Supporting Information

New charge-transfer complexes of 1,2,5-chalcogenadiazoles with tetrathiafulvalenes

Elena A. Chulanova,*[a,b] Ekaterina A. Radiush,[a] Yaser Balmohammadi,[c] Jens Beckmann,[d] Simon Grabowsky[c] and Andrey V. Zibarev[a]

[a] *Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk, Russia*

[b] *Institute for Applied Physics, University of Tübingen, 72076 Tübingen, Germany*
E-mail: elena.chulanova@uni-tuebingen.de (E. A. Chulanova)

[c] *Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, 3012 Bern, Switzerland*

[d] *Institute for Inorganic Chemistry and Crystallography, University of Bremen, 28359 Bremen, Germany*

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1. Single-crystal X-ray diffraction

Table S1 Crystallographic data for the complexes

Complex	**1**	**2**	**3**	**4**	**5'**
Empirical formula	$C_{10}H_4N_4S_5$	$C_{21}H_6N_{12}S_6Se_3$	$C_{12}H_4N_2F_4S_5$	$C_{11}H_6N_4S_3$	$C_{18}H_8N_8S_8Te_2$
Formula weight (g mol^{-1})	340.47	855.62	412.47	290.38	848.00
Temperature [K]	100.0	100.0	100.0	100.0	100.0
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	Cc	$P2_1/c$	$P\bar{1}$
a [Å]	6.6346(4)	7.3298(2)	9.8502(5)	11.0656(4)	7.5481(2)
b [Å]	13.3837(8)	7.8942(3)	10.6342(5)	8.8374(3)	7.7702(2)
c [Å]	15.6515(9)	26.3901(9)	14.8943(7)	12.0606(4)	12.5117(3)
α [°]	88.0932(2)	95.9690(10)	90	90	74.6450(10)
β [°]	86.315(2)	92.9840(10)	103.318(2)	104.261(2)	85.362(2)
γ [°]	79.276(3)	90.1160(10)	90	90	69.6810(10)
V [Å^3]	1362.33(14)	1516.63(9)	1518.20(13)	1143.07(7)	663.54(3)
Z	4	2	4	4	1
ρ_{calcd} [Mg m^{-3}]	1.660	1.874	1.805	1.687	2.122
μ [mm^{-1}]	0.839	4.088	0.802	0.632	2.855
F (000)	688	828	824	592	404
Θ range [°]	2.61–25.00	2.33–35.10	2.81–32.59	2.89–30.14	2.878–28.34
Crystal size [mm^3]	0.2×0.15×0.15	0.30×0.25×0.15	0.25×0.25×0.10	0.30 × 0.20 × 0.10	0.40×0.20×0.15
Index range	$-7 \le h \le 7$, $-15 \le k \le 15$, $-18 \le l \le 18$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-42 \le l \le 42$	$-14 \le h \le 14$, $-16 \le k \le 15$, $-22 \le l \le 22$	$-15 \le h \le 15$, $-12 \le k \le 12$, $-16 \le l \le 17$	$-10 \le h \le 10$, $-10 \le k \le 10$, $-16 \le l \le 16$
Reflections collected	33113	122898	34507	62097	22597
Independent reflections	4769 [R_{int} = 0.1174]	13406 [R_{int} = 0.0580]	5421 [R_{int} = 0.0487]	3357 [R_{int} = 0.0948]	3357 [R_{int} = 0.0354]
Completeness to θ [%]	99.7	99.9	100.0	100.0	100.0
Data / restraints / parameters	4769 / 0 / 343	13406 / 0 / 379	5421 / 2 / 208	3357 / 0 / 163	3302 / 0 / 163

Goodness of fit on F^2	1.096	1.044	1.038	1.083	1.102
R indices [I > 2σ(I)]	R_1 = 0.0579, wR_2 = 0.1440	R_1 = 0.0371, wR_2 = 0.0545	R_1 = 0.0352, wR_2 = 0.0637	R_1 = 0.0495, wR_2 = 0.1171	R_1 = 0.0195, wR_2 = 0.0402
R indices (all data)	R_1 = 0.0827, wR_2 = 0.1524	R_1 = 0.0644, wR_2 = 0.0595	R_1 = 0.0543, wR_2 = 0.0696	R_1 = 0.0689, wR_2 = 0.1254	R_1 = 0.0248, wR_2 = 0.0417
Largest diff. peak / hole, e Å^{-3}	0.718 / –0.510	0.635 / –0.683	0.356 / –0.375	0.114 / –0.441	0.819 / –0.783
CCDC	**2192018**	**2192019**	**2192020**	**2192021**	**2192022**

2. Powder X-ray diffraction

Powder XRD was applied to control structural authenticity of low-crystalline bulky samples, as well as thin films, of the studied complexes.

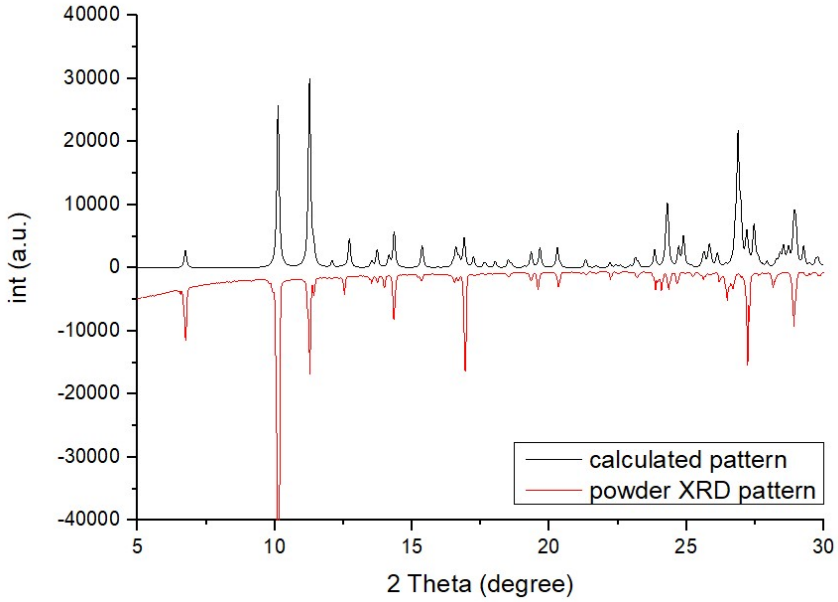

Figure S1. Powder XRD patterns of complex **2**: experimental (red) and calculated from the single-crystal data (black).

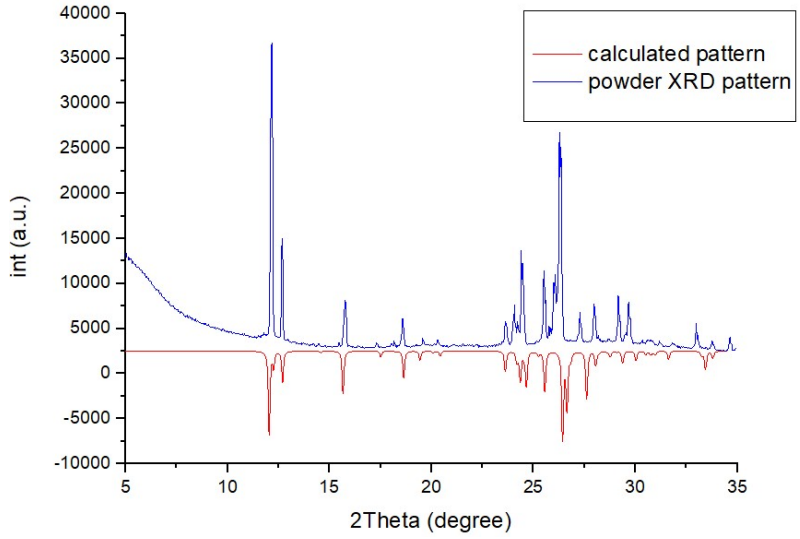

Figure S2. Powder XRD patterns of complex **3**: experimental (blue) and calculated from the single-crystal data (red).

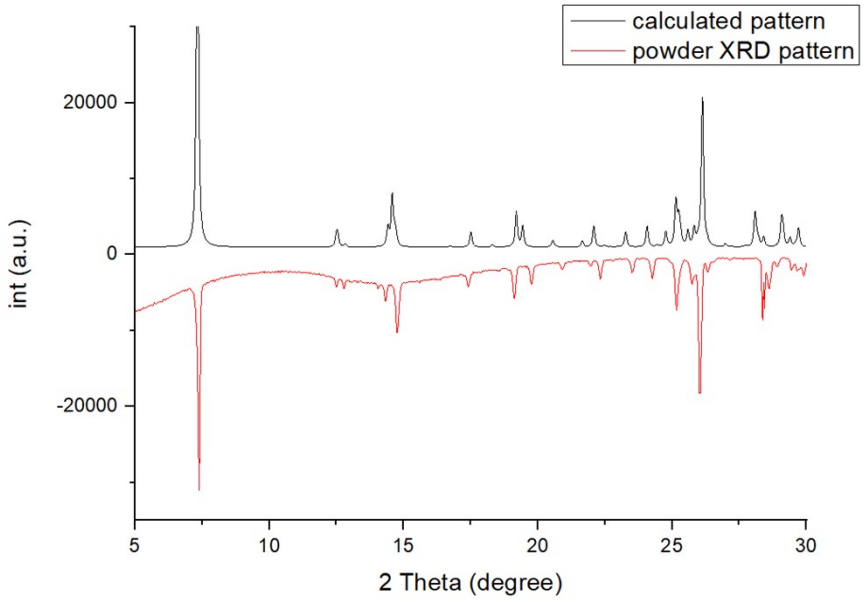

Figure S3. Powder XRD patterns of complex **5**: experimental (red) and calculated from the single-crystal data (black).

3. DFT calculations.

Below are the molecular geometries optimized at B97-D3/def2-tzvp level of theory with an effective core potential (ECP) for Te.

1

C	6.405040000000	7.832869000000	2.717517000000
C	6.781619000000	7.829503000000	4.024254000000
C	5.081151000000	8.245964000000	0.542417000000
H	4.243968000000	8.446275000000	-0.117156000000
C	6.372783000000	8.257703000000	0.174198000000
H	6.727798000000	8.462465000000	-0.829587000000
C	6.793466000000	8.281619000000	6.559250000000
H	6.423148000000	8.485556000000	7.557801000000
C	8.083380000000	8.324237000000	6.193169000000
H	8.909875000000	8.564187000000	6.853004000000
S	8.467378000000	7.906802000000	4.537792000000
S	5.625386000000	7.802257000000	5.352305000000
S	7.564725000000	7.868653000000	1.387477000000
S	4.715602000000	7.870055000000	2.205035000000
C	5.289749000000	11.251578000000	2.264497000000
C	5.416471000000	11.097946000000	3.690320000000
C	4.062346000000	11.317776000000	1.547694000000
C	4.331173000000	11.045988000000	4.608837000000
N	6.460749000000	11.296355000000	1.624602000000

N	6.685940000000	11.015285000000	4.100310000000
N	3.055267000000	11.348180000000	0.969896000000
N	3.425662000000	11.042294000000	5.336555000000
S	7.631026000000	11.133939000000	2.766309000000

2

S	-7.967863000000	1.173586000000	20.448970000000
S	-9.261456000000	1.785103000000	24.622420000000
S	-9.236581000000	3.593803000000	22.281670000000
S	-8.224311000000	-0.683617000000	22.730209000000
C	-8.468287000000	0.951649000000	22.118992000000
C	-8.943885000000	1.972510000000	22.897847000000
C	-7.383964000000	-0.454085000000	20.229368000000
C	-7.501297000000	-1.294436000000	21.267769000000
C	-9.738826000000	3.438218000000	24.873788000000
C	-9.717684000000	4.264337000000	23.812705000000
Se	-11.636237000000	2.855959000000	19.530654000000
N	-11.645455000000	1.082724000000	19.974325000000
N	-10.574710000000	2.563441000000	18.083326000000
N	-8.556613000000	0.273732000000	16.407386000000
N	-10.385264000000	-2.073082000000	19.361279000000
C	-10.266921000000	1.278217000000	18.071447000000
C	-10.863257000000	0.456703000000	19.111095000000
C	-10.621918000000	-0.941291000000	19.247562000000

C	-9.339718000000	0.746957000000	17.123354000000
Se	-12.378622000000	0.698977000000	22.626162000000
N	-12.624415000000	0.968438000000	24.408399000000
N	-12.622145000000	2.476016000000	22.260032000000
N	-13.058053000000	3.261733000000	26.975303000000
N	-13.134421000000	5.661667000000	23.460913000000
C	-12.838925000000	2.257709000000	24.598478000000
C	-12.844826000000	3.090396000000	23.407663000000
C	-13.022195000000	4.505661000000	23.429867000000
C	-12.980290000000	2.791721000000	25.915667000000
H	-7.211453000000	-2.338994000000	21.254205000000
H	-6.996119000000	-0.713653000000	19.250890000000
H	-10.039453000000	3.725728000000	25.875449000000
H	-10.006943000000	5.309127000000	23.833506000000

3

S	12.400857000000	-2.920511000000	3.151386000000
F	8.604020000000	-0.581352000000	2.723377000000
N	11.010032000000	-2.097220000000	3.349689000000
F	12.042336000000	-2.294231000000	-1.269947000000
C	11.514010000000	-2.188865000000	1.066143000000
F	8.092785000000	-0.078704000000	0.082981000000
F	9.752826000000	-0.912579000000	-1.849417000000
C	9.188007000000	-0.759286000000	0.447452000000

N	12.576282000000	-2.872670000000	1.533419000000
C	10.072708000000	-1.200028000000	-0.580220000000
C	10.610780000000	-1.742438000000	2.113118000000
C	11.224067000000	-1.896797000000	-0.288307000000
C	9.444455000000	-1.014847000000	1.776073000000
C	10.337662000000	2.492009000000	-0.228957000000
H	9.372829000000	2.941606000000	-0.434656000000
C	11.197570000000	2.059965000000	-1.163314000000
H	11.027226000000	2.108903000000	-2.233408000000
C	13.998216000000	-0.028819000000	4.298438000000
H	14.060188000000	-0.270207000000	5.354005000000
C	14.861066000000	-0.456139000000	3.361228000000
H	15.720266000000	-1.089356000000	3.553715000000
S	10.812487000000	2.338666000000	1.445585000000
S	12.713572000000	1.380961000000	-0.621517000000
S	12.692634000000	1.006933000000	3.788733000000
S	14.598403000000	0.062731000000	1.718516000000
C	13.079950000000	0.900181000000	2.066646000000
C	12.301181000000	1.448528000000	1.097800000000

4

S	4.323652000000	3.807981000000	7.947584000000
S	3.449409000000	2.317415000000	5.565310000000
C	4.009116000000	2.110343000000	8.134609000000

C	3.598947000000	1.433467000000	7.048280000000
C	3.979873000000	3.853201000000	6.224376000000
S	3.771108000000	5.029174000000	3.741237000000
S	4.645459000000	6.519689000000	6.123496000000
C	4.085444000000	6.726851000000	3.554273000000
C	4.495652000000	7.403712000000	4.640601000000
C	4.114861000000	4.983945000000	5.464449000000
S	0.915107000000	7.639795000000	4.135527000000
N	0.966452000000	5.278541000000	6.954257000000
N	0.045062000000	4.079340000000	4.472437000000
N	1.183978000000	7.279395000000	5.695631000000
N	0.399024000000	6.228871000000	3.519500000000
C	0.654225000000	3.176836000000	8.040643000000
C	-0.212255000000	1.999175000000	5.620637000000
C	0.405727000000	5.360303000000	4.563724000000
C	0.594519000000	3.986484000000	6.870876000000
C	0.138665000000	3.382319000000	5.620611000000
C	0.863746000000	5.966436000000	5.816853000000
C	-0.137222000000	1.258686000000	6.773931000000
C	0.296281000000	1.852760000000	7.993113000000
S	7.179968000000	1.198371000000	7.554836000000
N	7.128373000000	3.558596000000	4.735250000000
N	8.049522000000	4.758837000000	7.216656000000
N	6.911163000000	1.558152000000	5.994582000000

N	7.695805000000	2.609603000000	8.170370000000
C	7.440233000000	5.659963000000	3.648119000000
C	8.306651000000	6.838599000000	6.067675000000
C	7.689075000000	3.477776000000	7.125818000000
C	7.500093000000	4.850739000000	4.818173000000
C	7.955858000000	5.455424000000	6.068224000000
C	7.231209000000	2.871110000000	5.872890000000
C	8.231498000000	7.578664000000	4.914114000000
C	7.797994000000	6.984106000000	3.695170000000
H	-0.414021000000	0.207049000000	6.762430000000
H	0.343652000000	1.245413000000	8.894222000000
H	-0.544476000000	1.568400000000	4.679847000000
H	0.992807000000	3.649513000000	8.958350000000
H	3.356571000000	0.377583000000	7.025644000000
H	4.133770000000	1.686700000000	9.124536000000
H	3.960642000000	7.150540000000	2.564384000000
H	4.737895000000	8.459625000000	4.663269000000
H	7.750494000000	7.591132000000	2.793852000000
H	8.508217000000	8.630326000000	4.925217000000
H	7.101678000000	5.186912000000	2.730595000000
H	8.638880000000	7.269749000000	7.008292000000

5’

Te	7.380495000000	8.894695000000	0.156820000000

N	7.503781000000	8.282418000000	2.105042000000
N	8.136784000000	10.636697000000	0.918243000000
C	7.963916000000	9.248320000000	2.849890000000
C	8.317036000000	10.529153000000	2.209485000000
N	9.248845000000	12.525887000000	3.571626000000
C	8.838302000000	11.631763000000	2.951812000000
N	8.249218000000	9.014902000000	5.420538000000
C	8.119010000000	9.095090000000	4.268692000000
S	5.321634000000	12.743867000000	1.119353000000
S	4.455866000000	10.149664000000	2.208475000000
S	5.949849000000	13.986212000000	3.708897000000
S	4.948159000000	10.875768000000	5.045343000000
C	4.540431000000	11.207411000000	0.812686000000
C	5.364450000000	12.569890000000	2.870113000000
C	4.970501000000	11.366288000000	3.368728000000
C	5.972870000000	13.442971000000	5.461846000000
H	5.018816000000	13.716792000000	5.919561000000
H	6.770696000000	14.050492000000	5.906000000000
C	6.269933000000	11.965028000000	5.673046000000
H	7.221724000000	11.672561000000	5.229405000000
H	6.310988000000	11.747309000000	6.746009000000
S	3.371976000000	9.283398000000	-0.782924000000
S	4.205050000000	11.904418000000	-1.823645000000
S	1.661188000000	8.698135000000	-3.221762000000

S	2.555231000000	11.735311000000	-4.291877000000
C	4.093040000000	10.846783000000	-0.429592000000
C	2.643968000000	9.802419000000	-2.303995000000
C	3.035266000000	11.010881000000	-2.789314000000
C	2.544647000000	8.914912000000	-4.824149000000
H	3.595368000000	8.682599000000	-4.639843000000
H	2.125130000000	8.155365000000	-5.494139000000
C	2.367418000000	10.289383000000	-5.444659000000
H	1.364537000000	10.405184000000	-5.865951000000
H	3.114020000000	10.436146000000	-6.234368000000
Te	8.219790000000	12.412803000000	-1.056998000000
N	7.710940000000	12.995549000000	-2.934848000000
N	7.488638000000	10.606202000000	-1.656120000000
C	7.116689000000	12.003233000000	-3.552326000000
C	6.990749000000	10.711532000000	-2.874248000000
N	5.853022000000	8.675734000000	-3.993313000000
C	6.368017000000	9.588343000000	-3.488931000000
N	6.132611000000	12.247493000000	-5.943337000000
C	6.581914000000	12.162560000000	-4.875266000000

4. Hirshfeld surface analysis

Table S2 Interaction energy and its components (kJ mol^{-1}) for complexes **1**-**4** and **5**'. The reference molecule below the HS and the color-coded neighboring molecules are depicted in Figure 2, left column. Calculated at the B3LYP/6-31G(d,p) / B3LYP/dgdzvp levels of theory[a-c]

Molecule	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
			1		
	–1.7 / –1.7	–0.1 / –0.1	–1.7[b]	0.0 / 0.1	–3.3 / –3.2
	–6.6 / –7.3	–0.9 / –1.0	–7.2[b]	8.2 / 9.6	–8.9 / –8.9
	–1.1 / –2.1	–0.5 / –0.5	–10.9[b]	13.0 / 14.5	–3.0 / –3.1
	–4.0 / –6.0	–0.6 / –0.6	–7.0[a]	3.2 / 5.5	–8.8 / –9.4
	–7.0 / –10.6	–0.8 / –0.8	–12.2[b]	9.1 / 14.5	–13.0 / –13.5
	–3.9 / –5.3	–0.8 / –0.9	–7.1[b]	9.6 / 11.4	–4.9 / –5.3
	–9.2 / –9.8	–1.5 / –1.5	–4.2[b]	9.1 / 10.1	–8.9 / –8.8
	–4.9 / –8.2	–0.7 / –0.8	–9.7[b]	6.2 / 11.3	–10.3 / –10.7
	–29.1 / –40.8	–4.4 / –4.7	–43.6[b]	57.7 / 72.6	–36.4 / –39.8
	–6.1 / –8.1	–1.2 / –1.3	–10.5[b]	13.3 / 16.0	–8.3 / –8.7
	–7.0 / –7.6	–1.3 / –1.3	–4.5[b]	6.0 / 6.9	–8.6 / –8.6
	–16.2 / –25.8	–3.8 / –4.0	–35.7[b]	42.7 / 55.0	–24.6 / –27.4
	–1.8 / –2.1	–0.2 / –0.2	–2.8[b]	0.1 / 0.4	–4.4 / –4.6
	–7.7 / –9.5	–0.8 / –0.7	–9.7[b]	13.1 / 15.9	–9.0 / –9.2
	0.1 / 0.1	–0.1 / –0.1	–0.7[b]	0.0 / 0.0	–0.6 / –0.5
	–1.2 / –2.0	–1.0 / –1.0	–8.0[b]	6.1 / 8.3	–5.2 / –4.7
	1.0 / 1.0	0.0 / 0.0	–0.2[b]	0.0 / 0.0	0.8 / 0.8
			2		
	–14.4 / –23.0	–2.2 / –2.4	–23.3[b]	31.9 / 46.3	–17.5 / –17.7
	–0.5 / –0.5	–0.2 / –0.2	–1.2[b]	0.0 / 0.0	–1.6 / –1.7
	2.5 / 1.4	–1.1 / –1.2	–10.2[b]	7.9 / 10.7	–2.0 / –1.6
	–8.5 / –9.9	–0.9 / –0.8	–9.8[b]	12.8 / 15.1	–10.2 / –10.2
	–9.7 / –11.5	–1.6 / –1.6	–9.3[b]	14.3 / 17.0	–10.7 / –10.9
	–21.2 / –31.6	–3.6 / –3.8	–38.0[b]	41.3 / 58.1	–32.7 / –33.5
	–7.4 / –11.0	–0.9 / –0.9	–13.0[b]	22.5 / 27.7	–5.9 / –6.5

	–0.3 / –0.2	0.0 / 0.0	–0.2[b]	0.0 / 0.0	–0.4 / –0.4
			3		
	–16.9 / –33.0	–2.5 / –2.8	–49.0[b]	51.7 / 69.5	–30.5 / –36.6
	1.3 / 1.2	–0.2 / –0.2	–1.3[b]	0.0 / 0.0	0.1 / 0.1
	–5.7 / –7.2	–0.9 / –0.9	–9.5[b]	8.1 / 10.5	–10.0 / –10.0
	–10.1 / –12.5	–1.5 / –1.6	–9.9[b]	13.7 / 16.7	–12.0 / –12.7
	–10.9 / –13.7	–1.4 / –1.6	–11.4[b]	16.3 / 19.8	–12.5 / –13.3
	–10.7 / –12.9	–0.9 / –0.9	–10.3[b]	20.0 / 23.3	–8.6 / –8.9
	–3.6 / –4.1	–0.4 / –0.4	–6.4[b]	4.6 / 5.4	–6.9 / –6.9
	–0.4 / –0.5	–0.2 / –0.3	–5.0[b]	0.6 / 1.4	–4.5 / –4.2
	–1.9 / –2.9	–0.2 / –0.3	–7.1[b]	4.6 / 5.9	–5.5 / –5.8
	–14.6 / –25.2	–2.1 / –2.3	–41.7[b]	38.8 / 51.2	–29.3 / –33.0
	–2.2 / –4.2	–0.3 / –0.4	–8.3[b]	5.4 / 8.4	–6.4 / –6.7
	0.4 / 0.3	–0.1 / –0.1	–4.0[b]	1.7 / 2.2	–2.2 / –2.0
			4		
	0.0 / 0.0	–0.1 / –0.1	–0.9[b]	0.0 / 0.0	–0.9 / –0.9
	–0.2 / –0.1	–0.1 / –0.1	–1.0[b]	0.0 / 0.0	–1.1 / –1.0
	–5.7 / –6.9	–1.0 / –1.0	–10.7[b]	11.7 / 14.0	–8.9 / –8.6
	–5.9 / –7.5	–0.9 / –0.9	–8.9[b]	7.2 / 9.2	–10.1 / –10.6
	–4.1 / –4.5	–0.5 / –0.5	–3.0[b]	0.6 / 0.8	–6.9 / –7.3
	–7.9 / –10.0	–2.6 / –2.8	–10.2[b]	11.7 / 14.3	–11.9 / –12.7
	–12.5 / –27.8	–2.3 / –2.3	–50.4[b]	53.1 / 73.9	–26.0 / –29.3
	–6.8 / –7.5	–0.8 / –0.9	–12.2[b]	18.7 / 20.4	–6.8 / –6.6
	–1.1 / –1.1	–0.1 / –0.1	–1.2[b]	0.0 / 0.0	–2.2 / –2.3
			5'[c]		
	–1.1	–0.7	–4.7	–1.6	–2.5
	–21.2	–3.2	–28.3	48.8	–19.2
	–47.3	–4.4	–43.5	78.4	–42.7
	–14.4	–2.6	–6.5	13.1	–14.7
	–9.7	–2.4	–6.8	14.6	–9.0
	–8.2	–1.4	–10.3	7.2	–14.2
	–13.7	–1.5	–14.0	18.5	–16.4
	–22.1	–3.1	–29.6	36.9	–28.7

	–12.1	–0.8	–21.7	44.3	–4.8
	–1.5	–0.4	–1.9	0.1	–0.3
	–0.0	–0.2	–1.0	0.0	–1.0
	–1.1	–0.1	–0.6	0.0	–1.7
	–2.6	–0.2	–0.4	–0.0	–2.2
	–1.0	–0.0	–0.1	0.0	–0.9
	–0.6	–0.0	–0.2	0.0	–0.4
	–0.3	–0.0	–0.1	0.0	–0.4

[a] E_{tot} is the total interaction energy; and E_{ele}, E_{pol}, E_{dis} and E_{rep} are energies of electrostatic, polarization, dispersion and Pauli-repulsion interactions, respectively. E_{ele}, E_{pol}, E_{dis} and E_{rep} are given as absolute values without scale factor, whereas E_{tot} is the sum of the scaled[1] components. [b] The dispersion energies are independent of the level of theory as they are taken as sums of tabulated atomic Grimme terms. [c] For **5'**, only B3LYP/dgdzvp data are given because for the element Te, the basis set 6-31G(d,p) is not defined.

4. References

1 C. F. Mackenzie, P. R. Spackman, D. Jayatilaka and M. A. Spackman, *IUCrJ*, 2017, **4**, 575–587.