2)	1.125(4)
C1–X	1.681(2)	1.845(4)
X–C2	1.809(1)	1.944(3)
C2–C3	1.500(2)	1.500(4)
C3–O	1.212(1)	1.222(3)
C3–C4	1.480(2)	1.476(3)
C4–C5	1.390(2)	1.393(4)
C5–C6	1.380(2)	1.376(4)
C6–C7	1.370(2)	1.365(5)
C7–C8	1.382(2)	1.376(5)
C8–C9	1.375(2)	1.373(5)
C9–C4	1.381(2)	1.381(4)
X·····O	2.684(1)	2.722(2)
Bond angles (°)		
N–C1–X	176.6(2)	176.5(3)
C1–X–C2	98.0(1)	95.1(1)
X–C2–C3	106.4(1)	105.2(2)
C2–C3–O	119.0(1)	118.8(3)
C2–C3–C4	119.4(1)	119.6(3)
O–C3–C4	121.6(1)	121.6(3)
C3–C4–C5	122.5(1)	122.7(3)
C4–C5–C6	119.7(1)	120.1(3)
C5–C6–C7	120.7(2)	120.4(3)
C6–C7–C8	119.9(2)	120.1(4)
C7–C8–C9	119.7(2)	120.0(4)
C8–C9–C4	120.9(1)	120.7(3)
C9–C4–C5	119.1(1)	118.8(3)
C9–C4–C3	118.3(1)	118.5(3)

The carbonyl carbon atoms, C3, are not coplanar with the strictly planar phenyl rings, deviating by 0.050(2) Å (I) and 0.054(3) Å (II). The

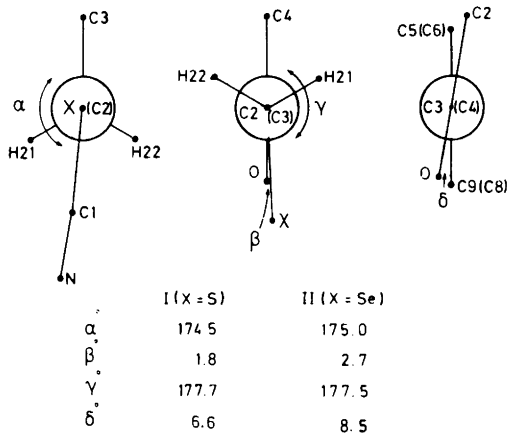

Fig. 2. Newman projections along the X–C2 bond (left), the C2–C3 bond (center) and the C3–C4 bond (right) together with torsion angles.

nonplanarity of carbonyl carbon atoms and other carbon atoms linked to phenyl rings is not uncommon, *e.g.* PhC(O)CH$_2$I[15] and several benzyl pseudohalides.[1] Relative to the plane of the phenyl ring, C3, O and X are, say, above, while N, C1 and C2 are located below this plane.

Fig. 2 shows general Newman projections, including calculated torsional angles; along the X–C2 bond (left), the C2–C3 bond (center) and the C3–C4 bond (right). For clarity of the latter projection, the distance of C3 from the phenyl ring plane is neglected. As shown in Fig. 1, and particularly by the projection along the C2–C3 bond, the C2–X and the C3–O bonds are very close to being *syn*-periplanar. This *"cis"*-conformation of the C=O and the C–X bonds has previously been observed in PhC(O)CH$_2$Cl,[16] in PhC(O)CH$_2$Br,[17] in 4-Cl–PhC(O)CH$_2$Br[18] and in 4-Br-PhC(O)CH$_2$Br.[19] In phenacyl iodide, PhC(O)CH$_2$I, however, the dihedral angle between the C=O and the C–I bonds is 93(3)°.[15] From the X–C2 projection, left, it is notable that the XCN groups are *anti*-periplanar to the C2–C3 bonds. In this respect, the two compounds differ from all other organic pseudohalides, RXCN, which so far have been studied by crystallographic methods (*cf.* Refs. 1 and 2).

Discussion

Conformational considerations. In molecules like I and II, free rotation may in principle be pos-

sible around no less than three bonds, the C(Ph)–C(C=O) bond, the C(C=O)–C(CH_2) bond and the C(CH_2)–X bond. Since substituents which might sterically impede conjugation between the phenyl group and the carbonyl group are absent, coplanarity between these two groups is favoured; *cf.* the torsional angles at only 6.6° (I) and 8.5° (II).

When considering the two compounds in the crystalline state as inorganic sulfur and selenium complexes[1], the observed torsional situation at the two remaining bonds can be accounted for. The two heteroatoms, S and Se, are acting as central atoms, and the organic group, $PhC(O)CH_2^-$, and the cyano group, NC^-, acting as ligands. "Secondary bonds"[20] to donor atoms, particularly to oxygen atoms, *trans* to one or both ligands, complete the coordination around the central atoms. Since the contact to a carbonyl oxygen atom *trans* to the cyano group is known to be considerably stronger than the contact *trans* to the organic group,[1] the direction of the X–CN bond will be determined by the direction of the strongest X–O contact.

In I and II, the carbonyl oxygen atom may in principle interact in several different ways with the heteroatoms; intra or intermolecularly *trans* to the cyano group but only intermolecularly *trans* to the organic group. The latter interaction is energetically the least favoured one and since no donor atoms, nitrogen or oxygen atoms, could be detected within 3.7 Å from the central atom *trans* to the organic group, one may conclude that these possible contacts are of no conformational influence. This study shows that it is the intramolecular interaction *trans* to the cyano group which is the one of predominating strength. This is to be expected from the low frequency carbonyl stretching bands. As a result of this interaction, the C=O and the C–X bonds are *"cis"* to each other and the compounds are nearly planar, *cf.*, Figs. 1 and 2. The intramolecular S–O and Se–O distances are quite short, being 2.684(2) and 2.722(2) Å, respectively, as compared with the corresponding sums of the van der Waals' radii, *i.e.* 3.32 and 3.42 Å.[21] Since these X–O contacts owing to the *"cis"* conformation are *syn*-periplanar to the C(CH_2)–C(C=O) bond, C2–C3, the *trans* effect will cause the XCN groups to be *anti*-periplanar to this bond, *Cf.* the Newman projection (left) in Fig. 2.

The X–C2–C3–O part of the molecules. The X–C2–C3 bond angles are only 106.4(1)° (I) and 105.2(2) (II). These bond angles are significantly less than 109.5°, the tetrahedral angle, and are in particular, less than the bond angle at the methylene carbon atom in benzyl compounds, 110–114°.[1] One may be tempted to conclude that these bond angles in I and II are diminished due to the intramolecular X–O interaction. However, in phenacyl iodide, $PhC(O)CH_2I$, where the C–I bond is *syn*-clinal to the C–C bond, this bond angle is also small, 107.2(6)°;[15] in diphenacylselenide, $(PhC(O)CH_2)_2Se$, where one of the oxygen atoms also interacts with the selenium atom, as in II, the Se–O distance is 2.874(1) Å; the bond angle at the methylene carbon atom is 109.6(4)°. The corresponding bond angle in the other half of the molecule, however, in which the oxygen atom is not coordinated to the selenium atom, is only 107.8(4)°.[22] Thus, the conclusion that there exists a simple relationship between the bond angle at the methylene carbon atom and the extent by which the carbonyl oxygen atom is intramolecularly coordinated in phenacyl compounds is dubious.

In both compounds, the C3C4C9 bond angle is significantly smaller than the C3C4C5 bond angle, ≃118.5 and ≃122.5°, respectively. It has been argued that since the carbonyl oxygen atom in phenacyl compounds is approximately coplanar with the phenyl ring and thus is fairly close to one of the two *ortho*-hydrogen atoms, H9 in Fig. 1, 2.44 Å, the oxygen atom may interact by hydrogen bonding.[19] The weakly acidic properties of aromatic hydrogen atoms, however, rather suggests that this difference in the bond angles at the carbonyl carbon atom is due to repulsion between the H5 atom and the methylene hydrogen atoms, H21 and H22.

The carbon-oxygen bond lengths are 1.212(1) Å (I) and 1.222(3) Å (II) and are as observed in recent accurate studies on phenacyl iodide, 1.216(6) Å,[15] and phenacyl kojate monohydrate, 1.220(3) Å.[23] The C=O bonds in the two compounds may therefore be characterized as pure C=O double bonds without significant contribution of the dipolar form. Although the intramolecular X–O interactions are fairly strong, there is no indication implicit in the bond lengths that these interactions are sufficiently strong to create any through-bond resonance of the type observed in 2-formyl-phenyltellurenyl bromide, 2–C(O)H-PhTeBr.[5]

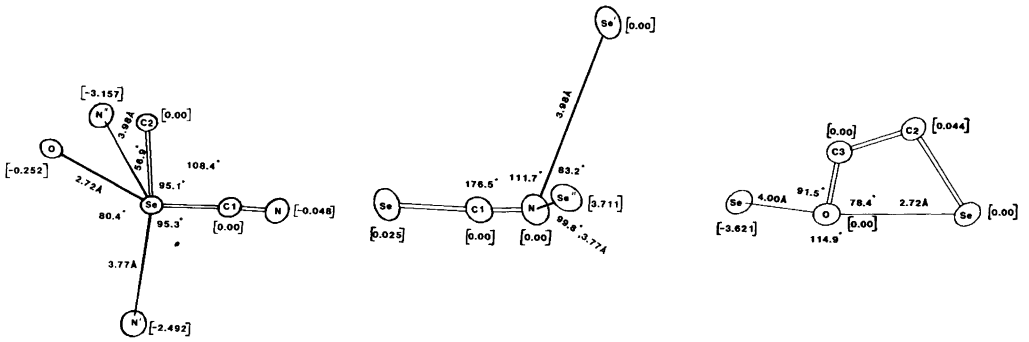

Fig. 3. Coordination around the selenium atom (left), the nitrogen atom (center) and the oxygen atom (right) in II.

Intermolecular contacts. Since no donor atoms could be detected at van der Waals' distances *trans* to the organic group, it may be appropriate to consider the compounds as three-coordinated sulfur and selenium complexes; the forth coordination site being vacant. However, in the recent structural study on benzyl- and 4-nitrobenzyl pseudohalides, it was suggested that coordinating interactions over distances significantly longer than those of van der Waals ought to be considered.[1,24]

Apart from the carbonyl oxygen atoms which undoubtedly are linked intramolecularly to the heteroatoms, no oxygen atoms or nitrogen atoms are found within 3.7 Å from the heteroatoms. Further away, one finds one oxygen atom and two nitrogen atoms with the following distances: S–O′ 3.94 Å, S–N′ 3.81 Å and S–N″ 3.94 Å; Se–O 4.00 Å, Se–N′ 3.77 Å and Se–N″ 3.98 Å. Provided these distances are indicative of some bonding interaction between the atoms, the sulfur and selenium atoms may be considered as six-coordinated, whereas the nitrogen atoms and the oxygen atoms are three-coordinated. Fig. 3 shows the coordination around the selenium atom, left, the nitrogen atom, center, and the oxygen atom, right, in II where the long contacts are included. The numbers in brackets show the

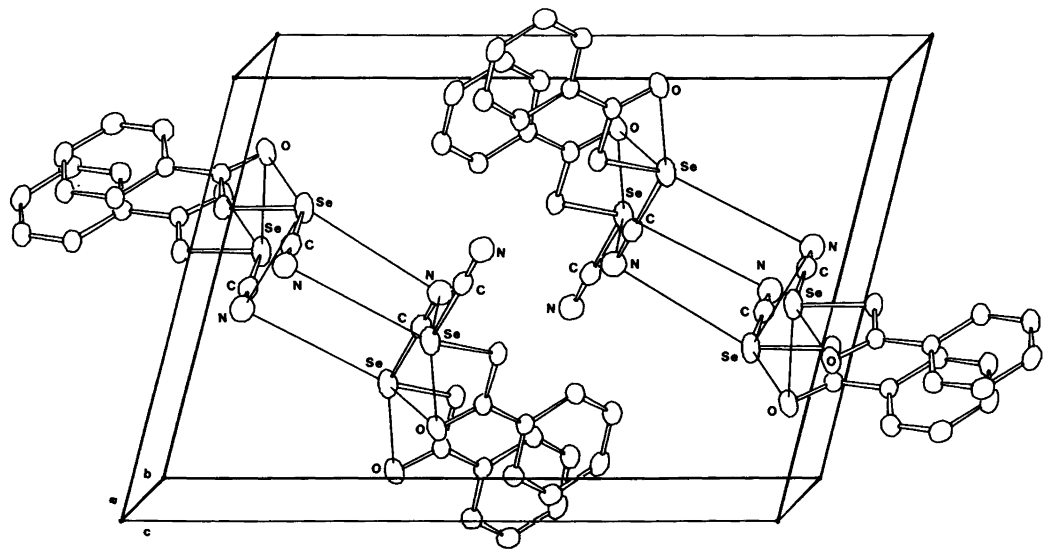

Fig. 4. Projection of the unit cell of II. The weak lines indicate the proposed intra- and intermolecular contacts.

Table 4. C=O frequencies of $PhC(O)CH_2SCN$ in various solvents together with intensities and calculated "cis"/"gauche" ratios, c/g

Solvents[a]	"Gauche" (cm^{-1})	Intensity	*"cis"* (cm^{-1})	Intensity	*c/g*
CCl_4	1710	2.0	1695	10.8	5.4
CH_2Cl_2	1703	2.3	1690	9.7	2.2
c-Hexane[b]	1713	≃0.5	1697	5.1	≃10.2
Et_3N	1710	2.1	1694	10.6	5.1
Et_2O	1708	4.2	1692	10.8	2.6
Dioxane	1705	4.7	1690	10.6	2.3
Pyridine	1701	3.9	1684	8.2	2.1
Benzene	1707	3.8	1691	10.5	2.8
Toluene	1707	3.3	1691	11.8	3.6
4-Xylene	1708	3.2	1691	10.8	3.4
Solid (KBr)	–	–	1678	–	
Solid (Nujol)	–	–	1677	–	
MeCN	1704	4.7	1688	8.2	1.7
4-Br−$PhC(O)CH_2SCN$					
MeCN	1701	4.6	1685	8.9	1.9
4-MeO−$PhC(O)CH_2SCN$					
MeCN	1688	4.5	1672	9.1	2.0

[a]0.04 M solutions. [b]0.02 M solution.

distance of the various atoms from the principal planes defined by C1−Se−C2, left, C1−N−Se′, center, and C3−O−Se″, right. For the sake of clarity, the oxygen atom above the principal in the left-hand drawing, 4.00 Å from the Se-atom, is omitted. Fig. 3 is also representative for I, since the suggested coordination around the corresponding atoms in I is most similar. Fig. 4 shows the unit cell content of II. The weak lines indicate the proposed intra and intermolecular contacts.

The proposed intermolecular contacts are admittedly very long as compared to those of van der Waals. Still, these exceedingly weak interactions seem to be of some importance when the complete three-dimensional crystal network is to be described. The molecules can hardly be linked together through the phenyl groups. The shortest C(Ph)−C(Ph) intermolecular distances found are C7−C8′, 3.843 Å and C7−C8″, 3.830 Å. The atoms involved are C7 (x,y,z), C8′ $(\bar{x}, -\frac{1}{2} + y, -\frac{1}{2} + z)$ and C8″ $(\bar{x}, \frac{1}{2} + y, -\frac{1}{2} - z)$. The phenyl groups of C8′ and C8″ are almost perpendicular and are thus not implying phenyl-phenyl interactions.

Comments on the structure of I and II in solution. Table 4 summarizes the results from the IR study. The presence of two prominent maxima in the C=O stretching region in most solvents, compared with only a single band in the solid state, suggests that rotational isomers are present in solution. The difference between the frequencies is fairly insensitive to the solvent, 14–17 cm^{-1} for I and 7–9 cm^{-1} for II, in I as observed for several phenacyl halides.[9,10] Since this difference between the two bands is independent of the solvent and the frequencies are fairly well correlated with known solvent effects upon carbonyl bands,[25] one may conclude that each band is characteristic for one rotational isomer.

It is notable that in tetrachloromethane and in cyclohexane, the two solvents of lowest dielectric constant and of lowest coordinating ability, only the low frequency band is essentially observed. Since the intramolecular X−O interactions may sustain in this class of solvents, the low frequency band is assigned to the *"cis"* conformation while the high frequency band is assigned to some other conformation, presumably a *syn*-clinal (*gauche*) one.[1] It is to be noted that the assignment made with regard to the two carbonyl bands is opposite to the generally accepted assignment

for the doublet observed in solutions of halomethylketones, $XCH_2C(O)R$, X=F, Cl, Br and I.[7–12] In the case of $PhC(O)CH_2SCN$, I, the two bands were sufficiently apart to permit the ratio between the two conformations to be calculated, *cf.* last column in Table 4. Apparently, the coordinating ability of the solvents will be the predominating factor with regard to the relative stability of the various rotational isomers of I and II and not the steric, the electrical or the mass effects as in the case of phenacyl halides and other halomethylketones.[7]

It is to be emphasized, however, that the problem with regard to the preferred conformation of molecules like I and II in solution is additionally complicated by the question of whether the carbonyl group remains coplanar with the phenyl group in the various types of solvents. Recent dipole moment studies[26] and NMR studies [27,28] have revealed that the simple picture of coplanarity of these two groups as observed for phenacyl compounds in the solid state[16–19,29] cannot be reliably applied in solution. Presumably, only detailed NMR studies at various temperatures and in various solvents[30] can lead to definite conclusions with regard to the structure of the various possible rotational isomers of compounds like I and II. A straightforward comparison of solid and solution state conformations of this class of compounds is not, at present, justified.

References

1. Maartmann-Moe, K., Sanderud, K. and Songstad, J. *Acta Chem. Scand. A 38* (1984) 187.
2. Corfield, G. C. In Patai, S., Ed., *The chemistry of Cyanates and Their Thio Derivatives,* Wiley, Chichester 1977, p. 131.
3. Renson, M. and Piette, J.-L. *Spectrochimica Acta 20* (1964) 1847.
4. Piette, J.-L. and Renson, M. *Spectrochmica Acta 29 A* (1973) 285.
5. Baivir, M., Llabres, G., Dideberg, O., Dupont, L. and Piette, J.-L. *Acta Crystallogr. B 30* (1974) 139.
6. Dereu, N. L. M., Zingaro, R. A. and Meyers, E. A. *Cryst. Struct. Comm. 10* (1981) 1353.
7. Jones, R. N. and Spinner, E. *Can. J. Chem. 36* (1958) 1020.
8. Laird, R. M. and Whitfield, S. E. *J. Chem. Research* (S) *1983,* 288.
9. Bilobrov, V. M., Anikeev, A. V. and Popov, A. F. *Organic Reactivity* (Tartu State University) *18* (1981) 190.
10. Bilobrov, V. M., Anikeev, A. V. and Popov, A. F. *Organic Reactivity* (Tartu State University) *19* (1982) 57.
11. Maltese, M. and Ercolani, C. *J. Chem. Soc. (B) 1970,* 1147.
12. Bellamy, L. J. *The Infrared Spectra of Complex Molecules,* Chapman and Hall, London and New York 1980, vol. 2, 2nd ed., p. 128.
13. Thorstenson, T. and Songstad, J. *Acta Chem. Scand. A 32* (1978) 133.
14. Maartmann-Moe, K., Rømming, C. and Songstad, J. *Acta Chem. Scand. A 36* (1982) 755.
15. Lere-Porte, J.-P., Bonniol, A., Petrissans, J. and Brianso, M.-C. *Acta Crystallogr. B 38* (1982) 1035.
16. Barrans, Y. and Maisseu, J.-J. *Compt. Rend. Acad Sc., Ser. C. 262* (1966) 91.
17. Gupta, M. P. and Prasad, S. M. *Acta Crystallogr. B 27* (1971) 1649.
18. Sinha, D. P. and Prasad, K. N. *Indian J. Phys. 56 A* (1982) 61.
19. Lau, B. W., Yoon, Y. K. and Suh, I.-H. *J. Korean Phys. Soc. 9* (1976) 29.
20. Alcock, N. W. *Inorg. Chem. Radiochem. 15* (1972) 1.
21. Bondi, A. *J. Phys. Chem. 68* (1964) 441.
22. Appa Rao, G. W. N., Seshasayee, M., Aravamudan, G. and Sowrirajan, S. *Acta Crystallogr. C 39* (1983) 620.
23. Phillips, S. E. V. and Truter, M. R. *J. Chem. Soc. Dalton Trans. 1975,* 1071.
24. Maartmann-Moe, K., Sanderud, K. and Songstad, J. *Acta Chem. Scand. B 36* (1982) 211.
25. Bellamy, L. J. and Williams, R. L. *Trans. Faraday Soc. 55* (1959) 14.
26. Mirarchi, D. and Ritchie, G. L. D. *Austr. J. Chem. 34* (1981) 1443.
27. Drakenberg, T., Sommer, J. M. and Jost, R. *Org. Magn. Res. 8* (1976) 579.
28. Drakenberg, T., Sommer, J. and Jost, R. *J. Chem. Soc. Perkin Trans 2* (1980) 363.
29. Kim, J. K. S., Boyko, E. R. and Carpenter, G. B. *Acta Crystallogr. 29 B* (1973) 1141.
30. RamaRao, M. and Bothner-By, A. A. *Org. Magn. Res. 8* (1976) 329.

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