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Energy Decomposition of the Intermolecular Interactions in Energetic Co-crystals

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Electronic Supplementary Information

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S1. The detail for interaction calculation

As shown in **Table S1,** DFT methods with different basis sets can give similar predictions, Combining with the accuracy and convergence of self-consistent field calculation in GAMESS, 6-311G(*d*,*p*) was chosen to estimate the interaction energies in DFT calculations. It's noted that a full electron basis set, 3-21G, was applied for halogen atoms, chlorine and iodine atoms to simplify the following BLW treatments instead of effective core potential basis sets. In order to improve the accuracy, a diffuse *d*-type function with exponent of 0.25 was added to 3-21G basis set for two halogen atoms like 6-31*(0.25) basis set.[1]

Table S1 The interaction energies of four pairs with different basis sets (unit: kJ/mol).

	Basis Set	PBE0	M06-2X	HF	MP2
CL-20/TNT-1	cc-pVTZ	-0.95	-31.48	12.02	-42.80
	6-311G(d,p)	-2.80	-34.72	10.69	-30.52
	6-311++G(d,p)	-2.01	-34.16	12.31	-37.47
CL-20/TNT-2	cc-pVTZ	-19.10	-31.87	-15.63	-31.70
	6-311G(d,p)	-20.29	-32.66	-18.27	-26.12
	6-311++G(d,p)	-20.54	-33.11	-17.48	-29.88
DADP/TCTNB-2	6-311G(d,p)/3-21G*(0.25)	-	-9.04	-	-
	6-311G(d,p)/[def2-QZVPP/def2-ecp]	-	-9.16	-	-
DADP/TITNB-2	6-311G(d,p)/3-21G*(0.25)	-	-17.99	-	-
	6-311G(d,p)/[def2-QZVPP/def2-ecp]	-	-18.86	-	-

Three hybird functionals, PBE0, B3LYP, and M06-2X were employed to evaluate the interaction energies in benchmark calculations. Moreover, Hatree-Fock, second order Møller−Plesset perturbation theory (MP2), and MP2.5 calculations were carried out for the comparison. And corresponding values at complete basis set (CBS) levelwere also obtained with the following two-point extrapolation[2] using Dunning's cc-pVXZ basis sets of X=2 (D) and 3(T):

$$E(\mathrm{HF}/X) = E(\mathrm{HF/CBS}) + A\exp(-\alpha\sqrt{X}) \quad (1)$$

and

$$E(\mathrm{corr}/X) = E(\mathrm{corr/CBS}) + BX^{-3} \quad (2)$$

The MP2.5 binding energies[3] were calculated according to the following equation:

$$\Delta E(\mathrm{MP2.5/CBS}) = \Delta E(\mathrm{MP2/CBS})' + 0.5\left[\Delta E(\mathrm{MP3}) - \Delta E(\mathrm{MP2})\right]_{\mathrm{smallbasis}} \quad (3)$$

where MP3 calculations were also carried out at cc-pVDZ level. And dispersion correction on the on the interaction description chose Grimme's 2010 scheme using DFT-D3 V3.01 package.

S2. Benchmark results

The eight complexes in CL-20/TNT, BTF/MATNB and TNT/AA was chosen for interaction benchmark calculation. And results were listed in **Table S2**.

Table S2 The interaction energies of molecule-pairs in three energetic cocrystals (Unit: kJ/mol)

	CL-20:TNT			BTF:MATNB			TNT:AA	
	1	2	3	1	2	3	1	2
Density Functional Theory Methods								
PBE0	-2.80	-20.29	-17.70	-5.83	-13.94	-5.65	-105.20	3.06
B3LYP	7.30	-16.21	-12.80	-1.02	-9.81	-3.67	-94.90	21.54
M06-2X	-34.72	-32.66	-32.27	-24.39	-29.05	-10.90	-105.15	-46.41
SCF and Post-SCF Methods								
HF	10.69	-18.27	-13.62	-7.18	-15.28	-4.35	-84.79	30.54
MP2	-30.52	-26.12	-29.70	-18.65	-23.02	-11.36	-81.35	-37.23
HF/CBS	15.13	-14.79	-10.02	-5.64	-13.62	-3.39	-86.74	32.85
MP2/CBS	-52.27	-36.36	-41.52	-32.86	-35.95	-15.36	-103.96	-66.32
MP2.5/CBS	**-43.33**	**-35.34**	**-38.47**	**-29.50**	**-33.97**	**-14.10**	**-105.55**	**-51.50**
SCF and Density Functional Theory methods with DFT-D3 correction								
HF-D3	-41.32	-41.59	-42.58	-32.52	-39.85	-14.44	-99.42	-43.54
PBE0-D3	-35.50	-35.19	-36.99	-21.18	-29.42	-12.27	-113.60	-40.09
B3LYP-D3	-38.69	-36.81	-38.77	-22.96	-31.45	-12.77	-107.61	-42.15
M06-2X-D3	**-42.79**	**-37.15**	**-39.10**	**-27.79**	**-33.04**	**-13.04**	**-106.92**	**-52.50**

Referring to the results from MP2.5/CBS, the combination with M06-2X and D3 dispersion correction can obtain reliable predictions. Therefore, in our work, M06-2X-D3 was employed mainly in following calculations and discussions.

S3. Lattice parameters predicted for five co-crystals

Table S3 Lattice Parameters of five Co-Crystals Calculated Using PBE-D2 Method and the Corresponding Experimental Values

Parameters	*a* (Å)	*b*(Å)	*c*(Å)	*α* (deg)	*β* (deg)	*γ*(deg)
			CL-20/TNT			
Cal.	9.774	19.691	25.231	90.0	90.0	90.0
Exp.	9.674	19.369	24.690	90.0	90.0	90.0
			BTF/MATNB			
Cal.	9.461	12.810	15.759	90.0	90.5	90.0
Exp.	9.332	12.604	15.476	90.0	90.6	90.0
			TNT/AA			
Cal.	6.489	8.760	14.369	85.8	80.5	67.8
Exp.	6.683	8.676	14.220	86.5	80.9	68.8
			DADP/TCTNB			
Cal.	10.360	10.360	9.462	89.2	89.2	94.5
Exp.	10.494	10.494	9.062	90.9	90.9	93.3
			DADP/TITNB			
Cal.	26.425	9.911	8.526	90.0	100.9	90.0
Exp.	25.909	10.006	8.250	90.0	97.7	90.0

S4. Results from BLW-EDA for different methods

Table S4 The results from BLW-EDA with several methods at the 6-311G(*d*,*p*) level (unit: kJ/mol).

	PBE0	B3LYP	M062X	HF	MP2*
		CL-20/TNT-1			
Frz	4.49	14.44	-26.94	15.62	-25.57
Frz+Disp_corr	-28.20	-31.56	-35.02	-36.39	
Disp**	-43.82	-47.18	-50.64	-52.01	-41.19
Pol	-3.40	-3.56	-4.31	-4.73	-4.73
CT	-3.90	-3.58	-3.46	-0.21	-0.21
		CL-20/TNT-2			
Frz	-11.16	-7.17	-23.74	-12.75	-20.61
Frz+Disp_corr	-26.07	-27.77	-28.23	-36.08	
Disp	-13.32	-15.02	-15.48	-23.33	-7.86
Pol	-3.57	-3.64	-3.75	-4.37	-4.37
CT	-5.56	-5.40	-5.17	-1.14	-1.14
		CL-20/TNT-3			
Frz	-7.97	-2.89	-22.75	-7.56	-23.64
Frz+Disp_corr	-27.26	-28.85	-29.58	-36.53	
Disp	-19.70	-21.29	-22.02	-28.97	-16.08
Pol	-3.58	-3.68	-3.94	-4.46	-4.46
CT	-6.15	-6.23	-5.57	-1.60	-1.60
		BTF/MATNB-1			
Frz	-1.51	3.23	-19.13	-2.61	-14.07
Frz+Disp_corr	-16.86	-18.71	-22.53	-27.95	
Disp	-14.25	-16.1	-19.92	-25.34	-11.46
Pol	-2.48	-2.59	-3.21	-4.33	-4.33
CT	-1.84	-1.66	-2.05	-0.25	-0.25
		BTF/MATNB-2			
Frz	-7.23	-3.04	-21.69	-8.45	-16.19
Frz+Disp_corr	-22.70	-24.69	-25.68	-33.02	
Disp	-14.25	-16.24	-17.23	-24.57	-7.74
Pol	-3.28	-3.55	-3.58	-5.02	-5.02
CT	-3.43	-3.21	-3.77	-1.81	-1.81
		BTF/MATNB-3			
Frz	-2.20	-0.20	-7.70	-2.26	-9.27
Frz+Disp_corr	-8.81	-9.30	-9.84	-12.36	
Disp	-6.55	-7.04	-7.58	-10.1	-7.01
Pol	-1.46	-1.47	-1.62	-1.75	-1.75
CT	-1.99	-2.00	-1.58	-0.34	-0.34
		TNT/AA-1			
Frz	35.66	47.88	23.17	30.38	33.82
Frz+Disp_corr	27.26	35.16	21.41	15.74	
Disp	-3.12	4.78	-8.97	-14.64	3.44
Pol	-54.35	-55.52	-55.42	-57.12	-57.12
CT	-86.52	-87.25	-72.90	-58.04	-58.04
		TNT/AA-2			
Frz	12.49	30.97	-35.76	36.25	-31.53
Frz+Disp_corr	-30.66	-32.72	-41.84	-37.83	
Disp	-66.91	-68.97	-78.09	-74.08	-67.78
Pol	-4.39	-4.07	-6.21	-4.94	-4.94
CT	-5.04	-5.37	-4.45	-0.76	-0.76

*At the MP2 level, the correlation energy is treated as dispersion correction energy according to local molecular orbital-EDA introduced by Li et al[4].

**Disp is the dispersion energy

Table S5. The results from BLW-EDA with several methods at the 6-311G(*d*,*p*)/3-21G*(0.25) level (unit: kJ/mol).

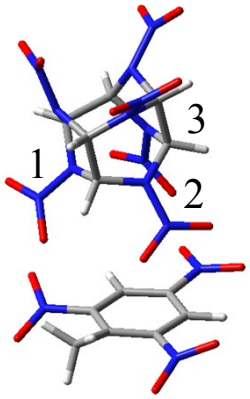
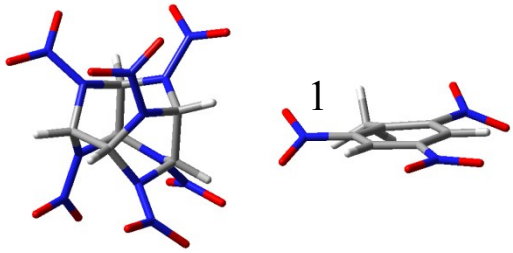
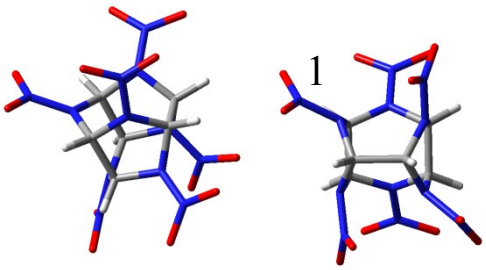
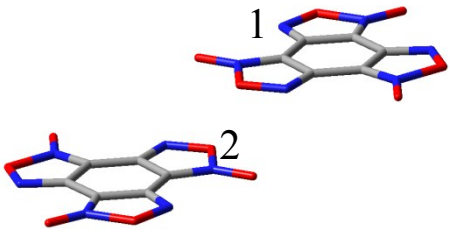
	PBE0	B3LYP	M062X	HF	MP2
		DADP:TCTNB-1			
Frz	-6.68	2.16	-30.2	-3.03	-
Frz+Disp	-35.95	-38.02	-37.12	-48.38	
Disp	-32.92	-34.99	-34.09	-45.35	
Pol	-3.17	-3.31	-3.49	-4.36	-
CT	-4.8	-4.51	-4.52	-1.25	-
		DADP:TCTNB-2			
Frz	-2.1	-4.38	-7.72	-4.07	-
Frz+Disp	-11.12	-10.97	-10.05	-13.99	
Disp	-7.05	-6.9	-5.98	-9.92	
Pol	-0.67	-0.68	-0.74	-0.91	-
CT	-1.26	-1.25	-0.58	-0.02	-
		DADP:TITNB-1			
Frz	2.86	-2.91	-14.91	1.28	-
Frz+Disp	-13.06	-13.45	-17.35	-16.29	
Disp	-14.34	-14.73	-18.63	-17.57	
Pol	-4.55	-4.6	-4.95	-5.46	-
CT	-8.54	-8.74	-6.59	-3.38	-
		DADP:TITNB-2			
Frz	5.88	1.6	-8.03	5.09	-
Frz+Disp	-6.19	-6.29	-9.85	-7.92	
Disp	-11.28	-11.38	-14.94	-13.01	
Pol	-3.03	-2.95	-3.14	-3.74	-
CT	-9.12	-9.48	-6.81	-3.56	-

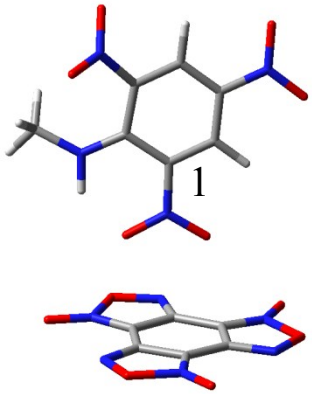
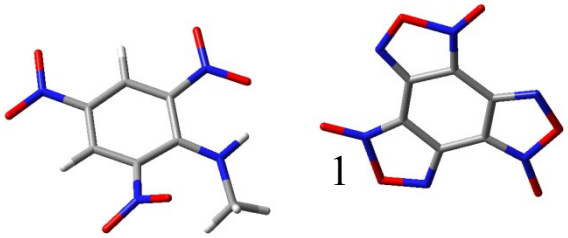
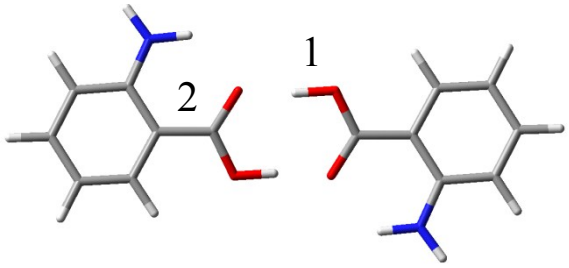
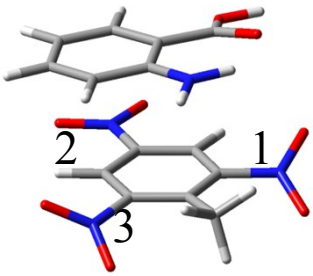
The dispersion energy for other methods can also be evaluated approximately referring to an exact E_{exchange} of HF:

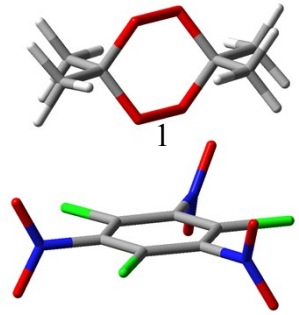
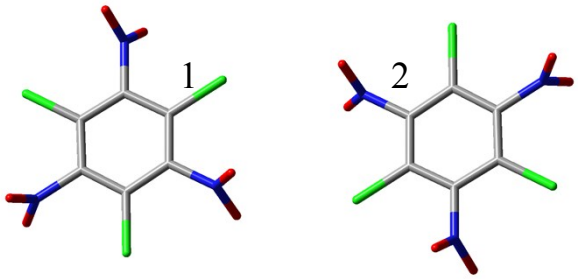
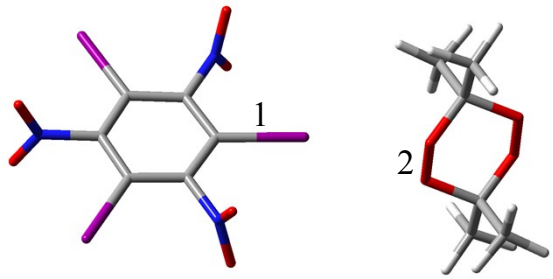
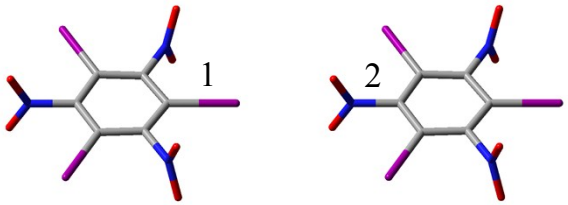
$$\Delta E_{\text{Disp}} \approx \Delta E_{\text{Frozen}} - \Delta E_{\text{Frozen}}\left(\text{HF}\right)$$

S5. BO variations in selected bonds caused by interactions

Table S6 BO variations in selected bonds caused by interactions

Complex	Bond	BO_{gas}	BO_{Pol}	BO_{CT}
CL-20/TNT-1 	**1 (N-NO_2)**	0.889	0.897	0.895
	2 (N-NO_2)	0.889	0.896	0.898
	3 (N-NO_2)	0.935	0.943	0.943
CL-20/TNT-2 	**1 (C-NO2)**	0.734	0.731	0.737
CL-20/TNT-3 	**1 (N-NO_2)**	0.886	0.900	0.904
BTF/MATNB-1 	**1 (C-N(=O))**	1.036	1.054	1.061
	2 (O-N(=O))	0.788	0.791	0.791
BTF/MATNB-2	**1 (C-NO_2)**	0.790	0.806	0.806

				
BTF/MATNB-3 	**1 (O-N(=O))**	0.779	0.782	0.782
TNT/AA-1 	**1 (O-H)**	0.886	0.790	0.737
	2 (C-C(=O))	1.033	1.069	1.063
TNT/AA-2 	**1 (C-NO_2)**	0.732	0.731	0.717
	2 (C-NO_2)	0.760	0.764	0.750
	3 (C-NO_2)	0.734	0.736	0.721

Complex	Bond	BO_{gas}	BO_{Pol}	BO_{CT}
DADP/TCTNB-1 	**1 (O-O)**	0.866	0.865	0.865
DADP/TCTNB-2 	**1(C-Cl)**	0.949	0.941	0.932
	2(C-NO_2)	0.693	0.689	0.688
DADP/TITNB-1 	**1(C-I)**	1.198	1.188	1.177
	2(O-O)	0.866	0.864	0.860
DADP/TITNB-2 	**1(C-I)**	1.198	1.190	1.170
	2(C-NO_2)	0.734	0.709	0.720

S6. References

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