Supporting informations

Solid state structure and solution behaviour of organoselenium(II) compounds containing 2-\{E(CH_2CH_2)_2NCH_2\}C_6H_4 groups (E = O, NMe)

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Solid state structure - supramolecular architectures

\[ \text{[2-{MeN(CH}_2\text{CH}_2)_2\text{NCH}_2}_2\text{C}_6\text{H}_4]}_2\text{Se}_2 \ (2) \]

- the crystal contains a 1:1 mixture of 1:1 mixtures of \((R_{N1}, S_{N3})\) and \((S_{N1}, R_{N3})\) isomers
- the crystal contains parallel chains built from either \((R_{N1}, S_{N3})\) or \((S_{N1}, R_{N3})\) isomers

**Figure S1.** View along \(c\) axis of the chain polymer of \((R_{N1}, S_{N3})\)-2 isomers based on intermolecular hydrogen contacts. Symmetry equivalent positions: \(H(3a)\) \((2.5-x, -0.5+y, 0.5-z)\). Intermolecular contacts within a chain: \(N(2)\ldots H(3a)_{\text{aryl}}\) 2.67 Å (c.f. \(\sum r_{vdw}(N,H)\) 2.74 Å). No further inter-chain contacts.
[2-{O(CH₂CH₂)₂NCH₂}C₆H₄]SeCl (3)

- the crystal contains only the S isomer
- intramolecular distances  Cl(1)···H(6) 2.67 Å  \[ \sum_{vdW}(Cl,H) 3.01 \text{ Å} \]

**Figure S2.** View of the chain polymer of S-2 isomers based on intermolecular hydrogen contacts (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: Cl(1a) (-0.5+x, 0.5-y, -z); H(7Bb) (0.5+x, 0.5-y, -z). Intermolecular contacts within a chain: Cl(1)···H(7Bb)\text{methylene} 2.89 Å.

**Figure S3.** View of a layer network built from parallel chains of S-2 isomers, connected through inter-chain hydrogen contacts (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: O(1a') (-0.5+x, -0.5-y, -z); H(7Ab'), H(11Ab') (0.5+x, -0.5-y, -z). Intermolecular contacts between chains: O(1)···H(7Ab')\text{methylene} 2.50 Å, O(1)···H(11Ab')\text{N-methylene-ring} 2.56 Å (c.f. \[ \sum_{vdW}(O,H) 2.60 \text{ Å} \]). No further inter-layer contacts.
Figure S4. View along $a$ axis of the layer network built from 4-HBr units through intermolecular hydrogen contacts (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: Se(1a) (x, y, 1+z); Se(1b) (x, y, -1+z); Se(1') (1.5-x, 0.5+y, 0.5+z); Se(1'') (1.5-x, -0.5+y, -0.5+z). Intermolecular contacts within a layer: Br(1)⋯H(11B'') N-methylene-ring 3.02 Å, Br(2)⋯H(8Aa) N-methylene-ring 3.05 Å, Br(2)⋯H(4'') aryl 3.06 Å.
Figure S5. View along c axis of the layer network in the crystal of 4·HBr.

Figure S6. View along c axis of the tridimensional network in the crystal of 4·HBr built through interlayer hydrogen contacts (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: H(5') (-0.5+x, 0.5-y, -1+z); O(1'') (0.5+x, 0.5-y, 1+z). Intermolecular contacts between layers: O(1)···H(5')aryl 2.37 Å (c.f. ∑vdw(O,H) 2.60 Å).
the crystal contains a 1:1 mixture of $R$ and $S$ isomers
- intramolecular distances $I(1)\cdots H(6)$ 2.96 Å
$\sum r_{vdW}(I,H)$ 3.35 Å

**Figure S7.** View of the dimer association of $R$ and $S$ isomers in the crystal of 5 (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: Se(1') $(2-x, -y, 1-z)$. Intermolecular contacts within the dimer unit: Se(1)···I(1') 3.96 Å; I(1)···H(9B') O-methylene-ring 3.28 Å (c.f. $\sum r_{vdW}(Se,I)$ 4.15 Å).

**Figure S8.** View of the columnar chain polymer in the crystal of 5 based on hydrogen contacts between dimer units (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: Se(1a') $(2-x, -y, 2-z)$; Se(1b) $(x, y, -1+z)$. Inter-dimer contacts within a chain: I(1)···H(5a')aryl 3.29 Å.

**Figure S9.** View along $c$ axis of the columnar chain polymer in the crystal of 5.
Figure S10. View along $c$ axis of the tridimesional network built from columnar chain polymers in the crystal of 5, through oxygen-hydrogen inter-chain contacts (only hydrogens involved in hydrogen contacts are shown). Inter-chain contacts: O(1)-···H(7B)$_{\text{methylene}}$ 2.51 Å (c.f. $\sum_{\text{vdW}}$ O,H 2.60 Å).
[2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]SeI (6)

- the crystal contains a 1:1 mixture of R and S isomers
- intramolecular distances  I(1)···H(6) 2.87 Å  \(\sum_{\text{vdW}(I,H)} 3.35 \text{ Å} \)

**Figure S11.** View along \(\alpha\) axis of the chain polymer of alternating S and R isomers in the crystal of 6 (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: Se(1a) (x, 1.5-y, 0.5+z); Se(1b) (x, 1.5-y, -0.5+z). Intermolecular contacts within a chain: I(1)···H₁₁Bbₙ-methylene-ring 3.31 Å. No further inter-chain contacts.
Solution behaviour

Figure S12. The aliphatic region of the $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 26ºC) of (a) [2-O(CH$_2$CH$_2$)$_2$NCH$_2$]C$_6$H$_5$; (b) [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeCl (3); (c) [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeI (5).

Figure S13. (a) The aliphatic region of the $^1$H NMR spectrum of [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeCl (3) (CDCl$_3$, 400 MHz, 26ºC), and (b) simulation of the $^1$H aliphatic region for 3 on the basis of the following parameters:

- $\delta$ 2.690 ppm [ddd, N-CH$_2$-CH$_2$, pro-trans-H$_{8,11}$, $^2$J$_{HH}$ 12.0, $^3$J$_{HH}$ 11.1, $^3$J$_{HH}$ 4.0 Hz];
- $\delta$ 3.110 ppm [d, N-CH$_2$-CH$_2$, pro-cis-H$_{8,11}$, $^2$J$_{HH}$ 12.0];
- $\delta$ 3.900 ppm [m, -CH$_2$-CH$_2$-O, H$_{9,10}$, $^3$J$_{HH}$ 11.1, $^3$J$_{HH}$ 4.0 Hz (with pro-trans-H$_{8,11}$)];
- $\delta$ 3.940 ppm [s, C$_6$H$_4$-CH$_2$-N, H$_7$].
Figure S14. $^1$H NMR spectra (CDCl$_3$) for [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]SeI (5) at (a) 26 °C (400 MHz), and (b) -30 °C (300 MHz).
[2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]₂Se₂ (2)

Figure S15. The 2D indirectly detected H,N-HMBC spectra (400 MHz, CDCl₃) for 2: (a) 26 °C; (b) 60 °C.

Figure S16. The 2D indirectly detected H,Se-HMBC spectra (400 MHz, CDCl₃) for 2: (a) 26 °C; (b) 60 °C.
[2-{O(CH₂CH₂)₂NCH₂}C₆H₄]SeCl (3)

Figure S17. The 2D indirectly detected H,N-HMBC spectra (400 MHz, CDCl₃) for 3, at 26 ºC.

Figure S18. The 2D indirectly detected H,Se-HMBC spectra (400 MHz, CDCl₃) for 3, at 26 ºC.
[2-{O(CH_2CH_2)_2NCH_2}C_6H_4]SeI (5)

**Figure S19.** The 2D indirectly detected H,N-HMBC spectra (400 MHz, C_6D_6) for 5, at 26 ºC.

**Figure S20.** The 2D indirectly detected H,Se-HMBC spectra (400 MHz, C_6D_6) for 5, at 26 ºC.
Figure S21. The 2D indirectly detected H,N-HMBC spectra (400 MHz) for 6: (a) 65 °C (C₆D₆); (b) 60 °C (CDCl₃).

Figure S22. The 2D indirectly detected H,Se-HMBC spectra (400 MHz, C₆D₆) for 6, at 65 °C.