Quantum Chemical Calculations of Monomer–Dimer Equilibria of Aromatic *C*-Nitroso Compounds

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Table S1. Gas-phase energies, standard enthalpies, standard Gibbs energies (at 298.15 K), counterpoise corrections, and chloroform energies of *Z*- and (C_2) *E*-nitrosobenzene dimers (in a.u.).

	E(g)	*H*°(g)	*G*°(g)	E_{CP}(g)	*E*($CHCl_3$)
B2PLYP-D3/6-311+G(2df,2p)					
Z-	-722.770421	-722.557218	-722.610808	0.005225	-722.795316
E-	-722.772195	-722.559004	-722.612714	0.005109	-722.791895
B3LYP-D3/6-311+G(2df,2p)					
Z-	-723.350954	-723.138175	-723.191436	0.002448	-723.376265
E-	-723.354805	-723.142047	-723.195276	0.002563	-723.374630
B97D/6-311+G(2df,2p)					
Z-	-722.830312	-722.622895	-722.676913	0.002532	-722.853635
E-	-722.830304	-722.622853	-722.676819	0.002652	-722.849762
DCD-PBEP86/6-311+G(2df,2p)					
Z-	-722.015357	-721.801906	-721.856127	0.007200	-722.040254
E-	-722.016304	-721.802862	-721.856525	0.006980	-722.036272
LC-ωPBE-D3/6-311+G(2df,2p)					
Z-	-722.811774	-722.594860	-722.647593	0.003134	-722.838753
E-	-722.813935	-722.597123	-722.649824	0.003004	-722.835339
M11/6-311+G(2df,2p)					
Z-	-722.935902	-722.721656	-722.774236	0.004908	-722.963317
E-	-722.941263	-722.726946	-722.779554	0.004515	-722.962228
PBE0/6-311+G(2df,2p)					
Z-	-722.490397	-722.276170	-722.329301	0.002827	-722.515686
E-	-722.495574	-722.281342	-722.334504	0.002749	-722.515071
PBE0DH/6-311+G(2df,2p)					
Z-	-722.485028	-722.268126	-722.320966	0.004338	-722.510850
E-	-722.489883	-722.272967	-722.325815	0.004204	-722.509740
TPSSh-D3/6-311+G(2df,2p)					
Z-	-723.405553	-723.193479	-723.247703	0.002950	-723.429687
E-	-723.408116	-723.196039	-723.249843	0.002876	-723.426782
ωB97X-D/6-311+G(2df,2p)					
Z-	-723.066769	-722.851767	-722.904850	0.002742	-723.093163
E-	-723.068227	-722.853290	-722.906505	0.002705	-723.089175
MP2/6-311+G(2df,2p)					
Z-	-721.662233				
E-	-721.658889				
MP4(SDQ)/may-cc-pVnZ [a]					
Z-	-721.98348				
E-	-721.98684				
CCSD/6-311+G(2df,2p) [b]					
Z-	-721.653507				
E-	-721.657933				

CCSD(T)/6-311+G(2df,2p) [b]			
Z-	-721.816799		
E-	-721.819752		
G4(MP2)			
Z-	-722.285207	-722.075503	-722.128987
E-	-722.287023	-722.077076	-722.130348
CBS-QB3			
Z-	-722.103591	-721.893234	-721.946608
E-	-722.106909	-721.896421	-721.949834
CBS-APNO			
Z-	-723.071294	-722.860635	-722.913305
E-	-723.072912	-722.862258	-722.914914

[a] At MP4(SDQ)/6-311+G(d,p) geometry, CBS extrapolation with $n = 2$–4; [b] At B2PLYP/6-311+G(d,p) geometry

Table S2. Gas-phase energies, standard enthalpies, standard Gibbs energies (at 298.15 K) and chloroform energies of nitrosobenzene (in a.u.).

	E(g)	$H°$(g)	$G°$(g)	E($CHCl_3$)
B2PLYP-D3/6-311+G(2df,2p)	-361.375350	-361.270902	-361.308567	-361.385259
B3LYP-D3/6-311+G(2df,2p)	-361.669066	-361.564828	-361.602424	-361.679207
B97D/6-311+G(2df,2p)	-361.405278	-361.303671	-361.341571	-361.415437
DCD-PBEP86/6-311+G(2df,2p)	-360.996114	-360.891645	-360.929346	-361.005766
LC-ωPBE-D3/6-311+G(2df,2p)	-361.396457	-361.290333	-361.327913	-361.406060
M11/6-311+G(2df,2p)	-361.461491	-361.356612	-361.394183	-361.471474
PBE0/6-311+G(2df,2p)	-361.236492	-361.131618	-361.169214	-361.246516
PBE0DH/6-311+G(2df,2p)	-361.233151	-361.126968	-361.164461	-361.243077
TPSSh-D3/6-311+G(2df,2p)	-361.692256	-361.588371	-361.626107	-361.702258
ωB97X-D/6-311+G(2df,2p)	-361.525812	-361.420589	-361.458151	-361.535624
MP2/6-311+G(2df,2p)	-360.811486			
MP4(SDQ)/may-cc-pVnZ [a]	-360.647139			
CCSD/6-311+G(2df,2p) [b]	-360.827751			
CCSD(T)/6-311+G(2df,2p) [b]	-360.902681			
G4(MP2)	-361.136550	-361.033654	-361.071313	
CBS-QB3	-361.043412	-360.940134	-360.977761	
CBS-APNO	-361.525936	-361.422445	-361.460036	

[a] At MP4(SDQ)/6-311+G(d,p) geometry, CBS extrapolation with n = 2–4;
[b] At B2PLYP-D3/6-311+G(d,p) geometry

Table S3. Gas-phase energies, standard enthalpies, standard Gibbs energies (at 298.15 K), counterpoise corrections, and DCE energies of *Z*-2-nitrosopyridine dimers (in a.u.).

	E(g)	$H°$(g)	$G°$(g)	E_{CP}(g)	E(DCE)
B2PLYP-D3/6-311+G(2df,2p)	-754.855721	-754.666543	-754.719271	0.005187	-754.882274
B3LYP-D3/6-311+G(2df,2p)	-755.438053	-755.249382	-755.301973	0.002493	-755.464978
B97D/6-311+G(2df,2p)	-754.905502	-754.721729	-754.775145	0.002583	-754.930438
DCD-PBEP86/6-311+G(2df,2p)	-754.078400	-753.888817	-753.941492	0.007089	-754.105029
LC-ωPBE-D3/6-311+G(2df,2p)	-754.885738	-754.692982	-754.745011	0.003137	-754.914449
M11/6-311+G(2df,2p)	-755.034945	-754.844441	-754.897001	0.004872	-755.064701
PBE0/6-311+G(2df,2p)	-754.558334	-754.368021	-754.420389	0.002859	-754.585126
PBE0DH/6-311+G(2df,2p)	-754.546271	-754.353486	-754.405484	0.004323	-754.573729
TPSSh-D3/6-311+G(2df,2p)	-755.490836	-755.302779	-755.355634	0.003024	-755.516667
ωB97X-D/6-311+G(2df,2p)	-755.145176	-754.954204	-755.006434	0.002799	-755.173247
MP2/6-311+G(2df,2p)	-753.733783				
MP4(SDQ)/may-cc-pVnZ [a]	-754.056650				
CCSD/6-311+G(2df,2p) [b]	-753.711198				
CCSD(T)/6-311+G(2df,2p) [b]	-753.467698				
G4(MP2)	-754.351853	-754.165529	-754.219093		
CBS-QB3	-754.170756	-753.984014	-754.037474		
CBS-APNO	-755.149963	-754.962375	-755.014363		

[a] At MP4(SDQ)/6-311+G(d,p) geometry, CBS extrapolation with n = 2–4; [b] At B2PLYP/6-311+G(d,p) geometry

Table S4. Gas-phase energies, standard enthalpies, standard Gibbs energies (at 298.15 K) and DCE energies of *anti*-2-nitrosopyridine (in a.u.).

	E(g)	*H*°(g)	*G*°(g)	*E*(DCE)
B2PLYP-D3/6-311+G(2df,2p)	-377.410827	-377.318496	-377.356279	-377.424432
B3LYP-D3/6-311+G(2df,2p)	-377.705202	-377.613094	-377.650813	-377.719051
B97D/6-311+G(2df,2p)	-377.435653	-377.346017	-377.384112	-377.449433
DCD-PBEP86/6-311+G(2df,2p)	-377.020945	-376.928504	-376.966303	-377.034258
LC-ωPBE-D3/6-311+G(2df,2p)	-377.427437	-377.333432	-377.371226	-377.440610
M11/6-311+G(2df,2p)	-377.504378	-377.411429	-377.449117	-377.518022
PBE0/6-311+G(2df,2p)	-377.262690	-377.169860	-377.207547	-377.276207
PBE0DH/6-311+G(2df,2p)	-377.256414	-377.162361	-377.199946	-377.269835
TPSSh-D3/6-311+G(2df,2p)	-377.727428	-377.635655	-377.673481	-377.741004
ωB97X-D/6-311+G(2df,2p)	-377.558558	-377.465459	-377.503169	-377.571999
MP2/6-311+G(2df,2p)	-376.841119			
MP4(SDQ)/may-cc-pVnZ [a]	-377.045762			
CCSD/6-311+G(2df,2p) [b]	-376.850836			
CCSD(T)/6-311+G(2df,2p) [b]	-376.927752			
G4(MP2)	-377.163795	-377.072751	-377.110418	
CBS-QB3	-377.071061	-376.979817	-377.017531	
CBS-APNO	-377.559655	-377.467774	-377.505521	

[a] At MP4(SDQ)/6-311+G(d,p) geometry, CBS extrapolation with $n = 2–4$;
[b] At B2PLYP-D3/6-311+G(d,p) geometry

Table S5. Nitrosobenzene and 2-nitrosopyridine CP-corrected gas-phase dimerization energies (in kJ/mol) obtained with various density functionals and 6-311+G(2df,2p) basis set, and corresponding mean average deviations (MAD) from the experimental values.

	nitrosobenzene		2-nitrosopyridine	
	Z-dimer	*E*-dimer	*Z*-dimer	MAD
APFD	-60.3	-66.4	-98.7	24.9
B2PLYP	-22.1	-32.0	-62.0	14.6
B2PLYP-D3	-38.1	-43.0	-75.8	**2.9**
B3LYP	-2.2	-17.8	-45.0	31.6
B3LYP-D3	-27.2	-37.4	-66.0	9.7
B97D	-45.2	-45.1	-83.0	7.0
B97-D3	-53.6	-53.1	-92.7	13.2
DSD-PBEP86	-41.8	-44.9	-77.2	**4.0**
LC-ωHPBE	-21.8	-32.2	-56.5	16.4
LC-ωPBE-D3	-41.3	-47.3	-72.8	**2.2**
M06-2X	-13.7	-27.8	-47.3	23.6
M11	-21.0	-36.1	-56.0	15.6
MN15	-22.0	-34.6	-57.9	15.1
PBE0	-38.3	-52.1	-79.0	**3.2**
PBE0-D3	-55.3	-64.4	-93.3	17.7
PBE0-D3(BJ)	-58.3	-65.6	-96.3	20.1
PBE0DH	-37.8	-50.9	-76.5	**1.8**
TPSSh	-21.7	-37.0	-64.3	12.3
TPSSh-D3(BJ)	-47.5	-54.4	-86.5	9.5
ωB97X-D	-32.6	-36.5	-66.3	8.1
Experiment	-37.2 [a]	-48.8 [a]	-73.8 [b]	

[a] Calculated from the experimental $\Delta_r G^*(CHCl_3)$ values (from ref. 3). [b] Calculated from the experimental $\Delta_r G^*$(DCE) value (this paper).