Supplementary Information

for:

Long-range Supramolecular Synthon Polymorphism: A Case Study of Two New Polymorphic Cocrystals of Ph_2Te_2 – 1,4-$C_6F_4I_2$.

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Energy frameworks

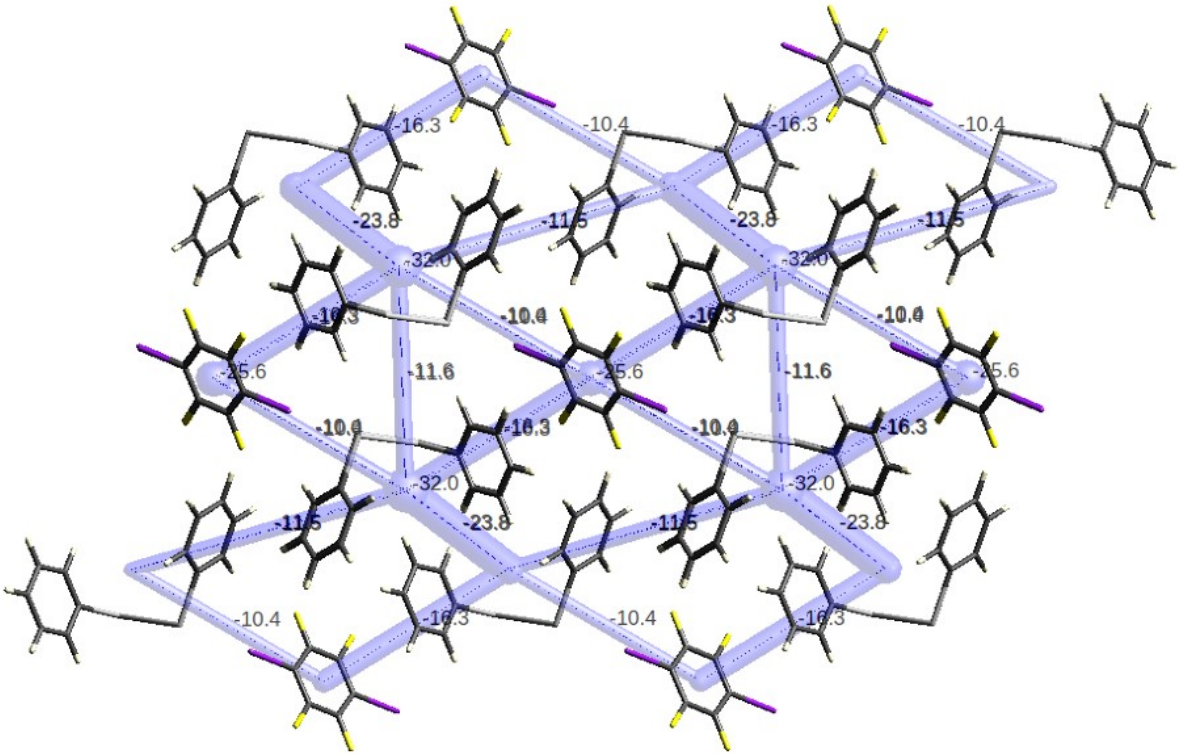


Figure S1

Showing the fragments of the energy framework **1α**. Intermolecular interaction energy values are given in kJ/mol

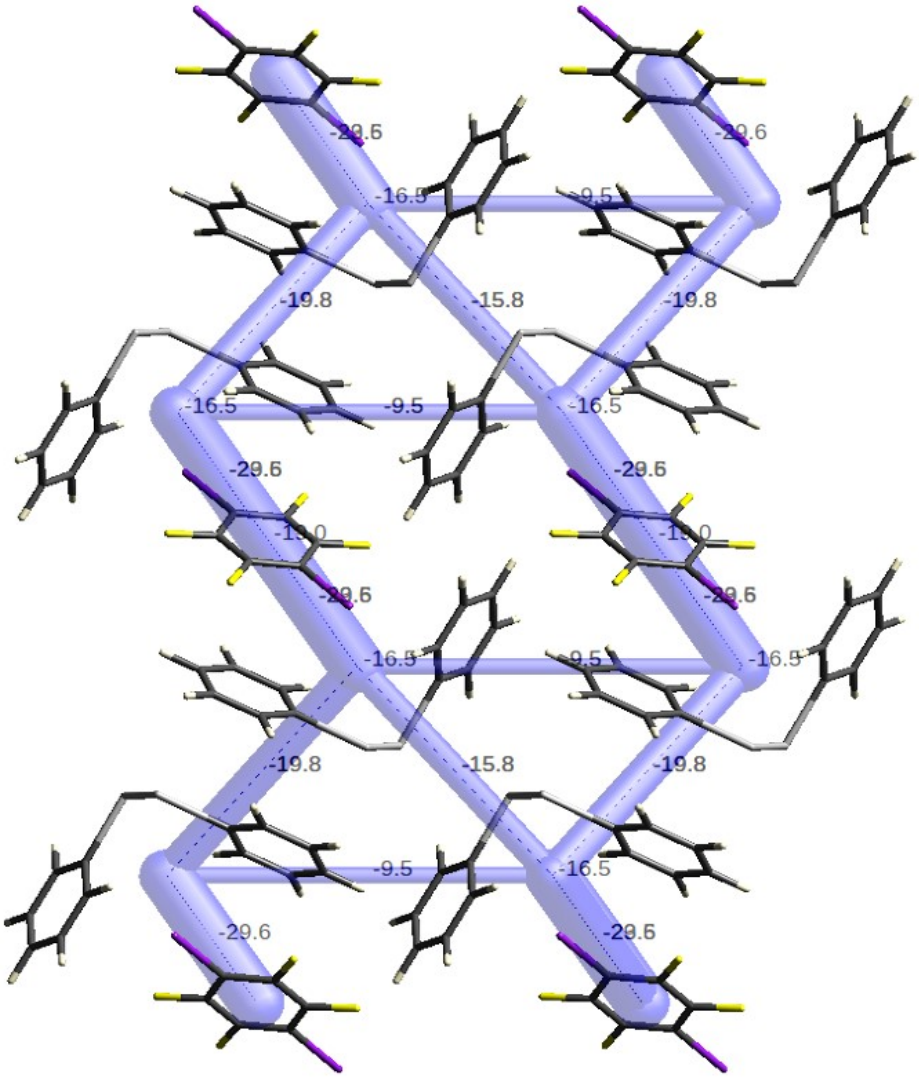


Figure S2
Showing the fragments of the energy framework **1β**. Intermolecular interaction energy values are given in kJ/mol

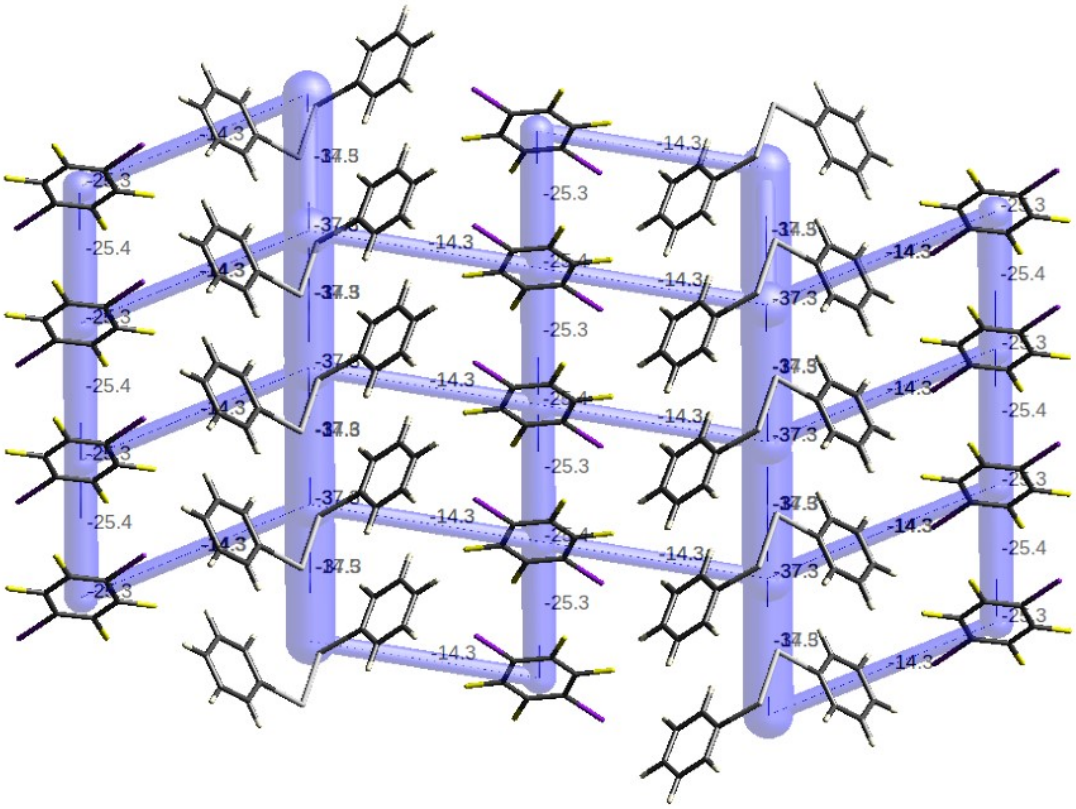


Figure S3
Showing the fragments of the energy framework of **1γ** . Intermolecular interaction energy values are given in kJ/mol

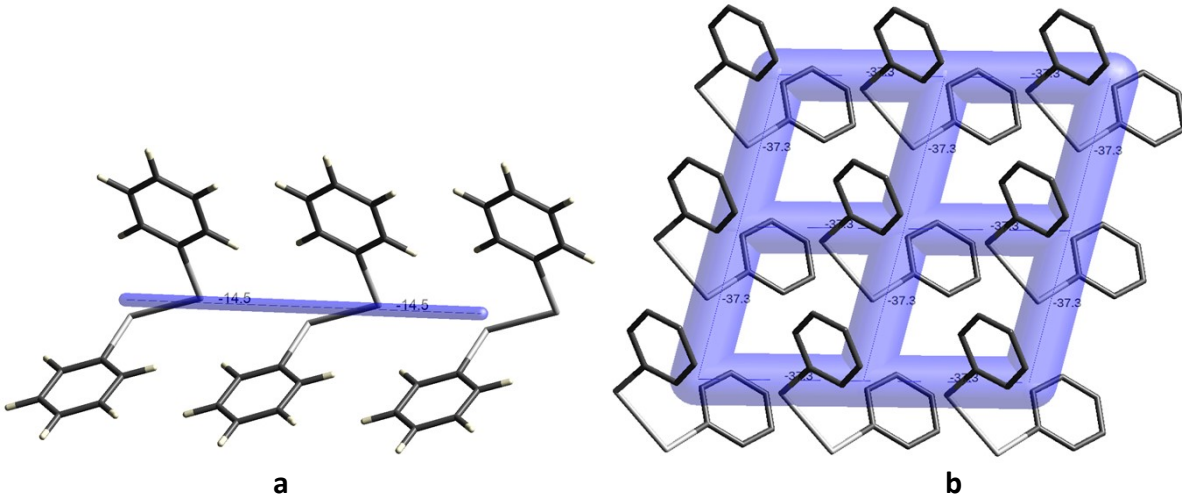
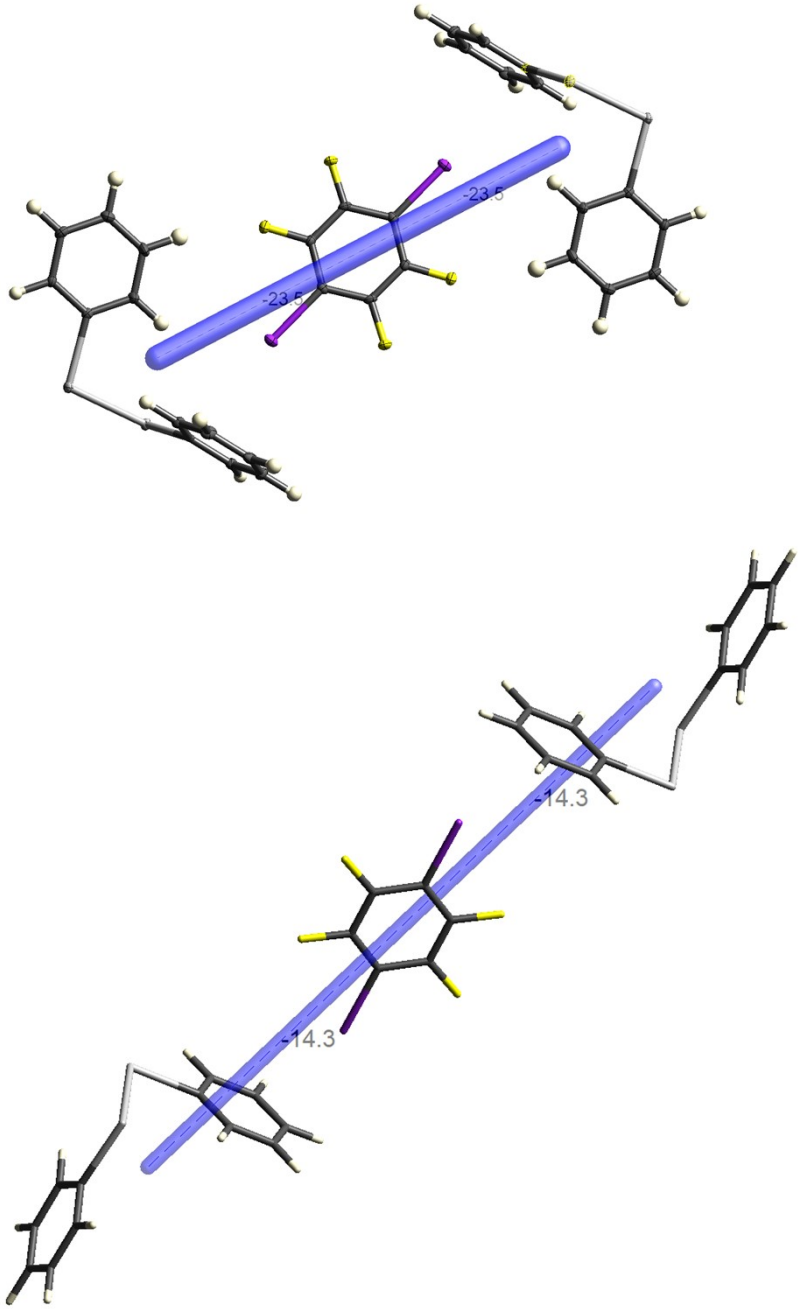


Figure S4
Showing the fragments of the energy framework of Ph2Te2 chains (a) **1β** and layers (b) **1γ** . Intermolecular interaction energy values are given in kJ/mol



a b

Figure S5
Showing the I---π(Ph) HaBs in the fragments of the energy framework (a) **1β** and (b) **1γ** . Intermolecular interaction energy values are given in kJ/mol

Periodic DFT calculations

Energy contributions

Table S1. Cohesion energies and their contributions for native and putative polymorphs of Ph2Te2 and Ph2Se2 as revealed by periodic DFT calculations.

	E_{cryst}^{total}/Z (a.u.)	$E_{mol\cdot cryst}^{total}$ (a.u.)	$E_{mol\cdot cryst}^{d3}$ (a.u.)	$E_{mol\cdot ghosts}^{PBE0}$ (a.u.)	$E_{mol\cdot isol}^{total}$ (a.u.)	E_{BSSE} (kcal/mol)	E_{def} (kcal/mol)	E_{latt} (kcal/mol)	E_{coh} (kcal/mol)
Ph2Te2 as Ph2Se2	-998.93537	-998.84675	-0.03310	-998.85047	-998.84926	23.10	1.58	-32.50	-30.92
Ph2Te2 as Ph2Te2	-998.93551	-998.84520	-0.03201	-998.85224	-998.84898	24.50	2.37	-32.17	-29.80
Ph2Se2 as Ph2Se2	-5265.40883	-5265.33601	-0.03128	-5265.33149	-5265.33722	16.79	0.76	-28.91	-28.15
Ph2Se2 as Ph2Te2	-5265.40482	-5265.33527	-0.03066	-5265.33086	-5265.33890	16.47	2.28	-27.17	-24.90

Table S2. Difference in some energy descriptors of putative and native polymorphs (kcal/mol).

	E_{cryst}^{total}/Z	$E_{mol\cdot cryst}^{total}$	$E_{mol\cdot ghosts}^{PBE0}$	$E_{mol\cdot isol}^{total}$
Ph_2Se_2 as Ph_2Te_2 - Ph_2Se_2 as Ph_2Se_2	2.51	0.46	0.39	-1.06
Ph_2Te_2 as Ph_2Se_2 - Ph_2Te_2 as Ph_2Te_2	0.09	-0.97	1.11	-0.18

Structural data

All crystals were calculated within the $P2_12_12_1$ space group (Z=4, SYMM 1/2+x,1/2-y,-z; SYMM -x,1/2+y,1/2-z; SYMM 1/2-x,-y,1/2+z).

Table S3. Experimental (DPHDSE02) and calculated fractional coordinates of native Ph_2Se_2 polymorph.

Atom	X_exp	Y_exp	Z_exp	X_calc	Y_calc	Z_calc
Se1	0.57419	0.22620	0.55357	-0.42514	0.23914	-0.44953
Se2	0.93083	0.29623	0.59578	-0.04749	0.30905	-0.40569
C1	0.54820	-0.00360	0.56790	-0.44994	0.00315	-0.43459
C2	0.34210	-0.07890	0.54700	0.33795	-0.07915	-0.45501
C3	0.30830	-0.24500	0.55650	0.30688	-0.24832	-0.44323
C4	0.47120	-0.33380	0.58600	0.48416	-0.33370	-0.41082
C5	0.68000	-0.25720	0.60660	-0.30346	-0.25111	-0.39143
C6	0.71520	-0.09390	0.59660	-0.26978	-0.08279	-0.40332
C7	0.83570	0.33580	0.67250	-0.15864	0.35003	-0.32797
C8	0.62990	0.27010	0.69620	-0.37519	0.28096	-0.30478
C9	0.58640	0.29290	0.75260	-0.42886	0.30436	-0.24671
C10	0.74020	0.38340	0.78430	-0.26789	0.39622	-0.21191
C11	0.94130	0.45230	0.76090	-0.05413	0.46694	-0.23561
C12	0.98950	0.42920	0.70430	0.00127	0.44476	-0.29362
H1	0.20973	-0.00934	0.52374	0.19598	-0.01313	-0.47948
H2	0.14936	-0.30432	0.53990	0.14179	-0.31219	-0.45925
H3	0.44084	-0.46224	0.59368	0.45722	-0.46482	-0.40058
H4	0.81202	-0.32642	0.63009	-0.16304	-0.31726	-0.36651
H5	0.87759	-0.03557	0.61173	-0.10333	-0.01836	-0.38843
H6	0.50453	0.20134	0.67065	-0.50000	0.20692	-0.33149
H7	0.42878	0.23864	0.77176	0.40337	0.24851	-0.22872
H8	0.70324	0.40119	0.82860	-0.30985	0.41232	-0.16645
H9	1.06213	0.52459	0.78649	0.07245	-0.45967	-0.20931
H10	1.14685	0.48421	0.68528	0.16967	-0.49924	-0.31141

Experimental cell unit parameters: 5.5878(11) 8.2521(17) 23.907(5)

Calculated cell unit parameters: 5.33945069 7.99110927 23.15620363

Table S4. Experimental (DPHDTE01) and calculated fractional coordinates of native Ph_2Te_2 polymorph.

Atom	X_exp	Y_exp	Z_exp	X_calc	Y_calc	Z_calc
Te1	0.81469	0.07162	0.08669	-0.20894	0.08381	0.08252
Te2	1.12347	0.32642	0.08037	0.14367	0.33394	0.07590
C1	0.78740	0.04530	0.16560	-0.22625	0.05577	0.16472
C2	0.95370	-0.05490	0.19050	-0.04467	-0.04418	0.19023
C3	0.92790	-0.07820	0.24110	-0.07236	-0.07162	0.24331
C4	0.73490	-0.00510	0.26770	-0.28173	0.00065	0.27094
C5	0.56720	0.09310	0.24270	-0.46173	0.10069	0.24546
C6	0.58860	0.11930	0.19190	-0.43493	0.12839	0.19238
C7	0.82700	0.49700	0.07970	-0.16728	-0.49101	0.07764
C8	0.74790	0.57190	0.12360	-0.23072	-0.40963	0.12315
C9	0.55000	0.68120	0.12270	-0.43982	-0.29903	0.12310
C10	0.42510	0.71790	0.07820	0.41381	-0.26896	0.07785
C11	0.50650	0.64570	0.03450	0.47955	-0.34938	0.03236
C12	0.70250	0.53630	0.03520	-0.31059	-0.45943	0.03216
H1	1.08620	-0.10780	0.17250	0.11648	-0.10178	0.16853
H2	1.04510	-0.14580	0.25780	0.06866	-0.15039	0.26308
H3	0.71760	-0.02180	0.30260	-0.30558	-0.02256	0.31233
H4	0.43340	0.14400	0.26090	0.37213	0.15654	0.26628
H5	0.47020	0.18650	0.17520	0.42043	0.20410	0.17238
H6	0.83080	0.54750	0.15430	-0.11854	-0.43270	0.15875
H7	0.49910	0.73160	0.15270	-0.48819	-0.23590	0.15868
H8	0.28670	0.79110	0.07770	0.24796	-0.18382	0.07799
H9	0.42600	0.67200	0.00370	0.36779	-0.32650	-0.00326
H10	0.75360	0.48700	0.00500	-0.26015	0.47773	-0.00343

Experimental cell unit parameters: 5.1523(14) 8.571(3) 26.799(7)

Calculated cell unit parameters: 4.90984374 8.45009815 25.64560249

Table S5. Calculated fractional coordinates of putative Ph_2Se_2 polymorph (Ph_2Se_2 as Ph_2Te_2).

Atom	X_calc	Y_calc	Z_calc
SE1	-0.18402	0.11221	0.08892
SE2	0.08429	0.35205	0.07896
C1	-0.21042	0.09787	0.16526
C2	-0.03135	0.00163	0.19404
C3	-0.06294	-0.01885	0.24876
C4	-0.27295	0.05678	0.27459
C5	-0.45057	0.15307	0.24585
C6	-0.42054	0.17382	0.19104
C7	-0.19048	-0.48274	0.07653
C8	-0.23224	-0.37323	0.11912
C9	-0.43862	-0.25943	0.11703
C10	0.39840	-0.25354	0.07275
C11	0.44406	-0.36151	0.02990
C12	-0.35057	-0.47584	0.03173
H1	0.13014	-0.05845	0.17348
H2	0.07490	-0.09550	0.27113
H3	-0.29969	0.03848	0.31724
H4	0.38395	0.21140	0.26558
H5	0.43852	0.24639	0.16817
H6	-0.10620	-0.37696	0.15391
H7	-0.47221	-0.17556	0.15059
H8	0.23680	-0.16478	0.07169
H9	0.31953	-0.35608	-0.00513
H10	-0.31566	0.43815	-0.00129

Calculated cell unit parameters: 5.11885479 7.90578813 24.99639665

Table S6. Calculated fractional coordinates of putative Ph_2Te_2 polymorph (Ph_2Te_2 as Ph_2Se_2).

Atom	X_calc	Y_calc	Z_calc
TE1	-0.33561	0.25516	-0.45583
TE2	0.06607	0.32287	-0.39189
C1	-0.36440	-0.00127	-0.43829
C2	0.42791	-0.08586	-0.45454
C3	0.39867	-0.24852	-0.43878
C4	-0.42641	-0.32567	-0.40610
C5	-0.21664	-0.24250	-0.39146
C6	-0.18444	-0.08113	-0.40797
C7	-0.12425	0.36264	-0.31464
C8	-0.33956	0.28292	-0.30130
C9	-0.44322	0.30404	-0.24816
C10	-0.33085	0.40307	-0.20819
C11	-0.11597	0.48165	-0.22172
C12	-0.01273	0.46316	-0.27492
H1	0.28517	-0.02692	-0.47847
H2	0.23562	-0.31357	-0.45109
H3	-0.45452	-0.45006	-0.39145
H4	-0.07758	-0.30249	-0.36654
H5	-0.01984	-0.01699	-0.39643
H6	-0.42519	0.20196	-0.33179
H7	0.38946	0.24118	-0.23783
H8	-0.41042	0.41851	-0.16652
H9	-0.02776	-0.44036	-0.19097
H10	0.15529	-0.47368	-0.28460

Calculated cell unit parameters: 5.11885479 7.90578813 24.99639665

Comparison of conformations

General comparison of theoretical and experimental conformations in crystals by the best mean square overlap of non-hydrogen atoms. Deviations were calculated for non-hydrogen atoms.[1]

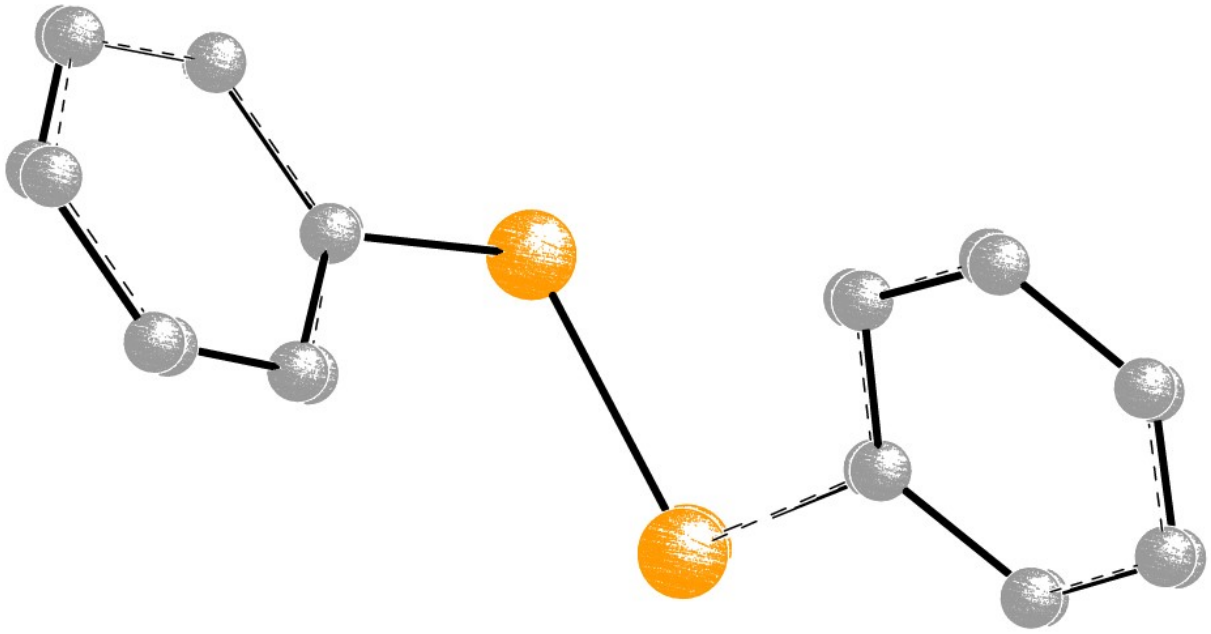


Figure S6
Ph_2Se_2 as Ph_2Se_2_exp and Ph_2Se_2 as Ph_2Se_2_cryst = 0.0697 Å (weighted r.m.s. deviation)

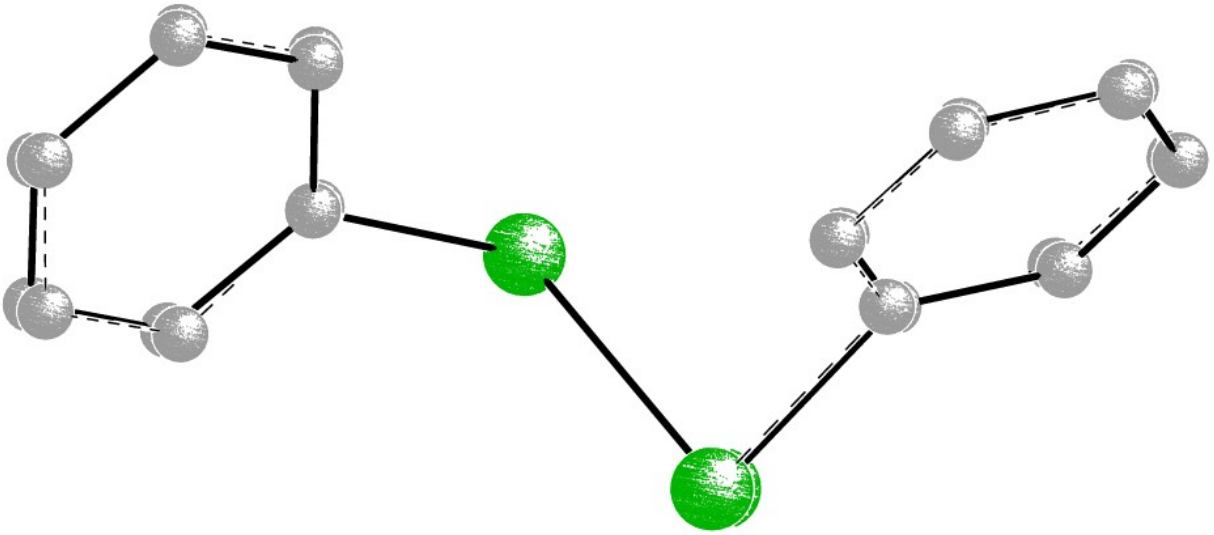


Figure S7
Ph_2Te_2 as Ph_2Te_2_exp and Ph_2Te_2 as Ph_2Te_2_cryst = 0.0797 Å (weighted r.m.s. deviation)

[1] Hereafter, the following abbreviations are used: exp - experiment; cryst - optimized crystal structure; isol - optimized isolated structure

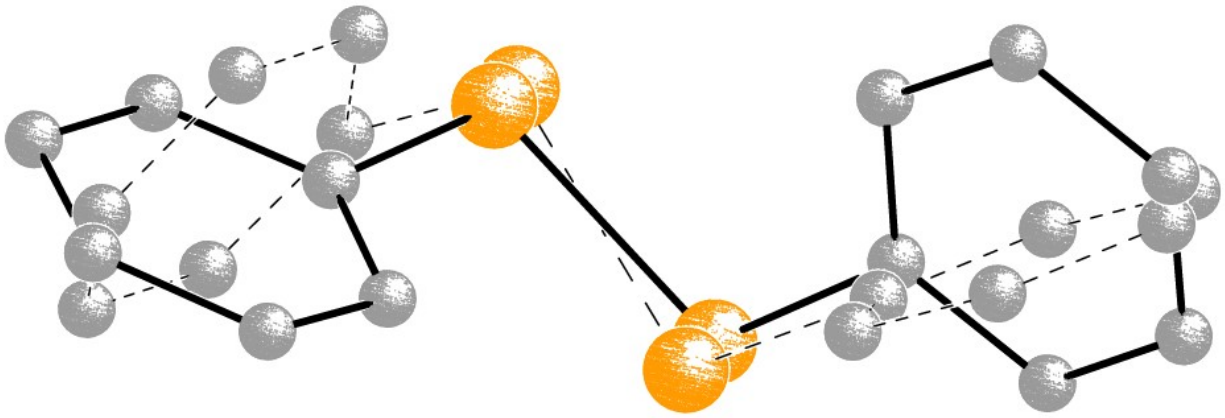


Figure S8
Ph_2Se_2 as Ph_2Se_2 exp and Ph_2Se_2 as Ph_2Te_2_cryst = 1.2161 Å (weighted R.M.S. deviation, conformational changes)

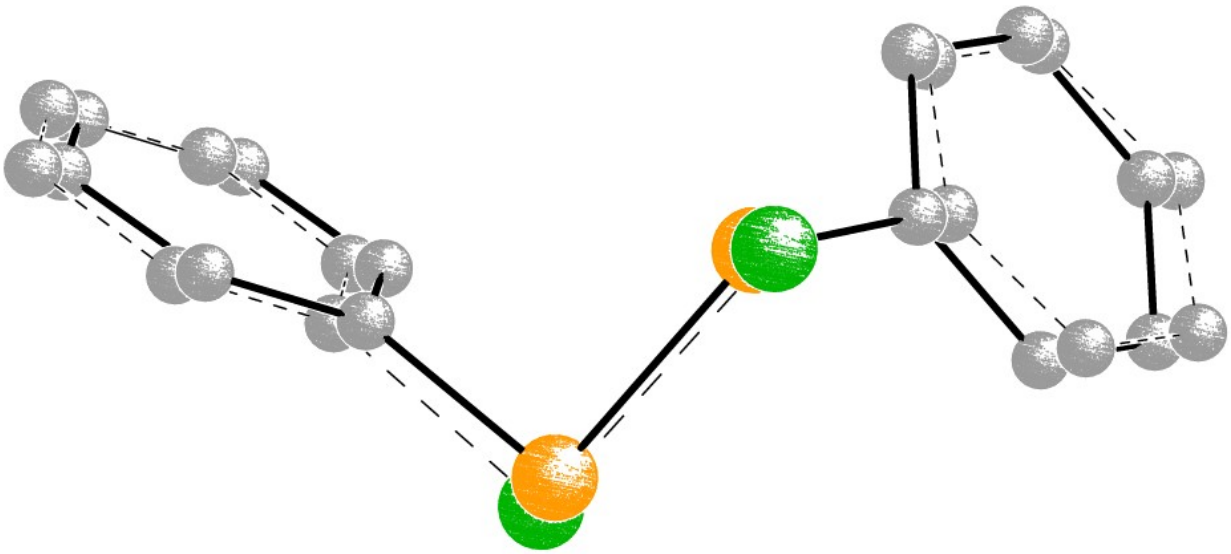


Figure S9
Ph_2Te_2 as Ph_2Te_2cryst and Ph_2Se_2 as Ph_2Te_2_cryst = 0.2390 Å (weighted r.m.s. deviation)

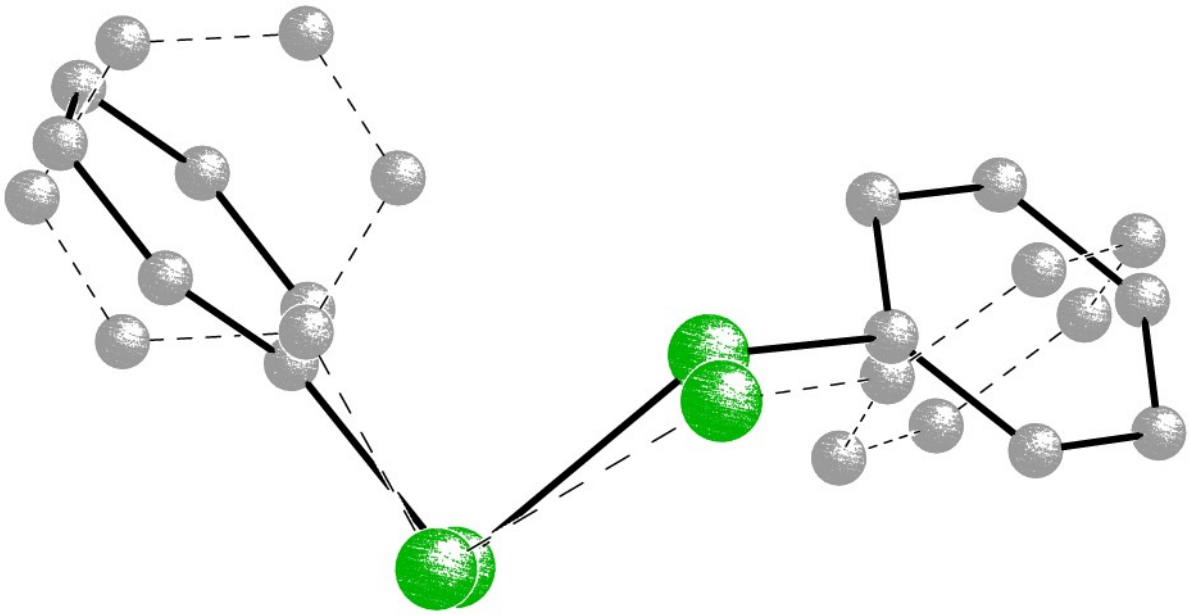


Figure S10
Ph_2Te_2 as Ph_2Te_2exp and Ph_2Te_2 as Ph_2Se_2_cryst = 1.1938 Å (weighted r.m.s. deviation, conformational changes)

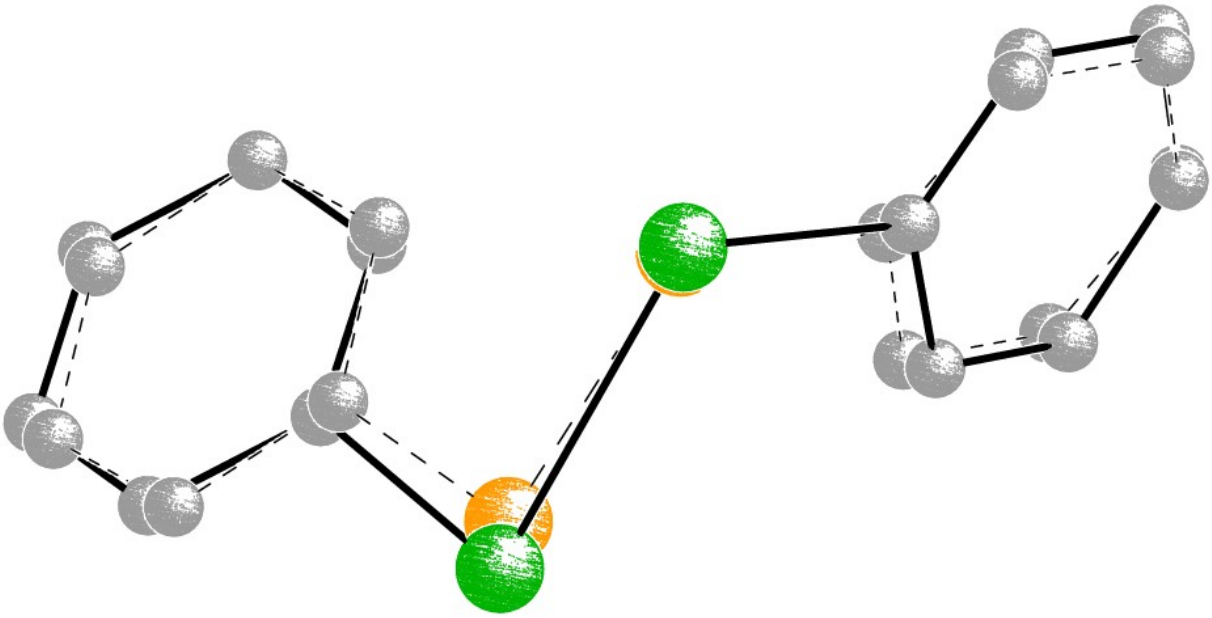


Figure S11
.Ph_2Se_2 as Ph_2Se_2 cryst and Ph_2Te_2 as Ph_2Se_2_cryst = 0.2066 Å (weighted r.m.s. deviation)

Comparison of theoretical conformations in crystals and isolated states by the best mean square overlap of non-hydrogen atoms. Deviations were calculated for non-hydrogen atoms.

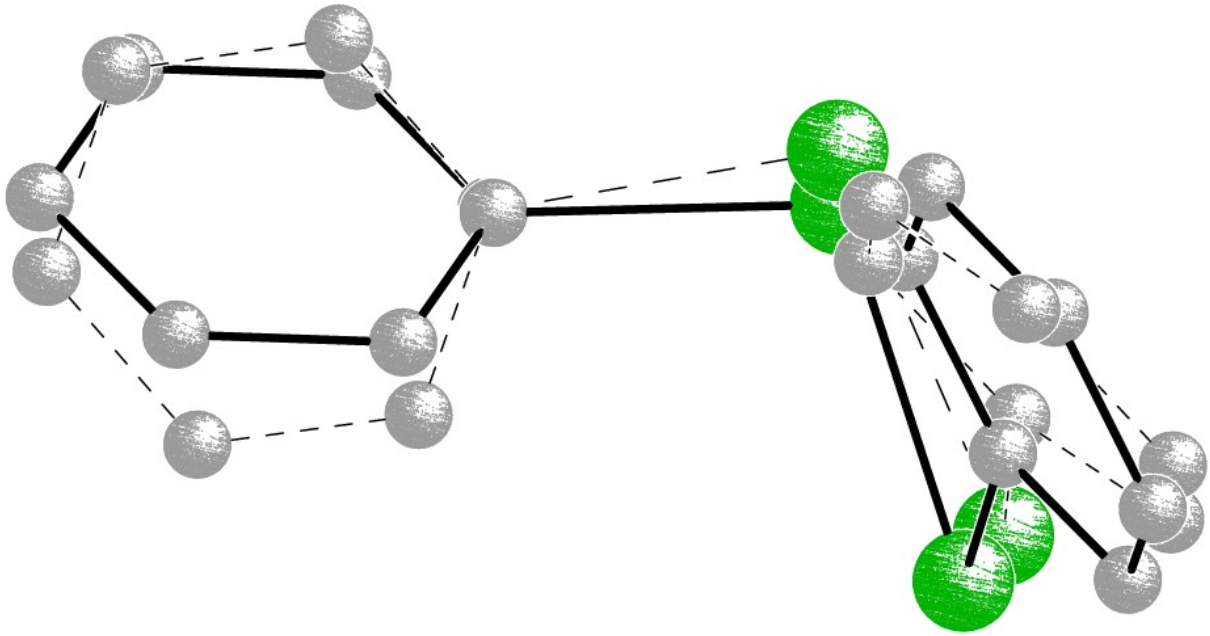


Figure S12
Ph_2Te_2 as Ph_2Se_2_isol and Ph_2Te_2 as Ph_2Se_2_cryst = 1.7944 Å (weighed r.m.s. deviation, a significant deformation. Note, $^{E_{def}}$ = 1.58 kcal/mol)

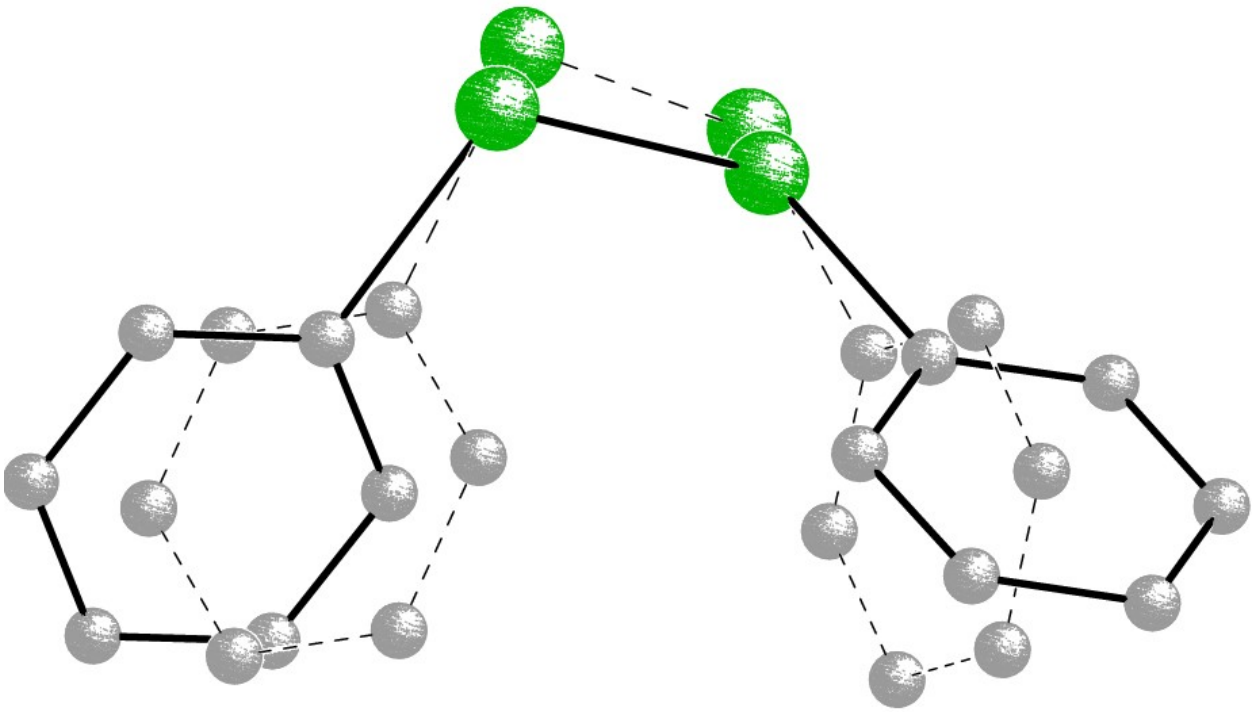


Figure S13
Ph_2Te_2 as Ph_2Se_2_isol and Ph_2Te_2 as Ph_2Te_2_isol = 1.4034 Å (weighed r.m.s. deviation, conformational changes)

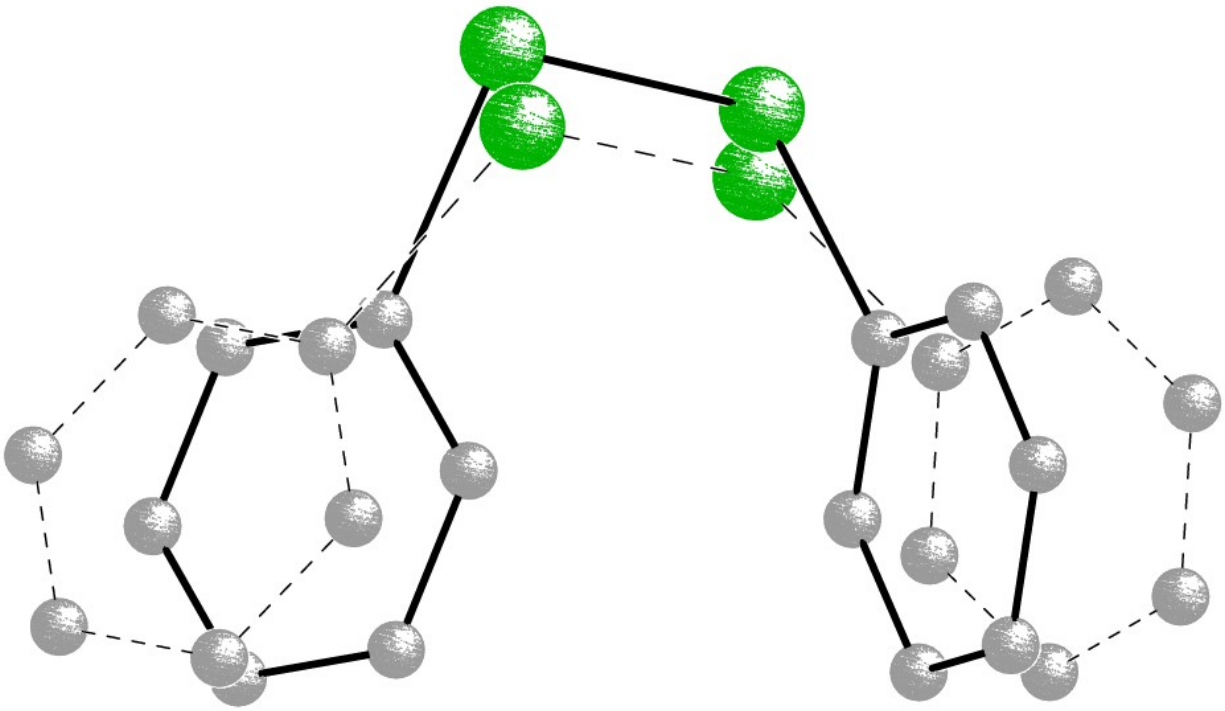


Figure S14
Ph_2Te_2 as Ph_2Te_2_isol and Ph_2Te_2 as Ph_2Te_2_cryst = 1.9922 Å (weighed r.m.s. deviation, a significant deformation. Note, $^{E_{def}}$ = 2.37 kcal/mol)

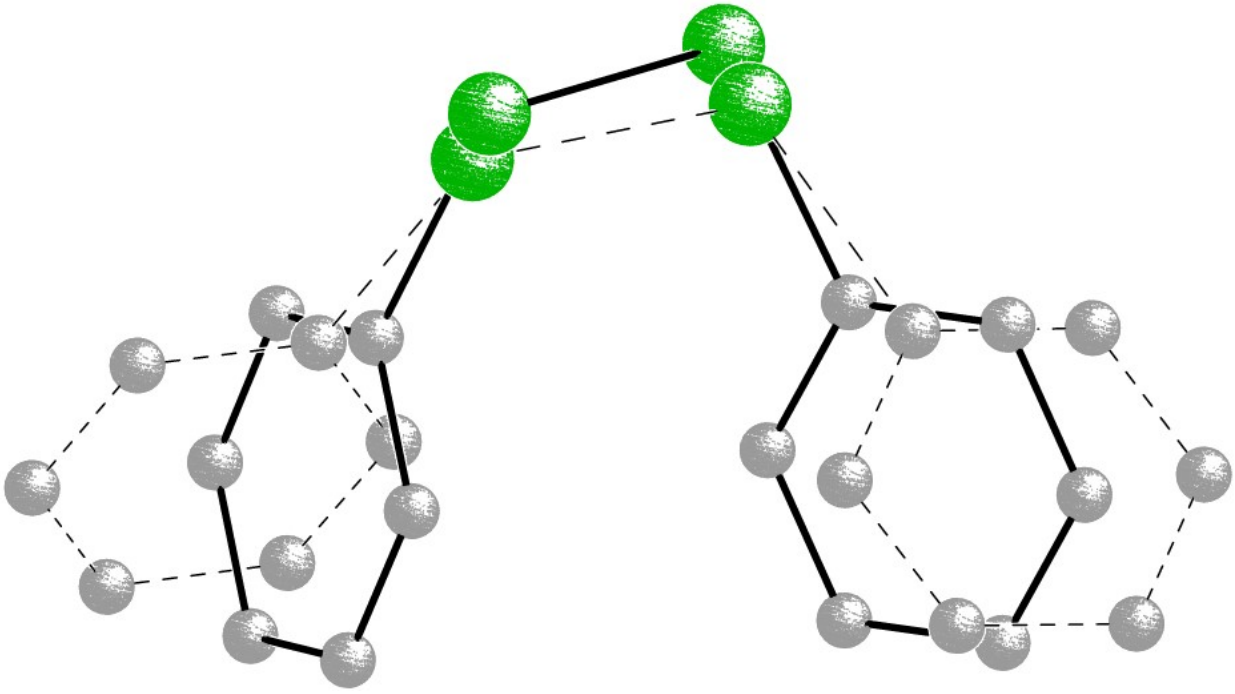


Figure S15
Ph_2Te_2 as Ph_2Te_2_isol and Ph_2Te_2 as Ph_2Se_2_isol = 1.4068 Å (weighed r.m.s. deviation, conformational changes)

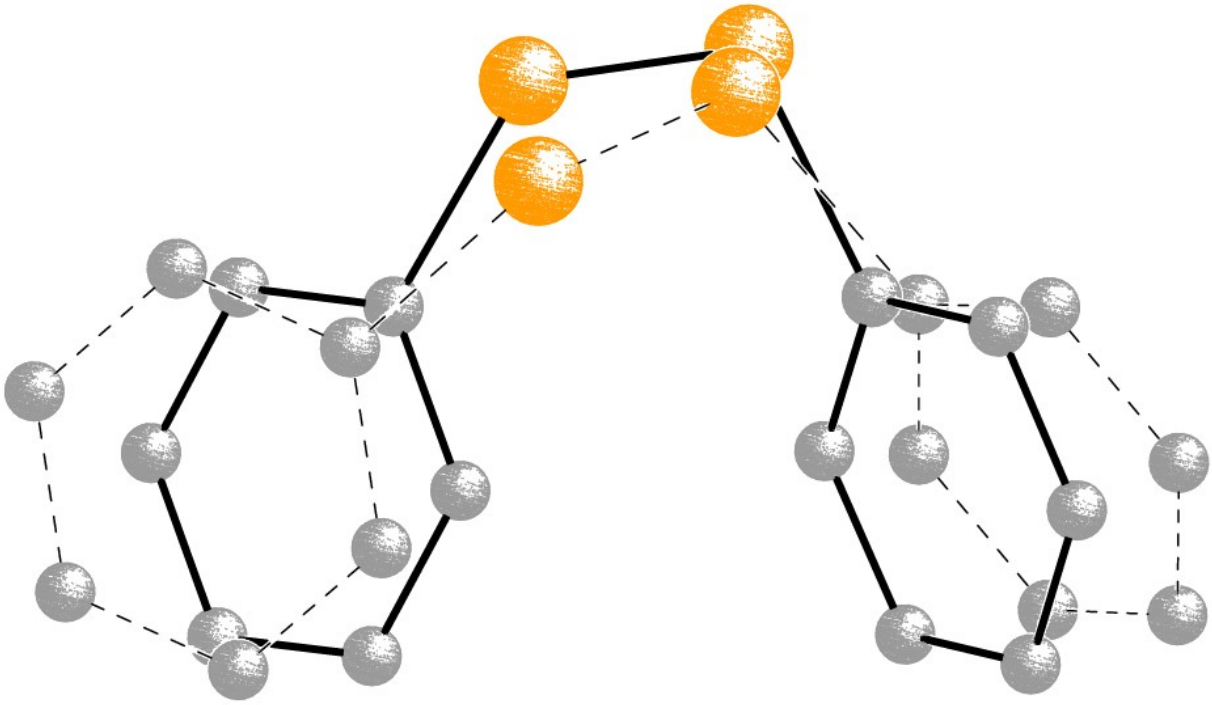


Figure S16
Ph_2Se_2 as Ph_2Te_2_isol and Ph_2Se_2 as Ph_2Te_2_cryst = 1.4571 Å (weighed r.m.s. deviation, a significant deformation. Note, $^{E_{def}}$ = 2.28 kcal/mol)

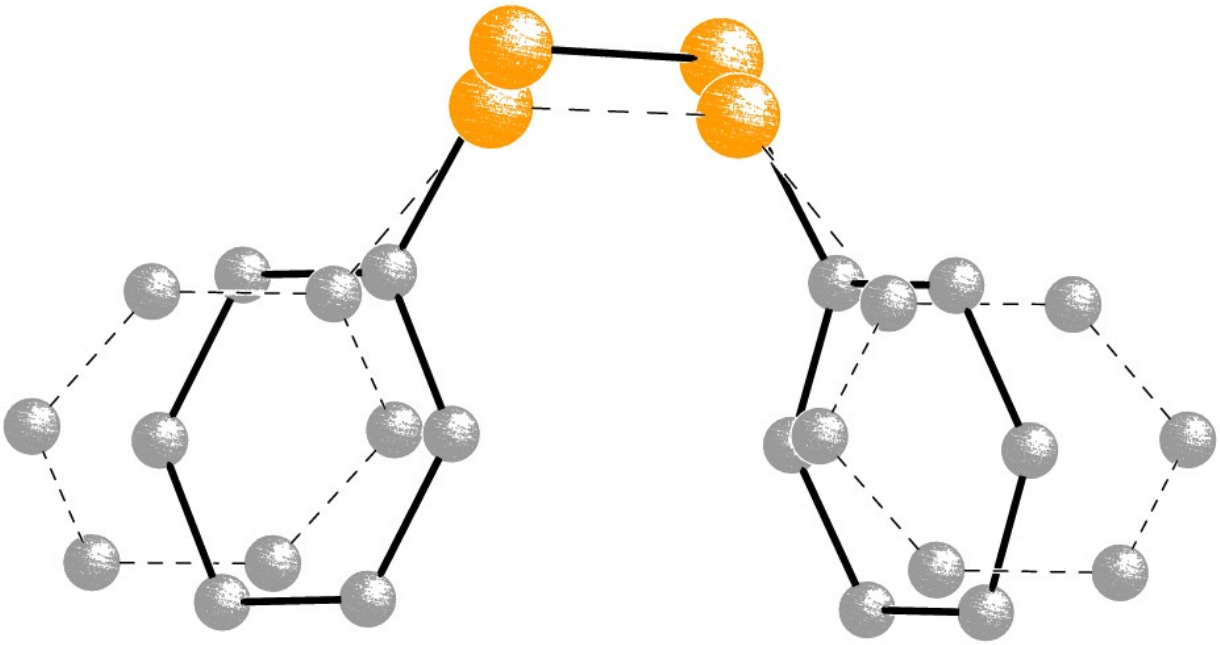


Figure S17
Ph_2Se_2 as Ph_2Te_2_isol and Ph_2Se_2 as Ph_2Se_2_isol = 1.3939 Å (weighed r.m.s. deviation, conformational changes)

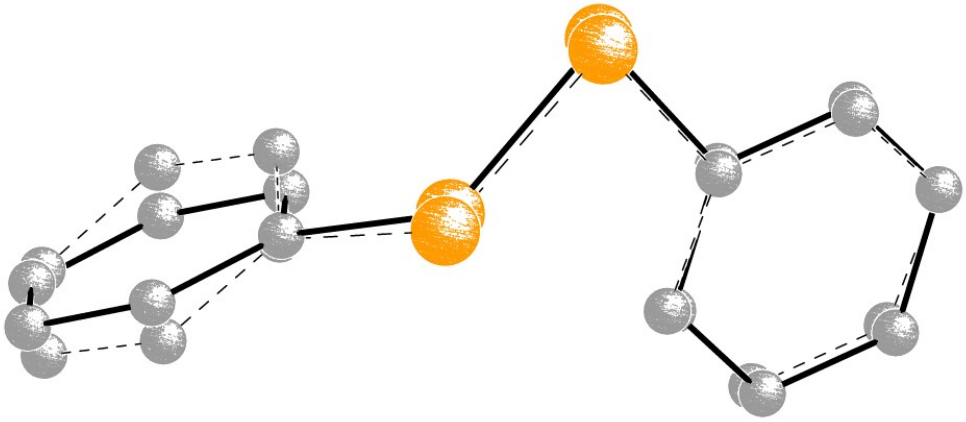


Figure S18
Ph_2Se_2 as Ph_2Se_2_isol and Ph_2Se_2 as Ph_2Se_2_cryst = 1.2749 Å (weighed r.m.s. deviation, a significant deformation. Note, $^{E_{def}}$ = 0.76 kcal/mol)

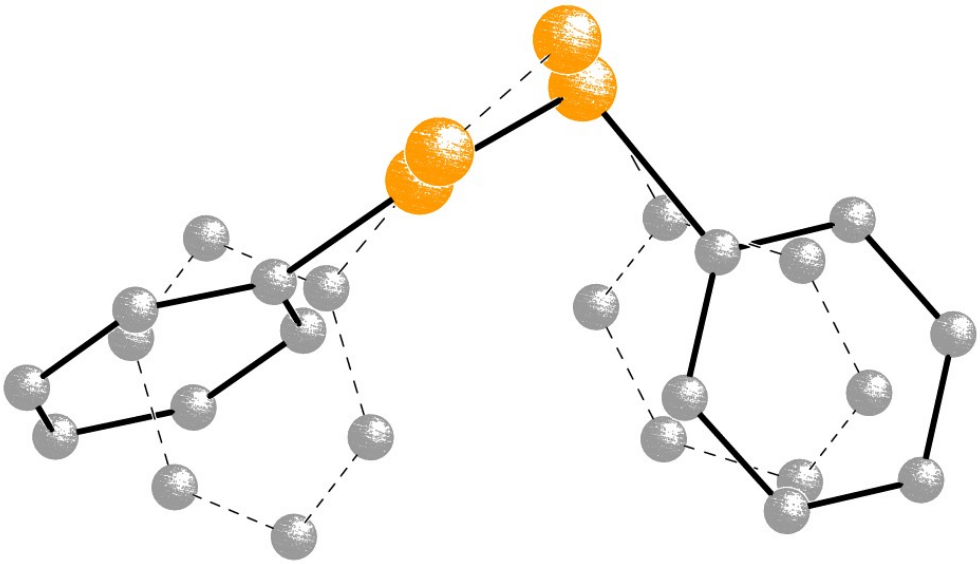
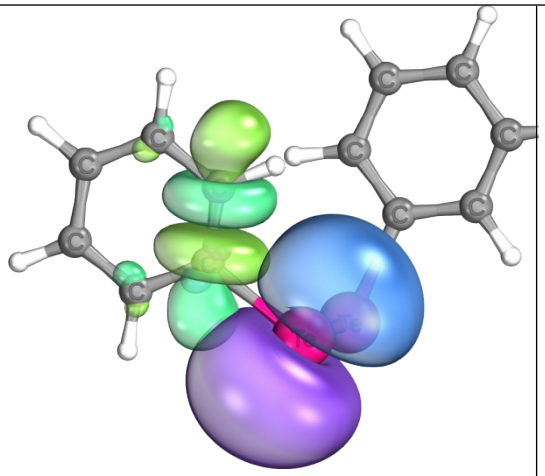
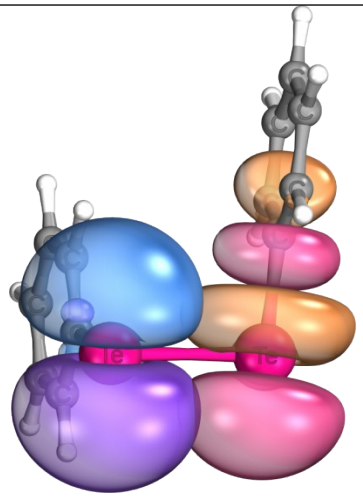


Figure S19
Ph_2Se_2 as Ph_2Se_2_isol and Ph_2Se_2 as Ph_2Te_2_isol = 1.3915 Å (weighed r.m.s. deviation, conformational changes)

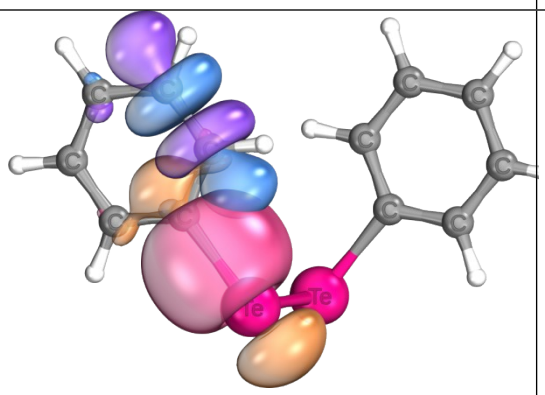
NBO analysis



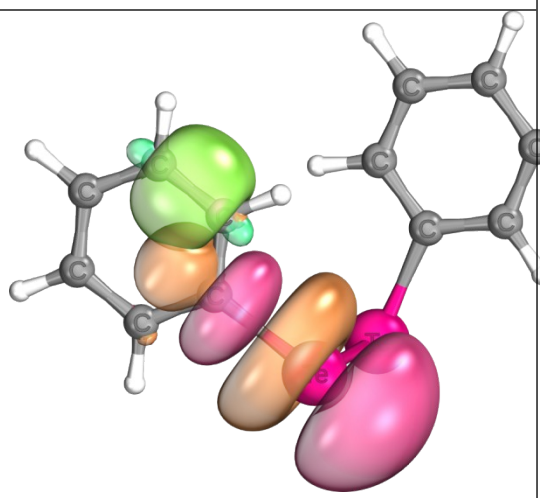
LP(Te)→σ*(C_i-C_o) 3.77 kcal/mol (4)



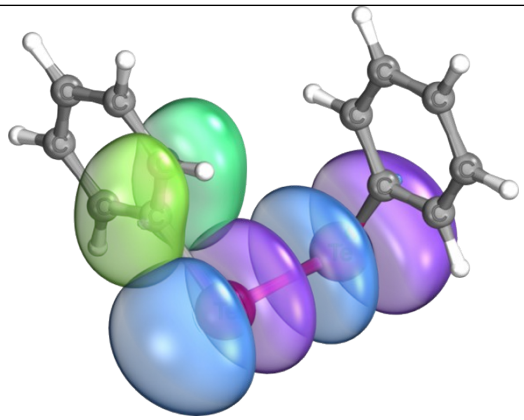
LP(Te)→σ*(Te-C_i) 5.89 kcal/mol (2)



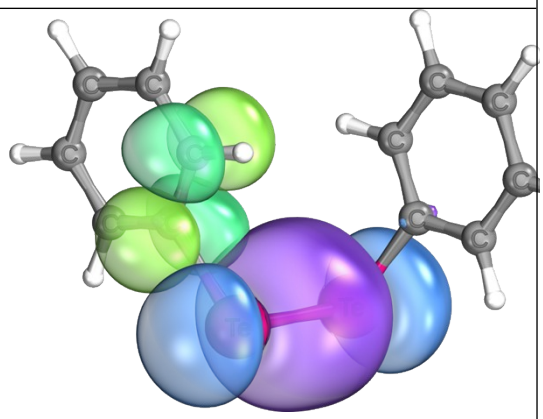
σ(Te-C_i)→σ*(C_o-C_m) 5.06 kcal/mol (4)



σ(C_o-C_m)→σ*(Te-C_i) 4.22 kcal/mol (4)



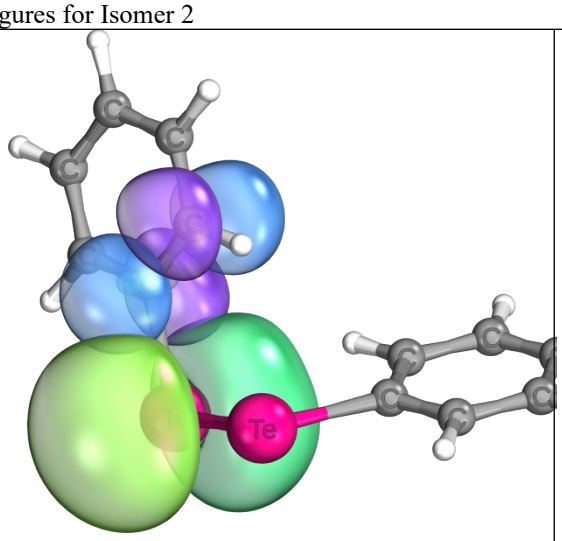
π(C_i-C_o)→σ*(Te-Te) 3.41 kcal/mol (2)



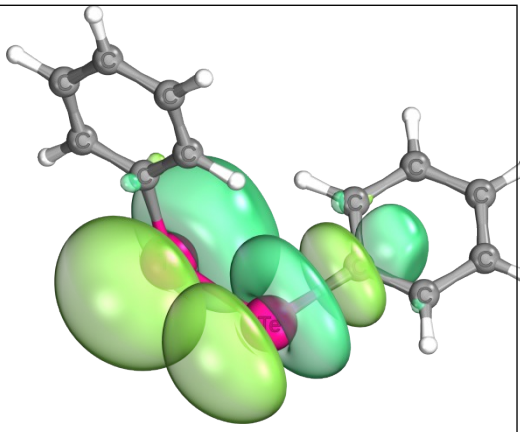
σ(Te-Te)→π*(C_i-C_o) 3.04 kcal/mol(2)

Figure S20. NBO donor-acceptor interaction orbital pairs in Ph_2Te_2 for α-like isomer along with stabilization energies. Number of similar interactions is given in parentheses.

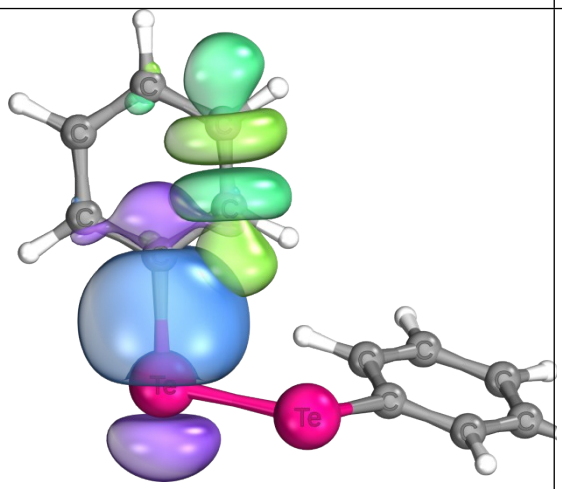
NBO Figures for Isomer 2



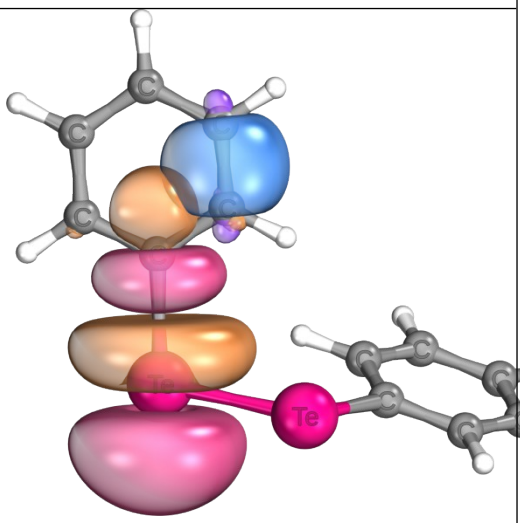
$LP(Te) \rightarrow \pi^*(C_i\text{-}C_o)$ 10.06 kcal/mol(2)



$LP(Te) \rightarrow \sigma^*(Te\text{-}C_i)$ 5.89 kcal/mol(2)



$\sigma(Te\text{-}C_i) \rightarrow \sigma^*(C_o\text{-}C_m)$ 4.87 kcal/mol (4)



$\sigma(C_o\text{-}C_m) \rightarrow \sigma^*(Te\text{-}C_i)$ 4.54 kcal/mol (4)

Figure S21. NBO donor-acceptor interaction orbital pairs in Ph_2Te_2 for β-like isomer along with stabilization energies. Number of similar interactions is given in parentheses.

Table S7. SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS for optimized isomer $\alpha_v Te_2Ph_2$

Threshold for printing: 0.50 kcal/mol

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
59. LP (1)Te 11	96. BD*(1) C 1- C 13	0.83	1.04	0.026
59. LP (1)Te 11	113. BD*(1) C 13- C 14	1.45	1.04	0.035
60. LP (2)Te 11	95. BD*(1) C 1- C 3	0.51	0.76	0.018
60. LP (2)Te 11	**96. BD*(1) C 1- C 13**	**3.77**	**0.75**	**0.047**
60. LP (2)Te 11	**112. BD*(1)Te 12- C 20**	**4.37**	**0.30**	**0.032**
60. LP (2)Te 11	**113. BD*(1) C 13- C 14**	**3.06**	**0.75**	**0.043**
60. LP (2)Te 11	122. BD*(2) C 20- C 23	0.70	0.24	0.012
60. LP (2)Te 11	330. RY (1)Te 12	1.00	0.83	0.026
61. LP (1)Te 12	120. BD*(1) C 20- C 21	1.46	1.04	0.035
61. LP (1)Te 12	121. BD*(1) C 20- C 23	0.82	1.04	0.026
62. LP (2)Te 12	97. BD*(2) C 1- C 13	0.70	0.24	0.012
62. LP (2)Te 12	104. BD*(1) C 5- C 23	0.51	0.76	0.018
62. LP (2)Te 12	**111. BD*(1)Te 11- C 13**	**4.37**	**0.30**	**0.032**
62. LP (2)Te 12	**120. BD*(1) C 20- C 21**	**3.05**	**0.75**	**0.043**
62. LP (2)Te 12	**121. BD*(1) C 20- C 23**	**3.78**	**0.75**	**0.047**
62. LP (2)Te 12	285. RY (1)Te 11	1.00	0.83	0.026
64. BD (1) C 1- C 3	**111. BD*(1)Te 11- C 13**	**4.22**	**0.69**	**0.048**
66. BD (2) C 1- C 13	**110. BD*(1)Te 11-Te 12**	**3.41**	**0.25**	**0.026**
66. BD (2) C 1- C 13	285. RY (1)Te 11	0.72	0.88	0.022
73. BD (1) C 5- C 23	**112. BD*(1)Te 12- C 20**	**4.22**	**0.69**	**0.048**
77. BD (1) C 9- C 21	**112. BD*(1)Te 12- C 20**	**4.27**	**0.69**	**0.048**
79. BD (1)Te 11-Te 12	**97. BD*(2) C 1- C 13**	**3.04**	**0.40**	**0.031**
79. BD (1)Te 11-Te 12	**122. BD*(2) C 20- C 23**	**3.04**	**0.40**	**0.031**
79. BD (1)Te 11-Te 12	377. RY (3) C 13	0.55	1.39	0.025
79. BD (1)Te 11-Te 12	500. RY (3) C 20	0.55	1.39	0.025
80. BD (1)Te 11- C 13	94. BD*(1) C 1- H 2	0.99	0.86	0.026
80. BD (1)Te 11- C 13	**95. BD*(1) C 1- C 3**	**5.06**	**0.98**	**0.063**
80. BD (1)Te 11- C 13	114. BD*(1) C 14- H 15	0.97	0.85	0.026
80. BD (1)Te 11- C 13	**115. BD*(1) C 14- C 16**	**4.85**	**0.98**	**0.062**
80. BD (1)Te 11- C 13	125. RY (1) C 1	1.68	1.79	0.049
80. BD (1)Te 11- C 13	402. RY (1) C 14	1.64	1.78	0.048
81. BD (1)Te 12- C 20	**104. BD*(1) C 5- C 23**	**5.05**	**0.98**	**0.063**
81. BD (1)Te 12- C 20	**108. BD*(1) C 9- C 21**	**4.85**	**0.98**	**0.062**
81. BD (1)Te 12- C 20	123. BD*(1) C 21- H 22	0.98	0.85	0.026
81. BD (1)Te 12- C 20	124. BD*(1) C 23- H 24	0.99	0.86	0.026
81. BD (1)Te 12- C 20	525. RY (1) C 21	1.64	1.78	0.048
81. BD (1)Te 12- C 20	557. RY (1) C 23	1.68	1.79	0.049
84. BD (1) C 14- C 16	**111. BD*(1)Te 11- C 13**	**4.27**	**0.69**	**0.048**
91. BD (2) C 20- C 23	**110. BD*(1)Te 11-Te 12**	**3.42**	**0.25**	**0.026**
91. BD (2) C 20- C 23	330. RY (1)Te 12	0.72	0.88	0.022

Table S8. SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

For optimized isomer β_v Te_2Ph_2

Threshold for printing: 0.50 kcal/mol

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
59. LP (1)Te 11	96. BD*(1) C 1- C 13	2.40	1.05	0.045
60. LP (2)Te 11	**97. BD*(2) C 1- C 13**	**10.06**	**0.25**	**0.045**
60. LP (2)Te 11	**112. BD*(1)Te 12- C 20**	**5.89**	**0.29**	**0.037**
60. LP (2)Te 11	124. BD*(1) C 23- H 24	0.98	0.64	0.022
60. LP (2)Te 11	330. RY (1)Te 12	0.87	0.93	0.025
61. LP (1)Te 12	121. BD*(1) C 20- C 23	2.40	1.05	0.045
62. LP (2)Te 12	94. BD*(1) C 1- H 2	0.98	0.64	0.022
62. LP (2)Te 12	**111. BD*(1)Te 11- C 13**	**5.89**	**0.29**	**0.037**
62. LP (2)Te 12	**122. BD*(2) C 20- C 23**	**10.06**	**0.25**	**0.045**
62. LP (2)Te 12	285. RY (1)Te 11	0.87	0.93	0.025
64. BD (1) C 1- C 3	**111. BD*(1)Te 11- C 13**	**4.54**	**0.67**	**0.049**
66. BD (2) C 1- C 13	286. RY (2)Te 11	1.03	0.74	0.025
73. BD (1) C 5- C 23	**112. BD*(1)Te 12- C 20**	**4.54**	**0.67**	**0.049**
77. BD (1) C 9- C 21	**112. BD*(1)Te 12- C 20**	**4.37**	**0.68**	**0.049**
79. BD (1)Te 11-Te 12	111. BD*(1)Te 11- C 13	0.66	0.47	0.016
79. BD (1)Te 11-Te 12	112. BD*(1)Te 12- C 20	0.66	0.47	0.016
79. BD (1)Te 11-Te 12	113. BD*(1) C 13- C 14	1.70	0.93	0.035
79. BD (1)Te 11-Te 12	120. BD*(1) C 20- C 21	1.70	0.93	0.035
80. BD (1)Te 11- C 13	94. BD*(1) C 1- H 2	0.95	0.86	0.026
80. BD (1)Te 11- C 13	**95. BD*(1) C 1- C 3**	**4.87**	**0.99**	**0.062**
80. BD (1)Te 11- C 13	110. BD*(1)Te 11-Te 12	0.56	0.43	0.014
80. BD (1)Te 11- C 13	114. BD*(1) C 14- H 15	1.05	0.85	0.027
80. BD (1)Te 11- C 13	**115. BD*(1) C 14- C 16**	**4.87**	**0.99**	**0.062**
80. BD (1)Te 11- C 13	125. RY (1) C 1	1.11	1.96	0.042
80. BD (1)Te 11- C 13	402. RY (1) C 14	1.58	1.80	0.048
81. BD (1)Te 12- C 20	**104. BD*(1) C 5- C 23**	**4.87**	**0.99**	**0.062**
81. BD (1)Te 12- C 20	**108. BD*(1) C 9- C 21**	**4.87**	**0.99**	**0.062**
81. BD (1)Te 12- C 20	110. BD*(1)Te 11-Te 12	0.56	0.43	0.014
81. BD (1)Te 12- C 20	123. BD*(1) C 21- H 22	1.05	0.85	0.027
81. BD (1)Te 12- C 20	124. BD*(1) C 23- H 24	0.95	0.86	0.026
81. BD (1)Te 12- C 20	525. RY (1) C 21	1.58	1.80	0.048
81. BD (1)Te 12- C 20	557. RY (1) C 23	1.11	1.96	0.042
84. BD (1) C 14- C 16	**111. BD*(1)Te 11- C 13**	**4.37**	**0.68**	**0.049**
91. BD (2) C 20- C 23	331. RY (2)Te 12	1.03	0.74	0.025

Table S9. SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS for 1α XRD geometry

Threshold for printing: 0.50 kcal/mol

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
59. LP (1)Te 11	97. BD*(1) C 1- C 13	0.83	1.05	0.026
59. LP (1)Te 11	112. BD*(1) C 13- C 14	1.45	1.05	0.035
60. LP (2)Te 11	97. BD*(1) C 1- C 13	3.78	0.76	0.048
60. LP (2)Te 11	111. BD*(1)Te 12- C 20	4.52	0.30	0.033
60. LP (2)Te 11	112. BD*(1) C 13- C 14	3.10	0.77	0.044
60. LP (2)Te 11	115. BD*(1) C 14- C 16	0.50	0.76	0.017
60. LP (2)Te 11	330. RY (1)Te 12	1.00	0.84	0.026
61. LP (1)Te 12	120. BD*(1) C 20- C 21	1.76	1.05	0.038
61. LP (1)Te 12	122. BD*(1) C 20- C 23	0.60	1.05	0.022
62. LP (2)Te 12	110. BD*(1)Te 11- C 13	4.98	0.30	0.035
62. LP (2)Te 12	120. BD*(1) C 20- C 21	2.55	0.76	0.039
62. LP (2)Te 12	121. BD*(2) C 20- C 21	0.98	0.25	0.014
62. LP (2)Te 12	122. BD*(1) C 20- C 23	3.68	0.77	0.048
62. LP (2)Te 12	285. RY (1)Te 11	1.02	0.86	0.026
64. BD (1) C 1- C 3	110. BD*(1)Te 11- C 13	4.22	0.70	0.048
71. BD (1) C 5- C 23	111. BD*(1)Te 12- C 20	4.52	0.69	0.050
77. BD (1) C 9- C 21	111. BD*(1)Te 12- C 20	4.30	0.69	0.049
78. BD (1)Te 11-Te 12	113. BD*(2) C 13- C 14	2.78	0.41	0.030
78. BD (1)Te 11-Te 12	121. BD*(2) C 20- C 21	2.75	0.41	0.030
79. BD (1)Te 11- C 13	94. BD*(1) C 1- H 2	0.99	0.86	0.026
79. BD (1)Te 11- C 13	95. BD*(1) C 1- C 3	4.84	1.01	0.062
79. BD (1)Te 11- C 13	114. BD*(1) C 14- H 15	0.99	0.86	0.026
79. BD (1)Te 11- C 13	115. BD*(1) C 14- C 16	4.96	0.99	0.063
79. BD (1)Te 11- C 13	125. RY (1) C 1	1.62	1.80	0.048
79. BD (1)Te 11- C 13	402. RY (1) C 14	1.64	1.79	0.048
80. BD (1)Te 12- C 20	102. BD*(1) C 5- C 23	4.86	1.00	0.062
80. BD (1)Te 12- C 20	108. BD*(1) C 9- C 21	5.02	1.00	0.063
80. BD (1)Te 12- C 20	123. BD*(1) C 21- H 22	1.01	0.86	0.026
80. BD (1)Te 12- C 20	124. BD*(1) C 23- H 24	1.04	0.85	0.027
80. BD (1)Te 12- C 20	525. RY (1) C 21	1.58	1.79	0.047
80. BD (1)Te 12- C 20	557. RY (1) C 23	1.63	1.79	0.048
82. BD (2) C 13- C 14	109. BD*(1)Te 11-Te 12	3.61	0.25	0.027
82. BD (2) C 13- C 14	285. RY (1)Te 11	0.73	0.90	0.023
84. BD (1) C 14- C 16	110. BD*(1)Te 11- C 13	4.40	0.69	0.049
90. BD (2) C 20- C 21	109. BD*(1)Te 11-Te 12	2.74	0.25	0.023
90. BD (2) C 20- C 21	330. RY (1)Te 12	0.70	0.89	0.022

Table S10. SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS for 1β XRD geometry

Threshold for printing: 0.50 kcal/mol

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
59. LP (1)Te 11	96. BD*(1) C 1- C 13	2.53	1.07	0.046
60. LP (2)Te 11	97. BD*(2) C 1- C 13	10.77	0.26	0.047
60. LP (2)Te 11	112. BD*(1)Te 12- C 20	5.77	0.30	0.037
60. LP (2)Te 11	124. BD*(1) C 23- H 24	1.54	0.63	0.028
60. LP (2)Te 11	330. RY (1)Te 12	0.86	0.95	0.025
61. LP (1)Te 12	121. BD*(1) C 20- C 23	2.53	1.07	0.046
62. LP (2)Te 12	94. BD*(1) C 1- H 2	1.54	0.63	0.028
62. LP (2)Te 12	111. BD*(1)Te 11- C 13	5.77	0.30	0.037
62. LP (2)Te 12	122. BD*(2) C 20- C 23	10.77	0.26	0.047
62. LP (2)Te 12	285. RY (1)Te 11	0.86	0.95	0.025
64. BD (1) C 1- C 3	111. BD*(1)Te 11- C 13	4.63	0.68	0.050
66. BD (2) C 1- C 13	286. RY (2)Te 11	1.10	0.75	0.026
73. BD (1) C 5- C 23	112. BD*(1)Te 12- C 20	4.64	0.68	0.050
77. BD (1) C 9- C 21	112. BD*(1)Te 12- C 20	4.52	0.68	0.050
79. BD (1)Te 11-Te 12	111. BD*(1)Te 11- C 13	0.69	0.47	0.016
79. BD (1)Te 11-Te 12	112. BD*(1)Te 12- C 20	0.69	0.47	0.016
79. BD (1)Te 11-Te 12	113. BD*(1) C 13- C 14	1.81	0.94	0.037
79. BD (1)Te 11-Te 12	120. BD*(1) C 20- C 21	1.81	0.94	0.037
80. BD (1)Te 11- C 13	94. BD*(1) C 1- H 2	0.97	0.86	0.026
80. BD (1)Te 11- C 13	95. BD*(1) C 1- C 3	4.81	1.01	0.062
80. BD (1)Te 11- C 13	110. BD*(1)Te 11-Te 12	0.56	0.43	0.014
80. BD (1)Te 11- C 13	114. BD*(1) C 14- H 15	1.06	0.85	0.027
80. BD (1)Te 11- C 13	115. BD*(1) C 14- C 16	4.86	1.00	0.062
80. BD (1)Te 11- C 13	125. RY (1) C 1	1.13	1.96	0.042
80. BD (1)Te 11- C 13	402. RY (1) C 14	1.61	1.82	0.048
81. BD (1)Te 12- C 20	104. BD*(1) C 5- C 23	4.81	1.01	0.062
81. BD (1)Te 12- C 20	108. BD*(1) C 9- C 21	4.86	1.00	0.062
81. BD (1)Te 12- C 20	110. BD*(1)Te 11-Te 12	0.56	0.43	0.014
81. BD (1)Te 12- C 20	123. BD*(1) C 21- H 22	1.06	0.85	0.027
81. BD (1)Te 12- C 20	124. BD*(1) C 23- H 24	0.97	0.86	0.026
81. BD (1)Te 12- C 20	525. RY (1) C 21	1.61	1.82	0.048
81. BD (1)Te 12- C 20	557. RY (1) C 23	1.13	1.96	0.042
84. BD (1) C 14- C 16	111. BD*(1)Te 11- C 13	4.52	0.68	0.050
91. BD (2) C 20- C 23	331. RY (2)Te 12	1.10	0.75	0.026

Table S11. Pair wise interaction energy contributions ($E_{AA'} = 0.5*(E_{dimer} - E_A - E_{A'})$) into lattice energies E_{latt} of native and putative polymorphs of Ph_2E_2 crystals. The sums of $E_{AA'}$ values are estimations of the E_{latt} values.

Bonding interactions in a dimer	Symmetry operation for a dimer	Pairwise energy $E_{AA'}$ (kcal·mol^{-1})
SEasSE, native polymorph		
Se…Se + CH…Se + stacking	x-1t; y; z;	-3.5
	x+1t; y; z;	-3.5
CH…pi	-x-1t; y+0.5-1t; -z+0.5-1t;	-2.6
	-x-1t; y+0.5; -z+0.5-1t;	-2.6
CH…pi	-x; y+0.5-1t; -z+0.5-1t;	-2.3
	-x; y+0.5; -z+0.5-1t;	-2.3
Se…Se	x+0.5-1t; -y+0.5; -z-1t;	-1.8
	x+0.5; -y+0.5; -z-1t;	-1.8
CH…pi	x+0.5-1t; -y+0.5-1t; -z-1t;	-1.6
	x+0.5; -y+0.5-1t; -z-1t;	-1.6
CH…pi + CH…Se	x; y-1t; z;	-1.6
	x; y+1t; z;	-1.6
CH…Se + CH…pi	x-1t; y-1t; z;	-1.2
	x+1t; y+1t; z;	-1.2
Sum of $E_{AA'}$		-29.2
SEasTE, putative polymorph		
Se…Se + CH…Se + stack	x-1t; y; z;	-3.5
	x+1t; y; z;	-3.5
CH…pi + CH…Se	-x; y+0.5-1t; -z+0.5;	-2.6
	-x; y+0.5; -z+0.5;	-2.6
CH…pi	-x-1t; y+0.5-1t; -z+0.5;	-1.9
	-x-1t; y+0.5; -z+0.5;	-1.9
CH…pi + CH…Se	x; y-1t; z;	-1.7
	x; y+1t; z;	-1.7
Se…Se + CH…Se	x+0.5-1t; -y+0.5; -z;	-1.7
	x+0.5; -y+0.5; -z;	-1.7
H…H + CH…Se	x-1t; y+1t; z;	-1.3
	x+1t; y-1t; z;	-1.3
CH…pi	x+0.5-1t; -y+0.5+1t; -z;	-1.2
	x+0.5; -y+0.5+1t; -z;	-1.2
Sum of $E_{AA'}$		-27.5
TEasSE, putative polymorph		
Te…Te + CH…Te + stacking	x-1t; y; z;	-4.0
	x+1t; y; z;	-4.0
Te…Te + CH…Te	x+0.5-1t; -y+0.5; -z-1t;	-3.0
	x+0.5; -y+0.5; -z-1t;	-3.0
CH…pi	-x-1t; y+0.5-1t; -z+0.5-1t;	-2.7
	-x-1t; y+0.5; -z+0.5-1t;	-2.7
CH…Te + CH…pi	-x; y+0.5-1t; -z+0.5-1t;	-2.5
	-x; y+0.5; -z+0.5-1t;	-2.5

CH…Te	x; y-1t; z; x; y+1t; z;	-1.9 -1.9
CH…pi	x+0.5-1t; -y+0.5-1t; -z-1t; x+0.5; -y+0.5-1t; -z-1t;	-1.6 -1.6
CH…Te	x-1t; y-1t; z; x+1t; y+1t; z;	-1.1 -1.1
Sum of $E_{AA'}$		-33.5

TEasTE, native polymorph		
Te…Te + CH…Te + stack	x-1t; y; z; x+1t; y; z;	-5.0 -5.0
Te…Te + CH…Te	x+0.5-1t; -y+0.5; -z; x+0.5; -y+0.5; -z;	-2.7 -2.7
CH…Te + CH…pi	-x; y+0.5-1t; -z+0.5; -x; y+0.5; -z+0.5;	-2.6 -2.6
stacking + Te…pi	x; y-1t; z; x; y+1t; z;	-2.0 -2.0
H…H + CH…pi	-x-1t; y+0.5-1t; -z+0.5; -x-1t; y+0.5; -z+0.5;	-1.8 -1.8
CH…Te + H…H	x-1t; y+1t; z; x+1t; y-1t; z;	-1.3 -1.3
CH…pi + H…H	x+0.5-1t; -y+0.5+1t; -z; x+0.5; -y+0.5+1t; -z;	-1.0 -1.0
Sum of $E_{AA'}$		-32.8

Table S12. SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS for optimized isomer α_v Se_2Ph_2

Threshold for printing: 0.50 kcal/mol

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
within unit 1				
41. LP (1)Se 11	78. BD*(1) C 1- C 13	0.84	1.08	0.027
41. LP (1)Se 11	95. BD*(1) C 13- C 14	2.26	1.08	0.044
42. LP (2)Se 11	77. BD*(1) C 1- C 3	0.58	0.78	0.019
42. LP (2)Se 11	**78. BD*(1) C 1- C 13**	**4.95**	**0.76**	**0.055**
42. LP (2)Se 11	**94. BD*(1)Se 12- C 20**	**4.27**	**0.37**	**0.035**
42. LP (2)Se 11	**95. BD*(1) C 13- C 14**	**3.48**	**0.77**	**0.046**
42. LP (2)Se 11	97. BD*(1) C 14- C 16	0.51	0.78	0.018
42. LP (2)Se 11	104. BD*(2) C 20- C 23	1.12	0.26	0.015
42. LP (2)Se 11	310. RY (1)Se 12	1.47	1.05	0.035
43. LP (1)Se 12	102. BD*(1) C 20- C 21	2.26	1.08	0.044
43. LP (1)Se 12	103. BD*(1) C 20- C 23	0.84	1.08	0.027
44. LP (2)Se 12	79. BD*(2) C 1- C 13	1.12	0.26	0.015
44. LP (2)Se 12	86. BD*(1) C 5- C 23	0.58	0.78	0.019
44. LP (2)Se 12	90. BD*(1) C 9- C 21	0.51	0.78	0.018
44. LP (2)Se 12	**93. BD*(1)Se 11- C 13**	**4.27**	**0.37**	**0.035**
44. LP (2)Se 12	**102. BD*(1) C 20- C 21**	**3.48**	**0.77**	**0.046**
44. LP (2)Se 12	**103. BD*(1) C 20- C 23**	**4.95**	**0.76**	**0.055**

44. LP (2)Se 12	267. RY (1)Se 11	1.47	1.05	0.035
46. BD (1) C 1- C 3	**93. BD*(1)Se 11- C 13**	**4.21**	**0.74**	**0.050**
48. BD (2) C 1- C 13	**92. BD*(1)Se 11-Se 12**	**4.66**	**0.28**	**0.032**
48. BD (2) C 1- C 13	267. RY (1)Se 11	1.05	1.08	0.030
55. BD (1) C 5- C 23	**94. BD*(1)Se 12- C 20**	**4.21**	**0.74**	**0.050**
59. BD (1) C 9- C 21	**94. BD*(1)Se 12- C 20**	**4.26**	**0.74**	**0.050**
61. BD (1)Se 11-Se 12	**79. BD*(2) C 1- C 13**	**3.90**	**0.44**	**0.037**
61. BD (1)Se 11-Se 12	**104. BD*(2) C 20- C 23**	**3.90**	**0.44**	**0.037**
61. BD (1)Se 11-Se 12	355. RY (3) C 13	0.65	1.38	0.027
61. BD (1)Se 11-Se 12	356. RY (4) C 13	0.60	2.39	0.034
61. BD (1)Se 11-Se 12	478. RY (3) C 20	0.65	1.38	0.027
61. BD (1)Se 11-Se 12	479. RY (4) C 20	0.60	2.39	0.034
62. BD (1)Se 11- C 13	76. BD*(1) C 1- H 2	0.75	0.92	0.023
62. BD (1)Se 11- C 13	**77. BD*(1) C 1- C 3**	**4.04**	**1.04**	**0.058**
62. BD (1)Se 11- C 13	96. BD*(1) C 14- H 15	0.73	0.91	0.023
62. BD (1)Se 11- C 13	**97. BD*(1) C 14- C 16**	**3.85**	**1.04**	**0.057**
62. BD (1)Se 11- C 13	107. RY (1) C 1	1.60	1.94	0.050
62. BD (1)Se 11- C 13	311. RY (2)Se 12	0.52	1.49	0.025
62. BD (1)Se 11- C 13	380. RY (1) C 14	1.51	1.96	0.049
63. BD (1)Se 12- C 20	**86. BD*(1) C 5- C 23**	**4.04**	**1.04**	**0.058**
63. BD (1)Se 12- C 20	**90. BD*(1) C 9- C 21**	**3.85**	**1.04**	**0.057**
63. BD (1)Se 12- C 20	105. BD*(1) C 21- H 22	0.73	0.91	0.023
63. BD (1)Se 12- C 20	106. BD*(1) C 23- H 24	0.75	0.92	0.023
63. BD (1)Se 12- C 20	268. RY (2)Se 11	0.52	1.49	0.025
63. BD (1)Se 12- C 20	503. RY (1) C 21	1.51	1.96	0.049
63. BD (1)Se 12- C 20	535. RY (1) C 23	1.60	1.94	0.050
66. BD (1) C 14- C 16	**93. BD*(1)Se 11- C 13**	**4.26**	**0.74**	**0.050**
73. BD (2) C 20- C 23	**92. BD*(1)Se 11-Se 12**	**4.66**	**0.28**	**0.032**
73. BD (2) C 20- C 23	310. RY (1)Se 12	1.05	1.08	0.030

Table S13. SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS for optimized isomer β_v Se_2Ph_2

Threshold for printing: 0.50 kcal/mol

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L) a.u.	F(L,NL) a.u.
41. LP (1)Se 22	93. BD*(1) C 12- C 21	3.32	1.10	0.054
41. LP (1)Se 22	521. RY (3)Se 23	0.52	1.68	0.026
42. LP (2)Se 22	85. BD*(1) C 6- C 8	0.58	0.77	0.019
42. LP (2)Se 22	**89. BD*(1) C 8-Se 23**	**6.07**	**0.36**	**0.042**
42. LP (2)Se 22	90. BD*(1) C 9- H 10	0.88	0.66	0.021
42. LP (2)Se 22	**94. BD*(2) C 12- C 21**	**14.21**	**0.27**	**0.055**
42. LP (2)Se 22	519. RY (1)Se 23	1.71	1.17	0.040
43. LP (1)Se 23	87. BD*(1) C 8- C 9	3.32	1.10	0.054
43. LP (1)Se 23	478. RY (3)Se 22	0.52	1.68	0.026
44. LP (2)Se 23	**88. BD*(2) C 8- C 9**	**14.18**	**0.27**	**0.055**
44. LP (2)Se 23	91. BD*(1) H 11- C 12	0.89	0.66	0.022
44. LP (2)Se 23	104. BD*(1) C 19- C 21	0.58	0.77	0.019
44. LP (2)Se 23	**105. BD*(1) C 21-Se 22**	**6.07**	**0.36**	**0.042**
44. LP (2)Se 23	476. RY (1)Se 22	1.71	1.17	0.040
50. BD (1) C 3- C 9	**89. BD*(1) C 8-Se 23**	**4.61**	**0.73**	**0.052**
51. BD (1) C 5- C 6	**89. BD*(1) C 8-Se 23**	**4.25**	**0.73**	**0.050**
54. BD (1) C 6- C 8	106. BD*(1)Se 22-Se 23	0.63	0.64	0.018
57. BD (2) C 8- C 9	520. RY (2)Se 23	1.65	0.90	0.034
58. BD (1) C 8-Se 23	81. BD*(1) C 3- C 9	3.88	1.05	0.057
58. BD (1) C 8-Se 23	82. BD*(1) C 5- C 6	3.92	1.05	0.057
58. BD (1) C 8-Se 23	86. BD*(1) C 6- H 24	0.80	0.90	0.024
58. BD (1) C 8-Se 23	90. BD*(1) C 9- H 10	0.73	0.92	0.023
58. BD (1) C 8-Se 23	106. BD*(1)Se 22-Se 23	0.70	0.53	0.017
58. BD (1) C 8-Se 23	198. RY (1) C 6	1.51	1.96	0.049
58. BD (1) C 8-Se 23	257. RY (1) C 9	1.00	2.11	0.041
58. BD (1) C 8-Se 23	478. RY (3)Se 22	0.80	1.62	0.032
59. BD (1) C 9- H 10	89. BD*(1) C 8-Se 23	0.53	0.61	0.016
60. BD (1) H 11- C 12	105. BD*(1) C 21-Se 22	0.53	0.61	0.016
61. BD (1) C 12- C 13	**105. BD*(1) C 21-Se 22**	**4.61**	**0.73**	**0.052**
63. BD (2) C 12- C 21	477. RY (2)Se 22	1.65	0.90	0.034
70. BD (1) C 17- C 19	**105. BD*(1) C 21-Se 22**	**4.25**	**0.73**	**0.050**
73. BD (1) C 19- C 21	106. BD*(1)Se 22-Se 23	0.64	0.64	0.018
74. BD (1) C 21-Se 22	91. BD*(1) H 11- C 12	0.73	0.92	0.023
74. BD (1) C 21-Se 22	**92. BD*(1) C 12- C 13**	**3.88**	**1.05**	**0.057**
74. BD (1) C 21-Se 22	**101. BD*(1) C 17- C 19**	**3.92**	**1.05**	**0.057**
74. BD (1) C 21-Se 22	103. BD*(1) C 19- H 20	0.80	0.90	0.024
74. BD (1) C 21-Se 22	106. BD*(1)Se 22-Se 23	0.71	0.53	0.017
74. BD (1) C 21-Se 22	294. RY (1) C 12	0.99	2.11	0.041
74. BD (1) C 21-Se 22	417. RY (1) C 19	1.52	1.96	0.049
74. BD (1) C 21-Se 22	521. RY (3)Se 23	0.80	1.62	0.032
75. BD (1)Se 22-Se 23	85. BD*(1) C 6- C 8	2.18	0.97	0.041
75. BD (1)Se 22-Se 23	89. BD*(1) C 8-Se 23	0.75	0.57	0.018
75. BD (1)Se 22-Se 23	104. BD*(1) C 19- C 21	2.19	0.97	0.041
75. BD (1)Se 22-Se 23	105. BD*(1) C 21-Se 22	0.75	0.57	0.019
75. BD (1)Se 22-Se 23	233. RY (4) C 8	0.60	2.20	0.032
75. BD (1)Se 22-Se 23	452. RY (4) C 21	0.60	2.20	0.032

Table S14. Selected NBOs composition and population (bonding/antibonding) in isomers of Se_2Ph_2 and Te_2Ph_2 in vacuo.

Ph2Se2 α_v

```
  61. (1.95403) BD ( 1)Se 11-Se 12
              ( 50.00%)   0.7071*Se 11 s(  5.78%)p16.19( 93.61%)d 0.10(  0.56%)
                                                  f 0.01(  0.05%)
              ( 50.00%)   0.7071*Se 12 s(  5.78%)p16.19( 93.61%)d 0.10(  0.56%)
                                                  f 0.01(  0.05%)
  62. (1.97530) BD ( 1)Se 11- C 13
              ( 44.91%)   0.6701*Se 11 s( 12.46%)p 7.00( 87.19%)d 0.03(  0.34%)
                                                  f 0.00(  0.02%)
              ( 55.09%)   0.7422* C 13 s( 24.91%)p 3.00( 74.84%)d 0.01(  0.20%)
                                                  f 0.00(  0.06%)
  63. (1.97530) BD ( 1)Se 12- C 20
              ( 44.91%)   0.6701*Se 12 s( 12.46%)p 7.00( 87.19%)d 0.03(  0.34%)
                                                  f 0.00(  0.02%)
              ( 55.09%)   0.7422* C 20 s( 24.91%)p 3.00( 74.84%)d 0.01(  0.20%)
                                                  f 0.00(  0.06%)
```

Ph2Se2 β_v

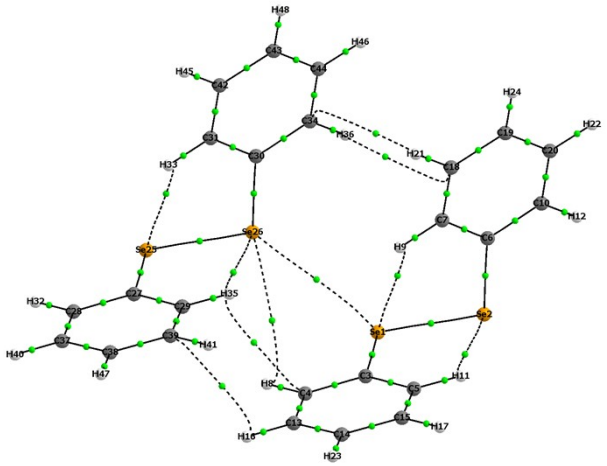
```
  75. (1.97601) BD ( 1)Se 22-Se 23
              ( 50.00%)   0.7071*Se 22 s(  7.08%)p13.03( 92.30%)d 0.08(  0.56%)
                                                  f 0.01(  0.06%)
              ( 50.00%)   0.7071*Se 23 s(  7.08%)p13.04( 92.30%)d 0.08(  0.56%)
                                                  f 0.01(  0.06%)

  74. (1.97530) BD ( 1) C 21-Se 22
              ( 54.03%)   0.7350* C 21 s( 23.96%)p 3.16( 75.77%)d 0.01(  0.21%)
                                                  f 0.00(  0.06%)
              ( 45.97%)   0.6780*Se 22 s( 12.80%)p 6.79( 86.86%)d 0.03(  0.33%)
                                                  f 0.00(  0.02%)

  58. (1.97532) BD ( 1) C  8-Se 23
              ( 54.02%)   0.7350* C  8 s( 23.96%)p 3.16( 75.77%)d 0.01(  0.21%)
                                                  f 0.00(  0.06%)
              ( 45.98%)   0.6781*Se 23 s( 12.80%)p 6.79( 86.86%)d 0.03(  0.33%)
                                                  f 0.00(  0.02%)
```

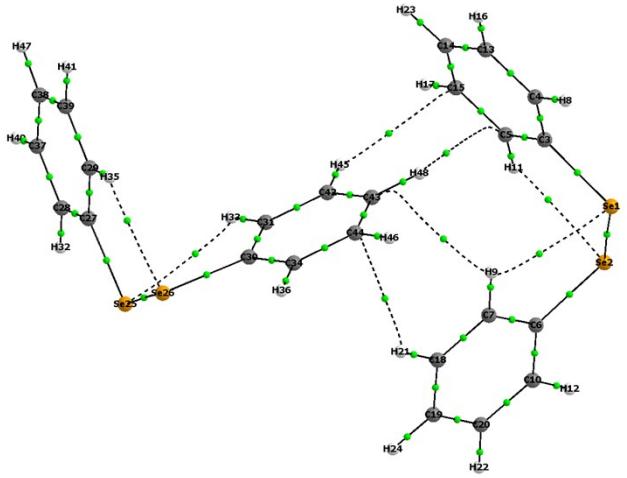
Ph2Te2 α_v

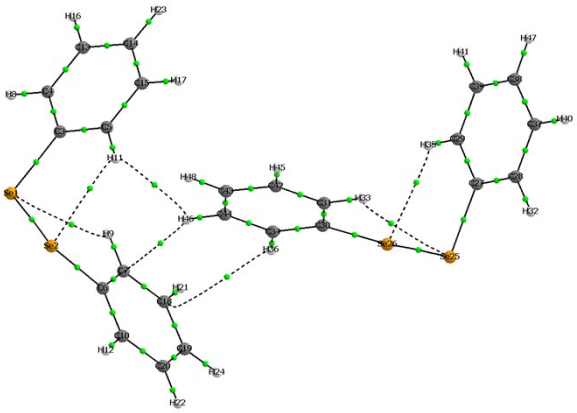
```
  79. (1.95869) BD ( 1)Te 11-Te 12
              ( 50.00%)   0.7071*Te 11 s(  5.62%)p16.70( 93.79%)d 0.11(  0.60%)
              ( 50.00%)   0.7071*Te 12 s(  5.62%)p16.70( 93.79%)d 0.11(  0.60%)

  80. (1.96845) BD ( 1)Te 11- C 13
              ( 39.76%)   0.6306*Te 11 s( 10.19%)p 8.79( 89.54%)d 0.03(  0.27%)
              ( 60.24%)   0.7761* C 13 s( 24.51%)p 3.07( 75.30%)d 0.01(  0.16%)
                                                  f 0.00(  0.03%)

  81. (1.96845) BD ( 1)Te 12- C 20
              ( 39.76%)   0.6306*Te 12 s( 10.19%)p 8.79( 89.54%)d 0.03(  0.27%)
              ( 60.24%)   0.7761* C 20 s( 24.51%)p 3.07( 75.30%)d 0.01(  0.16%)
                                                  f 0.00(  0.03%)
```

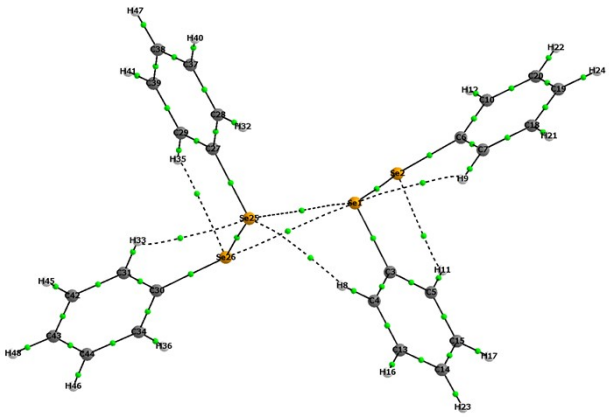
Ph2Te2 β_v

```
  79. (1.97566) BD ( 1)Te 11-Te 12
              ( 50.00%)   0.7071*Te 11 s(  6.64%)p13.97( 92.75%)d 0.09(  0.61%)
              ( 50.00%)   0.7071*Te 12 s(  6.64%)p13.97( 92.75%)d 0.09(  0.61%)
     80. (1.96887) BD ( 1)Te 11- C 13
              ( 40.76%)   0.6385*Te 11 s( 10.48%)p 8.52( 89.24%)d 0.03(  0.28%)
              ( 59.24%)   0.7697* C 13 s( 23.68%)p 3.21( 76.11%)d 0.01(  0.18%)
                                                  f 0.00(  0.03%)
  81. (1.96887) BD ( 1)Te 12- C 20
              ( 40.76%)   0.6385*Te 12 s( 10.48%)p 8.51( 89.24%)d 0.03(  0.28%)
              ( 59.24%)   0.7697* C 20 s( 23.68%)p 3.21( 76.11%)d 0.01(  0.18%)
                                                  f 0.00(  0.03%)
```









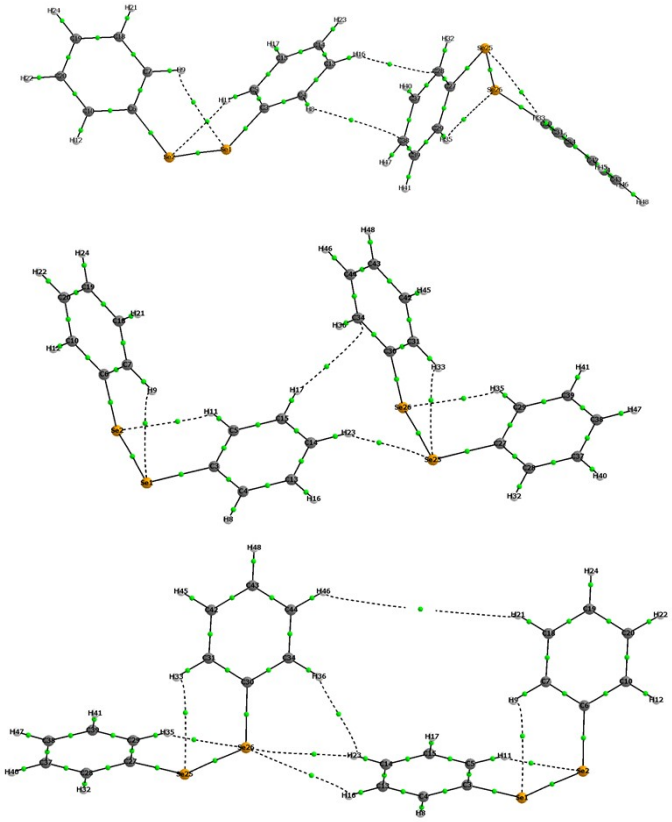
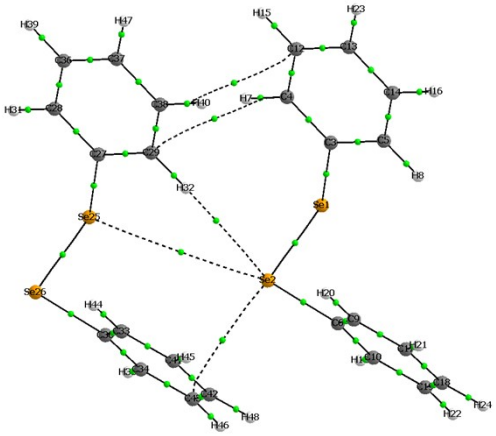
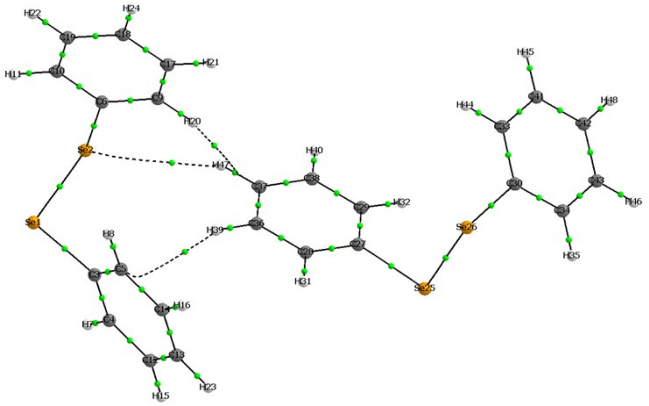
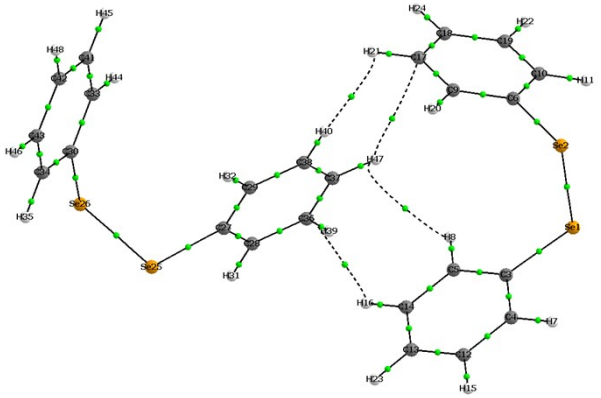
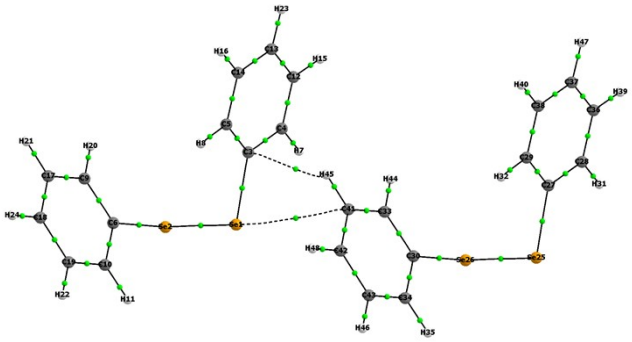


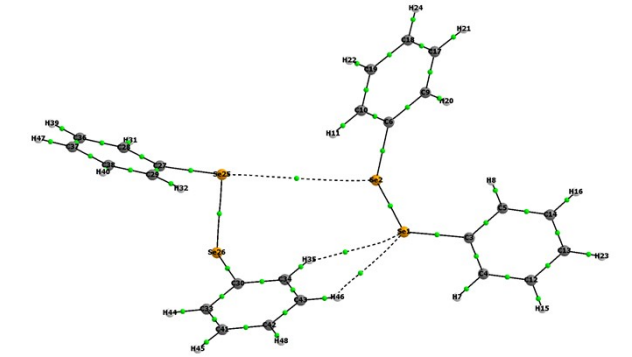
Figure 22
QTAIM atomic connectivity graphs for dimers from the native polymorph of Ph2Se2 (in the order of decreasing of absolute value of pairwise interaction energy).

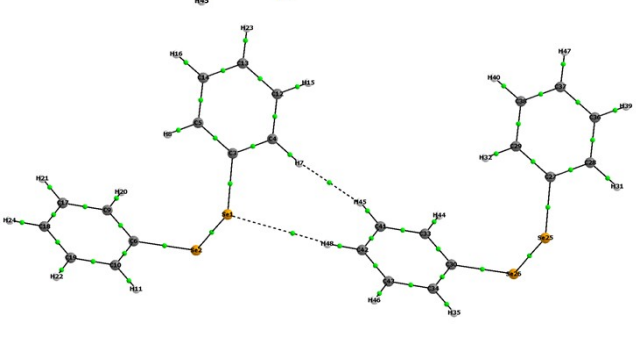












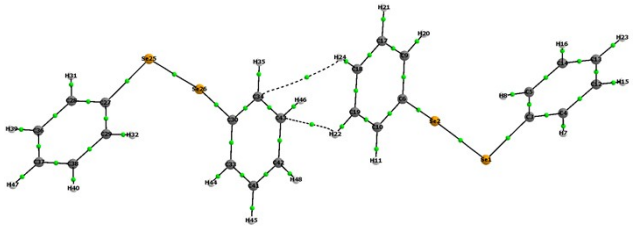
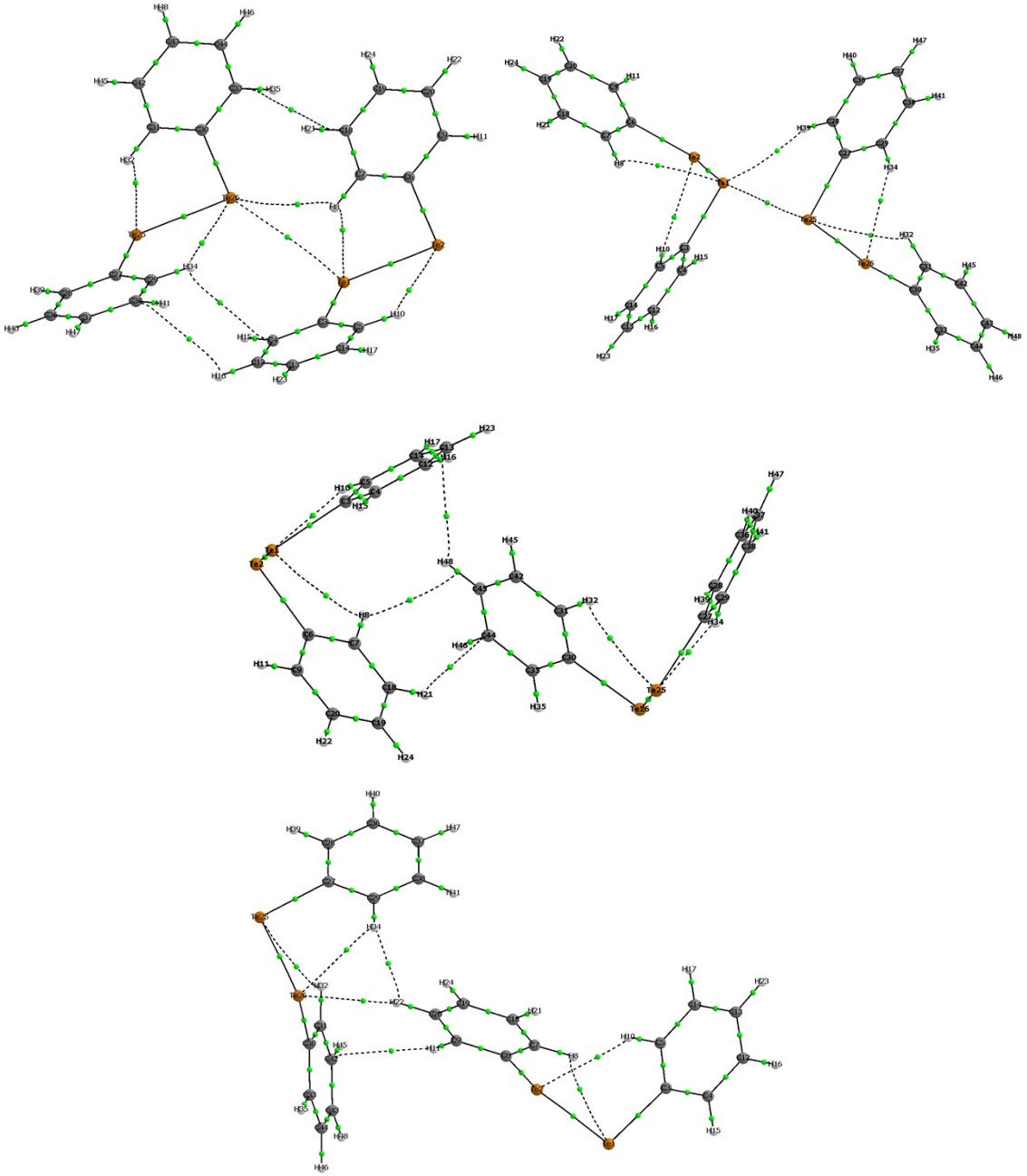


Figure 23
QTAIM atomic connectivity graphs for dimers from the putative polymorph of Ph2Se2 (in the order of decreasing of absolute value of pairwise interaction energy).



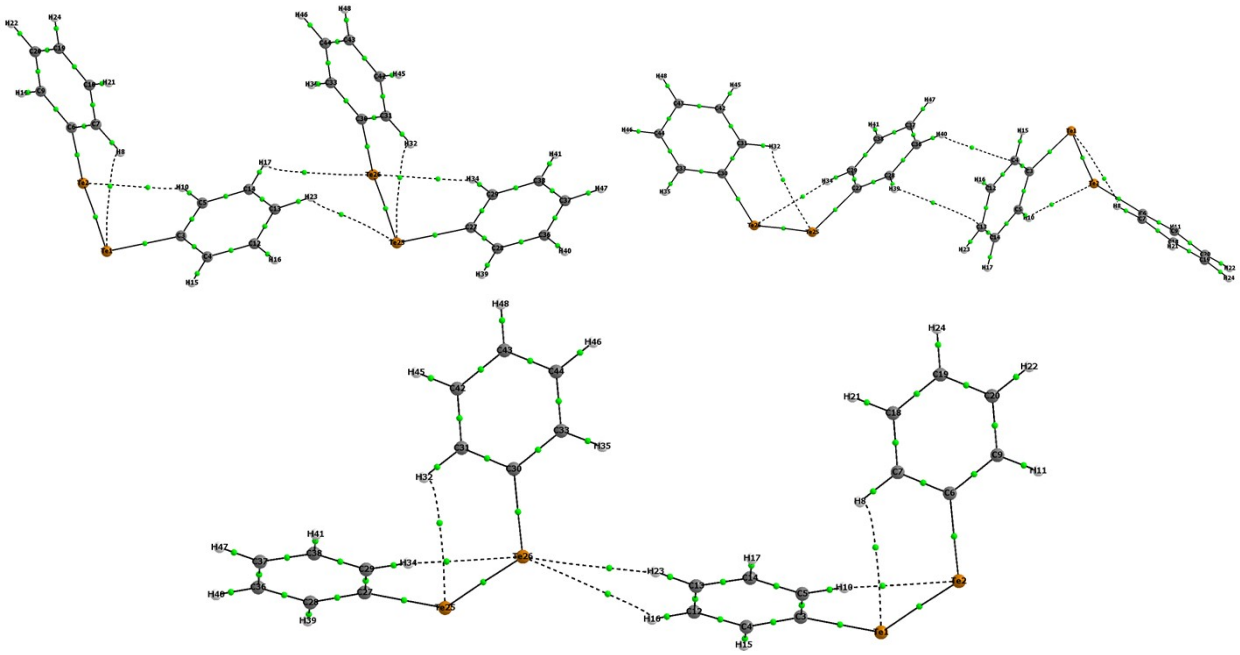


Figure 24
QTAIM atomic connectivity graphs for dimers from the putative polymorph of Ph2Te2 (in the order of decreasing of absolute value of pairwise interaction energy).

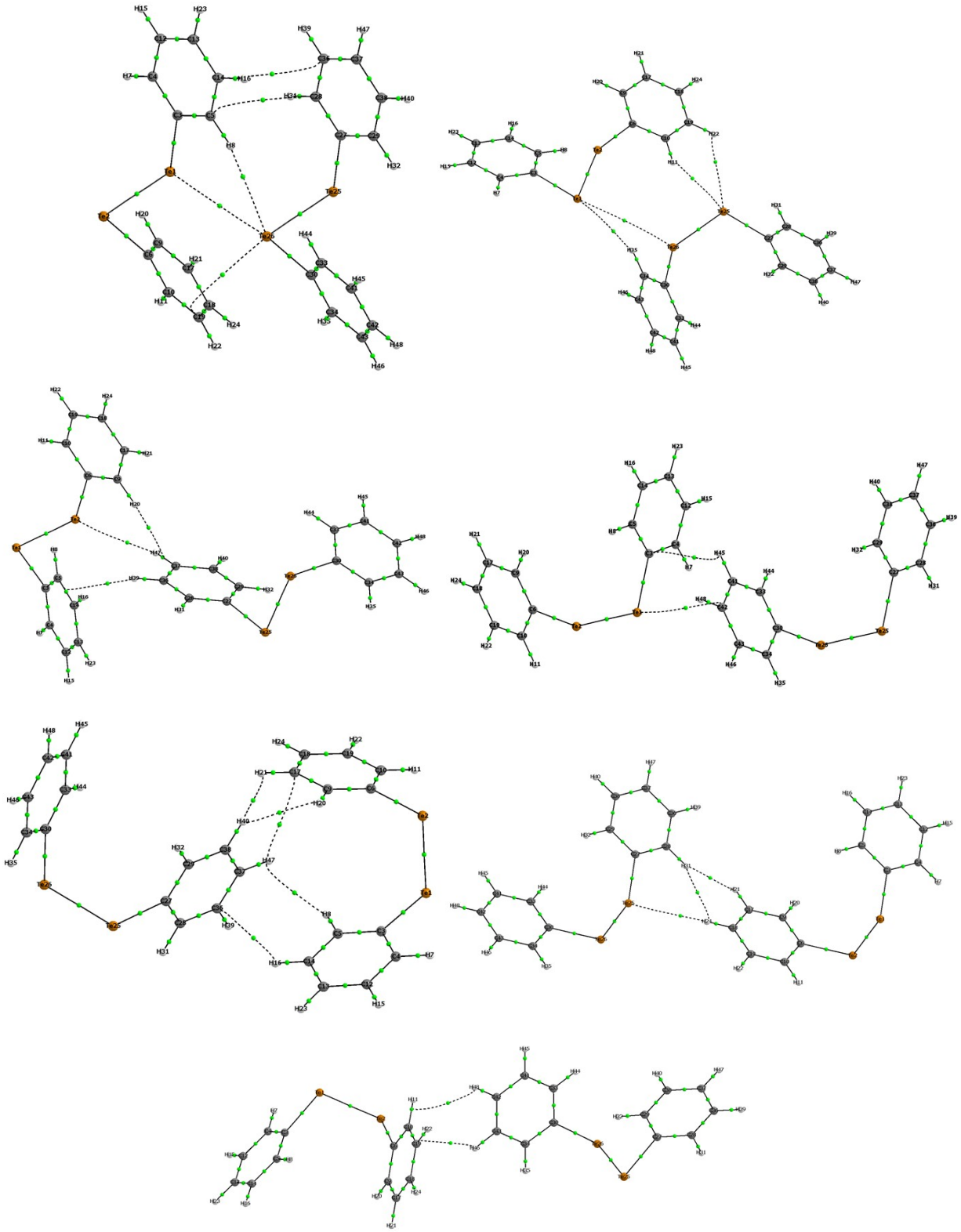


Figure 25
QTAIM atomic connectivity graphs for dimers from the native polymorph of Ph2Te2 (in the order of decreasing of absolute value of pairwise interaction energy).

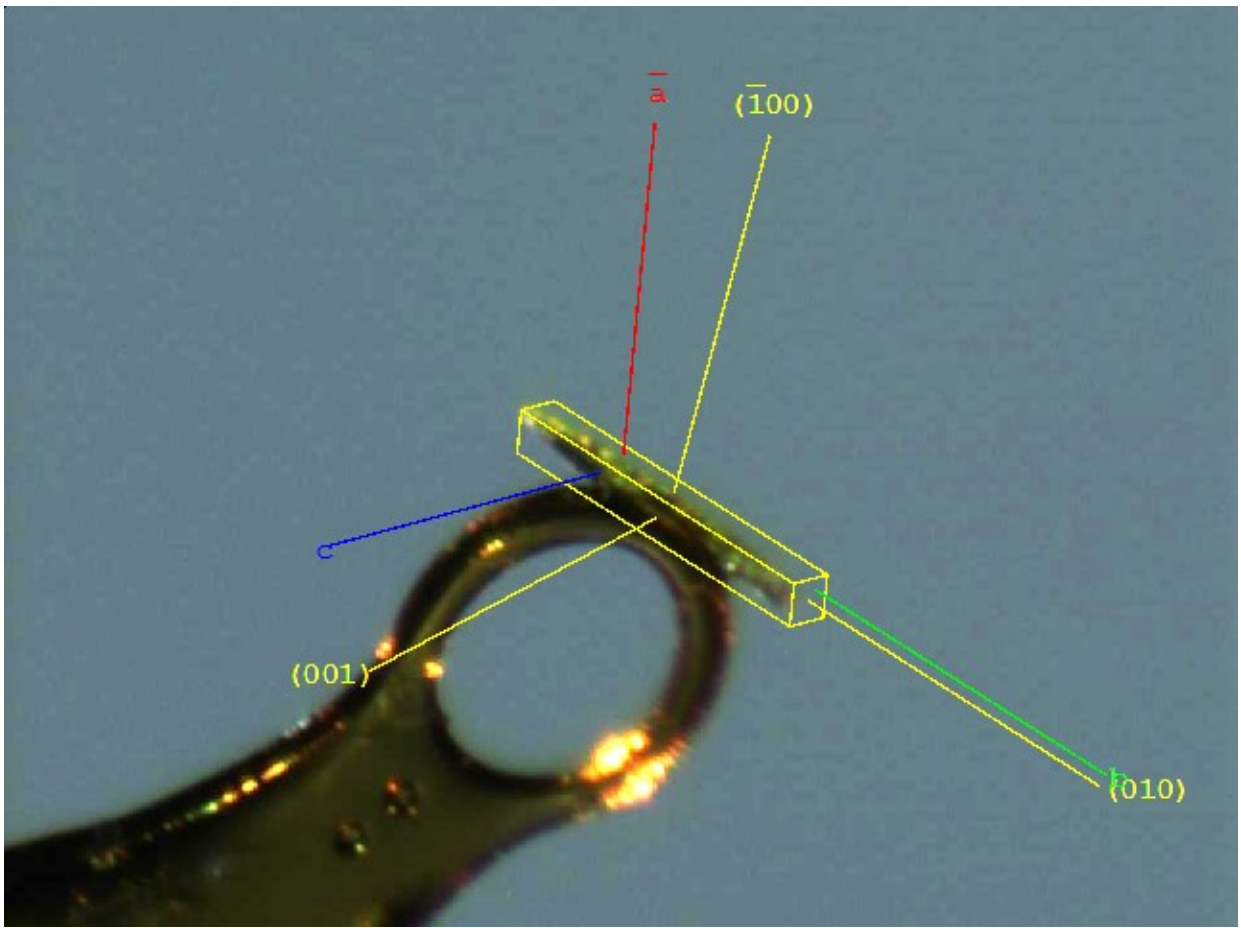


Figure S26
Micro photo of the acicular crystals of **1α** showing crystal faces and axis indexing.

$P2_1/n$	
cell_length_a	13.2557(10)
cell_length_b	5.3985(4)
cell_length_c	23.3604(18)
cell_angle_beta	103.761(1)

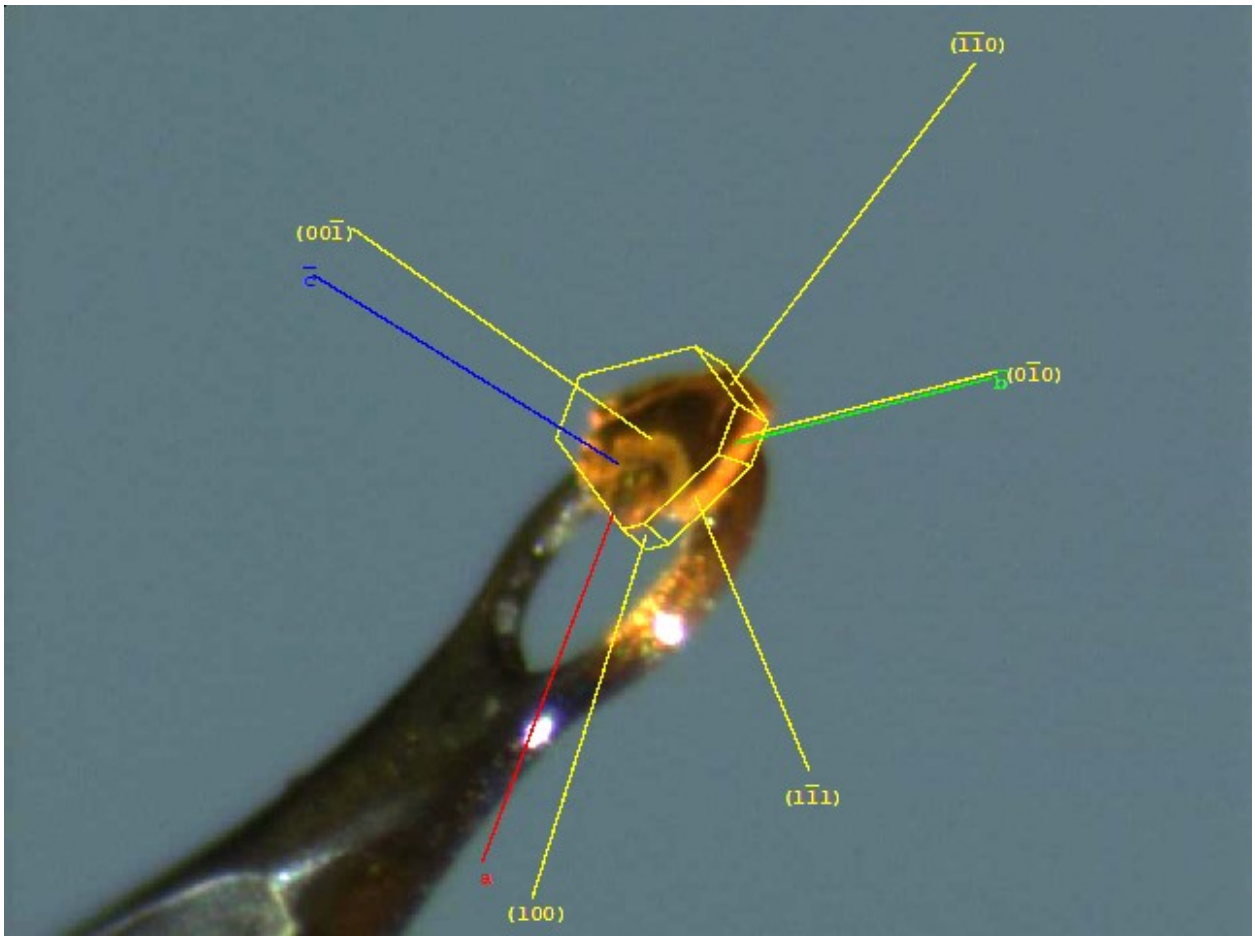


Figure S27
Micro photo of the acicular crystals of **1γ** showing crystal faces and axis indexing.

C2/c

cell_length_a	6.8200(4)
cell_length_b	8.6628(5)
cell_length_c	33.6106(19)
cell_angle_beta	92.684(2)