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A Theoretical Study on Weak Interactions in Phenylenediamine Homodimer Clusters

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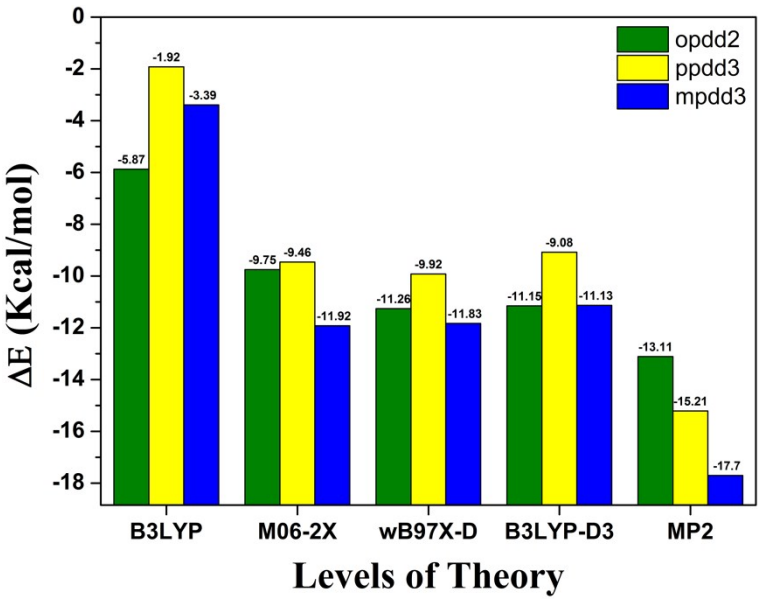

Fig S1. Interaction energies (kcal/mol) of the phenylenediamine homodimer clusters calculated at different levels of theory.

Interaction energies of phenylenediamine dimer (pdd) clusters calculated at traditional DFT B3LYP, dispersion-corrected DFT M06-2X, ωB97X-D, and B3LYP-D3 as well as the MP2 levels of theory are illustrated in Fig. S1 and also listed in Tables S1-S4. It is worth mentioning that the interaction energies of the pdd clusters obtained at the B3LYP level of theory largely differ from those calculated using dispersion-corrected DFT. This is because the B3LYP theory does not include the dispersion interaction, while the ωB97X-D functional includes empirical dispersion and treats hydrogen bonding and van der Waals forces more reasonable than conventional DFT.

Table S1. Interaction energies (kcal/mol) of all the phenylenediamine homodimer clusters calculated at the B3LYP/6-311++G(d,p) level of theory.

Dimer cluster	ΔE	BSSE	ZPVE	ΔE^{e}	ΔE^{e0}
opdd1	-6.41	0.79	1.30	-5.61	-4.31
opdd2	-6.49	0.62	1.54	-5.87	-4.33
opdd3	-5.05	0.54	1.07	-4.51	-3.44
ppdd1	-3.67	0.48	0.89	-3.19	-2.3
ppdd2	-3.65	0.63	0.90	-3.02	-2.12
ppdd3	-2.60	0.68	0.67	-1.92	-1.25
mpdd1	-4.84	0.71	1.00	-4.13	-3.13
mpdd2	-4.00	0.61	0.95	-3.39	-2.44
mpdd3	-3.44	0.60	0.68	-2.84	-2.16
mpdd4	-3.99	0.76	0.88	-3.23	-2.35
mpdd5	-3.76	0.48	0.79	-3.28	-2.49

ΔE^{e}: BSSE corrected interaction energy; ΔE^{e0}: BSSE+ZPE corrected interaction energy.

Table S2. Interaction energies (kcal/mol) of all the phenylenediamine homodimer clusters calculated at the M06-2X/6-311++G(d,p) level of theory.

Dimer cluster	ΔE	BSSE	ZPVE	ΔE^{e}	ΔE^{e0}
opdd1	-9.82	1.79	1.01	-8.03	-7.02
opdd2	-10.47	0.72	1.45	-9.75	-8.3
opdd3	-8.29	0.80	0.98	-7.49	-6.51
ppdd1	-9.01	1.06	1.02	-7.95	-6.93
ppdd2	-8.69	1.14	1.01	-7.55	-6.54
ppdd3	-10.81	1.35	1.15	-9.46	-8.31
mpdd1	-10.92	0.9	1.09	-10.02	-8.93
mpdd2	-13.37	1.44	1.26	-11.92	-10.66
mpdd3	-10.31	1.27	0.89	-9.03	-8.14
mpdd4	-12.43	1.41	0.74	-11.01	-10.27
mpdd5	-6.34	0.69	0.49	-5.65	-5.16

ΔE^{e}: BSSE corrected interaction energy; ΔE^{e0}: BSSE+ZPE corrected interaction energy.

Table S3. Interaction energies (kcal/mol) of all the phenylenediamine homodimer clusters calculated at the B3LYP-D3/6-311++G(d,p) level of theory.

Dimer cluster	ΔE	BSSE	ZPVE	ΔE^{e}	ΔE^{e0}
opdd1	-				
opdd2	-11.89	0.74	1.82	-11.15	-9.33
opdd3	-8.86	0.68	1.19	-8.18	-6.99
ppdd1					
ppdd2	-8.34	0.88	1.17	-7.46	-6.29
ppdd3	-10.26	1.18	1.30	-9.08	-7.78
mpdd1	-10.67	1.21	1.46	-9.46	-8.00
mpdd2	-12.26	1.13	1.34	-11.13	-9.79
mpdd3	-9.89	1.13	1.10	-8.76	-7.66
mpdd4	-11.79	1.23	1.17	-10.56	-9.39
mpdd5					

ΔE^{e}: BSSE corrected interaction energy; ΔE^{e0}: BSSE+ZPE corrected interaction energy.

Table S4. Interaction energies (kcal/mol) of all the phenylenediamine homodimer clusters calculated at different basis sets on the ωB97X-D and MP2 levels of theory.

Theory	opdd2		ppdd3		mpdd2	
	ΔE	ΔE^e	ΔE	ΔE^e	ΔE	ΔE^e
ωB97X-D/6-311++g(d,p)	-12	-11.26	-11.01	-9.92	-12.97	-11.83
ωB97X-D/6-311++g(2d,p)	-11.16	-10.68	-10.31	-9.56	-12.23	-11.54
ωB97X-D/6-311++g(3d,p)	-10.97	-10.54	-10.30	-9.50	-12.12	-11.34
ωB97X-D/6-311++g(2d,2p)	-11.03	-10.58	-9.94	-9.37	-11.83	-11.30
ωB97X-D/aug-cc-pvdz	-11.54	-10.22	-10.75	-9.44	-12.67	-11.28
ωB97X-D/aug-cc-pvtz	-10.70	-10.37	-9.61	-9.24	-11.39	-11.00
MP2/6-311++g(d,p)	-11.76	-8.13	-13.81	-7.89	-16.06	-10.15
MP2/aug-cc-pvtz	-13.11	-8.67	-15.21	-9.26	-17.70	-11.59

ΔE^e: BSSE corrected interaction energy.

Table S5. NBO analysis of the intermolecular weak interactions in the secondary stable pdd clusters calculated at the ωB97X-D/6-311++G(d,p) level of theory. The second-order perturbation energies $E^{(2)}_{i\rightarrow j^*}$ are in kcal/mol.

Dimer cluster	Donor	Acceptor	$E^{(2)}_{i\rightarrow j^*}$	Sum of $E^{(2)}_{i\rightarrow j^*}$
opdd1	LP (1) N2	BD*(1) N17-H30	10.10	20.20
	LP (1) N18	BD*(1) N1-H14	10.10	
ppdd1	LP (1) N1	BD*(1) N17-H19	2.32	4.03
	LP (1) N1	BD*(2) C23-C29	0.21	
	LP (1) N17	BD*(2) C7-C8	0.13	
	BD (2) C7-C8	BD*(2) C20-C21	0.21	
	BD (2) C20-C21	BD*(2) C7-C8	0.79	
	BD (2) C23-C29	BD*(2) N1-H2	0.15	
	BD (2) C23-C29	BD*(2) C8-H9	0.22	
mpdd4	LP (1) N17	BD*(1) N1-H3	1.57	3.97
	LP (1) N1	BD*(2) C24-C26	0.17	
	LP (1) N4	BD*(2) C27-C29	0.18	
	LP (1) N20	BD*(2) C8-C10	0.16	
	BD(2) C23-C31	BD*(1) C8-H9	0.15	
	BD(2) C24-C26	BD*(2) C7-C15	0.32	
	BD(2) C24-C26	BD*(1) C8-C10	0.62	
	BD(2) C27-C29	BD*(1) N4-H6	0.44	
	BD(2) C27-C29	BD*(2) C8-C10	0.36	

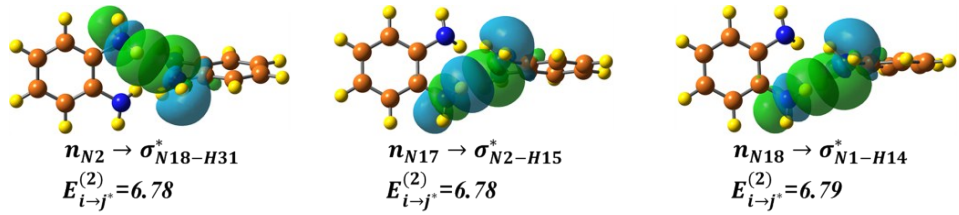

Fig. S2 Natural bond orbitals patterns showing N-H···N hydrogen bonding in the opdd clusters. All the second-order perturbative energy is in kcal/mol.

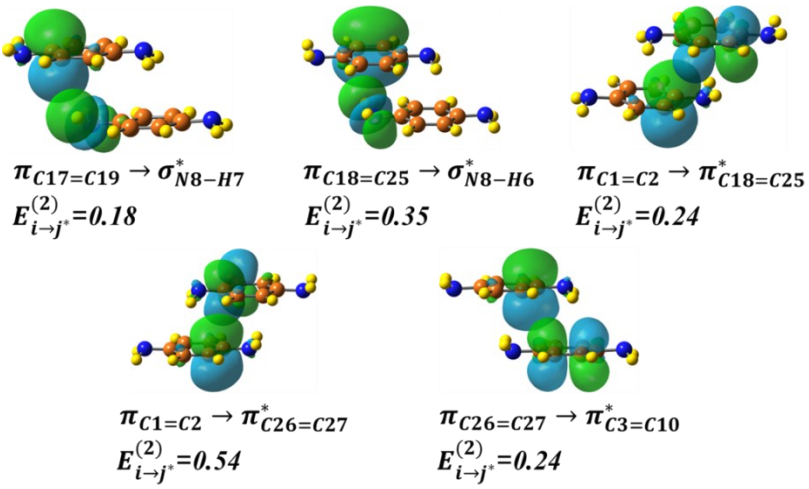

Fig. S3 Natural bond orbitals patterns showing N-H···π hydrogen bonding and π···π* interactions in the ppdd clusters. All the second-order perturbative energy is in kcal/mol.

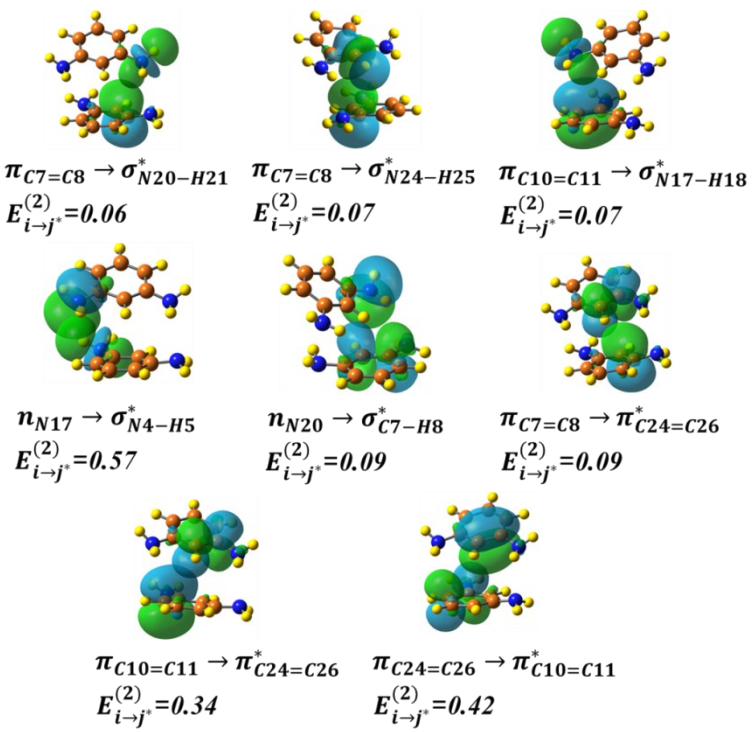

Fig. S4 Natural bond orbitals patterns showing the N-H···N, N-H···π, C-H···N, and π···π interactions in the mpdd clusters. All the second-order perturbative energy is in kcal/mol.

Table S5. Theoretical harmonic vibrational frequencies (cm^{-1}), their assignments and relative intensities (km/mol) of the N–H stretching modes of phenylenediamine monomers and their corresponding clusters calculated at the ωB97X-D/6-311++g(d,p) level of theory.

Geometry	Assignment	ν_{N-H}	IR intensity	Raman intensity
opd	ν_{as}	3670	151	20
	ν_{s}	3563	69	259
	ν_{s}	3561	21	72
opdd2	ν_{as}	3639	72	97
	ν_{as}	3638	29	127
	ν_{s}	3480	800	7
	ν_{s}	3462	122	100
	ν_{s}	3461	122	100
ppd	ν_{as}	3693	939	105
	ν_{s}	3596	228	366
ppdd3	ν_{as}	3690	201	114
	ν_{as}	3672	68	12
	ν_{s}	3595	161	487
	ν_{s}	3590	390	288
mpd	ν_{as}	3711	173	66
	ν_{as}	3610	221	319
mpdd3	ν_{as}	3711	361	66
	ν_{as}	3699	184	52
	ν_{as}	3695	153	54
	ν_{as}	3673	128	22
	ν_{s}	3597	159	204
	ν_{s}	3593	530	226
	ν_{s}	3584	230	96

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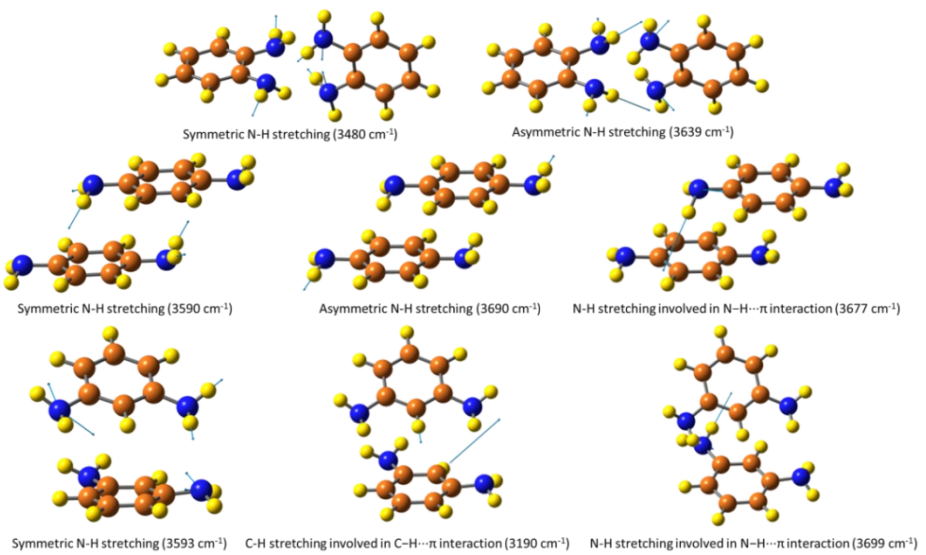

Fig. S5 The normal modes of N–H stretches of the pdd clusters calculated at the ωB97X-D/6-311++G(d,p) level of theory.