Electronic Supplementary Material (ESI) for CrystEngComm.

Supramolecular architectures featuring Se···N secondary-bonding interactions in crystals of selenium-rich molecules: A comparison with their congeners

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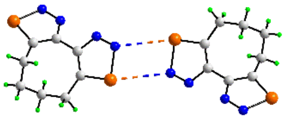
– ELECTRONIC SUPPLEMENTARY MATERIALS –

ESI Table S1. Supramolecular architectures formed by di-nuclear selenium molecules.

1. QAFBUY 4,5,6,7-tetrahydrocycloocta[1,2-d:8,7-d']bis[1,2,3]selenadiazole

H. Detert and D. Schollmeyer, *IUCr Data*, 2020, **5**, x201585.
https://doi.org/10.1107/S2414314620015850

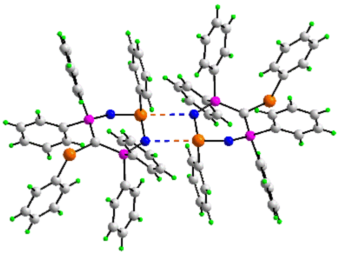


d(Se···N) = 3.381(9) Å; C–Se···N = 146.4(3)°; N–Se···N = 75.8(3)°; Se–N···Se = 104.2(3)°; N–N···Se = 134.8(6)°

{Centrosymmetric dimer *via* a {SeN···}$_2$ synthon involving one Se atom only. Longer Se···N contacts of 3.530(8) Å involving the second Se atom link the dimers into a zigzag chain *via* additional {SeN···}$_2$ synthons}

2. XIVPEX 1,3,3,5,5-pentaphenyl-4-(phenylseleno)-1-selena-3,5-diphospha-2,6-diazine

M. Nieger, D. Hanssgen and C. Mohr, Private Communication to the Cambridge Structural Database, Refcode XIVPEX, 2002.

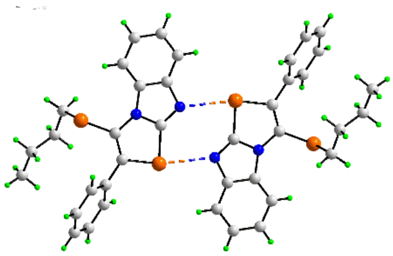


d(Se···N) = 3.023(3) Å; N–Se···N = 171.39(9) & 76.30(9)°; C–Se···N = 81.95(12)°; Se–N···Se = 103.70(10)°; P–Se···Se = 128.77(14)°

{Centrosymmetric dimer *via* four-membered {SeN···}$_2$ synthon}

3. TAXZEZ 3-(butylselanyl)-2-phenyl[1,3]selenazolo[3,2-a]benzimidazole

J. A. Roehrs, R. P. Pistoia, D. F. Back and G. Zeni, *Adv. Synth. Catal.*, 2012, **354**, 1791-1796.
https://doi.org/10.1002/adsc.201200075

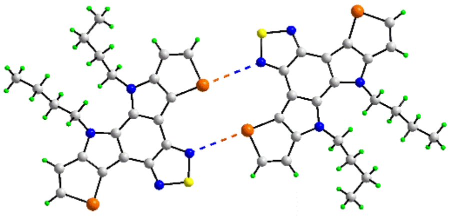


d(Se···N) = 2.9798(18) Å; N–Se···N = 167.79(7) & 82.72(7)°; C–Se···N = 113.72(13) & 142.40(14)°

{Only one of two Se atoms (ring) forms a contact leading to a centrosymmetric dimer *via* a $\{SeCN\cdots\}_2$ synthon}

4. VEHVIQ 10,11-dibutyl-10,11-dihydroselenopheno[3,2-b]selenopheno-[2',3':4,5]pyrrolo-[3,2-g][1,2,5]thiadiazolo[3,4-e]indole

S. Ghosh, S. Das, N. R. Kumar, A. R. Agrawal and S. S. Zade, *New J. Chem.*, 2017, **41**, 11568-11575. https://doi.org/10.1039/C7NJ02394D

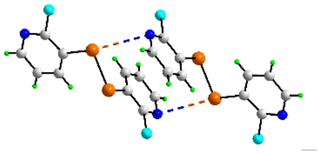


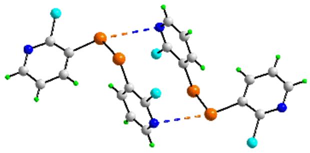
d(Se···N) = 3.433(3) Å; C–Se···N = 171.64(12) & 92.96(12)°; S–Se···N = 113.59(11)°; C–N···Se = 138.6(2)°

{Two-molecule aggregate constructed about a 10-membered $\{SeC_3N\cdots\}_2$ synthon and generated by 2-fold symmetry. A close transannular Se···Se contact of 3.4771(5) Å is noted}

5. DIHHEI bis(2-chloro-3-pyridyl)diselenide

K. K. Bhasin, N. Singh, S. Doomra, E. Arora, G. Ram, S. Singh, Y. Nagpal, S. K. Mehta and T. M. Klapötke, *Bioinorg. Chem. Appl.*, 2007, 069263. https://doi.org/10.1155/2007/69263





d(Se···N) = 3.378(7) Å; C–Se···N = 163.4(3)°; Se–Se···N = 83.53(14)°; (Cl)C–N···Se = 100.4(5)°; C–N···Se = 99.5(6)° {left-hand image}

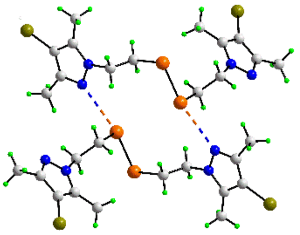
d(Se···N) = 3.413(8) Å; C–Se···N = 154.8(3)°; Se–Se···N = 86.11(14)°; (Cl)C–N···Se = 108.2(6)°; C–N···Se = 91.4(6)°

d(Se···N) = 3.451(7) Å; C–Se···N = 161.5(3)°; Se–Se···N = 79.61(13)°; Cl(C)–N···Se = 103.8(6)°; C–N···Se = 100.7(5)°

{Three independent molecules. One self-associates about a centre of inversion to form a two-molecule aggregate (first entry). The remaining molecules are also connected into a dimer with one of the Se···N interactions marginally longer than the cut-off distance criterion. For the centrosymmetric dimer, close intramolecular 1,4-Se···Cl contacts are noted: 3.117(3) & 3.140(2) Å; second dimer: 3.125(3) & 3.151(3) Å and 3.109(3) & 3.150(3) Å}

6. GIWXAO 1,2-bis(2-(4-bromo-3,5-dimethyl-1H-pyrzol-1-yl)ethyl)diselane

S. Pundir, S. K. Mehta, S. M. Mobin and K. K. Bhasin, *Ind. J. Heterocycl. Chem.*, 2017, **27**, 99-105.

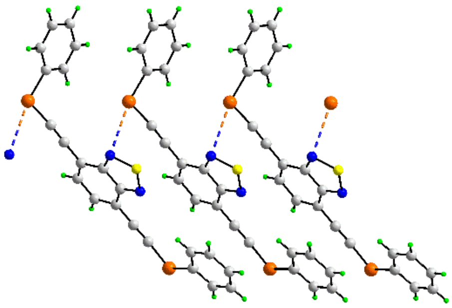


d(Se···N) = 3.141(6) Å; Se–Se···N = 168.61(12)°; C–Se···N = 75.8(3)°; N–N···Se = 127.3(5)°; C–N···Se = 127.4(4)°

{Only one Se atom forms a Se···N interactions, centrosymmetric dimer; {$Se_2C_2N_2\cdots$}$_2$ synthon; flat with CH_2CH_2 atoms lying to either side of the Se_2N_2 plane}

7. BAFKOM 4,7-bis[(phenylselanyl)ethynyl]-2,1,3-benzothiadiazole

C. H. Silveira, M. G. Fronza, R. A. Balaguez, A. M. E. Larroza, L. Savegnago, D. F. Back, B. A. Iglesias and D. Alves, *Dyes Pigm.*, 2021, **185**, 108910. https://doi.org/10.1016/j.dyepig.2020.108910

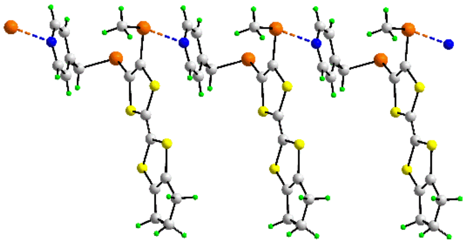


d(Se···N) = 3.345(3) Å; (Ph)C–Se···N = 162.90(9)° & C–Se···N = 77.96(11)°; (S)C–N···Se = 105.30(12)° & C–N···Se = 96.03(16)°

{One Se forms Se···N interactions with one of the two available N atoms to generate a linear chain. Weak Se···S interactions [3.6025(9) Å] involving the second Se atom link chains into a 2-D array}

8. NIBWOM 4-methylseleno-5-(4-picolylseleno)-4',5'-trimethylenetetrathiafulvalene

N. Benbellat, Y. Le Gal, S. Golhen, A. Gouasmia and L. Ouahab, *Synth. Met.*, 2012, **162**, 1789-1797. https://doi.org/10.1016/j.synthmet.2012.08.018

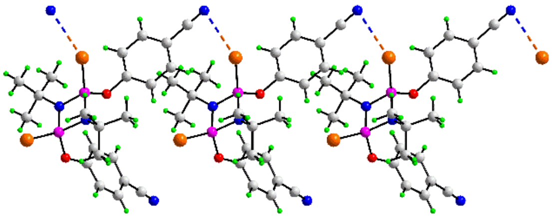


d(Se···N) = 3.360(7) Å; C–Se···N = 168.5(3) & 74.3(2)°; C–N···Se = 119.3(6) & 121.1(5)°

{Linear chain; an additional intra-chain Se···N contact of 3.546(8) Å involving the second Se atom is noted. Intra-chain 1,3-Se···S contacts are noted, involving both Se atoms, with the Se atom forming the shorter of the Se···N contacts, forming the longer Se···S contact, 3.139(2) *cf.* 3.091(2) Å}

9. BULQIK 4,4'-((1,3-di-t-butyl-2,4-diselenido-1,3,2,4-diazadiphosphetidine-2,4-diyl)bis(oxy))dibenzonitrile

Y. X. Shi, R. Z. Liang, K. A. Martin, N. Weston, S. Gonzalez-Calera, R. Ganguly, Y. Li, Y. Lu, A. J. M. Ribeiro, M. J. Ramos, P. A. Fernandes and F. Garcia, *Inorg. Chem.*, 2015, **54**, 6423-6432. https://doi.org/10.1021/acs.inorgchem.5b00735

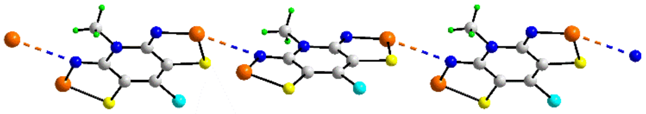


d(Se···N) = 3.365(3) Å; P–Se···N = 153.87(5)°; C–N···Se = 83.6(2)°

{Linear chain; only one of the selenide-Se atoms forms Se···N interactions. Intra-chain 1,3-Se···O contacts are noted, involving both Se atoms, with the Se atom forming the shorter of the Se···N contacts, forming the longer Se···S contact, 3.0912(17) *cf.* 2.9544(17) Å}

10. SUQQUR 8-chloro-4-methyl-4H-bis[1,2,3]thiaselenazolo[4,5-b:5',4'-e]pyridine radical

A. A. Leitch, X. Yu, S. M. Winter, R. A. Secco, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2009, **131**, 7112-7125. https://doi.org/10.1021/ja900853t

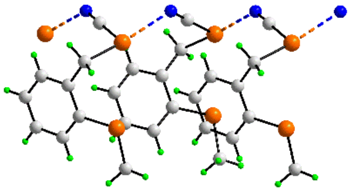


d(Se···N) = 3.001(5) Å; N–Se···N = 162.61(19)°; S–Se···N = 74.82(12)°; Se–N···Se = 81.28(18)°; C–N···Se = 162.6(4)°

{One of the two Se atoms associates *via* a Se···N interaction within a zigzag chain (glide). Weak Se···S interactions, *i.e.* 3.687(2) Å, involving the second Se atom connect chains into a 2-D array}

11. YUNSIK 2-(methylselanyl)benzyl selenocyanate

A. Lari, C. Bleiholder, F. Rominger and R. Gleiter, *Eur. J. Org. Chem.*, 2009, **2009**, 2765-2774. https://doi.org/10.1002/ejoc.200900108

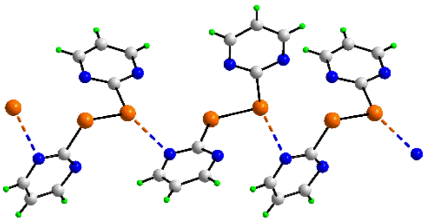


d(Se···N) = 3.125(4) Å; methylene-C–Se···N = 166.75(12)°; (N)C–Se···N = 72.72(12)°; C–N···Se = 135.0(3)°

{Only the Se(CN) atom forms Se···N contacts within a zigzag chain (glide symmetry)}

12. SEDZEI 2,2'-diselane-1,2-diyldipyrimidine

A. S. Hodage, C. P. Prabhu, P. P. Phadnis, A. Wadawale, K. I. Priyadarsini and V. K. Jain, *J. Organomet. Chem.*, 2012, **720**, 19-25. https://doi.org/10.1016/j.jorganchem.2012.08.035

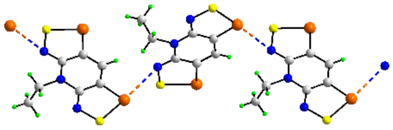


d(Se···N) = 3.349(14) Å; C–Se···N = 163.7(5)°; Se–Se···N = 90.0(2)°; C–N···Se = 120(1) & 126(1)°

{Dinuclear; one Se atom forms a Se···N(pyrimidyl) contact within a zigzag chain (glide symmetry); two intramolecular Se···N contacts are noted 3.325(12) & 3.349(13) Å with the interacting and non-interacting Se atoms, respectively}

13. HIGQOE 4-ethyl-4H-di((1,2,3)selenathiazolo)(4,5-b:5',4'-e)pyrid-3-yl radical

A. A. Leitch, J. L. Brusso, K. Cvrkalj, R. W. Reed, C. M. Robertson, P. A. Dube and R. T. Oakley, *Chem. Commun.*, 2007, 3368-3370. https://doi.org/10.1039/b708756j

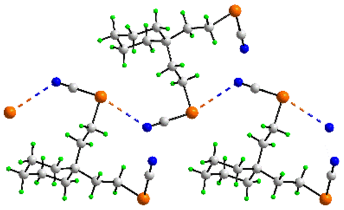


d(Se···N) = 3.405(3) Å; S–Se···N = 174.46(6)°; C–Se···N = 87.84(10)°; S–N···Se = 95.35(12)°; C–N···Se = 122.75(19)°

{Only one Se atom forms a Se···N interaction; zigzag chain (glide symmetry). Additional interactions: Se···Se contacts of 3.5833(6) Å, involving the Se forming the close Se···N interaction connect chains into a 2-D array, within which are supporting Se···S contacts of 3.6565(11) Å}

14. GOHMEW 1,1-bis(selenocyanatoethyl)cyclohexane

D. B. Werz, F. R. Fischer, S. C. Kornmayer, F. Rominger and R. Gleiter, *J. Org. Chem.*, 2008, **73**, 8021-8029. https://doi.org/10.1021/jo801378p

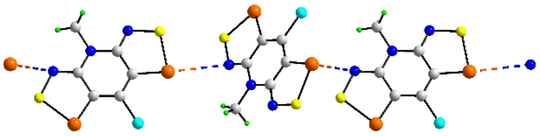


d(Se···N) = 3.199(2) Å; (N)C–Se···N = 145.69(8)°; C–Se···N = 76.77(8)°; C–N···Se = 126.28(17)°

{Only one Se atoms forms a Se···N interaction; helical chain (2_1). Additional but long Se···N contacts of 3.558(3) Å connect chains into a double-chain}

15. SUQRAY 8-chloro-4-methyl-4H-bis[1,2,3]selenathiazolo[4,5-b:5',4'-e]pyridine radical

A. A. Leitch, X. Yu, S. M. Winter, R. A. Secco, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2009, **131**, 7112-7125. https://doi.org/10.1021/ja900853t

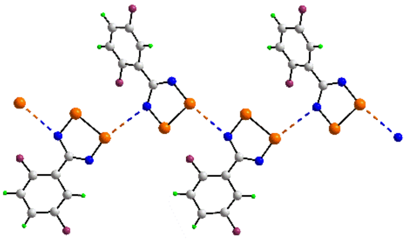


d(Se···N) = 3.234(3) Å; C–Se···N = 176.51(11)°; S–Se···N = 89.78(5)°; S–N···Se = 94.13(12)°; C–N···Se = 121.2(2)°

{One of the two Se atoms associates *via* a Se···N interaction within a helical (2_1) chain. Chains are connected into a 3-D architecture by a combination of Se···Se [3.5723(5) Å] interactions, involving the second Se atom, and Se···S [3.4304(10) & 3.4727(10) Å] interactions with the shorter separation involving the Se atom forming the Se···N interaction leading to the chain}

16. WERQEP 4-(2,5-Difluorophenyl)-1,2,3,5-diselenadiazolyl radical

L. Beer, A. W. Cordes, D. J. T. Myles, R. T. Oakley and N. J. Taylor, *CrystEngComm*, 2000, **2**, 109-114. https://doi.org/10.1039/b004875p



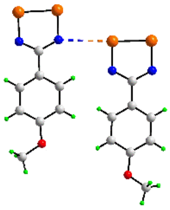
d(Se···N) = 3.15(2) Å; N–Se···N = 169.2(7)°; Se–Se···N = 101.7(4)°; Se–Se···N = 93.7(8)°; C–N···Se = 155(2)°

d(Se···N) = 3.33(2) Å; N–Se···N = 163.0(9)°; Se–Se···N = 106.0(4)°; Se–Se···N = 96.0(8)°; C–N···Se = 145(2)°

{Two independent di-nuclear molecules. One Se of each ring participates in Se···N interactions. The two independent molecules form a dimeric aggregate and these assemble within a helical chain (2_1). Supporting Se···Se [3.746(4) Å] interactions are also found within the chain. Shorter Se···Se contacts involving all Se atoms [3.279(5) & 3.313(5) Å] link chains into a double-chain}

17. WIMNEL10 4-(4-methoxyphenyl)-1,2,3,5-diselenadiazole

M. Parvez, R. T. Boeré and K. H. Moock, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 2118-2121. https://doi.org/10.1107/S0108270195004252

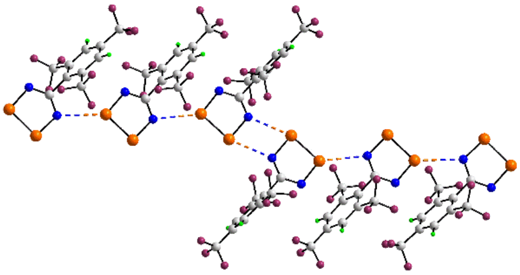


d(Se···N) = 3.415(13) Å; Se–Se···N = 157.8(2)°; N–Se···N = 89.3(5)°; Se–Se···N = 90.4(5)°; C–N···Se = 144(1)°

{Two independent di-nuclear molecules which are connected into a two-molecule aggregate *via* a single Se···N interaction. Another Se···N contact, *i.e.* 3.473(13) Å, between the first independent molecules only, link the aggregates into a linear chain. All Se atoms participate in a Se···Se interaction [3.193(3) to 3.579(3) Å] linking molecules into a 2-D array}

18. UBOJON 4-(2,4,6-tris(trifluoromethyl)phenyl)-1,2,3,5-diselenadiazolyl radical

R. L. Melen, R. J. Less, C. M. Pask and J. M. Rawson, *Inorg. Chem.*, 2016, **55**, 11747-11759. https://doi.org/10.1021/acs.inorgchem.6b01771



d(Se···N) = 2.840(9) Å; Se–Se···N = 161.05(16)°; N–Se···N = 72.6(3)°; Se–N···Se = 107.5(3)°; C–N···Se = 136.9(6)°

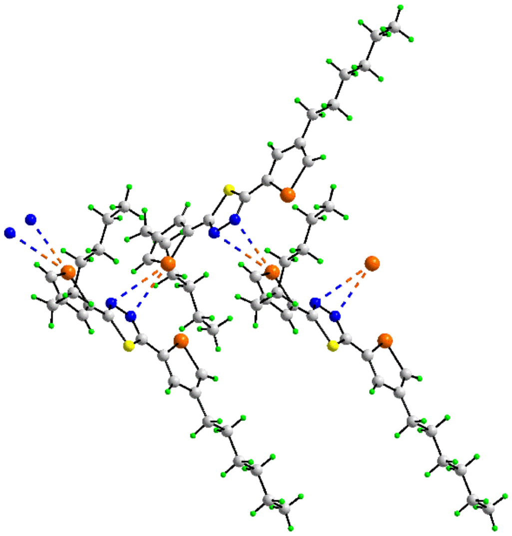
d(Se···N) = 3.254(8) Å; N–Se···N = 134.0(3)°; Se–Se···N = 129.93(13)°; Se–N···Se = 137.0(3)°; C–N···Se = 105.5(5)°

d(Se···N) = 3.288(9) Å; Se–Se···N = 135.29(14)°; N–Se···N = 130.2(3)°; Se–N···Se = 133.0(3)°; C–N···Se = 108.1(6)°

{Three independent molecules. One molecule employs two interactions involving Se, the second, one and the third, none. The aggregate is a centrosymmetric, six-molecule species. The aggregate is constructed about symmetric $\{SeN\cdots\}_2$ synthon, entry 1; connected to the core are two second independent molecules, entry 2, this effectively bridges to the terminal molecules, entry 3. All Se atoms participate in a Se···Se interaction [3.3204(17) to 3.3344(16) Å] linking molecules into a 1-D coordination polymer}

19. SIKWIT 2,5-bis(4-n-hexylselenophen-2-yl)-1,3,4-thiadiazole

H. Pang, P. J. Skabara, D. J. Crouch, W. Duffy, M. Heeney, I. McCulloch, S. J. Coles, P. N. Horton and M. B. Hursthouse, *Macromolecules*, 2007, **40**, 6585-6593. https://doi.org/10.1021/ma071242n



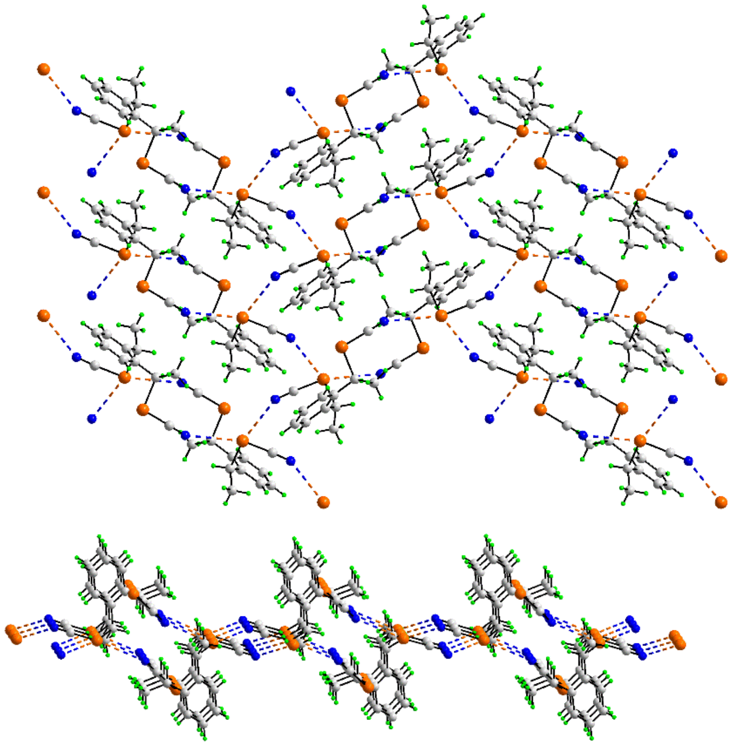
d(Se···N) = 3.048(6) Å; C–Se···N = 164.2(3) & 78.9(3)°; N–N···Se = 91.3(4)°; C–N···Se = 115.7(5)°

d(Se···N) = 3.369(6) Å; C–Se···N = 157.0(2) & 82.6(3)°; N–N···Se = 64.8(3)°; C–N···Se = 122.8(4)°

{Dinuclear; one Se atom forms two Se···N(thiadiazolyl) contact within a helical chain; two intramolecular Se···N contacts are noted 3.053(7) & 3.103(6) Å on either side of the ring, *i.e.* with the interacting and non-interacting Se atoms, respectively. Intermolecular Se···S [3.617(2) Å] contacts link chains into a 2-D array}

20. MAHHEM syn-(1,2-phenylene)bis(ethane-1,1-diyl) bis(selenocyanate)

H.-T. Huynh, O. Jeannin, E. Aubert, E. Espinosa and M. Fourmigué, *New J. Chem.*, 2021, **45**, 76-84. https://doi.org/10.1039/D0NJ05293K



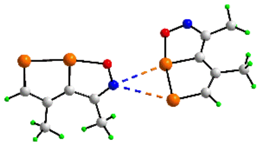
d(Se···N) = 3.283(7) Å; (N)C–Se···N = 162.6(2)°; C–Se···N = 75.12(17)°; C–N···Se = 149.3(6)°

d(Se···N) = 3.393(6) Å; C–Se···N = 167.36(17)°; (N)C–Se···N = 73.1(2)°; C–N···Se = 144.7(5)°

{Only one of the two Se atoms forms Se···N interactions but this forms two Se···N interactions; molecules are connected into a 2-D array with an undulating topology}

21. FIKYIH 3,4-dimethyl-1-oxa-6,6aλ^4-diselena-2-azapentalene

C. Allen, J. C. A. Boeyens, A. G. Briggs, L. Denner, A. J. Markwell, D. H. Reid and B. G. Rose, *J. Chem. Soc. Chem. Comm.*, 1987, 967-968. https://doi.org/10.1039/C39870000967



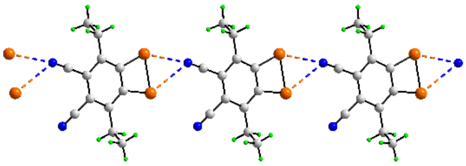
d(Se···N) = 3.213(10) Å; C–Se···N = 157.6(3)°; Se–Se···N = 70.8(2)°; O–Se···N = 117.9(3)°; O–N···Se = 94.7(6)°; C–N···Se = 140.1(7)°

d(Se···N) = 3.337(11) Å; C–Se···N = 152.3(4)°; Se–Se···N = 65.4(2)°; O–N···Se = 112.6(7)°; C–N···Se = 129.9(7)°

{One Se(II) and one Se(IV); two independent molecules connected by a pair Se···N interactions involving the Se atoms of one molecule only as the N atom is bifurcated; the Se(IV) atom forms the shorter interaction}

22. HOGBOW 2,5-diethyl-7,8-diselenabicyclo[4.2.0]octa-1,3,5-triene-3,4-dicarbonitrile

T. Kimura, T. Nakahodo, H. Fujihara and E. Suzuki, *Inorg. Chem.*, 2014, **53**, 4411-4417. https://doi.org/10.1021/ic5000765



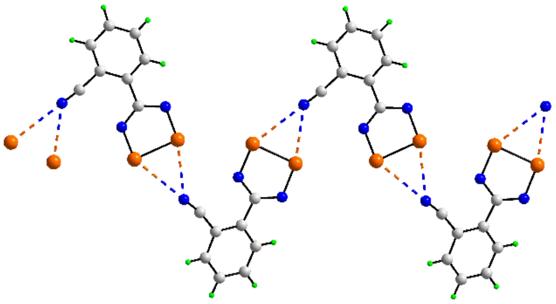
d(Se···N) = 3.049(5) Å; C–Se···N = 144.24(17)°; Se–Se···N = 69.07(10)°; C–N···Se = 172.2(5)°

d(Se···N) = 3.124(6) Å; C–Se···N = 140.24(17)°; Se–Se···N = 65.73(9)°; C–N···Se = 128.3(4)°

{Both Se atoms forms a Se···N interaction with the same, bifurcated N atom; linear chain}

23. PAHRUL 4-(2-cyanophenyl)-1,2,3,5-diselenadiazole radical

A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem.*, 1992, **31**, 1802-1808. https://doi.org/10.1021/ic00036a016



d(Se···N) = 2.96(2) Å; N–Se···N = 165.2(6)°; Se–Se···N = 72.65(8)°; C–N···Se = 133(1)°

d(Se···N) = 3.173(13) Å; N–Se···N = 151.1(5)°; Se–Se···N = 63.02(7)°; C–N···Se = 164(1)°

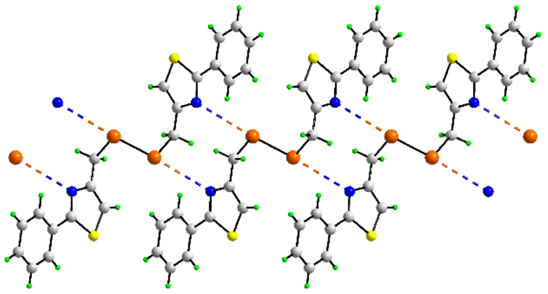
d(Se···N) = 2.97(2) Å; N–Se···N = 164.2(4)°; Se–Se···N = 72.2(4)°; C–N···Se = 136(2)°

d(Se···N) = 3.16(2) Å; N–Se···N = 150.9(5)°; Se–Se···N = 63.5(4)°; C–N···Se = 165(2)°

{Two independent molecules; four independent Se···N contacts. Each molecule forms two bifurcated Se···N(nitrile) contacts to give rise to an undulating zigzag chain. All Se atoms participate in Se···Se interactions [3.275(3) & 3.347(3) Å] to generate a double-chain}

24. FEYBAP 4,4'-[diselane-1,2-diylbis(methylene)]bis(2-phenyl-1,3-thiazole)

R. A. Popa, E. Licarete, M. Banciu and A. Silvestru, *Appl. Organomet. Chem.*, 2018, **32**, e4252. https://doi.org/10.1002/aoc.4252

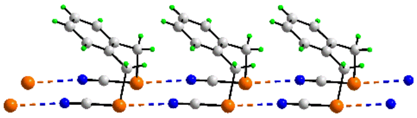


d(Se···N) = 3.342(3) Å; Se–Se···N = 171.91(6)°; C–Se···N = 77.85(14)°; C–N···Se = 113.40(2) & 119.97(3)°

{The molecule is centrosymmetric. Linear chain featuring two contacts per molecule; both Se atoms form Se···N interactions *via* centrosymmetric $\{SeC_2N\cdots\}_2$ synthons}

25. NARBIR ortho bis(selenocyanatato)xylene

S. L. W. McWhinnie, A. B. Brooks and I. Abrahams, *Acta Crystallogr., Sect. C: Struct. Chem.*, 1998, **54**, 126-128. https://doi.org/10.1107/S0108270197012262



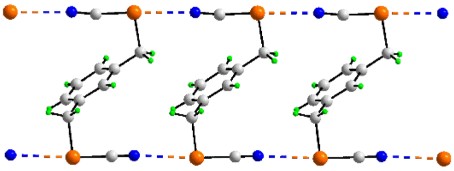
d(Se···N) = 2.969(9) Å; C–Se···N = 172.6(3) & 77.8(3)°; N–C···Se = 174.0(8)°

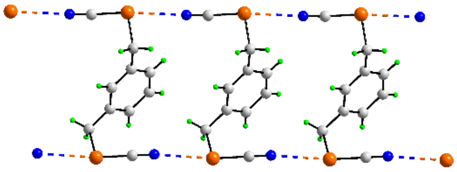
d(Se···N) = 2.985(8) Å; C–Se···N = 173.0(3) & 75.1(3)°; N–C···Se = 173.3(7)°

{Each Se forms a Se···N interaction to form a ladder}

26. FEDHUU 1,3-bis(selenocyanatomethyl)benzene

H.-T. Huynh, O. Jeannin and M. Fourmigué, *Chem. Commun.*, 2017, **53**, 8467-8469. https://doi.org/10.1039/C7CC04833E





d(Se···N) = 2.97(2) Å; (N)C–Se···N = 175.9(7)°; C–Se···N = 79.3(5)°; C–N···Se = 174(2)°

d(Se···N) = 3.02(2) Å; (N)C–Se···N = 175.7(7)°; C–Se···N = 80.6(5)°; C–N···Se = 176(2)°

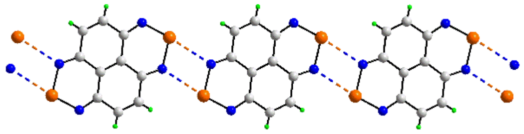
d(Se···N) = 3.01(2) Å; (N)C–Se···N = 172.9(7)°; C–Se···N = 78.5(5)°; C–N···Se = 172(2)°

d(Se···N) = 3.02(2) Å; (N)C–Se···N = 174.1(7)°; C–Se···N = 80.2(5)°; C–N···Se = 174(2)°

{Two independent molecules; each molecule self-associates to form a ladder. Entries 1 and 2 refer to the left-hand image. Intermolecular Se···Se interactions [3.739(2) Å] link chains into a 2-D for the chain in the right-hand image; analogous contacts [3.8509(18) Å] are found for the other chain}

27. NAPSEZ10 naphtho(1,8-cd:4,5-c'd')-bis(1,2,6)selenadiazine

A. Gieren, V. Lamm, R. C. Haddon and M. L. Kaplan, *J. Am. Chem. Soc.*, 1980, **102**, 5070-5073. https://doi.org/10.1021/ja00535a042

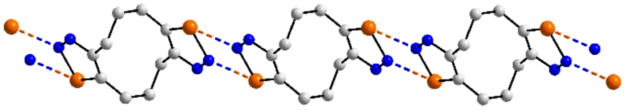


d(Se···N) = 2.90 Å; N–Se···N = 175.3 & 72.2°; Se–Se···N = 107.8°; C–N···Se = 131.3°

{No s.u. values; centrosymmetric molecule; flat tape}

28. ZEJKUU 4,5,6,10,11,12-hexahydrocylodeca(1,2-d:6,7-d')-bis(1,2,3)selenadiazole

G. A. Morales and F. R. Fronczek, *J. Chem. Crystallogr.*, 1994, **24**, 811-813. https://doi.org/10.1007/BF01668246

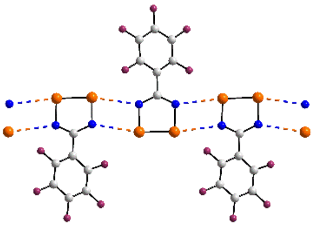


d(Se···N) = 3.094(15) Å; C–Se···N = 155.64(6)°; N–Se···N = 69.08(6)°; N–N···Se = 138.12(12)°; Se–N···Se = 110.92(6)°

{Centrosymmetric molecule. Linear ribbon}

29. UBOHOL 4-(pentafluorophenyl)-1,2,3,5-diselenadiazolyl radical

R. L. Melen, R. J. Less, C. M. Pask and J. M. Rawson, *Inorg. Chem.*, 2016, **55**, 11747-11759. https://doi.org/10.1021/acs.inorgchem.6b01771



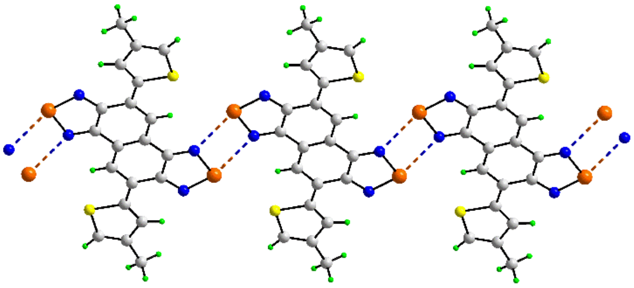
d(Se···N) = 3.092(6) Å; Se–Se···N = 165.43(11)°; N–Se···N = 80.8(2)°; Se–N···Se = 98.9(2)°; C–N···Se = 144.5(4)°

d(Se···N) = 3.097(6) Å; Se–Se···N = 168.72(11)°; N–Se···N = 80.5(2)°; Se–N···Se = 98.9(2)°; C–N···Se = 145.5(4)°

{Molecules assemble into a flat tape *via* non-symmetric {SeN···}$_2$ synthons; each Se forms a single interaction. Se···Se interactions involving both Se atoms [2-fold symmetry; 3.197(2) Å] link chains into a double-chain}

30. EJIYED 5,10-bis(4-methyl-2-thienyl)[1,2,5]selenadiazolo[3',4':5,6]naphtho[1,2-c][1,2,5]selenadiazole

K. Kawashima, I. Osaka and K. Takimiya, *Chem. Mater.*, 2015, **27**, 6558-6570.
https://doi.org/10.1021/acs.chemmater.5b03124

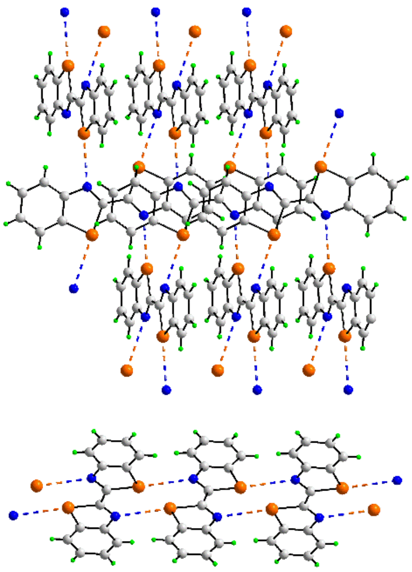


d(Se···N) = 2.966(3) Å; N–Se···N = 163.66(10) & 71.25(9)°; Se–N···Se = 108.75(10)°; C–N···Se = 143.84(19)°

{The molecule is centrosymmetric. Tape; both ring-Se atoms form Se···N interactions *via* centrosymmetric {SeN···}$_2$ synthons}

31. WULTOP 2,2'-bi-1,3-benzoselenazole

N. Biot and D. Bonifazi, *Chem.-Eur. J.*, 2020, **26**, 2904-2913.
https://doi.org/10.1002/chem.201904762

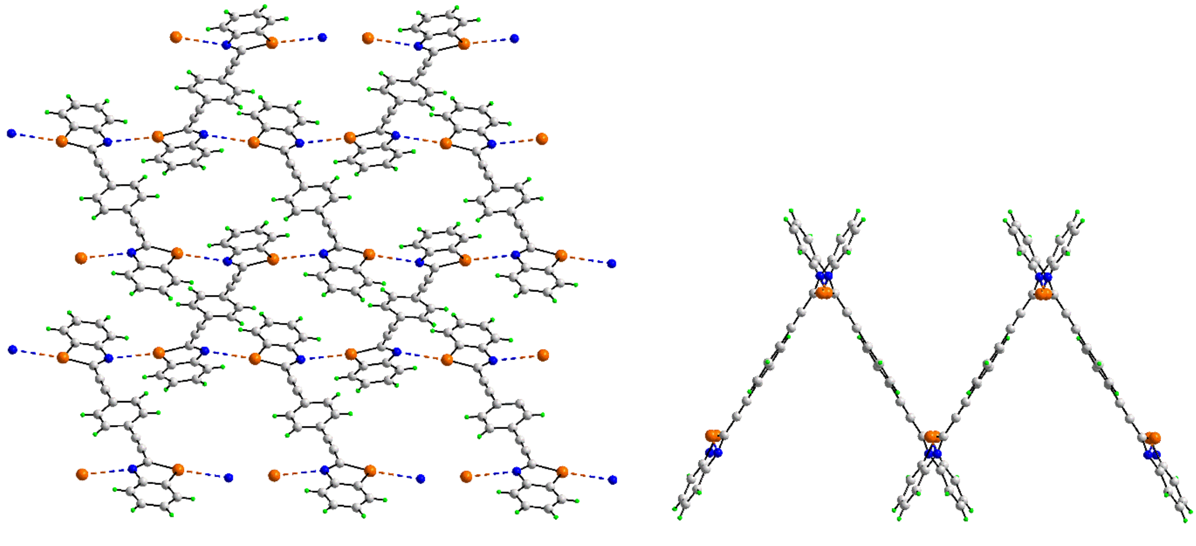


d(Se···N) = 3.234(4) Å; C–Se···N = 176.95(15) & 95.92(15)°; C–N···Se = 109.0(2) & 133.7(3)°

{Centrosymmetric, di-nuclear molecule. 2-D layer with a flat topology. Within the framework are long Se···Se contacts [3.7222(7) Å] with two contacts per Se atom}

32. **RUVWEM** 2,2'-(1,4-phenylenediethyne-2,1-diyl)bis(1,3-benzoselenazole)

A. Kremer, C. Aurisicchio, F. De Leo, B. Ventura, J. Wouters, N. Armaroli, A. Barbieri and D. Bonifazi, *Chem.-Eur. J.*, 2015, **21**, 15377-15387. https://doi.org/10.1002/chem.201501260

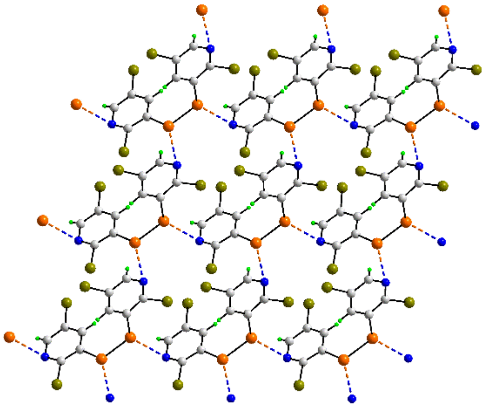


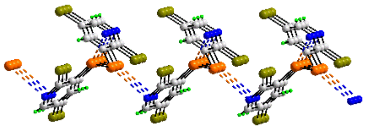
d(Se···N) = 3.381(5) Å; C–Se···N = 162.56(16) & 84.69(15)°; C–Se···Se = 109.2(3) & 131.5(3)°

{Dinuclear, centrosymmetric molecule; 2-D array; zigzag topology}

33. **ABOWUK** 1,2-bis(2,5-dibromopyrid-3-yl)diselenide

K. K. Bhasin and V. Arora, *Appl. Organomet. Chem.*, 2004, **18**, 359-362. https://doi.org/10.1002/aoc.659



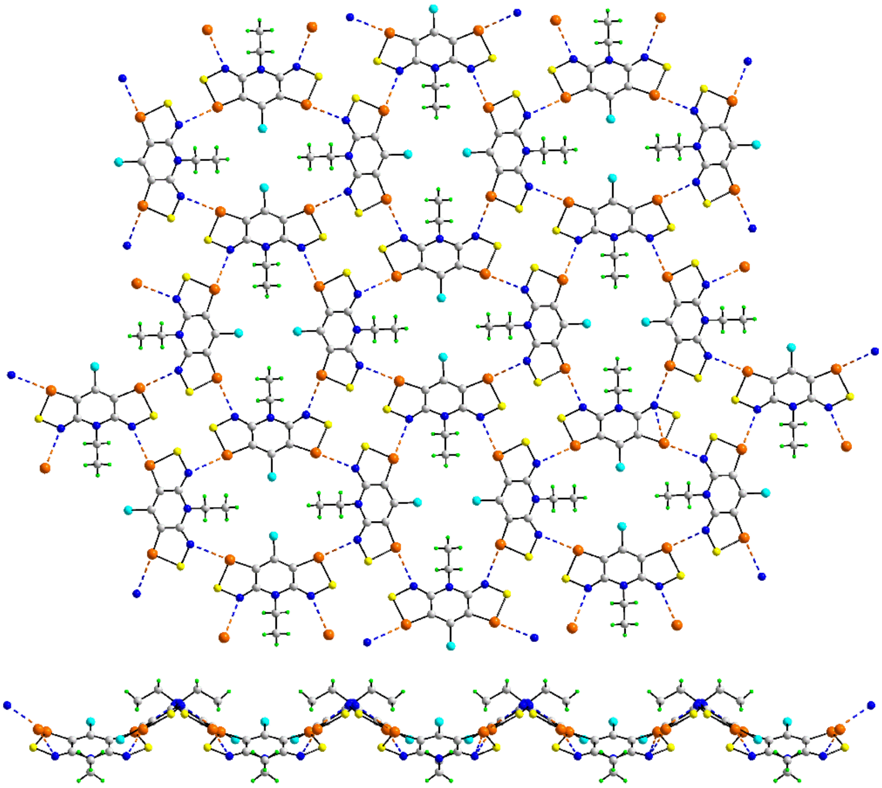


d(Se···N) = 3.414(9) Å; C–Se···N = 140.5(3)°; Se–Se···N = 117.24(14)°; C–N···Se = 99.8(6)° & (Br)C–N···Se = 98.1(5)°

{Molecule has 2-fold symmetry bisecting the Se–Se bond; each Se and N atom form Se···N interactions that project laterally to form a jagged 2-D array. Intramolecular Se···Br contacts [3.2095(14) Å] are noted}

34. YODSUG 8-chloro-4-ethyl-4H-bis((1,2,3)selenathiazolo)(4,5-b:5',4'-e)pyridinyl radical

C. M. Robertson, A. A. Leitch, K. Cvrkalj, R. W. Reed, D. J. T. Myles, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2008, **130**, 8414-8425. https://doi.org/10.1021/ja801070d

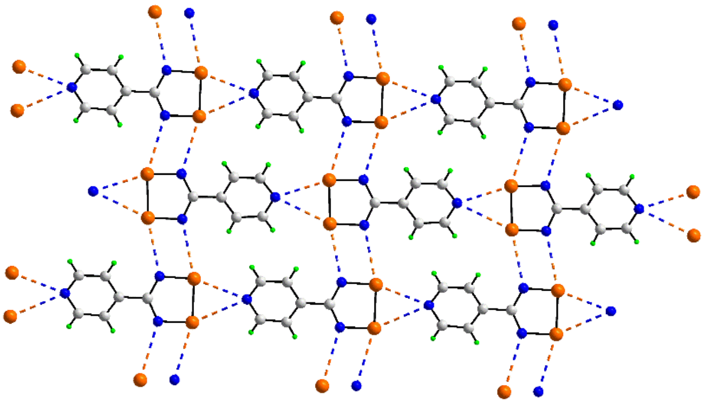


d(Se···N) = 3.279(2) Å; C–Se···N = 164.51(9)°; S–Se···N = 102.17(4)°; S–N···Se = 81.28(8)°; C–N···Se = 123.38(16)°

{The molecule has mirror symmetry. Each of the Se atoms participates in a Se···N interaction within a 2-D array, with a jagged topology. Close intermolecular Se…S and S···S interactions [3.4462(7) & 3.5451(9) Å] are noted along with intramolecular Se…Cl [3.3144(7) Å] contacts. At room temperature, the Se···N contact is 3.308(3) Å}

35. TINQIT 4-(3H-1,2,3,5-diselenadiazol-4-yl)pyridine radical

A. I. Taponen, J. W. L. Wong, K. Lekin, A. Assoud, C. M. Robertson, M. Lahtinen, R. Clérac, H. M. Tuononen, A. Mailman and R. T. Oakley, *Inorg. Chem.*, 2018, **57**, 13901-13911. https://doi.org/10.1021/acs.inorgchem.8b02416



1. d(Se···N) = 2.962(3) Å; N–Se···N = 162.77(8)°; Se–Se···N = 72.73(6)°; C–N···Se = 106.93(19) & 136.0(2)°

2. d(Se···N) = 3.172(3) Å; N–Se···N = 154.33(8)°; Se–Se···N = 63.09(6)°; C–N···Se = 94.43(19) & 149.0(2)°

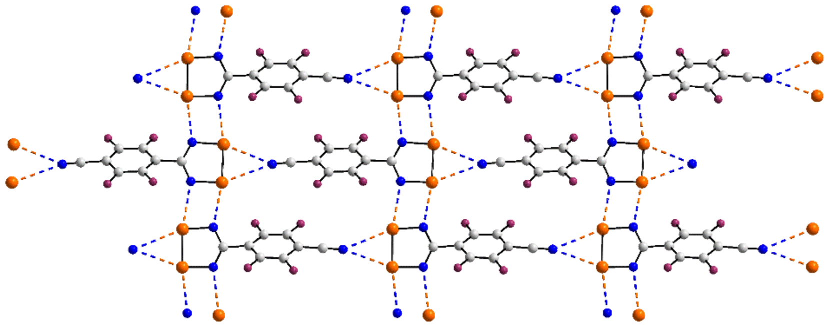
3. d(Se···N) = 3.169(3) Å; Se–Se···N = 154.38(5)°; N–Se···N = 75.71(9)°; Se–N···Se = 105.62(9)°; C–N···Se = 133.0(2)°

4. d(Se···N) = 3.212(3) Å; Se–Se···N = 154.52(5)°; N–Se···N = 74.46(9)°; Se–N···Se = 104.07(9)°; C–N···Se = 135.7(2)°

{The two Se atoms of the ring are connected to a common pyridyl-N atom, entries 1 & 2. The linear chains thus formed are connected into a flat 2-D array *via* tapes constructed about non-symmetric {SeN···}$_2$ synthons, entries 3 & 4. A double-layer is formed about a centre of inversion by Se···Se [3.2527(4) Å] interactions}

36. UBOJED 4-(4-cyano-2,3,5,6-tetrafluorophenyl)-1,2,3,5-diselenadiazolyl radical

R. L. Melen, R. J. Less, C. M. Pask and J. M. Rawson, *Inorg. Chem.*, 2016, **55**, 11747-11759. https://doi.org/10.1021/acs.inorgchem.6b01771



1. d(Se···N) = 3.085(12) Å; N–Se···N = 158.2(4)°; Se–Se···N = 69.5(3)°; C–N···Se = 163(1)°

2. d(Se···N) = 3.145(13) Å; N–Se···N = 155.2(4)°; Se–Se···N = 66.8(3)°; C–N···Se = 153(1)°

5. d(Se···N) = 3.039(12) Å; N–Se···N = 160.0(4)°; Se–Se···N = 69.9(3)°; C–N···Se = 162(1)°

6. d(Se···N) = 3.126(13) Å; N–Se···N = 155.6(4)°; Se–Se···N = 65.9(3)°; C–N···Se = 154(1)°

3. d(Se···N) = 3.188(14) Å; Se–Se···N = 163.5(2)°; N–Se···N = 82.3(4)°; Se–N···Se = 97.4(4)°; C–N···Se = 144(1)°

4. d(Se···N) = 3.192(13) Å; Se–Se···N = 167.6(2)°; N–Se···N = 82.3(4)°; Se–N···Se = 97.1(4)°; C–N···Se = 146(1)°

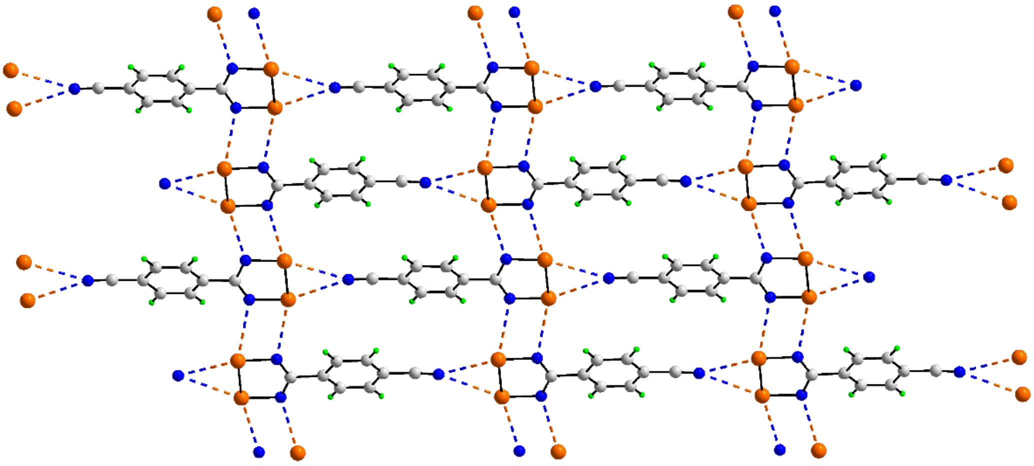
7. d(Se···N) = 3.146(12) Å; Se–Se···N = 166.1(2)°; N–Se···N = 81.5(4)°; Se–N···Se = 98.0(4)°; C–N···Se = 145.1(1)°

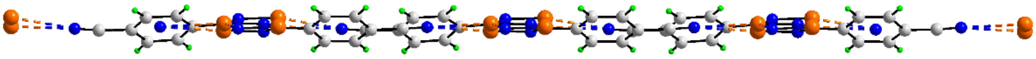
8. d(Se···N) = 3.145(12) Å; Se–Se···N = 168.4(2)°; N–Se···N = 81.2(4)°; Se–N···Se = 98.5(4)°; C–N···Se = 146.5(9)°

{Two independent molecules. The two Se atoms of the ring are connected to a common nitrile-N atom, entries 1 & 2. The linear chains thus formed are connected into a flat 2-D array *via* tapes constructed about non-symmetric $\{SeN\cdots\}_2$ synthons, entries 3 & 4; the pattern is also adopted by the second independent molecule, entries 5-8. The result is a flat 2-D array comprising alternating rows of independent molecules. Intra-layer Se···F interactions are apparent with the shortest of these being 3.066(7) Å. Three additional Se···F interactions [3.249(9), 3.296(9) & 3.439(6) Å} connect the 2-D array into a double-layer. These are connected into a 3-D architecture by Se···Se contacts [3.212(2) & 3.220(2) Å] involving all Se atoms}

37. PAHREV 4-(4-cyanophenyl)-1,2,3,5-diselenadiazole radical

A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem.*, 1992, **31**, 1802-1808. https://doi.org/10.1021/ic00036a016





1. d(Se···N) = 3.050(11) Å; Se–Se···N = 157.8(3)°; N–Se···N = 76.9(4)°; Se–N···Se = 103.8(4)°; C–N···Se = 135.9(9)°

2. d(Se···N) = 3.071(11) Å; Se–Se···N = 154.9(3)°; N–Se···N = 76.5(4)°; Se–N···Se = 102.7(4)°; C–N···Se = 137(1)°

3. d(Se···N) = 2.967(12) Å; Se–Se···N = 162.3(3)°; N–Se···N = 76.5(4)°; Se–N···Se = 104.2(4)°; C–N···Se = 141(1)°

4. d(Se···N) = 2.988(12) Å; Se–Se···N = 162.8(3)°; N–Se···N = 76.1(4)°; Se–N···Se = 103.1(4)°; C–N···Se = 141.0(9)°

5. d(Se···N) = 3.096(18) Å; N–Se···N = 159.9(5)°; Se–Se···N = 68.1(4)°; C–N···Se = 160(2)°

6. d(Se···N) = 3.01(2) Å; N–Se···N = 158.7(5)°; Se–Se···N = 68.0(4)°; C–N···Se = 156(2)°

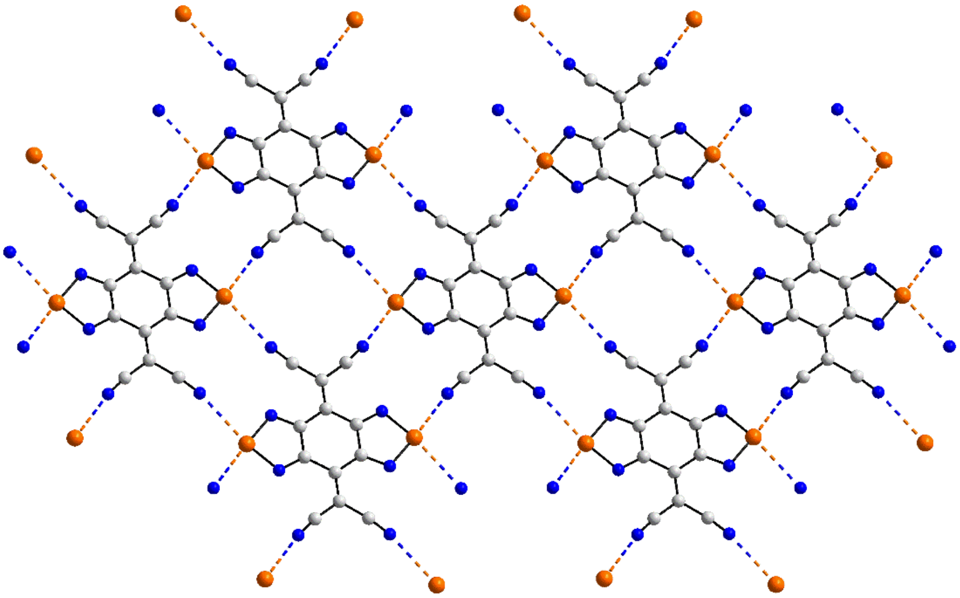
7. d(Se···N) = 3.106(18) Å; N–Se···N = 158.1(5)°; Se–Se···N = 68.3(4)°; C–N···Se = 159(2)°

8. d(Se···N) = 3.12(2) Å; N–Se···N = 157.3(5)°; Se–Se···N = 67.9(4)°; C–N···Se = 157(2)°

{Two independent molecules; eight independent Se···N contacts, four giving rise to a ribbon comprising alternating independent molecules *via* {SeN(ring)···}$_2$ synthons (entries 1 & 2 for the first {SeN(ring)···}$_2$ synthon, 3 & 4 for the second}; four involving bifurcated nitrile atoms which link the ribbons on either side into a flat, 2-D array. Double-layers feature Se···Se interactions [3.192(3) & 3.275(3) Å] between the independent molecules}

38. GEFVOC10 4H,8H-4,8-bis(dicyanomethylene)benzo(1,2-c:4,5-c')bis(1,2,5)selenadiazole

T. Suzuki, H. Fujii, Y. Yamashita, C. Kabuto, S. Tanaka, M. Harasawa, T. Mukai and T. Miyashi, *J. Am. Chem. Soc.*, 1992, **114**, 3034-3043. https://doi.org/10.1021/ja00034a041

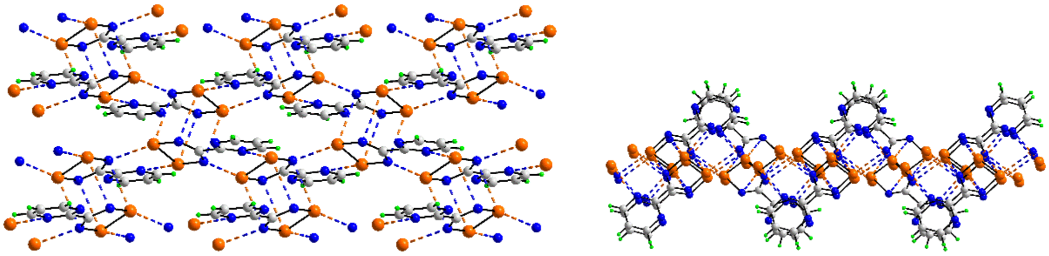


d(Se···N) = 2.940(4) Å; N–Se···N = 169.49(11) & 82.94(11)°; C–N···Se = 169.5(3)°

{The molecule is disposed over a site of symmetry 2/m; each Se atom form two Se···N interactions; grid comprising edge-shared 12-membered {···Se···NC$_3$N}$_2$ and 14-membered {SeNC$_4$N···}$_2$ synthons; flat, 2D array}

39. BARWUO 4-(2-pyrimidyl)-1,2,3,5-diselenadiazolyl radical

J. Wu, D. J. MacDonald, R. Clérac, I.-R. Jeon, M. Jennings, A. J. Lough, J. Britten, C. Robertson, P. A. Dube and K. E. Preuss, *Inorg. Chem.*, 2012, **51**, 3827-3839. https://doi.org/10.1021/ic3000284



1. d(Se···N) = 3.160(6) Å; Se–Se···N = 91.28(11)° & N–Se···N = 82.8(2)°; Se–N···Se = 98.1(2)° & C–N···Se = 86.8(4)°

2. d(Se···N) = 3.190(7) Å; Se–Se···N = 89.37(12)° & N–Se···N = 81.5(2)°; Se–N···Se = 97.6(3)° & C–N···Se = 87.1(4)°

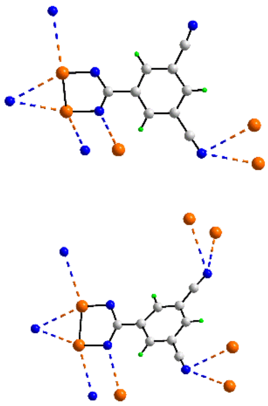
3. d(Se···N) = 3.152(6) Å; N–Se···N = 167.1(2)°; Se–Se···N = 88.00(11)°; Se–N···Se = 95.0(2)° & C–N···Se = 148.3(4)°

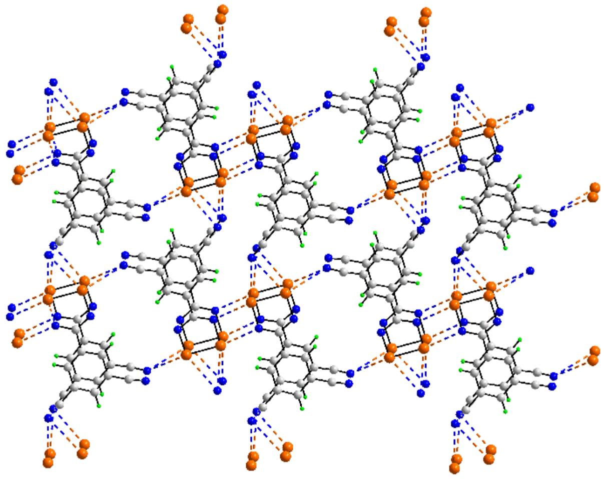
4. d(Se···N) = 2.949(6) Å; N–Se···N = 172.4(2)°; Se–Se···N = 97.14(12)°; C–N···Se = 97.3(4) & 147.3(5)°

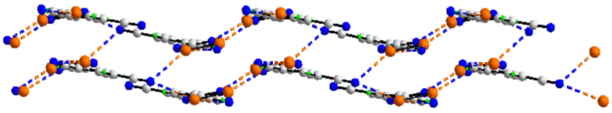
{Both Se and both N atoms of the diselenadiazolyl residue participate in Se···N interactions. Two centrosymmetrically related rings are connected *via* four Se···N interactions (entries 1 & 2) which define staves within the shape of a rectangle. Each Se atoms forms a second Se···N interaction, one with a diselenadiazolyl-N, entry 3, implying this N participates in two Se···N interactions with the second contact involving a 2-pyrimidyl-N atom (shortest Se···N separation, entry 4). The result is a 2-D grid. Within the layer, Se···Se interactions [3.4869(12) Å] also feature}

40. WAJGUJ 3,5-dicyanophenyl-1,2,3,5-diselenadiazolyl radical

W. M. Davis, R. G. Hicks, R. T. Oakley, B. Zhao and N. J. Taylor, *Can. J. Chem.*, 1993, **71**, 180-185. https://doi.org/10.1139/v93-026







1. d(Se···N) = 3.310(16) Å; N–Se···N = 154.2(5)°; Se–Se···N = 64.2(3)°; C–N···Se = 96(1)°

2. d(Se···N) = 3.311(16) Å; N–Se···N = 160.8(5)°; Se–Se···N = 73.4(3)°; C–N···Se = 135(1)°

3. d(Se···N) = 2.978(13) Å; Se–Se···N = 159.7(3)°; N–Se···N = 78.1(4)°; Se–Se···N = 104.3(5)°; C–N···Se = 139(1)°

4. d(Se···N) = 3.054(12) Å; Se–Se···N = 157.4(2)°; N–Se···N = 75.9(5)°; Se–Se···N = 101.6(5)°; C–N···Se = 137.9(9)°

5. d(Se···N) = 3.396(17) Å; Se–Se···N = 146.9(3)°; N–Se···N = 98.4(5)°; C–N···Se = 138(1)°

6. d(Se···N) = 3.047(14) Å; N–Se···N = 161.2(4)°; Se–Se···N = 70.0(3)°; C–N···Se = 142(1)°

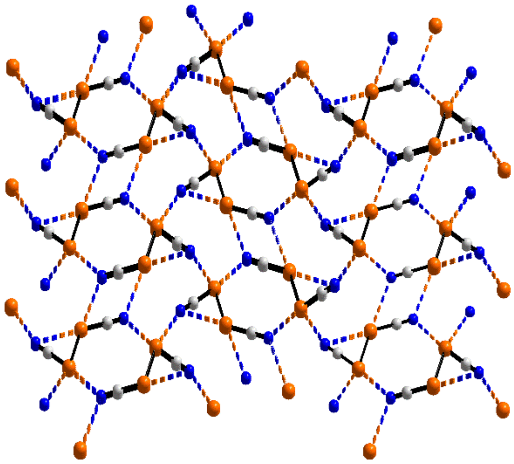
7. d(Se···N) = 3.136(15) Å; N–Se···N = 157.4(5)°; Se–Se···N = 65.9(3)°; C–N···Se = 101(1)°

8. d(Se···N) = 3.362(16) Å; Se–Se···N = 150.0(3)°; N–Se···N = 101.5(5)°; C–N···Se = 116(1)°

{Two independent molecules. First molecule: self-associates *via* Se···N(nitrile) interactions from the bifurcated nitrile molecule, entries 1 & 2. Adjacent Se and N atoms associate with equivalent atoms for the second independent molecule *via* a non-symmetric {SeN···}$_2$ synthon, entries 3 & 4. Each Se atom forms two contacts, with the second contact for the second Se atom being with a nitrile-N of the second independent molecule, entry 5. Second molecule: the two Se atoms of the ring self-associate with the bifurcated nitrile-N atoms, entries 6 & 7. Adjacent Se and N participate in the {SeN···}$_2$ as per entries 3 & 4. The other Se of the ring forms a single contact with a nitrile-N atom (self-association), entry 8. Common features: each Se forms two contacts. Only one nitrile-N in the first molecule forms bifurcated Se···N interactions, while both nitriles of the second molecule are bifurcated. Result: a double layer with the key interaction between layers being relating to entry 8. Double-layers are connected into a double double-layer *via* Se···Se interactions [3.217(2) & 3.261(2) Å] involving all Se atoms}

41. XUNHOF diselane-1,2-dicarbonitrile

C. J. Burchell, P. Kilian, A. M. Z. Slawin, J. D. Woollins, K. Tersago, C. Van Alsenoy and F. Blockhuys, *Inorg. Chem.*, 2006, **45**, 710-716. https://doi.org/10.1021/ic0515103



d(Se···N) = 2.877(4) Å; Se–Se···N = 164.33(8)°; C–Se···N = 69.44(16)°; C–N···Se = 158.7(4)°

d(Se···N) = 2.937(4) Å; C–Se···N = 172.89(16)°; Se–Se···N = 91.61(8)°; C–N···Se = 133.4(4)°

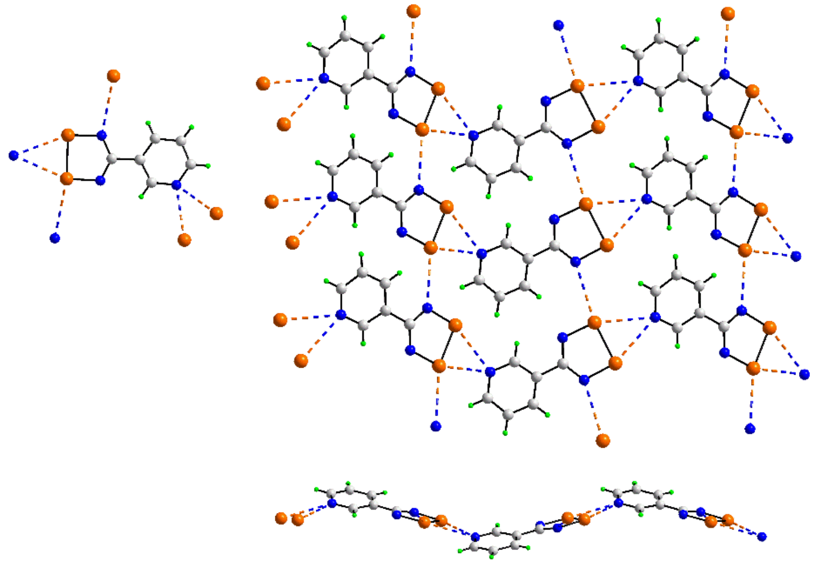
d(Se···N) = 3.157(4) Å; Se–Se···N = 165.35(8)°; C–Se···N = 71.11(15)°; C–N···Se = 127.7(3)°

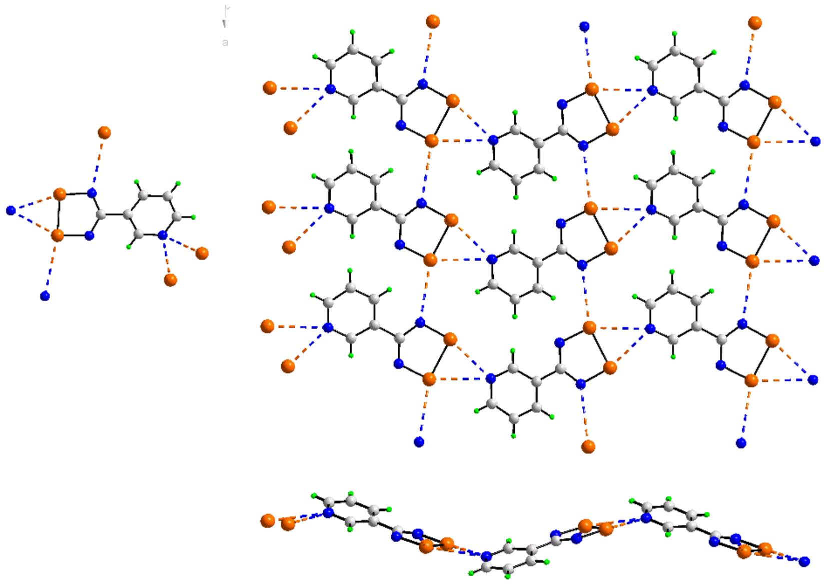
d(Se···N) = 3.199(5) Å; C–Se···N = 178.39(17)°; Se–Se···N = 82.40(7)°; C–N···Se = 93.0(3)°

{No symmetry. Each Se forms two Se···N(nitrile) contacts as does each nitrile-N atom. Entries 1 and 2 pertain to the first Se atom. The result is a 3-D architecture}

42. TINQAL 3-(3H-1,2,3,5-diselenadiazol-4-yl)pyridine radical

A. I. Taponen, J. W. L. Wong, K. Lekin, A. Assoud, C. M. Robertson, M. Lahtinen, R. Clérac, H. M. Tuononen, A. Mailman and R. T. Oakley, *Inorg. Chem.*, 2018, **57**, 13901-13911.
https://doi.org/10.1021/acs.inorgchem.8b02416





1. d(Se···N) = 3.065(3) Å; N–Se···N = 158.47(11)°; Se–Se···N = 68.12(6)°; C–N···Se = 95.2(2) & 143.4(2)°

2. d(Se···N) = 3.074(3) Å; N–Se···N = 158.92(11)°; Se–Se···N = 67.71(6)°; C–N···Se = 105.9(2) & 137.4(2)°

3. d(Se···N) = 3.411(3) Å; Se–Se···N = 161.09(6)°; N–Se···N = 100.38(11)°; Se–N···Se = 102.13(12)°; C–N···Se = 139.7(2)°

4. d(Se···N) = 2.906(3) Å; N–Se···N = 164.08(12)°; Se–Se···N = 73.94(7)°; C–N···Se = 107.6(2) & 135.4(3)°

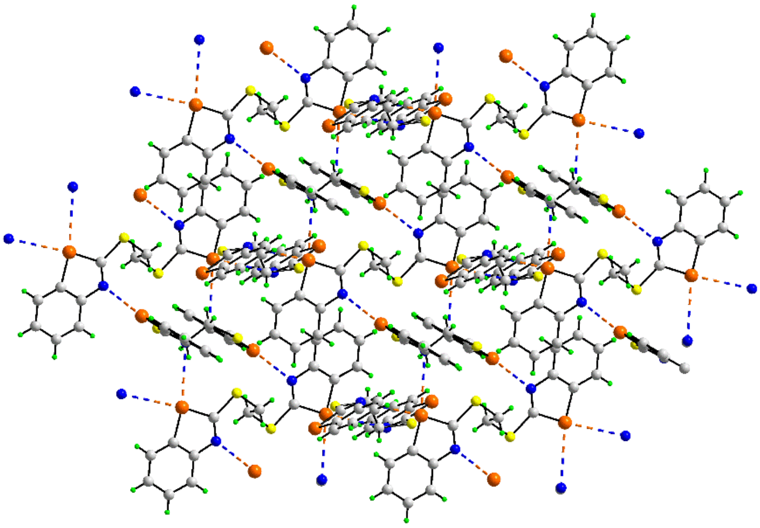
5. d(Se···N) = 3.174(3) Å; N–Se···N = 152.43(11)°; Se–Se···N = 61.62(6)°; C–N···Se = 93.0(2) & 145.0(2)°

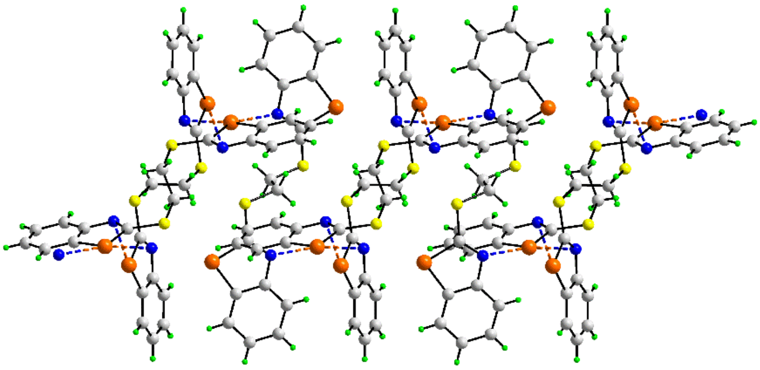
6. d(Se···N) = 3.406(3) Å; Se–Se···N = 155.68(6)°; N–Se···N = 103.12(11)°; Se–N···Se = 105.09(12)°; C–N···Se = 135.6(2)°

{Two independent molecules which form the same pattern of Se···N contacts, each self-associating only. The pyridyl-N bridges the Se atoms of a symmetry related molecule, entries 1 and 2. One of the Se atoms forms two contacts, the second with a ring-N atom of the same molecule, entry 3. The ring-N forms a single interaction, corresponding to entry 3. The corresponding contacts for the second independent molecule are listed as entries 4-6. Flat 2-D arrays eventuate in each case. The layers assemble into a 3-D architecture through Se···Se interactions [3.2404(5) & 3.3094(5) Å] formed between the independent molecules}

43. PUZWIQ 2,2'-(ethylenedisulfanyl)bis(benzoselenazole)

Z. Časar, I. Leban, A. Majcen-Le Maréchal and D. Lorcy, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1568-1573. https://doi.org/10.1039/b203317h





d(Se···N) = 3.227(3) Å; C–Se···N = 161.03(13) & 89.41(14)°; C–N···Se = 97.3(2) & 129.4(3)°

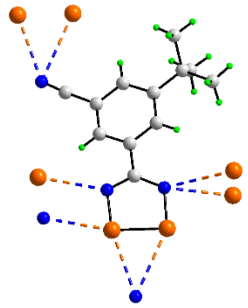
d(Se···N) = 3.375(4) Å; C–Se···N = 168.51(14) & 103.54(14)°; C–N···Se = 93.7(3) & 112.5(3)°

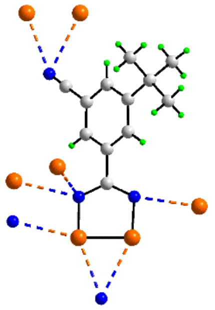
d(Se···N) = 3.234(3) Å; C–Se···N = 171.09(14) & 100.16(14)°; C–N···Se = 96.0(2) & 110.6(2)°

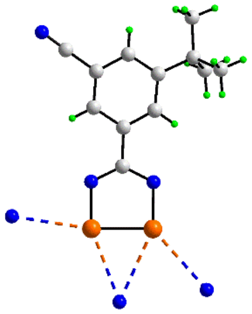
{There are three half molecules in the asymmetric-unit, each being disposed about a centre of inversion. The nature of the Se···N formed between the molecules differentiate them: the Se atoms in one molecule form two interactions, entries 1 & 2, in the second molecule, one (entry 3) and in the third, none. The ring-N donors are derived from each molecule. The result is a 2-D array. Each independent Se atom forms a 1,3-Se···S contact [3.0966(11), 3.1042(9) & 3.1209(9) Å]}

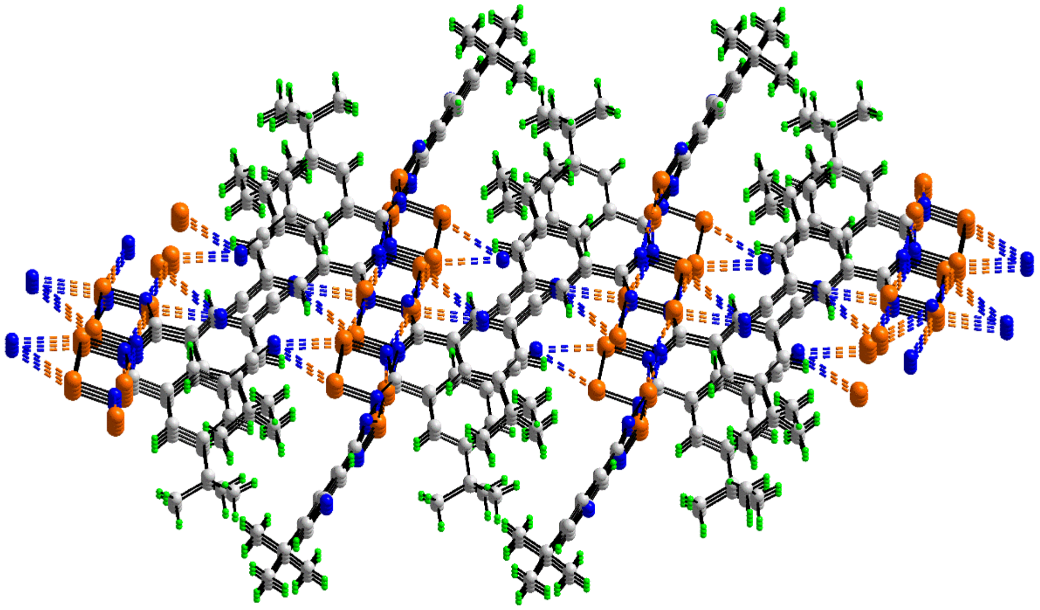
44. **PECXED02** 4-(3-cyano-5-t-butyl-phenyl)-3H-1,2,3,5-diselenadiazol-3-yl radical

R. T. Boere, Private Communication to the Cambridge Structural Database, Refcode PECXED02, 2020.









1. d(Se···N) = 2.997(3) Å; N–Se···N = 165.38(12)°; Se–Se···N = 75.55(7)°; C–N···Se = 135.5(3)°

2. d(Se···N) = 3.303(3) Å; N–Se···N = 153.08(12)°; Se–Se···N = 61.49(7)°; C–N···Se = 96.3(3)°

3. d(Se···N) = 2.894(4) Å; Se–Se···N = 167.81(7)°; N–Se···N = 77.19(13)°; Se–N···Se = 104.05(14)°; C–N···Se = 141.0(3)°

4. d(Se···N) = 2.933(4) Å; Se–Se···N = 165.86(7)°; N–Se···N = 76.08(13)°; Se–N···Se = 102.59(14)°; C–N···Se = 141.6(3)°

5. d(Se···N) = 3.063(4) Å; N–Se···N = 156.26(14)°; Se–Se···N = 69.57(7)°; Se–Se···N = 88.47(13)°; C–N···N = 153.7(3)°

6. d(Se···N) = 3.142(3) Å; N–Se···N = 152.99(13)°; Se–Se···N = 65.98(6)°; Se–Se···N = 91.50(12)°; C–N···N = 141.2(3)°

7. d(Se···N) = 2.926(4) Å; N–Se···N = 158.93(12)°; Se–Se···N = 68.70(8)°; C–N···Se = 144.3(3)°

8. d(Se···N) = 3.005(3) Å; N–Se···N = 156.52(12)°; Se–Se···N = 65.15(8)°; C–N···Se = 105.3(3)°

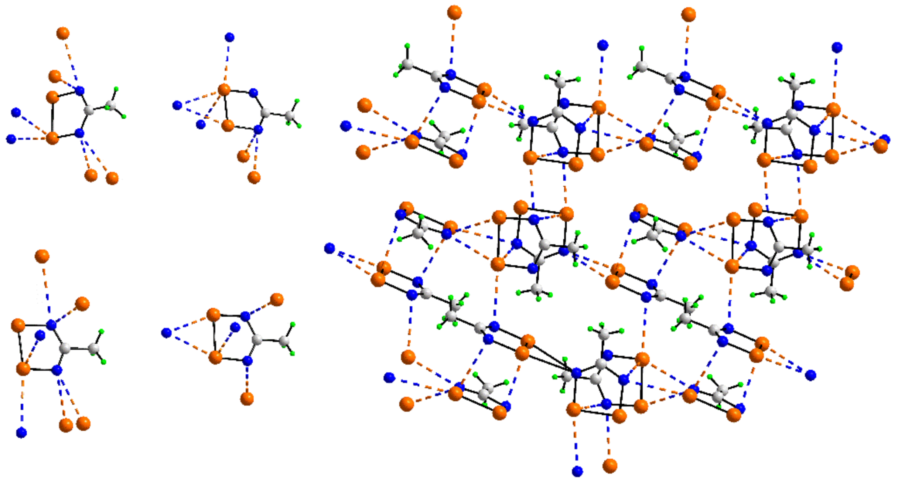
9. d(Se···N) = 3.216(4) Å; N–Se···N = 135.53(13)°; Se–Se···N = 129.79(7)°; Se–N···Se = 90.01(13)°; C–N···Se = 139.0(3)°

10. d(Se···N) = 3.101(4) Å; Se–Se···N = 170.07(7)°; N–Se···N = 80.71(14)°; Se–N···Se = 104.14(14)°; C–N···Se = 92.9(2)°

{Three independent molecules; 10 independent Se···N contacts. Two molecules associate to form a non-symmetric $\{\mathrm{SeN}\cdots\}_2$ synthon; first two entries. The Se atoms of two molecules self-associate by accepting bifurcated Se···N(nitrile) contacts; entries 3-6, while those of the third molecule accept bifurcated Se···N(ring) contacts, entries 7 and 8. Additional Se···N(ring) contacts are noted, *i.e.* single contacts between rings, entries 9 and 10. In the first two molecules, one Se forms two contacts and the other, one. For the third molecule, each Se forms two contacts. For the ring-N atoms, for the first two molecules, one N forms a single contact while the other forms two. For the third molecule, the ring-N atoms do not form contacts. Finally, the nitrile-N atoms of the first two molecules form two contacts whereas that of the third does not form a contact. The two interacting nitrile groups project to either side of layers comprising alternating hetero-rings to connect translationally related layers into a 2-D array. Within this array are also a relatively large number of Se···Se interactions ranging from a short 3.1453(5) to a long 3.7577(7) Å}

45. ZEXVON 4-methyl-1,2,3,5-diselenadiazole

C. D. Bryan, A. W. Cordes, R. T. Oakley and R. E. vonH. Spence, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 2402-2404. https://doi.org/10.1107/S0108270195006147



1. d(Se···N) = 3.009(14) Å; N–Se···N = 168.9(5)°; Se–Se···N = 79.5(3)°; Se–N···Se = 83.8(5)°; C–N···Se = 161(1)°

2. d(Se···N) = 3.346(15) Å; Se–Se···N = 79.2(2)°; N–Se···N = 92.1(5)°; Se–N···Se = 96.6(5)°; C–N···Se = 81.2(9)°

3. d(Se···N) = 2.971(14) Å; N–Se···N = 160.2(5)°; Se–Se···N = 69.3(3)°; Se–N···Se = 112.7(6)°; C–N···Se = 130(1)°

4. d(Se···N) = 3.048(15) Å; N–Se···N = 157.1(6)°; Se–Se···N = 65.7(3)°; Se–N···Se = 108.3(6)°; C–N···Se = 121(1)°

5. d(Se···N) = 3.186(14) Å; Se–Se···N = 80.9(3)°; N–Se···N = 92.7(5)°; Se–N···Se = 99.4(5)°; C–N···Se = 84.3(9)°

6. d(Se···N) = 3.300(13) Å; Se–Se···N = 169.7(3)°; N–Se···N = 95.1(5)°; Se–N···Se = 83.0(5)°; C–N···Se = 156(1)°

7. d(Se···N) = 3.051(11) Å; N–Se···N = 159.4(5)°; Se–Se···N = 68.4(3)°; Se–N···Se = 109.4(5)°; C–N···Se = 119(1)°

8. d(Se···N) = 3.076(13) Å; N–Se···N = 157.5(5)°; Se–Se···N = 67.3(3)°; Se–N···Se = 109.1(5)°; C–N···Se = 135(1)°

9. d(Se···N) = 3.054(15) Å; Se–Se···N = 161.9(3)°; N–Se···N = 84.4(5)° Se–N···Se = 110.7(6)°; C–N···Se = 102(1)°;

10. d(Se···N) = 3.215(14) Å; Se–Se···N = 82.2(3)°; N–Se···N = 94.8(5)°; Se–N···Se = 97.8(6)°; C–N···Se = 86(1)°

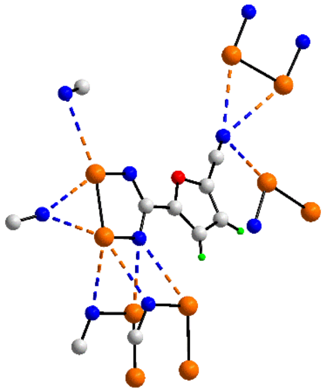
11. d(Se···N) = 3.343(15) Å; Se–Se···N = 79.7(3)°; N–Se···N = 95.0(4)°; Se–N···Se = 96.9(6)°; C–N···Se =84(1)°

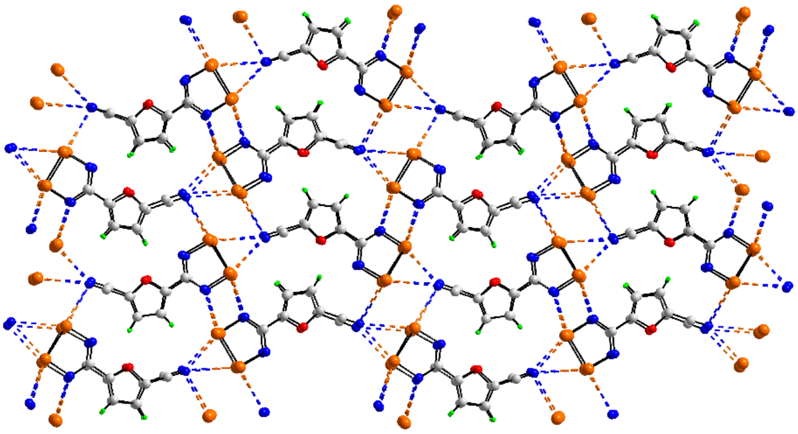
12. d(Se···N) = 3.452(14) Å; Se–Se···N = 174.5(3)°; N–Se···N = 95.0(4)°; Se–N···Se = 82.4(6)°; C–N···Se = 154(1)°

{Four independent molecules and each forms a distinctive pattern of Se···N interactions. First molecule connects to four different molecules: one Se atom of the ring forms two contacts with two ring-N atoms, entries 1 and 2, while the second Se atom does not form a contact. Each ring-N atom forms two contacts, entries 3-6. Entries 3 and 4 relate to the N atom connecting two Se atoms of the same ring. Entries 2 and 5 relate to the face-to-face contact between two rings. The second independent molecule: one Se atom forms a single contact, entry 7, while the other forms three contacts, entries 5, 8 & 9. Entries 7 and 8 refer to a ring-N bridging the Se atoms. Only one of the ring-N atoms forms Se···N interactions, entries 1 & 2. Entries 2 & 5 relate to the face-to-face contact between two rings. The third independent molecule: One Se atoms forms two contacts, entries 6 & 10, while the other does not form one. Each of the ring-N atoms forms two contacts. One, entries 11 & 12, forms contacts to two different molecules while the other bridges two Se atoms of a ring, entries 7 & 8. Entries 10 & 11 refer to contacts between the third and four independent molecules. The fourth independent molecule: one Se forms a single contact, entry 4, while the other forms two, entries 3 & 11. Entries 3 & 4 relate to a ring-N bridging two Se atoms of the ring. Each ring atom forms a single contact, entries 9 & 10. Net result: 2-D architecture. Close Se···Se contacts also feature in the crystal, *i.e.* within the 2-D array [shortest contact = 3.160(3) Å] and between layers to generate a 3-D architecture. For the latter, the Se···Se separations tended to be longer and range from 3.630(3) to 3.789(3) Å}

46. YIFHUQ 2-(1,2,3,5-diselenadiazol-4-yl)-5-cyanofuran

J. F. Britten, O. P. Clements, A. W. Cordes, R. C. Haddon, R. T. Oakley and J. F. Richardson, *Inorg. Chem.*, 2001, **40**, 6820-6824. https://doi.org/10.1021/ic010678v





1: d(Se···N) = 3.004(8) Å; N–Se···N = 164.5(3)°; Se–Se···N = 73.80(16)°; C–N···Se = 147.7(7)°

2: d(Se···N) = 3.241(8) Å; N–Se···N = 154.8(3)°; Se–Se···N = 62.8(15)°; C–N···Se = 150.8(7)°

3: d(Se···N) = 3.315(9) Å; Se–Se···N = 165.08(15)°; N–Se···N = 90.0(3)°; C–N···Se = 105.0(7)°

4: d(Se···N) = 2.974(10) Å; N–Se···N = 164.5(3)°; Se–Se···N = 74.2(2)°; C–N···Se = 145.7(7)°

5: d(Se···N) = 3.234(8) Å; N–Se···N = 153.7(3)°; Se–Se···N = 62.25(16)°; C–N···Se = 152.3(7)°

6: d(Se···N) = 3.459(9) Å; Se–Se···N = 158.80(16)°; N–Se···N = 83.8(3)°; C–N···Se = 111.8(7)°

7: d(Se···N) = 3.030(6) Å; Se–Se···N = 153.98(12)°; N–Se···N = 79.4(2)°; Se–N···Se = 106.1(3)°; C–N···Se = 127.8(5)°

8: d(Se···N) = 3.202(6) Å; Se–Se···N = 141.79(12)°; N–Se···N = 74.7(2)°; Se–N···Se = 99.3(3)°; C–N···Se = 136.0(5)°

9: d(Se···N) = 3.050(7) Å; Se–Se···N = 151.56(12)°; N–Se···N = 78.8(2)°; Se–N···Se = 108.0(3)°; C–N···Se = 125.3(5)°

10: d(Se···N) = 3.278(7) Å; Se–Se···N = 135.57(12)°; N–Se···N = 72.0(2)°; Se–N···Se = 100.0(2)°; C–N···Se = 131.9(5)°

11: d(Se···N) = 3.014(10) Å; N–Se···N = 165.6(3)°; Se–Se···N = 75.80(19)°; C–N···Se = 143.0(8)°

12: d(Se···N) = 3.317(8) Å; N–Se···N = 152.9(3)°; Se–Se···N = 61.74(16)°; C–N···Se = 151.7(7)°

13: d(Se···N) = 3.346(10) Å; Se–Se···N = 160.69(17)°; N–Se···N = 85.9(3)°; C–N···Se = 108.8(7)°

14: d(Se···N) = 3.025(10) Å; N–Se···N = 164.4(3)°; Se–Se···N = 73.56(19)°; C–N···Se = 143.4(8)°

15: d(Se···N) = 3.246(8) Å; N–Se···N = 154.2(3)°; Se–Se···N = 63.35(16)°; C–N···Se = 155.0(8)°

16: d(Se···N) = 3.274(9) Å; Se–Se···N = 158.53(17)°; N–Se···N = 90.9(3)°; C–N···Se = 101.9(7)°

17: d(Se···N) = 3.228(7) Å; Se–Se···N = 151.23(12)°; N–Se···N = 79.8(2)°; Se–N···Se = 103.0(3)°; C–N···Se = 129.9(5)°

18: d(Se···N) = 3.322(7) Å; Se–Se···N = 142.21(11)°; N–Se···N = 76.7(2)°; Se–N···Se = 100.2(2)°; C–N···Se = 134.6(5)°

19: d(Se···N) = 3.257(6) Å; Se–Se···N = 143.80(12)°; N–Se···N = 79.9(2)°; Se–N···Se = 105.6(3)°; C–N···Se = 122.3(5)°

20: d(Se···N) = 3.426(6) Å; Se–Se···N = 131.27(11)°; N–Se···N = 75.3(2)°; Se–N···Se = 98.6(2)°; C–N···Se = 130.0(5)°

21: d(Se···N) = 3.343(11) Å; Se–Se···N = 154.84(17)°; N–Se···N = 86.7(3)°; C–N···Se = 106.9(7)°

22: d(Se···N) = 3.218(9) Å; Se–Se···N = 164.70(18)°; N–Se···N = 90.3(3)°; C–N···Se = 105.3(7)°

23: d(Se···N) = 3.145(7) Å; Se–Se···N = 151.62(12)°; N–Se···N = 79.9(2)°; Se–N···Se = 105.8(3)°; C–N···Se = 127.1(5)°

24: d(Se···N) = 3.319(7) Å; Se–Se···N = 140.38(11)°; N–Se···N = 75.0(2)°; Se–N···Se = 98.9(2)°; C–N···Se = 135.2(5)°

25: d(Se···N) = 3.159(6) Å; Se–Se···N = 153.91(12)°; N–Se···N = 79.4(2)°; Se–N···Se = 102.9(3)°; C–N···Se = 133.0(5)°

26: d(Se···N) = 3.237(6) Å; Se–Se···N = 145.70(12)°; N–Se···N = 76.7(2)°; Se–N···Se = 100.7(3)°; C–N···Se = 136.1(5)°

27: d(Se···N) = 3.368(10) Å; Se–Se···N = 159.09(17)°; N–Se···N = 89.0(3)°; C–N···Se = 106.3(7)°

28: d(Se···N) = 3.348(9) Å; Se–Se···N = 165.13(17)°; N–Se···N = 85.2(3)°; C–N···Se = 108.6(7)°

29: d(Se···N) = 2.991(6) Å; Se–Se···N = 154.68(13)°; N–Se···N = 78.6(2)°; Se–N···Se = 107.8(3)°; C–N···Se = 126.8(5)°

30: d(Se···N) = 3.201(6) Å; Se–Se···N = 139.06(12)°; N–Se···N = 72.4(2)°; Se–N···Se = 100.2(3)°; C–N···Se = 135.5(5)°

31: d(Se···N) = 3.294(7) Å; Se–Se···N = 138.60(11)°; N–Se···N = 80.7(2)°; Se–N···Se = 104.4(3)°; C–N···Se = 118.6(5)°

32: d(Se···N) = 3.453(7) Å; Se–Se···N = 127.10(11)°; N–Se···N = 76.2(2)°; Se–N···Se = 98.1(2)°; C–N···Se = 125.9(5)°

33: d(Se···N) = 2.991(9) Å; N–Se···N = 168.1(3)°; Se–Se···N = 79.31(19)°; C–N···Se = 146.0(8)°

34: d(Se···N) = 3.424(8) Å; N–Se···N = 150.3(3)°; Se–Se···N = 59.13(15)°; C–N···Se = 150.9(8)°

35: d(Se···N) = 3.006(10) Å; N–Se···N = 161.1(3)°; Se–Se···N = 70.0(2)°; C–N···Se = 141.4(7)°

36: d(Se···N) = 3.102(8) Å; N–Se···N = 157.1(3)°; Se–Se···N = 65.54(17)°; C–N···Se = 152.9(7)°

37: d(Se···N) = 2.975(9) Å; N–Se···N = 164.8(3)°; Se–Se···N = 77.7(2)°; C–N···Se = 143.5(7)°

38: d(Se···N) = 3.252(8) Å; N–Se···N = 153.5(3)°; Se–Se···N = 61.93(16)°; C–N···Se = 153.8(7)°

39: d(Se···N) = 3.051(9) Å; N–Se···N = 163.9(3)°; Se–Se···N = 73.83(19)°; C–N···Se = 144.1(7)°

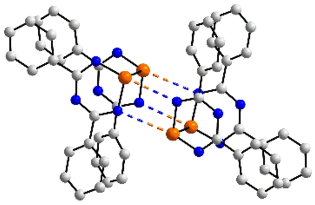
40: d(Se···N) = 3.274(8) Å; N–Se···N = 154.2(3)°; Se–Se···N = 63.50(16)°; C–N···Se = 152.5(7)°

{Eight independent molecules. A total of 40 Se···N contacts; two are marginally longer than 3.45 Å. All molecules form the same pattern of contacts. The first molecule (as does each molecule) participates in 10 independent contacts. The nitrile-N forms three contacts, two of which span the two Se atoms of a symmetry related ring, entries 1 and 2, and a Se of a second ring, entry 3. A symmetry related nitrile spans the two Se atoms of the ring, entries 4 and 5. One of these Se atoms also forms a second Se···N(nitrile) interaction with a different nitrile-N atom, entry 6. The other Se atom and adjacent N atom participate in the formation of two non-symmetric {SeN···}$_2$ synthons sharing one edge, entries 7-10. The second independent molecule: entries 11-20. The third molecule: entries 14, 15, 21, 11, 12, 22-26. The fourth molecule: entries 4, 5, 27, 1, 2, 28-32. The fifth: entries 33, 34, 22, 35, 36, 13, 9, 10, 19 and 20. The sixth: entries 35, 36, 28, 33, 34, 3, 7, 8, 17 and 18. Seventh: 37, 38, 6, 37, 38, 21, 23, 24, 29 and 30. Eighth: 39, 40, 16, 39, 40, 27, 25, 26, 31 and 32. Molecules seven and eight are exceptional in that the bifurcated Se···N(nitrile) interactions lead to the self-association between molecules. The result: 3-D assembly. The next closest Se···N interaction is 3.603(6) Å but this occurs within two pre-existing Se···N interactions. In addition, Se···Se contacts [range = 3.1893(12) to 3.7724(11) Å] feature within the 3-D architecture}

ESI Table S2. Supramolecular architectures formed by di-nuclear selenium molecules co-crystallised with other species.

47. DUVFEF10 bis(3,5-diphenyl-1,2,4,6-selenatriazine) acetonitrile solvate

R. T. Oakley, R. W. Reed, A. W. Cordes, S. L. Craig and J. B. Graham, *J. Am. Chem. Soc.*, 1987, **109**, 7745-7749. https://doi.org/10.1021/ja00259a024



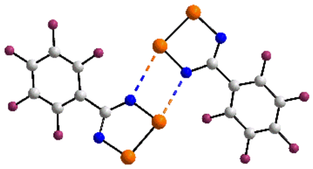
d(Se···N) = 3.032(7) Å; N–Se···N = 163.6(3) & 76.9(3)°; Se–Se···N = 67.60(17)°; Se–N···Se = 109.4(4)°; C–N···Se = 128.5(6)°

d(Se···N) = 3.235(8) Å; N–Se···N = 144.0(3) & 71.3(3)°; Se–Se···N = 118.10(18)°; Se–N···Se = 101.4(4)°; C–N···Se = 131.3(7)°

{Two independent Se-molecules and one solvent molecule. The two molecules associate to about a centre of inversion *via* four Se···N contacts to form a two-molecule aggregate with the appearance of a prism: there are also short interactions across the diagonal, *i.e.* with Se···N = 3.246(9) Å}

48. SOBPIL (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl radical bis(4-(pentafluorophenyl)-3H-1,2,3,5-diselenadiazol-3-yl radical)

M. A. Nascimento, E. Heyer, J. J. Clarke, H. J. Cowley, A. Alberola, N. Stephaniuk and J. M. Rawson, *Angew. Chem., Int. Ed.*, 2019, **58**, 1371-1375. https://doi.org/10.1002/anie.201812132



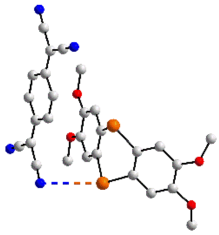
d(Se···N) = 2.914(6) Å; Se–Se···N = 166.66(11)°; N–Se···N = 76.45(19)°; Se–N···Se = 105.7(2)°; C–N···Se = 138.6(4)°

d(Se···N) = 3.024(6) Å; Se–Se···N = 164.15(11)°; N–Se···N = 73.48(19)°; Se–N···Se = 101.3(2)°; C–N···Se = 143.8(4)°

{Two independent dinuclear molecules which associate *via* a {···SeN}$_2$ synthon to form a two-molecule. These aggregate normal to the central plane *via* Se···Se contacts (3.1330(8) & 3.1895(7) Å) to form an octa-nuclear Se$_8$ aggregate. The outer staves (defined by the Se···Se contacts) are bridged by (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl-O atoms (2.897(5) & 2.996(4) Å)}

49. BOMDIQ 2,3,7,8-tetramethoxyselenanthrene 7,7,8,8-tetracyanoquinodimethane

W. Hinrichs and G. Klar, *J. Chem. Res. (S)*, 1982, 336-337.

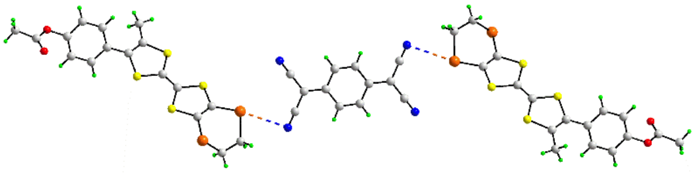


d(Se···N) = 3.45 Å; C–Se···N = 140.6 & 86.0°; C–N···Se = 95.4°

{1:1 co-crystal. Standard uncertainties not available. One Se forms Se···N interactions with one of the four available N atoms to generate a two-molecule aggregate}

50. ASIHUF 4-(4-acetoxyphenyl)-5-methyl-4',5'-ethylenediselenotetrathiafulvalene hemikis(tetracyano-4-quinodimethane)

L. Kaboub, J.-P. Legros, B. Donnadieu, A.-K. Gouasmia, L. Boudiba and J.-M. Fabre, *J. Mater. Chem.*, 2004, **14**, 351-362. https://doi.org/10.1039/b308514g

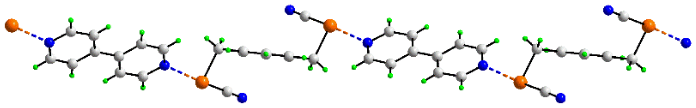


d(Se···N) = 3.260(7) Å; C–Se···N = 171.3(2)°; Se–Se···N = 70.3(3)°; C–N···Se = 95.7(5)°

{2:1 co-crystal; the tetracyano-4-quinodimethane molecules is centrosymmetric; one Se from each co-former and two N atoms from tetracyano-4-quinodimethane form Se···N interactions to generate a three-molecule aggregate. The Se atoms are proximate having a Se···Se separation of 3.4986(16) Å and each Se atom forms a 1,3-Se···S contact: 3.097(3) & 3.100(2) Å; the shorter contact involves the Se atom participating in the Se···N contact. Supramolecular tapes are formed *via* weak intermolecular Se···S interactions [3.709(3) Å]}

51. FEDJAC 1,3-bis(selenocyanatomethyl)benzene 4,4'-bipyridine

H.-T. Huynh, O. Jeannin and M. Fourmigué, *Chem. Commun.*, 2017, **53**, 8467-8469. https://doi.org/10.1039/C7CC04833E

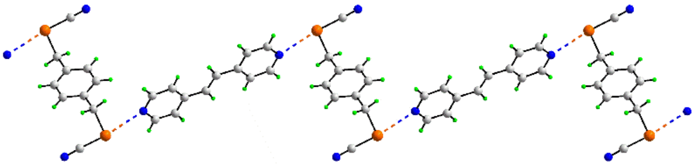


d(Se···N) = 2.830(2) Å; (N)C–Se···N = 177.18(9)°; C–Se···N = 84.30(9)°; C–N···Se = 107.4(2) & 137.06(19)°

{1:1 co-crystal; The 4,4'-bipyridyl molecule is centrosymmetric whereas the other molecule is bisected by a 2-fold axis of symmetry. Appearance of a flattened step-ladder but is twisted; both Se atoms form Se···N interactions}

52. FUNGIH (1,4-phenylene)bis(methylene) bis(selenocyanate) 4,4'-(ethene-1,2-diyl)dipyridine

V. Kumar, Y. Xu, C. Leroy and D. L. Bryce, *Phys. Chem. Chem. Phys.*, 2020, **22**, 3817-3824. https://doi.org/10.1039/C9CP06267J

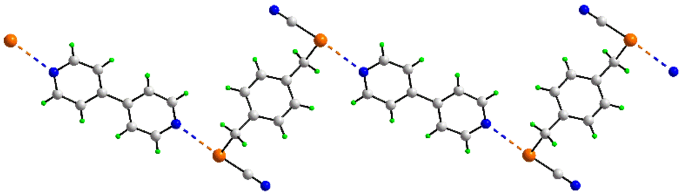


d(Se···N) = 2.865(2) Å; (N)C–Se···N = 167.84(9)°; C–Se···N = 83.00(8)°; C–Se···N = 105.56(18) & 138.63(19)°

{1:1 co-crystal; Each co-former is centrosymmetric. Step-ladder with twists; both Se atoms form Se···N interactions}

53. FEDJEG 1,4-bis(selenocyanatomethyl)benzene 4,4'-bipyridine

H.-T. Huynh, O. Jeannin and M. Fourmigué, *Chem. Commun.*, 2017, **53**, 8467-8469. https://doi.org/10.1039/C7CC04833E

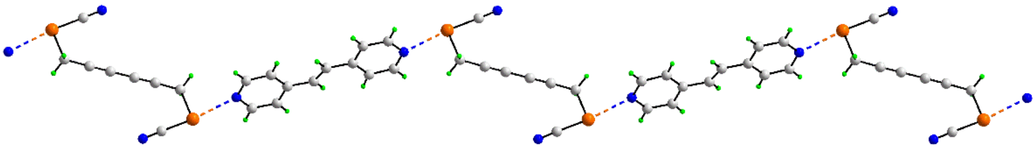


d(Se···N) = 2.897(2) Å; (N)C–Se···N = 176.70(11)°; C–Se···N = 83.00(10)°; C–N···Se = 108.1(2) & 136.2(2)°

{1:1 co-crystal; Each co-former is centrosymmetric. Step-ladder; both Se atoms form Se···N interactions}

54. QANSAD bis(selenocyanatomethyl)-butadyine 1,2-bis(4-pyridyl)ethylene

A. Dhaka, I.-R. Jeon, O. Jeannin, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2022, e202116650. https://doi.org/10.1002/anie.202116650

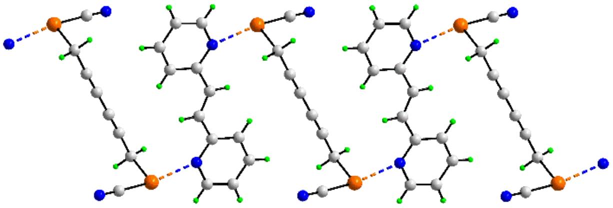


d(Se···N) = 2.7368(12) Å; (N)C–Se···N = 174.42(6)°; C–Se···N = 79.29(6)°; C–N···Se = 117.34(10) & 121.33(10)°

{1:1 co-crystal; Each co-former is centrosymmetric. Step-ladder; both Se atoms form Se···N interactions}

55. QANSEH bis(selenocyanatometh-yl)-butadyine 1,2-bis(2-pyridyl)ethylene

A. Dhaka, I.-R. Jeon, O. Jeannin, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2022, e202116650. https://doi.org/10.1002/anie.202116650

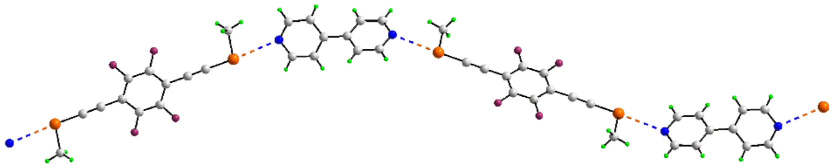


d(Se···N) = 2.792(3) Å; (N)C–Se···N = 172.37(14)°; C–Se···N = 81.39(13)°; C–N···Se = 107.4(2) & 132.0(3)°

{1:1 co-crystal; Each co-former is centrosymmetric. Step-ladder; both Se atoms form Se···N interactions}

56. IMOQUZ 4,4'-bipyridine 1,2,4,5-tetrafluoro-3,6-bis[(methylselanyl)ethynyl]benzene

A. Dhaka, O. Jeannin, I.-R. Jeon, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2020, **59**, 23583-23587. https://doi.org/10.1002/anie.202011981

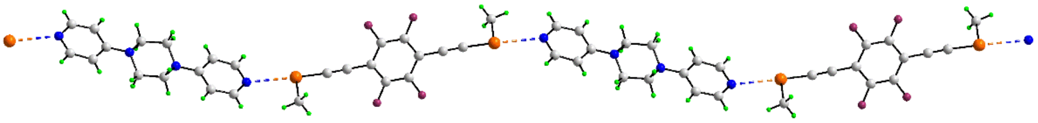


d(Se···N) = 3.055(3) Å; (C)C–Se···N = 176.09(11)°; C–Se···N = 80.01(11)°; C–N···Se = 105.78(18) & 134.83(19)°

{1:1 co-crystal; Se-compound disposed about a centre of inversion; bipyridine molecule disposed about a 2-fold axis; each Se atom forms a Se···N interaction to give a twisted chain}

57. IMORIO 1,2,4,5-tetrafluoro-3,6-bis[(methylselanyl)ethynyl]benzene 1,4-bis(pyridin-4-yl)piperazine

A. Dhaka, O. Jeannin, I.-R. Jeon, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2020, **59**, 23583-23587. https://doi.org/10.1002/anie.202011981

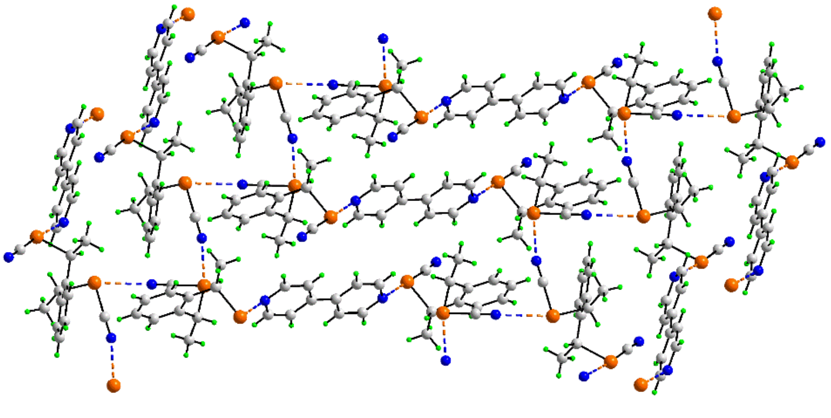


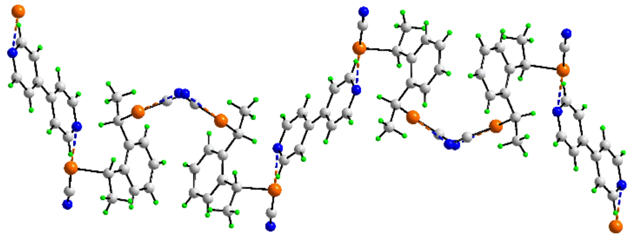
d(Se···N) = 2.995(2) Å; (C)C–Se···N = 171.58(11)°; C–Se···N = 78.55(13)°; C–N···Se = 103.93(19) & 141.0(2)°

{1:1 co-crystal; each co-former is disposed about a centre of inversion; each Se atom forms a Se···N interaction to give a twisted chain}

58. MAHHOW bis(anti-(1,2-phenylene)bis(ethane-1,1-diyl) bis(selenocyanate)) 4,4'-bipyridine

H.-T. Huynh, O. Jeannin, E. Aubert, E. Espinosa and M. Fourmigué, *New J. Chem.*, 2021, **45**, 76-84. https://doi.org/10.1039/D0NJ05293K





d(Se···N) = 3.003(4) Å; (N)C–Se···N = 173.62(13)°; C–Se···N = 82.52(10)°; C–N···Se = 104.7(3) & 128.2(3)°

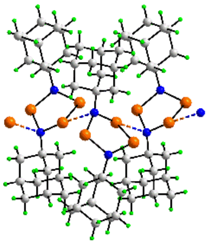
d(Se···N) = 3.198(3) Å; C–Se···N = 165.56(9)°; (N)C–Se···N = 71.16(11)°; C–N···Se = 131.2(2)°

{2:1 co-crystal; bipyridine co-former is located about a centre of inversion; one Se forms a Se···N interaction with the pyridyl-N atom, first entry, to form a three-molecule aggregate; within this aggregate, there is a supporting Se···N interaction to the second selenium atom, *i.e.* 3.482(3) Å; the other Se interacts with a symmetry related nitrile-N to which it is bonded to form a zigzag chain; the 2-D array has an undulating topology. Layers are connected into a 3-D architecture *via* Se···Se interactions [3.6669(8) Å]}

ESI Table S3. Supramolecular architectures formed by tri-nuclear selenium molecules.

59. IVEDAO 1,3-diadamantyl-1,3-diaza-2,4,5-triselenacyclopentane

T. Maaninen, H. M. Tuononen, G. Schatte, R. Suontamo, J. Valkonen, R. Laitinen and T. Chivers, *Inorg. Chem.*, 2004, **43**, 2097-2104. https://doi.org/10.1021/ic034944b

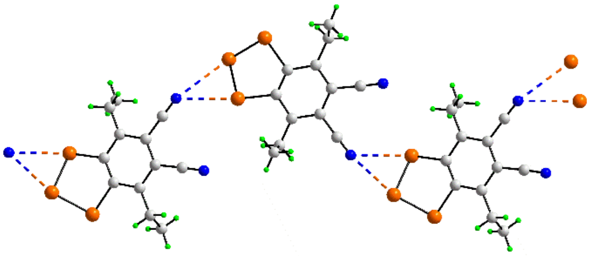


d(Se···N) = 3.166(4) Å; N–Se···N = 166.25(15)°; Se–Se···N = 100.82(8)°; Se–N···Se = 85.45(15) & 97.34(16)°; C–N···Se = 125.2(3)°

{Only one Se of the three Se atoms forms a Se···N interaction; helical chain (2$_1$). The crystal also features Se···Se contacts [2.5425(7) & 2.6340(7) Å] connecting the original chains into a double-chain}

60. SACMUF 5,6-dicyano-4,7-diethylbenzo(1,2,3)triselenole

T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara and T. Akasaka, *J. Org. Chem.*, 2004, **69**, 4716-4723. https://doi.org/10.1021/jo030354j



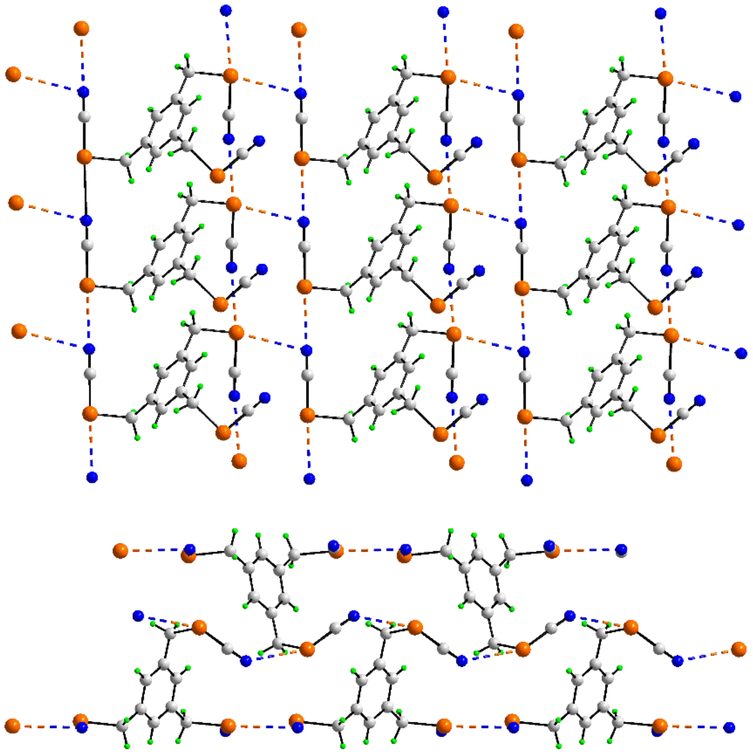
d(Se···N) = 3.119(12) Å; C–Se···N = 165.7(4)°; Se–Se···N = 74.2(3)°; C–N···Se = 128(1)°

d(Se···N) = 3.345(16) Å; Se–Se···N = 142.3(2) & 63.8(3)°; C–N···Se = 153(1)°

{Bay of three Se atoms; 1,2-Se atoms are connected to a bifurcated nitrile-N atom; helical chain}

61. PEYQIW (benzene-1,3,5-triyl)tris(methylene) tris(selenocyanate)

O. Jeannin, H.-T. Huynh, A. M. S. Riel and M. Fourmigué, *New J. Chem.*, 2018, **42**, 10502-10509. https://doi.org/10.1039/C8NJ00554K



d(Se···N) = 3.011(5) Å; (N)C–Se···N = 169.31(19)°; C–Se···N = 79.09(18)°; C–N···Se = 170.1(4)°

d(Se···N) = 3.023(5) Å; (N)C–Se···N = 168.48(19)°; C–Se···N = 79.52(19)°; C–N···Se = 168.6(4)°

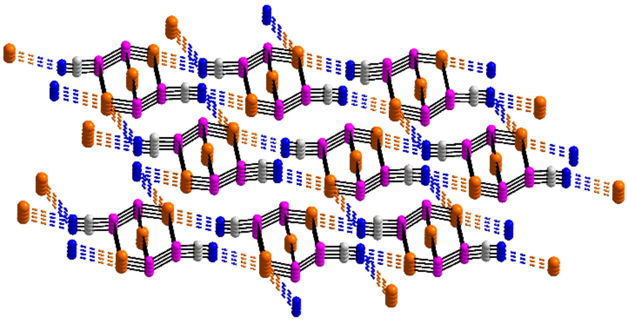
d(Se···N) = 3.379(6) Å; (C)C–Se···N = 171.01(18)°; (N)C–Se···N = 76.3(2)°; C–N···Se = 106.7(4)°

d(Se···N) = 3.243(8) Å; (N)C–Se···N = 156.5(3)°; C–Se···N = 75.1(3)°; C–N···Se = 140.2(7)°

{The molecule lacks symmetry, one Se forms two Se···N(nitrile) interactions, entries 1 & 3, the others two. The upper view shows linked ladders involving two of the Se atoms only; entry 2, with the longest Se···N separation is associated with the stave (entry 3). Indeed, within these ladders, the second set of staves formed by the second Se atom occur at separations greater than the sum of the van der Waals radii, *i.e.* 3.464(5) Å. The layers are linked into a double layer *via* contacts formed by the third Se atom, entry 4. Within the layer of the top view, there are close diagonal Se···Se interactions [3.7612(7) Å] within each ladder}

62. REQQIN exo,exo-α-dicyano-triselenatetraphosphorane

B. W. Tattershall, E. L. Sandham and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1997, 81-88. https://doi.org/10.1039/a604230i



d(Se···N) = 3.378(6) Å; P–Se···N = 163.78(11) & 68.51(10)°; C–Se···Se = 117.2(5)°

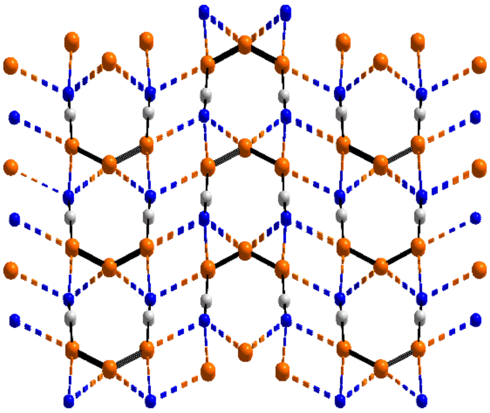
d(Se···N) = 3.310(6) Å; P–Se···N = 158.06(11) & 66.52(10)°; C–Se···Se = 154.5(5)°

d(Se···N) = 3.345(5) Å; P–Se···N = 149.55(10) & 75.64(11)°; C–Se···Se = 135.8(5)°

{Trinuclear molecule with two of three Se atoms forming Se···N(nitrile) interactions, one forms a single contact (entry 1) and the other two, one nitrile is bifurcated (entries 1 and 3), engaging two different molecules, resulting in a 3-D array. Referring to the diagram above, stacks of molecules are also liked by Se···Se contacts [3.6749(9) Å]}

63. **XUNHUL** triselane-1,3-dicarbonitrile

C. J. Burchell, P. Kilian, A. M. Z. Slawin, J. D. Woollins, K. Tersago, C. Van Alsenoy and F. Blockhuys, *Inorg. Chem.*, 2006, **45**, 710-716. https://doi.org/10.1021/ic0515103



d(Se···N) = 3.064(3) Å; Se–Se···N = 169.55(6) & 87.70(6)°; C–Se···N = 132.7(3)°

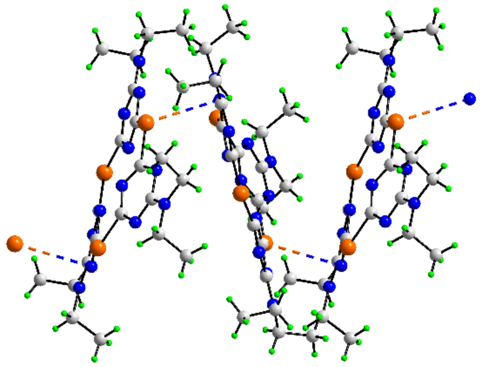
d(Se···N) = 3.029(3) Å; C–Se···N = 173.60(13)°; Se–Se···N = 87.6(6)°; C–N···Se = 113.9(3)°

d(Se···N) = 3.215(3) Å; Se–Se···N = 162.10(5)°; C–Se···N = 72.05(11)°; C–N···Se = 122.1(2)°

{The molecule is disposed about a mirror plane with the central Se lying on the plane. Each Se forms two Se···N(nitrile) contacts and each nitrile-N atom forms three contacts. Entry 1 refers to the Se atom lying on the mirror plane. The result is a 3-D architecture}

64. SAMHIZ N,N,N',N',N'',N''-hexaethyl-2,8,14-triselena-4,6,10,12,16,18,19,20,21-nonaazatetracyclo[13.3.1.13,7.19,13]henicosa-1(19),3(21),4,6,9(20),10,12,15,17-nonaene-5,11,17-triamine acetonitrile solvate

J. Thomas, W. Van Rosson, K. Van Hecke, L. Van Meervelt, M. Smet, W. Maes and W. Dehaen, *Chem. Commun.*, 2012, **48**, 43-45. https://doi.org/10.1039/c1cc15473g

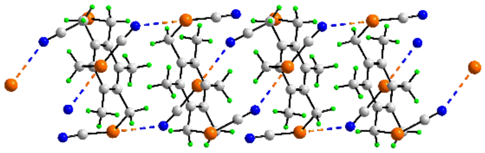


d(Se···N) = 3.441(4) Å; C–Se···N = 84.66(11) & 117.39(11)°; C–Se···N = 73.89(19) & 89.5(2)°

{Trinuclear; one Se atom forms a Se···N(triazine) contact within a helical chain (2_1 screw)}

65. XOBWOD bis(1,3,5-tris(selenocyanatomethyl)-2,4,6-trimethylbenzene) 1,4-dinitrobenzene

A. M. S. Riel, O. Jeannin, O. B. Berryman and M. Fourmigué, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. and Mat.*, 2019, **75**, 34-38. https://doi.org/10.1107/S2052520618017778



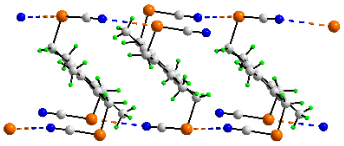
d(Se···N) = 2.989(8) Å; (N)C–Se···N = 175.3(2)°; C–Se···N = 80.41(17)°; Se–N···Se = 154.5(5)°

d(Se···N) = 3.063(4) Å; (N)C–Se···N = 178.8(2)°; C–Se···N = 81.78(16)°; Se–N···Se = 141.0(4)°

{2(Se):1 Co-crystal; the tri-nuclear Se compound has no symmetry but the co-former is situated about an inversion centre. Two of the Se atoms participate in Se···N(nitrile) interactions within a 1-D chain, *cf.* **XOBWIX**. Close Se···O [3.321(6) Å] and Se···Se [3.6444(12) Å] interactions involving the Se atom not forming a Se···N contact link chains into a 2-D array}

66. XOBWIX bis(1,3,5-tris(selenocyanatomethyl)-2,4,6-trimethylbenzene) benzoquinone

A. M. S. Riel, O. Jeannin, O. B. Berryman and M. Fourmigué, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. and Mat.*, 2019, **75**, 34-38. https://doi.org/10.1107/S2052520618017778



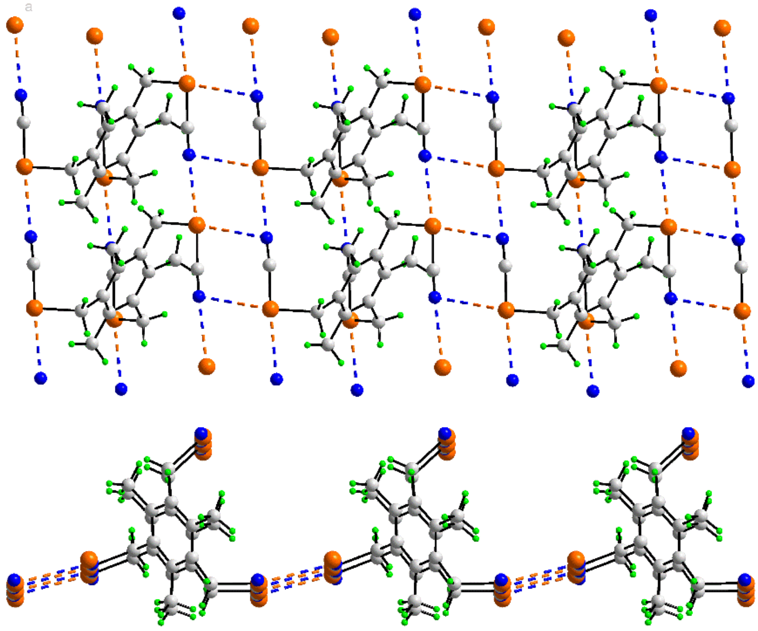
d(Se···N) = 3.192(9) Å; (N)C–Se···N = 174.7(3)°; C–Se···N = 79.7(2)°; Se–N···Se = 142.3(7)°

d(Se···N) = 3.315(6) Å; (N)C–Se···N = 177.1(3)°; C–Se···N = 80.3(2)°; Se–N···Se = 136.6(6)°

{2(Se):1 Co-crystal; the tri-nuclear Se compound has no symmetry but the co-former is situated about an inversion centre. Two of the Se atoms participate in Se···N(nitrile) interactions within a 1-D chain, *cf*. **XOBWOD**. Close Se···O interactions [2.966(6) Å] involving the Se atom not forming a Se···N contact link chains into a 2-D array}

67. PEYQOC (2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene) tris(selenocyanate) N,N-dimethylformamide solvate

O. Jeannin, H.-T. Huynh, A. M. S. Riel and M. Fourmigué, *New J. Chem.*, 2018, **42**, 10502-10509. https://doi.org/10.1039/C8NJ00554K



d(Se···N) = 2.964(3) Å; (N)C–Se···N = 176.10(11)°; C–Se···N = 80.34(10)°; C–N···Se = 179.1(2)°

d(Se···N) = 3.385(3) Å; (C)C–Se···N = 164.24(10)°; C–Se···N = 77.09(11)°; C–N···Se = 105.4(2)°

d(Se···N) = 2.972(3) Å; (N)C–Se···N = 173.82(11)°; C–Se···N = 77.21(11)°; C–N···Se = 176.7(3)°

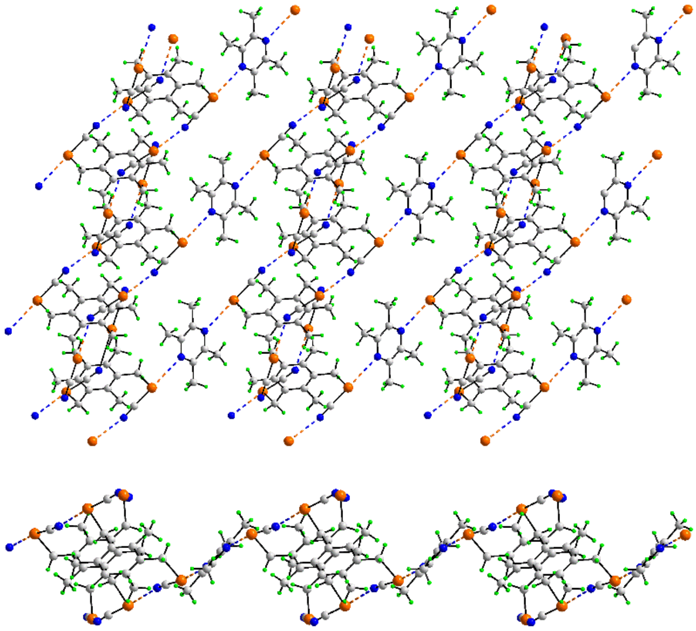
d(Se···N) = 3.318(3) Å; (C)C–Se···N = 172.40(10)°; C–Se···N = 77.74(10)°; C–N···Se = 107.6(2)°

d(Se···N) = 2.960(4) Å; (N)C–Se···N = 175.42(13)°; C–Se···N = 78.40(13)°; C–N···Se = 178.9(3)°

{1:1 (innocent) solvate. The molecule lacks symmetry, two Se atoms form two Se···N(nitrile) interactions, entries 1 & 2 and 3 & 4, the other Se, one. The former lead to linked ladders and a 2-D array with the longest Se···N separations being associated with the staves. The third Se projects to one side of the layer and is associated within a linear chain. The next longest Se···N separation in the crystal of 3.643(3) Å serves to link one ladder so a double-layer is formed. Within the layer of the top view, there are close diagonal Se···Se interactions [3.7452(5) Å] within each ladder}

68. XOBWET bis(1,3,5-tris(selenocyanatomethyl)-2,4,6-trimethylbenzene) tetramethylpyrazine

A. M. S. Riel, O. Jeannin, O. B. Berryman and M. Fourmigué, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. and Mat.*, 2019, **75**, 34-38. https://doi.org/10.1107/S2052520618017778



d(Se···N) = 3.171(5) Å; (N)C–Se···N = 172.64(18)°; C–Se···N = 77.52(13)°; C–N···Se = 115.7(3) & 126.3(3)°

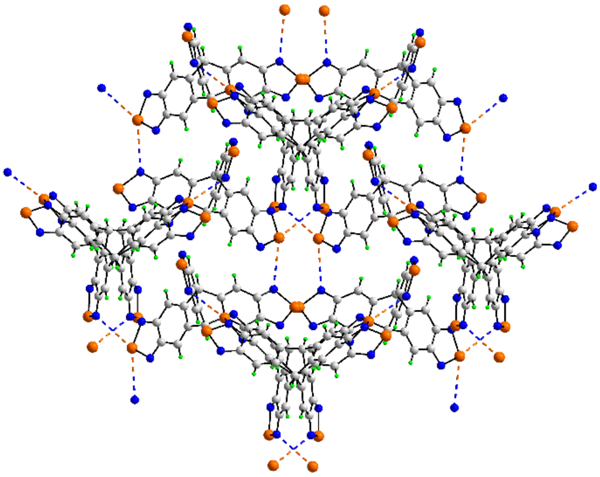
d(Se···N) = 3.029(6) Å; (N)C–Se···N = 175.03(18)°; C–Se···N = 78.56(15)°; C–N···Se = 164.4(4)°

d(Se···N) = 3.096(5) Å; (N)C–Se···N = 178.83(18)°; C–Se···N = 81.48(15)°; C–N···Se = 137.1(4)°

{2:1 Co-crystal; the tri-nuclear Se compound has no symmetry but the co-former is situated about an inversion centre. The tetramethylpyrazine links two molecules, entry 1. The other two independent contacts involve two nitrile-N atoms. Each Se atom forms a single interaction. The result is a jagged 2-D array. Layers are connected into a 3-D architecture via long Se···Se [3.7381(11) Å] interactions}

69. RANPOP triptycenetris(2,1,3-benzoselendiazole) unknown solvate

W. Yang, R. Jiang, C. Liu, B. Yu, X. Cai and H. Wang, *Cryst. Growth Des.*, 2021, **21**, 6497–6503. https://doi.org/10.1021/acs.cgd.1c00942

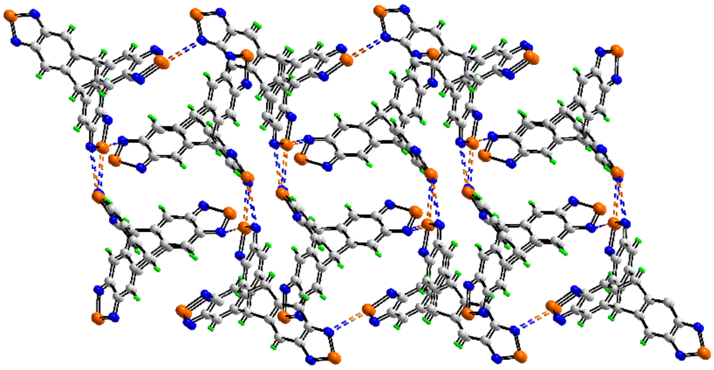


d(Se···N) = 3.328(9) Å; N–Se···N = 157.2(4) & 71.8(4)°; Se–N···Se = 122.2(4)°; C–N···Se = 114.4(6)°

{The molecule has 2-fold symmetry with the interacting Se atom lying on the axis, implying this atom forms two Se···N interactions, one with one N of each symmetry-related residue. A 3-D architecture eventuates}

70. RANPUV bis[triptycenetris(2,1,3-benzoselendiazole)] bis(tetrahydrofuran)

W. Yang, R. Jiang, C. Liu, B. Yu, X. Cai and H. Wang, *Cryst. Growth Des.*, 2021, **21**, 6497–6503. https://doi.org/10.1021/acs.cgd.1c00942



1. d(Se···N) = 3.269(6) Å; N–Se···N = 151.6(2) & 69.1(2)°; Se–N···Se = 97.3(2)°; C–N···Se = 148.1(5)°

2. d(Se···N) = 2.934(7) Å; N–Se···N = 167.9(2) & 78.3(2)°; Se–N···Se = 110.1(3)°; C–N···Se = 127.9(5)°

3. d(Se···N) = 3.237(7) Å; N–Se···N = 172.9(2) & 79.0(2)°; Se–N···Se = 113.4(3)°; C–N···Se = 116.5(5)°

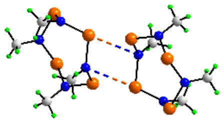
4. d(Se···N) = 3.356(7) Å; N–Se···N = 148.1(3) & 115.7(3)°; Se–N···Se = 92.3(3)°; C–N···Se = 112.7(5)°

{Two independent molecules with different patterns of Se···N interactions. One molecule employs one Se atom of one residue, entry 1, and a N atom of another in forming Se···N interactions, entry 3, respectively. The second molecule employs two Se atoms, one forms two contacts, entries 2 & 3, and the other, one contact, entry 4, and a N atom in forming interactions, *i.e.* from each residue. A non-symmetric {SeN···}$_2$ synthon is formed, *via* entries 1 & 2. The result is a 1-D tubular arrangement which is porous. The THF molecules are incorporated with the pores with the closest Se···O interaction being 3.357(8) Å *cf.* with the sum of the van der Waals radii of 3.42 Å}

ESI Table S4. Supramolecular architectures formed by tetra-nuclear selenium molecules.

71. MUHDEA 2,4,6,8-tetramethyl-1,3,5,7,2,4,6,8-tetraselenatetrazocane

A. J. Karhu, O. J. Pakkanen, J. M. Rautiainen, R. Oilunkaniemi, T. Chivers and R. S. Laitinen, *Inorg. Chem.*, 2015, **54**, 4990-4997. https://doi.org/10.1021/acs.inorgchem.5b00582

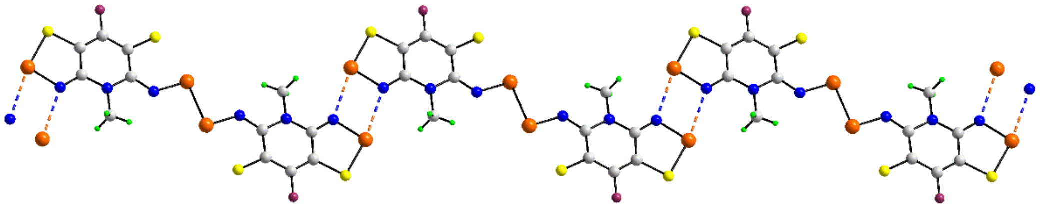


d(Se···N) = 3.225(8) Å; N–Se···N = 174.0(3) & 76.8(3)°; Se–N···Se = 87.4(3) & 103.2(3)°; C–N···Se = 93.8(6)°

{Centrosymmetric dimer; only one of four Se atoms form Se···N interactions; considerably longer Se···N interactions, *i.e.* 3.633(10) & 3.680(10) Å, link molecules into a 2-D array. Also featuring within the dimeric aggregate are Se···Se interactions [3.6290(16) Å] which encompass the {···SeN}$_2$ synthons leading to the dimer}

72. BUQGUQ01 5,5'-(diselane-1,2-diyldinitrilo)bis(7-fluoro-4-methyl-4,5-dihydro-6H-[1,2,3]thiaselenazolo[4,5-b]pyridine-6-thione radical)

K. Lekin, A. A. Leitch, J. S. Tse, X. Bao, R. A. Secco, S. Desgreniers, Y. Ohishi and R. T. Oakley, *Cryst. Growth Des.*, 2012, **12**, 4676-4684. https://doi.org/10.1021/cg3009255

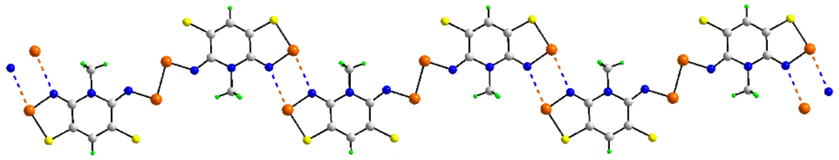


d(Se···N) = 2.85 Å; S–Se···N = 169.2°; N–Se···N = 78.3°; Se–N···Se = 101.7°; C–N···Se = 142.3°

{Standard uncertainties not available. Centrosymmetric molecule. Tape; only the ring-Se atoms form Se···N interactions *via* centrosymmetric {SeN···}$_2$ synthons. Within the chains are close 1,5-Se···S contacts [2.78 Å] between the exocyclic Se atoms as well as transannular Se···Se interactions [3.68 Å]. A 3-D architecture is formed through a number of Se···S interactions involving all Se atoms as well as all S atoms with contact distances of 3.12 and 3.67 Å; the longer separations involve the Se$_2$ units with the ring-S atoms}

73. NEBGUX 1,2-bis(4-methyl-6-thioxo-1,2,3-thiaselenazolo(4,5-b)pyridin-5-ylideneamino)diselenide

L. Beer, J. L. Brusso, R. C. Haddon, M. E. Itkis, H. Kleinke, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson, R. A. Secco and X. Yu, *J. Am. Chem. Soc.*, 2005, **127**, 18159-18170. https://doi.org/10.1021/ja055122b



At r.t.: d(Se···N) = 2.892(5) Å; S–Se···N = 171.07(11)°; N–Se···N = 78.97(18)°; Se–N···Se = 101.03(19)°; C–N···Se = 143.3(4)°

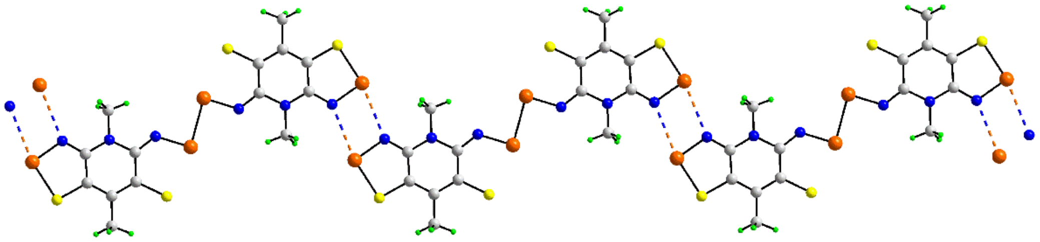
At 1.86 GPa: d(Se···N) = 2.86 Å

At 2.76 GPa: d(Se···N) = 2.70 Å

{Centrosymmetric molecule; flat tape. Within the chains are close 1,5-Se···S contacts [2.785(3) Å] between the exocyclic Se atoms as well as transannular Se···Se interactions [3.702(3) Å]. A 3-D architecture is formed through a number of Se···S interactions involving all Se atoms as well as all S atoms with contact distances of 3.177(2) & 3.633(3) Å; the longer separations involve the atoms of the Se_2 units and the ring-S atoms}

74. BUQHAX 1,2-bis(4,7-dimethyl-6-thioxo-1,2,3-thiaselenazolo(4,5-b)pyridin-2-ylideneamino)diselenide

A. A. Leitch, X. Yu, C. M. Robertson, R. A. Secco, J. S. Tse and R. T. Oakley, *Inorg. Chem.*, 2009, **48**, 9874-9882. https://doi.org/10.1021/ic901563n

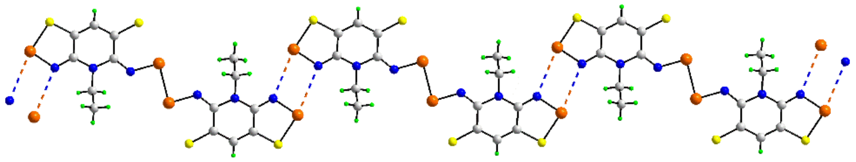


d(Se···N) = 2.98 Å; S–Se···N = 168.4°; N–Se···N = 76.4°; Se–N···Se = 103.6°; C–N···Se = 140.7°

{Centrosymmetric molecule. Tape as above. Within the chains are close 1,5-Se···S contacts [2.78 Å] between the exocyclic Se atoms as well as transannular Se···Se interactions [3.84 Å]. A 3-D architecture is formed through Se···S interactions involving the Se atoms forming the Se···N interactions only with thione-S atoms, with a contact distance of 3.62 Å}

75. XAKGUM 1,2-bis(4-ethyl-6-thioxo-1,2,3-thiaselenazolo(4,5-b)pyridin-2-ylideneamino)diselenide

L. Beer, J. L. Brusso, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed and J. F. Richardson, *Chem. Commun.*, 2005, 1543-1545. https://doi.org/10.1039/B416352D

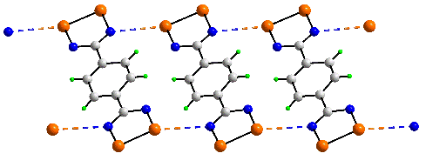


d(Se···N) = 3.239(3) Å; S–Se···N = 165.55(5)°; N–Se···N = 78.25(9)°; Se–N···Se = 101.75(10)°; C–N···Se = 141.76(18)°

{Centrosymmetric, di-nuclear molecule. Flat tape *via* {SeN(ring)···}$_2$ synthons. Within the chains are close 1,5-Se···S contacts [2.7849(9)] between the exocyclic Se atoms. A 3-D architecture is formed through Se···S interactions involving the Se atoms participating in the Se···N contacts and thione-S atoms, with a contact distance of 3.3348(9) Å}

76. VINJOR 1,4-bis(3,4-diselena-2,5-diazacyclopentadienyl)benzene

A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 582-588. https://doi.org/10.1021/ja00002a028



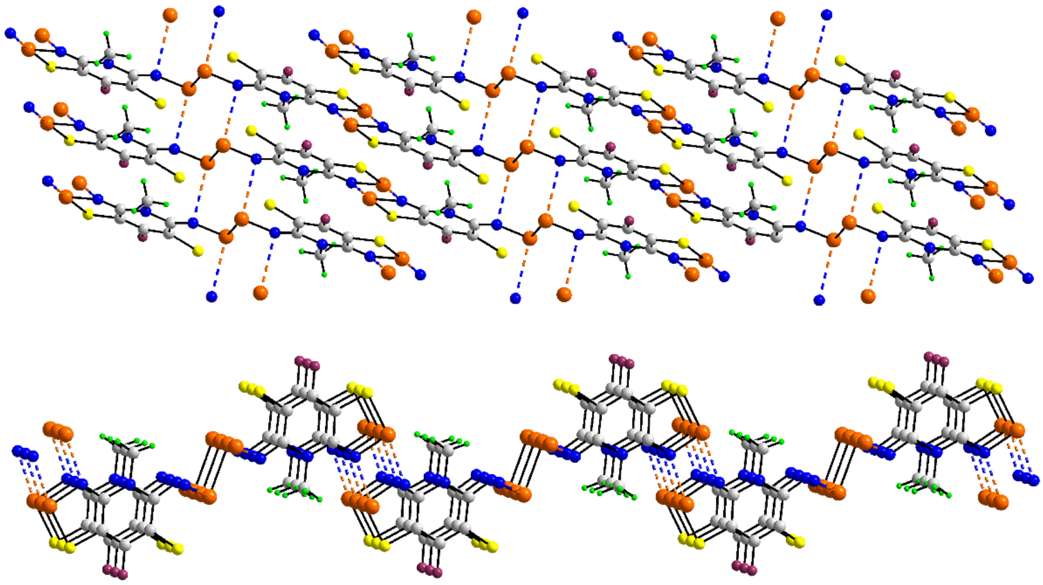
d(Se···N) = 3.43(3) Å; Se–Se···N = 155.6(5)°; N–Se···N = 91.0(9)°; Se–N···Se = 91(1)°; C–N···Se = 145(2)°

d(Se···N) = 3.44(3) Å; Se–Se···N = 152.1(4)°; N–Se···N = 90(1)°; Se–N···Se = 92.5(9)°; C–N···Se = 142(2)°

{Tetra-nuclear molecule. One Se of each ring associates with a translationally related molecule to form a tape. All of the Se atoms (three Se atoms form two contacts and one, three contacts) participate in Se···Se interactions [range: 3.253(6) to 3.792(7) Å] which link chains into a 3-D architecture. High-pressure structure determinations are available with further Se···N interactions: W. Yong, K. Lekin, R. P. C. Bauer, J. S. Tse, S. Desgreniers, R. A. Secco, N. Hirao and R. T. Oakley, *Inorg. Chem.*, 2019, **58**, 3550-3557 https://doi.org/10.1021/acs.inorgchem.9b00142}

77. BUQGUQ03 5,5'-(diselane-1,2-diyldinitrilo)bis(7-fluoro-4-methyl-4,5-dihydro-6H-[1,2,3]thiaselenazolo[4,5-b]pyridine-6-thione radical)

K. Lekin, A. A. Leitch, J. S. Tse, X. Bao, R. A. Secco, S. Desgreniers, Y. Ohishi and R. T. Oakley, *Cryst. Growth Des.*, 2012, **12**, 4676-4684. https://doi.org/10.1021/cg3009255



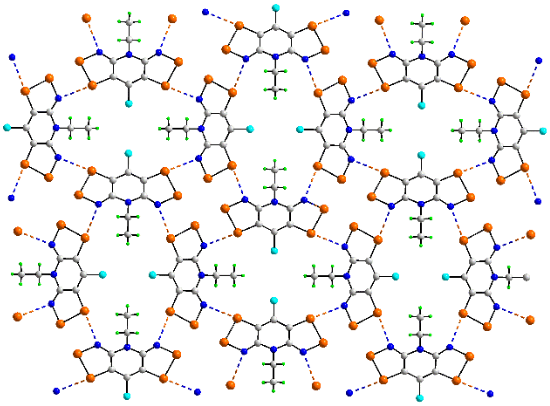
d(Se···N) = 2.45 Å; S–Se···N = 171.3°; N–Se···N = 79.4°; Se–N···Se = 100.6°; C–N···Se = 143.6°

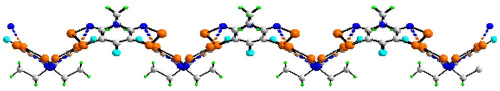
d(Se···N) = 3.03 Å; Se–Se···N = 97.3°; N–Se···N = 93.1°; Se–N···Se = 93.1°; C–N···Se = 91.4°

{Standard uncertainties not available. At 8.40 GPa. Centrosymmetric molecule. Tape as above but with a shorter separation (first entry); tapes are connected into a layer *via* longer Se···N interactions *via* centrosymmetric, six-membered {SeSeN···}$_2$ synthons. Within the chains are close 1,5-Se···S contacts [2.76 Å] between the exocyclic Se atoms as well as transannular Se···Se interactions [3.31 Å]. A 3-D architecture is formed through a number of Se···S interactions involving all Se atoms as well as all S atoms with each forming two contacts. The Se···S distances are 2.90 & 3.57 Å between the Se atom forming the Se···N contact and the thione-S, and 3.21 & 3.37 for those formed between the exocyclic-Se atom and the ring-S}

78. AFUDEL01 8-chloro-4-ethyl-4H-bis((1,2,3)diselenazolo)(4,5-b:5',4'-e)pyridinyl radical

C. M. Robertson, A. A. Leitch, K. Cvrkalj, R. W. Reed, D. J. T. Myles, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2008, **130**, 8414-8425. https://doi.org/10.1021/ja801070d





At 100 K: d(Se···N) = 3.339(7) Å; C–Se···N = 165.5(3)°; Se–Se···N = 97.49(12)°; Se–N···Se = 82.4(2)°; C–N···Se = 123.1(5)°

At r.t.: d(Se···N) = 3.378(5) Å; C–Se···N = 165.7(2)°; Se–Se···N = 97.82(9)°; Se–N···Se = 82.26(17)°; C–N···Se = 123.7(4)°

{Molecule has mirror symmetry bisecting the six-membered ring. Two of four Se atoms and the outer N atoms form Se···N interactions that project laterally to form a jagged 2-D array. One of the Se atoms forming a Se···N contact forms an intramolecular Se···Cl contact of 3.243(2) Å. Intra-layer Se···Se contacts are apparent, *i.e.* 3.4565(10) Å, leading to square Se$_4$ synthons, and 3.5849(11) Å, as well as inter-layer Se···Se contacts: 3.5566(10) and 3.7812(12) Å, within a 3-D architecture}

79. IZOXOL 8-bromo-4-ethyl-4H-bis(1,2,3)diselenazolo(4,5-b:5',4'-e)pyridin-3-yl radical

A. A. Leitch, K. Lekin, S. M. Winter, L. E. Downie, H. Tsuruda, J. S. Tse, M. Mito, S. Desgreniers, P. A. Dube, S. Zhang, Q. Liu, C. Jin, Y. Ohishi and R. T. Oakley, *J. Am. Chem. Soc.*, 2011, **133**, 6051-6060. https://doi.org/10.1021/ja200391j

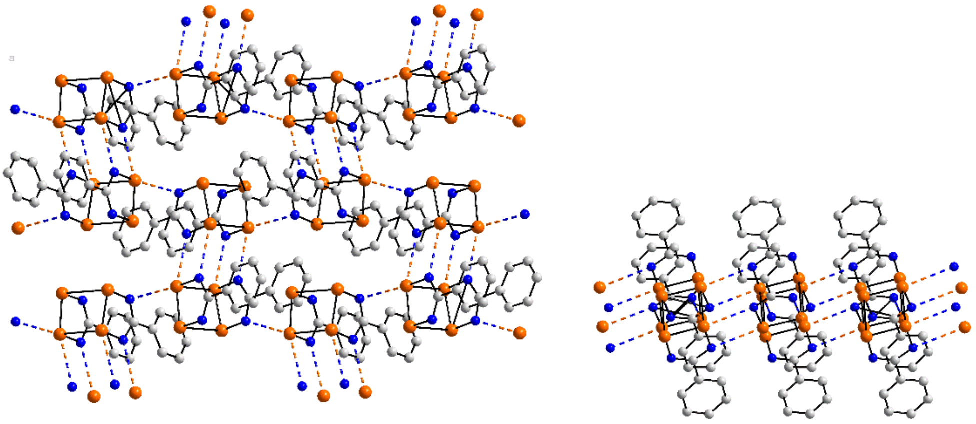
At r.t.: d(Se···N) = 3.397(5) Å; C–Se···N = 165.3(2)°; Se–Se···N = 98.23(9)°; Se–N···Se = 81.67(17)°; C–N···Se = 123.6(4)°

At r.t. and 8.91GPa: d(Se···N) = 2.97 Å; Se···Se come into play

{Isostructural with **AFUDEL01**}

80. JEFBIF 1,1':2,2'-bi(4-phenyl-1,2,3,5-diselenadiazole)

P. Del Bel Belluz, A. W. Cordes, E. M. Kristof, P. V. Kristof, S. W. Liblong and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, **111**, 9276-9278. https://doi.org/10.1021/ja00208a047



d(Se···N) = 3.187(12) Å; Se–Se···N = 163.7(2) & 70.5(2)°; N–Se···N = 83.7(4)°; Se–N···Se = 99.9(5)°; C–N···Se = 139.9(8)°

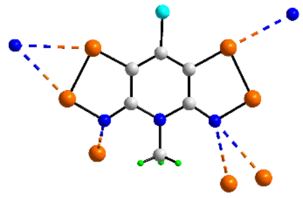
d(Se···N) = 3.301(12) Å; Se–Se···N = 157.5(2) & 110.4(2)°; N–Se···N = 80.1(4)°; Se–N···Se = 96.2(5)°; C–N···Se = 145.0(8)°

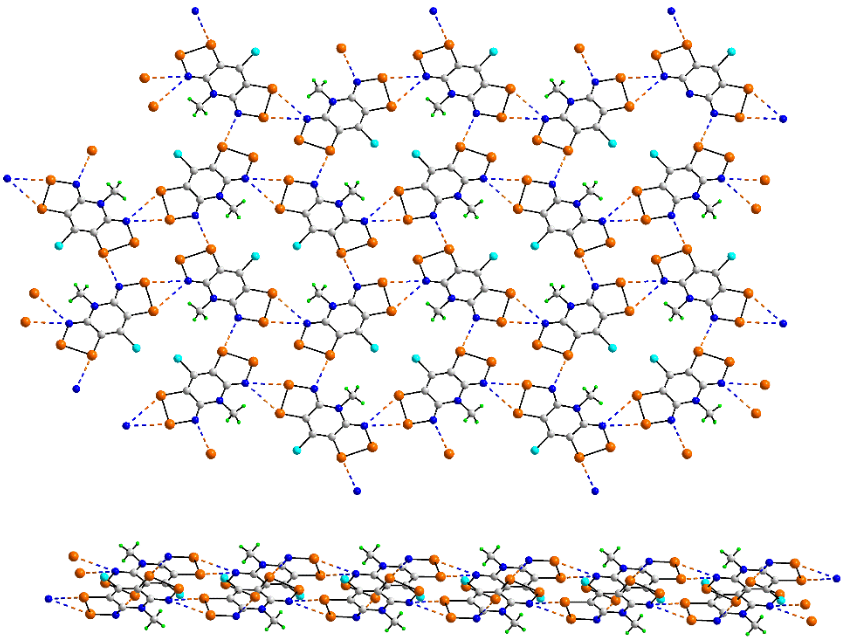
d(Se···N) = 3.091(13) Å; N–Se···N = 167.4(5)°; Se–Se···N = 88.5(2) & 99.6(2)°; Se–N···Se = 99.0(5)°; C–N···Se = 97.2(8)°

{Non-symmetric, U-shaped molecule by virtue of a close Se-Se bond [3.160(2) Å] and supporting Se…Se interaction [3.347(2) Å]. Only two Se of the four Se atoms interact, one of these forms two Se···N interactions (entries one and three); centrosymmetrically-related molecules are connected by four Se···N interactions (first and second entries); these are connected into a 2-D array}

81. **SUQREC** 8-chloro-4-methyl-4H-bis[1,2,3]diselenazolo[4,5-b:5',4'-e]pyridine radical

A. A. Leitch, X. Yu, S. M. Winter, R. A. Secco, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2009, **131**, 7112-7125. https://doi.org/10.1021/ja900853t





d(Se···N) = 3.115(3) Å; N–Se···N = 160.95(11)°; Se–Se···N = 71.62(5)°; Se–N···Se = 79.55(9)°; C–N···Se = 162.2(2)°

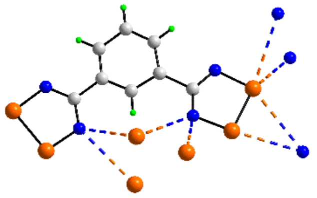
d(Se···N) = 3.264(3) Å; C–Se···N = 149.72(11)°; Se–Se···N = 64.94(5)°; Se–N···Se = 102.77(10)°; C–N···Se = 133.3(2)°

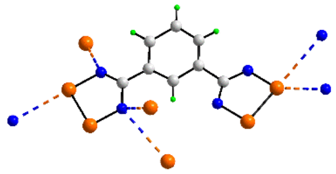
d(Se···N) = 3.026(3) Å; C–Se···N = 178.11(10)°; Se–Se···N = 91.49(6)°; Se–N···Se = 107.01(12)°; C–N···Se = 108.41(19)°

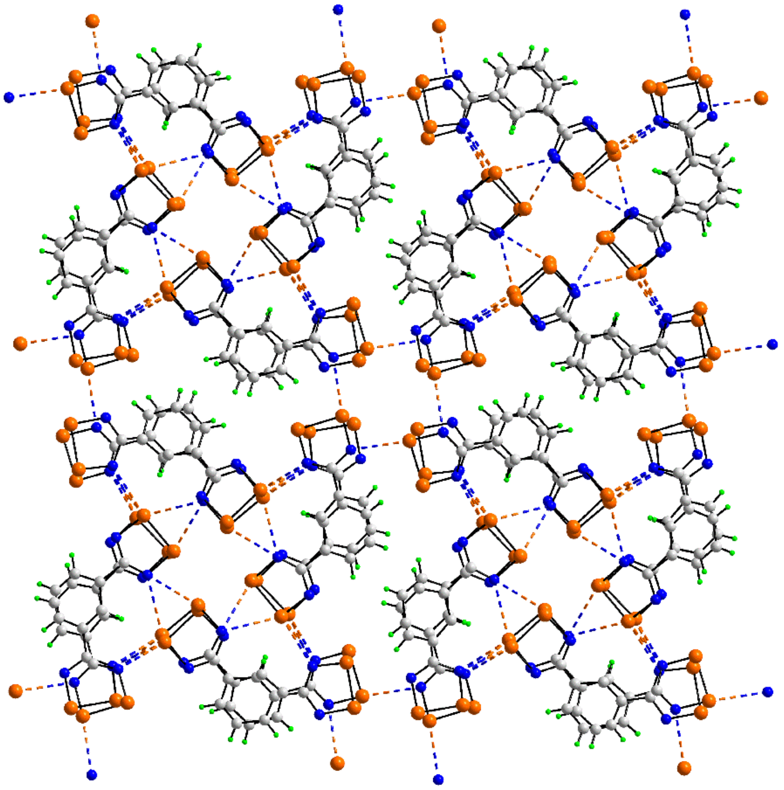
{Non-symmetric, tetra-nuclear molecule. Two Se atoms of one ring are connected to the same ring-N atom, entries 1 & 2. One Se of the second ring forms a single contact, entry 3. The N of the first ring forms a single contact, corresponding to entry 3 while the N of the second ring forms two contacts, corresponding to entries 1 & 2. The result is a flat 2-D array Within the larger cavities, Cl···Cl halogen bonding is evident (3.4029(14) Å *cf.* 3.50 Å for the sum of the van der Waals radii) along with intramolecular Se···Cl contacts [3.1962(11) & 3.2771(10) Å]. Within the layer, Se···Se interactions [3.3133(5) & 3.6999(5) Å], leading to a non-symmetric Se_4 synthon, and transannular Se···Se [3.5087(5) Å] interactions are apparent. Intermolecular Se···Se interactions [3.4488(5) & 3.7460(5) Å], involving Se atoms from both rings, feature within a 3-D architecture}

82. SOBSUX 1,3-phenylene-bis(1,2,3,5-diselenadiazolyl)

M. P. Andrews, A. W. Cordes, D. C. Douglass, R. M. Fleming, S. H. Glarum, R. C. Haddon, P. Marsh, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, G. W. Trucks, R. Tycko, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 3559-3568. https://doi.org/10.1021/ja00009a051







1. d(Se···N) = 3.29(3) Å; N–Se···N = 157(1)°; Se–Se···N = 73.0(5)°; Se–N···Se = 80(1)°; C–N···Se = 148(2)°

2. d(Se···N) = 3.43(3) Å; N–Se···N = 154.0(9)°; Se–Se···N = 66.6(5)°; Se–N···Se = 120(1)°; C–N···Se = 124(2)°

3. d(Se···N) = 3.25(3) Å; Se–Se···N = 152.8(5)°; N–Se···N = 101.0(9)°; Se–N···Se = 116(1)°; C–N···Se = 118(2)°

4. d(Se···N) = 3.37(3) Å; Se–Se···N = 146.0(5)°; N–Se···N = 82.7(9)°; Se–N···Se = 103(1)°; C–N···Se = 134(2)°

5. d(Se···N) = 3.37(3) Å; Se–Se···N = 148.5(5)°; N–Se···N = 102(1)°; Se–N···Se = 102(1)°; C–N···Se = 135(2)°

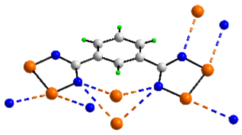
6. d(Se···N) = 3.44(3) Å; Se–Se···N = 133.9(5)°; N–Se···N = 104(1)°; Se–N···Se = 107(1)°; C–N···Se = 110(2)°

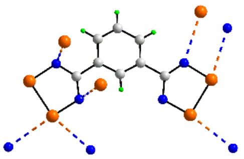
7. d(Se···N) = 3.11(3) Å; N–Se···N = 171(1)°; Se–Se···N = 95.0(5)°; Se–N···Se = 92(1)°; C–N···Se = 141(2)°

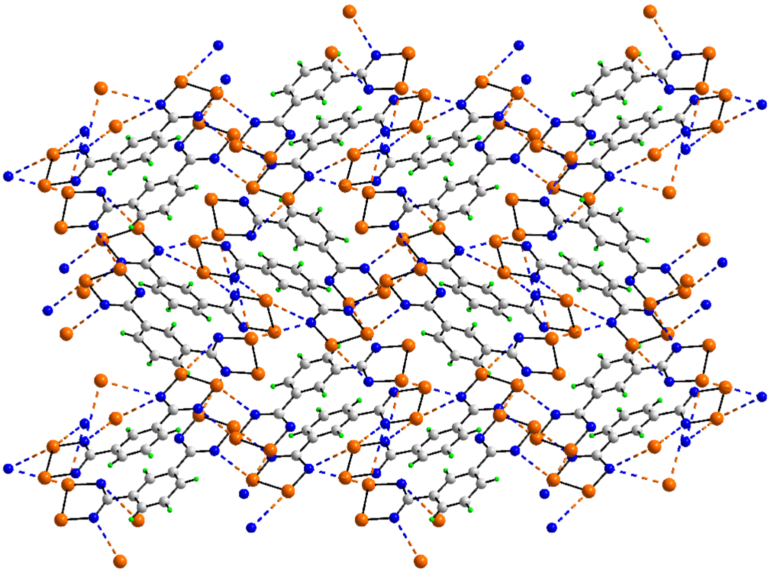
{Polymorph. Two independent tetra-nuclear molecules. For the first independent molecule, two Se atoms of one ring each form contacts, with both linked to a common ring-N atom, entries 1 and 2, with one Se forming two further contacts, entries 3 & 4. One N of each ring forms two Se···N contacts. For the ring with the participating Se atoms, the contacts correspond to entries 1 & 2. For the N atom of the second ring, the contacts correspond to entries 3 and 5. For the second independent molecule, one Se atom of each ring forms contacts. One Se forms two contacts, one corresponding to entry 5 and the other to entry 6. For the second ring, the Se atom forms a single interaction: entry 7. One N forms a single interaction (entry 7) while the other forms two interactions (entries 4 & 6). The result is a 3-D architecture. Extra, Se···Se, contacts are noted between the independent molecules within the square columns, *i.e.* 3.454(5), 3.529(5), 3.663(5) & 3.716(5) Å}

83. SOBSUX01 1,3-phenylene-bis(1,2,3,5-diselenadiazolyl)

A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer and J. V. Waszczak, *J. Am. Chem. Soc.*, 1992, **114**, 1729-1732.
https://doi.org/10.1021/ja00031a028







1. d(Se···N) = 3.432(15) Å; N–Se···N = 170.2(5)°; Se–Se···N = 92.5(2)°; Se–N···Se = 111.6(5)°; C–N···Se = 88(1)°

2. d(Se···N) = 3.025(13) Å; Se–Se···N = 163.9(2)°; N–Se···N = 76.2(4)°; Se–N···Se = 103.4(5)°; C–N···Se = 142(1)°

3. d(Se···N) = 3.153(16) Å; Se–Se···N = 153.4(3)°; N–Se···N = 75.4(5)°; Se–N···Se = 104.6(5)°; C–N···Se = 135(1)°

4. d(Se···N) = 3.353(16) Å; N–Se···N = 157.5(5)°; Se–Se···N = 93.5(3)°; Se–N···Se = 109.8(5)°; C–N···Se = 128(1)°

5. d(Se···N) = 3.024(13) Å; Se–Se···N = 164.1(2)°; N–Se···N = 75.8(4)°; Se–N···Se = 104.5(5)°; C–N···Se = 138(1)°

6. d(Se···N) = 3.239(13) Å; N–Se···N = 155.3(5)°; Se–Se···N = 91.0(3)°; Se–N···Se = 115.5(6)°; C–N···Se = 124(1)°

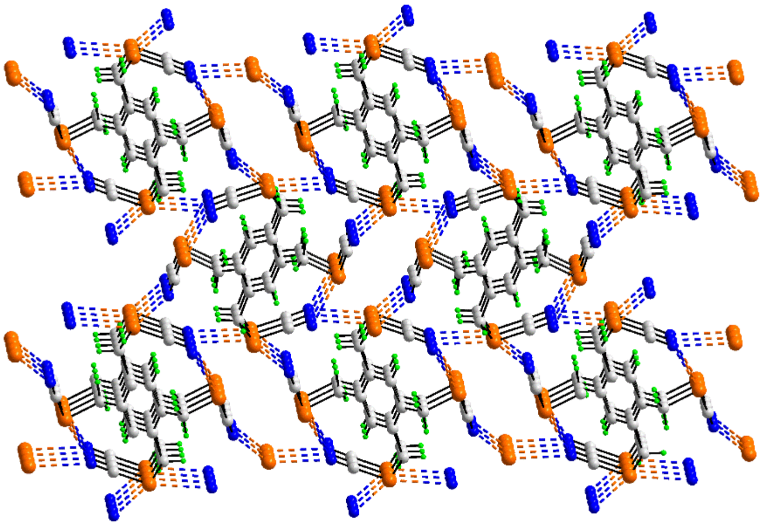
7. d(Se···N) = 3.311(14) Å; Se–Se···N = 145.6(3)°; N–Se···N = 74.2(5)°; Se–N···Se = 111.6(6)°; C–N···Se = 117(1)°

8. d(Se···N) = 3.039(15) Å; N–Se···N = 171.0(6)°; Se–Se···N = 97.1(3)°; Se–N···Se = 103.0(5)°; C–N···Se = 95(1)°

{Polymorph. Two independent tetra-nuclear molecules. For the first independent molecule, two Se atoms of one ring each form a contact, entries 1 and 2. One Se of the second ring forms two Se···N contacts, entries 3 and 4. For the first ring, one N forms a single interaction to complete a non-symmetric {···SeN}$_2$ synthon, entry 5. The second N links to two Se atoms, entries 4 & 6. One N only of the second ring forms two interactions: entry 3, to form a centrosymmetric {···SeN}$_2$ synthon, and entry 7. For the second independent molecule, the Se atoms of one ring each forms a single interaction. One interaction corresponds to entry 8. The second interaction along with a contact involving the adjacent N atoms completes the non-symmetric {···SeN}$_2$ synthon *via* entries 2 & 5. Only one Se of the second ring forms Se···N interaction, *i.e.* entries 6 & 7. Each of the N atoms of this second ring forms a single contact, *i.e.* entries 1 & 8. 3-D array. Extra, Se···Se, contacts are noted between the independent molecules aligned face-to-face, *i.e.* 3.125(3) & 3.411(3) Å and 3.196(3) & 3.203(3) Å, and longer lateral contacts: 3.780(3) Å}

84. PEYRET (benzene-1,2,4,5-tetrayl)tetrakis(methylene) tetrakis(selenocyanate)

O. Jeannin, H.-T. Huynh, A. M. S. Riel and M. Fourmigué, *New J. Chem.*, 2018, **42**, 10502-10509. https://doi.org/10.1039/C8NJ00554K



d(Se···N) = 3.085(5) Å; (N)C–Se···N = 164.0(2)°; C–Se···N = 79.3(2)°; C–N···Se = 155.6(4)°

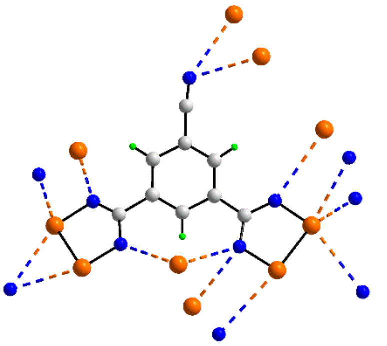
d(Se···N) = 3.302(7) Å; (C)C–Se···N = 167.6(2)°; C–Se···N = 72.5(2)°; C–N···Se = 159.6(6)°

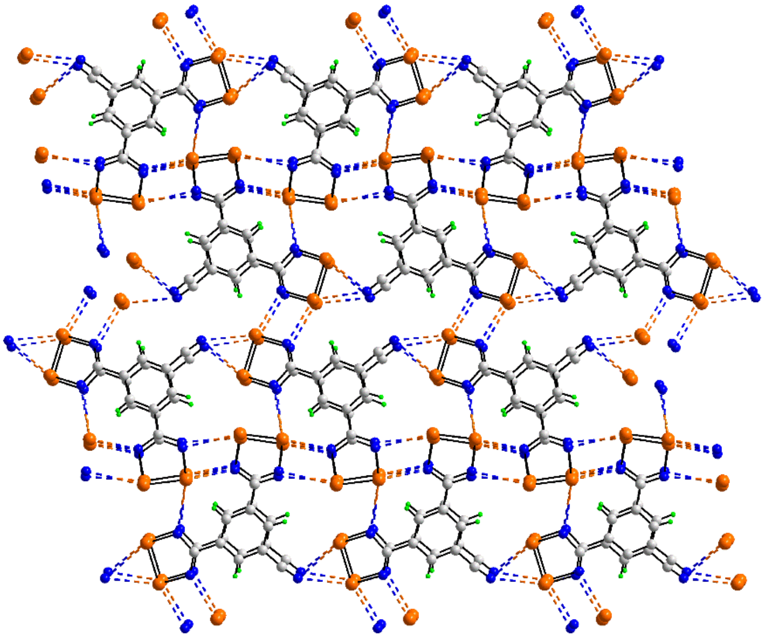
d(Se···N) = 3.370(6) Å; (N)C–Se···N = 170.0(3)°; C–Se···N = 79.41(17)°; C–N···Se = 124.8(4)°

{Centrosymmetric molecule. One independent Se atom forms two Se···N(nitrile) interactions, entries 1 & 2, and the other Se, one (entry 3). One independent nitrile forms one contact and the other two. The result is a 3-D array. The closest Se···Se contact is 3.9985(11) Å}

85. YAXWAV 3,5-bis(4,5-diselenaimidazol-2-yl)-benzonitrile

A. W. Cordes, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, S. R. Scott and J. V. Waszczak, *Chem. Mater.*, 1993, **5**, 820-825. https://doi.org/10.1021/cm00030a017





1: d(Se···N) = 3.055(14) Å; N–Se···N = 157.3(5)°; Se–Se···N = 69.3(3)°; C–N···Se = 152(1)°

2: d(Se···N) = 3.116(15) Å; N–Se···N = 155.2(5)°; Se–Se···N = 66.5(3)°; C–N···Se = 109(1)°

3: d(Se···N) = 3.104(15) Å; Se–Se···N = 150.2(2)°; N–Se···N = 88.2(5)°; Se–N···Se = 99.2(5)°; C–N···Se = 132.3(9)°

4: d(Se···N) = 3.406(13) Å; Se–Se···N = 158.0(2)°; N–Se···N = 79.2(5)°; Se–N···Se = 89.0(5)°; C–N···Se = 148.5(9)°

5: d(Se···N) = 3.108(12) Å; Se–Se···N = 151.1(2)°; N–Se···N = 92.0(5)°; Se–N···Se = 113.2(6)°; C–N···Se = 123.2(9)°

6: d(Se···N) = 3.243(16) Å; N–Se···N = 162.0(6)°; Se–Se···N = 75.6(2)°; Se–N···Se = 117.1(6)°; C–N···Se = 126(1)°

7: d(Se···N) = 3.300(13) Å; N–Se···N = 157.3(5)°; Se–Se···N = 75.5(2)°; Se–N···Se = 115.1(5)°; C–N···Se = 128.5(9)°

8: d(Se···N) = 3.444(12) Å; Se–Se···N = 140.0(2)°; N–Se···N = 91.4(5)°; Se–N···Se = 112.9(6)°; C–N···Se = 120(1)°

9: d(Se···N) = 2.877(12) Å; Se–Se···N = 163.5(3)°; N–Se···N = 77.7(5)°; Se–N···Se = 103.0(5)°; C–N···Se = 140.3(9)°

10: d(Se···N) = 2.902(14) Å; Se–Se···N = 161.7(3)°; N–Se···N = 76.7(4)°; Se–N···Se = 102.7(5)°; C–N···Se = 139(1)°

11: d(Se···N) = 3.107(15) Å; N–Se···N = 155.0(5)°; Se–Se···N = 68.9(3)°; C–N···Se = 110(1)°

12: d(Se···N) = 3.137(15) Å; N–Se···N = 152.2(4)°; Se–Se···N = 67.5(3)°; C–N···Se = 152(1)°

13: d(Se···N) = 3.355(15) Å; Se–Se···N = 144.4(2)°; N–Se···N = 74.4(5)°; Se–N···Se = 103.5(5)°; C–Se···Se = 124(1)°

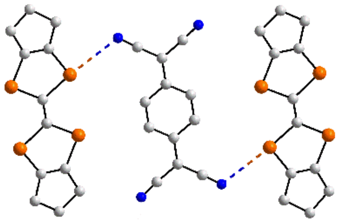
14: d(Se···N) = 3.394(13) Å; Se–Se···N = 151.9(2)°; N–Se···N = 73.8(5)°; Se–N···Se = 100.6(5)°; C–Se···Se = 140.3(9)°

{Two independent molecules with each forming a similar pattern of Se···N interactions. 14 independent contacts. Se···N contacts leading to self-association between molecules: the nitrile-N bridges two Se of one ring, entries 1 and 2, and molecules assemble into a supramolecular tape *via* {SeN···}$_2$ synthons, entries 3 and 4. Contacts between the independent molecules: ring-N atoms of two rings are bridged by a Se atom, entries 5 and 6, and one of the Se atoms participating in the formation of the tape, bridges two ring-N atoms, entries 7 and 8. The independent molecules also associate through a non-symmetric {SeN···}$_2$ synthon, entries 9 and 10. The equivalent interactions involving the second independent molecule only correspond to entries 11 and 12 [Se···N(nitrile)], and 13 and 14 (leading to tapes). In this scheme, for each molecule, two Se atoms form a single interaction, one forms two interactions and the fourth Se atom forms three interactions. Result: 3-D array. Additonal Se…Se contacts are present within the architecture such as transannular interactions within {SeN···}$_2$ synthons

[3.726(2) Å], supporting Se···N interactions: 3.534(3), 3.771(3) & 3.790(3) Å as well as face-to-face contacts between the rings: 3.170(4) & 3.284(4) Å and 3.227(4) & 3.259(4) Å}

86. BOWSUB bis(hexamethylenetetraselenafulvalene) 7,7,8,8-tetracyanoquinodimethane

T. J. Emge, W. A. Bryden, D. O. Cowan and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, 1982, **90**, 173-184. https://doi.org/10.1080/00268948208076180

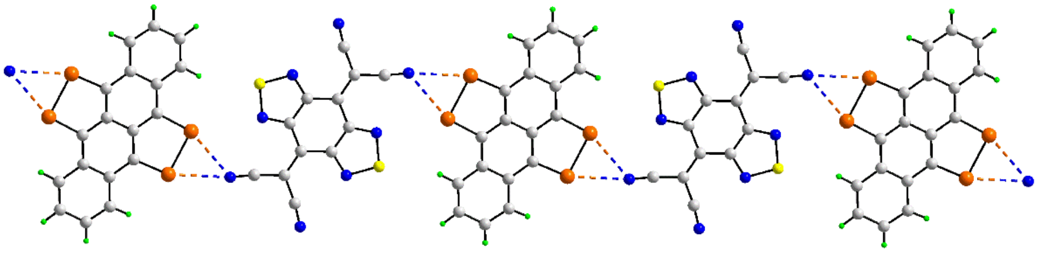


d(Se···N) = 3.29 Å; C–Se···N = 163.5 & 86.6°; C–N···Se = 113.3°

{2:1 co-crystal. Standard uncertainties not available. The tetracyano-4-quinodimethane molecule is centrosymmetric; one Se from each Se-co-former and two N atoms from tetracyano-4-quinodimethane form Se···N interactions to generate a three-molecule aggregate. A 2-D array features Se···Se interactions 3.6382(7) Å involving Se atoms not forming Se···N interactions}

87. PEFGUC01 naphthaceno(5,6-cd:11,12-c'd')-bis(1,2)diselenole 4,8-bis(di-cyanomethylene)-4H,8H-benzo(1,2-c:4,5-c')-bis(1,2,5)thiadiazole

K. Iwasaki, A. Ugawa, A. Kawamoto, Y. Yamashita, K. Yakushi, T. Suzuki and T. Miyashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 3350-3357. https://doi.org/10.1246/bcsj.65.3350



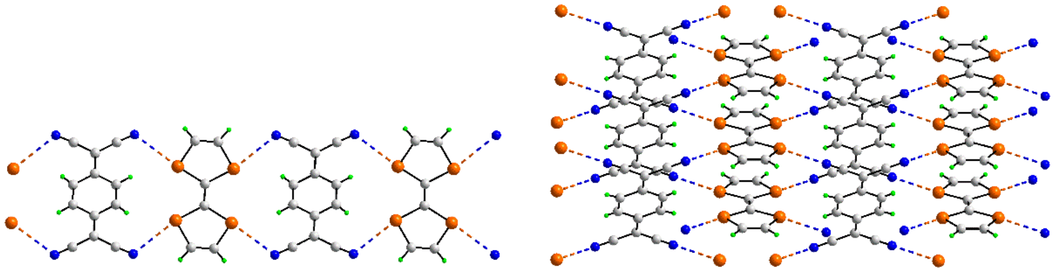
d(Se···N) = 3.084(3) Å; C–Se···N = 160.51(12)°; Se–Se···N = 68.32(6)°; C–N···Se = 164.7(3)°

d(Se···N) = 3.098(3) Å; C–Se···N = 158.57(13)°; Se–Se···N = 67.69(7)°; C–N···Se = 124.2(3)°

{1:1 co-crystal with each co-former disposed about a centre of inversion. The nitrile-N atoms of one nitrile is bifurcated, forming two Se···N(nitrile) interactions to Se to result in a linear chain. An intra-chain Se···N(ring) interaction of 3.578(3) Å is also apparent. A 2-D array features Se···Se interactions 3.6450(5) Å involving both Se atoms}

88. ZUGRUO 2,2',5,5'-tetraselenafulvalene 7,7,8,8-tetracyano-p-quinodimethane

P. W. R. Corfield and S. J. La Placa, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1996, **52**, 384-387.
https://doi.org/10.1107/S0108768195012286



d(Se···N) = 3.165(3) Å; C–Se···N = 169.54(8) & 77.59(12)°; N–Se···N = 122.1(2)°

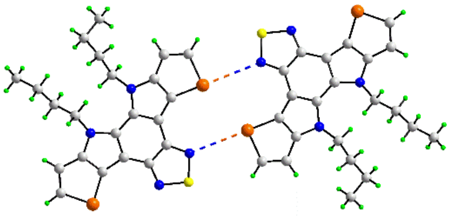
d(Se···N) = 3.177(3) Å; C–Se···N = 175.00(9) & 82.35(13)°; N–Se···N = 122.4(2)°

{1:1 Co-crystal with each co-former being centrosymmetric. Each Se and N atom forms a single contact to generate a 2-D array with a flat topology}

ESI Table S5. Supramolecular architectures formed by congeners of **1**-**88**.

4. VEHVIQ 10,11-dibutyl-10,11-dihydroselenopheno[3,2-b]selenopheno-[2',3':4,5]pyrrolo-[3,2-g][1,2,5]thiadiazolo[3,4-e]indole

S. Ghosh, S. Das, N. R. Kumar, A. R. Agrawal and S. S. Zade, *New J. Chem.*, 2017, **41**, 11568-11575. https://doi.org/10.1039/C7NJ02394D



d(Se···N) = 3.433(3) Å; C–Se···N = 171.64(12) & 92.96(12)°; S–Se···N = 113.59(11)°; C–N···Se = 138.6(2)°

{Two-molecule aggregate constructed about a 10-membered $\{SeC_3N\cdots\}_2$ synthon and generated by 2-fold symmetry. A close transannular Se···Se contact of 3.4771(5) Å is noted}

Monoclinic, *C*2/*c*: *a* = 24.223(1), *b* = 7.881(<1), *c* = 25.416(1) Å, β = 120.28(<1)°, *V* = 4189.9 Å^3, *Z′* = 1; T = 100 K

4S. VEHVOW 10,11-dibutyl-10,11-dihydro[1,2,5]thiadiazolo[3,4-e]thieno[3,2-b]thieno[2',3':4,5]pyrrolo[3,2-g]indole

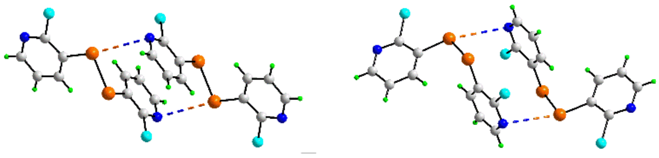
S. Ghosh, S. Das, N. R. Kumar, A. R. Agrawal and S. S. Zade, *New J. Chem.*, 2017, **41**, 11568-11575. https://doi.org/10.1039/C7NJ02394D

Monoclinic, *C*2/*c*: *a* = 20.674(<1), *b* = 14.342(<1), *c* = 16.341(<1) Å, β = 111.55(<1)°, *V* = 4506.7 Å^3, *Z′* = 1; T = room temp.

{No comparable supramolecular contact; no S···N contacts less than the sum of the van der Waals radii (3.35 Å). The closest intermolecular contact (3.67 Å) leads to a centrosymmetric dimer}

5. DIHHEI bis(2-chloro-3-pyridyl)diselenide

K. K. Bhasin, N. Singh, S. Doomra, E. Arora, G. Ram, S. Singh, Y. Nagpal, S. K. Mehta and T. M. Klapötke, *Bioinorg. Chem. Appl.*, 2007, 69263. https://doi.org/10.1155/2007/69263



d(Se···N) = 3.378(7) Å; C–Se···N = 163.4(3)°; Se–Se···N = 83.53(14)°; Cl(C)–N···Se = 100.4(5)°; C–N···Se = 99.5(6)° {left-hand image}

d(Se···N) = 3.413(8) Å; C–Se···N = 154.8(3)°; Se–Se···N = 86.11(14)°; Cl(C)–N···Se = 108.2(6)°; C–N···Se = 91.4(6)°

d(Se···N) = 3.451(7) Å; C–Se···N = 161.5(3)°; Se–Se···N = 79.61(13)°; Cl(C)–N···Se = 103.8(6)°; C–N···Se = 100.7(5)°

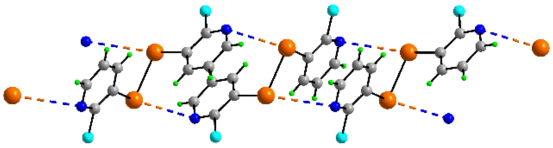
{Three independent molecules. One self-associates about a centre of inversion to form a two-molecule aggregate (first entry). The remaining molecules are also connected into a dimer with one of the Se···N interactions marginally longer than the cut-off distance criterion. For the centrosymmetric dimer, close intramolecular 1,4-Se···Cl contacts are noted: 3.117(3) & 3.140(2) Å; second dimer: 3.125(3) & 3.151(3) Å and 3.109(3) & 3.150(3) Å}

Monoclinic, $P2_1/c$: *a* = 11.390(2), *b* = 27.851(5), *c* = 11.849(2) Å, β = 112.98(<1)°, *V* = 3460.4 Å^3, *Z′* = 3; T = 93 K

5Te. DIHHAE bis(2-chloro-3-pyridyl)ditelluride

K. K. Bhasin, N. Singh, S. Doomra, E. Arora, G. Ram, S. Singh, Y. Nagpal, S. K. Mehta and T. M. Klapötke, *Bioinorg. Chem. Appl.*, 2007, 69263. https://doi.org/10.1155/2007/69263

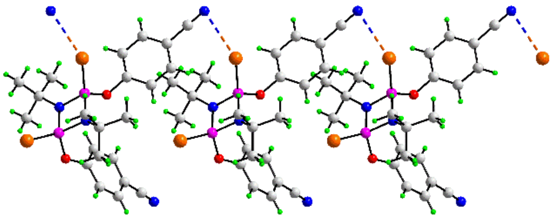
Monoclinic, $C2/c$: *a* = 11.611(1), *b* = 9.781(1), *c* = 12.076(1) Å, β = 113.717(2)°, *V* = 1255.7 Å^3, *Z′* = 0.5; T = 93 K



{The molecule has 2-fold symmetry and each Te atom forms a Te···N contact just beyond the sum of the van der Waals radii (3.62 cf. 3.61 Å) to form a twisted ribbon}

9. BULQIK 4,4'-((1,3-di-t-butyl-2,4-diselenido-1,3,2,4-diazadiphosphetidine-2,4-diyl)bis(oxy))dibenzonitrile

Y. X. Shi, R. Z. Liang, K. A. Martin, N. Weston, S. Gonzalez-Calera, R. Ganguly, Y. Li, Y. Lu, A. J. M. Ribeiro, M. J. Ramos, P. A. Fernandes and F. Garcia, *Inorg. Chem.*, 2015, **54**, 6423-6432. https://doi.org/10.1021/acs.inorgchem.5b00735



d(Se···N) = 3.365(3) Å; P–Se···N = 153.87(5)°; C–N···Se = 83.6(2)°

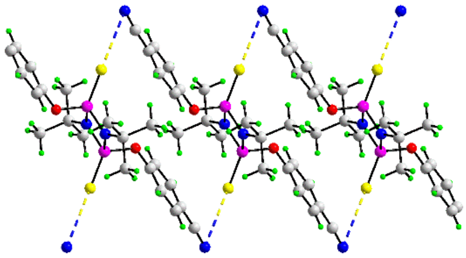
{Linear chain; only one of the selenide-Se atoms forms Se···N interactions. Intra-chain 1,3-Se···O contacts are noted, involving both Se atoms, with the Se atom forming the shorter of the Se···N contacts, forming the longer Se···S contact, 3.0912(17) *cf.* 2.9544(17) Å}

Monoclinic, $P2_1/c$: a = 17.315(<1), b = 16.567(<1), c = 9.006(<1) Å, β = 99.05(<1)°, V = 2551.4 Å^3, Z' = 1; T = 103 K

9S. BULQUW 4,4'-((1,3-di-t-butyl-2,4-disulfido-1,3,2,4-diazadiphosphetidine-2,4-diyl)bis(oxy))dibenzonitrile

Y. X. Shi, R. Z. Liang, K. A. Martin, N. Weston, S. Gonzalez-Calera, R. Ganguly, Y. Li, Y. Lu, A. J. M. Ribeiro, M. J. Ramos, P. A. Fernandes and F. Garcia, *Inorg. Chem.*, 2015, **54**, 6423-6432. https://doi.org/10.1021/acs.inorgchem.5b00735

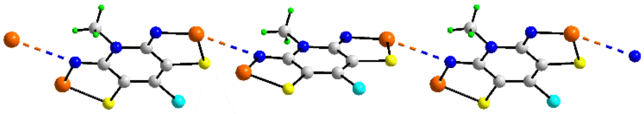
Triclinic, $P\bar{1}$: a = 8.660(3), b = 8.684(3), c = 17.225(5) Å, α = 88.33(1), β = 89.43(1), γ = 70.35(1)°, V = 1219.4 Å^3, Z' = 1; T = 103 K



{Two independent half molecules in the asymmetric-unit. No comparable supramolecular contact; no S···N contacts less than the sum of the van der Waals radii (3.35 Å). The closest intermolecular S···N contacts are 3.42 & 3.51 Å whereby each independent molecule self-associates into a linear chain; the chain sustained by the longer interaction is illustrated}

10. SUQQUR 8-chloro-4-methyl-4H-bis[1,2,3]thiaselenazolo[4,5-b:5',4'-e]pyridine radical

A. A. Leitch, X. Yu, S. M. Winter, R. A. Secco, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2009, **131**, 7112-7125. https://doi.org/10.1021/ja900853t



d(Se···N) = 3.001(5) Å; N–Se···N = 162.61(19)°; S–Se···N = 74.82(12)°; Se–N···Se = 81.28(18)°; C–N···Se = 162.6(4)°

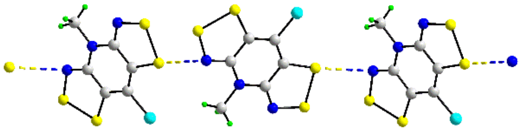
{One of the two Se atoms associates *via* a Se···N interaction within a zigzag chain (glide). Weak Se···S interactions, *i.e.* 3.687(2) Å, involving the second Se atom connect chains into a 2-D array}

Monoclinic, $P2_1/n$: a = 4.157(<1), b = 14.004(1), c = 16.489(1) Å, β = 94.34(<1)°, V = 957.0 Å^3, Z' = 1; T = room temp.

10S. MOSTIX01 8-chloro-4-methyl-4H-bis((1,2,3)dithiazolo)(4,5-b:5',4'-e)pyridin-3-yl radical

L. Beer, J. L. Brusso, A. W. Cordes, R. C. Haddon, M. E. Itkis, K. Kirschbaum, R. T. Oakley, D. S. MacGregor, A. A. Pinkerton and R. W. Reed, *J. Am. Chem. Soc.*, 2002, **124**, 9498-9509. https://doi.org/10.1021/ja026118s

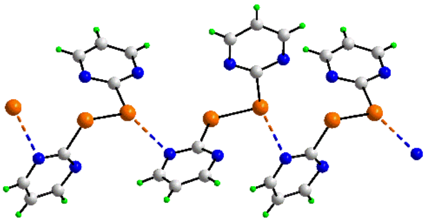
Orthorhombic, $P2_12_12_1$: a = 4.246(1), b = 15.194(5), c = 15.069(4) Å, V = 972.3 Å^3, Z' = 1; T = room temp.



{A similar pattern of supramolecular aggregation is found with d(S···N) = 3.17 Å but with the supramolecular chain being propagated by 2_1-screw symmetry}

12. SEDZEI 2,2'-diselane-1,2-diyldipyrimidine

A. S. Hodage, C. P. Prabhu, P. P. Phadnis, A. Wadawale, K. I. Priyadarsini and V. K. Jain, *J. Organomet. Chem.*, 2012, **720**, 19-25 https://doi.org/10.1016/j.jorganchem.2012.08.035



d(Se···N) = 3.349(14) Å; C–Se···N = 163.7(5)°; Se–Se···N = 90.0(2)°; C–N···Se = 120(1) & 126(1)°

{Dinuclear; one Se atom forms a Se···N(pyrimidyl) contact within a zigzag chain; two intramolecular Se···N contacts are noted 3.325(12) & 3.349(13) Å with the interacting and non-interacting Se atoms, respectively}

Tetragonal, $P\bar{4}2_1c$: a = 13.710(3), c = 10.929(3) Å, V = 2054.3 Å^3, Z' = 1; T = room temp.

12S. PYMSUL11 2,2'-disulfanediyldipyrimidine

G. K. Batsala, V. Dokorou, N. Kourkoumelis, M. J. Manos, A. J. Tasiopoulos, T. Mavromoustakos, M. Simčič, S. Golič-Grdadoinik and S. K. Hadjikakou, *Inorg. Chim. Acta*, 2012, **382**, 146-157 https://doi.org/10.1016/j.ica.2011.10.024

Tetragonal, $P\bar{4}2_1c$: a = 13.334(<1), c = 10.809(<1) Å, V = 1921.7 Å^3, Z' = 1; T = room temp.

{Similar chain with d(S···N) = 3.31 Å}

12S. PYMSUL12 2,2'-disulfanediyldipyrimidine

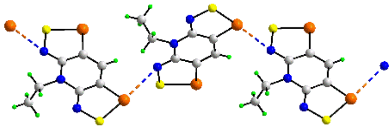
G. J. Corban, C. D. Antoniadis, S. K. Hadjikakou, N. Kourkoumelis, V. Yu. Tyurin, A. Dolgano, E. R. Milaeva, M. Kubicki, P. V. Bernhardt, E. R. T. Tiekink, S. Skoulika and N. Hadjiliadis, *Heteroat. Chem.*, 2012, **23**, 498-511 https://doi.org/10.1002/hc.21042

Triclinic, $P\bar{1}$: a = 7.040(<1), b = 9.671(<1), c = 15.005(1) Å, α = 86.43(<1), β = 81.15(<1), γ = 79.99(<1)°, V = 993.4 Å^3, Z' = 2; T = room temp.

{No comparable supramolecular association. One of the independent molecules self-associates over a centre of inversion but with d(S···N) = 3.40 Å}

13. HIGQOE 4-ethyl-4H-di((1,2,3)selenathiazolo)(4,5-b:5',4'-e)pyrid-3-yl radical

A. A. Leitch, J. L. Brusso, K. Cvrkalj, R. W. Reed, C. M. Robertson, P. A. Dube and R. T. Oakley, *Chem. Commun.*, 2007, 3368-3370. https://doi.org/10.1039/b708756j



d(Se···N) = 3.405(3) Å; S–Se···N = 174.46(6)°; C–Se···N = 87.84(10)°; S–N···Se = 95.35(12)°; C–N···Se = 122.75(19)°

{Only one Se atom forms a Se···N interaction; zigzag chain (glide symmetry). Additional interactions: Se···Se contacts of 3.5833(6) Å, involving the Se forming the close Se···N interaction connect chains into a 2-D array, within which are supporting Se···S contacts of 3.6565(11) Å}

Monoclinic, $P2_1/c$: a = 4.980(<1), b = 14.935(<1), c = 13.824(<1) Å, β = 99.94(<1)°, V = 1012.8 Å^3, Z' = 1; T = room temp.

13S. ENABIE 4-ethyl-4H-bis(1,2,3)dithiazolo(4,5-b:5',4'-e)pyrid-3-yl radical

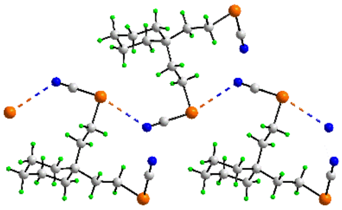
L. Beer, J. F. Britten, J. L. Brusso, A. W. Cordes, R. C. Haddon, M. E. Itkis, D. S. MacGregor, R. T. Oakley, R. W. Reed and C. M. Robertson, *J. Am. Chem. Soc.*, 2003, **125**, 14394-14403. https://doi.org/10.1021/ja0371350

Monoclinic, $P2_1/c$: a = 4.913(1), b = 14.764(5), c = 13.671(5) Å, β = 98.13(<1)°, V = 981.6 Å^3, Z' = 1; T = room temp.

{A supramolecular zigzag chain is formed but with d(S···N) = 3.47 Å}

14. GOHMEW 1,1-bis(selenocyanatoethyl)cyclohexane

D. B. Werz, F. R. Fischer, S. C. Kornmayer, F. Rominger and R. Gleiter, *J. Org. Chem.*, 2008, **73**, 8021-8029. https://doi.org/10.1021/jo801378p



d(Se···N) = 3.199(2) Å; (N)C–Se···N = 145.69(8)°; C–Se···N = 76.77(8)°; C–N···Se = 126.28(17)°

{Only one Se atoms forms a Se···N interaction; helical chain (2_1). Additional but long Se···N contacts of 3.558(3) Å connect chains into a double-chain}

Monoclinic, $P2_1/c$: a = 11.646(1), b = 10.434(1), c = 11.443(1) Å, β = 106.00(<1)°, V = 1336.6 Å^3, Z' = 1; T = 100 K.

14S. GOHMAS 1,1-bis(thiocyanatoethyl)cyclohexane

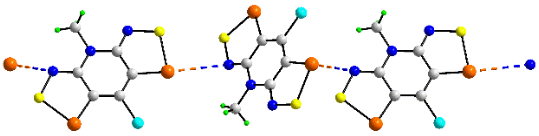
D. B. Werz, F. R. Fischer, S. C. Kornmayer, F. Rominger and R. Gleiter, *J. Org. Chem.*, 2008, **73**, 8021-8029. https://doi.org/10.1021/jo801378p

Monoclinic, $P2_1/c$: a = 11.662(<1), b = 10.341(<1), c = 11.519(<1) Å, β = 107.94(<1)°, V = 1321.6 Å^3, Z' = 1; T = 200 K.

{Similar supramolecular aggregation pattern with d(S···N) = 3.30 Å}

15. SUQRAY 8-chloro-4-methyl-4H-bis[1,2,3]selenathiazolo[4,5-b:5',4'-e]pyridine radical

A. A. Leitch, X. Yu, S. M. Winter, R. A. Secco, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2009, **131**, 7112-7125. https://doi.org/10.1021/ja900853t



d(Se···N) = 3.234(3) Å; C–Se···N = 176.51(11)°; S–Se···N = 89.78(5)°; S–N···Se = 94.13(12)°; C–N···Se = 121.2(2)°

{One of the two Se atoms associates *via* a Se···N interaction within a helical (2_1) chain. Chains are connected into a 3-D architecture by a combination of Se···Se [3.5723(5) Å] interactions, involving the second Se atom, and Se···S [3.4304(10) & 3.4727(10) Å] interactions with the shorter separation involving the Se atom forming the Se···N interaction leading to the chain}

Orthorhombic, $P2_12_12_1$: a = 4.193(<1), b = 15.141(<1), c = 16.153(<1) Å, V = 1025.6 Å^3, Z' = 1; T = room temp.

15S. MOSTIX01 8-chloro-4-methyl-4H-bis((1,2,3)dithiazolo)(4,5-b:5',4'-e)pyridin-3-yl radical

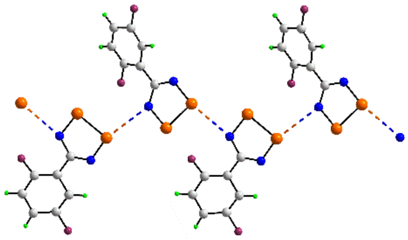
L. Beer, J. L. Brusso, A. W. Cordes, R. C. Haddon, M. E. Itkis, K. Kirschbaum, R. T. Oakley, D. S. MacGregor, A. A. Pinkerton and R. W. Reed, *J. Am. Chem. Soc.*, 2002, **124**, 9498-9509. https://doi.org/10.1021/ja026118s

Orthorhombic, $P2_12_12_1$: a = 4.246(1), b = 15.194(5), c = 15.069(4) Å, V = 972.3 Å^3, Z' = 1; T = room temp.

{A similar pattern of supramolecular aggregation is found with d(S···N) = 3.17 Å}

16. WERQEP 4-(2,5-difluorophenyl)-1,2,3,5-diselenadiazolyl radical

L. Beer, A. W. Cordes, D. J. T. Myles, R. T. Oakley and N. J. Taylor, *CrystEngComm*, 2000, **2**, 109-114. https://doi.org/10.1039/b004875p



d(Se···N) = 3.15(2) Å; N–Se···N = 169.2(7)°; Se–Se···N = 101.7(4)°; Se–Se···N = 93.7(8)°; C–N···Se = 155(2)°

d(Se···N) = 3.33(2) Å; N–Se···N = 163.0(9)°; Se–Se···N = 106.0(4)°; Se–Se···N = 96.0(8)°; C–N···Se = 145(2)°

{Two independent di-nuclear molecules. One Se of each ring participates in Se···N interactions. The two independent molecules form a dimeric aggregate and these assemble within a helical chain (2_1). Supporting Se···Se [3.746(4) Å] interactions are also found within the chain. Shorter Se···Se contacts involving all Se atoms [3.279(5) & 3.313(5) Å] link chains into a double-chain}

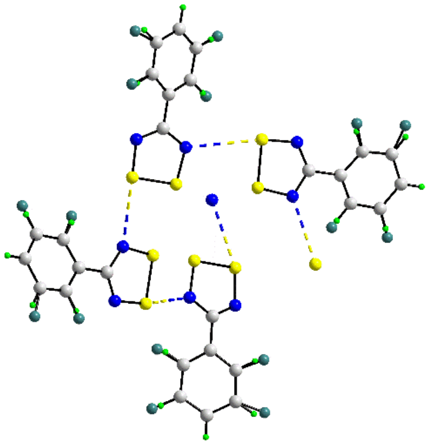
Monoclinic, $P2_1$: a = 7.305(3), b = 11.121(4), c = 11.198(4) Å, β = 111.44(2)°, V = 846.8 Å^3, Z' = 2; T = room temp.

16S. NIHBAH 4-(2,5-difluorophenyl)-1,2,3,5-dithiadiazolyl radical

A. J. Banister, A. S. Batsanov, O. G. Dawe, P. L. Herbertson, J. A. K. Howard, S. Lynn, I. May, J. N. B. Smith, J. M. Rawson, T. E. Rogers, B. K. Tanner, G. Antorrena and F. Palacio, *J. Chem. Soc., Dalton Trans.*, 1997, 2539-2542. https://doi.org/10.1039/a702881d

Tetragonal, $P4_2/n$: a = 21.277(3), c = 3.544(6) Å, V = 1604.4 Å^3, Z' = 1; T = 150 K

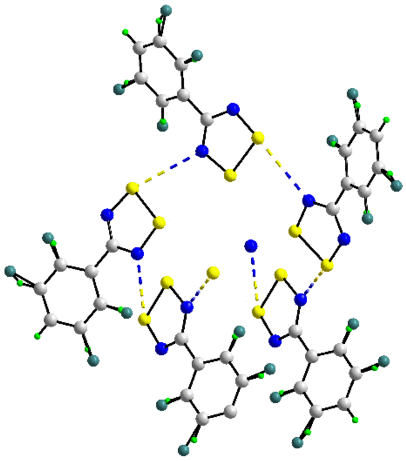
{A similar mode of connectivity with d(S···N) = 3.28 Å but leading to a helical chain with 4_2 symmetry}



16S. NIHBAH01 4-(2,5-difluorophenyl)-1,2,3,5-dithiadiazolyl radical

L. Beer, A. W. Cordes, D. J. T. Myles, R. T. Oakley and N. J. Taylor, *CrystEngComm*, 2000, **2**, 109-114. https://doi.org/10.1039/b004875p

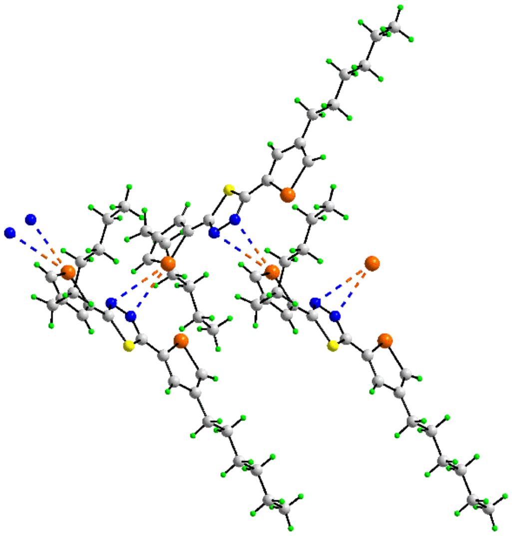
Tetragonal, *I*4$_1$/*a*: *a* = 30.214(2), *c* = 7.182(1) Å, *V* = 6556.3Å^3, *Z′* = 2; T = room temp.



{One of the two independent molecules adopts a similar mode of connectivity with d(S···N) = 3.32 Å but leading to a helical chain with 4$_1$ symmetry}

19. SIKWIT 2,5-bis(4-n-hexylselenophen-2-yl)-1,3,4-thiadiazole

H. Pang, P. J. Skabara, D. J. Crouch, W. Duffy, M. Heeney, I. McCulloch, S. J. Coles, P. N. Horton and M. B. Hursthouse, *Macromolecules*, 2007, **40**, 6585-6593. https://doi.org/10.1021/ma071242n



d(Se···N) = 3.048(6) Å; C–Se···N = 164.2(3) & 78.9(3)°; N–N···Se = 91.3(4)°; C–N···Se = 115.7(5)°

d(Se···N) = 3.369(6) Å; C–Se···N = 157.0(2) & 82.6(3)°; N–N···Se = 64.8(3)°; C–N···Se = 122.8(4)°

{Dinuclear; one Se atom forms two Se···N(thiadiazolyl) contact within a helical chain; two intramolecular Se···N contacts are noted 3.053(7) & 3.103(6) Å on either side of the ring, *i.e.* with the interacting and non-interacting Se atoms, respectively. Intermolecular Se···S [3.617(2) Å] contacts link chains into a 2-D array}

Orthorhombic, *Pbcn*: *a* = 38.796(3), *b* = 12.146(<1), *c* = 9.643(<1) Å, *V* = 4544.1 Å^3, *Z′* = 1; T = 120 K

19S. SIKWEP 2,5-bis(4-n-hexylthiophen-2-yl)-1,3,4-thiadiazole

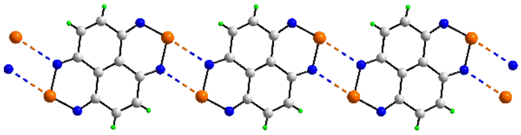
H. Pang, P. J. Skabara, D. J. Crouch, W. Duffy, M. Heeney, I. McCulloch, S. J. Coles, P. N. Horton and M. B. Hursthouse, *Macromolecules*, 2007, **40**, 6585-6593. https://doi.org/10.1021/ma071242n

Orthorhombic, *Pbcn*: *a* = 38.741(4), *b* = 12.055(1), *c* = 9.619(1) Å, *V* = 4492.1 Å^3, *Z′* = 1; T = 120 K

{The supramolecular architecture is formed but the d(S···N) separations are distinct with one, d(S···N) = 3.11 Å, being significantly shorter than the other, i.e. d(S···N) = 3.42 Å}

27. NAPSEZ10 naphtho(1,8-cd:4,5-c'd')-bis(1,2,6)selenadiazine

A. Gieren, V. Lamm, R. C. Haddon and M. L. Kaplan, *J. Am. Chem. Soc.*, 1980, **102**, 5070-5073. https://doi.org/10.1021/ja00535a042



d(Se···N) = 2.90 Å; N–Se···N = 175.3 & 72.2°; Se–Se···N = 107.8°; C–N···Se = 131.3°

{No s.u. values; centrosymmetric molecule; flat tape}

Monoclinic, $P2_1/a$: a = 15.099(8), b = 8.172(5), c = 3.863(5) Å, β = 92.35(2)°, V = 476.3 Å^3, Z' = 0.5; T = room temp.

27S. NAPTDZ10 naphtho(1,8-cd:4,5-c'd')-bis(1,2,6-thiadiazine)

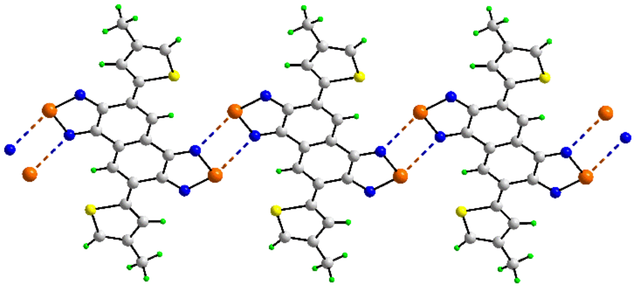
A. Gieren, V. Lamm, R. C. Haddon and M. L. Kaplan, *J. Am. Chem. Soc.*, 1979, **101**, 7277-7281. https://doi.org/10.1021/ja00518a024

Monoclinic, $P2_1/a$: a = 14.935(8), b = 8.304(6), c = 3.794(4) Å, β = 91.53(7)°, V = 470.4 Å^3, Z' = 0.5; T = room temp.

{The supramolecular architecture is the same with d(S···N) = 3.10 Å}

30. EJIYED 5,10-bis(4-methyl-2-thienyl)[1,2,5]selenadiazolo[3',4':5,6]naphtho[1,2-c][1,2,5]selenadiazole

K. Kawashima, I. Osaka and K. Takimiya, *Chem. Mater.*, 2015, **27**, 6558-6570. https://doi.org/10.1021/acs.chemmater.5b03124



d(Se···N) = 2.966(3) Å; N–Se···N = 163.66(10) & 71.25(9)°; Se–N···Se = 108.75(10)°; C–N···Se = 143.84(19)°

{The molecule is centrosymmetric. Linear tape; both ring-Se atoms form Se···N interactions *via* centrosymmetric {SeN···}$_2$ synthons}

Monoclinic, $P2_1/n$: a = 8.802(<1), b = 4.603(<1), c = 22.604(<1) Å, β = 90.60(<1)°, V = 915.8 Å^3, Z' = 0.5; T = 101 K

30O. EJIYAZ 5,10-bis(4-methyl-2-thienyl)[1,2,5]oxadiazolo[3',4':5,6]naphtho[1,2-c][1,2,5]oxadiazole

K. Kawashima, I. Osaka and K. Takimiya, *Chem. Mater.*, 2015, **27**, 6558-6570. https://doi.org/10.1021/acs.chemmater.5b03124

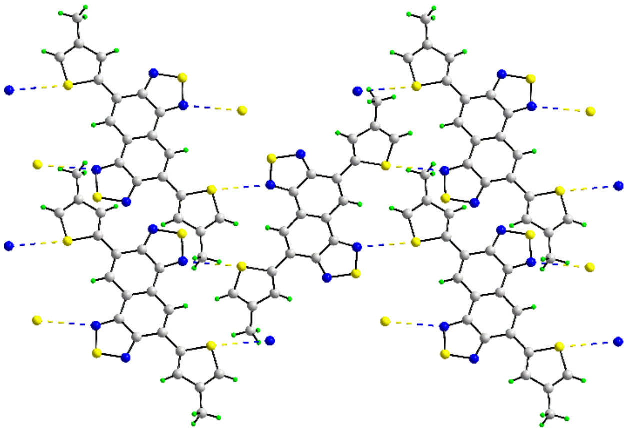
Monoclinic, $P2_1/n$: a = 4.746(<1), b = 10.044(<1), c = 17.881(<1) Å, β = 96.16(<1)°, V = 847.5 Å^3, Z' = 0.5; T = 103 K

{Centrosymmetric molecule. No O···N interactions less than the sum of the van der Waals radii (3.07 Å)}

30S. HAPKAM 5,10-bis(4-methyl-2-thienyl)[1,2,5]thiadiazolo[3',4':5,6]naphtho[1,2-c][1,2,5]thiadiazole

I. Osaka, M. Shimawaki, H. Mori, I. Doi, E. Miyazaki, T. Koganezawa and K. Takimiya, *J. Am. Chem. Soc.*, 2012, **134**, 3498-3507. https://doi.org/10.1021/ja210687r

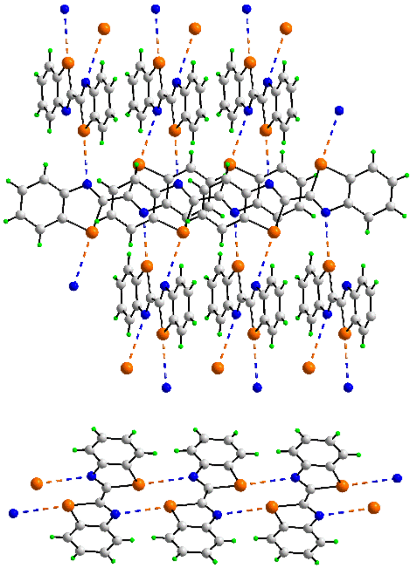
Monoclinic, $C2/c$: a = 11.796(1), b = 8.562(<1), c = 18.814(2) Å, β = 106.72(<1)°, V = 1819.7 Å^3, Z' = 0.5; T = room temp.



{Centrosymmetric molecule. A two-dimensional array features two acceptor and two donor S···N links per molecule with d(S···N) = 3.25 Å}

31. WULTOP 2,2'-bi-1,3-benzoselenazole

N. Biot and D. Bonifazi, *Chem.-Eur. J.*, 2020, **26**, 2904-2913. https://doi.org/10.1002/chem.201904762



d(Se···N) = 3.234(4) Å; C–Se···N = 176.95(15) & 95.92(15)°; C–N···Se = 109.0(2) & 133.7(3)°

{Centrosymmetric, di-nuclear molecule. 2-D layer with a flat topology. Within the framework are long Se···Se contacts [3.7222(7) Å] with two contacts per Se atom}

Monoclinic, $P2_1/c$: a = 9.065(1), b = 6.035(<1), c = 11.596(1) Å, β = 110.68(1)°, V = 593.5 Å^3, Z' = 0.5; T = room temp.

31O. NOGBOA01 2,2'-bibenzoxazole

C. M. Fitchett, C. Richardson and P. J. Steel, *Org. Biomol. Chem.*, 2005, **3**, 498-502. https://doi.org/10.1039/b416553e

Monoclinic, $P2_1/n$: a = 4.627(1), b = 16.480(2), c = 7.004(1) Å, β = 94.34(1)°, V = 532.5 Å^3, Z' = 0.5; T = 163 K

{Centrosymmetric molecule. Shortest intermolecular d(O···N) = 3.55 Å}

31S. FOCZON 2,2'-bibenzothiazole

C. M. Fitchett, C. Richardson and P. J. Steel, *Org. Biomol. Chem.*, 2005, **3**, 498-502. https://doi.org/10.1002/10.1039/b416553e

Monoclinic, $P2_1/c$: a = 8.993(1), b = 5.988(1), c = 11.445(2) Å, β = 110.87(1)°, V = 575.9 Å^3, Z' = 0.5; T = 168 K

{Centrosymmetric molecule. Similar array with d(S···N) = 3.26 Å}

31Te. WULTUV 2,2'-bi-1,3-benzotellurazole

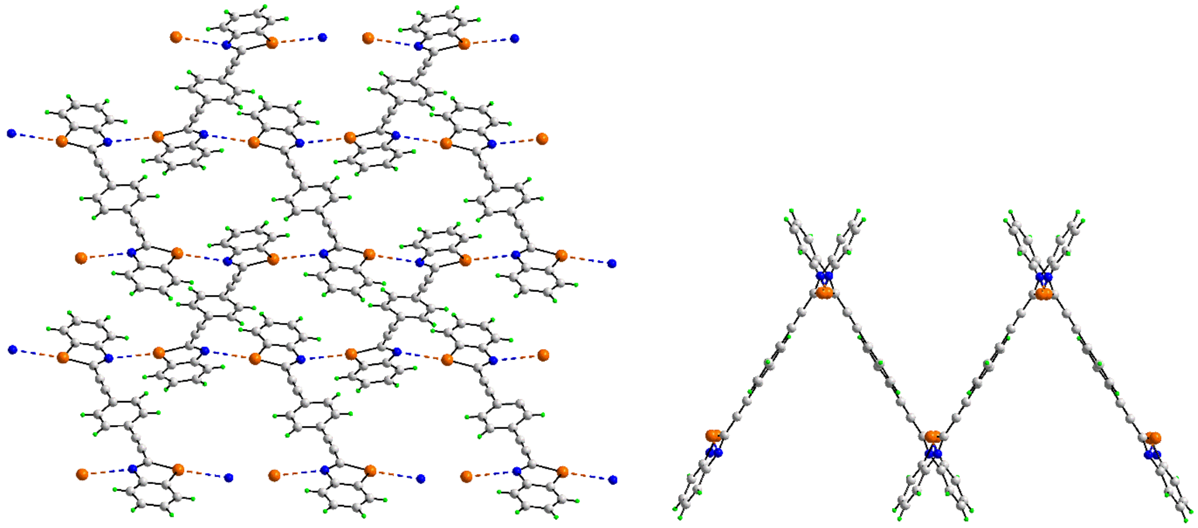
N. Biot and D. Bonifazi, *Chem.-Eur. J.*, 2020, **26**, 2904-2913. https://doi.org/10.1002/chem.201904762

Orthorhombic, *Pbca*: a = 11.565(<1), b = 11.928(<1), c = 18.640(1) Å, V = 2571.3 Å^3, Z' = 1; T = room temp.

{Non-symmetric. One tellurium atom forms a Te···N contact to generate a zigzag chain; d(Te···N) = 3.34 Å. The next closest contact is *ca* 4.8 Å}

32. RUVWEM 2,2'-(1,4-phenylenediethyne-2,1-diyl)bis(1,3-benzoselenazole)

A. Kremer, C. Aurisicchio, F. De Leo, B. Ventura, J. Wouters, N. Armaroli, A. Barbieri and D. Bonifazi, *Chem.-Eur. J.*, 2015, **21**, 15377-15387. https://doi.org/10.1002/chem.201501260



d(Se···N) = 3.381(5) Å; C–Se···N = 162.56(16) & 84.69(15)°; C–Se···Se = 109.2(3) & 131.5(3)°

{Dinuclear, centrosymmetric molecule; 2-D array; zigzag topology}

Monoclinic, $P2_1/c$: a = 19.170(1), b = 4.257(<1), c = 11.525(<1) Å, β = 98.60(<1)°, V = 930.0 $Å^3$, Z' = 0.5; T = room temp.

32O. RUVWIQ 2,2'-(1,4-phenylenediethyne-2,1-diyl)bis(1,3-benzoxazole)

A. Kremer, C. Aurisicchio, F. De Leo, B. Ventura, J. Wouters, N. Armaroli, A. Barbieri and D. Bonifazi, *Chem.-Eur. J.*, 2015, **21**, 15377-15387. https://doi.org/10.1002/chem.201501260

Monoclinic, $P2_1/c$: a = 15.416(3), b = 4.752(1), c = 11.923(3) Å, β = 98.52(1)°, V = 863.8 $Å^3$, Z' = 0.5; T = room temp.

{Centrosymmetric molecule. The closest intermolecular d(O···N) = 4.38 Å}

32S. RUVWOW 2,2'-(1,4-phenylenediethyne-2,1-diyl)bis(1,3-benzothiazole)

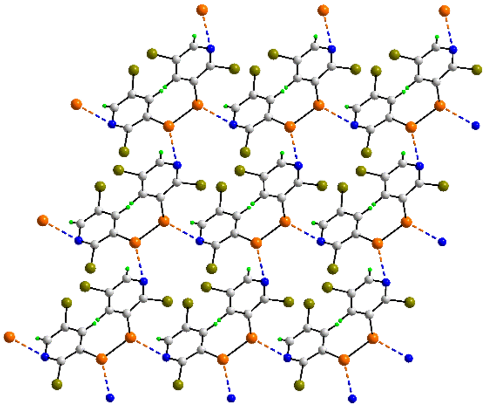
A. Kremer, C. Aurisicchio, F. De Leo, B. Ventura, J. Wouters, N. Armaroli, A. Barbieri and D. Bonifazi, *Chem.-Eur. J.*, 2015, **21**, 15377-15387. https://doi.org/10.1002/chem.201501260

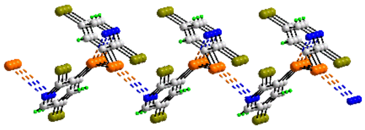
Monoclinic, $P2_1/c$: a = 15.423(<1), b = 5.028(<1), c = 11.902(<1) Å, 98.25(<1)°, V = 913.4 $Å^3$, Z' = 0.5; T = room temp.

{Centrosymmetric molecule. S/N atoms disordered. No d(S···N) < 4.0 Å}

33. ABOWUK 1,2-bis(2,5-dibromopyrid-3-yl)diselenide

K. K. Bhasin and V. Arora, *Appl. Organomet. Chem.*, 2004, **18**, 359-362. https://doi.org/10.1002/aoc.659





d(Se···N) = 3.414(9) Å; C–Se···N = 140.5(3)°; Se–Se···N = 117.24(14)°; (Br)C–N···Se = 98.1(5)° & C–N···Se = 99.8(6)°

{Molecule has 2-fold symmetry bisecting the Se–Se bond; each Se and N atom form Se···N interactions that project laterally to form a jagged 2-D array. Intramolecular Se···Br contacts [3.2095(14) Å] are noted}

Monoclinic, *C*2/*c*: *a* = 12.143(1), *b* = 9.103(<1), *c* = 14.274(1) Å, β = 113.30(<1)°, *V* = 1449.2 Å^3, *Z′* = 0.5; T = room temp.

33Te. FEGCIE bis(2,5-dibromo-3-pyridyl)-di-tellurium

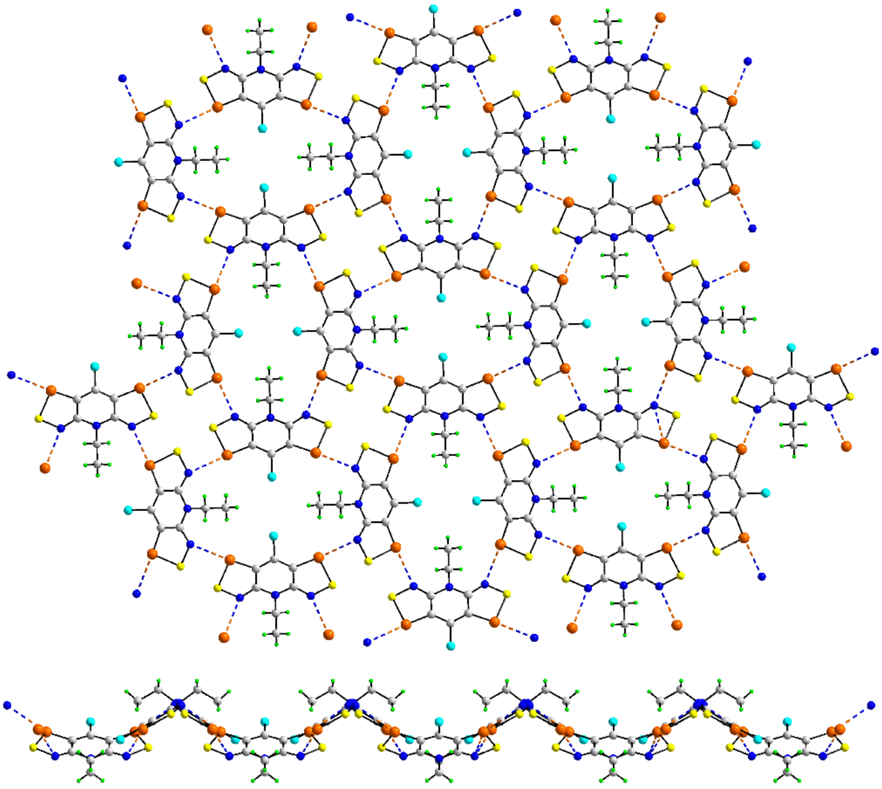
K. K. Bhasin, V. Arora, T. M. Klapötke and M.-J.Crawford, *Eur. J. Inorg. Chem.*, 2004, 4781-4788. https://doi.org/10.1002/ejic.200400297

Monoclinic, *C*2/*c*: *a* = 12.507(1), *b* = 9.452(1), *c* = 14.171(1) Å, β = 111.71(1)°, *V* = 1556.5 Å^3, *Z′* = 0.5; T = room temp.

{Same supramolecular pattern with d(Te···N) = 3.42 Å}

34. YODSUG 8-chloro-4-ethyl-4H-bis((1,2,3)selenathiazolo)(4,5-b:5',4'-e)pyridinyl radical

C. M. Robertson, A. A. Leitch, K. Cvrkalj, R. W. Reed, D. J. T. Myles, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2008, **130**, 8414-8425. https://doi.org/10.1021/ja801070d



d(Se···N) = 3.279(2) Å; C–Se···N = 164.51(9)°; S–Se···N = 102.17(4)°; S–N···Se = 81.28(8)°; C–N···Se = 123.38(16)°

{The molecule has mirror symmetry. Each of the Se atoms participates in a Se···N interaction within a 2-D array, with a jagged topology. Close intermolecular Se…S and S···S interactions [3.4462(7) & 3.5451(9) Å] are noted along with intramolecular Se…Cl [3.3144(7) Å] contacts. At room temperature, the Se···N contact is 3.308(3) Å}

Tetragonal, $P\bar{4}2_1m$: a = 16.056(<1), c = 4.160(<1) Å, V = 1072.5 Å^3, Z' = 0.5; T = room temp.

34S. MOSTOD 8-chloro-4-ethyl-4H-bis((1,2,3)dithiazolo)(4,5-b:5',4'-e)pyridin-3-yl radical

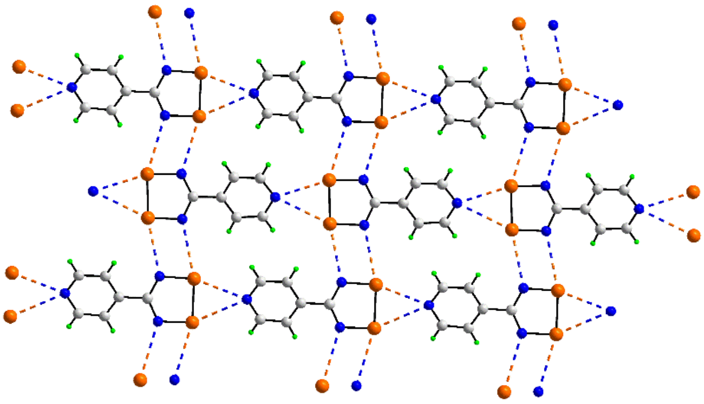
L. Beer, J. L. Brusso, A. W. Cordes, R. C. Haddon, M. E. Itkis, K. Kirschbaum, R. T. Oakley, D. S. MacGregor, A. A. Pinkerton and R. W. Reed, *J. Am. Chem. Soc.*, 2002, **124**, 9498-9509 https://doi.org/10.1021/ja026118s

Tetragonal, $P\bar{4}2_1m$: a = 15.886(4), c = 4.109(1) Å, V = 1036.9 Å^3, Z' = 0.5; T = room temp.

{Same supramolecular architecture but with d(S···N) = 3.40 Å}

35. TINQIT 4-(3H-1,2,3,5-diselenadiazol-4-yl)pyridine radical

A. I. Taponen, J. W. L. Wong, K. Lekin, A. Assoud, C. M. Robertson, M. Lahtinen, R. Clérac, H. M. Tuononen, A. Mailman and R. T. Oakley, *Inorg. Chem.*, 2018, **57**, 13901-13911. https://doi.org/10.1021/acs.inorgchem.8b02416



1. d(Se···N) = 2.962(3) Å; N–Se···N = 162.77(8)°; Se–Se···N = 72.73(6)°; C–N···Se = 106.93(19) & 136.0(2)°

2. d(Se···N) = 3.172(3) Å; N–Se···N = 154.33(8)°; Se–Se···N = 63.09(6)°; C–N···Se = 94.43(19) & 149.0(2)°

3. d(Se···N) = 3.169(3) Å; Se–Se···N = 154.38(5)°; N–Se···N = 75.71(9)°; Se–N···Se = 105.62(9)°; C–N···Se = 133.0(2)°

4. d(Se···N) = 3.212(3) Å; Se–Se···N = 154.52(5)°; N–Se···N = 74.46(9)°; Se–N···Se = 104.07(9)°; C–N···Se = 135.7(2)°

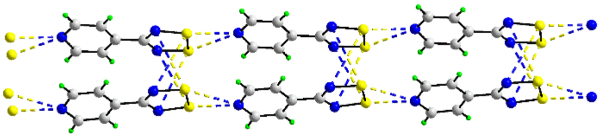
{The two Se atoms of the ring are connected to a common pyridyl-N atom, entries 1 & 2. The linear chains thus formed are connected into a flat 2-D array *via* tapes constructed about non-symmetric {SeN···}$_2$ synthons, entries 3 & 4. A double-layer is formed about a centre of inversion by Se···Se [3.2527(4) Å] interactions}

Monoclinic, *C*2/*c*: *a* = 16.385(1), *b* = 9.498(<1), *c* = 10.706(<1) Å, β = 120.39(<1)°, *V* = 1437.2 Å^3, *Z′* = 1; T = room temp.

35S. TINQEP 4-(3H-1,2,3,5-dithiadiazol-4-yl)pyridine radical

A. I. Taponen, J. W. L. Wong, K. Lekin, A. Assoud, C. M. Robertson, M. Lahtinen, R. Clérac, H. M. Tuononen, A. Mailman and R. T. Oakley, *Inorg. Chem.*, 2018, **57**, 13901-13911. https://doi.org/10.1021/acs.inorgchem.8b02416

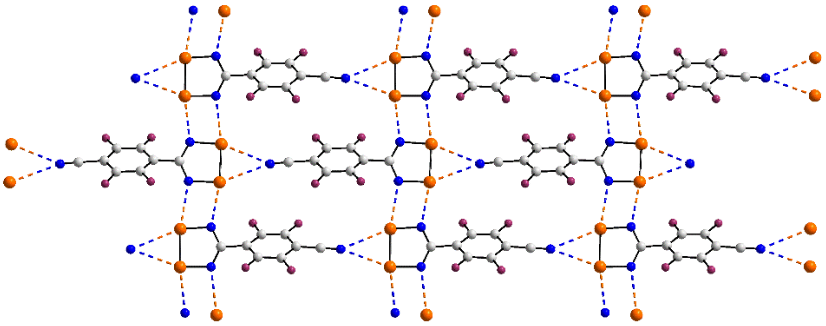
Monoclinic, *C*2/*c*: *a* = 15.460(<1), *b* = 8.979(1), *c* = 11.376(<1) Å, β = 119.89(<1)°, *V* = 684.6 Å^3, *Z′* = 1; T = room temp.



{The chains mediated by the pair of interactions to a common pyridyl-N ring persist with d(S···N) = 2.72 & 2.95 Å. However, the orthogonal interactions of **35** do not persist. Instead, very weak S···N interactions, d(S···N) = 3.56 & 3.60 Å, link chains into a double chain}

36. UBOJED 4-(4-cyano-2,3,5,6-tetrafluorophenyl)-1,2,3,5-diselenadiazolyl radical

R. L. Melen, R. J. Less, C. M. Pask and J. M. Rawson, *Inorg. Chem.*, 2016, **55**, 11747-11759. https://doi.org/10.1021/acs.inorgchem.6b01771



1. d(Se···N) = 3.085(12) Å; N–Se···N = 158.2(4)°; Se–Se···N = 69.5(3)°; C–N···Se = 163(1)°

2. d(Se···N) = 3.145(13) Å; N–Se···N = 155.2(4)°; Se–Se···N = 66.8(3)°; C–N···Se = 153(1)°

3. d(Se···N) = 3.188(14) Å; Se–Se···N = 163.5(2)°; N–Se···N = 82.3(4)°; Se–N···Se = 97.4(4)°; C–N···Se = 144(1)°

4. d(Se···N) = 3.192(13) Å; Se–Se···N = 167.6(2)°; N–Se···N = 82.3(4)°; Se–N···Se = 97.1(4)°; C–N···Se = 146(1)°

5. d(Se···N) = 3.039(12) Å; N–Se···N = 160.0(4)°; Se–Se···N = 69.9(3)°; C–N···Se = 162(1)°

6. d(Se···N) = 3.126(13) Å; N–Se···N = 155.6(4)°; Se–Se···N = 65.9(3)°; C–N···Se = 154(1)°

7. d(Se···N) = 3.146(12) Å; Se–Se···N = 166.1(2)°; N–Se···N = 81.5(4)°; Se–N···Se = 98.0(4)°; C–N···Se = 145.1(1)°

8. d(Se···N) = 3.145(12) Å; Se–Se···N = 168.4(2)°; N–Se···N = 81.2(4)°; Se–N···Se = 98.5(4)°; C–N···Se = 146.5(9)°

{Two independent molecules. The two Se atoms of the ring are connected to a common nitrile-N atom, entries 1 & 2. The linear chains thus formed are connected into a flat 2-D array *via* tapes constructed about non-symmetric $\{SeN\cdots\}_2$ synthons, entries 3 & 4; the pattern is also adopted by the second independent molecule, entries 5-8. The result is a flat 2-D array comprising alternating rows of independent molecules. Intra-layer Se···F interactions are apparent with the shortest of these being 3.066(7) Å. Three additional Se···F interactions [3.249(9), 3.296(9) & 3.439(6) Å} connect the 2-D array into a double-layer. These are connected into a 3-D architecture by Se···Se contacts [3.212(2) & 3.220(2) Å] involving all Se atoms}

Triclinic, $P\bar{1}$: a = 10.935(4), b = 11.174(4), c = 10.525(4) Å, α = 112.22(3), β = 118.09(2), γ = 63.58(3)°, V = 992.6 Å^3, Z' = 2; T = 180 K

36S. YOMXUT 4-(4-cyano-2,3,5,6-tetrafluorophenyl)-1,2,3,5-dithiadiazolyl radical

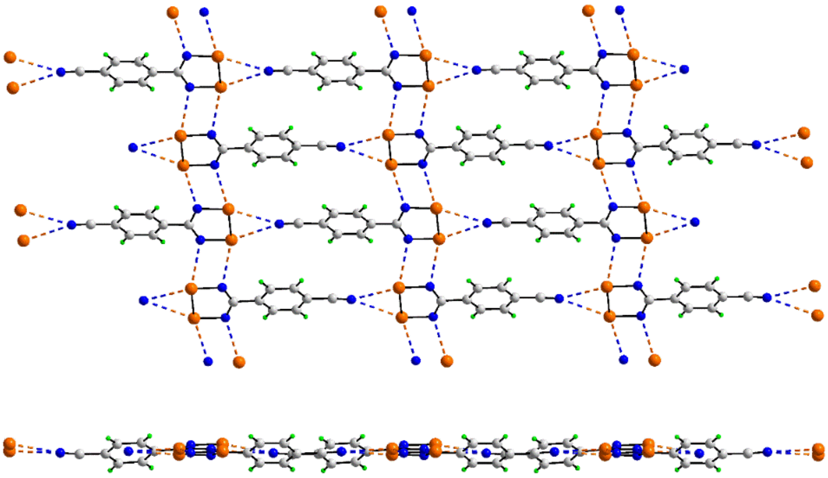
A. J. Banister, N. Bricklebank, W. Clegg, M. R. J. Elsegood, C. I. Gregory, I. Lavender, J. M. Rawson and B. K. Tanner, *Chem. Commun.*, 1995, 679-680. https://doi.org/10.1039/C39950000679

Triclinic, $P\bar{1}$: a = 7.574(6), b = 8.065(6), c = 9.509(7) Å, α = 65.73(3), β = 69.17(3), γ = 67.52(3)°, V = 475.5 Å^3, Z' = 1; T = 160 K

{The chain persists, mediated by the two interactions per nitrile-N atom with d(S···N) = 3.07 & 3.11 Å. The orthogonal contacts to generate the 2-D array are beyond the sum of the van der Waals radii, i.e. d(S···N) = 3.37 & 3.41 Å}

37. PAHREV 4-(4-cyanophenyl)-1,2,3,5-diselenadiazole radical

A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem.*, 1992, **31**, 1802-1808. https://doi.org/10.1021/ic00036a016



d(Se···N) = 3.050(11) Å; Se–Se···N = 157.8(3)°; N–Se···N = 76.9(4)°; Se–N···Se = 103.8(4)°; C–N···Se = 135.9(9)°

d(Se···N) = 3.071(11) Å; Se–Se···N = 154.9(3)°; N–Se···N = 76.5(4)°; Se–N···Se = 102.7(4)°; C–N···Se = 137(1)°

d(Se···N) = 2.967(12) Å; Se–Se···N = 162.3(3)°; N–Se···N = 76.5(4)°; Se–N···Se = 104.2(4)°; C–N···Se = 141(1)°

d(Se···N) = 2.988(12) Å; Se–Se···N = 162.8(3)°; N–Se···N = 76.1(4)°; Se–N···Se = 103.1(4)°; C–N···Se = 141.0(9)°

d(Se···N) = 3.096(18) Å; N–Se···N = 159.9(5)°; Se–Se···N = 68.1(4)°; C–N···Se = 160(2)°

d(Se···N) = 3.01(2) Å; N–Se···N = 158.7(5)°; Se–Se···N = 68.0(4)°; C–N···Se = 156(2)°

d(Se···N) = 3.106(18) Å; N–Se···N = 158.1(5)°; Se–Se···N = 68.3(4)°; C–N···Se = 159(2)°

d(Se···N) = 3.12(2) Å; N–Se···N = 157.3(5)°; Se–Se···N = 67.9(4)°; C–N···Se = 157(2)°

{Two independent molecules; eight independent Se···N contacts, four giving rise to a ribbon comprising alternating independent molecules *via* {SeN(ring)···}$_2$ synthons (entries 1 & 2 for the first {SeN(ring)···}$_2$ synthon, 3 & 4 for the second}; four involving bifurcated nitrile atoms which link the ribbons on either side into a flat, 2-D array. Double-layers feature Se···Se interactions [3.192(3) & 3.275(3) Å] between the independent molecules}

Triclinic, $P\bar{1}$: a = 10.478(4), b = 10.780(4), c = 9.432(4) Å, α = 107.16(3), β = 115.23(2), γ = 68.39(3)°, V = 883.9 Å^3, Z' = 2; T = room temp.

37S. PAHRAR 4-(4-cyanophenyl)-1,2,3,5-diselenadiazole radical

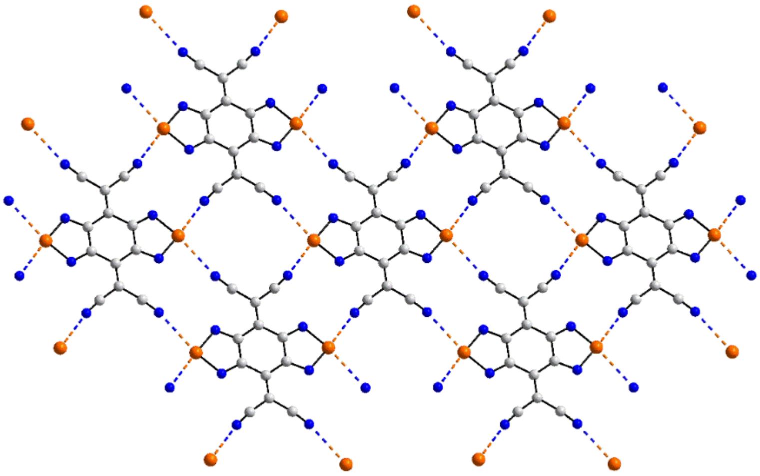
A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem.*, 1992, **31**, 1802-1808. https://doi.org/10.1021/ic00036a016

Triclinic, $P\bar{1}$: a = 10.466(3), b = 10.342(2), c = 9.169(2) Å, α = 104.97(2), β = 112.97(2), γ = 69.84(2)°, V = 848.9 Å^3, Z' = 2; T = room temp.

{Ostensibly, the same supramolecular pattern is observed. However, the chains involving the double interactions to nitrile-N comprise one independent molecule only: d(S···N) = 3.02 & 3.04 Å and 2 × 3.05 Å. The links between chains to form the 2-D array have d(S···N) = 3.21 & 3.26 and 3.17 & 3.21 Å}

38. GEFVOC10 4H,8H-4,8-bis(dicyanomethylene)benzo(1,2-c:4,5-c')bis(1,2,5)selenadiazole

T. Suzuki, H. Fujii, Y. Yamashita, C. Kabuto, S. Tanaka, M. Harasawa, T. Mukai and T. Miyashi, *J. Am. Chem. Soc.*, 1992, **114**, 3034-3043. https://doi.org/10.1021/ja00034a041



d(Se···N) = 2.940(4) Å; N–Se···N = 169.49(11) & 82.94(11)°; C–N···Se = 169.5(3)°

{The molecule is disposed over a site of symmetry 2/m; each Se atoms form two Se···N interactions; grid comprising edge-shared 12-membered {···Se···NC$_3$N}$_2$ and 14-membered {SeNC$_4$N···}$_2$ synthons; flat, 2D array}

Monoclinic, $C2/m$: a = 9.203(1), b = 13.388(1), c = 5.314(1) Å, β = 98.53(1)°, V = 647.5 Å^3, Z' = 0.25; T = room temp.

38S. FARSOG01 4H,8H-4,8-bis(dicyanomethylene)benzo(1,2-c:4,5-c')bis(1,2,5)thiadiazole

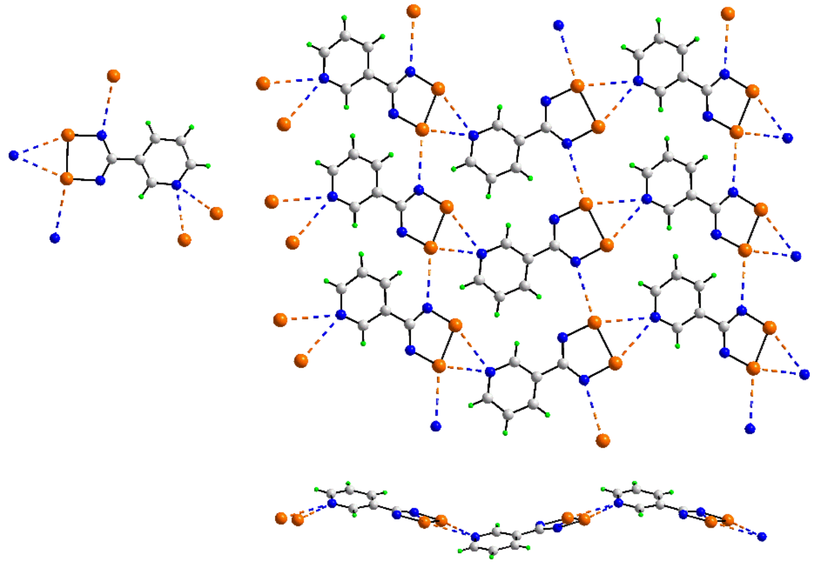
T. Suzuki, H. Fujii, Y. Yamashita, C. Kabuto, S. Tanaka, M. Harasawa, T. Mukai and T. Miyashi, *J. Am. Chem. Soc.*, 1992, **114**, 3034-3043. https://doi.org/10.1021/ja00034a041

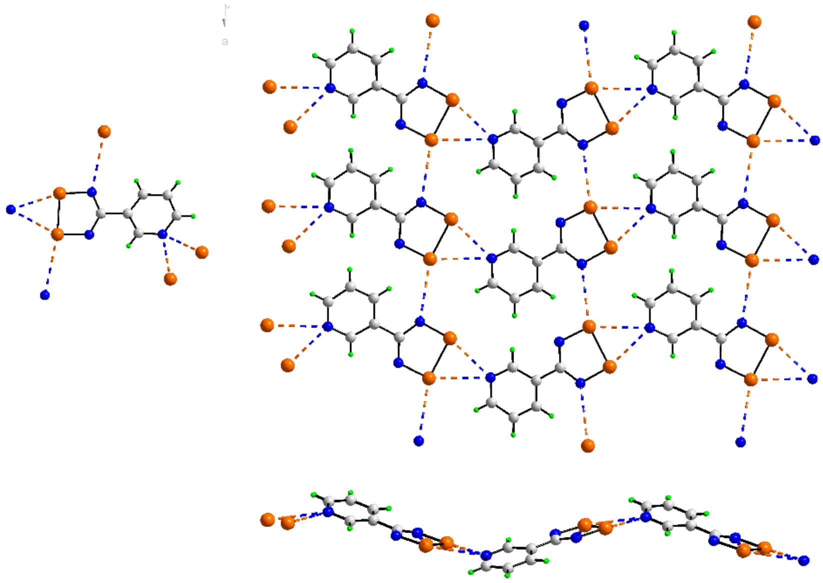
Monoclinic, $C2/m$: a = 8.999(1), b = 13.056(1), c = 5.535(1) Å, β = 99.15(2)°, V = 642.0 Å^3, Z' = 0.25; T = room temp.

{Same supramolecular aggregation with d(S···N) = 3.04 Å}

42. TINQAL 3-(3H-1,2,3,5-diselenadiazol-4-yl)pyridine radical

A. I. Taponen, J. W. L. Wong, K. Lekin, A. Assoud, C. M. Robertson, M. Lahtinen, R. Clérac, H. M. Tuononen, A. Mailman and R. T. Oakley, *Inorg. Chem.*, 2018, **57**, 13901-13911. https://doi.org/10.1021/acs.inorgchem.8b02416





1. d(Se···N) = 3.065(3) Å; N–Se···N = 158.47(11)°; Se–Se···N = 68.12(6)°; C–N···Se = 95.2(2) & 143.4(2)°

2. d(Se···N) = 3.074(3) Å; N–Se···N = 158.92(11)°; Se–Se···N = 67.71(6)°; C–N···Se = 105.9(2) & 137.4(2)°

3. d(Se···N) = 3.411(3) Å; Se–Se···N = 161.09(6)°; N–Se···N = 100.38(11)°; Se–N···Se = 102.13(12)°; C–N···Se = 139.7(2)°

4. d(Se···N) = 2.906(3) Å; N–Se···N = 164.08(12)°; Se–Se···N = 73.94(7)°; C–N···Se = 107.6(2) & 135.4(3)°

5. d(Se···N) = 3.174(3) Å; N–Se···N = 152.43(11)°; Se–Se···N = 61.62(6)°; C–N···Se = 93.0(2) & 145.0(2)°

6. d(Se···N) = 3.406(3) Å; Se–Se···N = 155.68(6)°; N–Se···N = 103.12(11)°; Se–N···Se = 105.09(12)°; C–N···Se = 135.6(2)°

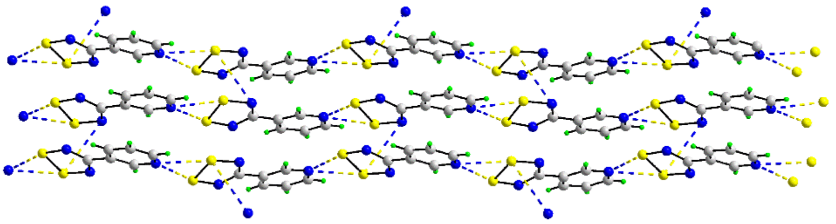
{Two independent molecules which form the same pattern of Se···N contacts, each self-associating only. The pyridyl-N bridges the Se atoms of a symmetry related molecule, entries 1 and 2. One of the Se atoms forms two contacts, the second with a ring-N atom of the same molecule, entry 3. The ring-N forms a single interaction, corresponding to entry 3. The corresponding contacts for the second independent molecule are listed as entries 4-6. Flat 2-D arrays eventuate in each case. The layers assemble into a 3-D architecture through Se···Se interactions [3.2404(5) & 3.3094(5) Å] formed between the independent molecules}

Monoclinic, $P2_1$: a = 6.152(<1), b = 16.523(<1), c = 7.301(<1) Å, β = 95.43(<1)°, V = 738.8 Å^3, Z' = 2; T = room temp.

42S. ASODUJ01 3-(3H-1,2,3,5-dithiadiazol-4-yl)pyridine radical

A. I. Taponen, J. W. L. Wong, K. Lekin, A. Assoud, C. M. Robertson, M. Lahtinen, R. Clérac, H. M. Tuononen, A. Mailman and R. T. Oakley, *Inorg. Chem.*, 2018, **57**, 13901-13911. https://doi.org/10.1021/acs.inorgchem.8b02416

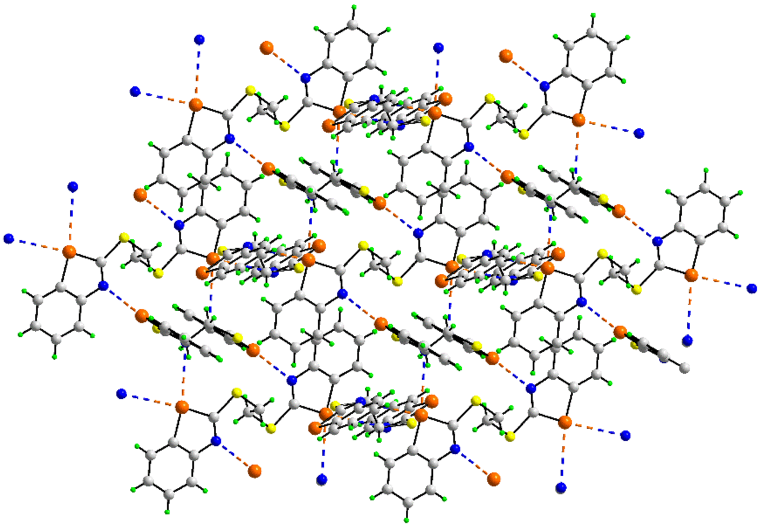
Monoclinic, $P2_1$: a = 6.313(<1), b = 15.861(<1), c = 7.108(<1) Å, β = 95.80(<1)°, V = 708.1 Å^3, Z' = 2; T = room temp.

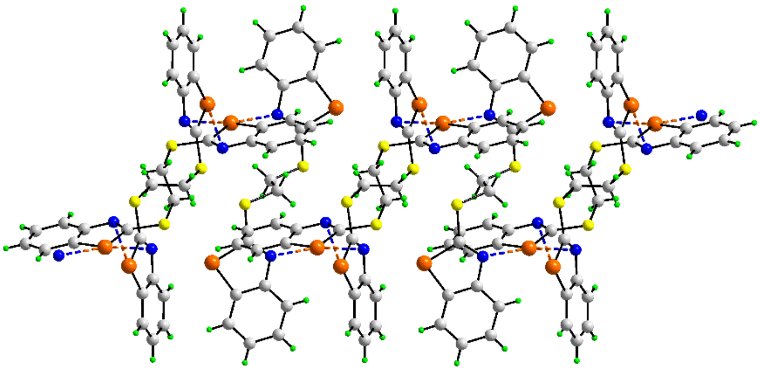


{Two independent zigzag chains are formed, d(S···N) = 2.85 & 2.97 Å and 2.87 & 2.96 Å. No further S···N contacts less the 3.50 Å are apparent. The next longest contact, i.e. d(S···N) = 3.55 Å, link the independent chains into a 2-D array}

43. **PUZWIQ** 2,2'-(ethylenedisulfanyl)bis(benzoselenazole)

Z. Časar, I. Leban, A. Majcen-Le Maréchal and D. Lorcy, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1568-1573. https://doi.org/10.1039/b203317h





d(Se···N) = 3.227(3) Å; C–Se···N = 161.03(13) & 89.41(14)°; C–N···Se = 97.3(2) & 129.4(3)°

d(Se···N) = 3.375(4) Å; C–Se···N = 168.51(14) & 103.54(14)°; C–N···Se = 93.7(3) & 112.5(3)°

d(Se···N) = 3.234(3) Å; C–Se···N = 171.09(14) & 100.16(14)°; C–N···Se = 96.0(2) & 110.6(2)°

{There are three half molecules in the asymmetric-unit, each being disposed about a centre of inversion. The nature of the Se···N formed between the molecules differentiate them: the Se atoms in one molecule form two interactions, entries 1 & 2, in the second molecule, one (entry 3) and in the third, none. The ring-N donors are derived from each molecule. The result is a 2-D array. Each independent Se atom forms a 1,3-Se···S contact [3.0966(11), 3.1042(9) & 3.1209(9) Å]}

Triclinic, $P\bar{1}$: a = 9.898(<1), b = 10.007(<1), c = 13.947(<1) Å, α = 102.75(<1), β = 104.03(<1), γ = 103.34(<1) °, V = 1246.9 Å^3, Z' = 1.5; T = room temp.

43S. **MACMOT** 2,2'-(1,2-ethanediyldithio)bis(1,3-benzothiazole)

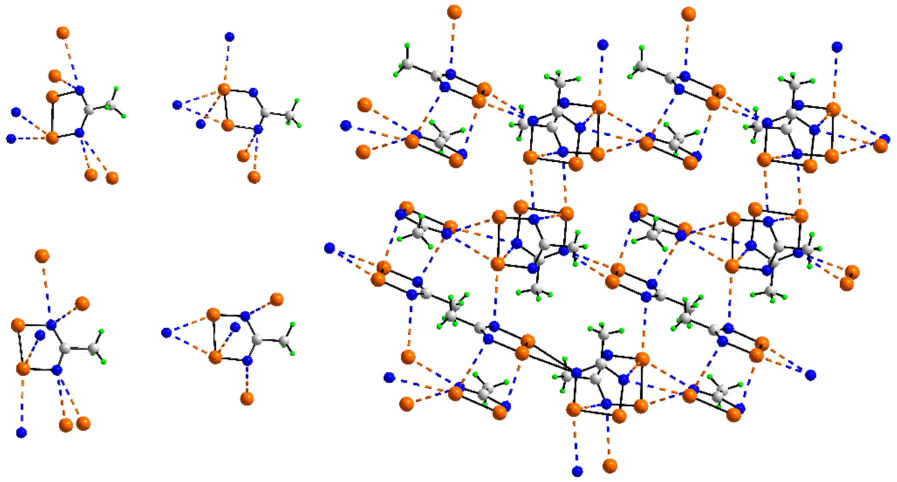
Q. Liu, D. Shi, C. Ma, F. Pan, R. Qu, K. Yu and J. Xu, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2003, **59**, o219-o220. https://doi.org/10.1107/S0108270103002257

Monoclinic, $P2_1/n$: a = 11.513(2), b = 10.711(2), c = 13.998(2) Å, β = 114.10(1)°, V = 1575.7 Å^3, Z' = 1; T = room temp.

{The closest S···N contacts is 3.59 Å which features between molecules assemble along the 2_1-screw axis}

45. ZEXVON 4-methyl-1,2,3,5-diselenadiazole

C. D. Bryan, A. W. Cordes, R. T. Oakley and R. E. vonH. Spence, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 2402-2404. https://doi.org/10.1107/S0108270195006147



1. d(Se···N) = 3.009(14) Å; N–Se···N = 168.9(5)°; Se–Se···N = 79.5(3)°; Se–N···Se = 83.8(5)°; C–N···Se = 161(1)°

2. d(Se···N) = 3.346(15) Å; Se–Se···N = 79.2(2)°; N–Se···N = 92.1(5)°; Se–N···Se = 96.6(5)°; C–N···Se = 81.2(9)°

3. d(Se···N) = 2.971(14) Å; N–Se···N = 160.2(5)°; Se–Se···N = 69.3(3)°; Se–N···Se = 112.7(6)°; C–N···Se = 130(1)°

4. d(Se···N) = 3.048(15) Å; N–Se···N = 157.1(6)°; Se–Se···N = 65.7(3)°; Se–N···Se = 108.3(6)°; C–N···Se = 121(1)°

5. d(Se···N) = 3.186(14) Å; Se–Se···N = 80.9(3)°; N–Se···N = 92.7(5)°; Se–N···Se = 99.4(5)°; C–N···Se = 84.3(9)°

6. d(Se···N) = 3.300(13) Å; Se–Se···N = 169.7(3)°; N–Se···N = 95.1(5)°; Se–N···Se = 83.0(5)°; C–N···Se = 156(1)°

7. d(Se···N) = 3.051(11) Å; N–Se···N = 159.4(5)°; Se–Se···N = 68.4(3)°; Se–N···Se = 109.4(5)°; C–N···Se = 119(1)°

8. d(Se···N) = 3.076(13) Å; N–Se···N = 157.5(5)°; Se–Se···N = 67.3(3)°; Se–N···Se = 109.1(5)°; C–N···Se = 135(1)°

9. d(Se···N) = 3.054(15) Å; Se–Se···N = 161.9(3)°; N–Se···N = 84.4(5)° Se–N···Se = 110.7(6)°; C–N···Se = 102(1)°;

10. d(Se···N) = 3.215(14) Å; Se–Se···N = 82.2(3)°; N–Se···N = 94.8(5)°; Se–N···Se = 97.8(6)°; C–N···Se = 86(1)°

11. d(Se···N) = 3.343(15) Å; Se–Se···N = 79.7(3)°; N–Se···N = 95.0(4)°; Se–N···Se = 96.9(6)°; C–N···Se =84(1)°

12. d(Se···N) = 3.452(14) Å; Se–Se···N = 174.5(3)°; N–Se···N = 95.0(4)°; Se–N···Se = 82.4(6)°; C–N···Se = 154(1)°

{Four independent molecules and each forms a distinctive pattern of Se···N interactions. First molecule connects to four different molecules: one Se atom of the ring forms two contacts with two ring-N atoms, entries 1 and 2, while the second Se atom does not form a contact. Each ring-N atom forms two contacts, entries 3-6. Entries 3 and 4 relate to the N atom connecting two Se atoms of the same ring. Entries 2 and 5 relate to the face-to-face contact between two rings. The second independent molecule: one Se atom forms a single contact, entry 7, while the other forms three contacts, entries 5, 8 & 9. Entries 7 and 8 refer to a ring-N bridging the Se atoms. Only one of the ring-N atoms forms Se···N interactions, entries 1 & 2. Entries 2 & 5 relate to the face-to-face contact between two rings. The third independent molecule: One Se atoms forms two contacts, entries 6 & 10, while the other does not form one. Each of the ring-N atoms forms two contacts. One, entries 11 & 12, forms contacts to two different molecules while the other bridges two Se atoms of a ring, entries 7 & 8. Entries 10 & 11 refer to contacts between the third and four independent molecules. The fourth independent molecule: one Se forms a single contact, entry 4, while the other forms two, entries 3 & 11. Entries 3 & 4 relate to a ring-N bridging two Se atoms of the ring. Each ring atom forms a single contact, entries 9 & 10. Net result: 2-D architecture. Close Se···Se contacts also feature in the crystal, *i.e.* within the 2-D array [shortest contact = 3.160(3) Å] and between layers to generate a 3-D architecture. For the latter, the Se···Se separations tended to be longer and range from 3.630(3) to 3.789(3) Å}

Triclinic, $P\bar{1}$: a = 8.649(1), b = 9.857(2), c = 12.375(3) Å, α = 102.11(2), β = 89.77(2), γ = 104.65(2)°, V = 996.7 Å^3, Z' = 2; T = room temp.

45S. JATNEX 4-methyl-1,2,3,5-dithiadiazole

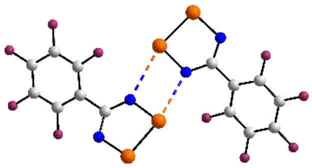
A. J. Banister, M. I. Hansford, Z. V. Hauptman, S. T. Waitand W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1989, 1705-1713. https://doi.org/10.1039/dt9890001705

Triclinic, $P\bar{1}$: a = 11.296(1), b = 12.498(1), c = 14.647(2) Å, α = 72.06(1), β = 77.85(1), γ = 77.30(1)°, V = 1896.3 Å^3, Z' = 8; T = room temp.

{A 3-D array features S···N numerous contacts between 2.86 and 3.25 Å}

48. SOBPIL (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl radical bis(4-(pentafluorophenyl)-3H-1,2,3,5-diselenadiazol-3-yl radical)

M. A. Nascimento, E. Heyer, J. J. Clarke, H. J. Cowley, A. Alberola, N. Stephaniuk and J. M. Rawson, *Angew. Chem., Int. Ed.*, 2019, **58**, 1371-1375. https://doi.org/10.1002/anie.201812132



d(Se···N) = 2.914(6) Å; Se–Se···N = 166.66(11)°; N–Se···N = 76.45(19)°; Se–N···Se = 105.7(2)°; C–N···Se = 138.6(4)°

d(Se···N) = 3.024(6) Å; Se–Se···N = 164.15(11)°; N–Se···N = 73.48(19)°; Se–N···Se = 101.3(2)°; C–N···Se = 143.8(4)°

{2:1 co-crystal. Two independent dinuclear molecules which associate *via* a {···SeN}$_2$ synthon to form a two-molecule. These aggregate normal to the central plane *via* Se···Se contacts (3.1330(8) & 3.1895(7) Å) to form an octa-nuclear Se$_8$ aggregate. The outer staves (defined by the Se···Se contacts) are bridged by (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl-O atoms (2.897(5) & 2.996(4) Å)}

Triclinic, *P*1̄: *a* = 7.559(<1), *b* = 13.324(<1), *c* = 15.848(<1) Å, α = 111.18(<1), β = 93.27(<1), γ = 105.51(<1)°, *V* = 1413.1 Å^3, *Z′* = 1; T = 170 K.

48S. SOBPEH (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl radical bis(4-(pentafluorophenyl)-3H-1,2,3,5-dithiadiazol-3-yl radical)

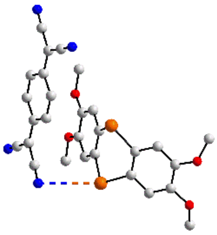
M. A. Nascimento, E. Heyer, J. J. Clarke, H. J. Cowley, A. Alberola, N. Stephaniuk and J. M. Rawson, *Angew. Chem., Int. Ed.*, 2019, **58**, 1371-1375. https://doi.org/10.1002/anie.201812132

Orthorhombic, *Fdd*2, *a* = 18.067(1), *b* = 17.834(1), *c* = 17.144(1) Å, *V* = 5523.8 Å^3, *Z′* = 0.5; T = 150 K.

{Two molecules are connected by a pair of S···S contacts with d(S···S) = 2.97 Å whereby two molecules sit atop of each other. Within this dimer, there are d(S···N) contacts of 3.57& 3.58 Å, being the closest intermolecular S···N contacts}

49. BOMDIQ 2,3,7,8-tetramethoxyselenanthrene 7,7,8,8-tetracyanoquinodimethane

W. Hinrichs and G. Klar, *J. Chem. Res. (S)*, 1982, 336-337.



d(Se···N) = 3.45 Å; C–Se···N = 140.6 & 86.0°; C–N···Se = 95.4°

{1:1 co-crystal. Standard uncertainties not available. One Se forms Se···N interactions with one of the four available N atoms to generate a two-molecule aggregate}

Monoclinic, *P*2₁/*c*: *a* = 10.481(5), *b* = 17.940(6), *c* = 13.818(6) Å, β = 94.99(4)°, *V* = 2588.3 Å^3, *Z′* = 1; T = room temp.

49S. MXTTCQ01 2,3,7,8-tetramethoxythianthrene 7,7,8,8-tetracyanoquinodimethane

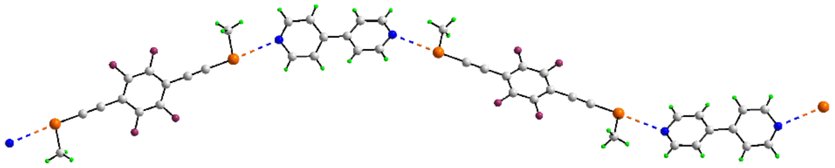
W. Hinrichs and G. Klar, *J. Chem. Res. (S)*, 1982, 336-337.

Monoclinic, *P*2₁/*c*: *a* = 10.441(3), *b* = 17.914(2), *c* = 13.757(3) Å, β = 94.31(2)°, *V* = 2565.8 Å^3, *Z′* = 1; T = room temp.

{Same supramolecular aggregate with d(S···N) = 3.43 Å}

56. IMOQUZ 4,4'-bipyridine 1,2,4,5-tetrafluoro-3,6-bis[(methylselanyl)ethynyl]benzene

A. Dhaka, O. Jeannin, I.-R. Jeon, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2020, **59**, 23583-23587. https://doi.org/10.1002/anie.202011981



d(Se···N) = 3.055(3) Å; (C)C–Se···N = 176.09(11) & 80.01(11)°; C–N···Se = 105.78(18) & 134.83(19)°

{1:1 co-crystal; Se-compound disposed about a centre of inversion; bipyridine molecule disposed about a 2-fold axis; each Se atom forms a Se···N interaction to give a twisted chain}

Monoclinic, *C*2/*c*: *a* = 17.986(1), *b* = 5.654(<1), *c* = 21.470(1) Å, β = 108.64(<1)°, *V* = 2068.6 Å^3, *Z′* = 0.5; T = room temp.

56Te. IMORAG 4,4'-bipyridine 1,2,4,5-tetrafluoro-3,6-bis[(methyltellelanyl)ethynyl]benzene

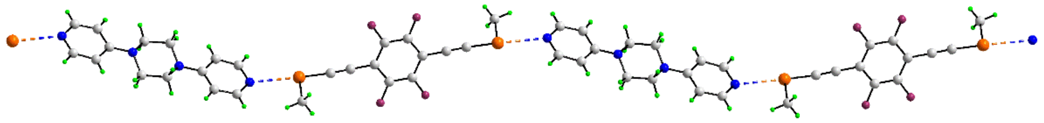
A. Dhaka, O. Jeannin, I.-R. Jeon, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2020, **59**, 23583-23587. https://doi.org/10.1002/anie.202011981

Monoclinic, *C*2/*c*: *a* = 17.927(<1), *b* = 5.698(<1), *c* = 22.219(<1) Å, β = 108.33(<1)°, *V* = 2154.6 Å^3, *Z′* = 0.5; T = room temp.

{Same supramolecular aggregate with d(Te···N) = 2.95 Å}

57. IMORIO 1,2,4,5-tetrafluoro-3,6-bis[(methylselanyl)ethynyl]benzene 1,4-bis(pyridin-4-yl)piperazine

A. Dhaka, O. Jeannin, I.-R. Jeon, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2020, **59**, 23583-23587. https://doi.org/10.1002/anie.202011981



d(Se···N) = 2.995(2) Å; (C)C–Se···N = 171.58(11) & 78.55(13)°; C–N···Se = 103.93(19) & 141.0(2)°

{1:1 co-crystal; each co-former is disposed about a centre of inversion; each Se atom forms a Se···N interaction to give a twisted chain}

Monoclinic, $P2_1/n$: a = 11.132(1), b = 5.915(<1), c = 19.168(3) Å, β = 95.68(<1)°, V = 1255.8 Å^3, Z' = 0.5; T = room temp.

57Te. IMOROU 1,2,4,5-tetrafluoro-3,6-bis[(methylyellanyl)ethynyl]benzene 1,4-bis(pyridin-4-yl)piperazine

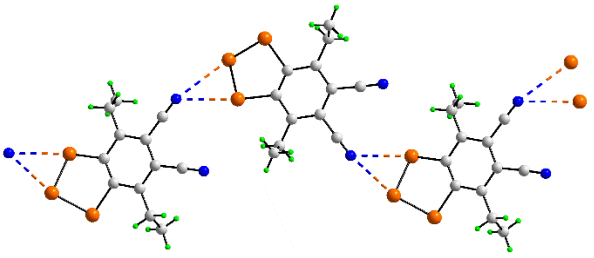
A. Dhaka, O. Jeannin, I.-R. Jeon, E. Aubert, E. Espinosa and M. Fourmigué, *Angew. Chem., Int. Ed.*, 2020, **59**, 23583-23587. https://doi.org/10.1002/anie.202011981

Monoclinic, $P2_1/n$: a = 11.338(<1), b = 5.928(<1), c = 19.258(<1) Å, β = 95.98(<1)°, V = 1287.4 Å^3, Z' = 0.5; T = room temp.

{Same supramolecular aggregate with d(Te···N) = 2.86 Å}

60. SACMUF 5,6-dicyano-4,7-diethylbenzo(1,2,3)triselenole

T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara and T. Akasaka, *J. Org. Chem.*, 2004, **69**, 4716-4723. https://doi.org/10.1021/jo030354j



d(Se···N) = 3.119(12) Å; C–Se···N = 165.7(4)°; Se–Se···N = 74.2(3)°; C–N···Se = 128(1)°

d(Se···N) = 3.345(16) Å; Se–Se···N = 142.3(2) & 63.8(3)°; C–N···Se = 153(1)°

{Bay of three Se atoms; 1,2-Se atoms are connected to a bifurcated nitrile-N atom; helical chain}

Orthorhombic, $P2_12_12_1$: a = 8.200(4), b = 9.501(4), c = 17.347(7) Å, V = 1351.5 Å^3, Z' = 1; T = room temp.

60S. SACMOZ 5,6-dicyano-4,7-diethylbenzo(1,2,3)trithiole

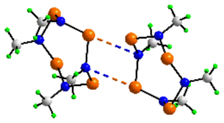
T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, I. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara and T. Akasaka, *J. Org. Chem.*, 2004, **69**, 4716-4723. https://doi.org/10.1021/jo030354j

Orthorhombic, $P2_12_12_1$: a = 7.969(<1), b = 9.257(<1), c = 16.860(2) Å, V = 1243.7 Å^3, Z' = 1; T = 93 K

{Same supramolecular aggregate with d(S···N) = 3.03 & 3.29 Å}

71. MUHDEA 2,4,6,8-tetramethyl-1,3,5,7,2,4,6,8-tetraselenatetrazocane

A. J. Karhu, O. J. Pakkanen, J. M. Rautiainen, R. Oilunkaniemi, T. Chivers and R. S. Laitinen, *Inorg. Chem.*, 2015, **54**, 4990-4997. https://doi.org/10.1021/acs.inorgchem.5b00582



d(Se···N) = 3.225(8) Å; N–Se···N = 174.0(3) & 76.8(3)°; Se–Se···N = 87.4(3) & 103.2(3)°; C–N···Se = 93.8(6)°

{Centrosymmetric dimer; only one of four Se atoms form Se···N interactions; considerably longer Se···N interactions, *i.e.* 3.633(10) & 3.680(10) Å, link molecules into a 2-D array. Also featuring within the dimeric aggregate are Se···Se interactions [3.6290(16) Å] which encompass the {···SeN}$_2$ synthons leading to the dimer}

Monoclinic, $P2_1/n$: a = 6.372(5), b = 12.724(5), c = 14.478(5) Å, β = 93.13(<1)°, V = 1172.1 Å^3, Z' = 1; T = 150 K

71S. TSTMIM 1,3,5,7-tetrasulfur-2,4,6,8-tetramethylimide

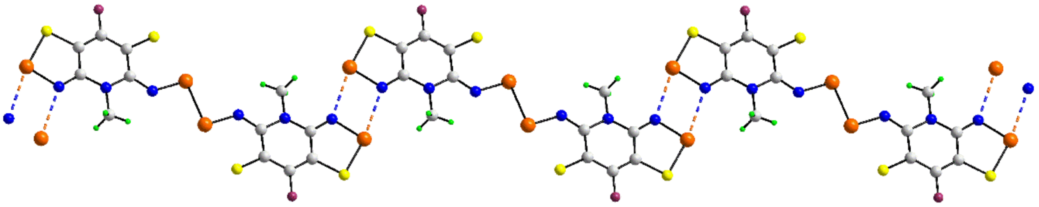
A. L. Macdonald and J. Trotter, *Can. J. Chem.*, 1973, **51**, 2504-2506. https://doi.org/10.1139/v73-377

Orthorhombic, $Fdd2$: a = 25.483(6), b = 15.842(3), c = 5.642(2) Å, V = 2277.7 Å^3, Z' = 0.5; T = room temp

{No intermolecular contacts less than 3.70 Å}

72. BUQGUQ01 5,5'-(diselane-1,2-diyldinitrilo)bis(7-fluoro-4-methyl-4,5-dihydro-6H-[1,2,3]thiaselenazolo[4,5-b]pyridine-6-thione radical)

K. Lekin, A. A. Leitch, J. S. Tse, X. Bao, R. A. Secco, S. Desgreniers, Y. Ohishi and R. T. Oakley, *Cryst. Growth Des.*, 2012, **12**, 4676-4684. https://doi.org/10.1021/cg3009255



d(Se···N) = 2.85 Å; S–Se···N = 169.2°; N–Se···N = 78.3°; Se–N···Se = 101.7°; C–N···Se = 142.3°

{Standard uncertainties not available. Centrosymmetric molecule. Tape; only the ring-Se atoms form Se···N interactions *via* centrosymmetric {SeN···}$_2$ synthons. Within the chains are close 1,5-Se···S contacts [2.78 Å] between the exocyclic Se atoms as well as transannular Se···Se interactions [3.68 Å]. A 3-D architecture is formed through a number of Se···S interactions involving all Se atoms as well as all S atoms with contact distances of 3.12 and 3.67 Å; the longer separations involve the Se$_2$ units with the ring-S atoms}

Monoclinic, *P*2$_1$/*c*: *a* = 4.284(<1), *b* = 13.466(<1), *c* = 15.898(1) Å, β = 79.30(<1)°, *V* = 901.2 Å^3, *Z′* = 0.5; T = room temp.

72S. HOJQII03 5,5'-(disulfanediyldinitrilo)bis(7-fluoro-4-methyl-4,5-dihydro-6H-[1,2,3]dithiazolo[4,5-b]pyridine-6-thione)

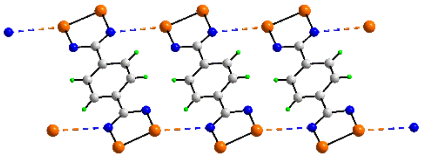
K. Lekin, H. Phan, S. M. Winter, J. W. L. Wong, A. A. Leitch, D. Laniel, W. Yong, R. A. Secco, J. S. Tse, S. Desgreniers, P. A. Dube, M. Shatruk and R. T. Oakley, *J. Am. Chem. Soc*, 2014, **136**, 8050-8062. https://doi.org/10.1021/ja502753t

Monoclinic, *P*2$_1$/*c*: *a* = 4.601(<1), *b* = 12.732(1), *c* = 15.912(1) Å, β = 78.95(<1)°, *V* = 914.9 Å^3, *Z′* = 0.5; T = room temp.

{Same supramolecular aggregation pattern with d(S···N) = 3.09 Å}

76. VINJOR 1,4-bis(3,4-diselena-2,5-diazacyclopentadienyl)benzene

A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 582-588.
https://doi.org/10.1021/ja00002a028



d(Se···N) = 3.43(3) Å; Se–Se···N = 155.6(5)°; N–Se···N = 91.0(9)°; Se–Se···N = 91(1)°; C–N···Se = 145(2)°

d(Se···N) = 3.44(3) Å; Se–Se···N = 152.1(4)°; N–Se···N = 90(1)°; Se–Se···N = 92.5(9)°; C–N···Se = 142(2)°

{Tetra-nuclear molecule. One Se of each ring associates with a translationally related molecule to form a tape. All of the Se atoms (three Se atoms form two contacts and one, three contacts) participate in Se···Se interactions [range: 3.253(6) to 3.792(7) Å] which link chains into a 3-D architecture. High-pressure structure determinations are available with further Se···N interactions: W. Yong, K. Lekin, R. P. C. Bauer, J. S. Tse, S. Desgreniers, R. A. Secco, N. Hirao and R. T. Oakley, *Inorg. Chem.*, 2019, **58**, 3550-3557 https://doi.org/10.1021/acs.inorgchem.9b00142}

Monoclinic, *P*2₁/*n*: *a* = 5.939(13), *b* = 18.764(16), *c* = 9.569(11) Å, β = 101.01(11)°, *V* = 1046.7 Å³, *Z′* = 1; T = room temp.

76S. VINJIL 1,4-bis(3,4-dithia-2,5-diazacyclopentadienyl)benzene

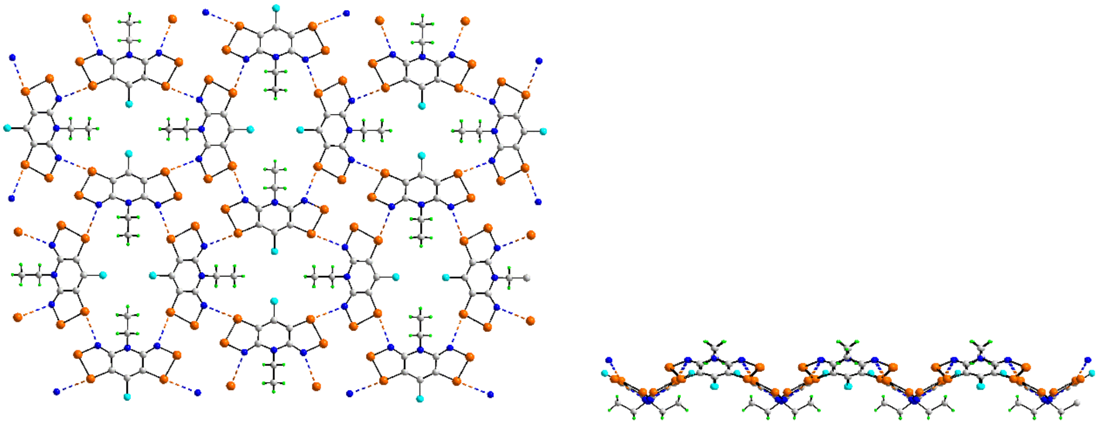
A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 582-588. https://doi.org/10.1021/ja00002a028

Monoclinic, *P*2₁/*n*: *a* = 5.858(5), *b* = 18.732(5), *c* = 9.340(3) Å, β = 101.82(5)°, *V* = 1003.2 Å³, *Z′* = 1; T = room temp.

{Same supramolecular aggregation with d(S···N) = 3.47 & 3.52 Å}

78. AFUDEL01 8-chloro-4-ethyl-4H-bis((1,2,3)diselenazolo)(4,5-b:5',4'-e)pyridinyl radical

C. M. Robertson, A. A. Leitch, K. Cvrkalj, R. W. Reed, D. J. T. Myles, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2008, **130**, 8414-8425. https://doi.org/10.1021/ja801070d



At 100 K: d(Se···N) = 3.339(7) Å; C–Se···N = 165.5(3)°; Se–Se···N = 97.49(12)°; Se–N···Se = 82.4(2)° & C–N···Se = 123.1(5)°

At r.t.: d(Se···N) = 3.378(5) Å; C–Se···N = 165.7(2)°; Se–Se···N = 97.82(9)°; Se–N···Se = 82.26(17)° & C–N···Se = 123.7(4)°

{Molecule has mirror symmetry bisecting the six-membered ring. Two of four Se atoms and the outer N atoms form Se···N interactions that project laterally to form a jagged 2-D array.

One of the Se atoms forming a Se···N contact forms an intramolecular Se···Cl contact of 3.243(2) Å. Intra-layer Se···Se contacts are apparent, *i.e.* 3.4565(10) Å, leading to square Se$_4$ synthons, and 3.5849(11) Å, as well as inter-layer Se···Se contacts: 3.5566(10) and 3.7812(12) Å, within a 3-D architecture}

Tetragonal, $P\bar{4}2_1m$: a = 16.180(1), c = 4.126(<1) Å, V = 1080.3 Å^3, Z' = 0.5; T = 100 K

78S. MOSTOD01 8-chloro-4-ethyl-4H-bis((1,2,3)dithiazolo)(4,5-b:5',4'-e)pyridinyl radical

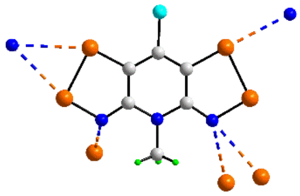
C. M. Robertson, A. A. Leitch, K. Cvrkalj, R. W. Reed, D. J. T. Myles, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2008, **130**, 8414-8425. https://doi.org/10.1021/ja801070d

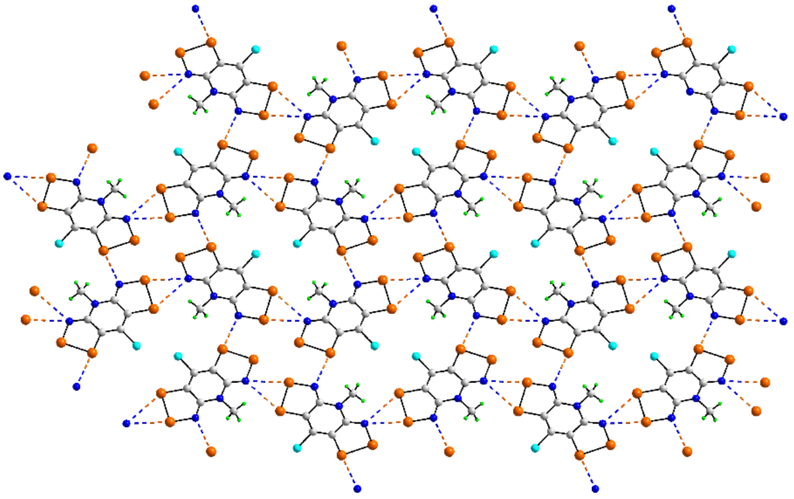
Tetragonal, $P\bar{4}2_1m$: a = 15.793(<1), c = 4.031(<1) Å, V = 1005.4 Å^3, Z' = 0.5; T = 100 K

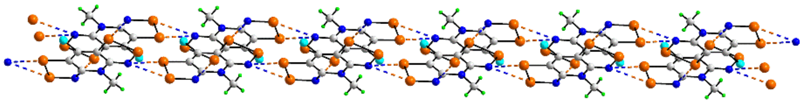
{Same supramolecular aggregation with d(S···N) = 3.35 Å}

81. SUQREC 8-chloro-4-methyl-4H-bis[1,2,3]diselenazolo[4,5-b:5',4'-e]pyridine radical

A. A. Leitch, X. Yu, S. M. Winter, R. A. Secco, P. A. Dube and R. T. Oakley, *J. Am. Chem. Soc.*, 2009, **131**, 7112-7125. https://doi.org/10.1021/ja900853t







d(Se···N) = 3.115(3) Å; N–Se···N = 160.95(11)°; Se–Se···N = 71.62(5)°; Se–N···Se = 79.55(9)°; C–N···Se = 162.2(2)°

d(Se···N) = 3.264(3) Å; C–Se···N = 149.72(11)°; Se–Se···N = 64.94(5)°; Se–N···Se = 102.77(10)°; C–N···Se = 133.3(2)°

d(Se···N) = 3.026(3) Å; C–Se···N = 178.11(10)°; Se–Se···N = 91.49(6)°; Se–N···Se = 107.01(12)°; C–N···Se = 108.41(19)°

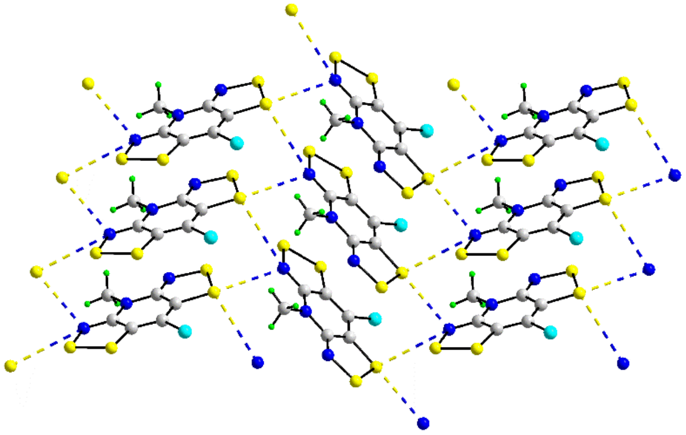
{Non-symmetric, tetra-nuclear molecule. Two Se atoms of one ring are connected to the same ring-N atom, entries 1 & 2. One Se of the second ring forms a single contact, entry 3. The N of the first ring forms a single contact, corresponding to entry 3 while the N of the second ring forms two contacts, corresponding to entries 1 & 2. The result is a flat 2-D array Within the larger cavities, Cl···Cl halogen bonding is evident (3.4029(14) Å *cf.* 3.50 Å for the sum of the van der Waals radii) along with intramolecular Se···Cl contacts [3.1962(11) & 3.2771(10) Å]. Within the layer, Se···Se interactions [3.3133(5) & 3.6999(5) Å], leading to a non-symmetric Se_4 synthon, and transannular Se···Se [3.5087(5) Å] interactions are apparent. Intermolecular Se···Se interactions [3.4488(5) & 3.7460(5) Å], involving Se atoms from both rings, feature within a 3-D architecture}

Monoclinic, $P2_1/n$: a = 4.198(<1), b = 14.318(<1), c = 16.765(<1) Å, β = 96.22(<1)°, V = 1001.7 Å^3, Z' = 1; T = room temp.

81S. MOSTIX01 8-chloro-4-methyl-4H-bis((1,2,3)dithiazolo)(4,5-b:5',4'-e)pyridin-3-yl radical

L. Beer, J. L. Brusso, A. W. Cordes, R. C. Haddon, M. E. Itkis, K. Kirschbaum, R. T. Oakley, D. S. MacGregor, A. A. Pinkerton and R. W. Reed, *J. Am. Chem. Soc.*, 2002, **124**, 9498-9509 https://doi.org/10.1021/ja026118s

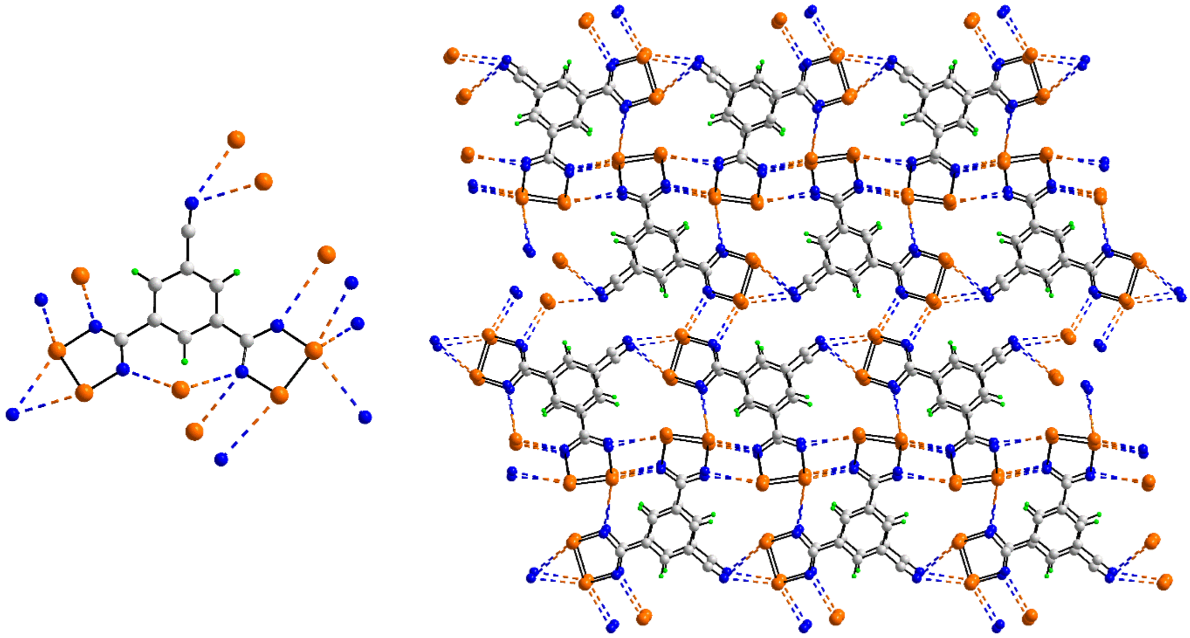
Orthorhombic, $P2_12_12_1$: a = 4.246(1), b = 15.194(5), c = 15.069(4) Å, V = 972.3 Å^3, Z' = 1; T = room temp.



{Chains are formed with d(S···N) = 3.17 Å but the next closest S···N contact is 3.60 Å and leads to a 2-D of a different topology}

85. YAXWAV 3,5-bis(4,5-diselenaimidazol-2-yl)-benzonitrile

A. W. Cordes, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, S. R. Scott and J. V. Waszczak, *Chem. Mater.*, 1993, **5**, 820-825. https://doi.org/10.1021/cm00030a017



1: d(Se···N) = 3.055(14) Å; N–Se···N = 157.3(5)°; Se–Se···N = 69.3(3)°; C–N···Se = 152(1)°

2: d(Se···N) = 3.116(15) Å; N–Se···N = 155.2(5)°; Se–Se···N = 66.5(3)°; C–N···Se = 109(1)°

3: d(Se···N) = 3.104(15) Å; Se–Se···N = 150.2(2)°; N–Se···N = 88.2(5)°; Se–N···Se = 99.2(5)°; C–N···Se = 132.3(9)°

4: d(Se···N) = 3.406(13) Å; Se–Se···N = 158.0(2)°; N–Se···N = 79.2(5)°; Se–N···Se = 89.0(5)°; C–N···Se = 148.5(9)°

5: d(Se···N) = 3.108(12) Å; Se–Se···N = 151.1(2)°; N–Se···N = 92.0(5)°; Se–N···Se = 113.2(6)°; C–N···Se = 123.2(9)°

6: d(Se···N) = 3.243(16) Å; N–Se···N = 162.0(6)°; Se–Se···N = 75.6(2)°; Se–N···Se = 117.1(6)°; C–N···Se = 126(1)°

7: d(Se···N) = 3.300(13) Å; N–Se···N = 157.3(5)°; Se–Se···N = 75.5(2)°; Se–N···Se = 115.1(5)°; C–N···Se = 128.5(9)°

8: d(Se···N) = 3.444(12) Å; Se–Se···N = 140.0(2)°; N–Se···N = 91.4(5)°; Se–N···Se = 112.9(6)°; C–N···Se = 120(1)°

9: d(Se···N) = 2.877(12) Å; Se–Se···N = 163.5(3)°; N–Se···N = 77.7(5)°; Se–N···Se = 103.0(5)°; C–N···Se = 140.3(9)°

10: d(Se···N) = 2.902(14) Å; Se–Se···N = 161.7(3)°; N–Se···N = 76.7(4)°; Se–N···Se = 102.7(5)°; C–N···Se = 139(1)°

11: d(Se···N) = 3.107(15) Å; N–Se···N = 155.0(5)°; Se–Se···N = 68.9(3)°; C–N···Se = 110(1)°

12: d(Se···N) = 3.137(15) Å; N–Se···N = 152.2(4)°; Se–Se···N = 67.5(3)°; C–N···Se = 152(1)°

13: d(Se···N) = 3.355(15) Å; Se–Se···N = 144.4(2)°; N–Se···N = 74.4(5)°; Se–N···Se = 103.5(5)°; C–Se···Se = 124(1)°

14: d(Se···N) = 3.394(13) Å; Se–Se···N = 151.9(2)°; N–Se···N = 73.8(5)°; Se–N···Se = 100.6(5)°; C–Se···Se = 140.3(9)°

{Two independent molecules with each forming a similar pattern of Se···N interactions. 14 independent contacts. Se···N contacts leading to self-association between molecules: the nitrile-N bridges two Se of one ring, entries 1 and 2, and molecules assemble into a supramolecular tape *via* {SeN···}$_2$ synthons, entries 3 and 4. Contacts between the independent molecules: ring-N atoms of two rings are bridged by a Se atom, entries 5 and 6, and one of the Se atoms participating in the formation of the tape, bridges two ring-N atoms, entries 7 and 8. The independent molecules also associate through a non-symmetric {SeN···}$_2$ synthon, entries 9 and 10. The equivalent interactions involving the second independent molecule only correspond to entries 11 and 12 [Se···N(nitrile)], and 13 and 14 (leading to tapes). In this scheme, for each molecule, two Se atoms form a single interaction, one forms two interactions and the fourth Se atom forms three interactions. Result: 3-D array. Additonal Se…Se contacts are present within the architecture such as transannular interactions within {SeN···}$_2$ synthons [3.726(2) Å], supporting Se···N interactions: 3.534(3), 3.771(3) & 3.790(3) Å as well as face-to-face contacts between the rings: 3.170(4) & 3.284(4) Å and 3.227(4) & 3.259(4) Å}

Monoclinic, $P2_1/c$: *a* = 7.124(4), *b* = 30.500(20), *c* = 10.874(2) Å, β = 105.46(3)°, *V* = 2277.2 Å^3, *Z′* = 2; T = room temp.

85S. YAXVUO 3,5-bis(4,5-dithiaimidazol-2-yl)-benzonitrile

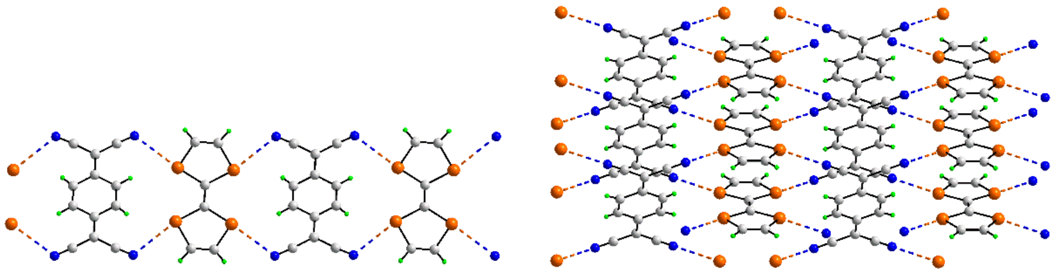
A. W. Cordes, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, S. R. Scott and J. V. Waszczak, *Chem. Mater.*, 1993, **5**, 820-825. https://doi.org/10.1021/cm00030a017

Monoclinic, $P2_1/c$: *a* = 7.000(20), *b* = 30.050(6), *c* = 10.713(8) Å, β = 104.80(10)°, *V* = 2178.7 Å^3, *Z′* = 2; T = room temp.

{A 3-D array features S···N numerous contacts between 2.96 and 3.28 Å}

88. ZUGRUO 2,2',5,5'-tetraselenafulvalene 7,7,8,8-tetracyano-p-quinodimethane

P. W. R. Corfield and S. J. La Placa, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1996, **52**, 384-387. https://doi.org/10.1107/S0108768195012286



d(Se···N) = 3.165(3) Å; C–Se···N = 169.54(8) & 77.59(12)°; N–Se···N = 122.1(2)°

d(Se···N) = 3.177(3) Å; C–Se···N = 175.00(9) & 82.35(13)°; N–Se···N = 122.4(2)°

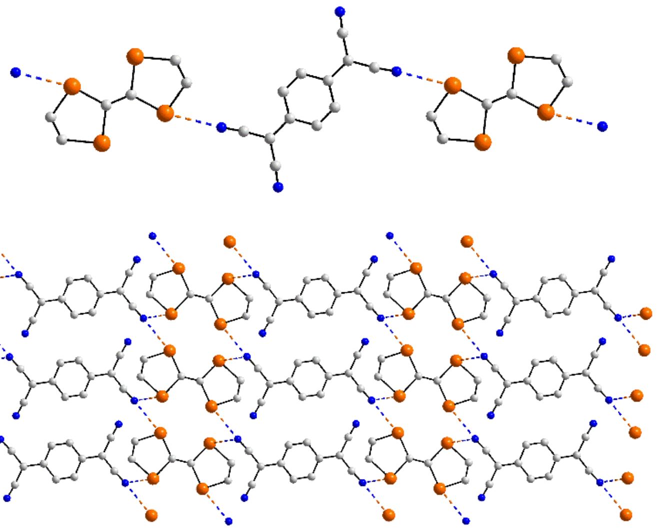
{1:1 Co-crystal with each co-former being centrosymmetric. Each Se and N atom forms a single contact to generate a 2-D array with a flat topology}

Monoclinic, $P2_1/c$: a = 12.505(<1), b = 3.872(<1), c = 18.504(<1) Å, β = 104.13(<1)°, V = 868.9 Å^3, Z' = 0.5; T = room temp.

88Te. VEVFIL tetratellurafulvalene tetracyanoquinodimethane

D. O. Cowan, M. D. Mays, T. J. Kistenmacher, T. O. Poehler, M. A. Beno, A. M. Kini, J. M. Williams, Y.-K. Kwok, K. D. Carlson, L. Xiao, J. J. Novoa and M.-H. Whangbo, *Mol. Cryst. Liq. Cryst*. 1990, **181**, 43-58; https://doi.org/10.1080/00268949008035991

Triclinic, $P\bar{1}$: a = 3.947(3), b = 7.397(4), c = 16.622(10) Å, α = 86.58(5), β = 83.27(6), γ = 80.69(6)°, V = 475.2 Å^3, Z' = 0.5; T = room temp.



{Chains are formed with d(Te···N) = 3.05 Å but the next closest Te···N contact is 3.78 Å (running horizontally across the page) and leads to a 2-D of a different topology as for **ECITAL** below; diagonally opposite nitrile-N atoms form both interactions}

88S. TTFTCQ01 $\Delta^{2,2'}$-bis-1,3-dithiole-7,7,8,8-tetracyanoquinodimethanide

T. J. Kistenmacher, T. E. Phillips and D. O. Cowan, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem*., 1974, **30**, 763-768. https://doi.org/10.1107/S0567740874003669

Monoclinic, $P2_1/c$: a = 12.298(6), b = 3.819(2), c = 18.468(8) Å, β = 104.46(4)°, V = 839.9 Å^3, Z' = 0.5; T = room temp.

{A similar supramolecular aggregation with d(S···N) = 3.20 & 3.25 Å}