

The Crystal Structure of 4-Nitrobenzyl Tellurocyanate, 4-Nitrobenzyl Selenocyanate, 4-Nitrobenzyl Thiocyanate and Benzyl Selenocyanate

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The structures of the title compounds, 4-NO₂-C₆H₄CH₂TeCN, I, 4-NO₂-C₆H₄CH₂SeCN, II, 4-NO₂-C₆H₄CH₂SCN, III, and C₆H₅CH₂SeCN, IV, have been determined by X-ray methods using diffractometer data collected at room temperature. The crystals are monoclinic, space group *P2₁/c*; I and II are isomorphous.

The C–X–C bond angles are 90.6(1)° in I, 94.0(1)° in II, 100.3(1)° in III and 96.0(2)° in IV. The X–C(CN) bond lengths, 2.060(4) Å in I, 1.844(3) Å in II, 1.680(2) Å in III and 1.829(4) Å in IV are distinctly shorter than the X–C(CH₂) bond lengths, 2.167(3) Å in I, 1.972(3) Å in II, 1.822(2) Å in III and 1.971(4) Å in IV.

The pseudohalide group is in all compounds *syn-clinal (gauche)* to the C(CH₂)–C(Ar) bond with torsion angles of 77.4° (I), 75.3° (II), 58.3° (III) and 64.0° (IV). The XCC plane makes angles of 98.0° (I), 96.9° (II), 101.9° (III) and 97.1° (IV) with the plane of the benzene ring.

The tellurium atom in I forms two fairly strong intermolecular bonds to oxygen atoms from neighbouring nitro groups of 2.949(2) and 3.182(3) Å. I may therefore in the crystalline state be considered as a distorted square planar tellurium(II) complex. II may similarly be viewed as a square planar selenium(II) complex with somewhat weaker Se–O bonds, 3.005(2) and 3.174(2) Å. In III, the sulfur atom is in principle only three-coordinated with a weak intermolecular S–O bond of 3.174(2) Å approximately *trans* to the cyano group. A very weak intermolecular S–N bond, 3.549(2) Å, approximately *trans* to the nitrobenzyl group, completes the three-dimensional network. In IV, the selenium atom is essentially four-coordinated with two weak intermolecular Se–N bonds, 3.107(4) and 3.641(4) Å, to neighbouring selenocyanate groups in a non-

planar arrangement. In all compounds the short intermolecular bond is *trans* to the cyano group.

The possible influence of van der Waals' contacts and also longer contacts than the van der Waals' ones upon the structure of the XCN group is discussed.

Organic thiocyanates, RSCN, are well-known to be a most important class of compounds both in organic and biological chemistry; for recent comprehensive reviews, *cf.* Refs. 1 and 2. The complex chemical behaviour of these substances appears to be due to their pronounced ability to act as ambident electrophilic species toward a number of nucleophiles combined with their potential to isomerize to the thermodynamically more stable isomers, the isothiocyanates, RNCS.³ To further complicate the chemistry of this class of compounds they also act as weak donors toward various acceptors.^{4,5} Fairly recently, several inorganic complexes with *N*-bonded organic thiocyanates have been synthesized and characterized.^{6–9}

More information on the electronic distribution in the SCN-group may contribute to the understanding of the chemistry of this class of compounds. X-ray crystallographic studies with emphasis on S–C(R) and S–C(CN) bond lengths, and also on (NC)C–S–C(R) and S–C–N bond angles appears to be a useful approach. Significant variations in the C–N bond length with the nature of the organic group are probably not to be anticipated.^{10–13} Several X-ray studies on organic thiocyanates have been

reported,¹⁴⁻²⁰ but the majority of these studies are of limited accuracy. Presently it is thus not known whether the SCN-group in RSCN deviates significantly from linearity,^{14,17} a deviation may have considerable influence upon the electronic distribution and hence the chemical properties of RSCN.^{21,22} Since compounds with greatly different organic groups have been examined it is not possible to draw any definite conclusions with regard to the effect of the organic group upon the electronic distribution in the thiocyanate group.

Organic thiocyanates also present a conformational problem, *cf.* Ref. 23. A number of microwave studies on simple aliphatic thiocyanates have appeared,²⁴⁻²⁷ and the *syn-clinal (gauche)* conformer is apparently the more stable one. Likewise, several spectroscopic studies have been done.²⁸⁻³¹ The results from the latter studies, however, appear somewhat contradictory with regard to the preferred conformation. The various results clearly indicate that the energy barrier between the two possible conformers considered, *i.e.* the *syn-clinal* and the *anti*, is fairly small. NMR studies on 2-phenylethyl thiocyanate³² and on the two 1,2-dithiocyanate-1-phenylpropanes³³ reveal that the solvating power and the dielectric constant of the solvent may be the determining factor with regard to the preferred conformation in solution.

Organic selenocyanates, RSeCN, are less known from a structural point of view. These compounds are known to be better electrophilic species both at the organic carbon atom; the selenocyanate ion being a better leaving group,^{34,35} and at the selenium atom and are also acting as better nitrogen donors than the corresponding thiocyanates.^{5,36,37} These observations are to be expected since the group moment of the SeCN-group is larger than that of the SCN-group.^{38,39} Detailed microwave spectra^{40,41} and spectroscopic studies⁴² on MeSeCN have been reported, but to the best of our knowledge only 1,4-diselenocyanatobenzene has been studied by X-ray methods.⁴³

Organic tellurocyanates, RTeCN, have just recently been synthesized⁴⁴⁻⁴⁶ and no structural information is presently available.

In an attempt to solve some of the many problems with regard to the chemical behaviour of compounds of the general type RXCN (X=S, Se and Te) we have undertaken a structural investigation on some crystalline examples of

sufficient stability. In the present study we report the crystal structures of:

- I 4-Nitrobenzyl tellurocyanate,
4-NO₂PhCH₂TeCN
- II 4-Nitrobenzyl selenocyanate,
4-NO₂PhCH₂SeCN
- III 4-Nitrobenzyl thiocyanate,
4-NO₂PhCH₂SCN
- IV Benzyl selenocyanate,
PhCH₂SeCN

Compound IV was included in the present investigation since the study of I and II revealed that the tellurium atom in I and the selenium atom in II form fairly strong intermolecular contacts with oxygen atoms from neighbouring nitro groups. In IV such intermolecular contacts to oxygen atoms are excluded.

A preliminary report on the preparation and the crystal structure of I has been published.⁴⁷

EXPERIMENTAL

Materials. The preparation and purification of the studied compounds together with some of their physical data have been published.^{47,48}

X-ray data and structure determinations. The crystals of I from dichloromethane, of II and III from benzene/diethyl ether and of IV from diethyl ether were suitable for the crystallographic study. An Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoK α radiation was used for the determination of cell parameters and for recording of intensity data. The cell parameters were for each of the compounds based upon least squares fits to the diffractometer settings of 25 independent reflections with $\lambda(\alpha_1)=0.70926$ Å and $\lambda(\alpha_2)=0.71354$ Å.⁴⁹

Intensity data ($\lambda=0.71073$ Å) were recorded at room temperature (~ 19 °C) using the ω -scan technique with variable scan speed; I: 3.5–0.4° min⁻¹; II: 3.5–0.5° min⁻¹; III: 3.5–0.5° min⁻¹; IV: 7.0–0.75° min⁻¹. Minimum scan width was 1.5° including 2×0.25° background scans. At intervals of 100 recordings the orientation of the crystals was checked. Three standard reflections were measured every 2 h and the intensity data later corrected in accordance with their variations. The minimum and maximum correction factors (averages in parenthesis) were I: 0.98, 1.03(1.00); II: 0.98, 1.01(0.99); III: 0.99,

Table 1. Crystal data and structural parameters.

Compound	I	II	III	IV
Mp. °C	123	122	85–86	72
Recryst. from	CH ₂ Cl ₂	Benzene/ether ^a	As II	Ether ^a
Cryst. system	Monoclinic	As I	As I	As I
<i>a</i> (Å)	4.749(1)	4.747(1)	8.342(1)	6.029(1)
<i>b</i> (Å)	16.717(2)	16.293(1)	15.495(1)	7.566(2)
<i>c</i> (Å)	11.753(2)	11.671(2)	7.044(1)	17.578(5)
β (°)	93.26(1)	94.41(1)	99.78(1)	95.25(2)
Volume (Å ³)	931.5(4)	899.9(3)	897.3(3)	798.5(6)
Temp. °C	~19°	As I	As I	As I
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	As I	As I	As I
<i>M</i>	289.75	241.11	194.21	196.11
<i>Z</i>	4	4	4	4
<i>F</i> (000)	544	472	400	384
<i>D</i> _c (g cm ⁻³)	2.066	1.779	1.438	1.631
Abs. coeff. (cm ⁻¹)	32.792	44.520	3.229	49.723
Cryst. dim. (mm)	~0.1×0.2×0.3	~0.2×0.2×0.2	~0.3×0.3×0.1	~0.3×0.1×0.1
Tr. coeff. min.-max.	0.746–0.774	0.443–0.562	Not corr.	0.481–0.678
Fudge factor, <i>p</i>	0.02	0.02	0.02	0.02
Scale factor	0.706	0.291	0.345	0.311
No. of refl.	2724	2615	2435	1564
No. of refl. >2 σ , <i>N</i>	2083	1659	1439	1075
<i>R</i>	0.027	0.036	0.039	0.037
<i>R</i> _w ^b	0.030	0.035	0.040	0.035
<i>S</i> =[$\sum w(\Delta F)^2/N-n$] ^{1/2}	1.181	1.481	1.429	1.403
Diff. Four. max. <i>e</i> Å ⁻³	0.22	0.40	0.08	0.30

^a Diethyl ether. ^b $R_w = [\sum w(\Delta F)^2 / \sum w F_o^{2}]^{1/2}$, $w^{-1} = \sigma(F^2) = \sigma^2(I) / 4Lp \cdot I$, $\sigma^2(I) = \sigma^2(I)_{\text{count}} + (pI)^2$.

1.04(1.02), IV: 1.00, 1.94(1.35). The reason for the notable corrections on IV was sublimation during the recording of the intensities; the crystal volume being reduced to about its original half. All crystallographically independent reflections with $\theta < 25^\circ$ were recorded.

The intensity data were corrected for Lorentz, polarization and, with the exception of IV, also for absorption; the latter corrections being based upon crystal faces and dimensions. The structure of the compounds were solved by interpretation of Patterson and Fourier density maps.

Atomic form factors and anomalous dispersion coefficients were taken from Ref. 50. Before the final cycles of the least squares refinement the hydrogen atoms were placed geometrically (C–H=0.95 Å) and fixed. Their attributed common fixed thermal parameter ($\beta=5$) was deducted from the individual values arrived at in previous iterations. Non-hydrogen atoms were refined anisotropically. The function minimized is $\sum w \Delta F^2$, the attributed weights correspond to the counting statistics plus 2% of the net intensity (fudge factor of 0.02). Reflections with

$I < 2\sigma(I)$ were excluded and considered unobserved in the least-squares refinement.

Table 1 summarizes the crystal data and other relevant information. Fractional atomic coordinates and thermal parameters are listed in Table 2. 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.

All computer programs used belong to the Enraf-Nonius Structure Determination Pack, version 17-1980.

RESULTS

An ORTEP drawing of I, 4-NO₂-PhCH₂TeCN, is shown in Fig. 1, including numbering of the atoms. For clarity the hydrogen atoms are omitted. In this drawing the tellurium atom, Te, the cyano carbon atom, C1, and the methylene carbon atom, C2, are in the plane of the paper. When considering the separate mole-

Table 2. Fractional atomic coordinates and their e.s.d. (Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B=4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+abc\cos\gamma B(1,2)+accos\beta B(1,3)+bcaB(2,3)]$)

	X	Y	Z	B(Å ²)		X	Y	Z	B(Å ²)
	I					II			
Te	0.02384(5)	0.45575(1)	0.31964(2)	3.052(4)	Se	0.02738(8)	0.45675(2)	0.30737(3)	3.775(7)
C1	0.2331(8)	0.5237(2)	0.2050(3)	3.94(8)	C1	0.2299(8)	0.5192(2)	0.2106(3)	4.17(8)
N1	0.3516(9)	0.5611(3)	0.1421(4)	6.2(1)	N1	0.3549(8)	0.5569(2)	0.1512(3)	6.21(9)
C2	-0.1718(7)	0.3857(2)	0.1816(3)	3.18(6)	C2	-0.1622(7)	0.3916(2)	0.1815(3)	3.64(7)
C3	0.0250(6)	0.3255(2)	0.1362(3)	2.63(5)	C3	0.0299(6)	0.3290(2)	0.1349(3)	3.05(6)
C4	0.0699(7)	0.2522(2)	0.1908(3)	3.08(6)	C4	0.0730(7)	0.2536(2)	0.1883(3)	3.53(7)
C5	0.2533(7)	0.1967(2)	0.1497(3)	3.17(6)	C5	0.2504(7)	0.1960(2)	0.1462(3)	3.67(7)
C6	0.3893(6)	0.2149(2)	0.0526(3)	2.64(5)	C6	0.3844(7)	0.2151(2)	0.0489(3)	3.10(6)
C7	0.3517(7)	0.2870(2)	-0.0041(3)	2.98(6)	C7	0.3486(7)	0.2894(2)	-0.0065(3)	3.43(7)
C8	0.1676(7)	0.3421(2)	0.0389(3)	2.98(6)	C8	0.1674(7)	0.3463(2)	0.0372(3)	3.41(7)
N2	0.5831(6)	0.1564(2)	0.0080(2)	3.36(6)	N2	0.5766(6)	0.1550(2)	0.0029(3)	4.06(6)
O1	0.7139(6)	0.1755(2)	-0.0757(2)	4.75(6)	O1	0.7041(6)	0.1753(2)	-0.0797(2)	5.77(6)
O2	0.6089(7)	0.0918(2)	0.0539(3)	5.24(7)	O2	0.6006(6)	0.0883(2)	0.0488(2)	6.21(7)
	III					IV			
S	0.04356(6)	0.58947(4)	0.20652(9)	4.68(1)	Se	0.15560(7)	0.29845(8)	0.46152(3)	4.23(1)
C1	0.1561(3)	0.5519(1)	0.4102(3)	4.04(5)	C1	0.4587(7)	0.2757(7)	0.4687(2)	3.8(1)
N1	0.2267(3)	0.5292(1)	0.5541(3)	6.01(5)	N	0.6469(6)	0.2665(7)	0.4749(3)	5.7(1)
C2	0.1969(2)	0.5936(2)	0.0509(3)	4.04(5)	C2	0.0914(7)	0.0786(7)	0.4035(3)	4.2(1)
C3	0.3399(2)	0.6494(1)	0.1276(3)	3.24(4)	C3	0.1746(7)	0.0763(6)	0.3257(2)	3.13(9)
C4	0.3264(2)	0.7388(1)	0.1182(3)	3.82(4)	C4	0.0484(8)	0.1526(7)	0.2649(3)	4.1(1)
C5	0.4585(3)	0.7904(1)	0.1847(3)	4.17(5)	C5	0.1208(9)	0.1456(7)	0.1933(3)	5.1(1)
C6	0.6025(2)	0.7509(1)	0.2618(3)	3.87(4)	C6	0.317(1)	0.0662(7)	0.1819(3)	5.1(1)
C7	0.6192(2)	0.6635(2)	0.2758(3)	3.96(4)	C7	0.4431(8)	-0.0092(7)	0.2413(3)	4.6(1)
C8	0.4864(3)	0.6127(1)	0.2072(3)	3.67(4)	C8	0.3719(7)	-0.0039(7)	0.3142(2)	3.6(1)
N2	0.7449(3)	0.8055(1)	0.3334(3)	5.77(5)					
O1	0.8681(2)	0.7700(2)	0.4152(3)	8.45(6)					
O2	0.7314(3)	0.8830(1)	0.3101(3)	9.18(6)					

cules only and neglecting differences in the intermolecular bonding system, the drawing in Fig. 1 of I is characteristic for all the four compounds and the tellurium atom is therefore termed X. In the case of IV, benzyl selenocyanate, which lacks the 4-nitro groups and thus contains only one nitrogen atom, this nitrogen atom is termed N and not N1 in the following tables. Intramolecular bond lengths and bond angles in the molecules are listed in Table 3.

The phenyl rings are in all compounds planar within experimental error; the maximum deviation from planarity was observed in III in which C4 and C7 were 0.006 and 0.007 Å, respectively, out of plane; *i.e.* 3 e.s.d. The methylene carbon atom, C2, in III and IV and some of the atoms belonging to the nitro groups in I, II and III are

slightly but significantly out of the phenyl ring plane. These deviations from coplanarity are summarized in Table 4.

Fig. 2 shows general Newman projections along the X-C2 bond (left hand side) and along the C2-C3 and the C3-C6 bonds (right-hand side). For clarity of the latter projections for compounds III and IV the distance of C2 from the phenyl ring plane is disregarded; *cf.* Table 4. It is apparent that in all compounds the XCN group is *syn-clinal (gauche)* to the C2-C3 bond. The torsional angles, however, differ significantly.

The coordination around the central atom in all four compounds is shown in Fig. 3 in which C1, the central element and C2 are in the plane of the paper and the distances of the various atoms

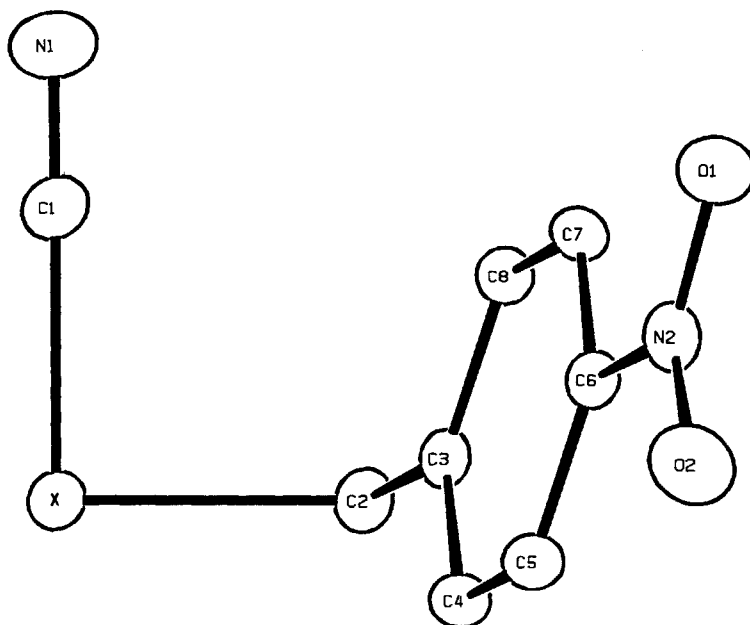


Fig. 1. ORTEP drawing of 4-NO₂-PhCH₂TeCN, I. The tellurium atom, X, the cyano carbon atom, C1, and the methylene carbon atom, C2, are in the plane of the paper.

from this plane are indicated in brackets. Fig. 4 shows the projections of the unit cells along the *a*-axis for I, the *c*-axis for III and the *b*-axis for IV; II is omitted since it is isomorphous with I. The weak lines indicate the proposed intermolecular interactions.

DISCUSSION

The compounds studied in the present investigation as well as numerous other compounds containing a heteroatom of some coordinating ability, may in principle be looked upon in two ways. In solution, particularly when dissolved in non-coordinating solvents, they act fundamentally as organic species and may be illustrated as shown in Figs. 1 and 2. In their crystalline state, however, and probably also in coordinating solvents, *i.e.* solvents with atoms of some Lewis basicity, the organic pseudohalides of the general type RXCN (X=Te, Se and S) may better be regarded as inorganic complexes with the heteroatom X as the central element. The organic group, R, and the cyano group, NC⁻, may thus be considered as ligands as shown in Fig. 3. In a discussion of results from structural studies of this

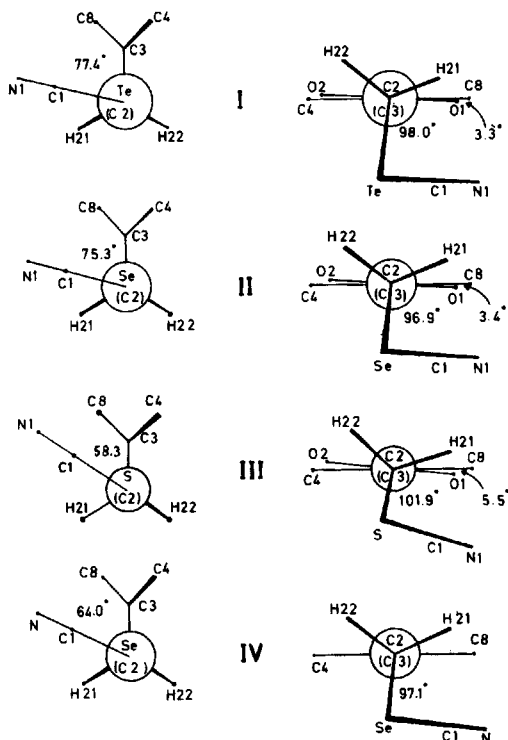


Fig. 2. Newman projections along the X-C2 bond (left) and along the C2-C3 and the C3-C6 bonds (right).

Table 3. Structural data.

	I	II	III	IV
Bonds lengths (Å)				
N1-C1	1.141(5)	1.129(4)	1.138(2)	1.132(4) ^a
C1-X	2.060(4)	1.844(3)	1.680(2)	1.829(4)
X-C2	2.167(3)	1.972(3)	1.822(2)	1.971(4)
C2-C3	1.492(4)	1.498(4)	1.498(2)	1.499(5)
C3-C4	1.394(4)	1.385(4)	1.391(2)	1.381(5)
C4-C5	1.379(4)	1.377(4)	1.377(3)	1.371(6)
C5-C6	1.377(4)	1.379(4)	1.375(3)	1.357(6)
C6-C7	1.384(4)	1.376(3)	1.364(3)	1.359(6)
C7-C8	1.385(4)	1.388(4)	1.378(2)	1.390(5)
C8-C3	1.390(4)	1.386(4)	1.378(2)	1.366(5)
C6-N2	1.460(4)	1.468(3)	1.475(2)	
N2-O1	1.235(3)	1.222(3)	1.220(3)	
N2-O2	1.210(4)	1.212(3)	1.215(3)	
Bond angles (°)				
N1-C1-X	179.3(4)	179.5(3)	175.9(2)	177.6(4) ^b
C1-X-C2	90.6(1)	94.0(1)	100.3(1)	96.0(2)
X-C2-C3	112.4(2)	112.4(2)	113.6(1)	114.6(3)
C2-C3-C4	120.7(3)	120.9(2)	120.3(2)	119.6(4)
C3-C4-C5	120.9(3)	121.2(2)	120.5(2)	119.7(4)
C4-C5-C6	118.5(3)	118.2(3)	118.2(2)	120.5(4)
C5-C6-C7	122.5(3)	122.5(3)	122.8(2)	120.4(4)
C6-C7-C8	118.1(3)	118.2(2)	118.4(2)	119.9(4)
C7-C8-C3	120.9(3)	120.7(2)	120.9(2)	119.7(4)
C8-C3-C2	120.3(3)	119.9(2)	120.4(2)	120.6(4)
C8-C3-C4	119.1(3)	119.2(3)	119.3(2)	119.8(4)
C5-C6-N2	119.0(3)	119.3(3)	118.7(2)	
C7-C6-N2	118.5(3)	118.2(3)	118.6(2)	
C6-N2-O1	117.9(3)	117.8(3)	117.9(2)	
C6-N2-O2	119.2(3)	118.4(3)	118.0(2)	
O1-N2-O2	122.9(3)	123.8(3)	124.1(2)	

^a The N-C1 bond length. ^b The N-C1-X bond angle.

Table 4. The distance of C2, N2, O1 and O2 in I, II and III and of C2 in IV from the phenyl ring plane (Å). (Positive value is defined as the opposite side of the XCN-part of the molecules, cf. right-hand side drawings in Fig. 2).

	I	II	III	IV
C2	-0.004(3)	-0.009(3)	0.030(2)	0.042(5)
N2	0.004(3)	0.009(3)	0.012(2)	
O1	-0.059(3)	-0.080(3)	-0.091(2)	
O2	0.064(3)	0.048(3)	0.099(2)	

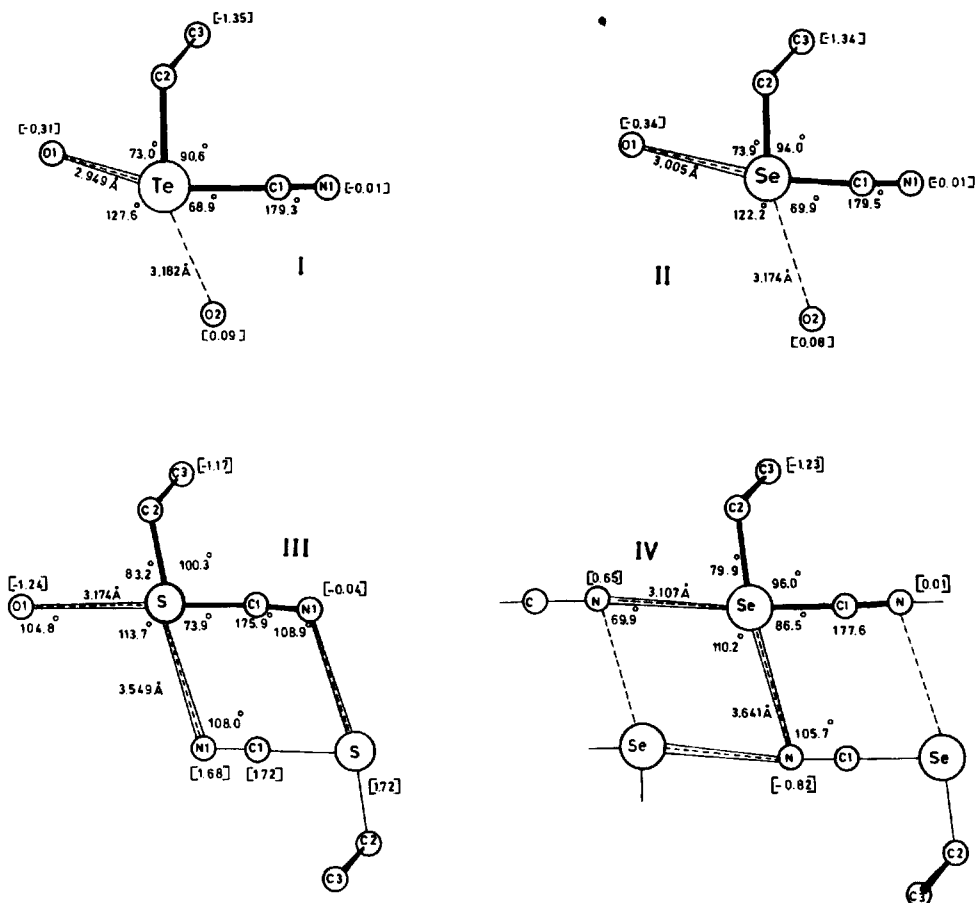


Fig. 3. The coordination around the central atoms, Te in I, Se in II and IV and S in III. The central atom, the cyano carbon atom, C1, and the methylene carbon atom, C2, are in the plane of the paper. Numbers in brackets indicate the distance in Å of the various atoms from this plane.

class of compounds it thus seems appropriate to consider both the organic and the inorganic aspects. It should be emphasized that in some instances, *cf.* III and IV in Fig. 3, the weakly coordinating nitrogen atom belonging to the cyano group⁶⁻⁹ may also be an important factor when describing the complete three-dimensional crystal network of organic pseudohalides, *cf.* Figs. 3 and 4.

The 4-nitrobenzyl group in I, II and III and the benzyl group in IV. The structural data on the organic part of the molecules as listed in Table 3 show the majority of the bond lengths and the bond angles to be as expected. The notable deviations from the expected values in the case of

IV like some of the aromatic carbon-carbon bond lengths are presumably due to the experimental difficulties caused by evaporation during data uptake, *cf.* Experimental. The calculated uncertainties in the case of IV are for all bond lengths and bond angles generally twice as large as for the remaining three compounds, *cf.* last column in Table 3.

The benzene ring is in all four compounds planar within experimental error but are in I, II and III significantly distorted with regard to the C-C-C bond angles as observed in numerous compounds containing one or more nitro groups.^{51,52} The bond angle at the carbon atom bearing the nitro group is thus in all three

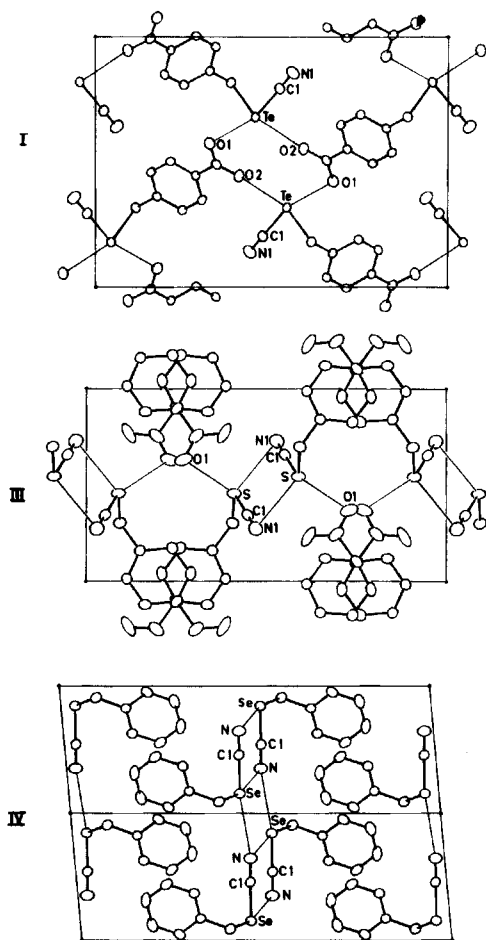


Fig. 4. The projections of the unit cell along the *a*-axis for I, the *c*-axis for III and the two adjacent cells along the *b*-axis for IV. The weak lines indicate the proposed intermolecular interactions.

compounds slightly but significantly larger than 120° while the two adjacent ones are slightly less, ~ 118 – 118.5° . No similar distortion is observed in IV which lacks the nitro group.

In compounds I, II and III it is observable that the N2–O1 bonds are all slightly longer than the N2–O2 bonds. This is coincidental with the degree of coordination between O1 and the heavy atom of the neighbouring molecule. Likewise, the bond angles C6–N2–O1 and C6–N2–O2 appear influenced by the coordination of the O1 oxygens. In I, the tellurocyanate,

the N2–O bond lengths and also the two C6–N2–O bond angles are different, a long N2–O1 bond to the fairly strongly coordinated oxygen atom, 1.234(3) Å, as compared with a short nitrogen–oxygen bond length, N2–O2, to the weakly coordinated oxygen atom, 1.210(3) Å. This latter bond length is actually within experimental error as observed in III, the thiocyanate, in which only a very weak interaction between one oxygen atom and the central sulfur atom is observed as mentioned above. In II, the corresponding selenocyanate, an apparently intermediate case is observed with regard to both N2–O bond lengths and C6–N2–O bond angles as anticipated from the intermolecular selenium–oxygen interactions as shown in Fig. 3.

Even the C6–N2 bond lengths seem correlated to the coordination of the oxygen atom, 1.460(4) Å in I, 1.468(3) Å in II and 1.475(2) Å in III. These bond lengths may not be significantly different but the trend is explainable as an increase in charge transfer from the oxygen atoms to the neighbouring heteroatoms which causes an increase in the residual positive charge on the nitrogen atoms and thus shortens the C6–N2 bonds. An inverse relationship between N–O bond lengths and C–N bond lengths in nitro-substituted aromatic compounds has actually been observed.⁵³ An increase in the coordination of the oxygen also causes a small decrease in the O1–N2–O2 bond angles, from $124.1(2)^\circ$ in III to $122.9(3)^\circ$ in I. In none of the compounds is the nitro group coplanar with the phenyl ring plane, *cf.* right hand drawings in Fig. 2. This lack of coplanarity in nitroaromatics is quite commonly observed and twist angles of more than 10° have occasionally been detected.⁵⁴ In III, the thiocyanate, the nitrogen atom belonging to the nitro group is probably slightly out of the phenyl ring plane, *cf.* Table 4.

The bond angle at the methylene carbon atom, the X–C2–C3 bond angle, is $112.4(2)^\circ$ in I and II, $113.6(1)^\circ$ in III and $114.6(3)^\circ$ in IV, *cf.* Table 4. This bond angle is thus in all four compounds slightly but significantly larger than 109.5° , the expected bond angle for a purely sp^3 hybridized carbon atom. This increase in the *s*-character of the methylene carbon atom in benzylic compounds, particularly in benzylic compounds containing electronegative substituents, is quite commonly observed, both in the solid state⁵⁵ and in the gas phase.^{56,57} It has previously been sug-

Table 5. A comparison between X-C(CH₂) bond lengths, X-C(CN) bond lengths and the sum of the covalent radii of X and C, $\Sigma R_{\text{cov.}}(\text{X}-\text{C})$. (Bond lengths in Å).

	I	II	III	IV
X-C(CH ₂)	2.167(3)	1.972(3)	1.822(2)	1.971(4)
X-C(CN)	2.060(4)	1.844(3)	1.680(2)	1.829(4)
$\Sigma R_{\text{cov.}}(\text{X}-\text{C})$	2.14	1.94	1.81	1.94
X-C(CH ₂)- $\Sigma R_{\text{cov.}}$	0.03	0.03	0.01	0.03
X-C(CH ₂)-X-C(CN)	0.107(7)	0.128(6)	0.142(4)	0.142(8)
$\Sigma R_{\text{cov.}}-\text{X}-\text{C}(\text{CN})$	0.08	0.10	0.13	0.11

gested⁵⁵ that this decrease of the *p*-character of the C-H bonds in benzylic compounds is the probable cause for their high acidities as compared with simple aliphatic species.⁵⁸ Finally it should be noted that in III and IV, the methylene carbon atom is distinctly out of the phenyl ring plane, *cf.* Table 4. Whether this deviation from the expected result, as was observed in the case of I and II, is due to electronic effects or to packing effects cannot be decided upon. However, since this deviation, particularly in the case of III, is considerable, 15 e.s.d., one should not neglect the possibility that similar deviations are to be observed in other benzylic compounds, particularly in the solid state.

The X-C bond lengths. Two sets of X-C bond lengths, the X-C(CH₂) bond lengths and the X-C(CN) bond lengths, emanate from the present study. These bond lengths and the sum of the covalent radii of the atoms from the VI main group, X, and the carbon atom, C, as given by $\Sigma R_{\text{cov.}}(\text{X}-\text{C})$ ⁵⁹ together with some calculated differences between these bond lengths are listed in Table 5.

In the tellurocyanate, I, and in the two selenocyanates, II and IV, the observed X-C(CH₂) bond lengths are somewhat longer, ~0.03 Å, than calculated from the covalent radii. In the case of III, the thiocyanate, however, the difference is only 0.01 Å and is hardly significant. As mentioned in the introduction no structural studies on alkyl tellurocyanates have previously been performed allowing direct comparisons. The available surveys on Te-C single bond lengths,^{60,61} however, leave no doubt that 2.14 Å is a most valid estimate for Te-C(aliph.); Te-C(arom.) bond lengths may actually be somewhat shorter, 2.11-2.12 Å.^{62,63} Thus, the Te-C(CH₂) bond of 2.167(3) Å as observed in I

appears to be exceptionally long.

The same conclusion can apparently also be made with regard to the Se-C(CH₂) bond of 1.972(3) Å in II and 1.971(4) Å in IV. Although comparisons of bond lengths determined by X-ray, by microwave and by electron diffraction are not entirely justifiable it is worth noticing that the Se-C(Me) bond length in MeSeCN^{40,41} and in Me₂Se⁶⁴ is 1.956 and 1.943 Å, respectively, and is thus in fair agreement with the bond length calculated from the covalent radii but not with the bond lengths as observed in the present study. The S-C(CH₂) bond length in III, 1.822(2) Å, on the other hand is comparable with those calculated from the covalent radii and is as observed in MeSCN^{25,26}, in EtSCN²⁷, in (NCSCH₂)₂¹⁴ and in CH₂(SCN)₂¹⁷. The S-C single bond may possibly be somewhat shorter in Me₂S, 1.802(2) Å, as determined by microwave,⁶⁵ and also in MeSCN when coordinated to a metal atom through the nitrogen atom.⁸

The notable length of the X-C(CH₂) bond in the tellurocyanate and in the two selenocyanates may well be due to the benzyl groups. Electron diffraction studies of benzyl halides^{56,57} have revealed that X-C bonds in this class of compounds are significantly longer than in the usual aliphatic systems. This elongation of the X-C bond from methyl to benzyl halides is highly dependent upon the halogen atom, 0.04-0.06 Å for C-Br and 0.02-0.04 Å for C-Cl⁵⁶ while probably negligible for C-F.⁶⁶ Provided a similar lengthening of the X-C(CH₂) bond in benzyl compounds takes place when descending the VI main group, the observed Te-C(CH₂) and Se-C(CH₂) bond lengths as observed in I, II and IV may be considered as real bond lengths. As in the case of the benzyl halides⁶⁶ these elongated bonds do not seem to contradict or to invalidate

the bond lengths as calculated from the covalent radii,⁵⁹ but may rather shed light upon the considerable kinetic instability of benzyl halides and of benzyl pseudohalides in solution.⁴⁸

As observed in numerous structural studies on organic pseudohalides the X–C(CN) bond lengths are significantly shorter than the X–C(CH₂) bond lengths. The difference range from 0.107(7) Å (I, X=Te), 0.128(6) Å (II, X=Se) to 0.142(4) Å (III, X=S) in the three 4-nitrobenzyl pseudohalides; cf. Table 5. Owing to the exceptionally long Te–C(CH₂) and Se–C(CH₂) bonds in these compounds of reasons outlined above, the difference between the sum of the covalent radii, $\Sigma R_{\text{cov.}}(\text{X}-\text{C})$ and the X–C(CN) bond lengths may well be a better measure for the double-bond character of the X–C(CN) bonds. This difference, 0.08 Å in the case of the tellurocyanate, 0.10–0.11 Å for the selenocyanates and 0.13 Å for the thiocyanate readily suggests that the bond order of the X–C(CN) bond is increasing when ascending the VI main group. In the case of organic thiocyanates it was originally suggested that this increase in the bond order of the S–C(CN) bond was due to some contribution of the pseudo-ionic structure as depicted by $\text{R}-\text{S}^{\delta+}=\text{C}=\text{N}^{\delta-}$.¹⁴ When only considering the X–C(CN) bond lengths in the examined organic pseudohalides one may thus be led to conclude that the onium character of the thiocyanate, III is more pronounced than in the selenocyanates, II and IV, and particularly in the tellurocyanate, I.

This conclusion, however, may not be correct and contrasts first of all with the results from dipole moment studies which clearly indicate that the group moment of SeCN in RSeCN exceeds that of SCN in corresponding RSCN by some 0.5D.^{38,39} Furthermore, the selenocyanates are generally regarded to act as better donors through the terminal nitrogen atom than do the thiocyanates.^{5,36,37} The ability of the heteroatom in RXCN to coordinate to even hard Lewis donors, particularly in the solid state, cf. Fig. 3, is undoubtedly increasing with increasing size of the heteroatom. Although the tellurium atom is superior to the selenium atom and particularly the sulfur atom to form square planar coordination complexes^{67,68} this ability may also be the result of a higher residual positive charge on the larger heteroatom in RXCN. This is to be anticipated from purely electronegativity

considerations. Finally it is worth mentioning that fairly strong coordination of the heavier heteroatoms in the solid state may result in an elongation of the X–C(CN) bond. In the complex anions formed from 4-nitrobenzyl tellurocyanate and halide anions, $[\text{4-NO}_2\text{-PhCH}_2\text{Te(X)CN}]^-$, X=Cl, Br and I, the Te–C(CN) bond lengths are comparable with the Te–C(CH₂) bond length.⁶⁸ Thus, the relative length of the X–C(CN) bonds in organic pseudohalides in the solid state may prove to be a poor measure of the onium character of the heteroatom, particularly when these compounds are dissolved in non-coordinating solvents.

Recent photoelectron spectral studies on MeSCN and MeSeCN have revealed that all bonds in MeSeCN are shifted by some 0.3 eV to lower ionization energy as compared with MeSCN in consistency with the easier ionization of Se as compared with S.⁶⁹ The narrowness of the π ionization band in MeSeCN points to a less bonding character of the π orbitals in the Se compound. This latter observation suggests that the X–C(CN) bond is less influenced by charge development on the heteroatom X the larger the heteroatom is. Through this decreasing conjugation between the cyano group and the heteroatom the larger the heteroatom is the terminal nitrogen atom will retain its negative charge irrespective of the onium character of the larger heteroatoms and RSeCN will thus act as better donors than RSCN. As anticipated,¹⁰⁻¹³ no relationship between the heteroatom and the C–N bond lengths could be detected, cf. first entry in Table 3.

Conformational considerations. All the compounds studied in the present investigation exist exclusively in the *syn*-clinal (*gauche*) conformation in the solid state cf. left-hand Newman projections in Fig. 2. Thus, the conformation in this class of compounds is independent upon the heteroatom, the extent by which the heteroatom is intermolecularly coordinated to donor atoms and to which donor atom, oxygen or nitrogen. So far, there seem to be no known exceptions to the “*gauche* effect”⁷⁰ with regard to the conformation of organic pseudohalides in the solid state.²³

The torsion angles, however, are significantly different, 77.4° in I, 75.0° in II, 58.3° in III and 64.0° in IV. There seems to be no simple correlation between the size of the heteroatom and the torsion angle. In the two isomorphous

compounds, I and II, these angles are most similar, while in II and IV, the two selenocyanates, the torsion angles are significantly different. This may indicate that lattice forces are the determining factor with regard to the magnitude of the torsion angle as long as the *syn*-clinal conformation is retained. It is interesting to note that the observed torsion angle in the thiocyanate, 58.3° , is identical with the angle determined in EtSCN by infrared and Raman investigations in vapour, liquid, amorphous and crystalline states.³⁰ The coincidence may be fortuitous but may also mean that at least in the case of organic thiocyanates a torsion angle of $\sim 60^\circ$ represents a distinct energetic minimum.

The C-Ph dihedral angles are most similar in the four compounds, $\sim 100^\circ$, and no distinct relationship between the size of the heteroatom and this dihedral angle is evident from this study; cf. right-hand Newman projections in Fig. 2. Presumably a dihedral angle of $\sim 100^\circ$ for this class of compounds causes a maximum separation between the heteroatom and the one *ortho*-carbon atom, C8. In benzyl fluoride⁵⁶ and in benzyl alcohol,⁵⁷ both compounds having small atoms linked to the methylene carbon atom, the dihedral angle is only $\sim 54^\circ$.

Coordination around the heteroatoms. In the 4-nitrobenzyl compounds, I, II and III, the C1-X-C2 bond angle increases from the tellurocyanate to the thiocyanate, $90.6(1)^\circ$ in I, $94.0(1)^\circ$ in II and $100.3(1)^\circ$ in III. The C1-Te-C2 bond angle and also the C1-Se-C2 bond angle fall at the low end of the range of these angles observed in other organotellurium and organoselenium compounds.⁶¹ The small bond angles in I and II may well be due to the fairly strong intermolecular contacts, cf. Fig. 3. Extensive "secondary bonding"⁷¹ seems to decrease the bond angle in divalent species from the VI group, presumably due to increased repulsion between the lone pairs on the central atoms when these are partly involved in some bonding. In the complex anions derived from 4-nitrobenzyl tellurocyanate and halide ions, $[4\text{-NO}_2\text{-PhCH}_2\text{Te}(\text{CN})\text{X}]^-$ in which the halide ions are strongly linked to the central atom *trans* to the cyano group, the C-Te-C bond angles are only $87.4(3)^\circ$ (X=Cl), $87.8(4)^\circ$ (X=Br) and $88.7(2)^\circ$ (X=I)⁶⁸ as compared with $90.6(1)^\circ$ in the parent tellurocyanate. As the intermolecular bonding system in IV is much weaker than in II, this may

explain the difference in the corresponding C1-Se-C2 angle, $96.0(2)$ and $94.0(1)^\circ$ in IV and II, respectively.

The two isomorphous compounds, I and II, are as anticipated most similar and the central elements form two strong intermolecular "secondary bonds" to oxygen atoms from neighbouring nitro groups. These two oxygen atoms are very close to the planes made by the two Te-C and the two Se-C bonds; the sum of the bond angles around the heteroatoms being $360.1(4)$ in I and $360.0(4)$ in II. These two compounds in their crystalline state may therefore be considered as slightly distorted square planar tellurium(II) and selenium(II) complexes. 4-Nitrobenzyl tellurocyanate owes undoubtedly its remarkable stability in the solid state to these intermolecular contacts. The intermolecular X-O distances, $2.949(1)$ and $3.182(1)$ Å in I and $3.005(1)$ and $3.174(1)$ Å in II are all significantly less than the sum of the van der Waals' radii, 3.58 (Te-O) and 3.42 Å (Se-O).^{71,72} The intermolecular bonds in I are therefore the stronger ones. Compound I one may also be classified as a six-coordinated complex since two oxygen atoms are located mutually opposite to the plane, $3.566(3)$ and $3.881(3)$ Å away from the central tellurium atom.

In both I and II and also in III and IV, the strongest intermolecular interactions is always *trans* to the cyano group. This observation is as expected in view of the *trans* effect, particularly the *σ-trans* effect of the 4-nitrobenzyl group which far exceeds that of the cyano group.⁷³

In compound III, 4-nitrobenzyl thiocyanate, a weak S-O interaction is observed, $3.174(1)$ Å, *trans* to the cyano group, but this oxygen atom is significantly away from the C1-S-C2 plane, 1.24 Å. The distance between the atoms is less than the sum of the van der Waals' radii, 3.32 Å.⁷² *Trans* to the nitrobenzyl group no oxygen atoms as in I and II could be detected. A nitrogen atom from a neighbouring thiocyanato group, however, was observed in a suitable position, 1.68 Å above the C1-S-C2 plane but no less than $3.549(2)$ Å away, cf. Fig. 3.

The van der Waals' distance for an S-N interaction, however, is only 3.35 Å and it may thus not be appropriate to consider a sulfur atom and a nitrogen atom, $3.549(2)$ Å apart, to be in any contact. However, in view of the regular pattern by which this compound, and for that

matter also compound IV, are built up in their crystalline state, it seems necessary also to consider distances significantly larger than van der Waals' distances as indicative of some bonding interaction, particularly distances between atoms with some residual charge of opposite sign due to Coulombic forces. This is indeed the case with regard to the sulfur atom and the nitrogen atom in organic thiocyanates as outlined above.

In IV, benzyl selenocyanate, no oxygen atoms are available and the lattice forces are entirely due to Se-N interactions. A fairly strong Se-N contact is observed *trans* to the cyano group, 3.107(3) Å, as compared with a van der Waals distance of 3.45 Å.^{71,72} This nitrogen atom is only 0.65 Å above the C1-Se-C2 plane. As in the thiocyanate, III, the fourth coordination site is approached by a nitrogen atom from a neighbouring selenocyanate group, 0.82 Å below the C1-Se-C2 plane, but 3.641(3) Å away from the selenium atom. When considering distances somewhat longer than van der Waals' ones, compounds III and IV may thus also be looked upon as square planar complexes, albeit highly distorted. The intermolecular unit as described for IV, *cf.* Fig. 3, is in principle quite similar to what has previously been observed in 1,4-diselenocyanatobenzene⁴³ and in selenium diselenocyanate,⁷⁴ the suggested intermolecular contacts, however, are significantly longer. It is apparent that when the geometry suggests directed interactions, "post-van der Waals'" contacts may not be disregarded, *cf.* Refs. 71 and 75.

The donor atoms. The bond angles at the coordinating donor atoms, oxygen and nitrogen are summarized in Table 6. Although packing effects may alter significantly the intermolecular

Table 6. A survey of intermolecular bond angles (°) at the oxygen atoms in compounds I, II and III and at the nitrogen atom in compounds III and IV. (Intermolecular bond distances in Å).

I	$\angle \text{Te}^{2.949(2)}\text{O1}---\text{N2}$	115.2
	$\angle \text{Te}^{3.182(2)}\text{O2}---\text{N2}$	152.2
II	$\angle \text{Se}^{3.005(2)}\text{O1}---\text{N2}$	116.9
	$\angle \text{Se}^{3.174(2)}\text{O2}---\text{N2}$	150.3
III	$\angle \text{S}^{3.174(2)}\text{O1}---\text{N2}$	104.8
	$\angle \text{S}^{3.549(2)}\text{N1}---\text{C1}$	108.0
IV	$\angle \text{Se}^{3.107(4)}\text{N}---\text{C1}$	167.3
	$\angle \text{Se}^{3.641(4)}\text{N}---\text{C1}$	105.7

bond angles a fairly systematic pattern seems to emerge from the present study.

When oxygen is involved in bonding interaction *trans* to the cyano group, *i.e.* the stronger interaction, *cf.* Fig. 3., the bond angle at the oxygen atom is $\sim 110^\circ$. *Trans* to the nitrobenzyl group the intermolecular bond at oxygen is $\sim 150^\circ$; *i.e.* the N-O bond is fairly collinear with the intermolecular O-X bond. When the terminal nitrogen atom from the pseudohalide group is the donor atom the opposite is the case; in the strong interaction the C-N bond is fairly collinear with the Se-N interaction, the bond angle is 167° in IV, while in the extremely weak interaction in III and IV the intermolecular X-N-C bond angle is 108.0° in III and 105.7° in IV. It is notable that in III in which the position *trans* to the cyano group is occupied by an oxygen atom, the nitrogen atom does not approach the coordination site *trans* to the 4 nitrobenzyl group collinearly but in a similar fashion to what is observed in IV.

Comments on the pseudohalide groups. In I and II the pseudohalide groups are linear within experimental error, the Te-C1-N1 and the Se-C1-N1 bond angles are $179.3(4)$ and $179.5(3)^\circ$, respectively. In these two compounds there is no evidence that the terminal nitrogen atom takes part in any "secondary bonding".

In III and IV the corresponding bond angles are $175.9(2)$ and $177.6(4)^\circ$, respectively and thus deviate significantly from linearity. In III a very weak contact with a neighbouring sulfur atom probably exists approximately at right angles to the N-C bond. The nitrogen atom is observed to be slightly tilted toward this sulfur atom resulting in a bent thiocyanate group. A fairly similar contact is observed in IV, but in this case a stronger contact which is collinear with the N-C1 bond also exists which straightens out the selenocyanate group. A less bent pseudohalide group is then observed in IV than in III.

These observations suggest that weak and even exceedingly weak "secondary bonding" to the terminal nitrogen atom may be the governing factor with regard to the pseudohalide groups being linear or bent. Bent pseudohalide groups are to be anticipated when this secondary bonding makes an angle significantly less than 180° with the pseudohalide group while linear groups may be found when the pseudohalide group is non-coordinated, as in I and II, or the nitrogen

atom is intermolecularly linked collinearly with the C–N bond. Since even very weak intermolecular contacts seem to play an important role, the presence of such contacts should be carefully looked for prior to any discussion on whether pseudohalide groups are linear or not.

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