

SUPPLEMENTARY MATERIAL

Evaluation of methods for calculating potential curves

Estimation of the best method for calculating stacking energies is based on good agreement with CCSD(T)/CBS energies,¹ obtained by method of Mackie and DiLabio.² Five model systems, shown in Fig. S1, were chosen: sandwich geometry (Fig. S1c), geometries with offset values between centroids Ω_1 and Ω_2 of -2.5 \AA and 2.5 \AA along Ω_1 -C direction (Fig. S1a and S1b) and geometries with the corresponding offset values of -2.5 \AA and 2.5 \AA along the orthogonal direction (Fig. S1d and S1e). Different methods, including MP2³ and D3 corrected⁴ DFT functionals, and few basis sets (cc-pVDZ⁵, cc-pVTZ⁶, aug-cc-pVDZ⁵⁻⁷ and 6-31++G**⁸) were tested. Results are given in Tables S1.

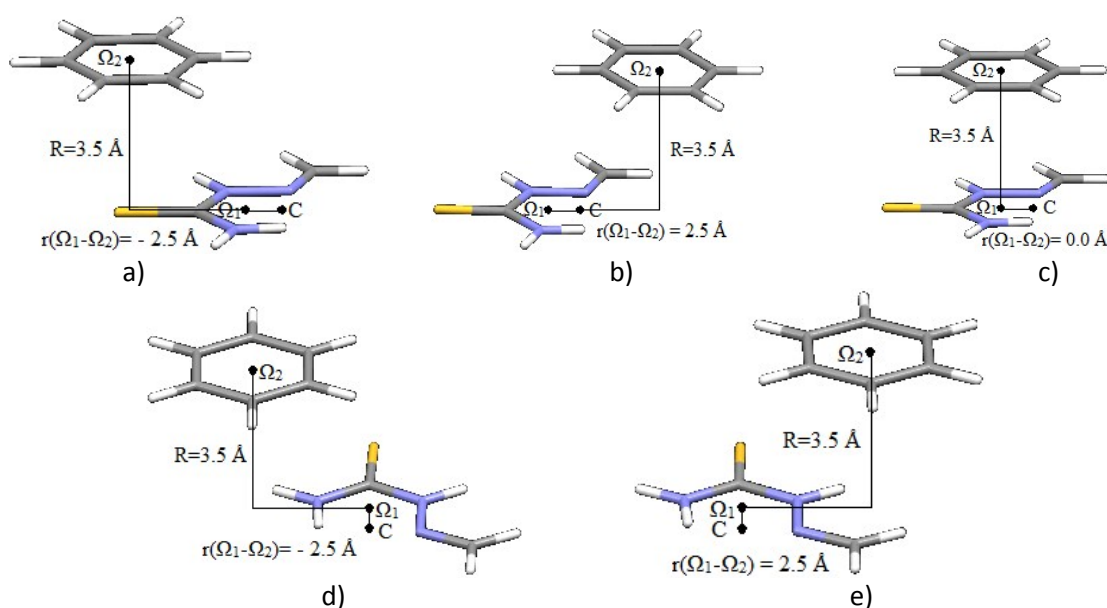


Fig. S1. Five orientations chosen for the selection of the method suitable for calculating potential curves; a) orientation 1; b) orientation 2; c) orientation 3; d) orientation 4; e) orientation 5

Tables S1. Interaction energies in kcal/mol, of the five model systems shown in Fig. S1, obtained by different methods

orientation 1	2-methylidenehydrazinecarbothioamide/benzene			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	0.26	-2.03	-2.68	-0.59
TPSS-D3	-1.35	-1.48	-1.76	-1.48
BLYP-D3	-1.32	-1.75	-1.74	-1.57
BP86-D3	-1.80	-2.26	-2.38	-2.10
PBE1PBE-D3	-0.99	-1.27	-1.50	-1.25
M05-D3	-0.83	-1.00	-1.50	-1.26
M06-D3	-2.01	-2.39	-2.93	-2.66
M052X-D3	-0.78	-1.32	-1.66	-1.36
M06HF-D3	-1.34	-1.43	-2.34	-1.75
CCSD(T)/CBS	-2.01			

orientation 2	2-methylidenehydrazinecarbothioamide/benzene			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-1.52	-2.63	-3.00	-1.96
TPSS-D3	-2.52	-2.62	-2.65	-2.56
BLYP-D3	-2.27	-2.37	-2.27	-2.22
BP86-D3	-2.22	-2.43	-2.43	-2.32
PBE1PBE-D3	-2.46	-2.62	-2.69	-2.60
M05-D3	-2.56	-2.63	-2.91	-2.84
M06-D3	-2.65	-2.76	-3.25	-3.15
M052X-D3	-2.35	-2.65	-2.83	-2.75
M06HF-D3	-2.33	-2.37	-2.87	-2.77
CCSD(T)/CBS	-2.63			

orientation 3	2-methylidenehydrazinecarbothioamide/benzene			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-1.80	-4.01	-4.62	-2.44
TPSS-D3	-3.54	-3.63	-3.72	-3.56
BLYP-D3	-3.66	-3.93	-3.74	-3.63
BP86-D3	-4.00	-4.36	-4.38	-4.18
PBE1PBE-D3	-3.31	-3.49	-3.60	-3.45
M05-D3	-3.44	-3.36	-3.81	-3.64
M06-D3	-4.19	-4.24	-5.09	-4.92
M052X-D3	-3.18	-3.46	-3.81	-3.69
M06HF-D3	-3.75	-3.38	-4.44	-4.33
CCSD(T)/CBS	-3.94			

orientation 4	2-methylidenehydrazinecarbothioamide/benzene			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-1.89	-3.02	-3.44	-2.38
TPSS-D3	-3.14	-3.18	-3.25	-3.20
BLYP-D3	-2.90	-2.95	-2.87	-2.85
BP86-D3	-2.90	-3.06	-3.09	-3.04
PBE1PBE-D3	-3.07	-3.20	-3.29	-3.24
M05-D3	-3.08	-3.14	-3.44	-3.39
M06-D3	-3.33	-3.49	-3.98	-3.94
M052X-D3	-2.93	-3.23	-3.42	-3.39
M06HF-D3	-3.22	-3.27	-3.83	-3.76
CCSD(T)/CBS	-3.13			

orientation 5	2-methylidenehydrazinecarbothioamide/benzene			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
MP2	-2.73	-4.43	-4.99	-3.46
TPSS-D3	-3.96	-4.11	-4.18	-4.15
BLYP-D3	-3.81	-4.06	-3.91	-3.93
BP86-D3	-4.02	-4.32	-4.34	-4.30
PBE1PBE-D3	-3.94	-4.14	-4.25	-4.24
M05-D3	-4.06	-4.08	-4.53	-4.50
M06-D3	-4.60	-4.70	-5.51	-5.46
M052X-D3	-3.96	-4.31	-4.59	-4.58
M06HF-D3	-4.48	-4.35	-5.21	-5.16
CCSD(T)/CBS	-4.37			

Parallel hydrogen/aromatic contacts of structural model A in crystal structures

Distribution of absolute torsion angle θ , that is defined as Ω_a - Ω_h - Ω'_a - Ω'_h torsion (Fig. S2) in parallel hydrogen/aromatic contacts of structural model A is shown in Fig. S3.

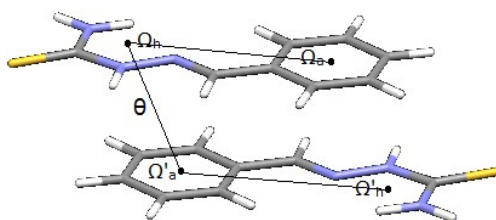


Fig. S2. Angle θ definition

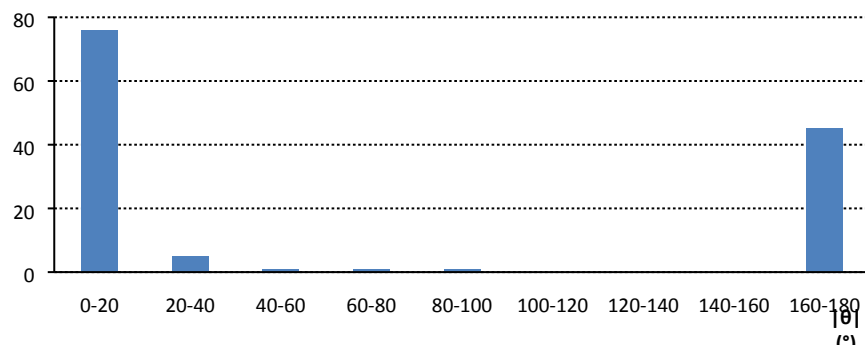


Fig. S3. Distribution of absolute torsion angle θ

Most of contacts have absolute torsion angle θ in the range of 0 to 20°, which corresponds to antiparallel position, shown in Fig. S2, providing the possibility for double interaction between different ring types. Another relatively numerous group of contacts has absolute torsion angle θ in the range of 160° to 180°, corresponding to parallel arrangement of molecules. Examples of both typical arrangements (parallel and antiparallel) is shown in Fig. S4.

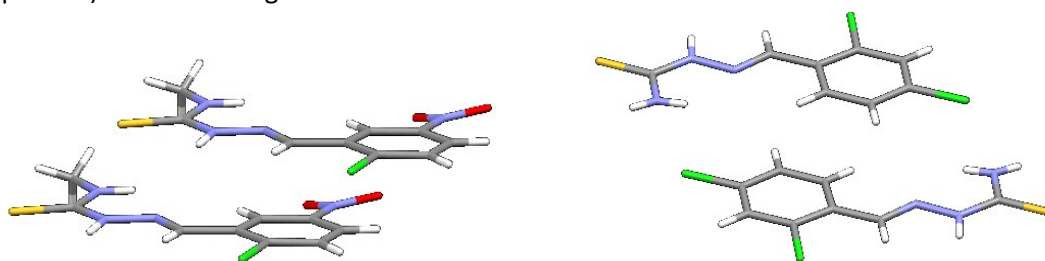
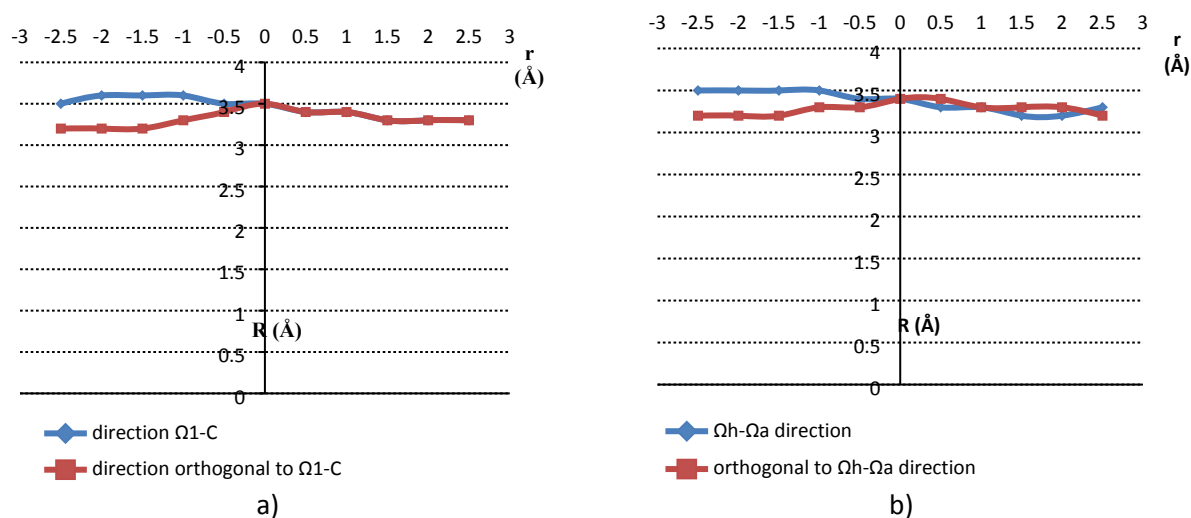
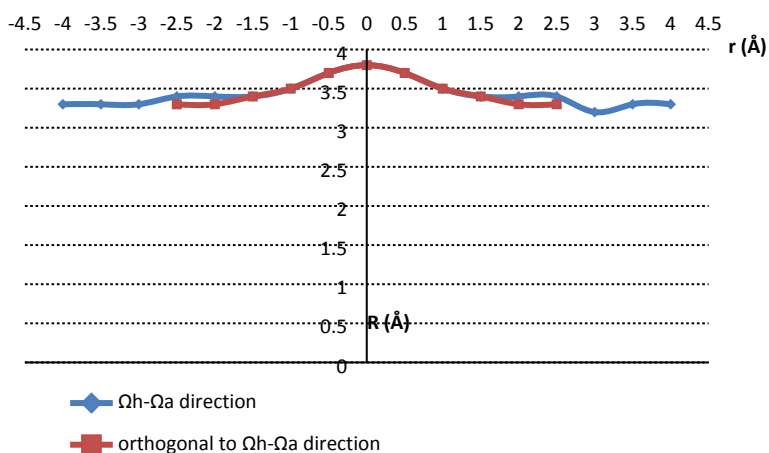


Fig. S4. a) parallel and b) antiparallel arrangement of molecules that have both ring types

Normal distances

Calculation of normal distances (Fig. S5) is in accord with the data from CSD search.





c)

Fig. S5. Normal distance dependences on offset values calculated on mp2/cc-pVTZ level; a) 2-methylidenehydrazinecarbothioamide/benzene dimer; b) antiparallel alignment of benzylidenehydrazinecarbothioamide dimer; c) parallel alignment of benzylidenehydrazinecarbothioamide dimer

Electrostatic potentials

Maps of electrostatic potentials for 2-methylidenehydrazinecarbothioamide⁹, thiosemicarbazide¹⁰, benzene and benzylidenehydrazinecarbothioamide molecules, calculated and visualized from wavefunction files using the Wavefunction Analysis Program (WFA-SAS)^{11,12} are shown in Figure S3. The wavefunctions were calculated on mp2/cc-pVTZ level of theory using Gaussian09 series of programs¹³. Electronic density is more delocalized in benzylidenehydrazinecarbothioamide molecule than it is in thiosemicarbazide and benzene molecules, since ESP extremes are less pronounced.

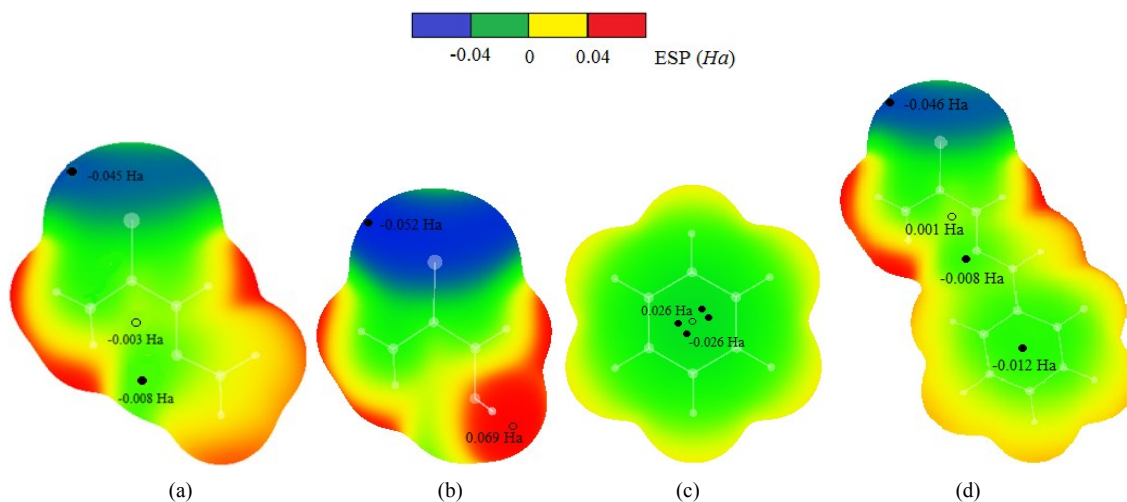


Figure S6. Electrostatic potential maps for (a) 2-methylidenehydrazinecarbothioamide (b) thiosemicarbazide (c) benzene and (d) benzylidenehydrazinecarbothioamide molecule; Values of some

important ESP maxima (empty circles) and minima (filled circles) in hartrees (H_a) are indicated onto the surfaces of the maps.

Notes and references

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