Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Hydrogen and Chalcogen Bonds in Crystals of Chalcogenadiazolecarboxylic Acids – Competition or Cooperation?

Jan Alfuth,[a]* Agnieszka Czapik,[b] Beata Zadykowicz,[c] Teresa Olszewska[a]

[a] *Department of Organic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland*
[b] *Department of Organic Stereochemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poznań 61-614, Poland*
[c] *Laboratory of Luminescence Research, Faculty of Chemistry, University of Gdańsk, 80-308 Gdańsk, Poland*

** Corresponding author: phone: +48 58 347 26 19; e-mail: jan.alfuth@pg.edu.pl*

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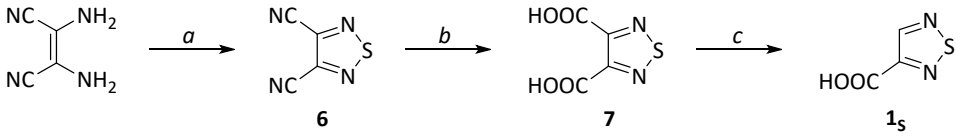
Nuclear Magnetic Resonance (NMR)

All the NMR spectra (^{1}H, ^{13}C) were recorded on the Varian Unity Inova 500 MHz spectrometer. The samples were dissolved in deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6). Chemical shifts are given in parts per million (ppm) and referenced to the appropriate residual solvent peak. Peaks are described as singlets (s), doublets (d), triplets (t), quartets (q), multiplets (m) and broad singlets (bs). All of the data were acquired and processed with MestReNova software.

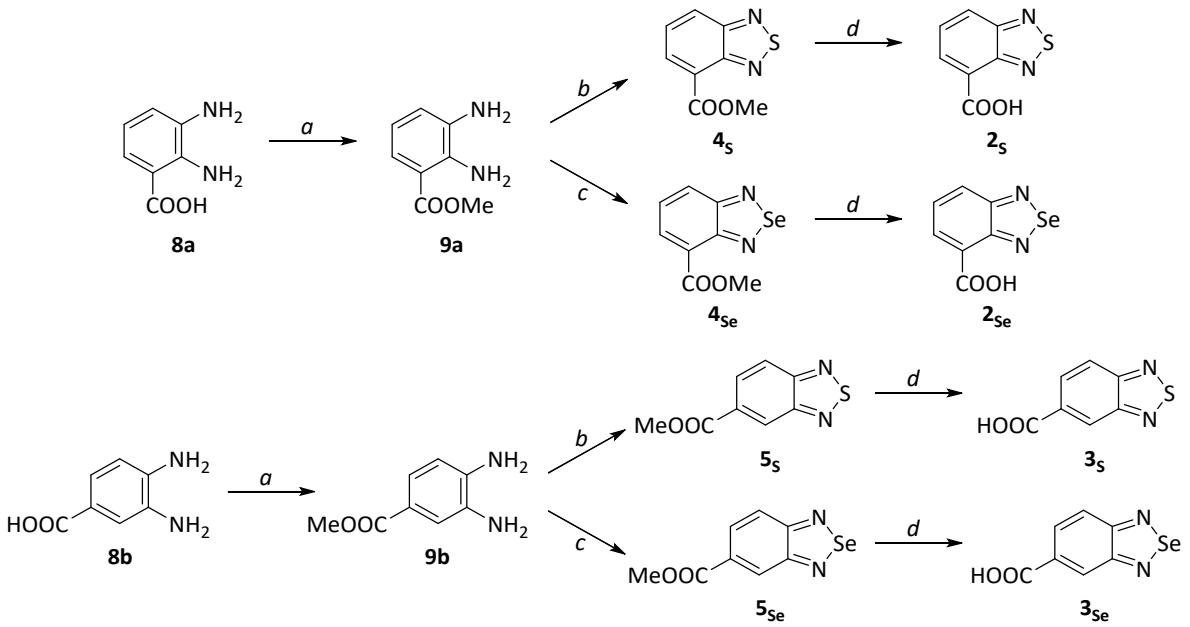
Experimental procedures

1,2,5-Thiadiazole-3-carboxylic acid (**1_S**) was prepared according to the route shown in Scheme S1 starting from 1,2,5-thiadiazole-3,4-dicarbonitrile (**6**), which was obtained from 2,3-diaminomaleonitrile and then hydrolysed following the procedure described in ref. S1. The obtained 1,2,5-thiadiazole-3,4-dicarboxylic acid (**7**) was then decarboxylated at about 200°C under vacuum.



Scheme S1 Synthetic route to obtain 1,2,5-thiadiazole-3-carboxylic acid (**1_S**): (*a*) $SOCl_2$, Py, CH_3CN, 0°C, then RT, 5h; (*b*) 6M HCl_{aq}, reflux, overnight; (*c*) 200°C, vacuum, 5 min.

2,1,3-Benzochalcogenadiazolecarboxylic acids **2**–**3** were synthesised according to the route shown in Scheme S2 using a slightly modified procedure presented in ref. S2. 2,3-Diaminobenzoic acid (**8a**) used in the synthesis was obtained according to the procedure presented in ref. S3. 3,4-Diaminobenzoic acid (**8b**) was purchased from Alfa Aesar.

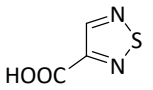


Scheme S2 Synthetic route to obtain the 2,1,3-benzochalcogenadiazolecarboxylic acids **2**–**3**: (*a*) $SOCl_2$, MeOH, 0°C, then 45°C, overnight; (*b*) $SOCl_2$, Et_3N, DCM, 0°C, then reflux, overnight; (*c*) SeO_2, anhydrous MeOH, reflux, 5 min; (*d*) 1M $NaOH_{aq}$, dioxane, RT, overnight, then 1M HCl_{aq}.

Preparation of 1,2,5-thiadiazole-3-carboxylic acid ($\mathbf{1_S}$)

1,2,5-Thiadiazole-3,4-dicarboxylic acid (**7**) (360 mg, 2.07 mmol) was placed in a round-bottom flask, vacuum was applied (with a water aspirator pump), and the substrate was heated to around 200°C for 5 minutes. The substrate melted and darkened and a colourless gas evolved (CO_2). The residue was cooled to room temperature, dissolved in AcOEt, filtered and evaporated to dryness. ^{13}C NMR spectra showed that the residue contained the unreacted substrate, so the product was purified by column chromatography on silica gel using hexane/AcOEt/AcOH mixture (7:3:1 v/v/v) as the eluent to give 130 mg (1 mmol, 48%) of pure 1,2,5-thiadiazole-3-carboxylic acid ($\mathbf{1_S}$).

1,2,5-thiadiazole-3-carboxylic acid ($\mathbf{1_S}$)



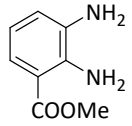
$\mathbf{1_S}$

White powder, mp 162–164°C. ^1H NMR (500 MHz, DMSO-d_6): δ 14.01 (bs, 1H), 9.22 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 161.73, 155.96, 154.32.

Crystals suitable for XRD analysis were obtained by dissolving $\mathbf{1_S}$ in a mixture of $PhCH_3$ and AcOEt and slow evaporation of the latter solvent at room temperature.

General procedure for preparation of methyl diaminobenzoates

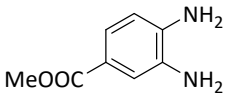
2,3-Diaminobenzoic acid (**8a**) or 3,4-diaminobenzoic acid (**8b**) (456 mg, 3 mmol) was placed in a two-neck round-bottom flask and dissolved in 25 ml of MeOH. The solution was cooled in an ice bath and $SOCl_2$ (2.2 ml, 3.57 g, 30 mmol, 10 eq) was added dropwise. The ice bath was removed and the mixture was stirred at 45°C overnight. The reaction mixture was cooled to room temperature and poured into a beaker containing 100 ml of water. The solution was neutralised with solid K_2CO_3 until the pH was basic and then extracted with AcOEt (4 times). The extracts were combined, dried over $MgSO_4$ and the solvent was removed. The oily residue was purified by column chromatography on silica gel using hexane/AcOEt mixture (1:1 v/v) as the eluent to give pure methyl 2,3-diaminobenzoate (**9a**) or methyl 3,4-diaminobenzoate (**9b**).



9a

methyl 2,3-diaminobenzoate (**9a**)

Yield: 68%. Brown oil. ^1H NMR (500 MHz, DMSO-d_6): δ 7.49 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.87 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.62 (dd, *J* = 8.1, 7.5 Hz, 1H), 4,48 (bs, 4H), 3.89 (s, 3H).



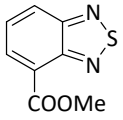
9b

methyl 3,4-diaminobenzoate (**9b**)

Yield: 74%. Light yellow crystalline solid. ^1H NMR (500 MHz, DMSO-d_6): δ 7.49 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.87 (s, 3H), 3,63 (bs, 4H).

General procedure for preparation of methyl 2,1,3-benzothiadiazolecarboxylates

Methyl 2,3-diaminobenzoate (**9a**) or methyl 3,4-diaminobenzoate (**9b**) (0.33 g, 2 mmol) was dissolved in 10 ml of DCM and then triethylamine (1.2 ml, 0.83 g, 8.16 mmol, 4 eq) was added. The solution was cooled in an ice bath and solution of $SOCl_2$ (0.29 ml, 0.476 g, 4 mmol, 2 eq) in 1 ml of DCM was added dropwise. The ice bath was removed and the mixture was refluxed overnight. Then the mixture was cooled and filtered through celite and evaporated. The product was purified by column chromatography on silica gel using hexane/AcOEt mixture (8:2 v/v) as the eluent to give pure $\mathbf{4_S}$ or $\mathbf{5_S}$.

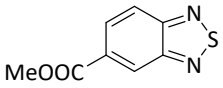


4_S

methyl 2,1,3-benzothiadiazole-4-carboxylate (**4_S**)

Yield: 81%. Straw-coloured solid, mp 95–96°C. ^{1}H NMR (500 MHz, $CDCl_3$): 8.41 (dd, *J* = 7.0, 1.2 Hz, 1H), 8.27 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.72 (dd, *J* = 8.8, 7.0 Hz, 1H), 4.10 (s, 3H).

Crystals suitable for XRD analysis were obtained by dissolving **4_S** in AcOEt and slow evaporation at room temperature.



5_S

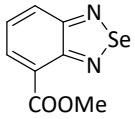
methyl 2,1,3-benzothiadiazole-5-carboxylate (**5_S**)

Yield: 63%. Straw-coloured solid, mp 84–86°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.23 (dd, *J* = 9.2, 1.6 Hz, 1H), 8.07 (d, *J* = 9.1 Hz, 1H), 4.03 (s, 3H).

Crystals suitable for XRD analysis were obtained by dissolving **5_S** in AcOEt and slow evaporation at room temperature.

General procedure for preparation of methyl 2,1,3-benzoselenadiazolecarboxylates

Methyl 2,3-diaminobenzoate (**9a**) or methyl 3,4-diaminobenzoate (**9b**) (0.33 g, 2 mmol) was dissolved in 7 ml of anhydrous MeOH and then a solution of SeO_2 (0.27 g, 2.4 mmol, 1.2 eq) in 2 ml of anhydrous MeOH was added in one portion. After several seconds, a grey precipitate was formed. The mixture was heated to reflux to dissolve all contents and the clear solution was left to slowly cool down to room temperature. Crystalline product (**4_{Se}** or **5_{Se}**) was filtered, washed with cold MeOH and dried.

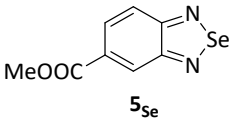


4_{Se}

methyl 2,1,3-benzoselenadiazole-4-carboxylate (**4_{Se}**)

Yield: 95%. Grey needles, mp 159–160°C. ^{1}H NMR (500 MHz, DMSO-d_6): 8.15 (dd, *J* = 6.8, 1.2 Hz, 1H), 8.12 (dd, *J* = 9.0, 1.2 Hz, 1H), 7.66 (dd, *J* = 9.0, 6.8 Hz, 1H), 3.93 (s, 3H).

Crystals of **4_{Se}** suitable for XRD analysis were grown from hot MeOH.



5_{Se}

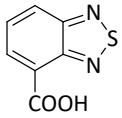
methyl 2,1,3-benzoselenadiazole-5-carboxylate (**5_{Se}**)

Yield: 75%. Grey needles, mp 143–144°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.45 (s, 1H), 7.96 (s, 2H), 3.94 (s, 3H).

Crystals of **5_{Se}** suitable for XRD analysis were grown from hot MeOH.

General procedure for preparation of 2,1,3-benzochalcogenadiazolecarboxylic acids

Methyl 2,1,3-benzochalcogenadiazolecarboxylate (**4_S**, **4_{Se}**, **5_S** or **5_{Se}**) (1 mmol) was dissolved in 5 ml of dioxane and 1.2 ml (1.2 mmol, 1.2 eq) of 1M $NaOH_{aq}$ was added and the mixture was stirred at room temperature overnight. Then 5 ml of distilled water was added and the mixture was extracted with AcOEt (to remove the unreacted ester). Then the aqueous solution was acidified with 1M HCl_{aq} and extracted with AcOEt (3 times). The extracts were combined, dried over $MgSO_4$ and the solvent was removed to give 2,1,3-benzochalcogenadiazolecarboxylic acids (**2_S**, **2_{Se}** or **3_S**).
In the case of **3_{Se}** the addition of 1M HCl_{aq} caused a grey precipitate to form, which was poorly soluble in most common solvents. The precipitate was filtered, washed with Et_2O and dried.

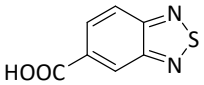


2_S

2,1,3-benzothiadiazole-4-carboxylic acid (**2_S**)

Yield: 81%. Cream-coloured solid, mp 185–189°C. ^{1}H NMR (500 MHz, DMSO-d_6): 13.39 (s, 1H), 8.36 (dd, *J* = 8.8, 1.1 Hz, 1H), 8.31 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.83 (dd, *J* = 8.8, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): 165.97, 155.53, 151.97, 133.47, 129.52, 126.29, 124.53.

Crystals suitable for XRD analysis were obtained by dissolving **2_S** in AcOEt and slow evaporation at room temperature.

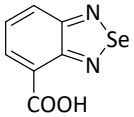


3_S

2,1,3-benzothiadiazole-5-carboxylic acid (**3_S**)

Yield: 85%. Cream-coloured solid, mp 220–222°C. ^{1}H NMR (500 MHz, DMSO-d_6): 13.58 (s, 1H), 8.64 (dd, *J* = 1.5, 0.9 Hz, 1H), 8.19 (dd, *J* = 9.1, 0.8 Hz, 1H), 8.16 (dd, *J* = 9.2, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): 167.11, 156.19, 154.26, 132.40, 129.34, 123.79, 121.92.

Crystals suitable for XRD analysis were obtained by dissolving **3_S** in AcOEt and slow evaporation at room temperature.

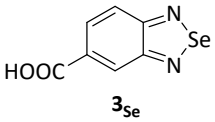


2_{Se}

2,1,3-benzoselenadiazole-4-carboxylic acid (**2_{Se}**)

Yield: 87%. Cream-coloured solid, mp 213–214°C. ^{1}H NMR (500 MHz, DMSO-d_6): 13.22 (s, 1H), 8.12 (dd, *J* = 6.8, 1.2 Hz, 1H), 8.09 (dd, *J* = 8.9, 1.2 Hz, 1H), 7.65 (dd, *J* = 9.0, 6.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): 166.46, 160.66, 156.91, 132.95, 128.85, 128.04, 126.06.

Crystals of **2_{Se}** suitable for XRD analysis were grown from hot dioxane.



3_{Se}

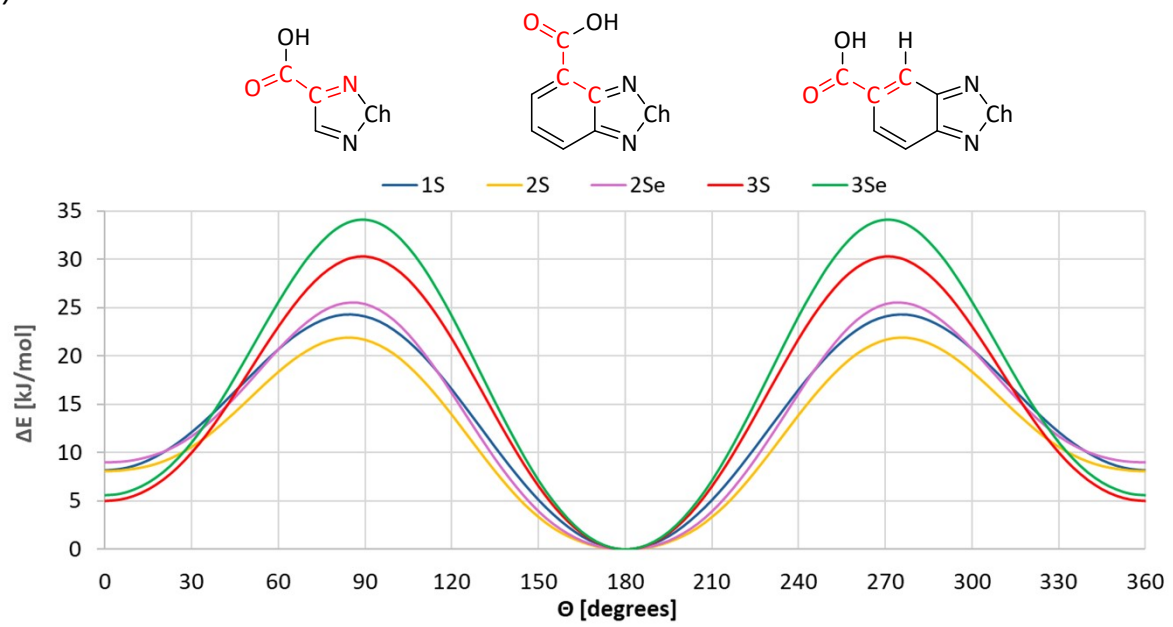
2,1,3-benzoselenadiazole-5-carboxylic acid (**3_{Se}**)

Yield: 68%. Grey solid, mp 286–287°C. ^{1}H NMR (500 MHz, DMSO-d_6): 13.47 (s, 1H), 8.41 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.96 (dd, *J* = 9.3, 1.7 Hz, 1H), 7.92 (dd, *J* = 9.3, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): 167.33, 161.15, 159.60, 131.61, 128.29, 125.85, 123.70.

Crystals suitable for XRD analysis were obtained by dissolving **3_{Se}** in a mixture of 1-butanol and THF and very slow evaporation at room temperature.

Theoretical calculations

a)



b)

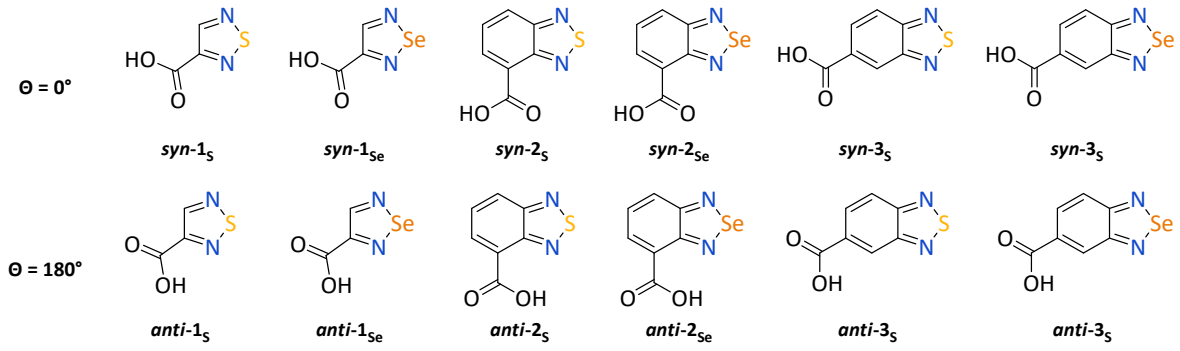
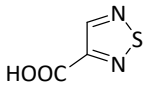
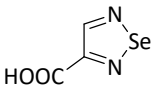
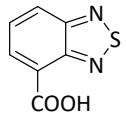
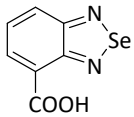
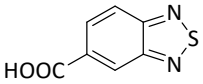
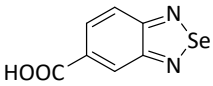
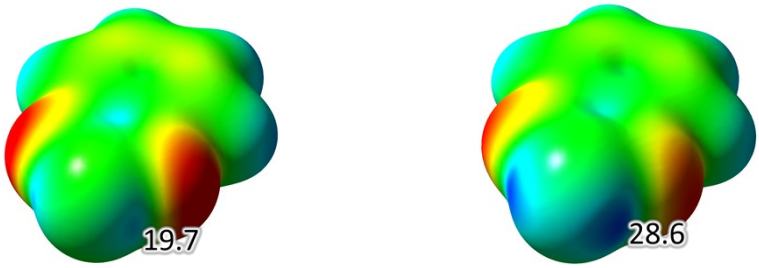


Figure S1 a) Potential energy surface scan for the rotation of carboxyl group through a C–C bond in the investigated molecules (**1**–**3**). Selected dihedral angle are marked in red (Ch = S or Se); b) Molecular structures of the *syn* and *anti* conformations of compounds **1**–**3**.

Table S1 The calculated intermolecular interaction energies (in kcal/mol) within synthons **A**, **B** and **D** formed by the studied compounds together with the optimised dimers. B3LYP/6-31++G** and B3LYP/6-31G** level of theory was used for the sulphur and selenium derivatives, respectively. Only centrosymmetric versions of the synthons **A**. For the synthon **B**, three different relative arrangements of molecules were chosen.

Compound	synthon				
	A	**B1**	**B2**	**B3**	**D**
 **1_S**	**–14.9**	**–1.9**	**–2.1**	**–0.8**	**–7.6**
 **1_{Se}**	**–15.4**	**–4.2**	**–4.3**	**–2.8**	**–9.6**
 **2_S**	**–15.2**	**–1.4**	**–1.7**	**–1.6**	**–7.2**
 **2_{Se}**	**–15.5**	**–3.2**	**–3.7**	**–3.5**	**–9.1**
 **3_S**	**–15.9**	**–1.5**	**–1.4**	**–1.5**	**–7.6**
 **3_{Se}**	**–16.3**	**–3.6**	**–3.4**	**–3.5**	**–9.7**



2,1,3-benzothiadiazole **2,1,3-benzoselenadiazole**

Figure S2 Molecular electrostatic potential maps of 2,1,3-benzochalcogenadiazoles mapped on 0.002 au electron density isosurface. The colour scale corresponds to values ranging from −0.04 (red) to +0.05 au (blue). The most positive ESP values for the σ-holes of S or Se are indicated in kcal/mol.

X-Ray crystallography

Table S2 Crystal data, data collection and structure refinement details for all structures.

	1$_S$	**2$_S$**	**3$_S$**	**4$_S$**	**5$_S$**
CCDC number	2332628	2332629	2332630	2332631	2332632
Chemical formula	$C_3H_2N_2O_2S$	$C_7H_4N_2O_2S$	$C_7H_4N_2O_2S$	$C_8H_6N_2O_2S$	$C_8H_6N_2O_2S$
Mr	130.13	180.18	180.18	194.21	194.21
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	130	100	130	130	130
a, *b*, *c* (Å)	3.68025 (19), 9.5291 (6), 13.5746 (7)	3.70347 (15), 6.3835 (3), 29.2533 (11)	6.9301 (4), 7.3617 (4), 8.2491 (4)	3.9220 (1), 17.4283 (4), 11.8780 (3)	20.3375 (6), 3.81288 (10), 22.5207 (7)
α, *β*, *γ* (°)	83.751 (5), 87.678 (4), 81.873 (5)	90, 92.866 (4), 90	91.500 (5), 107.919 (5), 115.929 (6)	90, 91.753 (2), 90	90, 109.866 (3), 90
V (Å^3)	468.32 (4)	690.72 (5)	353.71 (4)	811.53 (3)	1642.43 (9)
Z	4	4	2	4	8
D_x (Mg m^{-3})	1.846	1.733	1.692	1.590	1.571
Radiation type	Cu *Kα*	Mo *Kα*	Cu *Kα*	Cu *Kα*	Cu *Kα*
μ (mm^{-1})	5.29	0.42	3.71	3.28	3.24
Crystal size (mm)	0.40 × 0.15 × 0.05	0.30 × 0.04 × 0.02	0.20 × 0.17 × 0.05	0.55 × 0.04 × 0.03	0.50 × 0.05 × 0.02
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6541, 1932, 1889	5655, 1485, 1279	2715, 2715, 2521	7413, 1676, 1487	13639, 3379, 2983
R_{int}	0.036	0.038	0.045	0.037	0.032
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.135, 1.09	0.040, 0.081, 1.09	0.035, 0.097, 1.06	0.032, 0.089, 1.05	0.039, 0.107, 1.04
No. of parameters	147	110	114	119	237
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.87, –0.53	0.36, –0.29	0.33, –0.28	0.24, –0.38	0.44, –0.33

Table S2 Crystal data, data collection and structure refinement details for all structures. *(continued)*

	$\mathbf{2}_{Se}$	$\mathbf{3}_{Se}$	$\mathbf{4}_{Se}$	$\mathbf{5}_{Se}$
CCDC number	2332633	2332634	2332635	2332636
Chemical formula	$C_7H_4N_2O_2Se$	$C_7H_4N_2O_2Se$	$C_8H_6N_2O_2Se$	$C_8H_6N_2O_2Se$
Mr	227.08	227.08	241.11	241.11
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	130	130	130
a, *b*, *c* (Å)	12.8823 (6), 3.76622 (18), 15.6812 (8)	8.0711 (3), 7.5844 (2), 12.2026 (4)	10.02071 (14), 3.83488 (5), 21.0716 (3)	3.97381 (10), 6.41163 (17), 33.4053 (7)
α, *β*, *γ* (°)	90, 112.529 (6), 90	90, 105.733 (3), 90	90, 95.3939 (13), 90	90, 92.357 (2), 90
V (Å^3)	702.75 (7)	718.99 (4)	806.16 (2)	850.40 (4)
Z	4	4	4	4
D_x (Mg m^{-3})	2.146	2.098	1.987	1.883
Radiation type	Mo *Kα*	Cu *Kα*	Cu *Kα*	Cu *Kα*
μ (mm^{-1})	5.29	6.72	6.04	5.73
Crystal size (mm)	0.40 × 0.03 × 0.02	0.10 × 0.02 × 0.01	0.45 × 0.10 × 0.03	0.60 × 0.06 × 0.05
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5870, 1487, 1217	11740, 1498, 1462	6542, 1662, 1604	2689, 2689, 2664
R_{int}	0.055	0.037	0.024	0.059
$R[F^2 > 2\ \sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.083, 1.05	0.041, 0.111, 1.20	0.023, 0.059, 1.08	0.048, 0.114, 1.21
No. of parameters	110	113	119	121
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.82, –1.02	1.60, –0.67	0.32, –0.60	0.75, –0.78

Crystal structures of methyl 2,1,3-benzochalcogenadiazolecarboxylates

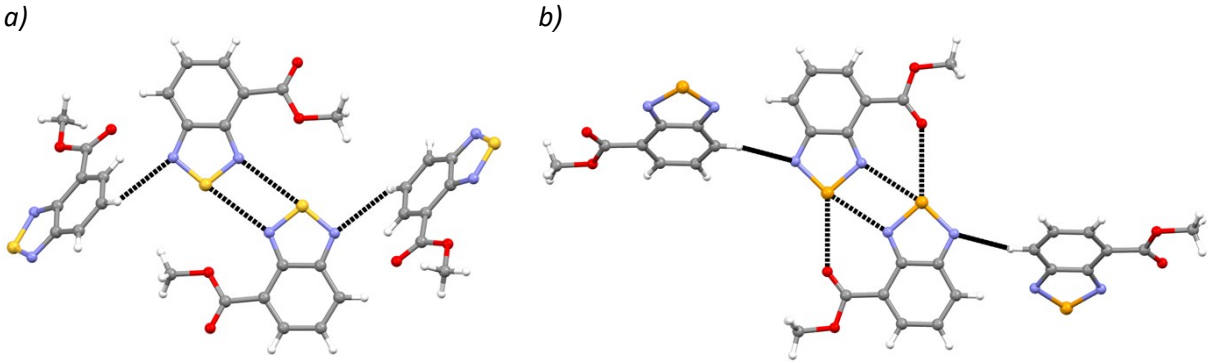


Figure S3 Crystal structures of $\mathbf{4_S}$ (a) and $\mathbf{4_{Se}}$ (b). In both cases molecules aggregate most importantly through $[Ch\cdots N]_2$ synthons. In the crystal lattice of $\mathbf{4_{Se}}$, additional Se···O=C interaction is present. The chalcogen-bonded dimers are connected by C_{Ar}–H···N HBs.

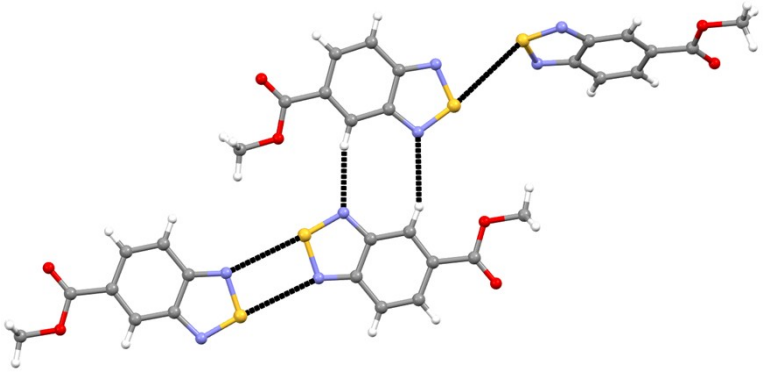


Figure S4 Crystal structure of $\mathbf{5_S}$. The asymmetric unit consists of two crystallographically independent molecules A and B. The molecules A form $[S\cdots N]_2$ synthons and the molecules B only contact with each other by S···S interactions. Molecules A and B contact each other laterally through C_{Ar}–H···N HBs.

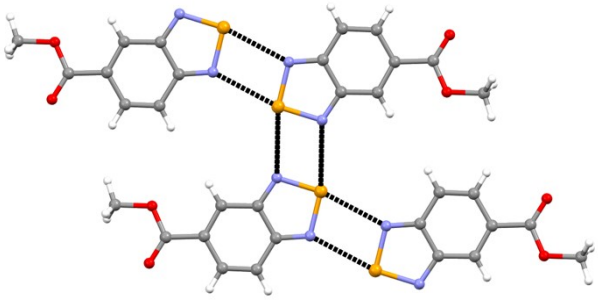


Figure S5 Crystal structure of $\mathbf{5_{Se}}$. The molecules aggregate into polymeric structures through centrosymmetric $[Se\cdots N]_2$ synthons.

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