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Supporting Information for Publication

The applicability of the dimeric heterosynthon concept to molecules with equivalent binding sites. A DFT study of crystalline urea-H₂O₂.

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Details of the solid-state DFT computations.

The default CRYSTAL09 options are used for the level of accuracy in evaluating the Coulomb and Hartree-Fock exchange series and a grid used in evaluating the DFT exchange-correlation contribution. Tolerance on energy controlling the self-consistent field convergence for geometry optimizations and frequencies computations is set to 1×10^{-8} and 1×10^{-11} hartree respectively. The number of points in the numerical first derivative calculation of the analytic nuclear gradients equals 2. The shrinking factor of the reciprocal space net is set to 3. Frequencies of normal modes were calculated within the harmonic approximation by numerical differentiation of the analytical gradient of the potential energy with respect to atomic position.^{s1} The IR intensities for normal modes were calculated from the dipole moment derivatives determined using well-localized Wannier functions of the unit cell to calculate the Born charge tensors.^{s1,s2}

In the two-component crystals with Z' = 1 the E_{latt} value computations may be carried out in the two separate steps.⁸ First, the urea-H₂O₂ dimer energy is computed. In this heterodimer urea and H₂O₂ molecules are held by N-Ht...O hydrogen bonds. Then, the interaction energy of the heterodimer with the surrounding molecules is evaluated. In so doing, the E_{latt} value of the solvate is written as:

$$E_{\text{latt}} = 2 E_{\text{HB}}(\text{N-Ht...O}) + 2 E_{\text{HB}}(\text{O-H...O}) + 2 E_{\text{HB}}(\text{N-Hc...O})$$
 (S1)

The first term on the r.h.s. of Eq. (S1) corresponds to the urea- H_2O_2 dimer energy. The factors of 2 in the terms on the r.h.s. of Eq. (S1) are caused by the symmetry of the crystal.

Fragment ^{a)}	Parameter	Exp. ¹²	PBE/6-31+G**
О-НО	<i>R</i> (OO), Å	2.616	2.611
	#(O-HO), deg.	174.5	171.9
N-HtO	<i>R</i> (NO), Å	2.996	2.955
	#(N-HO), deg.	163.8	161.8
N-HcO	<i>R</i> (NO), Å	2.964	2.965
	#(N-HO), deg.	162.1	158.5

Table S1. Parameters of the X-H...O fragments, where X = O and N, in the crystalline urea-H₂O₂: the X...O distance, R(X...O), and X-H...O angle, #(X-H...O). Experimental vs. theoretical values.

^{a)} see Fig. 1

Dimer ^{b)}	Gas phase	Acetonitrile
(I)	0.00 ^{c)}	19.96
(II)	14.64	0.00 ^d
(III)	23.37	5.19
(IV)	14.67	7.24
(V)	37.03	0.59
(VI)	3.34	17.70

Table S2. The relative energies ^{a)} of the urea- H_2O_2 dimers in the gas phase and acetonitrile computed at the PBE/6-31+G** level. The units are kJ/mol.

^{a)} Sum of electronic and thermal free energies; ^{b)} see Fig. S1; ^{d)} Total energy is -376.407862 a.u.; ^{e)} Total energy is -376.484507 a.u.



Fig. S1. The structures of the urea- H_2O_2 dimer.

Trimer ^{b)}	Gas phase	Acetonitrile
(a)	0.00 ^{c)}	29.33
(b)	13.85	6.49
(c)	17.07	0.0 ^{d)}
(d)	13.22	5.98
(e)	10.63	4.52
(f)	4.02	5.48
(g)	0.63	8.28

Table S3. The relative energies ^{a)} of the urea- $2(H_2O_2)$ structures in the gas phase and acetonitrile computed at the PBE/6-31+G** level. The units are kJ/mol.

^{a)} Sum of electronic and thermal free energies; ^{b)} see Fig. S2; ^{c)} Total energy is -527.811214 a.u.; ^{d)} Total energy is -527.912150 a.u.



Fig. S2. The structures of urea- $2(H_2O_2)$.

Trimer ^{b)}	Gas phase	Acetonitrile
(a)	27.36	0.00 ^d)
(b)	0.00 ^{c)}	25.10
(c)	21.34	17.66
(d)	8.49	14.10
(e)	_f)	3.10
(f)	10.79	4.10
(g)	16.02	8.03
(h)	15.27	14.48
(i)	11.97	10.79

Table S4. The relative energies ^{a)} of the 2(urea)- H_2O_2 structures in the gas phase and acetonitrile computed at the PBE/6-31+G** level. The units are kJ/mol.

^{a)} Sum of electronic and thermal free energies; ^{b)} see Fig. S3; ^{c)} Total energy is -601.415229 a.u.; ^{d)} Total energy is -601.514593 a.u.; ^(f) this structure was not localized.



Fig. S3. The structures of 2(urea)-H₂O_{2.}

References:

- s1. F. Pascale, C. M. Zicovich-Wilson, F. L. Gejo, B. Civalleri, R. Orlando and R. Dovesi, J. Comput. Chem., 2004, 25, 888-897.
- s2. C. M. Zicovich-Wilson, R. Dovesi and V. R. Saunders, J. Chem. Phys., 2001, 115, 9708-9718.