

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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Contents:	<i>page</i>
Table S1. MGAE109/05 database: zero-point-exclusive atomization energies	S-2
Table S2. IP13/3 and EA13/3 databases	S-4
Table S3. PA8 database	S-5
Table S4. HTBH38/04 database	S-6
Table S5. NHTBH38/04 databases	S-7
Table S6. Noncovalent interaction databases	S-9
Table S7. Interaction energies and sources of geometries in the S22 database	S-10
Table S8. TMAE9/05 and MLBE21/05 databases	S-11
Table S9. π system databases	S-12
Table S10. Spin-orbit contribution to bond energies in Table S8.	S-13
Table S11. Cartesian Coordinates for the HC7 database	S-14
Table S12. Cartesian coordinates for the DC10 database	S-20
Figure S1. Cumulenes and poly-ynes	S-24
Figure S2. Conjugated polyenes and protonated polyenes	S-25
Figure S3. Conjugated Schiff bases and protonated conjugated Schiff bases	S-26
Figure S4. Hydrogen bonded complexes in the S22 database	S-27
Figure S5. Dispersion-dominated complexes in the S22 database	S-28
Figure S6. Mixed complexes in the S22 database.	S-29

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

Molecule	D_e	Molecule	D_e	Molecule	D_e
CH (2I)	84.00	S ₂	101.67	H ₂ CCH	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 ₂ H ₆	534.66	SiF ₄	574.35
OH	107.09	CH ₃ Cl	395.51	C ₂ H ₅	603.75
OH ₂	232.60	CH ₃ SH	473.84	C ₄ H ₆ <i>d</i>	987.20
FH	141.18	HOCl	164.81	C ₄ H ₆ <i>e</i>	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 ₃ CHO	677.03
SiH ₃	227.58	AlF ₃	426.50	C ₂ H ₄ O	650.70
SiH ₄	322.40	BCl ₃	322.90	C ₂ H ₅ O	698.64
PH ₂	153.20	BF ₃	470.04	H ₃ COCH ₃	798.05
PH ₃	241.56	C ₂ Cl ₄	466.28	H ₃ CCH ₂ OH	810.36
SH ₂	182.60	C ₂ F ₄	589.36	C ₃ H ₄ <i>f</i>	703.20
ClH	106.48	C ₃ H ₄ <i>a</i>	704.79	C ₃ H ₄ <i>g</i>	682.74
HCCH	405.36	C ₄ H ₄ O	993.74	H ₃ CCOOH	803.04
H ₂ CCH ₂	563.51	C ₄ H ₄ S	962.73	H ₃ CCOCH ₃	977.96
H ₃ CCH ₃	712.80	C ₄ H ₅ N	1071.57	C ₃ H ₆	853.41
CN	180.58	C ₄ H ₆ <i>b</i>	1012.37	H ₃ CCHCH ₂	860.61
HCN	313.05	C ₄ H ₆ <i>c</i>	1004.13	C ₃ H ₈	1006.87
CO	259.27	C ₅ H ₅ N	1237.69	C ₂ H ₅ OCH ₃	1095.12
HCO	278.39	CCH	265.13	C ₄ H ₁₀ <i>h</i>	1303.04
H ₂ CO	373.82	CCl ₄	312.74	C ₄ H ₁₀ <i>i</i>	1301.32
H ₃ COH	513.22	CF ₃ CN	639.85	C ₄ H ₈ <i>j</i>	1149.01

N ₂	228.42	CF ₄	476.32	C ₄ H ₈ <i>k</i>	1158.61
H ₂ NNH ₂	438.60	CH ₂ OH	409.76	C ₅ H ₈ <i>l</i>	1284.28
NO	152.05	CH ₃ CN	615.84	C ₆ H ₆	1367.56
O ₂	120.22	CH ₃ NH ₂	582.56	CH ₃ CO	581.58
HOOH	268.57	CH ₃ NO ₂	601.27	(CH ₃) ₂ CH	900.75
F ₂	38.20	CHCl ₃	343.18	(CH ₃) ₃ C	1199.34
CO ₂	389.14	CHF ₃	457.50	H ₂ CCO	532.32
Si ₂	75.72	ClF ₃	125.33		
P ₂	117.09	H ₂	109.48		

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 ₂ O	171.8
C ₂ H ₂	156.6
SiH ₄	156.5
PH ₃	193.1
H ₂ S	173.7
HCl	137.1
H ₂	105.9

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

Reaction	best estimate	
	$V_f^\ddagger$	$V_r^\ddagger$
A + BC $\rightarrow$ AB + C		
1. H + HCl $\rightarrow$ H ₂ + Cl	5.7	8.7
2. OH + H ₂ $\rightarrow$ H + H ₂ O	5.7	21.2
3. CH ₃ + H ₂ $\rightarrow$ H + CH ₄	12.1	15.3
4. OH + CH ₄ $\rightarrow$ CH ₃ + H ₂ O	6.7	19.6
5. H + H ₂ $\rightarrow$ H ₂ + H	9.6	9.6
6. OH + NH ₃ $\rightarrow$ H ₂ O + NH ₂	3.2	12.7
7. HCl + CH ₃ $\rightarrow$ Cl + CH ₄	1.7	7.9
8. OH + C ₂ H ₆ $\rightarrow$ H ₂ O + C ₂ H ₅	3.4	19.9
9. F + H ₂ $\rightarrow$ HF + H	1.8	33.4
10. O + CH ₄ $\rightarrow$ OH + CH ₃	13.7	8.1
11. H + PH ₃ $\rightarrow$ PH ₂ + H ₂	3.1	23.2
12. H + HO $\rightarrow$ H ₂ + O	10.7	13.1
13. H + H ₂ S $\rightarrow$ H ₂ + HS	3.5	17.3
14. O + HCl $\rightarrow$ OH + Cl	9.8	10.4
15. NH ₂ + CH ₃ $\rightarrow$ CH ₄ + NH	8.0	22.4
16. NH ₂ + C ₂ H ₅ $\rightarrow$ C ₂ H ₆ + NH	7.5	18.3
17. C ₂ H ₆ + NH ₂ $\rightarrow$ NH ₃ + C ₂ H ₅	10.4	17.4
18. NH ₂ + CH ₄ $\rightarrow$ CH ₃ + NH ₃	14.5	17.8
19. <i>s-trans cis</i> -C ₅ H ₈ $\rightarrow$ <i>s-trans cis</i> -C ₅ H ₈	38.4	38.4

Table S5: NHTBH38/04 databases

Reactions	Best Estimate (kcal/mol)	
Heavy-atom transfer reactions		
$\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$	$V_{\text{f}}^{\neq}$	18.14
	$V_{\text{r}}^{\neq}$	83.22
$\text{H} + \text{FH} \rightarrow \text{HF} + \text{H}$	$V_{\text{f}}^{\neq}$	42.18
	$V_{\text{r}}^{\neq}$	42.18
$\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$	$V_{\text{f}}^{\neq}$	18.00
	$V_{\text{r}}^{\neq}$	18.00
$\text{H} + \text{FCH}_3 \rightarrow \text{HF} + \text{CH}_3$	$V_{\text{f}}^{\neq}$	30.38
	$V_{\text{r}}^{\neq}$	57.02
$\text{H} + \text{F}_2 \rightarrow \text{HF} + \text{F}$	$V_{\text{f}}^{\neq}$	2.27
	$V_{\text{r}}^{\neq}$	106.18
$\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}$	$V_{\text{f}}^{\neq}$	7.43
	$V_{\text{r}}^{\neq}$	61.01
Nucleophilic substitution reactions		
$\text{F}^- + \text{CH}_3\text{F} \rightarrow \text{FCH}_3 + \text{F}^-$	$V_{\text{f}}^{\neq}$	-0.34
	$V_{\text{r}}^{\neq}$	-0.34
$\text{F}^- \cdots \text{CH}_3\text{F} \rightarrow \text{FCH}_3 \cdots \text{F}^-$	$V_{\text{f}}^{\neq}$	13.38
	$V_{\text{r}}^{\neq}$	13.38
$\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}^-$	$V_{\text{f}}^{\neq}$	3.10
	$V_{\text{r}}^{\neq}$	3.10
$\text{Cl}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^-$	$V_{\text{f}}^{\neq}$	13.61
	$V_{\text{r}}^{\neq}$	13.61
$\text{F}^- + \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 + \text{Cl}^-$	$V_{\text{f}}^{\neq}$	-12.54
	$V_{\text{r}}^{\neq}$	20.11
$\text{F}^- \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^-$	$V_{\text{f}}^{\neq}$	2.89
	$V_{\text{r}}^{\neq}$	29.62
$\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^-$	$V_{\text{f}}^{\neq}$	-2.78
	$V_{\text{r}}^{\neq}$	17.33
$\text{OH}^- \cdots \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 \cdots \text{F}^-$	$V_{\text{f}}^{\neq}$	10.96
	$V_{\text{r}}^{\neq}$	47.20
Unimolecular and association reactions		
$\text{H} + \text{N}_2 \rightarrow \text{HN}_2$	$V_{\text{f}}^{\neq}$	14.69
	$V_{\text{r}}^{\neq}$	10.72

$\text{H} + \text{CO} \rightarrow \text{HCO}$	$V_{\text{f}}^{\neq}$	3.17
	$V_{\text{r}}^{\neq}$	22.68
$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CH}_2$	$V_{\text{f}}^{\neq}$	1.72
	$V_{\text{r}}^{\neq}$	41.75
$\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2$	$V_{\text{f}}^{\neq}$	6.85
	$V_{\text{r}}^{\neq}$	32.97
$\text{HCN} \rightarrow \text{HNC}$	$V_{\text{f}}^{\neq}$	48.16
	$V_{\text{r}}^{\neq}$	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 ₂ H ₄ ...F ₂	1.06	(H ₂ S) ₂	1.66	HeNe	0.04	(C ₂ H ₂) ₂	1.34
(HF) ₂	4.57	NH ₃ ...F ₂	1.81	(HCl) ₂	2.01	HeAr	0.06	(C ₂ H ₄) ₂	1.42
(H ₂ O) ₂	4.97	C ₂ H ₂ ...ClF	3.81	HCl...H ₂ S	3.35	Ne ₂	0.08	Sandwich (C ₆ H ₆) ₂	1.81
NH ₃ ...H ₂ O	6.41	HCN...ClF	4.86	CH ₃ Cl...HCl	3.55	NeAr	0.13	T-Shaped (C ₆ H ₆) ₂	2.74
(HCONH ₂) ₂	14.94	NH ₃ ...Cl ₂	4.88	HCN...CH ₃ SH	3.59	CH ₄ ...Ne	0.22	Parallel-Displaced (C ₆ H ₆) ₂	2.78
(HCOOH) ₂	16.15	H ₂ O...ClF	5.36	CH ₃ SH...HCl	4.16	C ₆ H ₆ ...Ne	0.47		
		NH ₃ ...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
<i>Hydrogen bonded complexes</i>		
(NH ₃) ₂ (C _{2h})	-3.17	CCSD(T)/QZ
(H ₂ O) 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
<i>Dispersion-dominated complexes</i>		
(CH ₄) ₂ (D _{3d})	-0.53	CCSD(T)/TZ
(C ₂ H 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
<i>Mixed complexes</i>		
Ethene...ethyne (C _{2v})	-1.53	CCSD(T)/QZ
Benzene...H ₂ O (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 ₂ O ⁺	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 ₂ O ⁺	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 $\Delta E_{\text{SO}} = E_{\text{SO}}(\text{A}) + E_{\text{SO}}(\text{B}) - E_{\text{SO}}(\text{AB})$, where $E_{\text{SO}}(\text{A})$ and $E_{\text{SO}}(\text{B})$ are the spin-orbit energies of atoms A and B and $E_{\text{SO}}(\text{AB})$ is the spin orbit energy of the diatomic molecules AB. In the case of CoO⁺, A is charged, i.e., A = Co⁺.

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

^d $\Delta E_{\text{SO}} \equiv nE_{\text{SO}}(\text{L}) + E_{\text{SO}}(\text{M}) - E_{\text{SO}}(\text{ML}_n)$, where n is the number of ligands, $E_{\text{SO}}(\text{L})$ is the spin-orbit energy of the ligand, $E_{\text{SO}}(\text{M})$ is the spin-orbit energy of the metal atom/ion, and $E_{\text{SO}}(\text{ML}_n)$ 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))

C6Cl6

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

C6F6

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

C6H6

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-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

P₄O₁₀

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

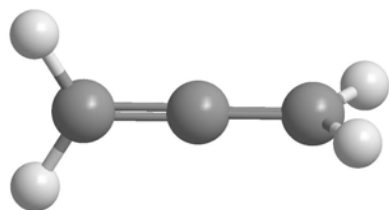
(CH₃O)₄Si

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

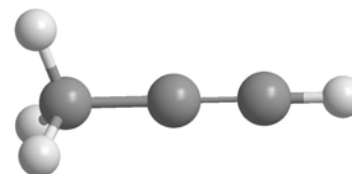
H	1.94932700	2.00293800	-0.97072200
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Urotopin (C₆N₄H₁₂)

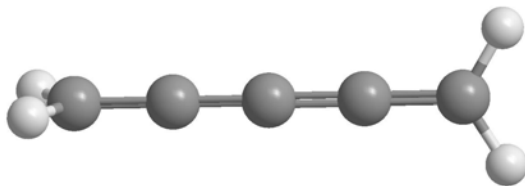
N	-0.86725400	-0.86725400	-0.86725400
C	0.00000000	0.00000000	-1.68026800
N	0.86725400	0.86725400	-0.86725400
C	0.00000000	1.68026800	0.00000000
N	-0.86725400	0.86725400	0.86725400
C	-1.68026800	0.00000000	0.00000000
C	0.00000000	-1.68026800	0.00000000
C	1.68026800	0.00000000	0.00000000
C	0.00000000	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



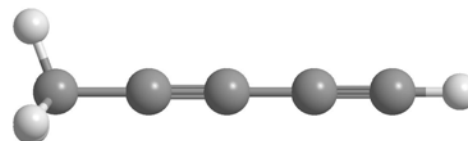
1: allene (C_3H_4)



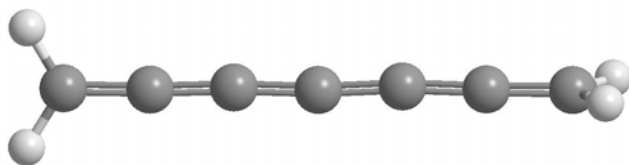
2: propyne (C_3H_4)



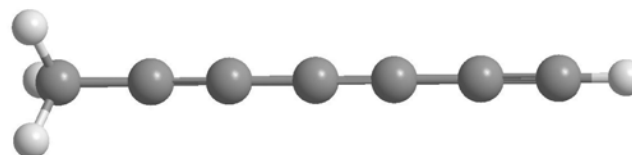
3: penta-1,2,3,4-tetraene (C_5H_4)



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



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



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

Figure S1. Structures of cumulenes and poly-ynes

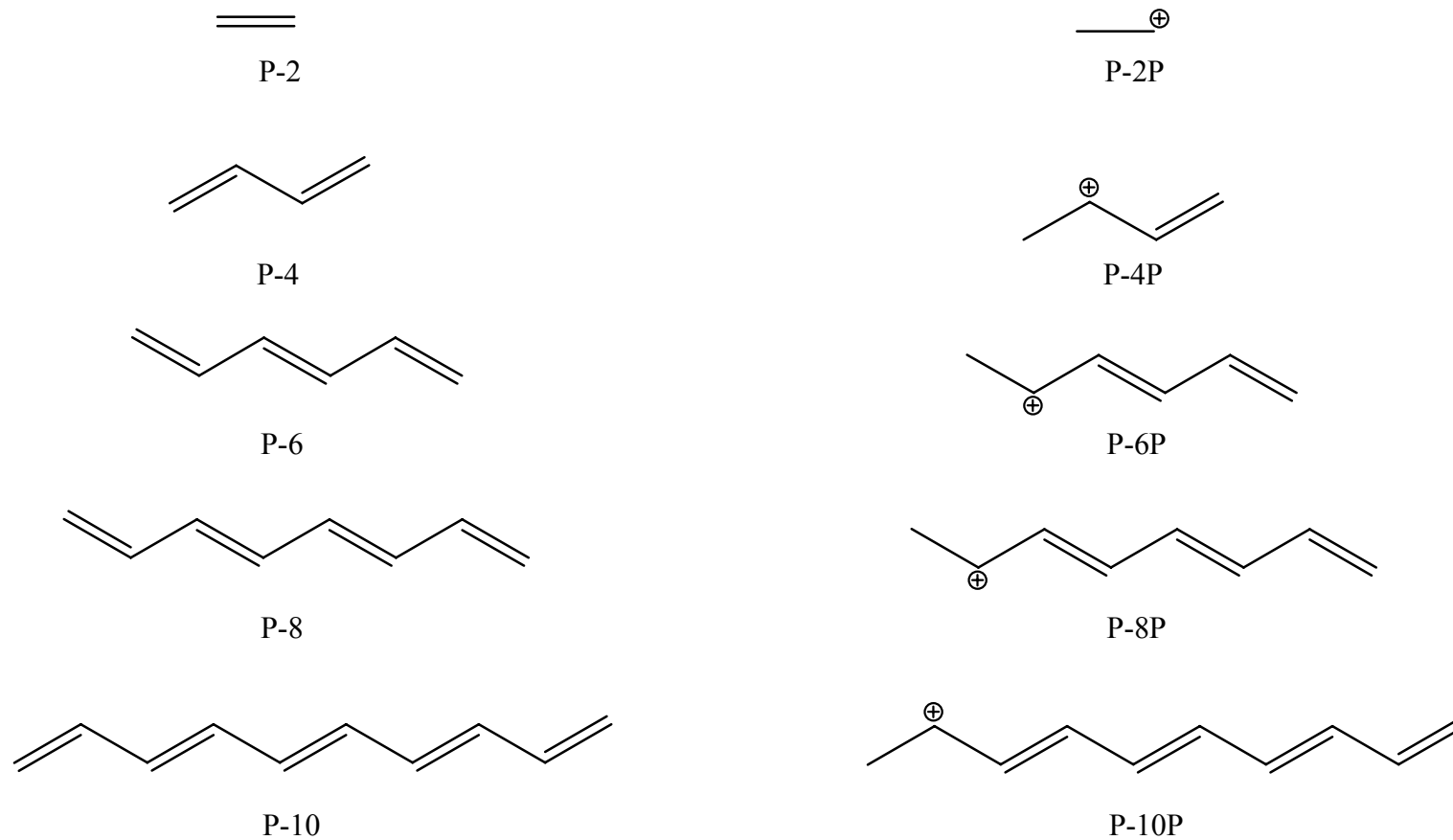


Figure S2. Structures of conjugated polyenes and protonated polyenes

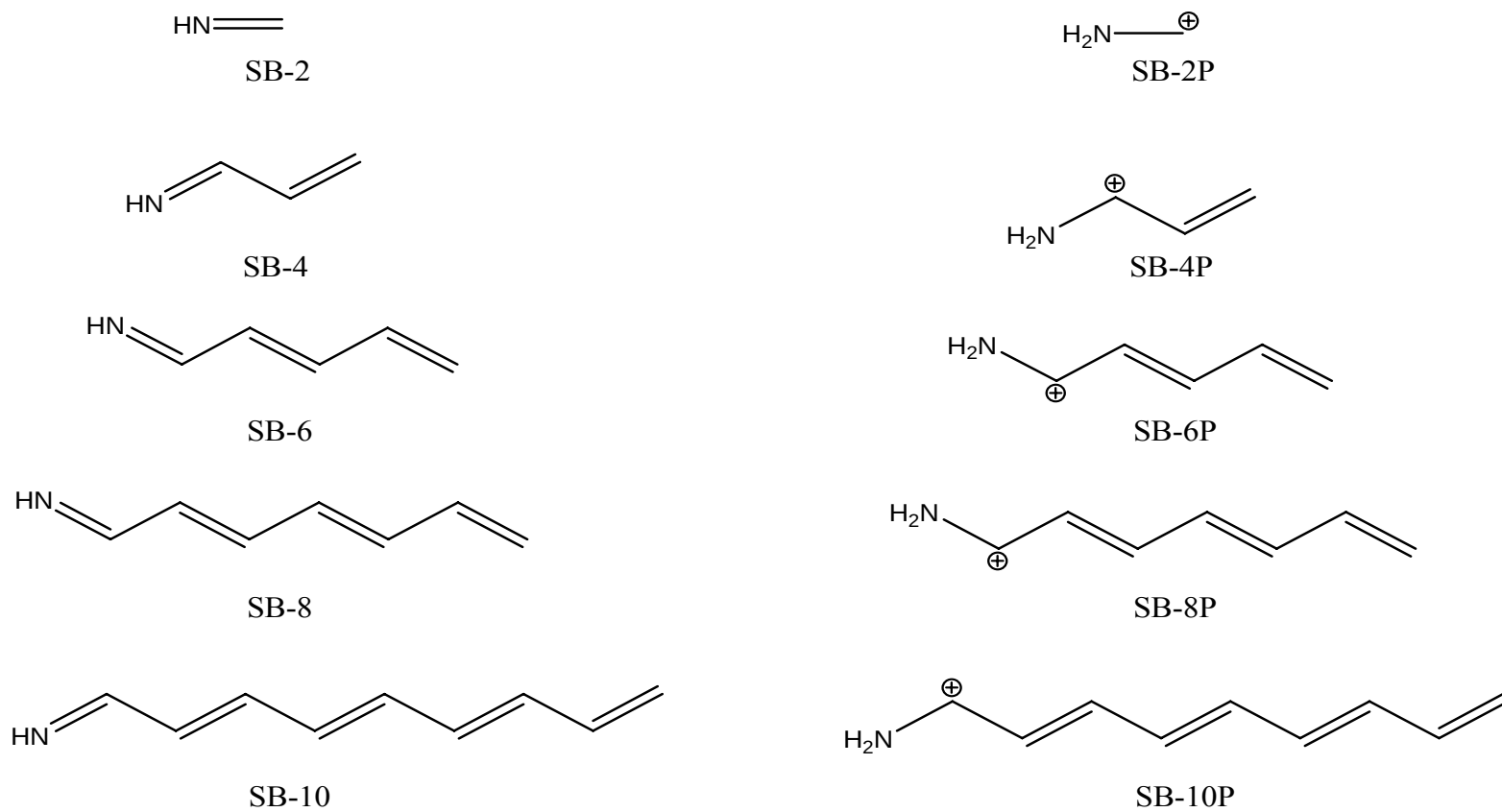


Figure S3. Structures of conjugated Schiff bases and protonated conjugated Schiff bases

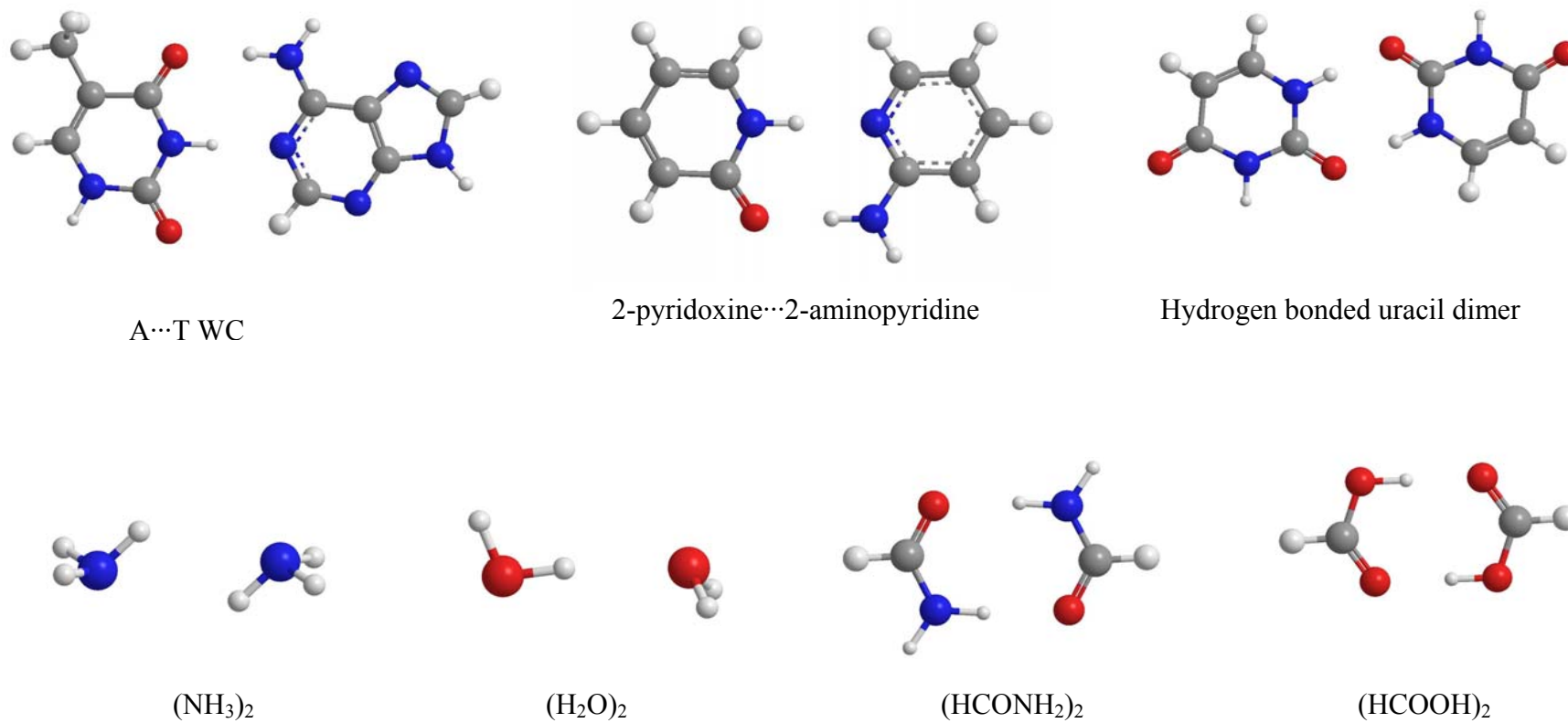


Figure S4. Structures of hydrogen bonded complexes in the S22 database

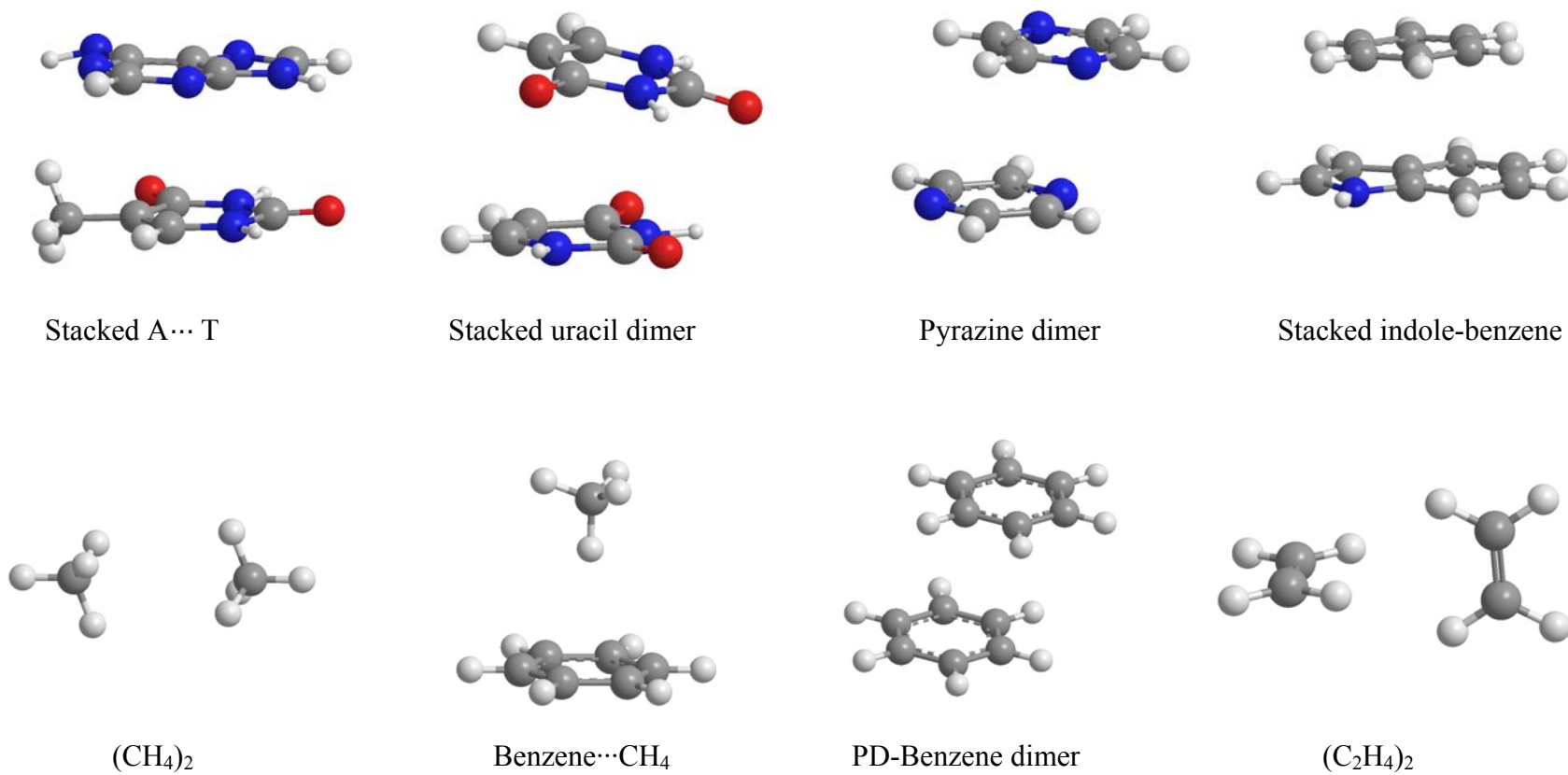
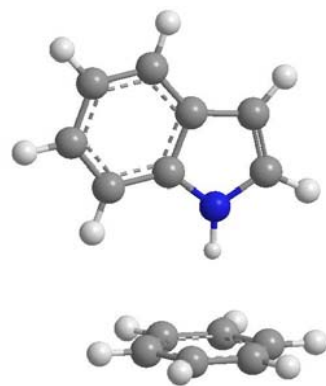
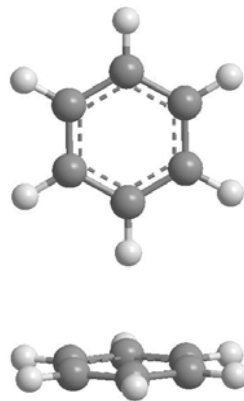


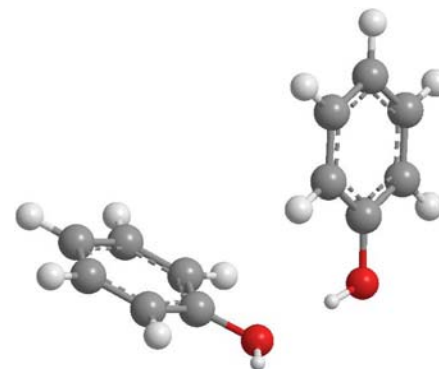
Figure S5. Structures of dispersion-dominated complexes in the S22 database



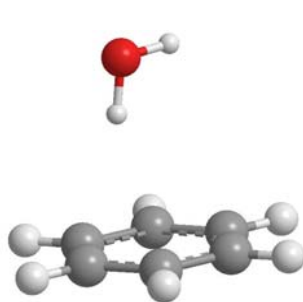
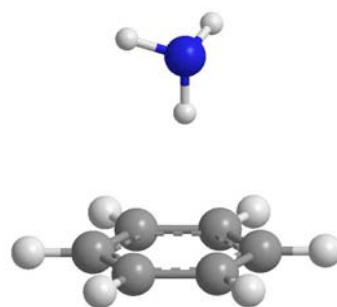
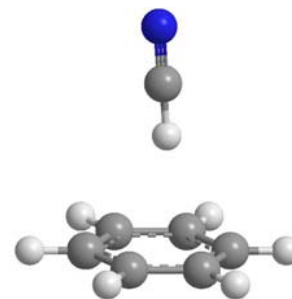
T-shaped indole...benzene



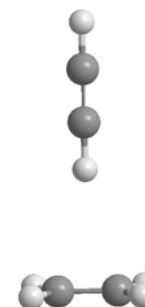
T-shaped benzene dimer



Phenol dimer

Benzene...H₂OBenzene...NH₃

Benzene...HCN



Ethene...ethyne

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