Synthesis and Molecular Structures of some Novel Anionic Diselenides†

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The anions $[Se(S)C{=}C(CN)_2]^{2-}$ (imnts) and $[Se_2C{=}C(CN)_2]^{2-}$ (imns) undergo oxidative dimerization reactions which have been studied by cyclic voltammetry. They proceed *via* a one-electron oxidation followed by a rapid chemical radical dimerization (EC_{irr} mechanism) with $E_{imnts} = -0.2$ V and $E_{imns} = -0.3$ V *versus* SCE. The resulting anionic diselenides have been characterized by X-ray structure analysis of $[NBu_4]_2[\{(NC)_2C{=}C(S)Se{-}\}_2]$ **1**, $[AsPh_4]_2[\{(NC)_2C{=}C(S)Se{-}\}_2]$ **2** and $[AsPh_4]_2[\{(NC)_2C{=}C(Se)Se{-}\}_2]$ **3**. The anions in **1**–**3** all exhibit a *trans* arrangement with an inversion centre bisecting the Se–Se bridges. The average Se–Se bond length is 2.330 Å. There are two types of bonds involving sp^2-hybridized carbon and different chalcogen atoms. The average Se–C bond distance involving selenium of the diselenide group is 1.936 Å and corresponds to a single bond. The chalcogen–carbon bonds involving anionic sulfur atoms of **1** and **2** as well as Se of **3** are 1.668, 1.669 and 1.81 Å respectively and seem indicative of some double-bond character with charge delocalization over the dimeric dianions.

Dithiocarbamates $[R_2NCS_2]^-$ and related 1,1-dithiolates $[R_2C{=}CS_2]^{2-}$ are readily oxidized by iodine or bromine in suitable solvents.[1,2] Reaction products are thiuram disulfides $[R_2NC(S)S{-}]_2$ and dianionic species $[\{R_2C{=}C(S)S{-}\}_2]^{2-}$. Recently we reported on the electrochemical oxidative dimerization reactions (1)–(3).[2–4] We showed by use of cyclic

$$2\,[S_2C{=}C(CN)_2]^{2-} \longrightarrow [\{(NC)_2C{=}C(S)S{-}\}_2]^{2-} + 2e^- \quad (1)$$

$$2\,[S(O)C{=}C(CN)_2]^{2-} \longrightarrow [\{(NC)_2C{=}C(O)S{-}\}_2]^{2-} + 2e^- \quad (2)$$

$$2\,[S_2C{=}N{-}S(O)_2{-}C_6H_4Cl\text{-}p]^{2-} \longrightarrow [\{p\text{-}ClC_6H_4{-}(O)_2S{-}N{=}C(S)S{-}\}_2]^{2-} + 2e^- \quad (3)$$

voltammetry[5] that the reactions proceed *via* a one-electron oxidation step followed by a rather rapid chemical radical dimerization[6] (EC_{irr} mechanism).

X-Ray structures of tetraphenylarsonium salts of the corresponding thiolatodisulfides revealed anions consisting of two mutually perpendicular planes of monomer fragments linked by a disulfide group.[2–4] In molecular compounds RSSR (R = Me, Et or Ph)[7–10] as well as in known negatively charged species[2–4] dihedral angles C–S–S–C are close to 90°. We showed by *ab initio* calculations on the characteristic S–S dihedral angle in dinegative model systems[4] that the *trans* form with C–S–S–C 180° is the most stable configuration taking into account only point-charge effects and electron–electron repulsion. The observed skew configuration is considered the result of a balance between the repulsion of negatively charged sulfur atoms and the overlap population in S–S bonds.[4]

Although it is known that rotation barriers decrease on going from sulfur to selenium (RSSR, $E \approx 28.5$ kJ mol^{-1}; RSeSeR, $E \approx 23.2$ kJ mol^{-1}),[11,12] most diselenides exhibit a skew conformation with dihedral angles C–Se–Se–C between 70 and 110° (see Table 1).[13–19] The reduction in rotation barriers and the increase in Se–Se bond lengths compared to disulfides led us to carry out a detailed structural analysis on the oxidation products of the monomeric species $[Se(S)C{=}C(CN)_2]^{2-}$ (isomaleonitrileselenolatethiolate, imnts) and $[Se_2C{=}C(CN)_2]^{2-}$ (isomaleonitrilediselenolate, imns) because it is expected that in dinegative diselenides the repulsion of negatively charged atoms should favour a *trans* configuration with dihedral angles near 180°.

Table 1 Distances and dihedral angles in various diselenides

Compound	d(Se–Se)/Å	d(Se–C)/Å	C–Se–Se–C/°	Ref.
Se_2Me_2	2.33	1.95	87.5	13
Se_2Ph_2	2.29	1.93	82	14
$Se_2(C_6F_5)_2$	2.32	1.91	75	15
$Se_2(CHPh_2)_2$	2.39	1.97	82	16
$Se_2(NC_4H_8O)_2$	2.33	2.28	104.5	17
$Se_2(C_6H_4Cl\text{-}p)_2$	2.33	1.93	74.5	18
$Se_2(CF_3)_2$	2.34	1.93	103.5	19

Experimental

The salts K_2[imnts] and K_2[imns] were prepared according to the literature.[20] Oxidation reactions were investigated by cyclic voltammetry (CV) using a PAR 361 scanning potentiostat with a three-electrode unit (platinum working electrode *versus* saturated calomel electrode, SCE). The solvent was MeCN with NBu_4ClO_4 as conduction salt in concentration 10^{-1} mol dm^{-3}. Concentrations of solutes were 10^{-4}–10^{-3} mol dm^{-3} and scan rates varied in the range 200–500 mV s^{-1}.

The compounds $[NBu_4]_2[\{(NC)_2C{=}C(S)Se{-}\}_2]$ **1**, $[AsPh_4]_2[\{(NC)_2C{=}C(S)Se{-}\}_2]$ **2** and $[AsPh_4]_2[\{(NC)_2C{=}C(Se)Se{-}\}_2]$ **3** were prepared by mixing solutions of K_2[imnts] (2.65 g, 0.01 mol) in acetone (100 cm^3) or K_2[imns] (3.12 g, 0.01 mol) in acetone (100 cm^3) with I_2 (0.63 g, 0.005 mol) in acetone (100 cm^3). The precipitated KI was removed and on addition of stoichiometric aqueous solutions of NBu_4Cl (5.56 g, 0.02 mol) **1** or $AsPh_4Cl$ (8.38 g, 0.02 mol) (**2**,**3**) precipitates were obtained,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

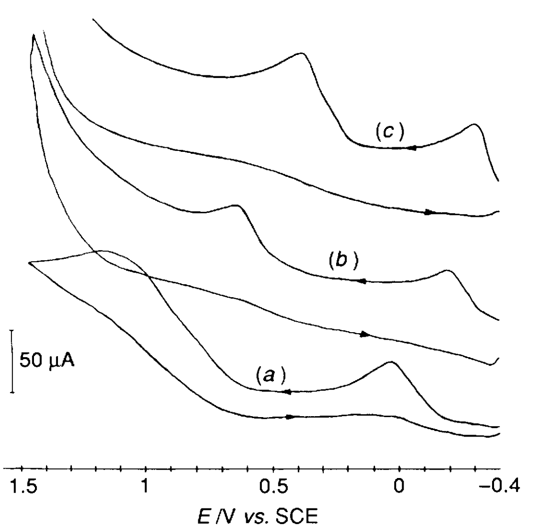
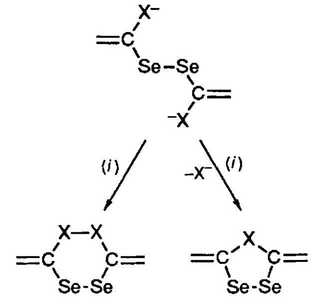


Fig. 1 Cyclic voltammograms of 10^{-4} mol dm^{-3} K_2[imnt] (*a*), K_2[imnts] (*b*) and K_2[imns] (*c*) containing 0.1 mol dm^{-3} NBu_4ClO_4 at scan rates of 200 mV s^{-1} in MeCN at 295 K



Scheme 1 X = S, $[\{(NC)_2C{=}C(S)Se{-}\}_2]^{2-}$ and related oxidation products; X = Se, $[\{(NC)_2C{=}C(Se)Se{-}\}_2]^{2-}$ and related oxidation products. (*i*) Oxidation

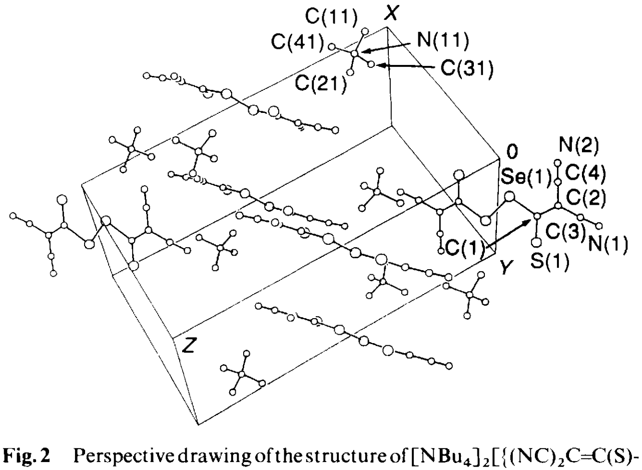


Fig. 2 Perspective drawing of the structure of $[NBu_4]_2[\{(NC)_2C{=}C(S){-}Se{-}\}_2]$ **1**. Within the NBu_4 groups only the α-carbon atoms are depicted for clarity

which were recrystallized from acetone–diethyl ether (Found: C, 55.70; H, 8.30; N, 9.60; S, 7.40. Calc. for $C_{40}H_{72}N_6S_2Se_2$ **1**: C, 55.90; H, 8.45; N, 9.80; S, 7.45. Found: C, 59.15; H, 3.50; N, 4.85; S, 5.70. Calc. for $C_{56}H_{80}As_2N_4S_2Se_2$ **2**: C, 58.95; H, 3.50; N, 4.90; S, 5.60. Found: C, 54.45; H, 3.20; N, 4.30. Calc. for $C_{56}H_{80}As_2N_4Se_4$ **3**: C, 54.50; H, 3.25; N, 4.55%).

Single crystals of compounds **1**–**3** were sealed in Lindemann glass capillaries and the crystal classes as well as preliminary lattice constants were obtained using the Weissenberg technique. No extinction conditions were observed for **2** and **3** while **1** showed extinctions in [0*k*0] for $k = 2n + 1$ and in (*h*0*l*) for $l = 2n + 1$. Diffraction intensities were collected at 295 K using a HUBER automatic four-circle diffractometer equipped with Mo-Kα radiation and a graphite monochromator. Data collection and processing parameters are summarized in Table 2.

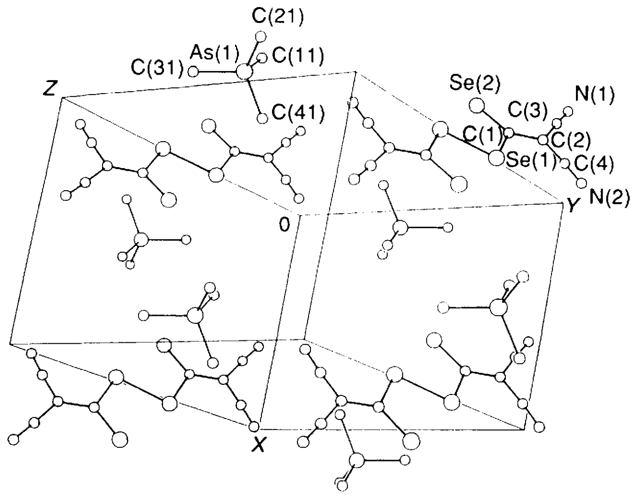


Fig. 3 Perspective view of the isomorphous structures of salts **2** and **3**. Within the $AsPh_4$ cations only the α-C atoms of the phenyl groups are depicted

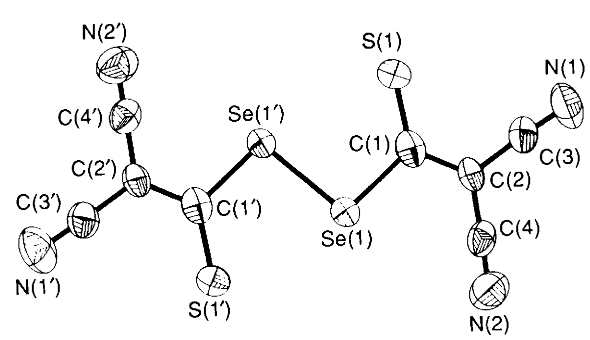


Fig. 4 Geometry and numbering scheme of the diselenide $[\{(NC)_2C{=}C(S)Se{-}\}_2]^{2-}$ present in salts **1** and **2**. Symmetry codes for primed atoms: 2 − *x*, −*y*, 1 − *z*, **1**; −*x*, −*y*, 1 − *z*, **2**

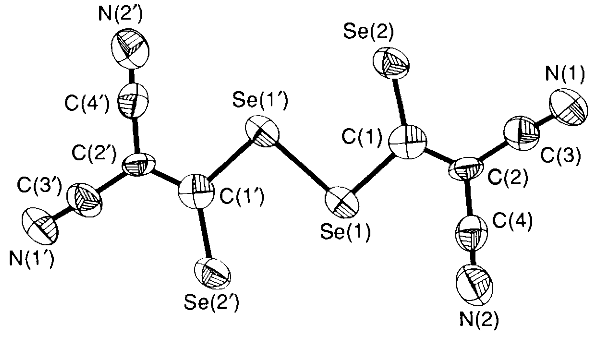


Fig. 5 Geometry and numbering scheme of the diselenide $[\{(NC)_2C{=}C(Se)Se{-}\}_2]^{2-}$ present in salt **3**. Symmetry code for primed atoms: −*x*, −*y*, 1 − *z*

The crystal structures were solved by direct methods. The hydrogen atoms of organic ligand parts were generated geometrically (C–H bonds fixed at 1.08 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms.

Computations were performed on a DEC MicroVAX-II computer and a PC-386 with SHELXS 86,[21] SHELX 76,[22] XTAL[23] and SCHAKAL.[24] Atomic positional parameters are

Table 2 Data collection and structure solution and refinement parameters[a]

Compound	**1**	**2**	**3**
Formula	$C_{40}H_{72}N_6$-S_2Se_2	$C_{56}H_{80}As_2$-$N_4S_2Se_2$	$C_{56}H_{80}$-$As_2N_4Se_4$
M	859.11	1140.86	1234.65
Colour and habit	Red, cube	Orange, prism	Orange, plate
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	12.1420(2)	9.307(2)	9.3274(2)
b/Å	9.3215(21)	11.313(3)	11.2400(3)
c/Å	20.7064(6)	13.165(3)	13.3160(3)
α/°	90.0	110.910(9)	110.248(9)
β/°	94.510(17)	96.010(10)	97.075(10)
γ/°	90.0	101.490(9)	100.668(9)
U/Å^3	2336(1)	1244.0(4)	1260.0(4)
Z	2	1	1
D_c/g cm^{-3}	1.22	1.52	1.63
μ/cm^{-1}	15.4	29.05	41.26
$F(000)$	908.0	570.0	605.85
Collection range/°	3–24	6–20	3–18
Reflections measured	6465	4501	1849
Unique reflections	3643	2251	1739
Reflections used	2472 [$F \geqslant 6\sigma(F)$]	1967 [$F \geqslant 4\sigma(F)$]	1411 [$F \geqslant 5\sigma(F)$]
Parameters refined	147	131	131
Maximum shift/e.s.d.	$< 10^{-3}$	−0.054	−0.001
R[b]	0.0597	0.0424	0.0640
R'[c]	0.0495	0.0390	0.0585

[a] Details in common: Mo-Kα radiation (λ = 0.710 73 Å). [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$ where $w = \sigma^{-2}(F_o)$.

Table 3 Atomic coordinates (× 10^4) for $[NBu_4]_2[\{(NC)_2C{=}C(S)$-$Se{-}\}_2]$ **1**

Atom	x	y	z
Se	9 814(1)	1 020(1)	4 682(1)
S	7 816(1)	−1 174(2)	4 529(1)
C(1)	8 406(5)	333(7)	4 291(3)
C(2)	7 967(5)	1 239(8)	3 796(3)
C(3)	6 955(6)	861(8)	3 445(3)
C(4)	8 521(6)	2 484(9)	3 604(3)
N(1)	6 162(5)	600(7)	3 132(3)
N(2)	8 979(6)	3 474(7)	3 455(3)
N(11)	7 406(4)	8 181(5)	6 962(2)
C(11)	7 463(5)	9 542(6)	6 561(3)
C(12)	6 471(5)	9 898(6)	6 098(3)
C(13)	6 594(5)	11 394(7)	5 809(3)
C(14)	5 727(5)	11 775(7)	5 290(3)
C(21)	6 489(5)	8 238(7)	7 406(3)
C(22)	6 554(5)	9 410(7)	7 909(3)
C(23)	5 668(5)	9 196(8)	8 391(3)
C(24)	5 735(6)	10 289(8)	8 908(3)
C(31)	7 162(5)	6 898(6)	6 520(3)
C(32)	7 991(5)	6 551(6)	6 046(3)
C(33)	7 578(5)	5 354(7)	5 588(3)
C(34)	8 425(6)	4 939(8)	5 134(3)
C(41)	8 521(5)	8 034(6)	7 326(3)
C(42)	8 650(5)	6 761(7)	7 770(3)
C(43)	9 854(6)	6 586(7)	8 039(3)
C(44)	10 271(6)	7 791(9)	8 432(3)

listed in Tables 3–5 and selected interatomic distances and bond angles in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 4 Atomic coordinates (× 10^4) for $[AsPh_4]_2[\{(NC)_2C{=}C(S)$-$Se{-}\}_2]$ **2**

Atom	x	y	z
Se	447(1)	747(1)	4616(1)
S	7376(2)	8784(2)	3218(2)
C(1)	8728(7)	113(6)	3438(5)
C(2)	8757(8)	904(7)	2841(6)
C(3)	7600(1)	563(7)	1931(7)
C(4)	0(1)	1931(9)	3075(6)
N(1)	6671(8)	437(7)	1204(6)
N(2)	1045(8)	2854(7)	3310(5)
As	2870(1)	6141(1)	2479(1)
C(11)	3543(5)	6913(4)	3863(4)
C(12)	3486(5)	8111(4)	4647(4)
C(13)	4504(5)	8680(4)	5651(4)
C(14)	5579(5)	8064(4)	5871(4)
C(15)	5636(5)	6866(4)	5087(4)
C(16)	4619(5)	6291(4)	4083(4)
C(21)	251(5)	5339(4)	2703(3)
C(22)	−734(5)	4366(4)	1776(3)
C(23)	−2126(5)	3742(4)	1886(3)
C(24)	−2532(5)	4090(4)	2924(3)
C(25)	−1547(5)	5063(4)	3850(3)
C(26)	−156(5)	5688(4)	3740(3)
C(31)	1930(4)	7449(4)	1982(4)
C(32)	3190(4)	8191(4)	1801(4)
C(33)	3036(4)	9078(4)	1309(4)
C(34)	1622(4)	9222(4)	998(4)
C(35)	362(4)	8480(4)	1179(4)
C(36)	516(4)	7593(4)	1671(4)
C(41)	2753(5)	4822(4)	1443(4)
C(42)	2926(5)	4910(4)	430(4)
C(43)	3381(5)	3936(4)	−366(4)
C(44)	3661(5)	2874(4)	−15(4)
C(45)	3488(5)	2787(4)	863(4)
C(46)	3033(5)	3761(4)	1659(4)

Results and Discussion

Electrochemical Work.—Fig. 1 gives typical cyclic voltammograms for imnt, imnts and imns. The voltammograms are very similar and exhibit two oxidation peaks on a positive scan while no reduction peaks in the reverse scan are observed (imnt, 0.05, 1.06; imnts, −0.2, 0.65; imns, −0.3, 0.4 V *vs.* SCE). We showed recently for imnt that the oxidation reaction in the first step at low potential is best characterized by assumption of an EC_{irr} mechanism.[2,6] By analogy, we propose a similar reaction in the first oxidative step for imnts and imns. A relatively slow oxidative radical formation is followed by rapid dimerization of the radical anions formed [equations (4) and (5)].

$$[Se(S,Se)C{=}C(CN)_2]^{2-} \rightleftharpoons [Se(S,Se)C{=}C(CN)_2]^{-} + e^{-} \quad (4)$$

$$2\,[Se(S,Se)C{=}C(CN)_2]^{-} \xrightarrow{k} [\{(NC)_2C{=}C(S,Se)Se{-}\}_2]^{2-} \quad (5)$$

Even at scan rates of 500 mV s^{-1} no reduction of radical anions is observed and the processes remain strictly irreversible. It can be seen from Fig. 1 that the oxidation potentials decrease with increasing selenium content in the series imnt > imnts > imns and this parallels the finding that imns is very sensitive to air-exposure while imnt is not.

The nature of the second oxidation reactions in the voltammograms of imnt, imnts and imns is still unknown. Although the processes are strictly irreversible, the constitution of the products formed is not entirely clear. As outlined earlier, the most probable reaction products constitute six- or five-membered ring systems (Scheme 1).[2]

X-Ray Work.—Compounds **2** and **3** are isomorphous. The

Table 5 Atomic coordinates (× 10^4) for $[AsPh_4]_2[\{(NC)_2C{=}C(Se)\text{-}Se\text{-}\}_2]$ **3**

Atom	*x*	*y*	*z*
Se(1)	431(2)	736(2)	4604(2)
Se(2)	7300(2)	8618(2)	3168(2)
C(1)	8700(2)	900(2)	3420(2)
C(2)	8730(2)	870(2)	2800(2)
C(3)	7550(3)	620(2)	1920(2)
C(4)	9950(3)	1960(3)	3070(2)
N(1)	6630(2)	450(2)	1200(2)
N(2)	970(2)	2820(2)	3290(2)
As	2115(2)	6156(2)	2530(2)
C(11)	3550(2)	6940(1)	3880(1)
C(!2)	3510(2)	8140(1)	4640(1)
C(13)	4530(2)	8710(1)	5630(1)
C(14)	5600(2)	8070(1)	5860(1)
C(15)	5650(2)	6870(1)	5100(1)
C(16)	4620(2)	6300(1)	4110(1)
C(21)	250(2)	5360(1)	2701(9)
C(22)	−760(2)	4410(1)	1787(9)
C(23)	−2140(2)	3800(1)	1898(9)
C(24)	−2520(2)	4150(1)	2922(9)
C(25)	−1520(2)	5100(1)	3836(9)
C(26)	−140(2)	5710(1)	3725(9)
C(31)	1910(1)	7440(1)	1960(1)
C(32)	3189(1)	8357(2)	1800(1)
C(33)	2990(1)	9050(1)	1280(1)
C(34)	1580(1)	9200(1)	950(1)
C(35)	330(1)	8470(1)	1130(1)
C(36)	490(1)	7590(1)	1630(1)
C(41)	2750(1)	4820(1)	1500(1)
C(42)	2960(1)	4920(1)	510(1)
C(43)	3440(1)	3960(1)	−260(1)
C(44)	3710(1)	2880(1)	−40(1)
C(45)	3500(1)	2780(1)	950(1)
C(46)	3020(1)	3750(1)	1720(1)

Table 6 Selected interatomic distances (Å) and angles (°). Symmetry codes for Se′: 2 − *x*, −*y*, 1 − *z* (**1**); −*x*, −*y*, 1 − *z* (**2,3**)

$[NBu_4]_2[\{(NC)_2C{=}C(S)Se\text{-}\}_2]$ **1**

Se–C(1)	1.942(6)	C(1)–Se–Se′	95.2(2)
Se–Se′	2.338(2)	Se(1)–C(1)–S(1)	122.6(3)
S–C(1)	1.668(7)	Se(1)–C(1)–C(2)	112.2(5)
C(1)–C(2)	1.401(9)	S(1)–C(1)–C(2)	125.2(5)
C(2)–C(3)	1.421(9)	C(1)–C(2)–C(3)	119.2(6)
C(2)–C(4)	1.414(10)	C(1)–C(2)–C(4)	122.5(6)
C(3)–N(1)	1.145(9)	C(3)–C(2)–C(4)	118.2(6)
C(4)–N(2)	1.133(10)	C(2)–C(3)–N(1)	175.9(8)
		C(2)–C(4)–N(2)	179.0(8)
		C(1)–Se–Se′–C(1′)	180(2)
N(11)–C(11)	1.521(7)	C(11)–N(11)–C(21)	111.9(4)
N(11)–C(21)	1.501(7)	C(11)–N(11)–C(31)	110.1(4)
N(11)–C(31)	1.519(7)	C(21)–N(11)–C(31)	106.1(4)
N(11)–C(41)	1.504(7)	C(11)–N(11)–C(41)	105.8(4)
		C(21)–N(11)–C(41)	112.2(4)
		C(31)–N(11)–C(41)	110.8(4)

$[AsPh_4]_2[\{(NC)_2C{=}C(S)Se\text{-}\}_2]$ **2**

Se–C(1)	1.926(7)	C(1)–Se–Se′	94.2(2)
Se–Se′	2.325(3)	C(2)–C(1)–S	125.8(5)
S–C(1)	1.669(7)	C(2)–C(1)–Se	111.8(4)
C(1)–C(2)	1.38(1)	S–C(1)–Se	122.4(5)
C(2)–C(3)	1.42(1)	C(1)–C(2)–C(3)	121.9(6)
C(2)–C(4)	1.43(1)	C(1)–C(2)–C(4)	121.0(7)
C(3)–N(1)	1.15(1)	C(3)–C(2)–C(4)	117.0(8)
C(4)–N(2)	1.15(1)	N(1)–C(3)–C(2)	178.5(9)
		N(2)–C(4)–C(2)	176(1)
		C(1)–Se–Se′–C(1′)	180(4)
As–C(21)	1.884(6)	C(21)–As–C(31)	109.5(2)
As–C(31)	1.887(6)	C(21)–As–C(11)	112.1(2)
As–C(11)	1.889(5)	C(21)–As–C(41)	106.6(2)
As–C(41)	1.893(5)	C(31)–As–C(11)	108.7(2)
		C(31)–As–C(41)	108.8(3)
		C(11)–As–C(41)	111.1(2)

$[AsPh_4]_2[\{(NC)_2C{=}C(Se)Se\text{-}\}_2]$ **3**

Se(1)–C(1)	1.94(2)	C(1)–Se(1)–Se(1)	94.6(7)
Se(1)–Se(1′)	2.328(4)	Se(1)–C(1)–Se(2)	122(1)
Se(2)–C(1)	1.81(2)	Se(1)–C(1)–C(2)	112(1)
C(1)–C(2)	1.38(4)	Se(2)–C(1)–C(2)	126(1)
C(2)–C(3)	1.42(3)	C(1)–C(2)–C(3)	122(2)
C(2)–C(4)	1.42(3)	C(1)–C(2)–C(4)	120(2)
C(3)–N(1)	1.14(3)	C(3)–C(2)–C(4)	118(2)
C(4)–N(2)	1.14(3)	C(2)–C(3)–N(1)	177(3)
		C(2)–C(4)–N(2)	177(3)
		C(1)–Se(1)–Se(1′)–C(1′)	180(1)
As–C(11)	1.92(1)	C(11)–As–C(21)	110.7(6)
As–C(21)	1.88(1)	C(11)–As–C(31)	109.2(5)
As–C(31)	1.88(2)	C(11)–As–C(41)	112.2(6)
As–C(41)	1.90(1)	C(21)–As–C(31)	108.6(6)
		C(21)–As–C(41)	106.5(5)
		C(31)–As–C(41)	109.7(6)

packings of the cations and anions in **1** and **2** and **3**, respectively, are depicted in Figs. 2 and 3, while Figs. 4 and 5 show the anions in **1**–**3** as well as the atom numbering schemes.

In the crystal structures of salts **1**–**3** the anions exhibit a *trans* arrangement with C(S,Se)Se–Se(Se,S)C 180° and an inversion centre bisecting the Se–Se bridges. The average Se–Se distance is 2.330 Å and corresponds to bond lengths reported for other diselenides[13–19] or for α-Se.[25] The uncommon *trans* configuration is achieved by repulsion effects of negatively charged terminal S or Se atoms together with reduced torsional barriers in diselenides as discussed above.[11,12]

The Se–Se as well as Se–C and S–C bond lengths in salt **2** are slightly compressed compared to those in **1** caused by packing effects of the larger $AsPh_4$ cation in **2**. This compression is also reflected by a significant increase in density when going from **1** to **2** (Table 2).

The Se–C bond lengths in salts **1**–**3** are similar and agree well with a value of 1.93 Å suggested by Pauling.[26] In spite of this the terminal S–C bonds in **1** and **2** (1.67 Å) as well as the terminal Se–C bond in **3** (1.81 Å) are remarkably short and exhibit some double-bond character. Bond distances between sp^2-hybridized carbon and sulfur are usually in the range 1.76–1.78 Å,[27,28] while the length of the double bond in solid CS_2 at −140 °C is 1.56 Å.[29] Compared to this, C–S bond lengths in conjugated molecules like $H_2C(CS\text{-}NH_2)_2$ [30] or $(CSNH_2)_2$ [31] are 1.674 and 1.665 Å, respectively, and show a strong correlation to the values observed in **1** and **2**. The bonding features are very similar for the diselenide in **3**. While C–Se single bonds are usually in the range 1.93–2.28 Å,[13–19] The C–Se bond in selenourea $[CSe(NH_2)_2]$ is 1.88 Å.[32] It is obvious that the negative charge within the diselenides in **1**–**3** is not localized on the terminal S and Se atoms, but must be delocalized to some extent as is the case in imnt.[33] The C–C and C–N bond lengths in dimeric imnts and imns agree well with those observed in the monomeric fragments.[33,34] The bonding within the cations in **1**–**3** shows no remarkable features and need not be discussed.[34,35]

Acknowledgements

Financial support from Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

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Received 20*th March* 1992; *Paper* 2/01493I