Hindered rotational barriers in conjugated donor – acceptor substituted systems: calculations *vs*. experiments

Mark Sigalov,[a] Vladimir Lokshin,[b] Nina Larina,[b†] and Vladimir Khodorkovsky*

[a] *Dept. of Chemistry, Ben-Gurion Univ. of the Negev, Beer-Sheva, 84105, Israel.*
[b] *Aix Marseille Université, CNRS, CINaM UMR 7325, 13288, Marseille, France. E-mail: khodor@cinam.univ-mrs.fr*

Table 1. Calculated for derivative **1** energies in chloroform: a) electronic energies, b) ZPE corrected energies, c) free energies at 166 K.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311++G(2df,2p)				
a	-385.02723	-385.01245	-385.02712	-385.01244
b	-384.89051	-384.87652	-384.89041	-384.87655
c	-384.90652	-384.89233	-384.9053	-384.89132
APFD/6-311++G(2df,2p)				
a	-384.69686	-384.6821	-384.69675	-384.68208
b	-384.55963	-384.54561	-384.55954	-384.54568
c	-384.57565	-384.56115	-384.57443	-384.56045
B2PLYPD/6-311++G(2df,2p)				
a	-384.21075	-384.19632	-384.21062	-384.19631
b	-384.56242	-384.54876	-384.56239	-384.54882
c	-384.57799	-384.56419	-384.57729	-384.56359
M062X/6-311++G(2df,2p)				
a	-384.85319	-384.83951	-384.85307	-384.8395
b	-384.71515	-384.70212	-384.71504	-384.70222
c	-384.73145	-384.71746	-384.72992	-384.71698

Table 2. Calculated for derivative **1** barriers to rotation: TS_A and TS_D (one-state approximation), B_A and B_D (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_A	B'_D	δ_D	$1-\delta_D$	B_D
B3LYP/6-311++G(2df,2p)											
a	9.27	0.07	9.28	9.21	0.01	0.99	9.21	0.07	0.99	0.01	0.07
b	8.78	0.06	8.76	8.70	0.01	0.99	8.70	0.06	0.99	0.01	0.06
c	8.90	0.77	9.54	8.77	0.08	0.92	8.78	0.75	0.92	0.08	0.76
APFD/6-311++G(2df,2p)											
a	9.26	0.07	9.27	9.21	0.01	0.99	9.21	0.07	0.99	0.01	0.07
b	8.80	0.06	8.75	8.70	0.01	0.99	8.70	0.06	0.99	0.07	0.06
c	9.10	0.77	9.54	8.77	0.08	0.92	8.80	0.74	0.92	0.08	0.76
B2PLYPD/6-311++G(2df,2p)											
a	9.05	0.08	9.06	8.98	0.01	0.99	8.98	0.08	0.99	0.01	0.08
b	8.57	0.02	8.53	8.52	0.00	1,00	8.52	0.02	1,00	0.00	0.02
c	8.66	0.44	9.04	8.60	0.05	0.95	8.60	0.44	0.95	0.05	0.44
M062X/6-311++G(2df,2p)											
a	8.58	0.08	8.59	8.52	0.01	0.99	8.52	0.07	0.99	0.01	0.08
b	8.18	0.07	8.11	8.04	0.01	0.99	8.05	0.07	0.99	0.01	0.07
c	8.78	0.96	9.08	8.12	0.11	0.89	8.19	0.89	0.90	0.10	0.95

[†] Present address: *Thales DIS France SA, Avenue du Pic de Bertagne, 13420 Gèmenos, France*

Table 3. Calculated for derivative **2** energies in toluene: a) electronic energies, b) ZPE corrected energies, c) free energies at 198 K.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-460.24494	-460.22832	-460.23804	-460.22316
b	-460.10324	-460.08749	-460.0971	-460.08302
c	-460.12355	-460.10762	-460.11716	-460.10286
B3LYP/aug-cc-pvDZ				
a	-460.1615	-460.14469	-460.15404	-460.13898
b	-460.01977	-460.00405	-460.01332	-459.99925
c	-460.04003	-460.02414	-460.03338	-460.0191
B3LYP/6-311++G(2df,2p)				
a	-460.26225	-460.24557	-460.25506	-460.2401
b	-460.12017	-460.1044	-460.11377	-460.09964
c	-460.14046	-460.12452	-460.13382	-460.11948
APFD/6-311++G(2df,2p)				
a	-459.87508	-459.85835	-459.8675	-459.85251
b	-459.73249	-459.71669	-459.72616	-459.71205
c	-459.75275	-459.73679	-459.74622	-459.7319
B2PLYPD/6-311++G(2df,2p)				
a	-459.32627	-459.3101	-459.32027	-459.30556
b	-459.74773	-459.73232	-459.74133	-459.72737
c	-459.768	-459.75241	-459.76135	-459.74718
M062X/6-311++G(2df,2p)				
a	-460.06526	-460.05009	-460.05852	-460.04453
b	-459.92152	-459.90703	-459.91557	-459.90234
c	-459.94178	-459.92707	-459.93556	-459.92214
MP2/6-311++G(2df,2p)				
a	-459.18165	-459.16737	-459.17541	-459.16214
b	-459.03825	-459.0248	-459.03283	-459.02031
c	-459.05856	-459.04491	-459.05288	-459.04013

Table 4. Calculated for derivative **2** barriers to rotation: TS_A and TS_D (one-state approximation), B_A and B_D (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_A	B'_D	δ_D	$1-\delta_D$	B_D
B3LYP/6-311+G(2d,p)											
a	10.43	4.33	13.67	9.34	0.32	0.68	9.68	3.98	0.71	0.29	4.23
b	9.88	3.85	12.69	8.84	0.30	0.70	9.15	3.53	0.72	0.28	3.76
c	10.00	4.01	12.98	8.97	0.31	0.69	9.29	3.69	0.72	0.28	3.92
B3LYP/aug-cc-pvDZ											
a	10.55	4.68	14.13	9.45	0.33	0.67	9.81	4.32	0.69	0.31	4.57
b	9.86	4.05	12.88	8.83	0.31	0.69	9.15	3.72	0.71	0.29	3.95
c	9.97	4.17	13.13	8.96	0.32	0.68	9.28	3.85	0.71	0.29	4.08
B3LYP/6-311++G(2df,2p)											
a	10.47	4.51	13.90	9.39	0.33	0.67	9.74	4.16	0.70	0.30	4.41
b	9.90	4.02	12.88	8.87	0.31	0.69	9.19	3.70	0.71	0.29	3.92
c	10.00	4.17	13.17	9.00	0.32	0.68	9.32	3.85	0.71	0.29	4.07
APFD/6-311++G(2df,2p)											
a	10.50	4.76	14.16	9.41	0.34	0.66	9.77	4.39	0.69	0.31	4.64
b	9.91	3.97	12.83	8.85	0.31	0.69	9.18	3.64	0.72	0.28	3.88
c	10.02	4.10	13.08	8.99	0.31	0.69	9.31	3.78	0.71	0.29	4.00
B2PLYPD/6-311++G(2df,2p)											
a	10.15	3.77	13.00	9.23	0.29	0.71	9.50	3.50	0.73	0.27	3.69
b	9.67	4.02	12.78	8.76	0.31	0.69	9.05	3.73	0.71	0.29	3.93
c	9.78	4.17	13.06	8.89	0.32	0.68	9.18	3.89	0.70	0.30	4.09
M062X/6-311++G(2df,2p)											
a	9.52	4.23	13.01	8.78	0.33	0.67	9.02	3.99	0.69	0.31	4.16
b	9.09	3.73	12.04	8.30	0.31	0.69	8.55	3.49	0.71	0.29	3.66
c	9.23	3.90	12.32	8.42	0.32	0.68	8.68	3.65	0.70	0.30	3.83
MP2/6-311++G(2df,2p)											
a	8.96	3.92	12.24	8.33	0.32	0.68	8.53	3.71	0.70	0.30	3.85
b	8.44	3.40	11.26	7.86	0.30	0.70	8.03	3.22	0.71	0.29	3.35
c	8.57	3.56	11.57	8.00	0.31	0.69	8.17	3.39	0.71	0.29	3.51

Table 5. Calculated for derivative **3** energies in toluene: a) electronic energies, b) ZPE corrected energies, c) free energies at 181 K.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-519.02671	-519.01361	-519.01509	-519.00622
b	-518.81719	-518.80474	-518.80622	-518.79797
c	-518.83782	-518.82449	-518.82578	-518.817
B3LYP/aug-cc-pvDZ				
a	-518.9319	-518.91843	-518.91935	-518.91025
b	-518.72226	-518.70989	-518.71084	-518.70254
c	-518.74265	-518.7297	-518.73033	-518.72157
B3LYP/6-311++G(2df,2p)				
a	-519.04713	-519.03395	-519.0344	-519.02559
b	-518.83707	-518.82468	-518.82511	-518.81691
c	-518.85765	-518.84453	-518.84465	-518.83593
APFD/6-311++G(2df,2p)				
a	-518.60864	-518.59517	-518.5958	-518.58676
b	-518.39742	-518.38498	-518.38534	-518.37725
c	-518.41776	-518.40475	-518.40479	-518.39625
B2PLYPD/6-311++G(2df,2p)				
a	-517.93248	-517.91949	-517.92242	-517.91316
b	-518.39239	-518.37992	-518.38167	-518.37308
c	-518.41261	-518.39957	-518.40112	-518.39204
M062X/6-311++G(2df,2p)				
a	-518.81395	-518.80102	-518.80244	-518.79316
b	-518.60147	-518.58938	-518.58614	-518.58219
c	-518.62176	-518.60909	-518.61005	-518.60112

Table 6. Calculated for derivative **3** barriers to rotation: TS_A (one-state approximation) and B_A (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_A	B'_D	δ_D	$1-\delta_D$	B_D
B3LYP/6-311+G(2d,p)											
a	8.22	7.29	12.86	5.57	0.57	0.43	7.07	5.79	0.55	0.45	6.61
b	7.81	6.88	12.06	5.18	0.57	0.43	6.68	5.38	0.55	0.45	6.21
c	8.36	7.56	13.06	5.51	0.58	0.42	7.16	5.90	0.55	0.45	6.81
B3LYP/aug-cc-pvDZ											
a	8.45	7.88	13.59	5.71	0.58	0.42	7.30	6.29	0.54	0.46	7.14
b	7.76	7.17	12.37	5.20	0.58	0.42	6.69	5.69	0.54	0.46	6.49
c	8.13	7.73	13.23	5.50	0.58	0.42	7.03	6.19	0.53	0.47	7.01
B3LYP/6-311++G(2df,2p)											
a	8.27	7.99	13.52	5.53	0.59	0.41	7.15	6.37	0.53	0.47	7.22
b	7.77	7.51	12.65	5.15	0.59	0.41	6.71	5.95	0.53	0.47	6.77
c	8.23	8.16	13.63	5.47	0.60	0.40	7.12	6.51	0.52	0.48	7.37
APFD/6-311++G(2df,2p)											
a	8.45	8.06	13.73	5.67	0.59	0.41	7.30	6.43	0.53	0.47	7.29
b	7.81	7.58	12.66	5.08	0.60	0.40	6.71	5.95	0.53	0.47	6.81
c	8.16	8.14	13.50	5.36	0.60	0.40	7.05	6.45	0.52	0.48	7.33
B2PLYPD/6-311++G(2df,2p)											
a	8.15	6.31	12.12	5.81	0.52	0.48	7.03	5.09	0.58	0.42	5.80
b	7.83	6.73	12.12	5.39	0.56	0.44	6.74	5.38	0.56	0.44	6.13
c	8.18	7.21	12.91	5.70	0.56	0.44	7.09	5.82	0.55	0.45	6.58
M062X/6-311++G(2df,2p)											
a	8.11	7.22	13.05	5.82	0.55	0.45	7.09	5.95	0.54	0.46	6.64

b	7.59	9.62	12.10	2.48	0.80	0.20	6.54	5.56	0.54	0.46	7.75
c	7.95	7.35	12.95	5.60	0.57	0.43	6.94	6.02	0.54	0.46	6.73

Table 7. Calculated for derivative **3** barriers to rotation: TS_A and TS_D (one-state approximation), B_A and B_D (three-state approximation). The Me group of the CH_3-C(O)- substituent is in its rotational transition state at TS_A, TS_D and TSD_A.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311++G(2df,2p)				
a	-519.04713	-519.03191	-519.03247	-519.02365
b	-518.83707	-518.82288	-518.82338	-518.81529
c	-518.85765	-518.84246	-518.84292	-518.83409
APFD/6-311++G(2df,2p)				
a	-518.60864	-518.59295	-518.59357	-518.58468
b	-518.39742	-518.38253	-518.38333	-518.37531
c	-518.41776	-518.40211	-518.40274	-518.39409
M062X/6-311++G(2df,2p)				
a	-518.81395	-518.79855	-518.79962	-518.7908
b	-518.60147	-518.58724	-518.58811	-518.58017
c	-518.62176	-518.60677	-518.60744	-518.59892

Table 8. Calculated for derivative **3** barriers to rotation: TS_A (one-state approximation) and B_A (three-state approximation). The Me group of the CH_3-C(O)- substituent is in its rotational transition state at TS_A, TS_D and TSD_A.

	TS_A=B'$_A$	TS_D=B"$_D$	TS_{DA}	B"$_A$	δ_A	1-δ_A	B_A	B'$_D$	δ_D	1-δ_D	B_D
B3LYP/6-311++G(2df,2p)											
a	9.55	9.20	14.73	5.53	0.62	0.38	8.04	6.69	0.55	0.45	8.06
b	8.90	8.59	13.67	5.08	0.63	0.37	7.48	6.18	0.55	0.45	7.50
c	9.53	9.24	14.78	5.54	0.63	0.37	8.04	6.75	0.54	0.46	8.10
APFD/6-311++G(2df,2p)											
a	9.85	9.46	15.04	5.58	0.63	0.37	8.26	6.77	0.55	0.45	8.25
b	9.34	8.84	13.87	5.03	0.64	0.36	7.78	6.09	0.56	0.44	7.63
c	9.82	9.43	14.85	5.43	0.63	0.37	8.22	6.64	0.55	0.45	8.18
M062X/6-311++G(2df,2p)											
a	9.66	8.99	14.53	5.53	0.62	0.38	8.09	6.44	0.56	0.44	7.86
b	8.93	8.38	13.37	4.98	0.63	0.37	7.46	5.91	0.56	0.44	7.29
c	9.41	8.99	14.33	5.35	0.63	0.37	7.89	6.44	0.55	0.45	7.84

Table 9. Calculated for derivative **3** energies in toluene: a) electronic energies, b) ZPE corrected energies, c) free energies at 133 K.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-519.02671	-519.01361	-519.01509	-519.00622
b	-518.81719	-518.80474	-518.80622	-518.79797
c	-518.83109	-518.8181	-518.8195	-518.81094
B3LYP/aug-cc-pvDZ				
a	-518.9319	-518.91843	-518.91935	-518.91025
b	-518.72226	-518.70989	-518.71084	-518.70254
c	-518.73601	-518.7233	-518.72407	-518.7155
B3LYP/6-311++G(2df,2p)				
a	-519.04713	-519.03395	-519.0344	-519.02559
b	-518.83707	-518.82468	-518.82511	-518.81691
c	-518.85094	-518.8381	-518.83838	-518.82987
APFD/6-311++G(2df,2p)				
a	-518.60864	-518.59517	-518.5958	-518.58676
b	-518.39742	-518.38498	-518.38534	-518.37725
c	-518.41114	-518.39836	-518.39856	-518.3902
B2PLYPD/6-311++G(2df,2p)				
a	-517.93248	-517.91949	-517.92242	-517.91316
b	-518.39239	-518.37992	-518.38167	-518.37308
c	-518.40603	-518.39323	-518.39489	-518.38601
M062X/6-311++G(2df,2p)				
a	-518.81395	-518.80102	-518.80244	-518.79316
b	-518.60147	-518.58938	-518.58614	-518.58219
c	-518.61516	-518.60273	-518.60386	-518.5951

Table 10. Calculated for derivative **3** barriers to rotation: TS_D (one-state approximation) and B_D (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_D	B'_D	δ_D	$1-\delta_D$	B_A
B3LYP/6-311+G(2d,p)											
a	8.22	7.29	12.86	5.57	0.57	0.43	7.07	5.79	0.55	0.45	6.61
b	7.81	6.88	12.06	5.18	0.57	0.43	6.68	5.38	0.55	0.45	6.21
c	8.15	7.27	12.64	5.37	0.58	0.42	6.97	5.67	0.55	0.45	6.56
B3LYP/aug-cc-pvDZ											
a	8.45	7.88	13.59	5.71	0.58	0.42	7.30	6.29	0.54	0.46	7.14
b	7.76	7.17	12.37	5.21	0.58	0.42	6.69	5.69	0.54	0.46	6.49
c	7.98	7.49	12.87	5.38	0.58	0.42	6.89	5.98	0.54	0.46	6.79
B3LYP/6-311++G(2df,2p)											
a	8.27	7.99	13.52	5.53	0.59	0.41	7.15	6.37	0.53	0.47	7.22
b	7.77	7.51	12.65	5.15	0.59	0.41	6.71	5.95	0.53	0.47	6.77
c	8.06	7.88	13.22	5.34	0.60	0.40	6.96	6.26	0.53	0.47	7.11
APFD/6-311++G(2df,2p)											
a	8.45	8.06	13.73	5.67	0.59	0.41	7.30	6.43	0.53	0.47	7.29
b	7.81	7.58	12.66	5.08	0.60	0.41	6.71	5.95	0.53	0.47	6.81
c	8.02	7.89	13.14	5.25	0.60	0.40	6.91	6.23	0.53	0.47	7.10
B2PLYPD/6-311++G(2df,2p)											
a	8.15	6.31	12.12	5.81	0.52	0.48	7.03	5.09	0.58	0.42	5.80
b	7.83	6.73	12.12	5.39	0.56	0.44	6.74	5.38	0.56	0.44	6.13
c	8.03	6.99	12.56	5.57	0.56	0.44	6.94	5.62	0.55	0.45	6.38
M062X/6-311++G(2df,2p)											
a	8.11	7.22	13.05	5.82	0.55	0.45	7.09	5.95	0.54	0.46	6.64
b	7.59	9.62	12.10	2.48	0.80	0.20	6.54	5.56	0.54	0.46	7.75

c	7.80	7.09	12.59	5.50	0.56	0.44	6.79	5.79	0.54	0.46	6.49

Table 11. Calculated for derivative **4** energies in methylene chloride: a) electronic energies, b) ZPE corrected energies, c) free energies at 208 K.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-479.6987	-479.67885	-479.68465	-479.67046
b	-479.51681	-479.49788	-479.50353	-479.49007
c	-479.54000	-479.52061	-479.52554	-479.51183
B3LYP/aug-cc-pvDZ				
a	-479.61224	-479.59209	-479.59727	-479.58288
b	-479.43005	-479.4113	-479.41641	-479.40293
c	-479.45298	-479.43412	-479.43842	-479.42471
B3LYP/6-311++G(2df,2p)				
a	-479.71763	-479.69762	-479.70242	-479.68825
b	-479.53521	-479.51632	-479.52092	-479.50752
c	-479.55824	-479.53919	-479.54295	-479.52929
APFD/6-311++G(2df,2p)				
a	-479.3114	-479.29143	-479.29612	-479.28197
b	-479.12811	-479.10931	-479.11378	-479.10033
c	-479.15102	-479.13212	-479.13579	-479.12207
B2PLYPD/6-311++G(2df,2p)				
a	-478.69682	-478.67816	-478.68482	-478.67097
b	-479.12853	-479.11025	-479.11569	-479.10245
c	-479.15162	-479.13284	-479.13766	-479.12414
M062X/6-311++G(2df,2p)				
a	-479.50345	-479.4856	-479.48996	-479.47682
b	-479.31895	-479.30217	-479.30641	-479.29395
c	-479.34177	-479.3249	-479.32836	-479.31562
MP2/6-311++G(2df,2p)				
a	-478.54232	-478.52663	-478.53225	-478.51971
b	-478.35816	-478.34325	-478.34883	-478.33699
c	-478.38107	-478.36581	-478.37083	-478.35869

Table 12. Calculated for derivative **4** barriers to rotation: TS_A (one-state approximation) and B_A (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_A	B'_D	δ_D	$1-\delta_D$	B_D
B3LYP/6-311+G(2d,p)											
a	12.46	8.82	17.72	8.90	0.50	0.50	10.67	7.05	0.60	0.40	8.11
b	11.88	8.33	16.78	8.45	0.50	0.50	10.15	6.63	0.60	0.40	7.66
c	12.17	9.07	17.68	8.60	0.51	0.49	10.43	7.24	0.59	0.41	8.32
B3LYP/aug-cc-pvDZ											
a	12.64	9.39	18.42	9.03	0.51	0.49	10.87	7.55	0.59	0.41	8.64
b	11.77	8.56	17.02	8.46	0.50	0.50	10.12	6.90	0.59	0.41	7.89
c	11.83	9.14	17.74	8.60	0.52	0.48	10.27	7.47	0.58	0.42	8.44
B3LYP/6-311++G(2df,2p)											
a	12.56	9.54	18.44	8.89	0.52	0.48	10.79	7.65	0.59	0.41	8.76
b	11.85	8.97	17.38	8.41	0.52	0.48	10.19	7.19	0.59	0.41	8.23
c	11.95	9.59	18.17	8.57	0.53	0.47	10.36	7.81	0.57	0.43	8.83
APFD/6-311++G(2df,2p)											
a	12.53	9.59	18.47	8.88	0.52	0.48	10.78	7.69	0.58	0.42	8.80
b	11.80	8.99	17.43	8.44	0.52	0.48	10.17	7.26	0.58	0.42	8.27
c	11.86	9.56	18.17	8.61	0.53	0.47	10.32	7.85	0.57	0.43	8.82
B2PLYPD/6-311++G(2df,2p)											
a	11.71	7.53	16.22	8.69	0.46	0.54	10.09	6.13	0.62	0.38	7.00
b	11.47	8.06	16.37	8.31	0.49	0.51	9.9	6.50	0.60	0.40	7.44

c	11.78	8.76	17.24	8.48	0.51	0.49	10.16	7.08	0.59	0.41	8.07
M062X/6-311++G(2df,2p)											
a	11.20104	8.47	16.71	8.25	0.51	0.49	9.74	6.97	0.58	0.42	7.84
b	10.52961	7.87	15.69	7.82	0.50	0.50	9.18	6.51	0.59	0.41	7.30
c	10.58609	8.41	16.41	7.99	0.51	0.49	9.32	7.09	0.57	0.43	7.84
MP2/6-311++G(2df,2p)											
a	9.85	6.32	14.19	7.87	0.45	0.55	8.75	5.44	0.62	0.38	5.98
b	9.36	5.85	13.28	7.43	0.44	0.56	8.28	5.01	0.62	0.38	5.53
c	9.58	6.43	14.04	7.62	0.46	0.54	8.51	5.53	0.61	0.39	6.07

Table 13. Calculated for derivative **4** energies in toluene: a) electronic energies, b) ZPE corrected energies, c) free energies at 133 K.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-479.6943	-479.67521	-479.68159	-479.66729
b	-479.51247	-479.4942	-479.50044	-479.48692
c	-479.5258	-479.50715	-479.51308	-479.49948
B3LYP/aug-cc-pvDZ				
a	-479.60788	-479.58851	-479.59424	-479.57976
b	-479.42576	-479.40767	-479.41336	-479.39983
c	-479.43887	-479.42066	-479.42599	-479.41239
B3LYP/6-311++G(2df,2p)				
a	-479.71328	-479.69404	-479.69948	-479.68513
b	-479.53092	-479.51269	-479.51798	-479.50443
c	-479.54406	-479.52571	-479.53062	-479.51699
APFD/6-311++G(2df,2p)				
a	-479.30707	-479.28776	-479.29321	-479.27881
b	-479.12379	-479.10558	-479.1108	-479.09722
c	-479.13685	-479.11856	-479.12342	-479.10976
B2PLYPD/6-311++G(2df,2p)				
a	-478.69252	-478.67435	-478.68167	-478.66753
b	-479.12442	-479.10662	-479.11271	-479.09929
c	-479.13801	-479.11952	-479.12532	-479.11182
M062X/6-311++G(2df,2p)				
a	-479.49932	-479.48188	-479.48701	-479.47351
b	-479.31482	-479.29837	-479.30344	-479.29067
c	-479.32786	-479.31133	-479.31605	-479.30319
MP2/6-311++G(2df,2p)				
a	-478.53866	-478.52316	-478.52943	-478.51658
b	-478.35445	-478.3398	-478.34601	-478.33392
c	-478.36744	-478.35272	-478.35863	-478.34645

Table 14. Calculated for derivative **4** barriers to rotation: TS_D (one-state approximation) and B_D (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_A	B'_D	δ_D	$1-\delta_D$	B_D
B3LYP/6-311+G(2d,p)											
a	11.98	7.98	16.95	8.97	0.47	0.53	10.39	6.56	0.61	0.39	7.43
b	11.46	7.55	16.03	8.48	0.47	0.53	9.89	6.15	0.62	0.38	7.01
c	11.70	7.98	16.52	8.53	0.48	0.52	10.07	6.45	0.61	0.39	7.38
B3LYP/aug-cc-pvDZ											
a	12.15	8.56	17.65	9.09	0.49	0.51	10.57	7.07	0.60	0.40	7.96
b	11.35	7.78	16.27	8.49	0.48	0.52	9.86	6.41	0.61	0.39	7.24
c	11.43	8.08	16.62	8.53	0.49	0.51	9.94	6.68	0.60	0.40	7.52
B3LYP/6-311++G(2df,2p)											
a	12.07	8.66	17.66	9.00	0.49	0.51	10.51	7.16	0.59	0.41	8.05
b	11.44	8.12	16.62	8.50	0.49	0.51	9.94	6.69	0.60	0.40	7.54
c	11.51	8.43	16.99	8.55	0.50	0.50	10.02	6.96	0.59	0.41	7.83
APFD/6-311++G(2df,2p)											
a	12.12	8.70	17.73	9.04	0.49	0.51	10.55	7.19	0.59	0.41	8.08
b	11.43	8.15	16.67	8.52	0.49	0.51	9.94	6.73	0.60	0.40	7.58
c	11.48	8.43	17.00	8.57	0.50	0.50	10.01	6.99	0.59	0.41	7.84
B2PLYPD/6-311++G(2df,2p)											
a	11.40	6.81	15.68	8.87	0.43	0.57	9.97	5.71	0.64	0.36	6.41
b	11.17	7.35	15.77	8.42	0.47	0.53	9.70	6.07	0.62	0.38	6.86
c	11.60	7.96	16.43	8.47	0.48	0.52	9.99	6.45	0.61	0.39	7.37
M062X/6-311++G(2df,2p)											
a	10.94	7.72	16.20	8.47	0.48	0.52	9.65	6.55	0.60	0.40	7.25
b	10.32	7.14	15.15	8.01	0.47	0.53	9.10	6.05	0.60	0.40	6.71
c	10.37	7.41	15.48	8.10	0.48	0.52	9.17	6.31	0.59	0.41	6.96
MP2/6-311++G(2df,2p)											
a	9.73	5.79	13.86	8.06	0.42	0.58	8.76	5.10	0.63	0.37	5.54
b	9.19	5.30	12.88	7.59	0.41	0.59	8.25	4.64	0.64	0.36	5.06
c	9.24	5.53	13.17	7.64	0.42	0.58	8.31	4.86	0.63	0.37	5.28

Table 15. Calculated for derivative **5** energies in toluene: a) electronic energies, b) ZPE corrected energies, c) free energies at RT.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-495.66868	-495.64335	-495.65234	-495.63594
b	-495.49902	-495.47496	-495.48377	-495.46815
c	-495.53562	-495.51097	-495.5186	-495.50239
B3LYP/aug-cc-pvDZ				
a	-495.58309	-495.55786	-495.56588	-495.5496
b	-495.41323	-495.38948	-495.39765	-495.38215
c	-495.44948	-495.42555	-495.43253	-495.41643
B3LYP/6-311++G(2df,2p)				
a	-495.68775	-495.66272	-495.6704	-495.6543
b	-495.5176	-495.49394	-495.50151	-495.48616
c	-495.55402	-495.53009	-495.53635	-495.5204
APFD/6-311++G(2df,2p)				
a	-495.27214	-495.24767	-495.25501	-495.2393
b	-495.10104	-495.07754	-495.08502	-495.0701
c	-495.13731	-495.11359	-495.11975	-495.10425
B2PLYPD/6-311++G(2df,2p)				
a	-494.64628	-494.62533	-494.63331	-494.61907
b	-495.10801	-495.0861	-495.09343	-495.07918
c	-495.14441	-495.12182	-495.12812	-495.11327
M062X/6-311++G(2df,2p)				
a	-495.46978	-495.44978	-495.45533	-495.44195
b	-495.29762	-495.27873	-495.28433	-495.27163
c	-495.33371	-495.31452	-495.319	-495.30568
MP2/6-311++G(2df,2p)				
a	-494.49916	-494.48155	-494.48794	-494.47538
b	-494.32772	-494.311	-494.31733	-494.30553
c	-494.3649	-494.34664	-494.35213	-494.33961

Table 16. Calculated for derivative **5** barriers to rotation: TS_A (one-state approximation) and B_A (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_A	B'_D	δ_D	$1-\delta_D$	B_D
B3LYP/6-311+G(2d,p)											
a	15.89	10.25	20.54	10.29	0.50	0.50	13.09	7.46	0.64	0.36	9.24
b	15.10	9.57	19.37	9.80	0.49	0.51	12.42	6.95	0.64	0.36	8.63
c	15.47	10.68	20.85	10.17	0.51	0.49	12.88	7.97	0.62	0.38	9.64
B3LYP/aug-cc-pvDZ											
a	15.83	10.80	21.02	10.22	0.51	0.49	13.10	7.91	0.62	0.38	9.71
b	14.90	9.78	19.50	9.73	0.50	0.50	12.32	7.18	0.63	0.37	8.82
c	15.02	10.64	20.74	10.10	0.51	0.49	12.62	8.12	0.61	0.39	9.65
B3LYP/6-311++G(2df,2p)											
a	15.71	10.89	20.99	10.10	0.52	0.48	13.01	7.98	0.62	0.38	9.78
b	14.85	10.10	19.73	9.63	0.51	0.49	12.30	7.43	0.62	0.38	9.09
c	15.02	11.09	21.10	10.01	0.53	0.47	12.64	8.46	0.60	0.40	10.03
APFD/6-311++G(2df,2p)											
a	15.36	10.75	20.61	9.86	0.52	0.48	12.73	7.88	0.62	0.38	9.65
b	14.75	10.05	19.42	9.36	0.52	0.48	12.15	7.26	0.63	0.37	9.01
c	14.88	11.02	20.75	9.73	0.53	0.47	12.47	8.28	0.60	0.40	9.93
B2PLYPD/6-311++G(2df,2p)											
a	13.15	8.14	17.07	8.94	0.48	0.52	10.94	6.13	0.64	0.36	7.42
b	13.75	9.15	18.09	8.94	0.51	0.49	11.37	6.72	0.63	0.37	8.25
c	14.18	10.22	19.54	9.32	0.52	0.48	11.86	7.68	0.61	0.39	9.22
M062X/6-311++G(2df,2p)											

a	12.55	9.07	17.46	8.40	0.52	0.48	10.55	6.91	0.60	0.40	8.21
b	11.85	8.34	16.31	7.97	0.51	0.49	9.96	6.35	0.61	0.39	7.57
c	12.04	9.23	17.59	8.36	0.52	0.48	10.29	7.30	0.59	0.41	8.43
MP2/6-311++G(2df,2p)											
a	11.05	7.04	14.92	7.88	0.47	0.53	9.38	5.55	0.63	0.37	6.49
b	10.49	6.52	13.92	7.40	0.47	0.53	8.85	5.07	0.64	0.36	5.99
c	11.46	8.01	15.87	7.86	0.50	0.50	9.68	6.19	0.61	0.39	7.30

Table 17. Calculated for derivative **5** energies in toluene: a) electronic energies, b) ZPE corrected energies, c) free energies at 201 K.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-495.66868	-495.64335	-495.65234	-495.63594
b	-495.49902	-495.47496	-495.48377	-495.46815
c	-495.52098	-495.49664	-495.50481	-495.48891
B3LYP/aug-cc-pvDZ				
a	-495.58309	-495.55786	-495.56588	-495.5496
b	-495.41323	-495.38948	-495.39765	-495.38215
c	-495.43499	-495.41119	-495.41871	-495.40293
B3LYP/6-311++G(2df,2p)				
a	-495.68775	-495.66272	-495.6704	-495.6543
b	-495.5176	-495.49394	-495.50151	-495.48616
c	-495.53946	-495.5157	-495.52255	-495.50693
APFD/6-311++G(2df,2p)				
a	-495.27214	-495.24767	-495.25501	-495.2393
b	-495.10104	-495.07754	-495.08502	-495.0701
c	-495.12282	-495.09928	-495.10601	-495.09082
B2PLYPD/6-311++G(2df,2p)				
a	-494.64628	-494.62533	-494.63331	-494.61907
b	-495.10801	-495.0861	-495.09343	-495.07918
c	-495.12987	-495.10763	-495.1144	-495.09987
M062X/6-311++G(2df,2p)				
a	-495.46978	-495.44978	-495.45533	-495.44195
b	-495.29762	-495.27873	-495.28433	-495.27163
c	-495.3193	-495.30031	-495.30529	-495.29231
MP2/6-311++G(2df,2p)				
a	-494.49916	-494.48155	-494.48794	-494.47538
b	-494.32772	-494.311	-494.31733	-494.30553
c	-494.35005	-494.33249	-494.33836	-494.32621

Table 18. Calculated for derivative **5** barriers to rotation: TS_D (one-state approximation) and B_D (three-state approximation).

	$TS_A=B'_A$	$TS_D=B''_D$	TS_{DA}	B''_A	δ_A	$1-\delta_A$	B_A	B'_D	δ_D	$1-\delta_D$	B_D
B3LYP/6-311+G(2d,p)											
a	15.89	10.25	20.54	10.29	0.50	0.50	13.09	7.46	0.64	0.36	9.26
b	15.10	9.57	19.37	9.80	0.49	0.51	12.42	6.95	0.64	0.36	8.63
c	15.27	10.15	20.12	9.98	0.50	0.50	12.65	7.48	0.63	0.37	9.15
B3LYP/aug-cc-pvDZ											
a	15.83206	10.80	21.02	10.22	0.51	0.49	13.10	7.91	0.62	0.38	9.71
b	14.90335	9.78	19.50	9.73	0.50	0.50	12.32	7.18	0.63	0.37	8.82
c	14.93473	10.22	20.12	9.90	0.51	0.49	12.46	7.66	0.62	0.38	9.24
B3LYP/6-311++G(2df,2p)											
a	15.71	10.89	20.99	10.10	0.52	0.48	13.01	7.98	0.62	0.388	9.78
b	14.85	10.10	19.73	9.63	0.51	0.49	12.30	7.43	0.62	0.38	9.09
c	14.91	10.61	20.41	9.80	0.52	0.48	12.46	7.96	0.61	0.39	9.58
APFD/6-311++G(2df,2p)											
a	15.36	10.75	20.61	9.86	0.52	0.48	12.73	7.88	0.62	0.38	9.65
b	14.75	10.05	19.42	9.36	0.52	0.48	12.15	7.26	0.63	0.37	9.01
c	14.77	10.55	20.08	9.53	0.53	0.47	12.28	7.80	0.61	0.39	9.48
B2PLYPD/6-311++G(2df,2p)											
a	13.15	8.14	17.07	8.94	0.48	0.52	10.94	6.13	0.64	0.36	7.42
b	13.75	9.15	18.09	8.94	0.51	0.49	11.37	6.72	0.63	0.37	8.25
c	13.96	9.71	18.83	9.12	0.52	0.48	11.61	7.21	0.62	0.38	8.75
M062X/6-311++G(2df,2p)											
a	12.55	9.07	17.46	8.40	0.52	0.48	10.55	6.91	0.60	0.40	8.21
b	11.85	8.34	16.31	7.97	0.51	0.49	9.96	6.35	0.61	0.39	7.57
c	11.92	8.79	16.94	8.15	0.52	0.48	10.10	6.83	0.60	0.40	8.00
MP2/6-311++G(2df,2p)											
a	11.05	7.04	14.92	7.88	0.47	0.53	9.38	5.55	0.63	0.37	6.49
b	10.49	6.52	13.92	7.40	0.47	0.53	8.85	5.07	0.64	0.36	5.99
c	11.02	7.34	14.96	7.62	0.49	0.51	9.29	5.67	0.62	0.38	6.70

Table 19. Calculated for derivative **6** energies in methylene chloride: a) electronic energies, b) ZPE corrected energies, c) free energies at RT.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-979.07004	-979.05004	-979.04871	-979.03853
b	-978.7278	-978.70965	-978.70784	-978.69874
c	-978.77814	-978.76004	-978.75737	-978.74712
B3LYP/aug-cc-pvDZ				
a	-978.90032	-978.87964	-978.87861	-978.86769
b	-978.55808	-978.53968	-978.53776	-978.52839
c	-978.60814	-978.59002	-978.58687	-978.57671
B3LYP/6-311++G(2df,2p)				
a	-979.10665	-979.08669	-979.08447	-979.0743
b	-978.76355	-978.74545	-978.74284	-978.73378
c	-978.81376	-978.79566	-978.79231	-978.78213
APFD/6-311++G(2df,2p)				
a	-978.29664	-978.27694	-978.27385	-978.26417
b	-977.95177	-977.93375	-977.93039	-977.92156
c	-978.00175	-977.98382	-977.97961	-977.96968
M062X/6-311++G(2df,2p)				
a	-978.68783	-978.6722	-978.66794	-978.66042
b	-978.34136	-978.32742	-978.32267	-978.31611
c	-978.39144	-978.37747	-978.37197	-978.36397

Table 20. Calculated for derivative **6** barriers to rotation: TS_A (one-state approximation) and B_A (three-state approximation).

	$TS_A=B''_A$	$TS_D=B'_D$	TS_{DA}	B''_D	δ_D	$1-\delta_D$	B_D	B'_A	δ_A	$1-\delta_A$	B_A
B3LYP/6-311+G(2d,p)											
a	12.55	13.38	19.77	7.22	0.63	0.37	11.13	8.64	0.56	0.44	10.84
b	11.39	12.53	18.24	6.86	0.62	0.38	10.39	7.84	0.57	0.43	9.86
c	11.36	13.03	19.47	8.11	0.58	0.42	10.98	8.48	0.56	0.44	10.11
B3LYP/aug-cc-pvDZ											
	12.98	13.62	20.48	7.50	0.63	0.37	11.38	9.10	0.56	0.44	11.25
	11.55	12.75	18.63	7.08	0.62	0.38	10.60	8.03	0.57	0.43	10.03
	11.37	13.35	19.72	8.35	0.58	0.42	11.23	8.49	0.57	0.43	10.13
B3LYP/6-311++G(2df,2p)											
	12.53	13.92	20.30	7.77	0.62	0.38	11.57	8.73	0.57	0.43	10.89
	11.36	13.00	18.68	7.32	0.61	0.39	10.77	7.91	0.58	0.42	9.90
	11.36	13.46	19.85	8.49	0.57	0.43	11.33	8.51	0.57	0.43	10.14
APFD/6-311++G(2df,2p)											
	12.36	14.30	20.38	8.01	0.61	0.39	11.83	8.55	0.58	0.42	10.76
	11.31	13.42	18.96	7.65	0.60	0.40	11.09	7.87	0.58	0.42	9.88
	11.25	13.89	20.12	8.87	0.56	0.44	11.68	8.44	0.58	0.42	10.07
M062X/6-311++G(2df,2p)											
	9.81	12.48	17.20	7.39	0.57	0.43	10.29	6.91	0.60	0.40	8.64
	8.75	11.73	15.84	7.10	0.55	0.45	9.65	6.19	0.61	0.39	7.75
	8.77	12.22	17.24	8.47	0.51	0.49	10.38	6.86	0.60	0.40	8.01

Table 21. Calculated for derivative **7** energies in toluene: a) electronic energies, b) ZPE corrected energies, c) free energies at RT.

	GS	TS_A	TS_D	TS_{DA}
B3LYP/6-311+G(2d,p)				
a	-326.01184	-325.98517	-325.98286	-325.9723
b	-325.87691	-325.85164	-325.84942	-325.8397
c	-325.91001	-325.88384	-325.88155	-325.87089
B3LYP/6-311++G(2df,2p)				
a	-326.02487	-325.99793	-325.99479	-325.98421
b	-325.88969	-325.8642	-325.86115	-325.85141
c	-325.92288	-325.89645	-325.8933	-325.88263
B3LYP/aug-cc-pvDZ				
a	-325.94854	-325.92168	-325.91891	-325.90826
b	-325.81379	-325.78839	-325.78578	-325.77598
c	-325.84705	-325.82062	-325.81792	-325.8072
B3LYP/aug-cc-pvTZ				
a	-326.03575	-326.0089	-326.00584	-325.99526
b	-325.90074	-325.87532	-325.87237	-325.86264
c	-325.93387	-325.90755	-325.90452	-325.89385
APFD/aug-cc-pvDZ				
a	-325.67743	-325.65068	-325.6477	-325.63689
b	-325.54221	-325.51675	-325.51385	-325.50389
c	-325.57538	-325.54894	-325.54594	-325.53508
APFD/6-311++G(2df,2p)				
a	-325.74411	-325.71728	-325.71373	-325.70305
b	-325.60847	-325.58293	-325.57945	-325.56964
c	-325.64158	-325.61513	-325.61153	-325.60081
B2PLYPD/6-311++G(2df,2p)				
a	-325.33296	-325.30805	-325.30613	-325.29596
b	-325.60917	-325.5846	-325.58202	-325.5724
c	-325.6421	-325.61663	-325.61398	-325.60351
M062X/6-311++G(2df,2p)				
a	-325.86775	-325.84367	-325.84022	-325.83045
b	-325.73106	-325.70817	-325.70488	-325.69588
c	-325.76421	-325.74023	-325.73702	-325.72697
MP2/6-311++G(2df,2p)				
a	-325.22791	-325.20405	-325.20176	-325.19203
b	-325.09091	-325.06838	-325.06623	-325.05737
c	-325.12385	-325.10032	-325.09835	-325.0885

Table 22. Calculated for derivative **7** barriers to rotation: TS_D (one-state approximation) and B_D (three-state approximation)

	$TS_A=B''_A$	$TS_D=B'_D$	TS_{DA}	B''_D	δ_D	$1-\delta_D$	B_D	B'_A	δ_A	$1-\delta_A$	B_A
B3LYP/6-311+G(2d,p)											
a	16.74	18.19	24.81	8.08	0.67	0.33	14.89	9.92	0.60	0.40	14.01
b	15.86	17.25	23.35	7.49	0.68	0.32	14.12	9.23	0.60	0.40	13.24
c	16.42	17.86	24.55	8.13	0.67	0.33	14.64	9.91	0.60	0.40	13.79
B3LYP/6-311++G(2df,2p)											
a	16.91	18.88	25.51	8.61	0.66	0.34	15.41	10.10	0.60	0.40	14.21
b	15.0	17.91	24.02	8.03	0.67	0.33	14.61	9.41	0.61	0.39	13.42
c	16.59	18.56	25.26	8.67	0.66	0.34	15.17	10.09	0.60	0.40	13.99
B3LYP/aug-cc-pvDZ											
a	16.85	18.59	25.28	8.42	0.67	0.33	15.20	10.07	0.60	0.40	14.15
b	15.94	17.58	23.73	7.79	0.67	0.33	14.36	9.36	0.61	0.39	13.34
c	16.59	18.28	25.01	8.42	0.66	0.34	14.96	10.05	0.60	0.40	13.96
B3LYP/aug-cc-pvTZ											
a	16.85	18.77	25.41	8.56	0.66	0.34	15.33	10.08	0.60	0.40	14.16
b	15.95	17.80	23.91	7.96	0.67	0.33	14.53	9.38	0.61	0.39	13.37
c	16.52	18.42	25.11	8.60	0.66	0.34	15.06	10.06	0.60	0.40	13.93
APFD/aug-cc-pvDZ											
a	16.79	18.66	25.44	8.65	0.66	0.34	15.25	10.19	0.60	0.40	14.14
b	15.98	17.80	24.05	8.07	0.66	0.34	14.53	9.51	0.60	0.40	13.42
c	16.59	18.47	25.29	8.70	0.66	0.34	15.11	10.18	0.60	0.40	14.01
APFD/6-311++G(2df,2p)											
a	16.84	19.06	25.77	8.93	0.65	0.35	15.55	10.21	0.60	0.40	14.21
b	16.03	18.21	24.37	8.34	0.66	0.34	14.83	9.53	0.61	0.39	13.49
c	16.60	18.86	25.59	8.99	0.65	0.35	15.39	10.19	0.60	0.40	14.05
B2PLYPD/6-311++G(2df,2p)											
a	15.63	16.84	23.22	7.59	0.67	0.33	13.81	9.40	0.59	0.41	13.11
b	15.42	17.04	23.07	7.66	0.67	0.33	13.92	9.15	0.60	0.40	12.93
c	15.98	17.65	24.22	8.23	0.66	0.34	14.45	9.77	0.60	0.40	13.48
M062X/6-311++G(2df,2p)											
	15.11	17.28	23.41	8.30	0.65	0.35	14.09	9.31	0.60	0.40	12.80
	14.36	16.43	22.08	7.71	0.65	0.35	13.38	8.69	0.61	0.39	12.13
	15.05	17.06	23.37	8.32	0.64	0.36	13.95	9.4	0.60	0.40	12.78
MP2/6-311++G(2df,2p)											
	14.97	16.41	22.52	7.54	0.66	0.34	13.44	9.08	0.60	0.40	12.60
	14.14	15.49	21.05	6.91	0.67	0.33	12.67	8.38	0.60	0.40	11.84
	14.77	16.00	22.18	7.42	0.67	0.33	13.13	9.05	0.59	0.41	12.43

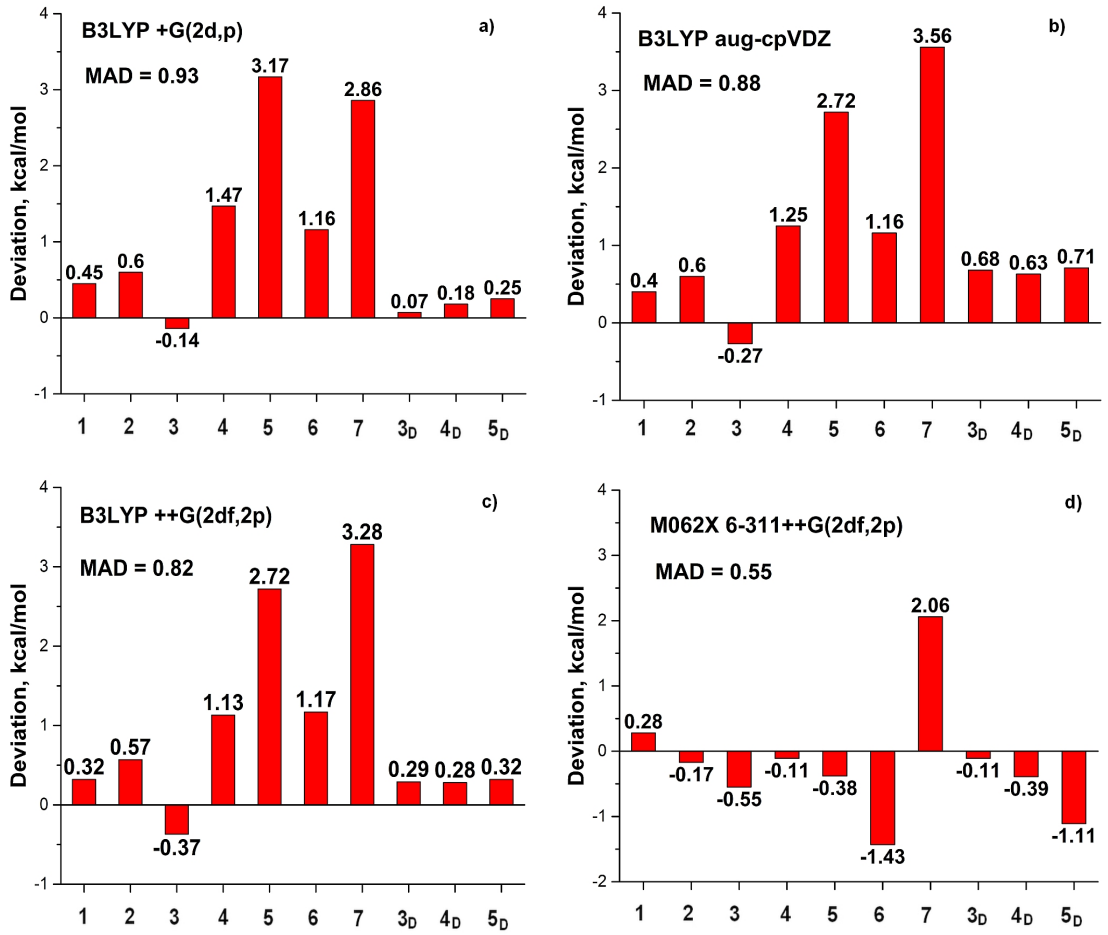

Figure 1S. Deviations of calculated using one-state approximation barriers $B_A = TS_A$ (derivatives **1** – **6**) and $B_D = TS_D$ (derivatives **3** – **5**, **7**) from the experimental.

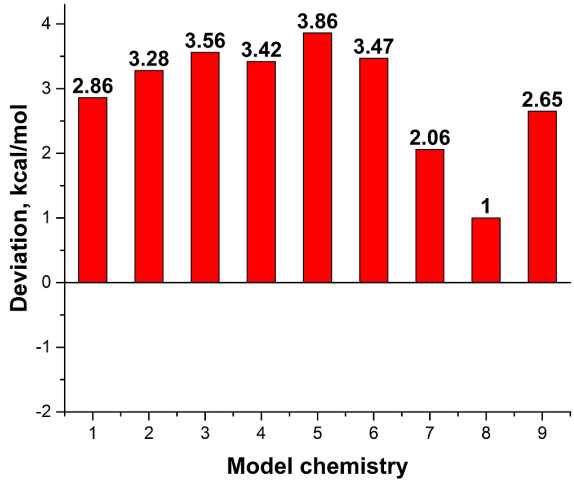

Figure 2S. Deviations of calculated using one-state approximation barrier B_D for derivative **7** $B_D = TS_D$ (at 298.15 K) from the experimental value. 1 – B3LYP/6-311+G(2d,p); 2 – B3LYP/aug-cc-pVDZ; 3 – B3LYP/6-311++G(2df,2p); 4 – B3LYP/aug-cc-pVTZ; 5 – APFD/6-311++G(2df,2p); 6 – APFD/aug-cc-pVDZ; 7 – M062X/6-311++G(2df,2p); 8 – MP2/6-311++G(2df,2p); 9 – B2PLYPD/6-311++G(2df,2p).

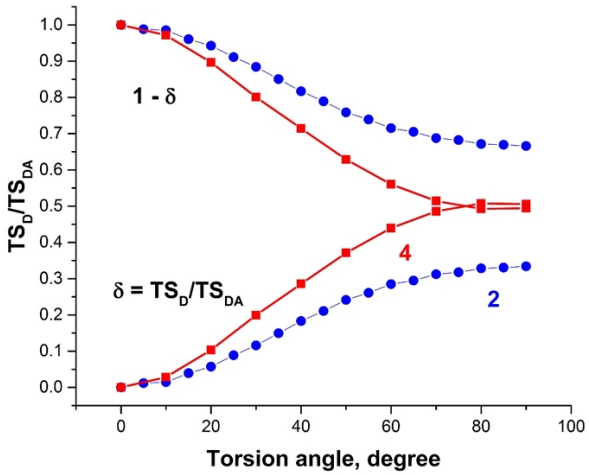

Figure 3S. Variation of δ and 1 - δ values with varying torsion angles, blue: derivative **2**, red: derivative **4**.

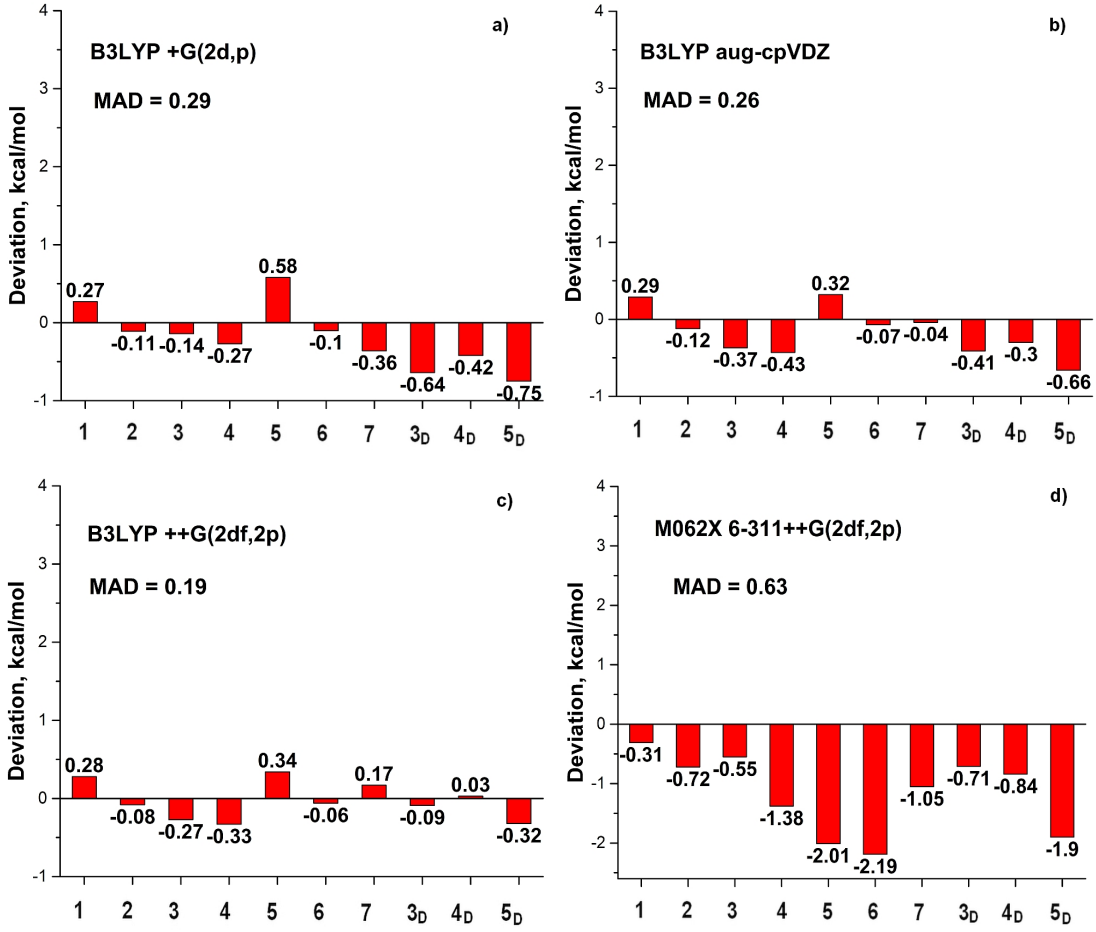

Figure 4S. Deviations of calculated using three-state approximation barriers B_A (derivatives **1** – **6**) and $B_D = TS_D$ (derivatives **3** – **5**, **7**) from the experimental.

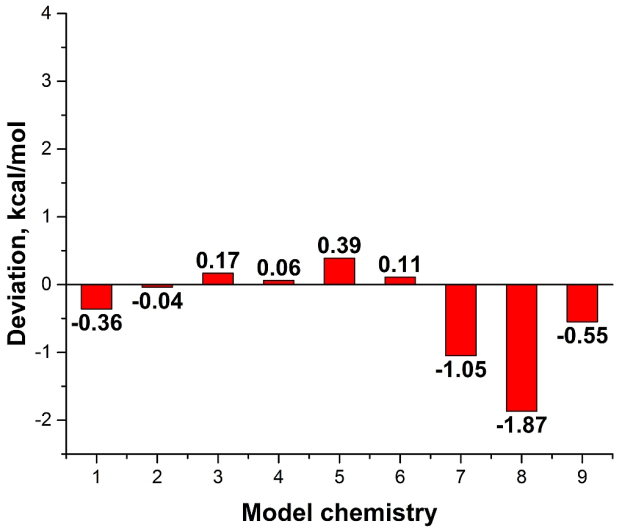

Figure 5S. Deviations of calculated using three-state approximation barrier B_D for derivative **7** (at 298.15 K) from the experimental value. 1 – B3LYP/6-311+G(2d,p); 2 – B3LYP/aug-cc-pVDZ; 3 – B3LYP/6-311++G(2df,2p); 4 – B3LYP/aug-cc-pVTZ; 5 – APFD/6-311++G(2df,2p); 6 – APFD/aug-cc-pVDZ; 7 – M062X/6-311++G(2df,2p); 8 – MP2/6-311++G(2df,2p); 9 – B2PLYPD/6-311++G(2df,2p).