Supplementary data for article:.

Blagojević, J. P.; Zarić, S. D. Stacking Interactions of Hydrogen-Bridged Rings-Stronger than the Stacking of Benzene Molecules. *Chemical Communications* **2015**, *51* (65), 12989–12991. https://doi.org/10.1039/c5cc04139b

Journal Name

ARTICLE TYPE

-Supplementary material-

Full Name,[*a] **Full Name**[a,b] **and Full Name**[b]

5 **Distribution of interplanar angle and absolute of torsion angles $H_1\Omega_1\Omega_2H_2$ (θ_1) and $A_1\Omega_1\Omega_2A_2$ (θ_2)**

Interplanar angle and absolute torsion angle $H_1\Omega_1\Omega_2H_2$ (θ_1) and $A_1\Omega_1\Omega_2A_2$ (θ_2) distributions, indicating the preferred antiparallel orientation of the middle planes of saturated five-membered hydrogen-bridged rings with planar surroundings of all atoms in the ring, are given in Fig. S1 and S2, respectively.
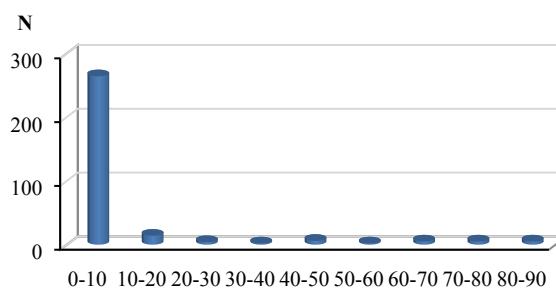
10 Fig. S1. Interplanar angle distributions
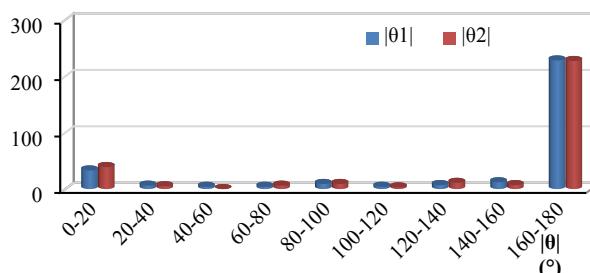
Fig. S2. Distributions of absolute values of torsion angles $H_1\Omega_1\Omega_2H_2$ ($|\theta_1|$) and $A_1\Omega_1\Omega_2A_2$ ($|\theta_2|$). Centroid and atom labelling is consistent with the scheme given in Fig 1.

## Evaluation of methods for calculating potential curves

15
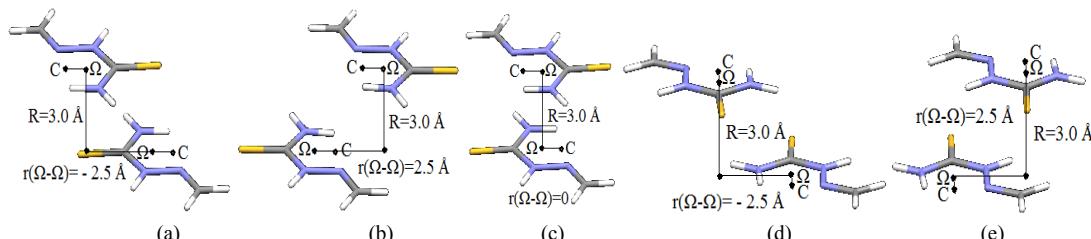
Figure S3. Model systems of 2-methylidenehydrazinecarbothioamide, used for the evaluation of different methods: a) orientation 1; b) orientation 2; c) orientation 3; d) orientation 4; e) orientation 5
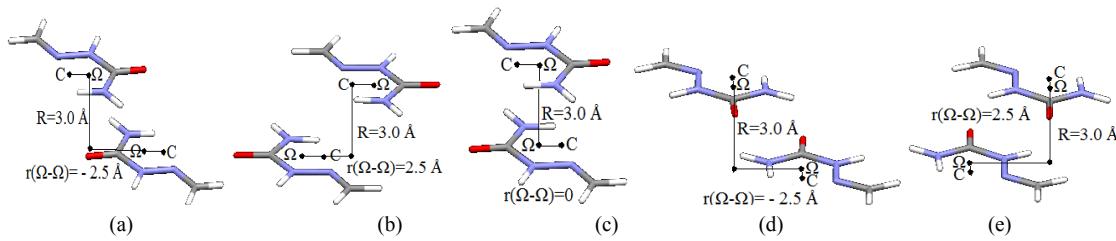
Figure S4. Model systems of 2-methylidenehydrazinecarboxamide, used for the evaluation of different methods: a) orientation 1; b) orientation 2; c) orientation 3; d) orientation 4; e) orientation 5

5

Several model systems (Figures S3 and S4) were chosen for the estimation of interaction energies at CCSD(T) level at complete basis set, by performing the method of Mackie and DiLabio[1]. Model systems are composed of dimers, having antiparallel middle molecular planes and offset values of -2.5 Å and 2.5 Å along Ω-C direction (orientations 1 and 2, respectively- Figures S3 and S4), 0.0 Å (orientation 3- Figures S3 and S4), -2.5 Å and 2.5 Å along the direction orthogonal to Ω-C direction (orientations 4 and 5, respectively-

10 Figures S3 and S4). Distances between middle molecular planes in all model systems are 3.0 Å. Calculated interaction energies at CCSD(T)/CBS level are given in Tables S1-S5. Møller-Plessett perturbation theory of the second order (MP2)[2] and several D3 corrected[3] 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. Basis set effect was also tested by applying several basis sets: cc-pVDZ[4], cc-pVTZ[5], aug-cc-pVDZ[4-6]and 6-31++G**[7]. The results are given in Tables S1-S5 for all five orientations. with the values obtained by methods that

15 were chosen for calculation of potential curves pointed out within a box. The selected method for calculating potential curves in the Ω-C direction is BLYP-d3/cc-pVDZ, since this method gives good results in orientations 2 (Table S1) and 3 (Table S3), while M06HF-d3/cc-pVDZ and M052X-d3/6-31++G** methods were chosen for calculating potential curves for 2-methylidenehydrazinecarbothioamide and 2-methylidenehydrazinecarboxamide, respectively, in the orthogonal direction, since they give good results in orientations 3 (Table S3), 4 (Table S4), and 5 (Table S5). Neither of the selected methods gives particulary good results for orientations 1, but this is of no great

20 importance, since energies are not high.

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 Figures S3 and S4

25

orientation 1	2-methylidenehydrazinecarbothioamide				2-methylidenehydrazinecarboxamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	4.99	0.22	-0.58	3.63	1.63	-0.48	-1.13	0.58
TPSS-D3	1.77	1.65	0.96	1.18	-0.48	-0.77	-0.95	-0.74
BLYP-D3	2.62	2.04	1.90	2.12	-1.17	-1.36	-1.39	-1.07
BP86-D3	0.60	-0.15	-0.49	-0.21	-0.85	-1.43	-1.54	-1.21
PBE1PBE-D3	2.01	1.66	1.20	1.36	-0.37	-0.87	-1.01	-0.80
M05-D3	3.51	3.45	2.75	3.00	-0.68	-1.02	-1.45	-1.29
M06-D3	1.18	0.29	-0.22	0.05	-1.13	-1.98	-2.21	-2.11
M052X-D3	2.05	1.06	0.56	0.79	-0.63	-1.47	-1.67	-1.55
M06HF-D3	-0.36	-0.96	-2.43	-1.61	-1.10	-1.68	-2.34	-2.56
CCSD(T)/CBS	**-0.72**				**-1.92**			

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 Figures S3 and S4

orientation 2	2-methylidenehydrazinecarbothioamide				2-methylidenehydrazinecarboxamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-0.27	-1.59	-1.90	-0.70	0.55	-0.72	-1.03	0.08
TPSS-D3	-2.16	-2.19	-2.23	-2.13	-1.48	-1.54	-1.60	-1.50
BLYP-D3	-2.28	-2.24	-2.13	-2.03	-1.60	-1.58	-1.51	-1.41
BP86-D3	-2.03	-2.26	-2.25	-2.12	-1.36	-1.62	-1.64	-1.50
PBE1PBE-D3	-2.04	-2.21	-2.25	-2.16	-1.37	-1.57	-1.63	-1.54
M05-D3	-2.15	-2.22	-2.40	-2.38	-1.55	-1.65	-1.85	-1.83
M06-D3	-1.60	-2.03	-2.25	-2.34	-1.02	-1.52	-1.74	-1.78

	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
M052X-D3	-1.69	-2.12	-2.20	-2.18	-1.06	-1.50	-1.60	-1.56
M06HF-D3	-1.36	-1.73	-2.02	-2.22	-0.68	-1.07	-1.37	-1.60
CCSD(T)/CBS	**-2.23**				**-1.54**			

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 Figures S3 and S4

orientation 3	2-methylidenehydrazinecarbothioamide				2-methylidenehydrazinecarboxamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	0.74	-2.76	-3.49	-0.58	2.53	-0.25	-0.83	1.28
TPSS-D3	-2.29	-2.36	-2.72	-2.86	-0.41	-0.58	-0.93	-0.99
BLYP-D3	-2.89	-3.37	-3.14	-3.18	-1.16	-1.53	-1.42	-1.38
BP86-D3	-3.64	-4.24	-4.35	-4.40	-1.41	-1.96	-2.10	-2.03
PBE1PBE-D3	-2.07	-2.34	-2.59	-2.75	-0.31	-0.65	-0.89	-0.97
M05-D3	-1.67	-1.73	-2.14	-2.19	-0.23	-0.46	-0.86	-0.92
M06-D3	-3.33	-3.94	-4.54	-4.71	-1.23	-2.00	-2.33	-2.42
M052X-D3	-2.07	-2.68	-3.22	-3.45	-0.30	-0.99	-1.40	-1.50
M06HF-D3	-3.58	-3.73	-5.20	-5.53	-1.25	-1.65	-2.77	-3.28
CCSD(T)/CBS	**-3.64**				**-1.54**			

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 Figures S3 and S4

orientation 4	2-methylidenehydrazinecarbothioamide				2-methylidenehydrazinecarboxamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-1.57	-2.74	-3.07	-2.03	0.35	-0.75	-1.01	-0.24
TPSS-D3	-3.39	-3.29	-3.37	-3.45	-1.70	-1.72	-1.85	-1.94
BLYP-D3	-3.37	-3.26	-3.14	-3.19	-1.73	-1.74	-1.69	-1.75
BP86-D3	-3.29	-3.35	-3.33	-3.41	-1.63	-1.79	-1.83	-1.89
PBE1PBE-D3	-3.27	-3.32	-3.40	-3.48	-1.57	-1.72	-1.83	-1.92
M05-D3	-3.12	-3.18	-3.41	-3.48	-1.50	-1.64	-1.85	-1.95
M06-D3	-3.03	-3.50	-3.68	-3.86	-1.21	-1.68	-1.81	-1.96
M052X-D3	-2.83	-3.23	-3.32	-3.50	-1.17	-1.59	-1.69	-1.80
M06HF-D3	-3.28	-3.69	-4.16	-4.36	-1.34	-1.78	-2.22	-2.47
CCSD(T)/CBS	**-3.27**				**-1.57**			

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 Figures S3 and S4

| orientation 5	2-methylidenehydrazinecarbothioamide				2-methylidenehydrazinecarboxamide			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	0.20	-4.37	-5.05	-1.19	-0.14	-3.50	-4.27	-2.02
TPSS-D3	-2.95	-3.29	-3.71	-3.79	-2.60	-3.02	-3.39	-3.51
BLYP-D3	-2.71	-3.34	-3.43	-3.35	-3.15	-3.74	-3.83	-3.79
BP86-D3	-4.37	-5.15	-5.42	-5.38	-3.60	-4.42	-4.69	-4.67
PBE1PBE-D3	-3.08	-3.56	-3.90	-4.01	-2.80	-3.41	-3.72	-3.86
M05-D3	-2.03	-2.16	-2.87	-2.92	-2.70	-3.05	-3.71	-3.88
M06-D3	-4.08	-4.91	-5.77	-6.05	-3.56	-4.60	-5.23	-5.52
M052X-D3	-3.14	-4.35	-4.63	-4.82	-3.14	-4.38	-4.66	-4.87
M06HF-D3	-5.30	-6.45	-7.32	-7.33	-4.56	-5.64	-6.49	-7.07
CCSD(T)/CBS	**-5.31**				**-4.89**			

Potential curves

Potential curves obtained by moving molecules along Ω-C direction and along the orthogonal direction are shown in Fig S5.

(a)

(b)
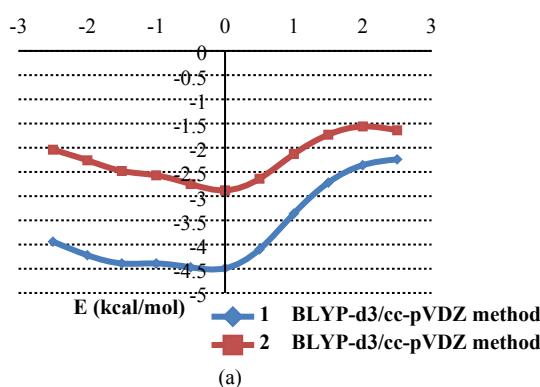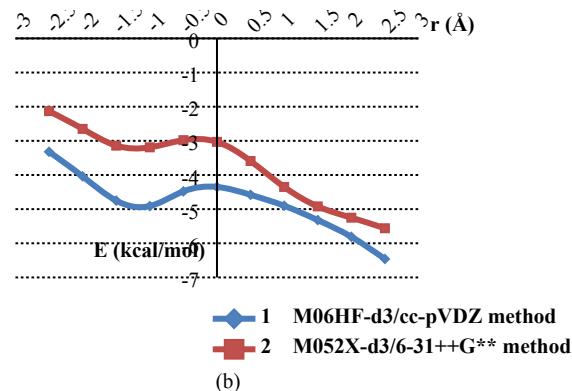
Fig S5. (a) Potential curves for offset values varied in the Ω-C direction; (b) Potential curves for offset values varied orthogonal to Ω-C direction

Normal distances

Figure S6 shows normal distance dependencies on offset values.

a)

b)
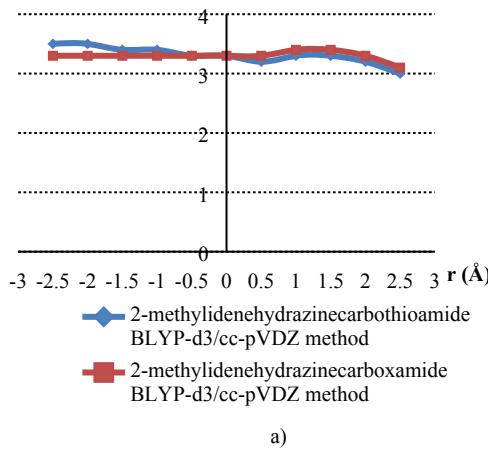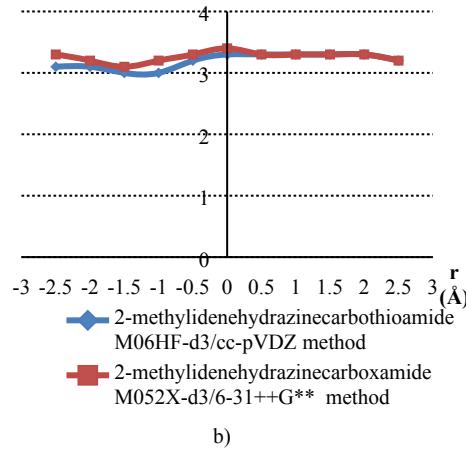
Figure S6. Normal distance dependencies on offset values; a) Ω-C direction; b) orthogonal to Ω-C direction

Normal distances are approximately constant, in the range between 3.0 and 3.5 Å, which is in accord with the results of crystal structure analysis (Fig. 2).

Electrostatic potentials

Maps of electrostatic potentials for 2-methylidenehydrazinecarbothioamide and 2-methylidenehydrazinecarboxamide molecules, calculated and visualized from wavefunction files using the Wavefunction Analysis Program (WFA-SAS)[8,9] are shown in Figure S7. The wavefunctions were calculated on mp2/cc-pVTZ level of theory using Gaussian09 series of programs[10]. Electronic density is more localized on oxygen atom in case of 2-methylidenehydrazinecarboxamide than it is localized on sulphur atom in case of 2-methylidenehydrazinecarbothioamide.
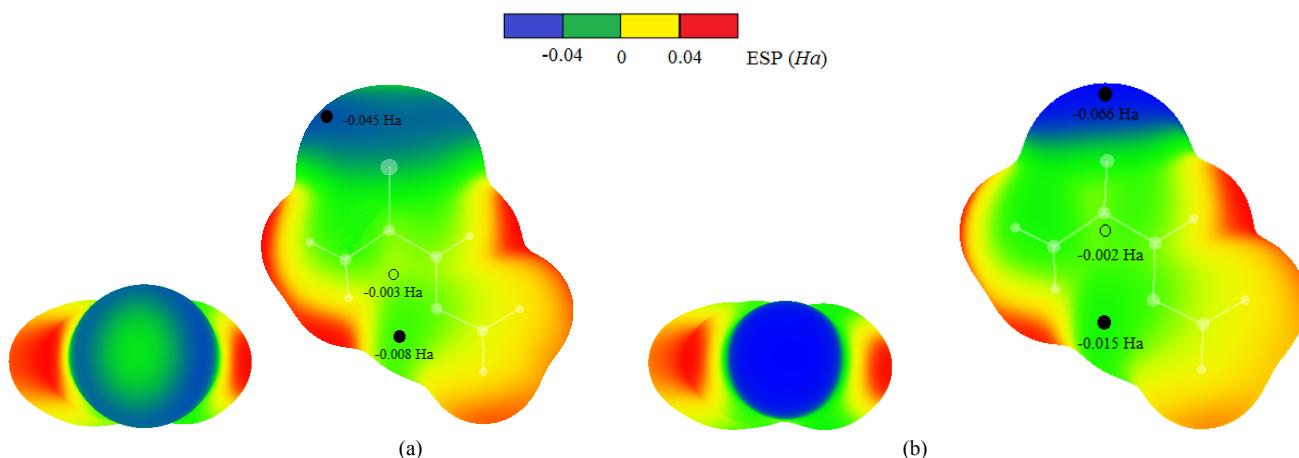
Figure S7. Side and top views of electrostatic potential maps for (a) 2-methylidenehydrazinecarbothioamide and (b) 2-methylidenehydrazinecarboxamide molecule; Values of some important ESP maxima (empty circles) and minima (filled circles) in hartrees (*Ha*) are indicated onto the surfaces of the maps.

Notes and references

[a] *Address, Address, Town, Country. Fax: XX XXXX XXXX; Tel: XX XXXX XXXX; E-mail: xxxx@aaa.bbb.ccc*
[b] *Address, Address, Town, Country. Fax: XX XXXX XXXX; Tel: XX XXXX XXXX; E-mail: xxxx@aaa.bbb.ccc*

1   I. D. Mackie, G. A. DiLabio, *J. Chem. Phys,* 2011, **135**, 1343181.
2   C. Møller, M. S. Plesset, *Phys. Rev*, 1934, **46**, 618–622.
3   S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys*, 2010, **132**, 154104.
4   T. H. Dunning Jr, *J. Chem. Phys*, 1989, **90**, 1007–1023.
5   R. A. Kendall, T. H. Dunning Jr, R. J. Harrison, *J. Chem. Phys*, 1992, **96**, 6796–6806.
6   D. E. Woon, T. H. Dunning Jr, *J. Chem. Phys*, 1993, **98**, 1358–1371.
7   R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys*, 1980, **72**, 650-654.
8   F. A. Bulat, A. Toro-Labbe, WFA: A suite of programs to analyse wavefunctions, *unpublished*.
9   F. A. Bulat, A. Toro-Labbe, T. Brinck, J. S. Murray, P. Politzer, *J. Mol. Model*, 2010, **16**, 1679–1691.
10 Gaussian 09 (Revision D.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.