Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Insight into melting point differences of dinitroimidazoles and dinitropyrazoles from the view of intermolecular interactions

Junnan Wu [a,b], Siwei Song [c], Xiujuan Qi [d*], Haijun Yang [a*] and Yi Wang [c*]

[a]School of Materials and Chemistry, Southwest University of Science and Technology, Mianyang, 621010, China.

[b]Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, 621000, China.

[c]School of Astronautics, Northwestern Polytechnical University, Xi'an, 710072, China.

[d]School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an, 710072, China.

Table of contents

S1: SAPT calculations of three computational standards.

S2: BEC calculations for ten dinitroimidazole and dinitropyrazole molecules.

S1: SAPT calculations of three computational standards.

(A) Time comparison of three computational standards

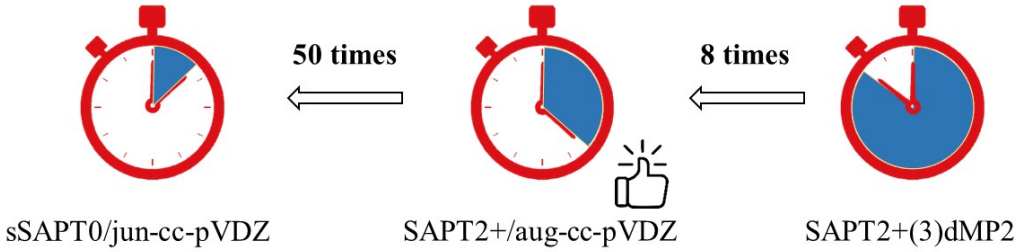

Fig. S1. Time comparison of three computational standards: Bronze(left), Silver(middle), Gold(right).

We used the same computing resources to measure the time consumption of three different computational standards (Bronze, Silver, Gold), as shown in Figure S1. For the binding energy calculation of the same dimer, the computational time for the gold standard is approximately 8 times than that of the silver standard, and the computational time for the silver standard is approximately 50 times than that of the copper standard. Generally, the computational time for the silver standard is acceptable.

(B) Accuracy comparison of three computational standards

The SAPT calculation results of DNP-4 without structural optimization are presented in Table S1 – S4. Among which, the difference between the calculation results of the silver standard and the bronze standard is larger than that between the gold standard and the silver standard. In consideration of the balance of the computational costs and accuracy, we opted for the SAPT2+/aug-cc-pVDZ (Silver) standard.

Table S1. The ELECTRO binding energy in cluster of DNP-4. The unit of energy is kJ/mol.

DIMER	Bronze-level	Silver-level	Gold-level	Silver - Bronze	Gold - Silver
1	5.400357	3.262513	3.739815	-2.13784	0.477302
2	-16.505	-15.5157	-14.9519	0.9893	0.5638
3	-0.93439	-5.46853	-3.10123	-4.53414	2.3673
4	-4.36169	-2.47186	-3.04926	1.88983	-0.5774
5	-10.532	-12.0941	-9.76569	-1.5621	2.32841
6	-16.7205	-13.3411	-12.9895	3.3794	0.3516
7	-4.36167	-2.47185	-3.04926	1.88982	-0.57741
8	-10.532	-12.0941	-9.76567	-1.5621	2.32843

9	-24.2905	-22.8991	-21.5248	1.3914	1.3743
10	-8.1276	-6.72706	-6.75112	1.40054	-0.02406
11	-10.2719	-8.78813	-8.28464	1.48377	0.50349
12	-8.12762	-6.72707	-6.75114	1.40055	-0.02407
13	-16.5049	-15.5157	-14.9519	0.9892	0.5638
14	5.400362	3.262507	3.739805	-2.13786	0.477298

Table S2. The EXCHANGE binding energy in cluster of DNP-4. The unit of energy is kJ/mol.

DIMER	Bronze-level	Silver-level	Gold-level	Silver - Bronze	Gold - Silver
1	0.370237	0.485258	0.46098	0.115021	-0.024278
2	13.35503	16.41993	15.88969	3.0649	-0.53024
3	20.77027	21.95669	20.85773	1.18642	-1.09896
4	2.957165	3.351602	3.195954	0.394437	-0.155648
5	13.84872	16.94227	16.20303	3.09355	-0.73924
6	9.494145	11.45021	10.98908	1.956065	-0.46113
7	2.957167	3.351605	3.195957	0.394438	-0.155648
8	13.84871	16.94226	16.20302	3.09355	-0.73924
9	24.98392	28.18462	26.86316	3.2007	-1.32146
10	11.06349	12.83167	12.26378	1.76818	-0.56789
11	8.433219	9.898303	9.418889	1.465084	-0.479414
12	11.06348	12.83166	12.26377	1.76818	-0.56789
13	13.35503	16.41993	15.88969	3.0649	-0.53024
14	0.370237	0.485258	0.46098	0.115021	-0.024278

Table S3. The INDUCTION binding energy in cluster of DNP-4. The unit of energy is kJ/mol.

DIMER	Bronze-level	Silver-level	Gold-level	Silver - Bronze	Gold - Silver
1	-0.32158	-0.2614	-0.22303	0.06018	0.03837
2	-4.11614	-4.54441	-2.98652	-0.42827	1.55789
3	-3.36175	-3.27212	-2.66216	0.08963	0.60996
4	-1.26897	-1.18383	-0.95672	0.08514	0.22711
5	-3.20636	-3.8117	-2.27335	-0.60534	1.53835
6	-2.32297	-2.56033	-1.94311	-0.23736	0.61722
7	-1.26897	-1.18384	-0.9567	0.08513	0.22714
8	-3.20635	-3.81171	-2.27335	-0.60536	1.53836
9	-4.19468	-4.66586	-3.25148	-0.47118	1.41438

10	-2.22523	-2.34994	-1.16669	-0.12471	1.18325
11	-1.51299	-1.74678	-1.20878	-0.23379	0.538
12	-2.22523	-2.34991	-1.16668	-0.12468	1.18323
13	-4.11614	-4.5444	-2.98654	-0.42826	1.55786
14	-0.32158	-0.2614	-0.22305	0.06018	0.03835

Table S4. The DISPERSION binding energy in cluster of DNP-4. The unit of energy is kJ/mol.

DIMER	Bronze-level	Silver-level	Gold-level	Silver - Bronze	Gold - Silver
1	-2.81717	-3.58687	-3.72735	-0.7697	-0.14048
2	-15.1795	-19.9831	-20.5712	-4.8036	-0.5881
3	-29.7586	-34.821	-35.2657	-5.0624	-0.4447
4	-5.42273	-6.89236	-7.06001	-1.46963	-0.16765
5	-15.3385	-21.0313	-21.8578	-5.6928	-0.8265
6	-10.9908	-15.0307	-15.6197	-4.0399	-0.589
7	-5.42273	-6.89236	-7.06002	-1.46963	-0.16766
8	-15.3385	-21.0313	-21.8578	-5.6928	-0.8265
9	-28.8778	-38.485	-39.904	-9.6072	-1.419
10	-14.0213	-18.6186	-19.1737	-4.5973	-0.5551
11	-10.4379	-14.6768	-15.4517	-4.2389	-0.7749
12	-14.0213	-18.6186	-19.1737	-4.5973	-0.5551
13	-15.1795	-19.9831	-20.5712	-4.8036	-0.5881
14	-2.81717	-3.58687	-3.72735	-0.7697	-0.14048

(C) The fitting results under Bronze medal standard

We calculated the binding energy in clusters for ten molecules under the bronze medal standard. The linear regression of the highest dimer binding energy and T_m (Fig. S2a), as well as the linear regression of the sum of the largest several binding energies and T_m (Fig. S2b), both perform relatively poorly compared to the silver standard. The energy difference between the bronze standard and the silver standard is consistently above 5 kJ/mol for each dimer's binding energy, which will be the main reason.

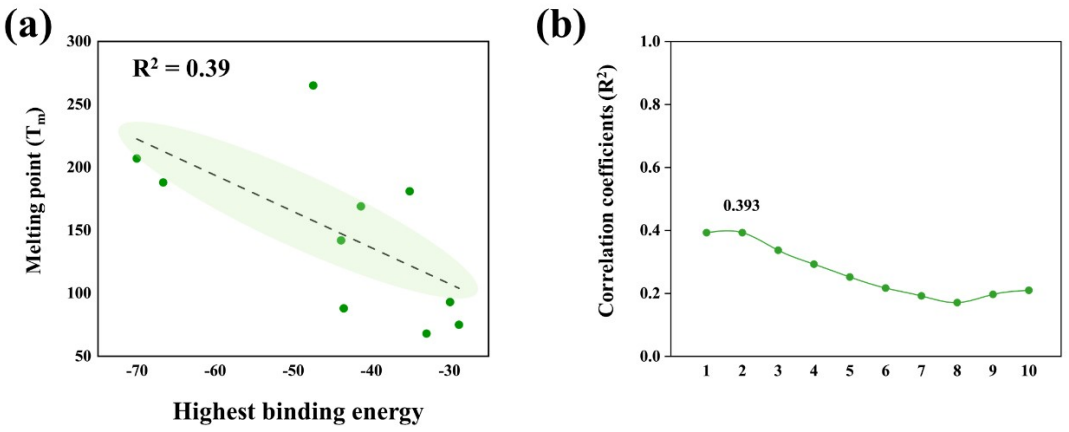

Fig. S2 (a) Correlation between melting point (T_m) and highest dimer binding energy; (b) Correlation coefficients (R^2) of the linear analysis between the sum of the largest several binding energies and T_m.

(D) The difference of key values between SAPT0 and SAPT2+

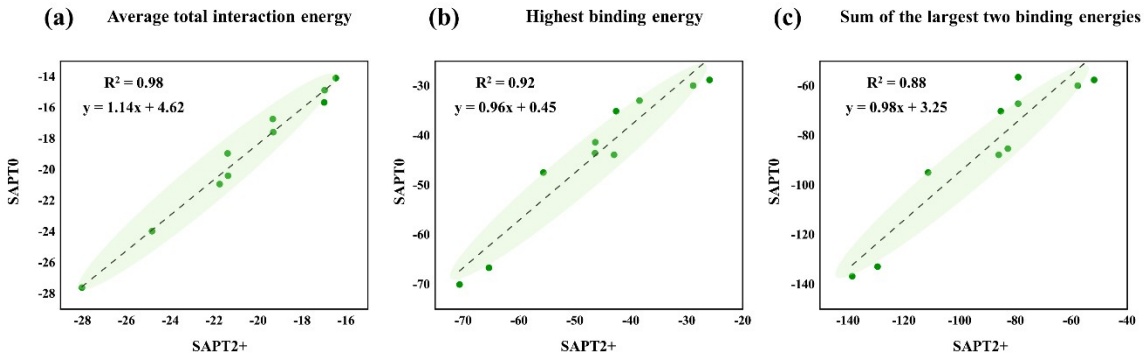

Fig. S3 (a) Average total interaction energy (E_{avg}) of SAPT0 and SAPT2+; (b) Highest binding energy of SAPT0 and SAPT2+; (c) Sum of the largest two binding energies of SAPT0 and SAPT2+.

In the fitting process, three crucial data points (average total interaction energy, highest binding energy and sum of the largest two binding energies) were chosen to compare the outcomes of SAPT0 and SAPT2+. We conducted a linear fitting of the results obtained from SAPT0 and SAPT2+ calculations. Remarkably, for the E_{avg} value (Fig S3 a), the R^2 is as high as 0.98, indicating that it is justifiable to convert the results from SAPT0 to SAPT2+ using a specific formula.

When considering highest binding energy (Fig. S3 b), it was observed that the values derived from SAPT0 were mostly lower than those obtained from SAPT2+, with a difference ranging from 5 to 10 kJ mol^{-1} and R^2 decreased to 0.92.

When considering sum of the largest two binding energies (Fig. S3 c), it was observed that

SAPT0 consistently yielded noticeably lower values than SAPT2+ in DNI-1, DNP-1, and DNP-4, with differences exceeding 20 kJ mol^{-1}, rendering an R^2 value of 0.88 unacceptable.

S2: BEC calculations for ten dinitroimidazole and dinitropyrazole molecules.

The BEC calculation results for all molecules are presented in Table S5 -S14. The total energy of dimer in Fig.3 is the sum of electro, exchange, induction and dispersion energy of dimer. The E_{avg} in Fig.3 is the average of the total energy of dimer.

Table S5. The binding energy in cluster of DNI-1. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	1.230839	0.327304	-0.29456	-2.74815
2	-8.40958	19.91597	-4.78642	-25.5495
3	-0.93128	19.59501	-5.10485	-21.6021
4	-14.127	15.5527	-4.44019	-22.0339
5	-59.4513	69.27462	-29.3577	-36.1066
6	-15.8907	9.37217	-3.21696	-11.8939
7	-4.15908	2.682918	-1.81489	-6.60416
8	-0.93129	19.59498	-5.10487	-21.6021
9	-14.127	15.55272	-4.4402	-22.0339
10	-13.4499	19.29629	-6.74325	-14.1829
11	-8.40958	19.91597	-4.78645	-25.5495
12	1.230834	0.327304	-0.29456	-2.74815
13	-59.4513	69.27462	-29.3577	-36.1066
14	-4.15907	2.682901	-1.81483	-6.60415
15	-13.4498	19.29628	-6.74325	-14.1829

Table S6. The binding energy in cluster of DNI-2. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-18.2369	23.87636	-6.7072	-28.1576
2	-8.03066	3.798876	-1.55766	-6.54774
3	-29.9834	36.49029	-9.72308	-49.2929
4	-88.9089	118.1932	-47.3984	-52.5307
5	-16.4721	16.26616	-4.00481	-24.0482
6	5.433253	2.292254	-1.35743	-7.19682
7	-85.9227	115.7017	-45.3125	-52.2643

8	-12.4516	31.95687	-6.68068	-36.8984
9	-21.4567	12.51603	-2.70826	-17.4901
10	-11.3329	9.072323	-2.65353	-9.80028
11	4.686325	6.915105	-2.25963	-5.9195
12	-6.00866	2.731554	-1.42261	-5.42677

Table S7. The binding energy in cluster of DNI-3. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-11.3329	9.072323	-2.65353	-9.80028
2	-3.42382	4.598126	-2.71481	-7.03421
3	1.700667	0.458169	-0.39379	-3.95445
4	2.85682	2.388816	-0.93582	-6.34066
5	-17.9406	17.22891	-4.8262	-19.7271
6	-82.1374	101.3388	-45.6863	-38.9026
7	-10.615	26.51716	-5.88922	-35.096
8	-14.7228	20.30564	-5.36984	-28.0911
9	-14.8952	20.22005	-3.8049	-24.8866
10	-17.9406	17.22892	-4.82627	-19.7271
11	-12.9396	11.88902	-2.56324	-17.7299
12	-79.1469	98.81235	-42.4482	-41.2006
13	-3.42382	4.598104	-2.71485	-7.0342

Table S8. The binding energy in cluster of DNI-4. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-12.0198	14.75289	-3.2491	-11.068
2	4.400382	3.475591	-1.1814	-6.4732
3	-8.51244	24.89786	-6.17814	-32.3942
4	-3.97422	2.944825	-1.8763	-6.97584
5	-0.10501	3.926853	-0.93034	-6.60641
6	-28.6388	28.19601	-9.1078	-24.3668
7	-28.3434	29.3081	-9.41599	-28.2119
8	-30.6867	26.28607	-7.32366	-31.273
9	-16.3007	21.52474	-5.10233	-25.1923
10	-1.06601	5.23362	-3.09965	-8.92222
11	-12.6437	8.191615	-2.68794	-8.25044

12	-30.6867	26.28611	-7.32361	-31.273
13	-8.51244	24.89787	-6.17811	-32.3942
14	-16.3007	21.52474	-5.10226	-25.1923

Table S9. The binding energy in cluster of DNI-5. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-0.47413	1.351718	-0.15885	-4.58691
2	-0.47413	1.351717	-0.15884	-4.58691
3	-15.855	21.46507	-7.05716	-16.7868
4	-15.5683	15.73331	-3.62743	-22.1585
5	-1.6704	9.40812	-1.28527	-13.4787
6	1.637102	7.073546	-1.87549	-15.0174
7	-20.5978	29.49924	-7.62028	-28.4432
8	-1.67039	9.408109	-1.28525	-13.4787
9	1.637111	7.073548	-1.87547	-15.0174
10	-15.855	21.46504	-7.05713	-16.7868
11	-21.4174	20.16044	-5.04712	-22.5426
12	-20.5977	29.49923	-7.62031	-28.4432
13	-21.4174	20.1605	-5.04712	-22.5426
14	-15.5683	15.7333	-3.62741	-22.1585

Table S10. The binding energy in cluster of DNI-6. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-11.7535	16.85764	-4.42097	-13.5892
2	-11.6503	9.916474	-3.34968	-15.0222
3	4.181835	3.488767	-1.76358	-7.95628
4	-5.53348	8.687221	-3.29429	-14.8031
5	-11.6503	9.916469	-3.34968	-15.0222
6	-24.8085	18.33237	-6.22732	-13.2155
7	4.181849	3.488762	-1.76356	-7.95628
8	-11.7535	16.85765	-4.42097	-13.5892
9	-7.39676	25.62401	-6.49727	-35.5071
10	-5.53348	8.687222	-3.29432	-14.8031
11	-5.3944	16.95653	-4.85948	-25.8573
12	-5.39441	16.95657	-4.85953	-25.8573

13	-7.39675	25.62402	-6.49727	-35.5072
14	-24.8085	18.33237	-6.22728	-13.2155

Table S11. The binding energy in cluster of DNP-1. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-41.1522	43.98907	-17.9013	-27.5534
2	4.648337	2.019233	-0.82619	-5.3786
3	-41.1522	43.98908	-17.9013	-27.5534
4	-11.5175	21.43873	-3.67792	-25.5826
5	-0.56373	0.671296	-0.21217	-3.66769
6	-19.8107	28.39436	-6.09518	-36.111
7	-11.5175	21.4388	-3.67789	-25.5826
8	-15.5427	17.4991	-3.71336	-25.3209
9	-2.17905	7.265884	-1.22814	-12.7962
10	-15.5427	17.49914	-3.71325	-25.3209
11	-3.41405	7.89912	-1.35148	-13.4296
12	-19.8107	28.39435	-6.09509	-36.111
13	-3.41404	7.899123	-1.35153	-13.4296

Table S12. The binding energy in cluster of DNP-2. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-14.0432	18.75868	-4.03497	-24.6857
2	-11.6548	11.61819	-2.54749	-13.4671
3	-40.6864	42.99877	-19.0329	-29.633
4	-28.5734	35.86662	-15.1987	-24.7585
5	-12.4316	26.44399	-3.76744	-24.3457
6	-14.0432	18.7587	-4.03499	-24.6857
7	-8.04272	10.75347	-2.49539	-15.0666
8	-7.63007	8.941291	-2.14726	-13.2633
9	-14.9437	23.77617	-6.07132	-20.1552
10	1.322282	4.102119	-0.74882	-8.90157
11	0.126042	15.03299	-3.32379	-26.4733
12	-12.4316	26.444	-3.76744	-24.3458
13	-8.04273	10.75345	-2.49538	-15.0666

Table S13. The binding energy in cluster of DNP-3. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	-24.1	28.28391	-6.94145	-24.607
2	0.776057	3.001439	-0.89264	-5.46086
3	4.101448	7.722697	-2.38303	-16.2587
4	4.697791	3.501146	-1.12624	-6.95349
5	6.295849	7.183608	-1.99507	-13.2392
6	-23.8731	16.79265	-7.67994	-21.5631
7	-12.2622	21.7227	-3.95151	-30.3046
8	-20.2868	19.53356	-5.34355	-21.2052
9	-2.3238	24.30708	-6.27527	-31.9576
10	-3.07124	11.84708	-3.08055	-14.5859
11	-41.3132	44.39527	-16.1957	-21.8584
12	-23.873	16.79265	-7.68001	-21.5631
13	-44.2071	30.28846	-12.3096	-20.1731
14	-41.3133	44.3953	-16.1957	-21.8584

Table S14. The binding energy in cluster of DNP-4. The unit of energy is kJ/mol.

DIMER	ELECTRO	EXCHANGE	INDUCTION	DISPERSION
1	3.464689	0.58243	-0.31707	-3.85917
2	-20.1518	29.23541	-7.69087	-24.6646
3	-2.06612	4.103386	-1.25624	-7.62554
4	-6.20785	23.33565	-3.28373	-36.2956
5	-16.6636	23.83426	-4.73533	-24.1155
6	-2.06612	4.10339	-1.25623	-7.62554
7	-15.2225	13.76345	-3.35024	-16.4145
8	-16.6636	23.83424	-4.7353	-24.1155
9	-6.81594	11.74346	-2.03401	-18.1855
10	-24.0343	28.8828	-4.68733	-38.6063
11	-6.81594	11.74346	-2.03405	-18.1855
12	-7.99134	11.30739	-1.88169	-15.4119
13	-20.1518	29.23541	-7.6908	-24.6646
14	3.46469	0.582429	-0.31702	-3.85917