

Supplementary Material: Very Strong Parallel Interactions Between Two Saturated Acyclic Groups Closed with Intramolecular Hydrogen Bonds Forming Hydrogen-Bridged Rings

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1. Analysis of Geometric Parameters of CSD Search

Analysis of geometric parameters of crystal structures is performed for derivatives of thiosemicarbazide, semicarbazide and glycolamide separately. The results are presented in Figures S1–S4.

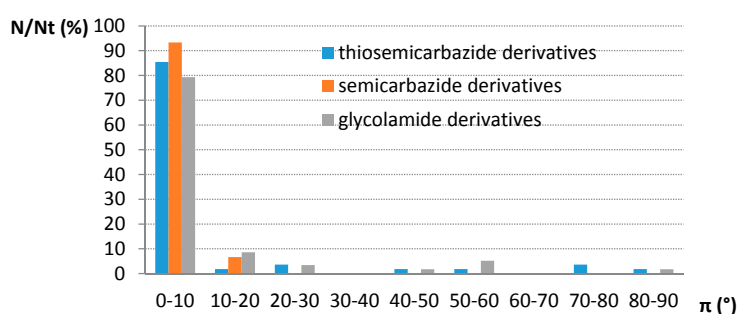


Figure S1. Interplanar angle (π) distributions of hydrogen-bridged rings of the derivatives of the molecules chosen for calculations; Nt stands for the total number of contacts of one group of derivatives.

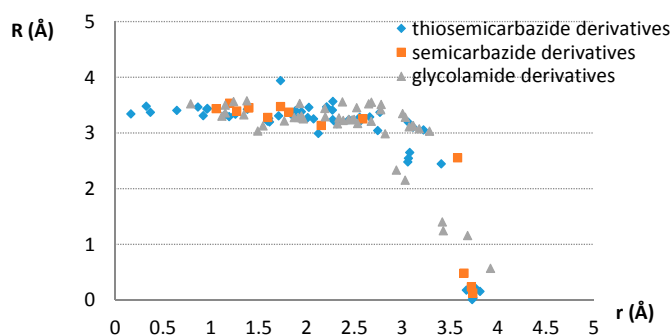


Figure S2. Interplanar distances (R) of contacts having parallel ring planes ($\pi \leq 10^\circ$), plotted as a function of offset values of the two centroids (r) of the derivatives of the molecules chosen for calculations.

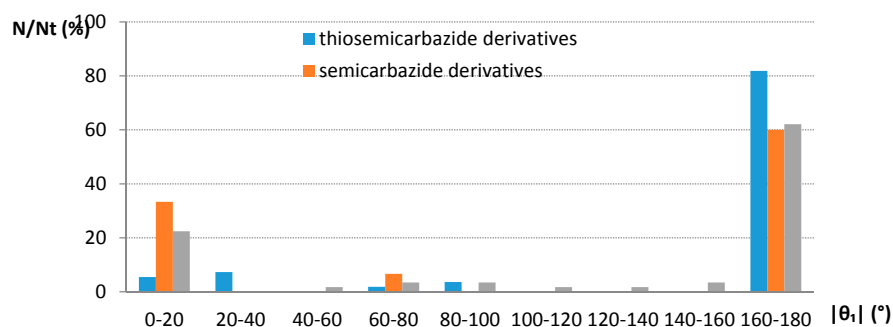


Figure S3. Torsion angle $H_1\Omega_1\Omega_2H_2$ distributions for the derivatives of the molecules chosen for calculations; Nt stands for the total number of contacts of one group of derivatives.

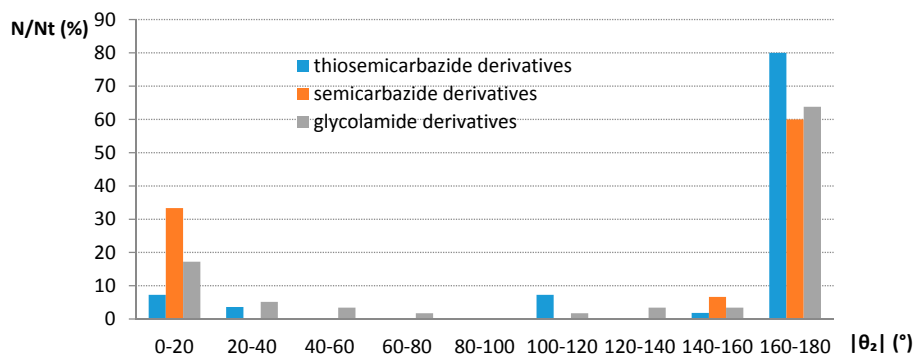


Figure S4. Torsion angle $A_1\Omega_1\Omega_2A_2$ distributions for the derivatives of the molecules chosen for calculations; Nt stands for the total number of contacts of one group of derivatives.

2. Optimized Geometries of Thiosemicarbazide, Semicarbazide and Glycolamide Dimers

The starting geometries for the optimization of the dimers were geometries at the potential curves minima (Figure 8) shown in Figure 9. Geometries of optimized dimers of thiosemicarbazide, semicarbazide and glycolamide molecules are given in Figure S5.

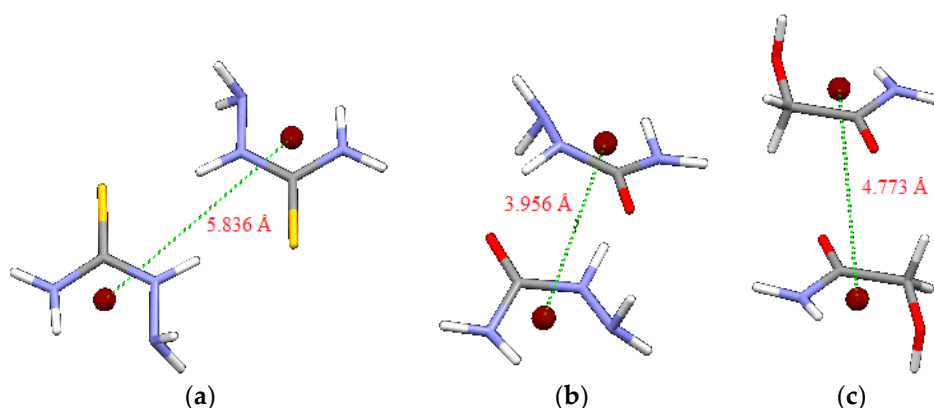


Figure S5. Optimized dimers of (a) thiosemicarbazide (b) semicarbazide and (c) glycolamide molecules.

The most stable dimer geometry of thiosemicarbazide does not correspond to stacking interactions. Optimized dimers of semicarbazide and glycolamide, however, are very similar to geometries corresponding to minima on potential curves presented in Figure 9b,c. Energies of optimized dimers are -20.34 kcal/mol for thiosemicarbazide dimer, -16.42 kcal/mol for semicarbazide dimer and -5.90 kcal/mol for glycolamide dimer. Energies are obtained using methods by which the minima in Figure 9 are obtained.

3. Examples from Crystal Structures and Melting Points

In the crystal structures from the CSD we found thiosemicarbazide that satisfy criteria 1–7 from Materials and methods section. Although, we did not find semicarbazide and glycolamide that satisfy these criteria, we found derivatives of semicarbazide and glycolamide satisfying the criteria. Derivatives of semicarbazide and glycolamide, that are considered, have substituents only on donor nitrogen atom (labeled D in Figure 1b). Selected examples from crystal structures are presented in Figure S6.

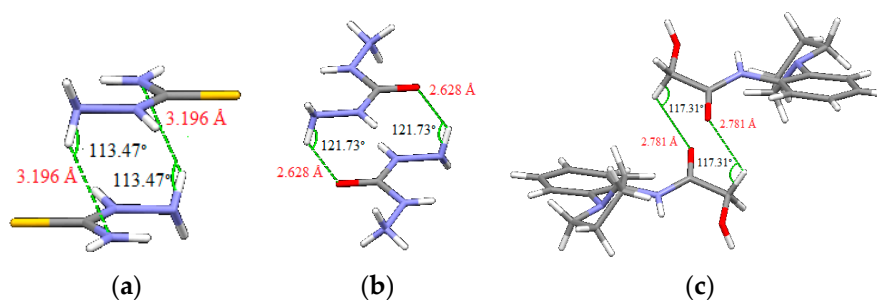


Figure S6. Selected examples of crystal structures from CSD, representing typical orientations of (a) thiosemicarbazide molecules (refcode TSCRBZ01), (b) species similar to semicarbazide molecule (refcode XOWNIH) and (c) species similar to glycolamide molecule (refcode POXWOP) with hydrogen bonds displayed.

Experimental melting points of thiosemicarbazide and carbonylhydrazide, similar hydrogen-bridged species with intermolecular hydrogen bonds (Figure S6a,b), are 180 °C and 153–158 °C, respectively [1], which is in accordance with calculated interaction energy in dimers of thiosemicarbazide and semicarbazide, since interaction in thiosemicarbazide is stronger (Table 2).

4. The Cooperative Effect of Intermolecular Hydrogen Bonds

Evaluation of Methods for Calculating Potential Curves

Several model systems (Figure S7) were chosen for the estimation of interaction energies at CCSD(T) level at complete basis set, by performing the method of Mackie and DiLabio [2].

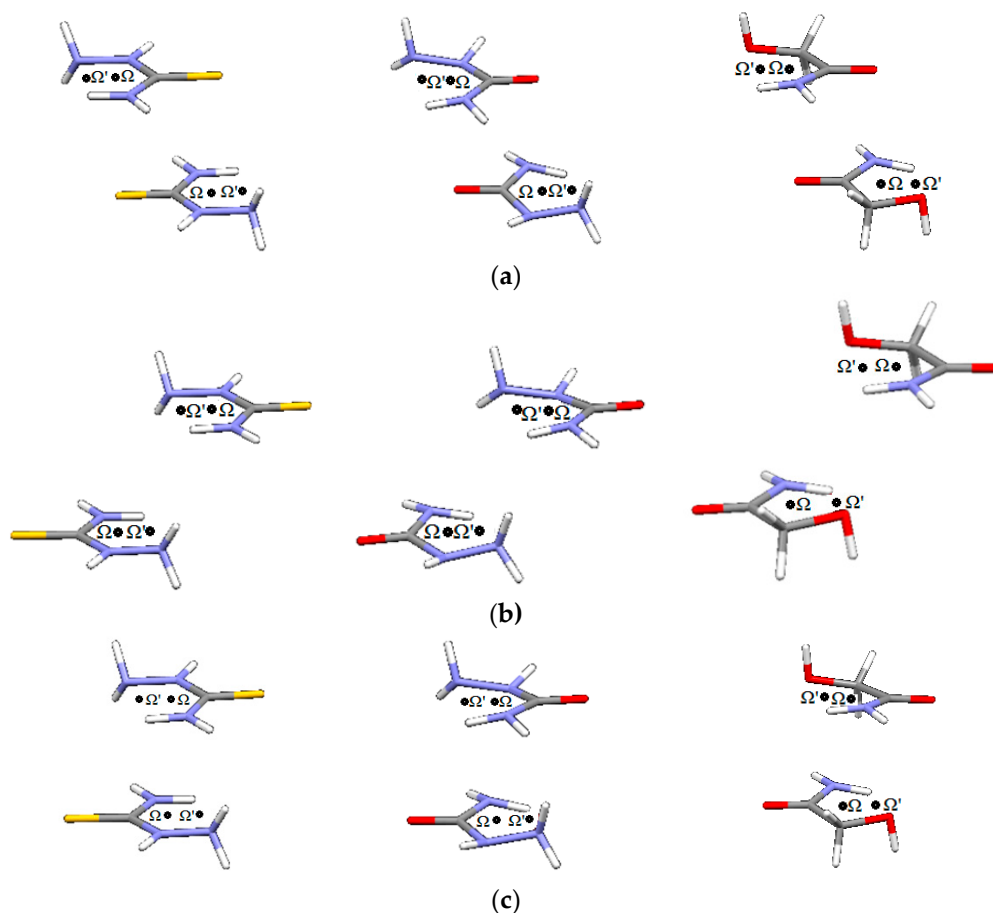


Figure S7. *Cont.*

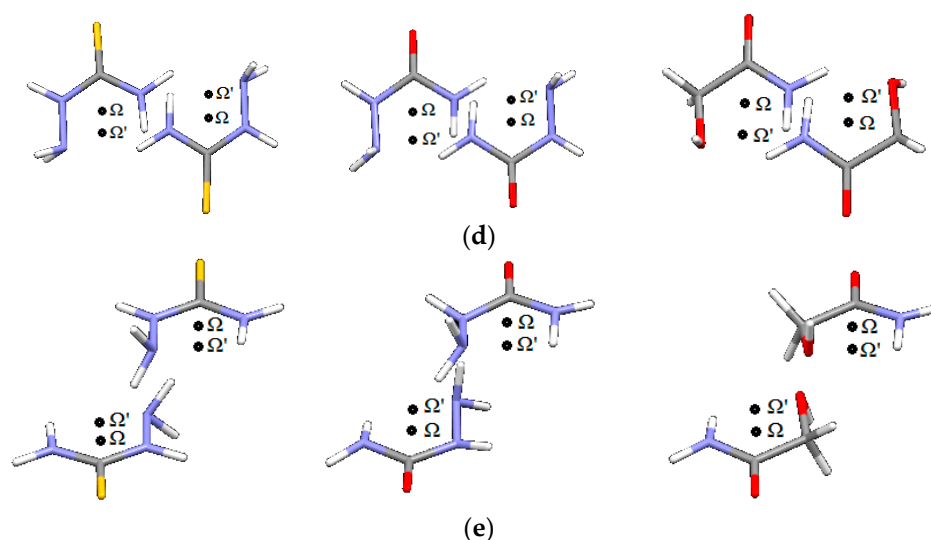


Figure S7. Model systems chosen for the estimation of CCSD(T)/CBS interaction energies; (a) orientation 1- offset values $-2.5 \text{ \AA}$ along $\Omega-\Omega'$ direction, normal distance $3.5 \text{ \AA}$; (b) orientation 2- offset values $2.5 \text{ \AA}$ along $\Omega-\Omega'$ direction, normal distance $3.5 \text{ \AA}$; (c) orientation 3- offset values $0.0 \text{ \AA}$, normal distance $3.5 \text{ \AA}$; (d) orientation 4- offset values $-2.5 \text{ \AA}$ along the direction orthogonal to $\Omega-\Omega'$ direction, normal distance $3.5 \text{ \AA}$; (e) orientation 5- offset values $2.5 \text{ \AA}$ along the direction orthogonal to $\Omega-\Omega'$ direction, normal distance $3.5 \text{ \AA}$

Model systems are composed of dimers, having antiparallel middle molecular planes and offset values of $-2.5 \text{ \AA}$ and $2.5 \text{ \AA}$ along $\Omega-\Omega'$ direction (orientations 1 and 2, respectively—Figure S7), $0.0 \text{ \AA}$ (orientation 3—Figure S7), $-2.5 \text{ \AA}$ and $2.5 \text{ \AA}$ along the direction orthogonal to $\Omega-\Omega'$ direction (orientations 4 and 5, respectively—Figure S7). Distances between middle molecular planes in all model systems are $3.5 \text{ \AA}$. Calculated interaction energies at CCSD(T)/CBS level are given in Tables S1–S5. Møller-Plesett perturbation theory of the second order (MP2) [3] and several D3 corrected [4] DFT functionals were tested in order to find less time-consuming methods for the calculation of potential curves, which approximately reproduce CCSD(T)/CBS interaction energies, of the dimers in the mutual positions selected to be model systems (Figure S7). Basis set effect was also tested by applying several basis sets: cc-pVDZ [5], cc-pVTZ [6], aug-cc-pVDZ [5–7] and 6-31++G** [8]. The results are given in Tables S1–S5 for all five orientations shown in Figure S7. The selected methods for calculating potential curves in the $\Omega-\Omega'$ direction are BP86-d3/6-31++G**, M052X-d3/cc-pVTZ and BLYP-d3/aug-cc-pVDZ for thiosemicarbazide, semicarbazide and glycolamide dimers, respectively (Figure 8a), since these methods give good results in orientations 1 (Table S1), 2 (Table S2) and 3 (Table S3), while TPSS-d3/aug-cc-pVDZ, TPSS-d3/cc-pVTZ and BLYP-d3/aug-cc-pVDZ methods were chosen for calculating potential curves in the orthogonal direction (Figure 8b), since they give good results in orientations 3 (Table S3), 4 (Table S4), and 5 (Table S5).

Table S1. Interaction energies in kcal/mol, obtained by MP2 method and different D3 corrected DFT functionals, by using several basis sets and energies at CCSD(T)/CBS level, calculated on model systems corresponding to orientation 1 in the Figure S7a.

Method	Thiosemicarbazide				Semicarbazide				Glycolamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-3.31	-5.70	-6.60	-4.30	-1.52	-2.69	-3.40	-2.49	-0.91	-1.99	-2.29	-1.11
TPSS-D3	-5.72	-6.00	-6.30	-6.10	-3.20	-3.44	-3.77	-3.53	-2.60	-2.60	-2.65	-2.36
BLYP-D3	-6.08	-6.46	-6.53	-6.41	-3.28	-3.42	-3.68	-3.47	-2.98	-2.86	-2.79	-2.52
BP86-D3	-6.12	-6.77	-6.99	-6.82	-2.65	-3.08	-3.37	-3.09	-2.50	-2.60	-2.58	-2.24
PBE1PBE-D3	-5.44	-5.88	-6.16	-6.00	-3.09	-3.50	-3.83	-3.61	-2.47	-2.63	-2.67	-2.38
M05-D3	-5.81	-6.00	-6.62	-6.36	-3.36	-3.87	-4.44	-4.34	-2.67	-2.87	-3.01	-2.79
M06-D3	-6.04	-6.56	-7.37	-7.23	-3.24	-4.03	-4.29	-4.27	-2.43	-2.98	-3.02	-2.78
M052X-D3	-5.30	-5.94	-6.47	-6.41	-3.06	-3.88	-4.16	-4.03	-2.31	-2.71	-2.75	-2.51
M06HF-D3	-6.02	-6.41	-7.47	-7.12	-2.96	-3.62	-4.05	-4.07	-2.25	-2.47	-2.69	-2.44
CCSD(T)/CBS			-6.74				-3.91				-2.79	

Table S2. Interaction energies in kcal/mol, obtained by MP2 method and different D3 corrected DFT functionals, by using several basis sets and energies at CCSD(T)/CBS level, calculated on model systems corresponding to orientation 2 in the Figure S7b.

Method	Thiosemicarbazide				Semicarbazide				Glycolamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-1.05	-1.60	-1.75	-1.26	-1.31	-1.89	-1.97	-1.50	-0.73	-0.93	-1.09	-0.74
TPSS-D3	-2.31	-2.22	-2.23	-2.17	-2.75	-2.65	-2.61	-2.58	-1.70	-1.51	-1.54	-1.49
BLYP-D3	-2.30	-2.11	-2.01	-1.93	-2.81	-2.59	-2.43	-2.40	-1.48	-1.18	-1.13	-1.09
BP86-D3	-1.82	-1.82	-1.74	-1.67	-2.34	-2.34	-2.20	-2.18	-1.05	-0.88	-0.85	-0.75
PBE1PBE-D3	-2.13	-2.16	-2.16	-2.12	-2.55	-2.57	-2.53	-2.52	-1.51	-1.45	-1.48	-1.42
M05-D3	-2.15	-2.22	-2.30	-2.28	-2.58	-2.64	-2.68	-2.65	-1.43	-1.55	-1.67	-1.61
M06-D3	-1.49	-1.77	-1.71	-1.78	-1.88	-2.20	-2.11	-2.12	-1.41	-1.41	-1.45	-1.45
M052X-D3	-1.71	-2.01	-2.00	-1.98	-2.09	-2.37	-2.35	-2.35	-1.25	-1.42	-1.47	-1.42
M06HF-D3	-1.49	-1.72	-1.75	-1.76	-1.80	-1.99	-2.06	-2.03	-1.22	-1.11	-1.21	-1.26
CCSD(T)/CBS			-1.95				-2.24				-1.28	

Table S3. Interaction energies in kcal/mol, obtained by MP2 method and different D3 corrected DFT functionals, by using several basis sets and energies at CCSD(T)/CBS level, calculated on model systems corresponding to orientation 3 in the Figure S7c.

Method	Thiosemicarbazide				Semicarbazide				Glycolamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-3.46	-5.21	-5.71	-4.00	-1.07	-2.63	-2.94	-1.68	1.25	0.06	-0.02	1.00
TPSS-D3	-5.79	-5.95	-6.00	-5.78	-3.44	-3.64	-3.71	-3.48	-0.94	-0.75	-0.78	-0.70
BLYP-D3	-6.20	-6.26	-6.11	-5.94	-3.87	-3.95	-3.86	-3.64	-1.14	-0.87	-0.71	-0.64
BP86-D3	-5.77	-6.22	-6.19	-6.01	-3.40	-3.82	-3.79	-3.54	-0.92	-0.84	-0.74	-0.62
PBE1PBE-D3	-5.57	-5.89	-5.98	-5.81	-3.31	-3.69	-3.76	-3.55	-0.82	-0.73	-0.76	-0.74
M05-D3	-5.94	-6.05	-6.45	-6.31	-3.59	-3.88	-4.15	-4.00	-0.83	-0.88	-0.99	-0.95
M06-D3	-5.66	-6.18	-6.54	-6.61	-3.34	-4.08	-4.22	-4.13	-0.38	-0.76	-0.68	-0.85
M052X-D3	-5.32	-5.92	-6.13	-6.08	-2.99	-3.69	-3.81	-3.63	-0.05	-0.22	-0.25	-0.32
M06HF-D3	-5.33	-5.88	-6.44	-6.39	-2.97	-3.56	-3.99	-3.95	-0.09	0.07	-0.19	-0.47
CCSD(T)/CBS		-6.04				-3.61				-0.65		

Table S4. Interaction energies in kcal/mol, obtained by MP2 method and different D3 corrected DFT functionals, by using several basis sets and energies at CCSD(T)/CBS level, calculated on model systems corresponding to orientation 4 in the Figure S7d.

Method	Thiosemicarbazide				Semicarbazide				Glycolamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-1.35	-1.87	-2.14	-1.42	-0.47	-0.98	-1.18	-0.68	-0.99	-1.44	-1.55	-1.12
TPSS-D3	-2.63	-2.47	-2.51	-2.38	-1.84	-1.76	-1.84	-1.77	-2.18	-2.11	-2.05	-2.04
BLYP-D3	-2.32	-2.08	-2.01	-1.89	-1.71	-1.56	-1.54	-1.46	-2.00	-1.85	-1.69	-1.68
BP86-D3	-2.11	-2.02	-2.01	-1.88	-1.44	-1.45	-1.48	-1.37	-1.75	-1.72	-1.63	-1.58
PBE1PBE-D3	-2.50	-2.47	-2.54	-2.43	-1.73	-1.76	-1.85	-1.78	-2.06	-2.09	-2.07	-2.04
M05-D3	-2.34	-2.38	-2.60	-2.49	-1.72	-1.75	-1.95	-1.90	-1.99	-2.07	-2.15	-2.13
M06-D3	-2.17	-2.45	-2.61	-2.56	-1.27	-1.49	-1.64	-1.61	-1.81	-1.94	-2.05	-2.08
M052X-D3	-2.16	-2.40	-2.54	-2.49	-1.43	-1.66	-1.77	-1.70	-1.80	-1.99	-2.03	-2.00
M06HF-D3	-2.17	-2.44	-2.73	-2.67	-1.32	-1.52	-1.82	-1.85	-1.70	-1.86	-2.04	-2.10
CCSD(T)/CBS		-2.27				-1.55				-1.77		

Table S5. Interaction energies in kcal/mol, obtained by MP2 method and different D3 corrected DFT functionals, by using several basis sets and energies at CCSD(T)/CBS level, calculated on model systems corresponding to orientation 5 in the Figure S7e).

Method	Thiosemicarbazide				Semicarbazide				Glycolamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-6.69	-8.15	-8.42	-6.98	-4.93	-6.27	-6.39	-5.62	2.90	1.53	1.66	2.93
TPSS-D3	-8.71	-8.65	-8.58	-8.69	-6.99	-7.04	-6.99	-7.26	1.63	1.69	1.78	1.87
BLYP-D3	-9.03	-8.90	-8.62	-8.74	-7.22	-7.24	-7.03	-7.26	1.33	1.52	1.73	1.90
BP86-D3	-8.93	-9.06	-8.85	-9.01	-7.11	-7.33	-7.16	-7.43	1.27	1.22	1.43	1.60
PBE1PBE-D3	-8.71	-8.79	-8.76	-8.86	-7.07	-7.22	-7.19	-7.47	1.41	1.38	1.48	1.55
M05-D3	-8.46	-8.46	-8.66	-8.75	-6.71	-6.93	-7.01	-7.29	1.68	1.64	1.70	1.74
M06-D3	-7.89	-8.23	-8.35	-8.59	-6.44	-7.04	-7.01	-7.40	0.89	0.49	0.70	0.56
M052X-D3	-8.24	-8.64	-8.76	-8.85	-6.69	-7.22	-7.22	-7.53	1.38	1.15	1.22	1.29
M06HF-D3	-8.58	-8.86	-9.41	-9.15	-7.17	-7.55	-7.93	-8.22	0.85	0.64	0.65	0.63
CCSD(T)/CBS			-8.60				-7.03				0.91	

5. Normal distances

Figure S8 shows normal distance dependencies on offset values.

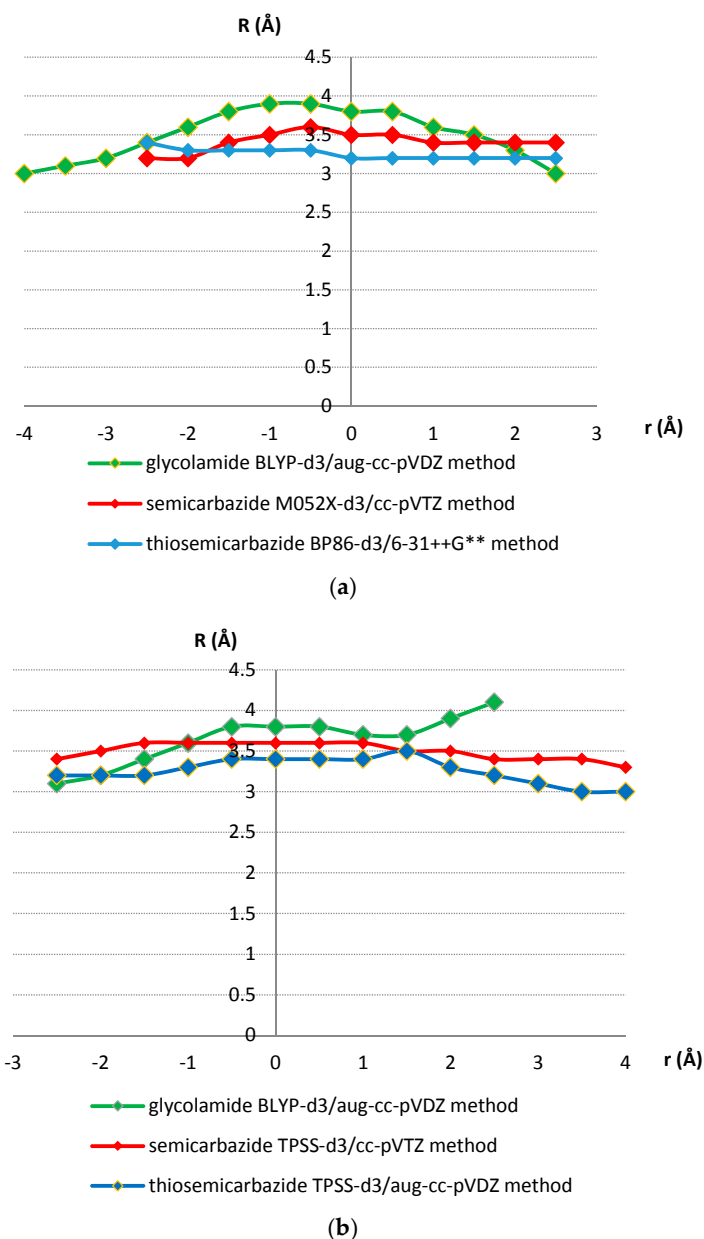


Figure S8. Normal distance dependencies on offset values; (a) Ω - Ω' direction; (b) orthogonal to Ω - Ω' direction.

Normal distances are approximately constant in case of thiosemicarbazide and semicarbazide, mostly in the range between 3.0 and 3.5 Å, which is in accord with the results of crystal structure analysis (Figure 3). The trends concerning glycolamide are slightly different.

6. Correlation Energies

Correlation energies, calculated as differences in CCSD(T)/CBS and HF/CBS energies, obtained by the method of Mackie and DiLabio [2], for all five orientations of thiosemicarbazide and semicarbazide dimers presented in Figure S7, are given in Table S6.

Table S6. Correlation energies in kcal/mol for the selected dimers of thiosemicarbazide and semicarbazide molecules.

Geometry	Thiosemicarbazide	Semicarbazide
orientation 1	−6.68	−2.97
orientation 2	−2.05	−2.27
orientation 3	−5.35	−4.45
orientation 4	−2.04	−1.83
orientation 5	−5.04	−4.22

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