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# Intermolecular and Very Strong Intramolecular C–Se···O/N Chalcogen Bonds in Nitrophenyl Selenocyanate Crystals

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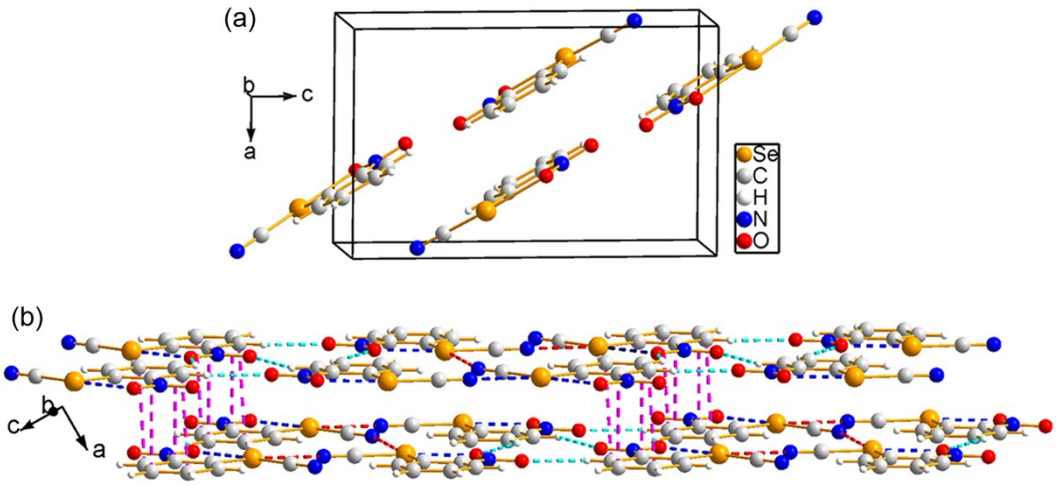


**Fig. S1** (a) The crystal cell unit of crystal **1a**, (b) The 3D supramolecular structure of crystal **1a** constructed by C–Se···N, C–Se···O chalcogen bonds, C–H···O hydrogen bond as well as π–hole···π–hole bonds.

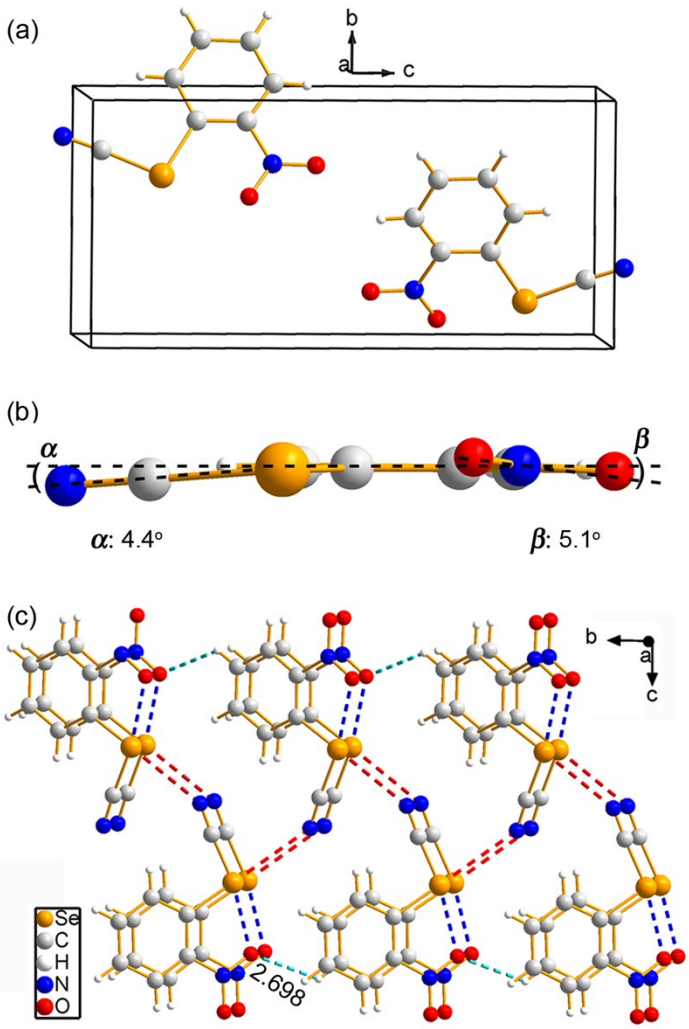


**Fig. S2** (a) The crystal cell unit of crystal **1b**, (b) The torsion angle between –CN/plane of $–NO_2$ and the plane of phenyl ring, (c) The 3D supramolecular structure of crystal **1b** constructed by C–Se···N, C–Se···O chalcogen bonds, C–H···O hydrogen bond as well as π–hole···π–hole bonds (distance in Å).

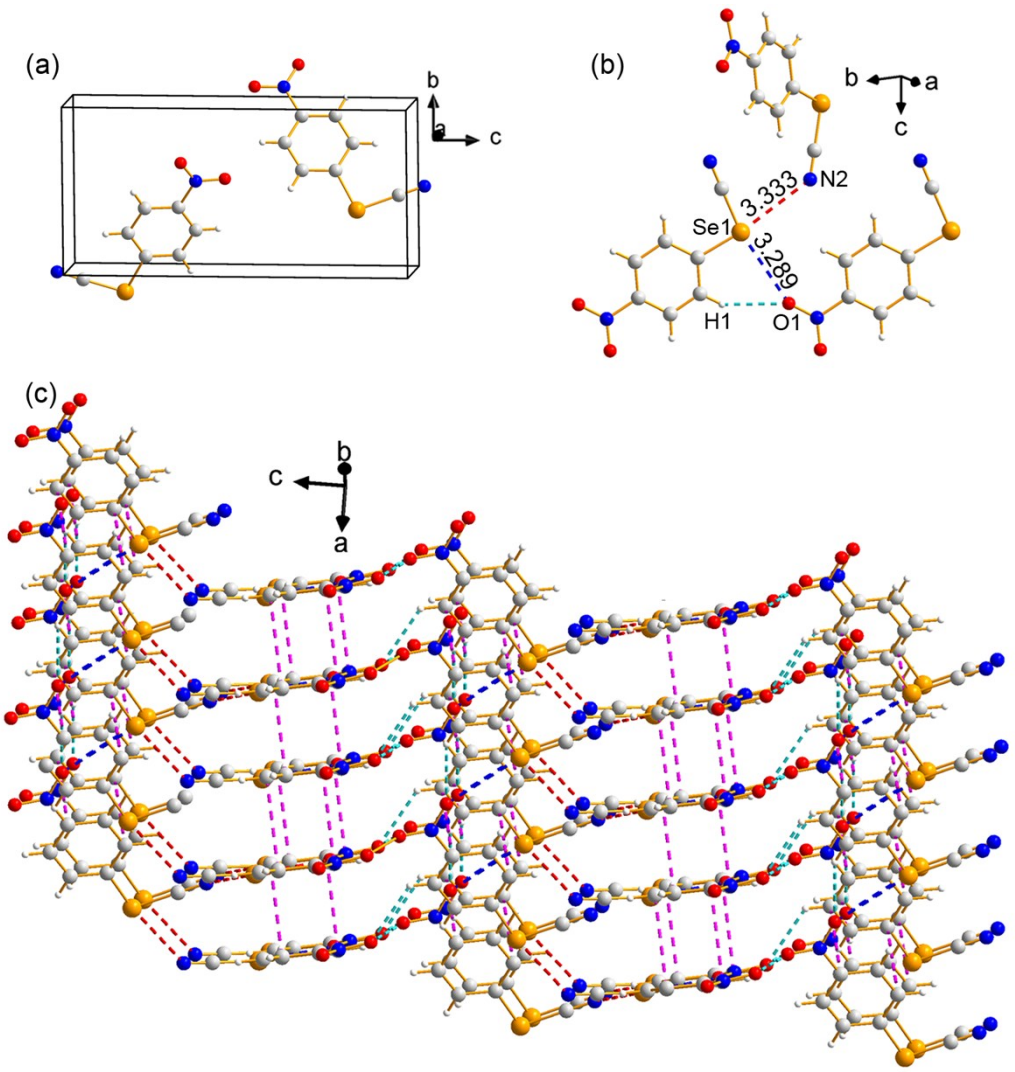


**Fig. S3** (a) The crystal cell unit of crystal **2**, (b) The bifurcated chalcogen bonds formed by Se atom of one *p*–NSC molecule with the N and O atoms from other adjacent two molecules (distance in Å), (c) The 3D supramolecular structure of crystal **2** constructed by C–Se···N, C–Se···O chalcogen bonds, C–H···O hydrogen bond as well as π–hole···π–hole bonds.

**Table S1**. The main bonding properties and geometrical parameters of crystals.

| Crystals | Interactions | *d*/(Å) | | *θ*/° |
|---|---|---|---|---|
| **1a** | C7–Se1···O2 (x, y, z) | 2.5145(18) | –26.5% | 169.83(8) |
| | C6–Se1···N2 (–x, y–0.5, 0.5–z) | 3.259(2) | –5.5% | 175.50(7) |
| | $\pi_h \cdots \pi_h$ (C1···C3, 1–x, 1–y, –z) | 3.447(3) | –6.8% | |
| | $\pi_h \cdots \pi_h$ (C2···C4, 1–x, 1–y, –z) | 3.538(3) | –4.4% | |
| | C2–H2···O1 (–x+1, y+0.5, –z-0.5) | 2.541(3) | –6.5% | 135.4 |
| | C3–H3···O2 (x, y+1, z) | 2.671(3) | –1.8% | 126.9 |
| **1b** | C7–Se1···O1 (x, y, z) | 2.525(3) | –25.5% | 170.06(12) |
| | C1–Se1···N2 (–x–1, y–0.5,–z–2) | 3.222(4) | –6.6% | 178.90(10) |
| | $\pi_h \cdots \pi_h$ (C1···C2, 1–x, 1–y, –z) | 3.588(4) | –3.0% | |
| | $\pi_h \cdots \pi_h$ (C4···C5, 1–x, 1–y, –z) | 3.594(5) | –2.9% | |
| | C4–H4···O2 (x+1, y+1, z) | 2.698(5) | –0.8% | 126.3 |
| **2** | C6–Se1···N2 (–x–1, y–0.5, –z–2) | 3.333(5) | –3.4% | 173.34(12) |
| | C7–Se1···O1 (x+1, y–1, z) | 3.289(4) | –3.8% | 166.79(14) |
| | $\pi_h \cdots \pi_h$ (C2···C3, x+1, y, z) | 3.550(5) | –4.0% | |
| | $\pi_h \cdots \pi_h$ (C5···C6, x–1, y, z) | 3.556(5) | –3.9% | |
| | C1–H1···O1 (x+1, y–1, z) | 2.564(5) | –5.7% | 152.4 |
| | C2–H2···O2 (–x–1, y–0.5, –z–1) | 2.575(5) | –5.3% | 128.6 |

The percentages represent the shortening degree of bonding length comparing to the sum of vdW radii of interacting atoms.

**Table S2**. The chalcogen bond interactions, second–order perturbation stabilization energies $E^2$ (in kJ·mol$^{-1}$) and the amount of charge transfer $\Delta q$ (in *a.u.*) of the selected units in crystal by NBO analysis.

| Crystals | Bonds | Donor | Acceptor | $E^2$ | $E^2_{total}$ | $\Delta q$ |
|---|---|---|---|---|---|---|
| **1a** | C–Se···N | LP(1)N7 | BD*(1)Se16–C17 | 6.28 | 6.28 | 0.0045 |
| | C–Se···O | LP(1)O4 | BD*(1)Se1–C3 | 15.31 | 62.34 | |
| | | LP(2)O4 | BD*(1)Se1–C3 | 47.03 | | |
| | | LP(1)O19 | BD*(1)Se16–C18 | 14.48 | 50.59 | |
| | | LP(2)O19 | BD*(1)Se16–C18 | 36.11 | | |
| **1b** | C–Se···N | LP(1)N16 | BD*(1)Se17–C21 | 5.65 | 6.53 | 0.0041 |
| | | BD(2)C15–N16 | BD*(1)Se17–C21 | 0.88 | | |
| | C–Se···O | LP(1)O2 | BD*(1)Se3–C15 | 14.81 | 58.87 | |
| | | LP(2)O2 | BD*(1)Se3–C15 | 44.06 | | |
| | | LP(1)O18 | BD*(1)Se17–C19 | 16.02 | 60.45 | |
| | | LP(2)O18 | BD*(1)Se17–C19 | 44.43 | | |
| **2** | C–Se···N | LP(1)N17 | BD*(1)Se1–C2 | 3.05 | 3.05 | 0.0031 |
| | C–Se···O | LP(1)O17 | BD*(1)Se1–C3 | 2.43 | 3.39 | 0.0018 |
| | | LP(2)O17 | BD*(1)Se1–C3 | 0.96 | | |

"LP" for 1–center valence lone pair, "BD" for 2–center bonding and "BD*" for 2–center antibonding.