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Supporting information for article:

Electronic criterion for categorizing the chalcogen and halogen bonds: sulfur–iodine interactions in crystals

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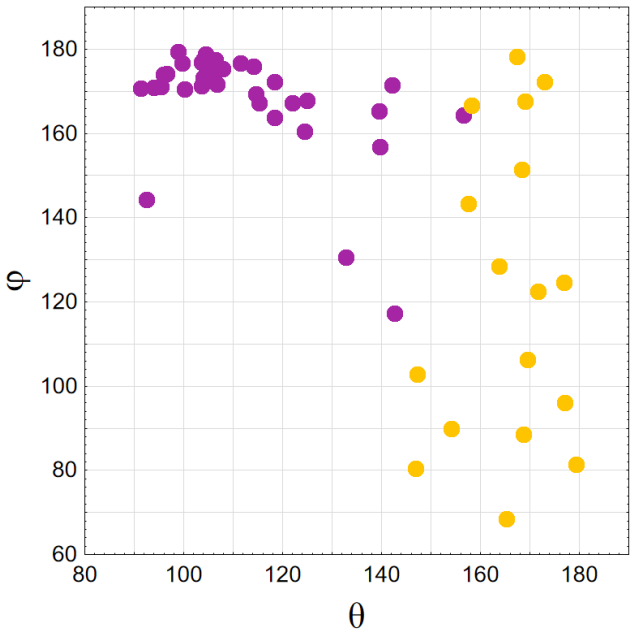

1 Scatterplot of θ,° and φ,° angles for S...I interactions in the set of considered crystals

Table S1 Calculated geometrical characteristics of S…I interactions for the test sample of crystals

Refcode	References	Noncovalent interaction	θ_{calc}, °	θ_{exp}, °	φ_{calc}, °	φ_{exp}, °	$d(S\ldots I)_{calc}$, Å	$d(S\ldots I)_{exp}$, Å
BIYDUK	Takemura *et al.*, 2014*a*	S(1)…I(1)	118.3	107.8	172.3	172.2	3.3119	3.3085
CUZDEH	Knight *et al.*, 2010	S(1)…I(1)	107.8	108.6	175.4	176.6	3.5696	3.5038
DUBGEO	Hubscher *et al.*, 2015	S(1)…I(1)	114.7	115.7	169.4	168.8	3.5870	3.6073
FAJPUB	Herbstein*et al.*, 1986	S(1)…I(1)	105.2	107.0	175.9	176.7	2.8386	2.8248
FAJPUB		S(2)…I(3)	106.2	107.2	176.3	176.1	2.8157	2.8055
FAJPUB		S(2)…I(2)	179.4	177.7	81.5	82.4	3.7090	3.7087
FAJRAJ	Herbstein*et al.*, 1986	S(1)…I(1)	103.6	102.7	171.3	173.0	2.8080	2.8025
FAJRAJ		S(2)…I(3)	114.1	114.7	175.9	177.0	2.9085	2.9012
GIGBED	Minkwitz *et al.*, 1988	S(1)…I(1)	111.4	113.8	176.8	175.6	3.2110	3.2106
GOJMUP	Behl *et al.*, 2012	S(2)…I(1)	139.8	139.4	156.8	154.9	3.6753	3.7080
GUDJUL	Ohta *et al.*,	S(2)…I(1)	115.2	117.7	167.2	165.3	3.5590	3.5363

	2009							
HIZQOY	Takemura *et al.,* 2014*b*	S(1)…I(1)	91.3	103.7	170.8	171.0	3.2030	3.2644
HOVLUA	SweeKuan Yen *et al.,* 2009	S(1)…I(3)	168.7	169.5	88.5	92.7	3.7113	3.6597
HOVLUA		S(1)…I(2)	169.0	166.7	167.6	166.3	3.6284	3.6194
ICILEL	Batsanov *et al.,* 2001	S(2)…I(4)	118.3	119.8	163.7	163.0	3.4931	3.5411
ICILEL		S(3)…I(1)	132.8	132.0	130.6	131.8	3.6796	3.7310
IFOSUL01	Wolstenholme *et al.,* 2006	S(5)…I(1)	104.4	104.6	178.8	177.1	3.4514	3.5153
IFOSUL01		S(1)…I(1A)	147.0	146.2	80.5	80.9	3.6924	3.7678
LEXSEN	Csehe*t al.,* 2007	S(1)…I(2)	124.9	123.0	167.8	167.3	3.6223	3.6407
NAHTIC	Rajesh Goud *et al.,* 2016	S(1)…I(1)	93.9	92.6	170.9	171.1	3.4160	3.1258
NAKROH	Werz *et al.,* 2005	S(1)…I(2)	154.1	161.9	89.9	96.2	3.8042	3.6462
NAKROH		S(1)…I(3)	168.3	163.9	151.5	151.5	3.7255	3.6442
NAKROH		S(2)…I(3)	165.2	172.8	68.5	69.8	3.8445	3.7700
NEPJIB	Makarov *et al.,* 2001	S(2)…I(1)	124.4	124.1	160.5	165.0	3.6949	3.7211
NEPJIB		S(4)…I(1)	147.2	148.5	102.8	103.3	3.7933	3.9056
NICSIB	Bock *et al.,* 1997	S(1)…I(1)	103.6	102.6	176.9	177.6	2.7831	2.7472
NICSIB		S(2)…I(3)	95.4	94.2	171.0	170.3	3.1026	3.1230
PEGZUY	Szlachcic *et al.,* 2013	S(2)…I(1)	106.3	104.5	177.5	177.8	2.8209	2.7845
PEGZUY		S(1)…I(2)	142.2	146.8	171.5	174.6	3.5141	3.5957
PIPXUJ	Kyoung-Soon Shin *et al.,* 2017	S(1)…I(2)	92.5	91.2	144.3	144.9	3.6772	3.7019
PIPXUJ		S(4)…I(1)	122.0	121.9	167.3	167.9	3.6516	3.6366
PUSREA	Blake *et al.,* 1998	S(4)…I(7)	100.2	120.2	170.6	172.9	2.8928	2.8400
PUSREA		S(3)…I(5)	99.6	99.3	176.7	178.8	2.8768	2.8281
PUSREA		S(1)…I(1)	98.8	99.9	179.4	178.4	2.8123	2.7963
PUSRUQ	Blake *et al.,* 1998	S(1)…I(1B)	106.8	172.7	171.7	107.4	3.1925	3.2132
REBZON	Bock *et al.,*1996	S(1)…I(1)	96.6	96.3	174.3	173.3	3.1367	3.1488
REBZON		S(2)…I(2)	103.9	103.3	177.5	178.4	3.0020	3.0250
SEJQAC	Bol'shakov *et al.,* 2017	S(4)…I(4)	157.6	160.0	143.3	144.0	3.6725	3.6302
SEJQAC		S(3)…I(4)	167.4	173.3	178.2	178.3	3.4570	3.4072
SEJQAC		S(1)…I(4)	169.5	174.0	106.4	104.0	3.4171	3.4322
SEJQAC		S(1)…I(2)	171.7	174.1	122.6	125.2	3.2471	3.4312
SEJQAC		S(3)…I(2)	177.1	178.1	96.2	98.3	3.3736	3.5113

WEDHAQ	Aragoni *et al.,* 2012	S(1)…I(3)	172.0	173.0	173.1	172.2	3.7842	3.7790
WURGUM	Tamilselvi *et al.,* 2012	S(1)…I(3)	156.6	156.2	164.4	163.1	3.5283	3.5970
WURGUM		S(2)…I(2)	158.2	162.3	166.6	174.8	3.4108	3.5080
WURGUM		S(3)…I(2)	176.9	177.0	124.6	124.6	3.7487	3.6680
XEPXUN	MijoonLee *et al.,* 2012	S(2)...I(1)	106.4	104.4	174.8	173.6	3.4740	3.4741
YEWPAR	Cristiani *et al.,* 1993	S(3)…I(5)	104.0	104.5	173.2	174.5	2.9341	2.9336
YEWPAR		S(1)…I(1)	104.8	101.6	173.6	173.5	2.8534	2.8803
YEWPAR		S(1)…I(4)	142.6	144.4	117.3	118.0	3.7242	3.7427
YEWPAR		S(1)…I(6)	163.7	166.5	128.4	130.7	3.7342	3.7342
YEWPAR		S(2)…I(3)	95.9	104.2	174.1	175.1	2.8650	2.8650

Table S2 Calculated topological characteristics of electron density in bond critical points for S…I interactions in considerate crystals

Refcode	Noncovalent interaction	$\rho(r_{bcp})$	ED_{min}
BIYDUK	S(1)…I(1)	0.0171	0.0171
CUZDEH	S(1)…I(1)	0.0109	0.0109
DUBGEO	S(1)…I(1)	0.0106	0.0106
FAJPUB	S(1)…I(1)	0.0426	0.0426
FAJPUB	S(2)…I(3)	0.0439	0.0438
FAJPUB	S(2)…I(2)	0.0086	0.0086
FAJRAJ	S(1)…I(1)	0.0449	0.0448
FAJRAJ	S(2)…I(3)	0.0369	0.0368
GIGBED	S(1)…I(1)	0.0201	0.0200
GOJMUP	S(2)…I(1)	0.0080	0.008
GUDJUL	S(2)…I(1)	0.0099	0.0099
HIZQOY	S(1)…I(1)	0.0209	0.0209
HOVLUA	S(1)…I(3)	0.0088	0.0087
HOVLUA	S(1)…I(2)	0.0087	0.0087
ICILEL	S(2)…I(4)	0.0118	0.0118
ICILEL	S(3)…I(1)	0.0089	0.0089
IFOSUL01	S(5)…I(1)	0.0124	0.0124
IFOSUL01	S(1)…I(1A)	0.0092	0.0092
LEXSEN	S(1)…I(2)	0.0060	0.0088
NAHTIC	S(1)…I(1)	0.0239	0.0239
NAKROH	S(1)…I(2)	0.0075	0.0075
NAKROH	S(1)…I(3)	0.0078	0.0078
NAKROH	S(2)…I(3)	0.0066	0.0066
NEPJIB	S(2)…I(1)	0.0072	0.0072
NEPJIB	S(4)…I(1)	0.0073	0.0073
NICSIB	S(1)…I(1)	0.0461	0.0466
NICSIB	S(2)…I(3)	0.0269	0.0269
PEGZUY	S(2)…I(1)	0.0436	0.0436
PEGZUY	S(1)…I(2)	0.0118	0.0117
PIPXUJ	S(1)…I(2)	0.0094	0.0093
PIPXUJ	S(4)…I(1)	0.0085	0.0084
PUSREA	S(4)…I(7)	0.0384	0.0384

PUSREA	S(3)…I(5)	0.0447	0.0447
PUSREA	S(1)…I(1)	0.0395	0.0395
PUSRUQ	S(1)…I(1B)	0.0228	0.0228
REBZON	S(1)…I(1)	0.0252	0.0252
REBZON	S(2)…I(2)	0.0315	0.0314
SEJQAC	S(4)…I(4)	0.0083	0.0083
SEJQAC	S(3)…I(4)	0.0118	0.0118
SEJQAC	S(1)…I(4)	0.0138	0.0138
SEJQAC	S(1)…I(2)	0.0200	0.0200
SEJQAC	S(3)…I(2)	0.0158	0.0157
WEDHAQ	S(1)…I(3)	0.0068	0.0067
WURGUM	S(1)…I(3)	0.0105	0.0105
WURGUM	S(2)…I(2)	0.0139	0.0139
WURGUM	S(3)…I(2)	0.0079	0.0079
XEPXUN	S(2)...I(1)	0.0129	0.0129
YEWPAR	S(3)…I(5)	0.0355	0.0355
YEWPAR	S(1)…I(1)	0.0409	0.0408
YEWPAR	S(1)…I(4)	0.0092	0.0092
YEWPAR	S(1)…I(6)	0.0078	0.0078
YEWPAR	S(2)…I(3)	0.0395	0.0395

Basis sets for S (Francl *et al.*, 1982; Gill *et al.*, 1992) and I (Towler, 1995) atoms in CRYSTAL format:

```
16 5
0 0 6 2. 1.
  21917.1000000          0.0018690
3301.4900000           0.0142300
 754.1460000           0.0696960
 212.7110000           0.2384870
  67.9896000           0.4833070
  23.0515000           0.3380740
0 1 6 8. 1.
    423.7350000          -0.0023767           0.0040610
    100.7100000          -0.0316930           0.0306810
     32.1599000          -0.1133170           0.1304520
     11.8079000           0.0560900           0.3272050
      4.6311000           0.5922550           0.4528510
      1.8702500           0.4550060           0.2560420
0 1 3 6. 1.
      2.6158400          -0.2503740          -0.0145110
      0.9221670           0.0669570           0.3102630
      0.3412870           1.0545100           0.7544830
0 1 1 0. 1.
      0.1171670           1.0000000           1.0000000
0 3 1 0. 1.
      0.6500000           1.0000000

53 11
0 0 9 2.0 1.11463
  3796580.0      0.0000486
   557679.0      0.0003926
   120134.0      0.0022873
    30906.4      0.011153
     8941.5      0.046196
     2853.97     0.153983
     1012.96     0.349652
403.354  0.429635
169.853  0.20006
```

```
0 1 7 8.0 1.13163
   10780.9000     -0.0002564   0.0010711
    2503.2700     -0.0060868   0.0097716
     769.8280     -0.051254    0.057486
     274.7070     -0.147205    0.219537
     111.3650      0.112441    0.461365
      51.8016      0.578709    0.455975
      25.2655      0.472067    0.215153
0 1 6 8.0 1.15719
    231.9100     0.0065595    -0.013354
     91.9272    -0.0265300    -0.066906
     38.3184   -0.316678     0.0087493
     17.4017   -0.036354     0.828479
8.14936  0.902330    1.302420
3.88355  0.457207    0.442669
0 3 6 10.0 1.0
    407.3970    0.013328
    121.6230    0.093425
     45.5984    0.30357
     18.9713    0.470024
      8.4500    0.30913
3.65671  0.053371
0 1 3 8.0 1.0
9.05308  -2.34517     -0.083203
4.91160  -0.545076    0.308103
      2.31586   5.55305      0.713035
0 1 1 7.0 1.0
      1.13401     1.0         1.0
0 3 3 10.0 1.0
6.76221  0.221231
2.69744  0.563316
1.09895  0.414919
0 3 1 0.0 1.0
      0.419302   1.0
0 1 1 0.0 1.0
      0.557375   1.0         1.0
0 1 1 0.0 1.0
      0.226293   1.0         1.0
0 1 1 0.0 1.0
      0.08542     1.0         1.0
```

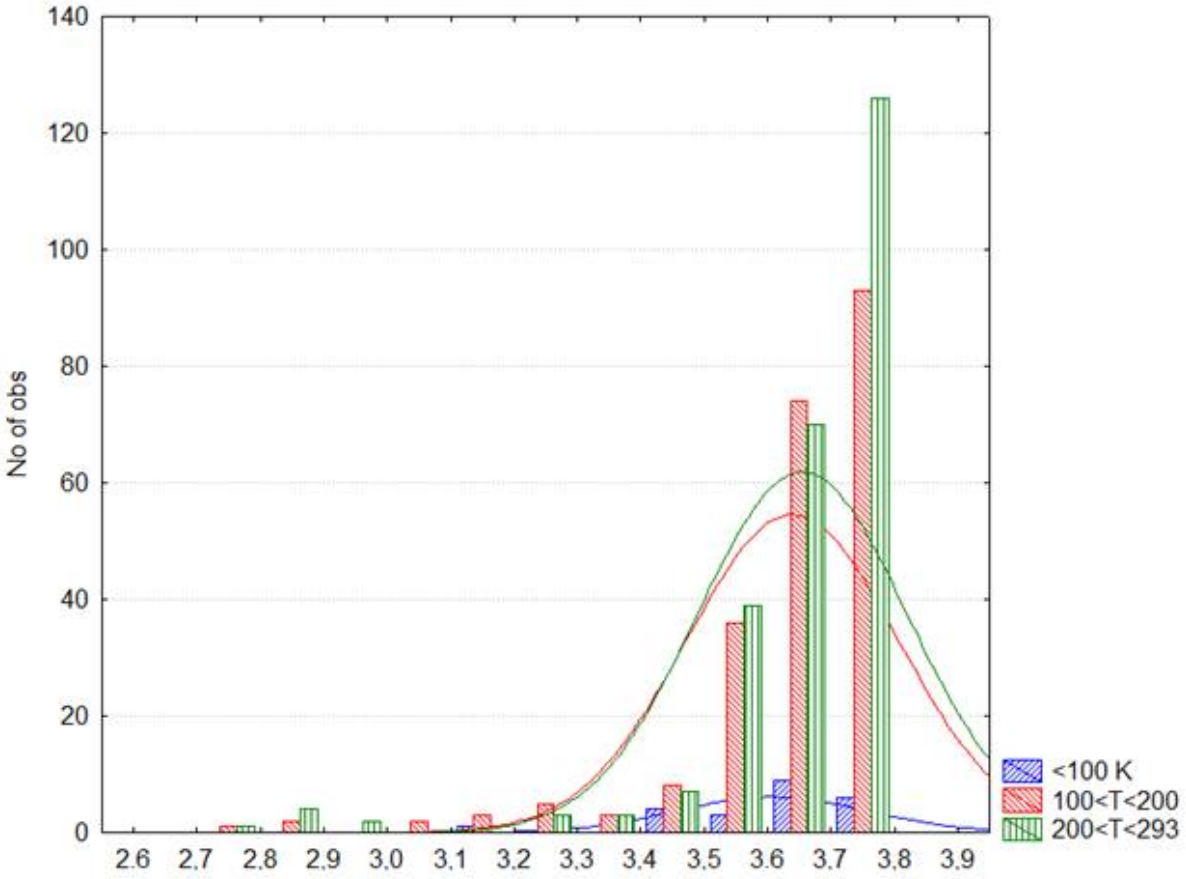

Figure S1 Histrogram of S…I distances (Å) distribution and the effect of X-Ray refinement temperature on it

The mean value of S…I contacts length is as follows:

a) 3. 6404 Å for all contacts without taking into account the temperature of X-ray refinement;

b) 3.6497 Å (+0.0093 Å comparing to complete subset above mentioned in (a)) for contacts in the structures refined in the temperature range 200 – 293 K;

c) 3.6338 Å (-0.0066 Å comparing to complete subset above mentioned in (a)) for the temperature range 100 – 200 K;

d) 3.6017 Å (-0.0387 Å comparing to complete subset above mentioned in (a)) for the temperatures 6 – 100 K.

Table S3 Comparison of geometric characteristics: S…I distance, φ and θ angles depending on the X-Ray refinement temperature

REFCODE	Temperature, K	S…I distance, Å	θ,°	φ,°	S…I change, Å*
CILHIO40	100	3.722	165.8	105.7	-0.052
CILHIO41	150	3.739	166.2	105.7	-0.035
CILHIO42	200	3.757	166.6	105.6	-0.017
CILHIO43	250	3.774	167.1	105.5	0.000
EGOPUN	173	3.632	85.5	81.5	0.000
		3.756	80.7	76.6	0.000
EGOPUN01	90	3.608	85.1	81.5	-0.024

		3.724	80.8	76.3	-0.032
IFOSUL	RT	3.498	104.4	177.3	0.000
IFOSUL01	113	3.768	146.2	80.9	**
		3.515	104.6	177.1	+0.017
ISAMAR	120	3.728	134.7	163.7	**
		3.744	151.9	149.4	+0.028
ISAMAR01	RT	3.716	153.2	148.8	0.000
PELXUZ	150	3.751	158.6	61.8	**
		3.721	157.8	87.1	-0.043
PELHUZ01	RT	3.764	158.2	87.4	0.000
PIPYEO	RT	3.719	177.3	91.6	0.000
PIPYEO01	150	3.649	178.1	91.5	-0.070
PIPYEO02	100	3.627	177.8	92.1	-0.092
		3.762	156.4	90.6	**
QINCUN	RT	3.729	146.9	130.9	0.000
QINCUN01	20	3.62	146.0	128.8	-0.109
		3.737	164.0	87.4	**
QINCUN02	150	3.778	163.5	88.0	**
		3.657	147.7	129.5	-0.072
QINCUN03	100	3.639	147.2	129.1	-0.090
		3.761	163.6	87.7	**
QINDOI	RT	3.728	140.9	130.0	0.000
QINDOI01	20	3.721	164.4	86.5	**
		3.623	145.1	128.9	-0.105
QINDOI02	150	3.758	164.6	86.7	**
		3.667	144.5	128.7	-0.061
QINPEK	RT	3.724	147.4	131.4	0.000
QINPEK01	20	3.71	163.8	88.1	**
		3.589	148.3	129.7	-0.135
QINPEK02	150	3.765	163.2	88.6	**
		3.644	148.5	129.8	-0.080
XIVBAF	RT	3.562	167.9	92.4	0.000
		3.749	169.9	72.4	0.000
XIVBAF01	100	3.715	170.2	72.6	-0.026
		3.536	167.9	91.6	-0.034

*with respect to the structure determined at the highest temperature
** Newly observed contacts in low-temperature determination

For two structures IFOSUL and ISAMAR we observe elongation of the exact S…I distances with decrease of temperatures in conditions of X-ray experiment, in all other cases we observe expectable shortening. The shortening value for the exact contacts in several structures is much higher than the shortening for the mean values discussed above: for example, in QINPEK, QINDOI and QINCUN, where the difference is above 0.1 Å. The values of φ and θ angles differ not significantly: the maximum change achieves 4.5° for QINDOI structure. In several cases we observe the emergence of new rather long S…I contacts in low-temperature structures due to overall shortening of intermolecular distances and compression of crystal packings.

As we cannot directly take into account the effect of the temperature in quantum-chemical calculations, we still can compare the differences in S…I distances for different temperature of experiments and with the change of method and approximation used in calculations. In both cases we obtained the similar results: Δ(S…I) in B3LYP calculation of HOVLUA with respect to its crystal structure (Δ=0.032 Å, Table 1) is very similar to Δ= 0.039 Å which follows from consideration of the CSD structures determined in the temperature range 6-100 K. These values are close and we can reliably reproduce the experimental structural features from theoretic point of view for crystals without low-temperature phase transitions.

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