Supporting Information for:

The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06 Functionals and Twelve Other Functionals

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Table S1: MGAE109/05 database of zero-point-exclusive atomization energies (kcal/mol)

Molecule	D_e	Molecule	D_e	Molecule	D_e
CH ($^2\Pi$)	84.00	S_2	101.67	H_2CCH	445.79
CH_2 ($^3B_1$)	190.72	Cl_2	57.98	$HCOOCH_3$	785.26
CH_2 ($^1A_1$)	181.37	SiO	192.08	HCOOH	500.98
CH_3 ($^2A''_2$)	307.44	SC	171.11	NF_3	204.53
CH_4	420.11	SO	125.22	PF_3	363.87
NH	83.67	ClO	64.49	SH	86.98
NH_2	181.90	ClF	61.48	$SiCl_4$	384.94
NH_3	297.90	Si_2H_6	534.66	SiF_4	574.35
OH	107.09	CH_3Cl	395.51	C_2H_5	603.75
OH_2	232.60	CH_3SH	473.84	C_4H_6 *d*	987.20
FH	141.18	HOCl	164.81	C_4H_6 *e*	1001.61
SiH_2 ($^1A_1$)	151.79	SO_2	258.62	HCOCOH	633.35
SiH_2 ($^3B_1$)	131.05	$AlCl_3$	306.26	CH_3CHO	677.03
SiH_3	227.58	AlF_3	426.50	C_2H_4O	650.70
SiH_4	322.40	BCl_3	322.90	C_2H_5O	698.64
PH_2	153.20	BF_3	470.04	H_3COCH_3	798.05
PH_3	241.56	C_2Cl_4	466.28	H_3CCH_2OH	810.36
SH_2	182.60	C_2F_4	589.36	C_3H_4 *f*	703.20
ClH	106.48	C_3H_4 *a*	704.79	C_3H_4 *g*	682.74
HCCH	405.36	C_4H_4O	993.74	H_3CCOOH	803.04
H_2CCH_2	563.51	C_4H_4S	962.73	H_3CCOCH_3	977.96
H_3CCH_3	712.80	C_4H_5N	1071.57	C_3H_6	853.41
CN	180.58	C_4H_6 *b*	1012.37	H_3CCHCH_2	860.61
HCN	313.05	C_4H_6 *c*	1004.13	C_3H_8	1006.87
CO	259.27	C_5H_5N	1237.69	$C_2H_5OCH_3$	1095.12
HCO	278.39	CCH	265.13	C_4H_{10} *h*	1303.04
H_2CO	373.82	CCl_4	312.74	C_4H_{10} *i*	1301.32
H_3COH	513.22	CF_3CN	639.85	C_4H_8 *j*	1149.01

N_2	228.42	CF_4	476.32	C_4H_8 [k]	1158.61
H_2NNH_2	438.60	CH_2OH	409.76	C_5H_8 [l]	1284.28
NO	152.05	CH_3CN	615.84	C_6H_6	1367.56
O_2	120.22	CH_3NH_2	582.56	CH_3CO	581.58
HOOH	268.57	CH_3NO_2	601.27	$(CH_3)_2CH$	900.75
F_2	38.20	$CHCl_3$	343.18	$(CH_3)_3C$	1199.34
CO_2	389.14	CHF_3	457.50	H_2CCO	532.32
Si_2	75.72	ClF_3	125.33		
P_2	117.09	H_2	109.48		

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[a] propyne

[b] *trans*-1,3-butadiene

[c] 2-butyne

[d] bicylobutane

[e] cyclobutene

[f] allene

[g] cyclopropene

[h] isobutane

[i] antiperiplanar butane

[j] cyclobutane

[k] isobutene

[l] spiropentane

Table S2: Zero-point-exclusive ionization potentials (IP13/3) and electron affinities (EA13/3) databases (kcal/mol)

	IP	EA
C	259.7	29.1
S	238.9	47.9
SH	238.9	53.3
Cl	299.1	83.4
Cl_2	265.3	55.6
OH	299.1	42.1
O	313.9	33.7
O_2	278.9	10.8
P	241.9	17.2
PH	234.1	23.2
PH_2	226.3	29.4
S_2	216.0	38.5
Si	187.9	31.9

Table S3. Zero-point-exclusive proton affinities (PA8) database (kcal/mol)

Molecule	proton affinities
NH_3	211.9
H_2O	171.8
C_2H_2	156.6
SiH_4	156.5
PH_3	193.1
H_2S	173.7
HCl	137.1
H_2	105.9

Table S4: HTBH38/04 database (kcal/mol)

Reaction	best estimate	
A + BC → AB + C	$V_f^{\neq}$	$V_r^{\neq}$
1. H + HCl → H_2 + Cl	5.7	8.7
2. OH + H_2 → H + H_2O	5.7	21.2
3. CH_3 + H_2 → H + CH_4	12.1	15.3
4. OH + CH_4 → CH_3 + H_2O	6.7	19.6
5. H + H_2 → H_2 + H	9.6	9.6
6. OH + NH_3 → H_2O + NH_2	3.2	12.7
7. HCl + CH_3 → Cl + CH_4	1.7	7.9
8. OH + C_2H_6 →H_2O + C_2H_5	3.4	19.9
9. F + H_2 → HF + H	1.8	33.4
10. O + CH_4 →OH + CH_3	13.7	8.1
11. H + PH_3→ PH_2 + H_2	3.1	23.2
12. H + HO → H_2 +O	10.7	13.1
13. H + H_2S → H_2 + HS	3.5	17.3
14. O + HCl → OH + Cl	9.8	10.4
15. NH_2 + CH_3→ CH_4 + NH	8.0	22.4
16. NH_2 + C_2H_5 → C_2H_6 + NH	7.5	18.3
17. C_2H_6 + NH_2 → NH_3 + C_2H_5	10.4	17.4
18. NH_2 + CH_4 → CH_3 + NH_3	14.5	17.8
19. *s-trans cis*-C_5H_8 → *s-trans cis*-C_5H_8	38.4	38.4

Table S5: NHTBH38/04 databases

Reactions		Best Estimate (kcal/mol)
Heavy-atom transfer reactions		
$H + N_2O \rightarrow OH + N_2$	$V_f^{\neq}$	18.14
	$V_r^{\neq}$	83.22
$H + FH \rightarrow HF + H$	$V_f^{\neq}$	42.18
	$V_r^{\neq}$	42.18
$H + ClH \rightarrow HCl + H$	$V_f^{\neq}$	18.00
	$V_r^{\neq}$	18.00
$H + FCH_3 \rightarrow HF + CH_3$	$V_f^{\neq}$	30.38
	$V_r^{\neq}$	57.02
$H + F_2 \rightarrow HF + F$	$V_f^{\neq}$	2.27
	$V_r^{\neq}$	106.18
$CH_3 + FCl \rightarrow CH_3F + Cl$	$V_f^{\neq}$	7.43
	$V_r^{\neq}$	61.01
Nucleophilic substitution reactions		
$F^- + CH_3F \rightarrow FCH_3 + F^-$	$V_f^{\neq}$	–0.34
	$V_r^{\neq}$	–0.34
$F^-\cdots CH_3F \rightarrow FCH_3 \cdots F^-$	$V_f^{\neq}$	13.38
	$V_r^{\neq}$	13.38
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	$V_f^{\neq}$	3.10
	$V_r^{\neq}$	3.10
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	$V_f^{\neq}$	13.61
	$V_r^{\neq}$	13.61
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	$V_f^{\neq}$	–12.54
	$V_r^{\neq}$	20.11
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	$V_f^{\neq}$	2.89
	$V_r^{\neq}$	29.62
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	$V_f^{\neq}$	–2.78
	$V_r^{\neq}$	17.33
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	$V_f^{\neq}$	10.96
	$V_r^{\neq}$	47.20
Unimolecular and association reactions		
$H + N_2 \rightarrow HN_2$	$V_f^{\neq}$	14.69
	$V_r^{\neq}$	10.72

$H + CO \rightarrow HCO$	$V_f^{\neq}$	3.17
	$V_r^{\neq}$	22.68
$H + C_2H_4 \rightarrow CH_3CH_2$	$V_f^{\neq}$	1.72
	$V_r^{\neq}$	41.75
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	$V_f^{\neq}$	6.85
	$V_r^{\neq}$	32.97
$HCN \rightarrow HNC$	$V_f^{\neq}$	48.16
	$V_r^{\neq}$	33.11

Table S6: Noncovalent interaction databases (kcal/mol)

HB6/04		CT7/04		DI6/04		WI7/05		PPS5/05	
Complex	D_e	Complex	D_e	Complex	D_e	Complex	D_e	Complex	D_e
$(NH_3)_2$	3.15	$C_2H_4\cdots F_2$	1.06	$(H_2S)_2$	1.66	HeNe	0.04	$(C_2H_2)_2$	1.34
$(HF)_2$	4.57	$NH_3\cdots F_2$	1.81	$(HCl)_2$	2.01	HeAr	0.06	$(C_2H_4)_2$	1.42
$(H_2O)_2$	4.97	$C_2H_2\cdots ClF$	3.81	$HCl\cdots H_2S$	3.35	Ne_2	0.08	Sandwich $(C_6H_6)_2$	1.81
$NH_3\cdots H_2O$	6.41	$HCN\cdots ClF$	4.86	$CH_3Cl\cdots HCl$	3.55	NeAr	0.13	T-Shaped $(C_6H_6)_2$	2.74
$(HCONH_2)_2$	14.94	$NH_3\cdots Cl_2$	4.88	$HCN\cdots CH_3SH$	3.59	$CH_4\cdots Ne$	0.22	Parallel-Displaced $(C_6H_6)_2$	2.78
$(HCOOH)_2$	16.15	$H_2O\cdots ClF$	5.36	$CH_3SH\cdots HCl$	4.16	$C_6H_6\cdots Ne$	0.47		
		$NH_3\cdots ClF$	10.62			$(CH_4)_2$	0.51		
Average	8.37		4.63		3.07		0.22		0.22

Table S7: Interaction energies (kcal/mol) and sources of geometries in the S22 database [a]

Complex (symmetry)	Best Estimate [b]	Geometries [b]
Hydrogen bonded complexes		
$(NH_3)_2$ (C_{2h})	–3.17	CCSD(T)/QZ
$(H_2O)_2$ (C_s)	–5.02	CCSD(T)/QZ
Formic acid dimer (C_{2h})	–18.61	CCSD(T)/TZ
Formamide dimer (C_{2h})	–15.96	CCSD(T)/TZ
Uracil dimer (C_{2h})	–20.65	MP2/TZ-CP
2-pyridoxine···2-aminopyridine (C_1)	–16.71	MP2/TZ-CP
Adenine···thymine WC (C_1)	–16.37	MP2/TZ-CP
Dispersion-dominated complexes		
$(CH_4)_2$ (D_{3d})	–0.53	CCSD(T)/TZ
$(C_2H_4)_2$ (D_{2d})	–1.51	CCSD(T)/QZ
Benzene···CH_4 (C_3)	–1.50	MP2/TZ-CP
Benzene dimer (C_{2h})	–2.73	MP2/TZ-CP
Pyrazine dimer (C_s)	–4.42	MP2/TZ-CP
Uracil dimer (C_2)	–10.12	MP2/TZ-CP
Indole·benzene (C_1)	–5.22	MP2/TZ-CP
Adenine···thymine stack (C_1)	–12.23	MP2/TZ-CP
Mixed complexes		
Ethene···ethyne (C_{2v})	–1.53	CCSD(T)/QZ
Benzene···H_2O (C_s)	–3.28	MP2/TZ-CP
Benzene···NH_3 (C_s)	–2.35	MP2/TZ-CP
Benzene···HCN (C_s)	–4.46	MP2/TZ-CP
Benzene dimer (C_{2v})	–2.74	MP2/TZ-CP
Indole···benzene T-shaped (C_1)	–5.73	MP2/TZ-CP
Phenol dimer (C_1)	–7.05	MP2/TZ-CP

[a] The best estimate are taken from a paper by Jurecka et al.

[b] P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).

Table S8: TMAE9/05 and MLBE21/05 databases (kcal/mol)

TMAE9/05		MLBE21/05	
Molecule	D_e	Molecule	D_e
Ag_2	38.30	AgH	54.00
Cr_2	36.00	BeO	104.80
Cu_2	47.20	CoH	45.60
CuAg	40.90	CoO^+	76.10
Mo_2	103.90	$CoOH^+$	73.80
Ni_2	47.60	$CrCH_3^+$	28.80
V_2	64.20	CuH_2O^+	38.80
Zr_2	70.80	FeH	36.90
ZrV	61.90	$Fe(CO)_5$	148.70 [a]
Ag_2	38.30	FeO	102.60
		FeS	76.70
		LiCl	113.90
		LiO	82.00
		MgO	59.19
		$MnCH_3^+$	51.90
		$NiCH_2^+$	76.30
		$Ni(CO)_4$	147.50 [a]
		RhC	139.20
		VCO^+	28.80
		VO	149.90
		VS	106.90

[a] average of breaking five or four carbonyl bonds to metal. All other values in this table are breaking one metal-metal or metal-ligand bond.

Table S9: π system databases (kcal/mol)[a]

π		PA-P5		PA-SB5	
E2-E1	-1.40	P-2	167.81	SB-2	214.46
E4-E3	-8.80	P-4	193.45	SB-4	226.15
E6-E5	-14.30	P-6	209.68	SB-6	233.44
		P-8	219.67	SB-8	238.16
		P-10	225.95	SB-10	240.97

[a] See Figure S1, S2, and S3 for the structures of the molecules in these databases.

Table S10: Spin-orbit contributions (kcal/mol) to bond energies in Table S8.[a]

TMAE9/05		MLBE21/05	
Molecule	ΔE_{SO}	Molecule	ΔE_{SO}
Ag_2	0	AgH	0
Cr_2	0	BeO	-0.02 [b]
Cu_2	0	CoH	-0.37 [b]
CuAg	0	CoO^+	-0.76 [b]
Mo_2	0	$CoOH^+$	-2.19 [c]
Ni_2	-5.56 [b]	$CrCH_3^+$	0
V_2	-1.83 [b]	CuH_2O^+	0
Zr_2	-3.30 [b]	FeH	-0.12 [b]
ZrV	-2.98 [b]	$Fe(CO)_5$	-1.52 [d]
Ag_2	0	FeO	-0.09 [b]
		FeS	-1.2 [b]
		LiCl	-0.84 [b]
		LiO	0.14 [b]
		MgO	-0.02 [b]
		$MnCH_3^+$	0
		$NiCH_2^+$	-1.72 [c]
		$Ni(CO)_4$	-2.78 [d]
		RhC	-4.34 [b]
		VCO^+	0
		VO	-0.94 [b]
		VS	-1.47 [b]

[a] The values in this table are added to the nonrelativistic DFT results before they are compared to the experimental values in the TMAE9/05 and MLBE12/05 databases.

[b] $\Delta E_{SO} = E_{SO}(A) + E_{SO}(B) - E_{SO}(AB)$, where $E_{SO}(A)$ and $E_{SO}(B)$ are the spin-orbit energies of atoms A and B and $E_{SO}(AB)$ is the spin orbit energy of the diatomic molecules AB. In the case of CoO^+, A is charged, i.e., $A = Co^+$.

[c] $\Delta E_{SO} = E_{SO}(L) + E_{SO}(M^+) - E_{SO}(ML^+)$, where L denotes ligand..

[d] $\Delta E_{SO} \equiv nE_{SO}(L) + E_{SO}(M) - E_{SO}(ML_n)$, where n is the number of ligands, $E_{SO}(L)$ is the spin–orbit energy of the ligand, $E_{SO}(M)$ is the spin–orbit energy of the metal atom/ion, and $E_{SO}(ML_n)$ is the spin–orbit energy of the metal–ligand complex.

Table S11: Cartesian coordinates for the HC7 database (MP2/6-311+G(d,p))

$(CH)_{12}$	Structure **1**		
C	0.00000200	0.87844600	1.79651700
C	-0.76075800	-0.43922200	1.79651700
H	-1.33205900	-0.76905400	2.65844700
C	0.76075600	-0.43922400	1.79651700
C	-1.19981100	-0.69271100	0.35388600
H	0.00000900	1.53812400	2.65844700
C	1.19981100	-0.69271100	0.35388600
H	1.33205000	-0.76907000	2.65844700
H	0.00000100	2.47465400	0.24764000
C	-0.76075600	0.43922400	-1.79651700
H	-2.14311400	-1.23732600	0.24764000
C	1.19981100	0.69271100	-0.35388600
C	0.00000000	-1.38542300	-0.35388600
C	0.76075800	0.43922200	-1.79651700
H	2.14311300	-1.23732800	0.24764000
C	0.00000000	1.38542300	0.35388600
C	-1.19981100	0.69271100	-0.35388600
C	-0.00000200	-0.87844600	-1.79651700
H	-2.14311300	1.23732800	-0.24764000
H	-0.00000100	-2.47465400	-0.24764000
H	2.14311400	1.23732600	-0.24764000
H	-0.00000900	-1.53812400	-2.65844700
H	-1.33205000	0.76907000	-2.65844700
H	1.33205900	0.76905400	-2.65844700

$(CH)_{12}$	Structure **22**		
C	-0.21673000	1.39209600	0.44477800
C	0.33719600	-0.00231100	0.75980200
C	-1.61011800	1.46871200	-0.11967300
C	-2.58179300	0.51845600	-0.19001100
C	-0.09322900	-1.02609600	-0.32353700
C	-2.51607500	-0.91225300	0.11531400
C	-1.39293700	-1.66637500	0.03140400
C	0.86933800	1.95515800	-0.45830700
C	1.87687400	0.07979500	0.59746900
H	-1.90445300	2.47193100	-0.43547200
C	1.13487900	-1.88337000	-0.49180000
H	-3.55542400	0.86732000	-0.53621500
H	-3.46019200	-1.39914300	0.35453200
H	-1.43339300	-2.73325600	0.24833500
H	0.72787000	2.83769800	-1.07845100
H	1.13491500	-2.83617500	-1.01618300
C	2.01724300	1.25619000	-0.35203900

C	2.23015900	-1.26181800	-0.01115800
H	2.94135300	1.49513200	-0.87271200
H	3.24645600	-1.64186400	-0.07817300
H	0.03867300	-0.37388100	1.74556700
H	-0.22596400	1.99145400	1.37279200
H	2.40908800	0.26571100	1.54099700
H	-0.24776100	-0.45403600	-1.25846900

$(CH)_{12}$ Structure **31**

C	0.99460900	-0.08470500	0.00000000
C	1.06353700	-0.98511000	1.20240100
C	1.06353700	-0.98511000	-1.20240100
C	0.09250300	-1.89110800	-1.52164900
C	0.09250300	-1.89110800	1.52164900
C	-1.01080800	-2.28759600	-0.68842600
C	-1.01080800	-2.28759600	0.68842600
H	1.86995500	0.57477800	0.00000000
H	1.91554300	-0.87845300	1.87331800
H	1.91554300	-0.87845300	-1.87331800
H	0.17078400	-2.38930800	2.48776000
H	0.17078400	-2.38930800	-2.48776000
H	-1.85756700	-2.76147200	-1.18320600
H	-1.85756700	-2.76147200	1.18320600
C	-0.25099700	0.83978800	0.00000000
C	-0.26820400	3.05711100	0.73349800
C	-0.26820400	3.05711100	-0.73349800
C	-0.25860700	1.77067300	1.17810700
C	-0.25860700	1.77067300	-1.17810700
H	-0.27107200	3.94740600	1.35435600
H	-0.27107200	3.94740600	-1.35435600
H	-0.25679100	1.43911000	2.21079900
H	-0.25679100	1.43911000	-2.21079900
H	-1.15447300	0.21251300	0.00000000

Adamantane

C	0.88830000	0.88830000	0.88830000
C	-0.88830000	-0.88830000	0.88830000
C	-0.88830000	0.88830000	-0.88830000
C	0.88830000	-0.88830000	-0.88830000
C	0.00000000	0.00000000	1.77300000
C	0.00000000	0.00000000	-1.77300000
C	0.00000000	1.77300000	0.00000000
C	0.00000000	-1.77300000	0.00000000
C	1.77300000	0.00000000	0.00000000
C	-1.77300000	0.00000000	0.00000000
H	1.52220000	1.52220000	1.52220000

H	-1.52220000	-1.52220000	1.52220000
H	-1.52220000	1.52220000	-1.52220000
H	1.52220000	-1.52220000	-1.52220000
H	2.42310000	-0.62630000	0.62630000
H	2.42310000	0.62630000	-0.62630000
H	-2.42310000	-0.62630000	-0.62630000
H	-2.42310000	0.62630000	0.62630000
H	-0.62630000	2.42310000	0.62630000
H	0.62630000	2.42310000	-0.62630000
H	0.62630000	-2.42310000	0.62630000
H	-0.62630000	-2.42310000	-0.62630000
H	-0.62630000	0.62630000	2.42310000
H	0.62630000	-0.62630000	2.42310000
H	0.62630000	0.62630000	-2.42310000
H	-0.62630000	-0.62630000	-2.42310000

bicycle[2.2.2]octane

C	0.00000000	0.00000000	1.29556600
C	0.13323900	1.43538200	0.76413300
C	-0.13323900	1.43538200	-0.76413300
C	0.00000000	0.00000000	-1.29556600
C	1.17645800	-0.83308000	0.76413300
C	1.30969700	-0.60230300	-0.76413300
C	-1.30969700	-0.60230300	0.76413300
C	-1.17645800	-0.83308000	-0.76413300
H	0.00000000	0.00000000	2.39192200
H	-0.56975700	2.09994300	1.27952100
H	1.14315200	1.80708900	0.97868600
H	0.56975700	2.09994300	-1.27952100
H	-1.14315200	1.80708900	-0.97868600
H	0.00000000	0.00000000	-2.39192200
H	0.99340900	-1.89354300	0.97868600
H	2.10348200	-0.55654700	1.27952100
H	2.13656000	0.08645400	-0.97868600
H	1.53372500	-1.54339500	-1.27952100
H	-2.13656000	0.08645400	0.97868600
H	-1.53372500	-1.54339500	1.27952100
H	-0.99340900	-1.89354300	-0.97868600
H	-2.10348200	-0.55654700	-1.27952100

Ethyne

C	0.00000000	0.00000000	0.60810700
C	0.00000000	0.00000000	-0.60810700
H	0.00000000	0.00000000	-1.67310000
H	0.00000000	0.00000000	1.67310000

Ethylene

C	0.00000000	0.00000000	-0.00932300
C	0.00000000	0.00000000	1.32978100
H	0.92631100	0.00000000	-0.57490800
H	-0.92631100	0.00000000	-0.57490800
H	0.92631100	0.00000000	1.89536600
H	-0.92631100	0.00000000	1.89536600

Ethane

C	0.00000000	0.00000000	0.76445100
C	0.00000000	0.00000000	-0.76445100
H	0.00000000	1.01971100	1.15903100
H	-0.88309500	-0.50985500	1.15903100
H	0.88309500	-0.50985500	1.15903100
H	0.00000000	-1.01971100	-1.15903100
H	-0.88309500	0.50985500	-1.15903100
H	0.88309500	0.50985500	-1.15903100

Methane

C	0.00000000	0.00000000	0.00000000
H	0.62940400	0.62940400	0.62940400
H	-0.62940400	-0.62940400	0.62940400
H	-0.62940400	0.62940400	-0.62940400
H	0.62940400	-0.62940400	-0.62940400

Hexane

C	1.41786200	2.88438300	0.00000000
C	-1.41786200	-2.88438300	0.00000000
C	0.00806500	0.76414000	0.00000000
C	-0.00806500	-0.76414000	0.00000000
C	-1.41786200	-1.35537100	0.00000000
C	1.41786200	1.35537100	0.00000000
H	-2.43571800	-3.28614900	0.00000000
H	2.43571800	3.28614900	0.00000000
H	0.90180600	3.27133900	0.88475400
H	0.90180600	3.27133900	-0.88475400
H	-0.90180600	-3.27133900	-0.88475400
H	-0.90180600	-3.27133900	0.88475400
H	1.95990100	0.98623800	-0.87982600
H	1.95990100	0.98623800	0.87982600
H	-1.95990100	-0.98623800	-0.87982600
H	-1.95990100	-0.98623800	0.87982600
H	-0.53702800	1.13115300	0.88065100
H	-0.53702800	1.13115300	-0.88065100
H	0.53702800	-1.13115300	-0.88065100
H	0.53702800	-1.13115300	0.88065100

2,2,3,3-Tetramethylbutane

C	0.00000000	0.00000000	0.78490900
C	0.00000000	0.00000000	-0.78490900
C	-0.86687300	1.14120200	1.34190800
C	1.42174600	0.18013400	1.34190800
C	-0.55487300	-1.32133500	1.34190800
C	0.86687300	1.14120200	-1.34190800
C	-1.42174600	0.18013400	-1.34190800
C	0.55487300	-1.32133500	-1.34190800
H	-0.59633900	2.11091100	0.91090600
H	-1.93145600	0.96682800	1.15785800
H	-0.72484300	1.20960400	2.42686600
H	1.80302500	1.18927600	1.15785800
H	1.40996900	0.02293000	2.42686600
H	2.12627200	-0.53901100	0.91090600
H	-1.52993300	-1.57190000	0.91090600
H	0.12843000	-2.15610300	1.15785800
H	-0.68512600	-1.23253400	2.42686600
H	0.59633900	2.11091100	-0.91090600
H	1.93145600	0.96682800	-1.15785800
H	0.72484300	1.20960400	-2.42686600
H	-1.80302500	1.18927600	-1.15785800
H	-1.40996900	0.02293000	-2.42686600
H	-2.12627200	-0.53901100	-0.91090600
H	1.52993300	-1.57190000	-0.91090600
H	-0.12843000	-2.15610300	-1.15785800
H	0.68512600	-1.23253400	-2.42686600

n-Octane

C	-0.16146400	4.47867500	0.00000000
C	-0.84061900	3.10866500	0.00000000
C	0.16146400	1.95379600	0.00000000
C	-0.50208600	0.57653500	0.00000000
C	0.50208600	-0.57653500	0.00000000
C	-0.16146400	-1.95379600	0.00000000
C	0.84061900	-3.10866500	0.00000000
C	0.16146400	-4.47867500	0.00000000
H	-0.89492500	5.29077300	0.00000000
H	0.47278100	4.59601600	0.88488300
H	0.47278100	4.59601600	-0.88488300
H	-1.49008500	3.01809600	-0.87994800
H	-1.49008500	3.01809600	0.87994800
H	0.81284600	2.04088900	-0.88074500
H	0.81284600	2.04088900	0.88074500
H	-1.15296200	0.48868100	-0.88091800

H	-1.15296200	0.48868100	0.88091800
H	1.15296200	-0.48868100	-0.88091800
H	1.15296200	-0.48868100	0.88091800
H	-0.81284600	-2.04088900	-0.88074500
H	-0.81284600	-2.04088900	0.88074500
H	1.49008500	-3.01809600	-0.87994800
H	1.49008500	-3.01809600	0.87994800
H	-0.47278100	-4.59601600	-0.88488300
H	0.89492500	-5.29077300	0.00000000
H	-0.47278100	-4.59601600	0.88488300

Table S12: Cartesian coordinates for the DC10 database (MP2/6-311+G(d,p))

C_6Cl_6

C	0.00000000	1.40687300	0.00000000
C	1.21838700	0.70343600	0.00000000
C	1.21838700	-0.70343600	0.00000000
C	0.00000000	-1.40687300	0.00000000
C	-1.21838700	-0.70343600	0.00000000
C	-1.21838700	0.70343600	0.00000000
Cl	2.70545600	1.56199600	0.00000000
Cl	2.70545600	-1.56199600	0.00000000
Cl	0.00000000	-3.12399200	0.00000000
Cl	-2.70545600	-1.56199600	0.00000000
Cl	-2.70545600	1.56199600	0.00000000
Cl	0.00000000	3.12399200	0.00000000

C_6F_6

C	0.00000000	1.39491400	0.00000000
C	1.20803100	0.69745700	0.00000000
C	1.20803100	-0.69745700	0.00000000
C	0.00000000	-1.39491400	0.00000000
C	-1.20803100	-0.69745700	0.00000000
C	-1.20803100	0.69745700	0.00000000
F	2.36044000	1.36280100	0.00000000
F	2.36044000	-1.36280100	0.00000000
F	0.00000000	-2.72560200	0.00000000
F	-2.36044000	-1.36280100	0.00000000
F	-2.36044000	1.36280100	0.00000000
F	0.00000000	2.72560200	0.00000000

C_6H_6

C	0.00000000	1.39870000	0.00000000
C	1.21130000	0.69940000	0.00000000
C	1.21130000	-0.69940000	0.00000000
C	0.00000000	-1.39870000	0.00000000
C	-1.21130000	-0.69940000	0.00000000
C	-1.21130000	0.69940000	0.00000000
H	0.00000000	2.48200000	0.00000000
H	2.14940000	1.24100000	0.00000000
H	2.14940000	-1.24100000	0.00000000
H	0.00000000	-2.48200000	0.00000000
H	-2.14940000	-1.24100000	0.00000000
H	-2.14940000	1.24100000	0.00000000

Cl_2

Cl	0.00000000	0.00000000	1.01226400
Cl	0.00000000	0.00000000	-1.01226400

HCl

Cl	0.00000000	0.00000000	0.07072500
H	0.00000000	0.00000000	-1.20233200

HCN

C	0.00000000	0.00000000	-0.50938900
N	0.00000000	0.00000000	0.66194900
H	0.00000000	0.00000000	-1.57731300

$HCN\text{-}BF_3$

B	0.00000000	0.00000000	-0.89451800
F	0.00000000	1.32217700	-0.97407100
F	-1.14503900	-0.66108800	-0.97407100
F	1.14503900	-0.66108800	-0.97407100
N	0.00000000	0.00000000	1.53744300
C	0.00000000	0.00000000	2.70601400
H	0.00000000	0.00000000	3.77431400

BF_3

B	0.00000000	0.00000000	0.00000000
F	0.00000000	1.31834100	0.00000000
F	1.14171700	-0.65917100	0.00000000
F	-1.14171700	-0.65917100	0.00000000

O_3

O	0.00000000	1.09353100	-0.22311500
O	0.00000000	0.00000000	0.44623000
O	0.00000000	-1.09353100	-0.22311500

P_4

P	-0.78054400	0.78054400	-0.78054400
P	0.78054400	-0.78054400	-0.78054400
P	0.78054400	0.78054400	0.78054400
P	-0.78054400	-0.78054400	0.78054400

PF_5

P	0.00000000	0.00000000	0.00000000
F	0.00000000	1.56086200	0.00000000
F	1.35174600	-0.78043100	0.00000000
F	-1.35174600	-0.78043100	0.00000000
F	0.00000000	0.00000000	1.59704700
F	0.00000000	0.00000000	-1.59704700

P_4O_{10}

P	1.01976100	-1.01976100	1.01976100
O	0.00000000	0.00000000	1.77700700
P	-1.01976100	1.01976100	1.01976100
O	0.00000000	1.77700700	0.00000000
P	1.01976100	1.01976100	-1.01976100
O	1.77700700	0.00000000	0.00000000
O	-1.77700700	0.00000000	0.00000000
P	-1.01976100	-1.01976100	-1.01976100
O	0.00000000	0.00000000	-1.77700700
O	0.00000000	-1.77700700	0.00000000
O	-1.85643800	-1.85643800	-1.85643800
O	1.85643800	-1.85643800	1.85643800
O	-1.85643800	1.85643800	1.85643800
O	1.85643800	1.85643800	-1.85643800

SF6

S	0.00000000	0.00000000	0.00000000
F	0.00000000	0.00000000	1.58989400
F	0.00000000	1.58989400	0.00000000
F	0.00000000	0.00000000	-1.58989400
F	-1.58989400	0.00000000	0.00000000
F	1.58989400	0.00000000	0.00000000
F	0.00000000	-1.58989400	0.00000000

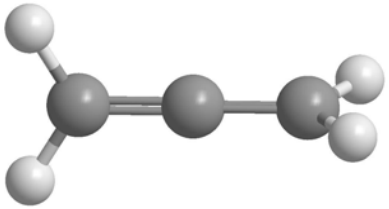
$(CH_3O)_4Si$

Si	0.00000000	0.00000000	0.00000000
O	0.00000000	1.38380600	0.88297800
O	-1.38380600	0.00000000	-0.88297800
O	0.00000000	-1.38380600	0.88297800
O	1.38380600	0.00000000	-0.88297800
C	-1.13138000	1.83776900	1.62225200
C	-1.83776900	-1.13138000	-1.62225200
C	1.13138000	-1.83776900	1.62225200
C	1.83776900	1.13138000	-1.62225200
H	-0.87459500	2.80675000	2.05289300
H	-2.00293800	1.94932700	0.97072200
H	-1.37494100	1.14202000	2.43234600
H	-2.80675000	-0.87459500	-2.05289300
H	-1.14202000	-1.37494100	-2.43234600
H	-1.94932700	-2.00293800	-0.97072200
H	0.87459500	-2.80675000	2.05289300
H	2.00293800	-1.94932700	0.97072200
H	1.37494100	-1.14202000	2.43234600
H	2.80675000	0.87459500	-2.05289300
H	1.14202000	1.37494100	-2.43234600

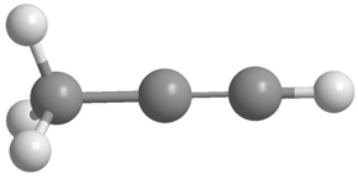
H	1.94932700	2.00293800	-0.97072200

Urotopin ($C_6N_4H_{12}$)

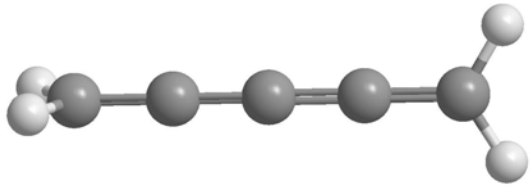
N	-0.86725400	-0.86725400	-0.86725400
C	0.00000000	0.00000000	-1.68026800
N	0.86725400	0.86725400	-0.86725400
C	0.00000000	1.68026800	0.00000000
N	-0.86725400	0.86725400	0.86725400
C	-1.68026800	0.00000000	0.00000000
C	0.00000000	-1.68026800	0.00000000
C	1.68026800	0.00000000	0.00000000
C	0.00000000	0.00000000	1.68026800
N	0.86725400	-0.86725400	0.86725400
H	0.63057000	-0.63057000	-2.31706600
H	-0.63057000	0.63057000	-2.31706600
H	0.63057000	2.31706600	0.63057000
H	-0.63057000	2.31706600	-0.63057000
H	-2.31706600	0.63057000	-0.63057000
H	-2.31706600	-0.63057000	0.63057000
H	0.63057000	-2.31706600	-0.63057000
H	-0.63057000	-2.31706600	0.63057000
H	2.31706600	-0.63057000	-0.63057000
H	2.31706600	0.63057000	0.63057000
H	-0.63057000	-0.63057000	2.31706600
H	0.63057000	0.63057000	2.31706600



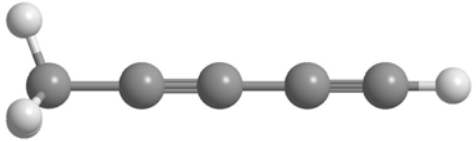
1: allene (C_3H_4)



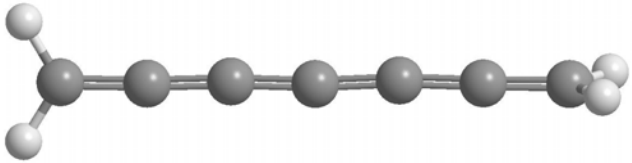
2: propyne (C_3H_4)



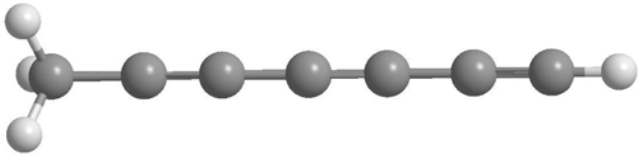
3: penta-1,2,3,4-tetraene (C_5H_4)



4: penta-1,3-diyne (C_5H_4)



5: hepta-1,2,3,4,5,6-hexaaene (C_7H_4)



6: hepta-1,3,5-triyne (C_7H_4)

Figure S1. Structures of cumulenes and poly-ynes

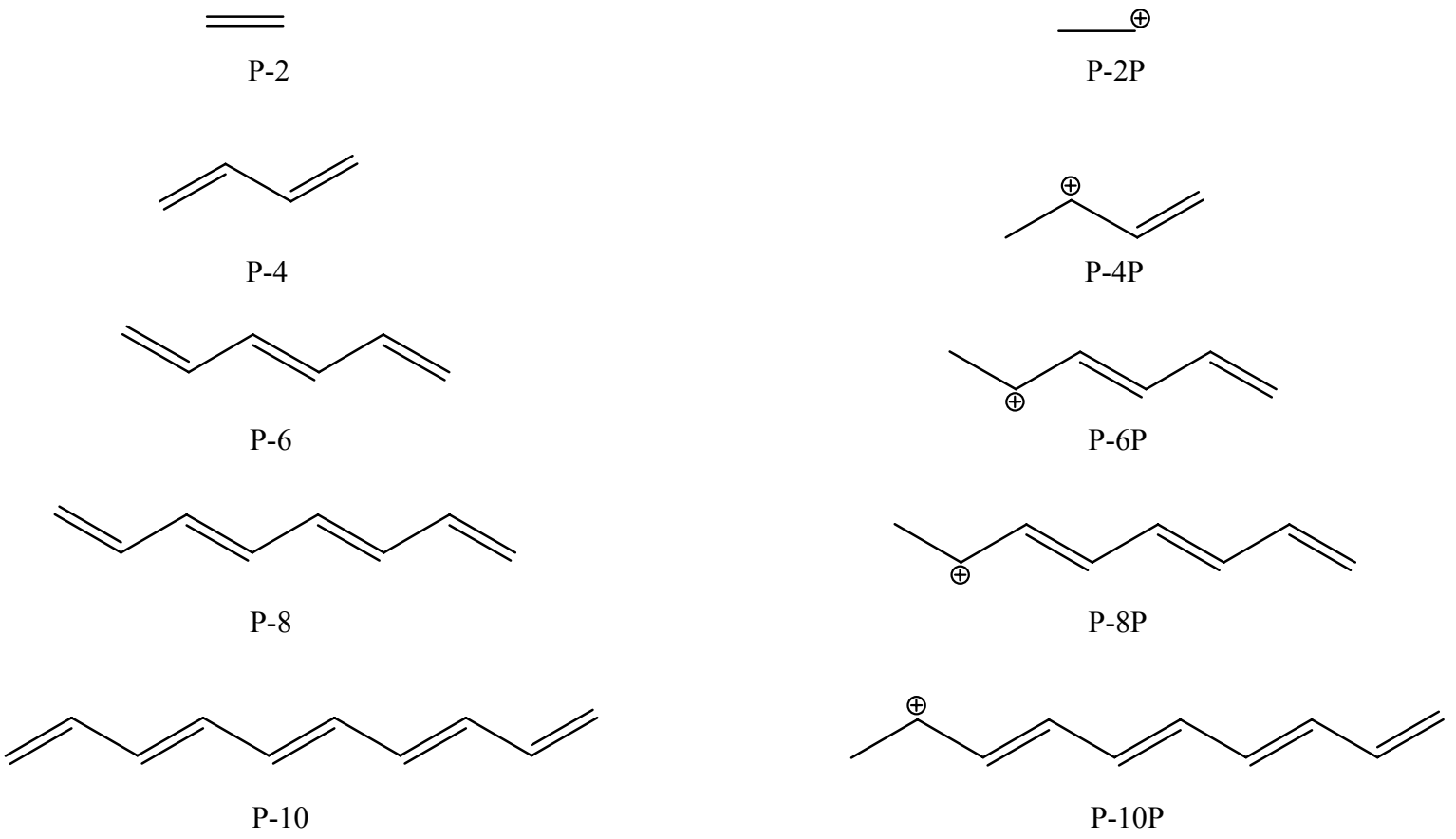


Figure S2. Structures of conjugated polyenes and protonated polyenes

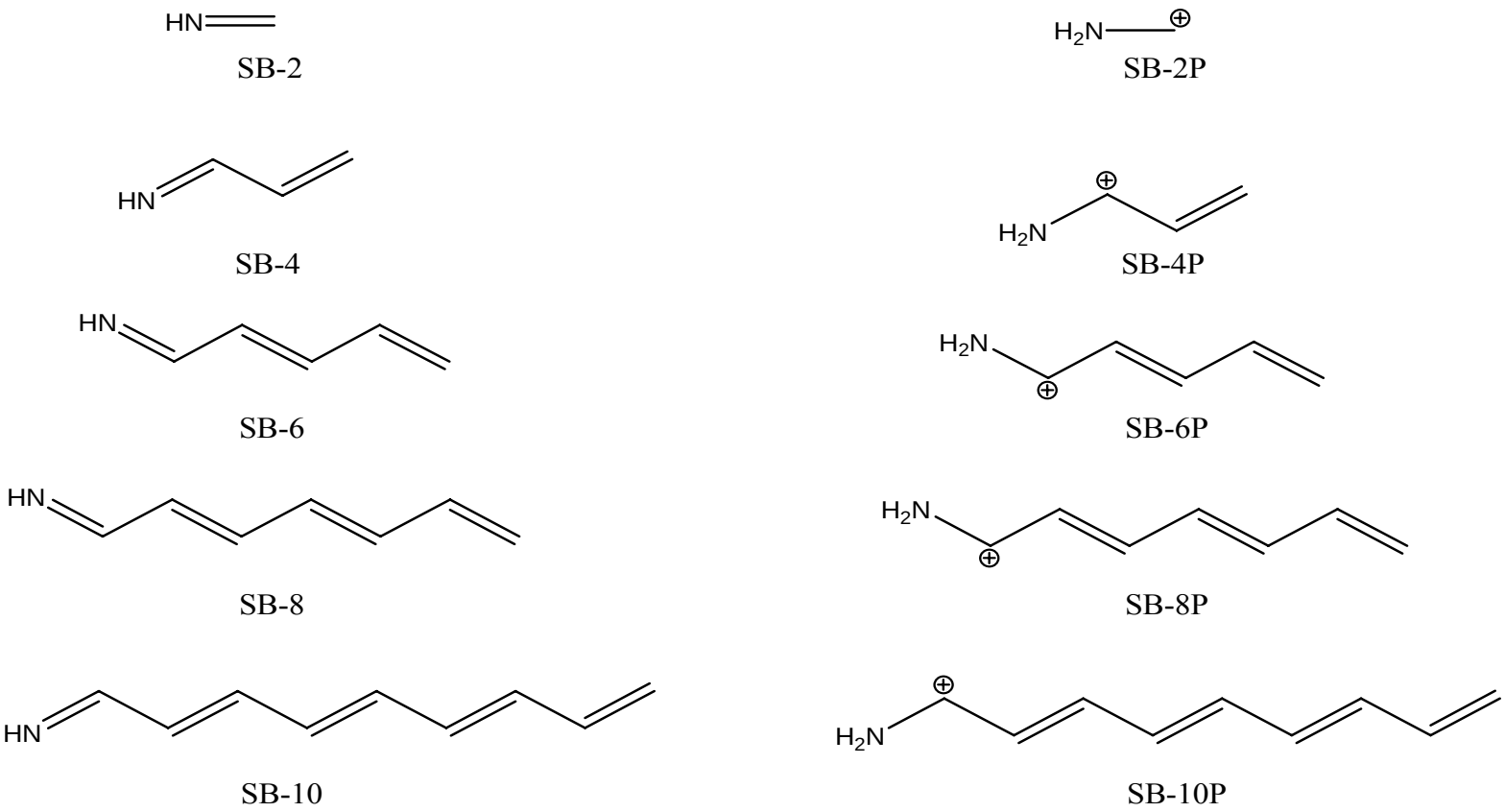
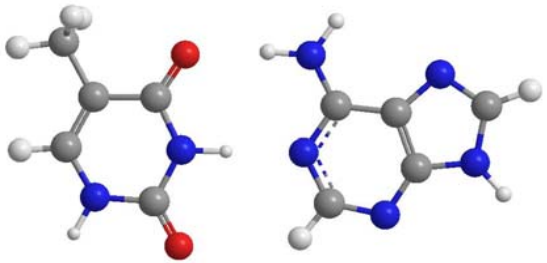
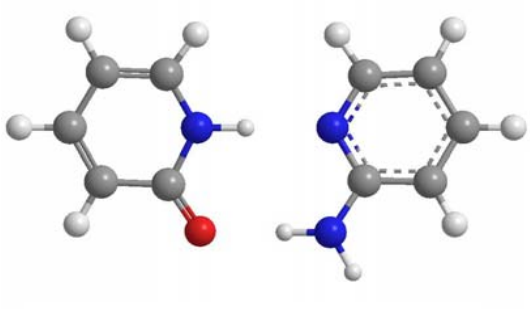


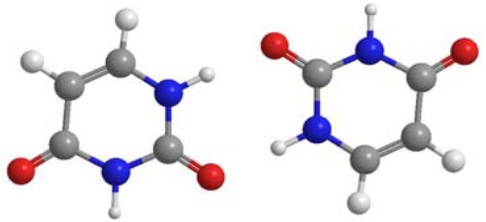
Figure S3. Structures of conjugated Schiff bases and protonated conjugated Schiff bases



A···T WC



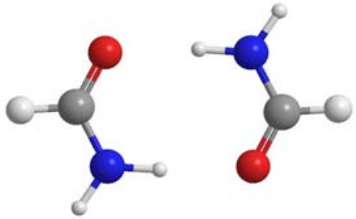
2-pyridoxine···2-aminopyridine



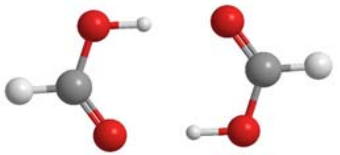
Hydrogen bonded uracil dimer

$(NH_3)_2$

$(H_2O)_2$



$(HCONH_2)_2$



$(HCOOH)_2$

Figure S4. Structures of hydrogen bonded complexes in the S22 database

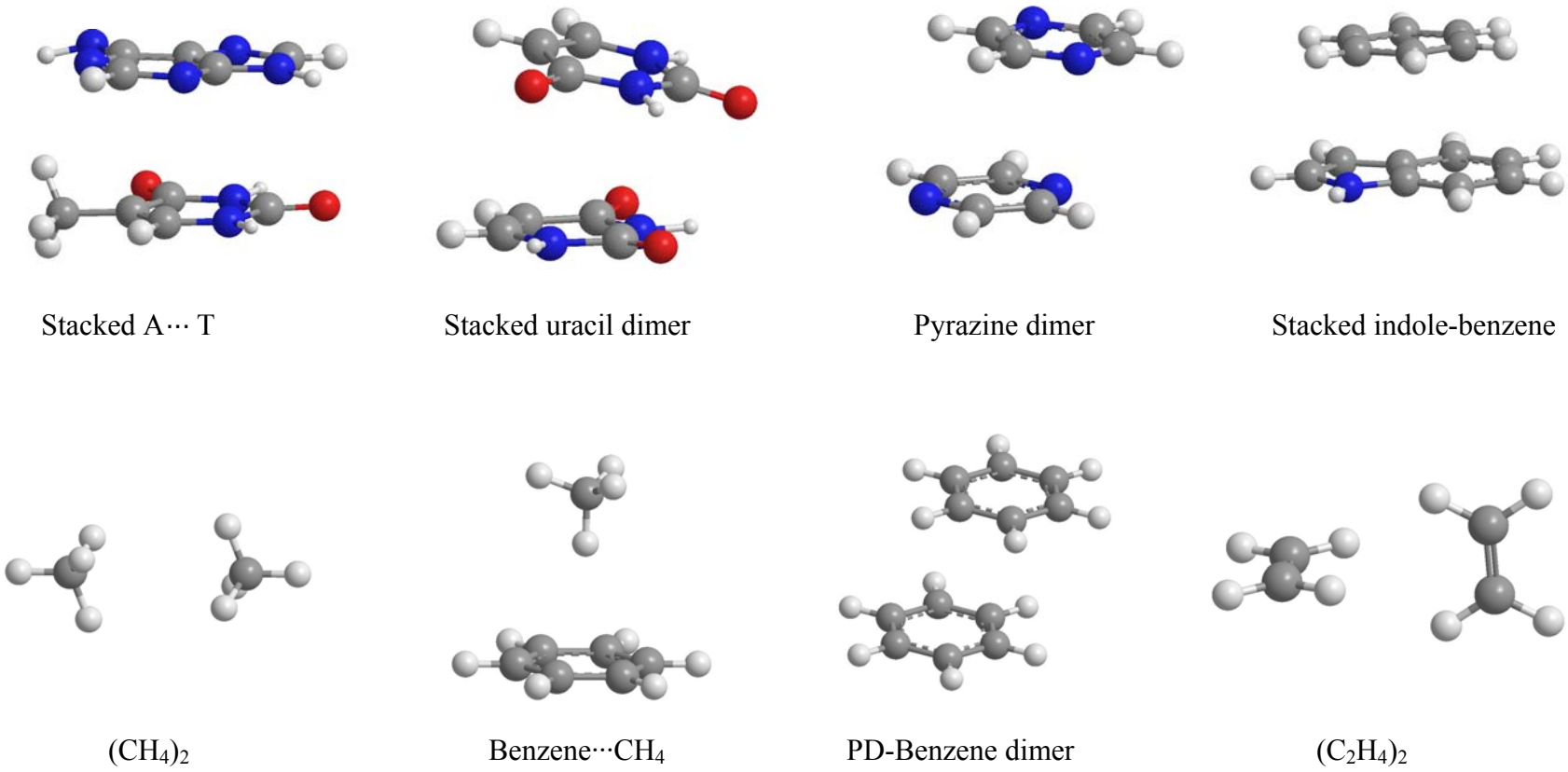
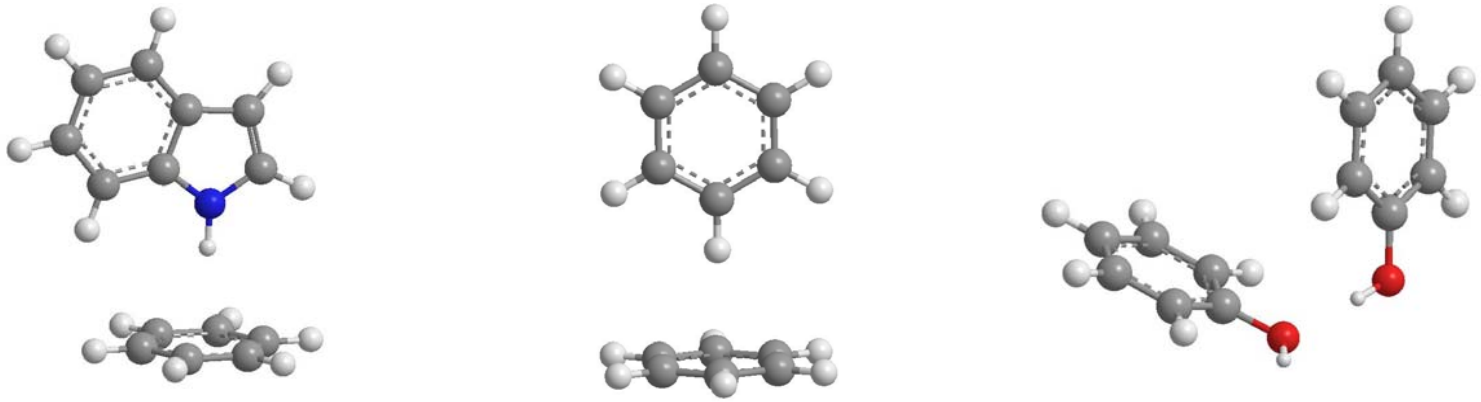


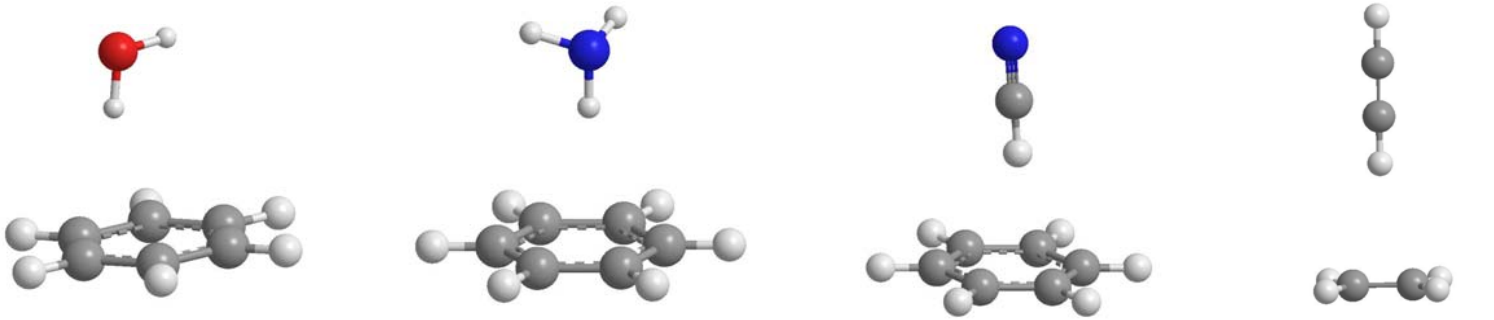
Figure S5. Structures of dispersion-dominated complexes in the S22 database



T-shaped indole···benzene

T-shaped benzene dimer

Phenol dimer



Benzene···H2O

Benzene···NH_3

Benzene···HCN

Ethene···ethyne

Figure S6. Structures of mixed complexes in the S22 database.