Structural and Thermodynamic Characterization of Polyphenylbenzenesnes

(Supporting Information)

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TABLE S1. Experimental results for the combustion of 1,2,4-triphenylbenzene, at T = 298.15 K.

	1	2	3	4	5	6	7	8
m(cpd.) / g	0.0222665	0.0163486	0.0235737	0.0163612	0.0313414	0.0150225	0.0357712	0.0281151
T_i / ºC	25.00038	25.00019	25.00244	25.02438	24.99294	25.04856	24.93494	24.99505
T_f / ºC	25.42773	25.32838	25.45226	25.34938	25.57883	25.34857	25.60690	25.52633
ΔT_{ad} / K	0.4578939	0.3362819	0.4843376	0.3365177	0.6442328	0.3090592	0.7353964	0.5780589
ε_i (cont.) / (J.K^{-1})	1.0165	1.0098	1.0180	1.0099	1.0267	1.0083	1.0317	1.0231
ε_f (cont.) / (J.K^{-1})	1.0512	1.0353	1.0547	1.0353	1.0755	1.0317	1.0874	1.0669
$-\Delta U$(IBP)[a] / J	890.5163	653.7586	942.0087	654.2094	1253.2843	600.7838	1430.7527	1124.5360
$-\Delta U$(ignition) / J	0.921	0.917	0.912	0.926	0.937	0.894	0.956	0.850
ΔU_Σ / J	0.491	0.351	0.523	0.351	0.718	0.320	0.834	0.636
$-\Delta U$(carbon) / J	0.122	0.261	0.795	0.145	0.317	0.155	0.00	0.165
$-\Delta_c u^o$(cpd.) / J·g^{-1}	39976.93	39983.03	39971.66	39972.94	39975.38	39981.19	39974.03	39980.77
$-\langle\Delta_c u^o\rangle$[b] / J·g^{-1} = 39977.0 ± 1.5 (0.0037 %)								

[a] ΔU(IBP) does not include ΔU(ignition): ΔU_{IBP}(as defined by equation 6);
m(cpd.) is the mass of compound burnt in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ε_i (cont.) is the energy equivalent of the contents in the initial state; ε_f (cont.) is the energy equivalent of the contents in the final state; ΔT_{ad} is the corrected temperature rise; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(ignition) is the electric energy for the ignition; ΔU_Σ is the standard state correction, ΔU(carbon) is the energy of combustion of the carbon residue formed, and $\Delta_c u^o$ is the standard massic energy of combustion.
[b] Mean value and given error as the standard deviation of the mean.

TABLE S2. Experimental results for the combustion of 1,2,4,5-tetraphenylbenzene, at T = 298.15 K.

	1	2	3	4	5	6	7
m(cpd.) / g	0.43875	0.28125	0.32428	0.44116	0.39232	0.36176	0.38857
m'(fuse) / g	0.00282	0.00260	0.00264	0.00292	0.00229	0.00227	0.00289
T_i / ºC	25.00105	25.00086	25.00109	25.00040	25.00137	25.00128	25.00085
T_f / ºC	26.20620	25.81395	25.92180	26.20899	26.08934	26.01503	26.08158
ΔT_{ad} / K	1.1267989	0.7235379	0.8330957	1.1327176	1.0063778	0.9298540	0.9990620
ε_i (cont.) / (J.K^{-1})	14.87	14.70	14.75	14.88	14.82	14.79	14.82
ε_f (cont.) / (J.K^{-1})	15.49	15.09	15.20	15.50	15.37	15.30	15.37
$\Delta m(H_2O)$ / g	1.6	1.0	3.0	-1.0	-2.7	-1.7	-0.3
$-\Delta U$(IBP)[a] / J	17542.56	11262.28	12974.68	17622.39	15649.56	14463.40	15545.82
$-\Delta U(HNO_3)$ / J	0.35	0.15	0.19	0.19	0.28	0.28	0.25
$-\Delta U$(ignition) / J	0.93	0.90	0.94	0.94	0.97	1.03	0.97
$\Delta U_{\sum}$ / J	9.80	6.05	7.05	9.86	8.66	7.93	8.58
$-\Delta U$(carbon) / J	0.99	0.99	0.00	22.77	35.64	5.94	0.00
$-m'\cdot\Delta_c u^o$(fuse) / J	45.80	42.22	42.87	47.42	37.19	36.86	46.93
$-\Delta_c u^o$(cpd.) / J·g^{-1}	39855.82	39871.87	39852.69	39864.78	39860.52	39870.12	39862.04
$-\langle\Delta_c u^o\rangle$[b] / J·g^{-1} = 39862.5 ± 2.7 (0.0067 %)				<%CO_2 recovery> = (100.13 ± 0.11)			

[a] ΔU(IBP) includes ΔU(ignition): ΔU_{IBP}(as defined by equation 6) + ΔU(ignition);
m(cpd.) is the mass of compound burnt in each experiment; m'(fuse) is the mass of the fuse (cotton) used in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ε_i (cont.) is the energy equivalent of the contents in the initial state; ε_f (cont.) is the energy equivalent of the contents in the final state; $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 2900.0 g; ΔT_{ad} is the corrected temperature rise; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(ignition) is the electric energy for the ignition; $\Delta U_{\sum}$ is the standard state correction; ΔU(carbon) is the energy of combustion of the carbon residue formed; $\Delta_c u^o$ (fuse) is the massic energy of combustion of the fuse (cotton) and $\Delta_c u^o$ is the standard massic energy of combustion.
[b] Mean value and given error as the standard deviation of the mean.

TABLE S3. Experimental results for the combustion of hexaphenylbenzene, at T = 298.15 K.

	1	2	3	4	5	6	7	8	9	10
m(cpd.) / g	0.0226284	0.0150088	0.0138859	0.0224696	0.0123217	0.0189004	0.0209448	0.0332435	0.0258486	0.0232630
T_i / ºC	24.99528	25.04220	25.07283	25.00746	25.12930	25.00479	25.00306	24.98735	25.00313	25.00524
T_f / ºC	25.43057	25.34063	25.34647	25.43820	25.36521	25.37626	25.41043	25.60466	25.49244	25.45129
ΔT_{ad} / K	0.4634300	0.3077996	0.2845833	0.4602905	0.2523370	0.3874481	0.4290316	0.6807148	0.5291644	0.4767100
ε_i (cont.) / (J.K^{-1})	1.0164	1.0080	1.0067	1.0162	1.0050	1.0122	1.0145	1.0280	1.0199	1.0170
ε_f (cont.) / (J.K^{-1})	1.0503	1.0304	1.0275	1.0499	1.0234	1.0406	1.0459	1.0778	1.0586	1.0519
$-\Delta U$(IBP)[a] / J	901.3066	598.2820	553.0878	895.1900	490.3041	753.3352	834.3391	1324.2946	1029.3435	927.1735
$-\Delta U$(ignition) / J	0.908	0.943	0.940	0.913	0.946	0.953	0.907	0.953	0.849	0.896
ΔU_Σ / J	0.506	0.324	0.298	0.503	0.262	0.416	0.465	0.777	0.587	0.522
$-\Delta U$(carbon) / J	1.145	0.663	0.772	0.993	1.140	0.739	1.016	1.789	1.426	0.842
$-\Delta_c u^o$(cpd.) / J·g^{-1}	39859.00	39884.59	39864.89	39861.96	39863.20	39875.18	39861.41	39866.63	39854.46	39869.96
$-\langle\Delta_c u^o\rangle$[b] / J·g^{-1} = 39866.1 ± 2.7 (0.0069 %)										

[a] ΔU(IBP) does not include ΔU(ignition): ΔU_{IBP}(as defined by equation 6);
m(cpd.) is the mass of compound burnt in each experiment; T_i is the initial temperature rise; T_f is the final temperature rise; ε_i (cont.) is the energy equivalent of the contents in the initial state; ε_f (cont.) is the energy equivalent of the contents in the final state; ΔT_{ad} is the corrected temperature rise; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(ignition) is the electric energy for the ignition; ΔU_Σ is the standard state correction, ΔU(carbon) is the energy of combustion of the carbon residue formed, and $\Delta_c u^o$ is the standard massic energy of combustion.
[b] Mean value and given error as the standard deviation of the mean.

TABLE S4. Experimental results obtained for the sublimation of 1,2,4-triphenylbenzene in the Knudsen/Quartz crystal effusion apparatus.

	T / K	Δt_i / s	(df/dt) / Hz·s^{-1}	p / Pa	T^{-1} / K^{-1}	ln p
1	359.20	3892.7	-0.2747	0.0143	0.002784	-4.2486
	361.20	2219.4	-0.3504	0.0183	0.002769	-4.0025
	363.20	2219.1	-0.4426	0.0231	0.002753	-3.7662
	364.20	2218.7	-0.4944	0.0259	0.002746	-3.6540
	365.20	2219.6	-0.5581	0.0293	0.002738	-3.5314
	366.20	2220.3	-0.6249	0.0328	0.002731	-3.4170
	367.20	2219.1	-0.7016	0.0369	0.002723	-3.2999
	368.20	2220.2	-0.7883	0.0415	0.002716	-3.1820
	369.20	2221.7	-0.8846	0.0466	0.002709	-3.0654
	370.20	2098.3	-0.9930	0.0524	0.002701	-2.9485
	Δm / mg	2.27	W / Hz·mg^{-1}	$6.13 \cdot 10^3$		
	Δf / Hz	-13908.60				
2	361.19	2218.7	-0.3457	0.0181	0.002769	-4.0119
	362.19	2220.2	-0.3916	0.0205	0.002761	-3.8861
	363.19	2221.2	-0.4397	0.0231	0.002753	-3.7688
	364.20	2219.0	-0.4964	0.0261	0.002746	-3.6462
	365.19	2219.9	-0.5562	0.0293	0.002738	-3.5309
	366.19	2220.5	-0.6253	0.0330	0.002731	-3.4125
	367.19	2224.3	-0.7050	0.0372	0.002723	-3.2912
	368.19	2222.0	-0.7906	0.0418	0.002716	-3.1752
	369.19	2220.4	-0.8882	0.0470	0.002709	-3.0575
	370.19	2124.2	-0.9970	0.0528	0.002701	-2.9406
	Δm / mg	2.43	W / Hz·mg^{-1}	$6.09 \cdot 10^3$		
	Δf / Hz	-14805.49				
3	360.19	3923.6	-0.3103	0.0161	0.002776	-4.1267
	361.19	2219.4	-0.3503	0.0182	0.002769	-4.0041
	362.19	2220.0	-0.3917	0.0204	0.002761	-3.8911
	363.20	2217.7	-0.4435	0.0232	0.002753	-3.7654
	364.20	2218.2	-0.4950	0.0259	0.002746	-3.6543
	365.20	2219.6	-0.5567	0.0291	0.002738	-3.5354
	366.20	2219.4	-0.6277	0.0329	0.002731	-3.4139
	367.20	2222.5	-0.7034	0.0369	0.002723	-3.2988
	368.20	2223.7	-0.7891	0.0415	0.002716	-3.1824
	369.20	2224.0	-0.8892	0.0468	0.002709	-3.0616
	370.20	2510.0	-0.9953	0.0525	0.002701	-2.9476
	Δm / mg	---	W / Hz·mg^{-1}	---		
	Δf / Hz	-15368.73				

TABLE S5. Experimental results obtained for the sublimation of 1,2,4,5-tetraphenylbenzene in the Knudsen/Quartz crystal effusion apparatus.

	T / K	Δt_i / s	(df/dt) / Hz·s^{-1}	p / Pa	T^{-1} / K^{-1}	ln p
1	440.28	3890.4	-0.2913	0.1346	0.002271	-2.0051
	442.29	2219.1	-0.3537	0.1639	0.002261	-1.8088
	444.30	2218.9	-0.4267	0.1982	0.002251	-1.6187
	446.31	2219.3	-0.5116	0.2381	0.002241	-1.4351
	448.31	2218.8	-0.6176	0.2881	0.002231	-1.2446
	450.32	2219.0	-0.7460	0.3487	0.002221	-1.0534
	452.33	2221.4	-0.8939	0.4188	0.002211	-0.8703
	454.34	2220.6	-1.0735	0.5041	0.002201	-0.6850
	456.34	2197.5	-1.2863	0.6053	0.002191	-0.5020
	Δm / mg	20.86	W / Hz·mg^{-1}	681.8		
	Δf / Hz	-14222.06				
2	441.28	2219.3	-0.3366	0.1543	0.002266	-1.8687
	443.29	2217.8	-0.4058	0.1865	0.002256	-1.6795
	445.29	2221.6	-0.4844	0.2231	0.002246	-1.5003
	447.30	2220.2	-0.5832	0.2692	0.002236	-1.3124
	449.31	2223.6	-0.6979	0.3229	0.002226	-1.1305
	451.31	2224.0	-0.8361	0.3877	0.002216	-0.9476
	453.32	2221.5	-1.0036	0.4663	0.002206	-0.7629
	455.33	2114.2	-1.2069	0.5621	0.002196	-0.5762
	Δm / mg	19.34	W / Hz·mg^{-1}	688.2		
	Δf / Hz	-13310.25				
3	439.29	4505.7	-0.2706	0.1230	0.002276	-2.0958
	441.29	2219.6	-0.3242	0.1476	0.002266	-1.9130
	443.30	2218.4	-0.3920	0.1789	0.002256	-1.7208
	445.31	2219.8	-0.4760	0.2178	0.002246	-1.5244
	447.32	2220.3	-0.5689	0.2608	0.002236	-1.3438
	449.33	2222.6	-0.6806	0.3128	0.002226	-1.1623
	451.33	2222.6	-0.8223	0.3787	0.002216	-0.9709
	453.34	3706.0	-0.9807	0.4527	0.002206	-0.7925
	Δm / mg	17.47	W / Hz·mg^{-1}	692.8		
	Δf / Hz	-12102.66				

TABLE S6. Experimental results obtained for the sublimation of hexaphenylbenzene in the Knudsen/Quartz crystal effusion apparatus.

	T / K	Δt_i / s	(df/dt) / Hz·s^{-1}	p / Pa	T^{-1} / K^{-1}	ln p
1	491.44	4473.2	-0.2336	0.0947	0.002035	-2.3573
	493.45	2219.4	-0.2781	0.1129	0.002027	-2.1810
	495.46	2219.8	-0.3275	0.1333	0.002018	-2.0152
	497.47	2220.5	-0.3858	0.1573	0.002010	-1.8496
	499.48	2219.4	-0.4530	0.1851	0.002002	-1.6868
	501.49	2220.4	-0.5336	0.2185	0.001994	-1.5211
	503.50	2222.5	-0.6227	0.2554	0.001986	-1.3648
	505.51	2221.1	-0.7282	0.2993	0.001978	-1.2062
	507.52	2223.0	-0.8525	0.3511	0.001970	-1.0466
	509.52	2114.6	-0.9923	0.4095	0.001963	-0.8929
	Δm / mg	17.89	W / Hz·mg^{-1}	694.8		
	Δf / Hz	-12430.74				
2	492.46	4477.7	-0.2383	0.0965	0.002031	-2.3384
	494.47	2219.4	-0.2788	0.1131	0.002022	-2.1792
	496.47	2218.8	-0.3294	0.1339	0.002014	-2.0106
	498.48	2220.2	-0.3886	0.1583	0.002006	-1.8433
	500.49	2219.8	-0.4539	0.1853	0.001998	-1.6860
	502.50	2219.8	-0.5376	0.2199	0.001990	-1.5147
	504.51	2219.6	-0.6254	0.2563	0.001982	-1.3614
	506.52	2220.7	-0.7330	0.3010	0.001974	-1.2007
	508.53	2220.4	-0.8605	0.3541	0.001966	-1.0383
	510.54	2103.7	-0.9906	0.4084	0.001959	-0.8956
	Δm / mg	17.94	W / Hz·mg^{-1}	696.2		
	Δf / Hz	-12490.53				

TABLE S7. Experimental results obtained for 1,2,4-triphenylbenzene where a and b are from the Clausius-Clapeyron equation $\ln\left(p/\mathrm{Pa}\right)=a-b\cdot\left(\mathrm{K}/T\right)$, and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}\left(\langle T\rangle\right)/R$; R = 8.314472 J·K^{-1}·mol^{-1}.

Experience nº	a	b	r^2	$\langle T\rangle$	$p\left(\langle T\rangle\right)$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}\left(\langle T\rangle\right)$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{0}\left(\langle T\rangle\right)$
		K		K	Pa	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
1	39.41 ± 0.10	15681 ± 36	1.0000	365.40	0.0300	130.4 ± 0.3	231.9 ± 0.8
2	39.95 ± 0.07	15879 ± 27	1.0000	365.69	0.0311	132.0 ± 0.2	236.5 ± 0.6
3	39.46 ± 0.12	15701 ± 45	0.9999	365.20	0.0293	130.5 ± 0.4	232.4 ± 1.0
Global results				365.43		131.0 ± 0.3	234.2 ± 0.7

TABLE S8. Experimental results obtained for 1,2,4,5-tetraphenylbenzene where a and b are from the Clausius-Clapeyron equation $\ln\left(p/\mathrm{Pa}\right)=a-b\cdot\left(\mathrm{K}/T\right)$, and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}\left(\langle T\rangle\right)/R$; R = 8.314472 J·K^{-1}·mol^{-1}.

Experience nº	a	b	r^2	$\langle T\rangle$	$p\left(\langle T\rangle\right)$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}\left(\langle T\rangle\right)$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{0}\left(\langle T\rangle\right)$
		K		K	Pa	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
1	40.67 ± 0.08	18791 ± 38	1.0000	446.31	0.2392	155.8 ± 0.3	241.5 ± 0.7
2	39.91 ± 0.17	18437 ± 76	0.9999	448.30	0.2958	153.3 ± 0.6	236.1 ± 1.4
3	40.08 ± 0.15	18530 ± 65	0.9999	446.32	0.2379	154.1 ± 0.6	237.5 ± 1.4
Global results				446.98		154.4 ± 0.5	238.4 ± 1.2

TABLE S9. Experimental results obtained for hexaphenylbenzene where a and b are from the Clausius-Clapeyron equation $\ln\left(p/\mathrm{Pa}\right)=a-b\cdot\left(\mathrm{K}/T\right)$, and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}\left(\langle T\rangle\right)/R$; R = 8.314472 J·K^{-1}·mol^{-1}.

Experience nº	a	b	r^2	$\langle T\rangle$	$p\left(\langle T\rangle\right)$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}\left(\langle T\rangle\right)$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{0}\left(\langle T\rangle\right)$
		K		K	Pa	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
1	38.82 ± 0.09	20234 ± 47	1.0000	500.48	0.2005	168.2 ± 0.4	227.0 ± 0.8
2	38.69 ± 0.13	20204 ± 66	0.9999	501.50	0.2016	168.0 ± 0.6	225.9 ± 1.1
Global results				500.99		168.1 ± 0.5	226.5 ± 0.9

TABLE S10. Crystal Data and Structure Refinement for 1,2,4-triphenylbenzene and 1,2,4,5-tetraphenylbenzene.

	1,2,4-Triphenylbenzene	**1,2,4,5-Tetraphenylbenzene**
empirical formula	$C_{24}H_{18}$	$C_{30}H_{22}$
formula weight	M_r = 306.38 mol.dm^{-3}	M_r = 382.48 mol.dm^{-3}
temp/K	123 (2) K	123 (2) K
λ/Å	0.71073 Å	0.71073 Å
crystal system	Orthorhombic, *Pbca*	Triclinic, *P-1*
cell constants	a = 10.3007(3) Å, b = 17.7674(5) Å, c = 18.3474(5) Å.	a = 5.8806 (12) Å, b = 7.4537 (15)) Å, c = 11.829 (2) Å, α = 83.746 (8)°, β = 89.648(8)°, γ = 81.157 (8)°
volume	V = 3357.88 (16)Å^3	V = 509.26 (18) Å^3
molecules per unit cell, Z	8	1
D_x	1.212 Mg m^{-3}	1.247 Mg m^{-3}
F(000)	1296	202
crystal size/shape/colour	0.40 × 0.40 × 0.16 mm (Plate, colourless)	0.34 × 0.06 × 0.02 mm (Needle, colourless)
θ range for data collection	3.02–27.5°	1.7–27.1°
Cell parameters	from 6418 reflections	from 1835 reflections
Absorption Coefficient	μ= 0.07 mm^{-1}	μ= 0.07 mm^{-1}
Radiation source:	fine-focus sealed tube	fine-focus sealed tube
Monochromator:	graphite	graphite
θ range	θ_{min} = 2.2°; θ_{max} = 33.3°; ω scans	θ_{min} = 1.7°; θ_{max} = 27.1°; ω scans
limiting indices	−15→14, −27→26, l = −28→24	h = −7→5 k = −9→9 l = −13→11
reflections collected/unique	57626 / 6418; 5001 with $I > 2\sigma(I)$; R_{int} = 0.031	3434 / 1835; 1289 with $I > 2\sigma(I)$; R_{int} = 0.025
Max and Min transmission	T_{min} = 0.973, T_{max} = 0.989	T_{min} = 0.976, T_{max} = 0.999
data/restraints/parameters	6418 / 0 / 217	1835 / 0 / 136
goodness-off-fit on F2	1.030	1.184
final R indices	$R[F^2 > 2\sigma(F^2)]$ = 0.046; $wR(F^2)$ = 0.121	$R[F^2 > 2\sigma(F^2)]$ = 0.054; $wR[(F^2 > 2\sigma(F^2)]$ =
final R indices (all data)	R = 0.064; $wR(F^2)$ = 0.137	R = 0.0863; $wR(F^2)$ = 0.180
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.40 e Å^{-3} and −0.23 e Å^{-3}	0.22 e Å^{-3} and −0.25 e Å^{-3}
refinement method	full matrix least-squares on F2	full matrix least-squares on F2
CCDC No.	736467	703163

The complete set of structural parameters in CIF format is available as an Electronic Supplementary Publication from the Cambridge Crystallographic Data Centre. Details may be obtained from The Director CCDC, 12 Union Road, Cambridge, CB21EZ, UK, e-mail:deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk, on request, quoting the depositary numbers ccdc 736467 and 703163.

TABLE S11. Total electronic energies (E_{el}) for the compounds considered in this work at the MP2/cc-pVDZ and B3LYP/6-311++G(d,p) levels of theory. The results for E_{el} obtained using the spin-component-scaled MP2 (SCS-MP2) approach are also shown.

Compound	E_{el} / Hartree		
	MP2	SCS-MP2	DFT
Benzene	-231.50645	-231.48534	-232.31130
Biphenyl	-461.85166	-461.80018	-463.42282
o-dPhB	-692.19797	-692.11467	-694.52848
m-dPhB	-692.19750	-692.11549	-694.53414
p-dPhB	-692.19741	-692.11544	-694.53450
123tPhB	-922.54480	-922.42938	-925.63321
124tPhB	-922.54435	-922.43041	-925.64008
135tPhB	-922.54394	-922.43126	-925.64542
1245TPhB	-1152.89177	-1152.74576	-1156.74572

TABLE S12. Phenyl-phenyl torsional potential energy profile in *o*-dPhB (σ_{int} = 2), calculated at the MP2/cc-pVDZ level of theory.

Φ(Ph-Ph) / º	**E_{el} (0 K) / Hartree**	**$\Delta_{rel}E_{el}$ / kJ·mol^{-1}**
0	-692.18581	31.9
30	-692.19570	6.0
52.085	-692.19797	0.0
60	-692.19774	0.6
90	-692.19434	9.5
120	-692.19779	0.5
127.915	-692.19797	0.0
150	-692.19570	6.0
180	-692.18581	31.9
210	-692.19570	6.0
232.085	-692.19797	0.0
240	-692.19779	0.5
270	-692.19434	9.5
300	-692.19774	0.6
307.915	-692.19797	0.0
330	-692.19570	6.0
360	-692.18581	31.9

TABLE S13. Phenyl-phenyl torsional potential energy profile in *p*-dPhB (σ_{int} = 2), calculated at the MP2/cc-pVDZ level of theory.

Φ(Ph-Ph) / º	E_{el} **(0 K) / Hartree**	$\Delta_{rel}E_{el}$ **/ kJ·mol^{-1}**
0	-692.19290	11.8
41.941	-692.19741	0.0
90	-692.19426	8.3
138.059	-692.19741	0.0
180	-692.19290	11.8
221.941	-692.19741	0.0
270	-692.19426	8.3
318.059	-692.19741	0.0
360	-692.19290	11.8

TABLE S14. Phenyl-phenyl torsional potential energy profile for the central phenyl substituent in 123tPhB (σ_{int} = 2), calculated at the MP2/cc-pVDZ level of theory.

Φ(Ph-Ph) / º	E_{el} **(0 K) / Hartree**	$\Delta_{rel}E_{el}$ **/ kJ·mol^{-1}**
0	-692.17365	63.9 **(58.8)**
30	-692.19342	12.0
52.085	-692.19797	0.0
60	-692.19750	1.2
90	-692.19071	19.1
120	-692.19760	1.0
127.915	-692.19797	0.0
150	-692.19342	12.0
180	-692.17365	63.9 **(58.8)**
210	-692.19342	12.0
232.085	-692.19797	0.0
240	-692.19760	1.0
270	-692.19071	19.1
300	-692.19750	1.2
307.915	-692.19797	0.0
330	-692.19342	12.0
360	-692.17365	63.9 **(58.8)**

The barrier height (in bold) was calculated for the 123tPhB molecule. The remaining values were derived according to the *o*-dPhB torsional profile.

Optimized geometries, in Cartesians coordinates, of the molecules considered in this work, at the MP2/cc-pVDZ level of theory.

1. Benzene

1	6	0	0.000000	1.405732	0.000000
2	6	0	1.217400	0.702866	0.000000
3	6	0	1.217400	-0.702866	0.000000
4	6	0	0.000000	-1.405732	0.000000
5	6	0	-1.217400	-0.702866	0.000000
6	6	0	-1.217400	0.702866	0.000000
7	1	0	0.000000	2.500950	0.000000
8	1	0	2.165887	1.250475	0.000000
9	1	0	2.165887	-1.250475	0.000000
10	1	0	0.000000	-2.500950	0.000000
11	1	0	-2.165887	-1.250475	0.000000
12	1	0	-2.165887	1.250475	0.000000

2. Biphenyl

1	6	0	0.000000	0.000000	-0.742542
2	6	0	-0.445550	1.130518	-1.463190
3	6	0	-0.444428	1.130940	-2.867336
4	6	0	0.000000	0.000000	-3.574331
5	6	0	0.444428	-1.130940	-2.867336
6	6	0	0.445550	-1.130518	-1.463190
7	6	0	0.000000	0.000000	0.742542
8	6	0	0.445550	1.130518	1.463190
9	6	0	0.444428	1.130940	2.867336
10	6	0	0.000000	0.000000	3.574331
11	6	0	-0.444428	-1.130940	2.867336
12	6	0	-0.445550	-1.130518	1.463190
13	1	0	-0.818406	2.003207	-0.915547
14	1	0	-0.800472	2.012706	-3.410900
15	1	0	0.000000	0.000000	-4.669355
16	1	0	0.800472	-2.012706	-3.410900
17	1	0	0.818406	-2.003207	-0.915547
18	1	0	0.818406	2.003207	0.915547
19	1	0	0.800472	2.012706	3.410900
20	1	0	0.000000	0.000000	4.669355
21	1	0	-0.800472	-2.012706	3.410900
22	1	0	-0.818406	-2.003207	0.915547

3. o-terphenyl

1	6	0	0.080119	-0.706619	1.243822
2	6	0	0.150247	-1.389274	2.478405
3	6	0	0.072897	-0.698867	3.698051
4	6	0	-0.072897	0.698867	3.698051
5	6	0	-0.150247	1.389274	2.478405
6	6	0	-0.080119	0.706619	1.243822
7	1	0	0.297452	-2.475292	2.471119
8	1	0	0.136026	-1.248844	4.643047
9	1	0	-0.136026	1.248844	4.643047
10	1	0	-0.297452	2.475292	2.471119
11	6	0	-0.211062	1.483833	-0.017842
12	6	0	-1.162287	1.122279	-0.997772
13	6	0	0.601056	2.617197	-0.241331
14	6	0	-1.292565	1.874761	-2.175084
15	1	0	-1.802564	0.250007	-0.828668
16	6	0	0.473264	3.367386	-1.422758
17	1	0	1.350048	2.895194	0.509242
18	6	0	-0.473264	2.997298	-2.393600
19	1	0	-2.037443	1.585345	-2.924240
20	1	0	1.116500	4.238774	-1.586759
21	1	0	-0.573219	3.580602	-3.315083
22	6	0	0.211062	-1.483833	-0.017842
23	6	0	-0.601056	-2.617197	-0.241331

24	6	0	1.162287	-1.122279	-0.997772
25	6	0	-0.473264	-3.367386	-1.422758
26	1	0	-1.350048	-2.895194	0.509242
27	6	0	1.292565	-1.874761	-2.175084
28	1	0	1.802564	-0.250007	-0.828668
29	6	0	0.473264	-2.997298	-2.393600
30	1	0	-1.116500	-4.238774	-1.586759
31	1	0	2.037443	-1.585345	-2.924240
32	1	0	0.573219	-3.580602	-3.315083

4. m-terphenyl

1	6	0	-2.513033	0.004163	-0.003483
2	6	0	-3.584501	0.576469	0.717966
3	6	0	-4.796943	-0.115618	0.868054
4	6	0	-4.957262	-1.392325	0.301615
5	6	0	-3.897005	-1.971901	-0.417069
6	6	0	-2.685487	-1.278831	-0.569572
7	6	0	-1.230654	0.735023	-0.163807
8	6	0	-1.218402	2.118182	-0.451498
9	6	0	0.000035	2.801989	-0.591734
10	6	0	1.218436	2.118131	-0.451534
11	6	0	1.230662	0.734985	-0.163829
12	6	0	-0.000001	0.059736	-0.019450
13	1	0	-3.453228	1.559060	1.184626
14	1	0	-5.615203	0.338575	1.437158
15	1	0	-5.902506	-1.932353	0.419732
16	1	0	-4.017264	-2.962517	-0.868661
17	1	0	-1.870726	-1.721371	-1.153454
18	1	0	-2.166613	2.648645	-0.591788
19	1	0	0.000060	3.870785	-0.831869
20	1	0	2.166626	2.648619	-0.591880
21	1	0	-0.000101	-1.001005	0.257199
22	6	0	2.513034	0.004129	-0.003497
23	6	0	2.685395	-1.278970	-0.569349
24	6	0	3.584572	0.576535	0.717740
25	6	0	3.896897	-1.972051	-0.416817
26	1	0	1.870592	-1.721673	-1.153056
27	6	0	4.797016	-0.115543	0.867850
28	1	0	3.453444	1.559220	1.184254
29	6	0	4.957247	-1.392365	0.301647
30	1	0	4.017073	-2.962769	-0.868210
31	1	0	5.615336	0.338761	1.436776
32	1	0	5.902482	-1.932414	0.419781

5. p-terphenyl

1	6	0	5.034897	-1.186393	-0.263081
2	6	0	3.630866	-1.186205	-0.264563
3	6	0	2.909989	0.000000	0.000000
4	6	0	3.630867	1.186205	0.264564
5	6	0	5.034898	1.186393	0.263080
6	6	0	5.741889	0.000000	0.000000
7	6	0	1.426367	0.000000	0.000000
8	6	0	0.701041	-1.057021	0.594821
9	6	0	-0.701039	-1.057018	0.594819
10	6	0	-1.426368	0.000000	0.000000
11	6	0	-0.701038	1.057018	-0.594819
12	6	0	0.701041	1.057021	-0.594821
13	6	0	-2.909981	0.000000	0.000000
14	6	0	-3.630868	-1.186179	-0.264658
15	6	0	-5.034896	-1.186373	-0.263163
16	6	0	-5.741895	0.000000	0.000000
17	6	0	-5.034897	1.186373	0.263163
18	6	0	-3.630868	1.186179	0.264658
19	1	0	5.578497	-2.112715	-0.477884
20	1	0	3.083414	-2.106171	-0.497923
21	1	0	3.083414	2.106171	0.497923
22	1	0	5.578496	2.112715	0.477884
23	1	0	6.836905	0.000000	0.000000

24	1	0	1.244330	-1.867447	1.093728
25	1	0	-1.244302	-1.867401	1.093827
26	1	0	-1.244301	1.867406	-1.093819
27	1	0	1.244329	1.867451	-1.093721
28	1	0	-3.083440	-2.106123	-0.498162
29	1	0	-5.578497	-2.112685	-0.478006
30	1	0	-6.836910	0.000000	0.000000
31	1	0	-5.578497	2.112685	0.478005
32	1	0	-3.083439	2.106123	0.498162

6. 1,2,3-triphenylbenzene

1	6	0	0.000029	-0.709196	0.000017
2	6	0	-1.228184	-1.426135	0.024768
3	6	0	-1.212925	-2.837874	0.018143
4	6	0	0.000132	-3.542524	0.000034
5	6	0	1.213137	-2.837788	-0.018104
6	6	0	1.228299	-1.426050	-0.024762
7	6	0	-0.000051	0.780087	0.000027
8	6	0	-0.671523	1.496311	-1.014616
9	6	0	-0.667386	2.900547	-1.016920
10	6	0	-0.000222	3.606917	0.000038
11	6	0	0.667007	2.900620	1.017005
12	6	0	0.671302	1.496385	1.014697
13	1	0	-2.165952	-3.377283	0.057560
14	1	0	0.000171	-4.637877	0.000058
15	1	0	2.166205	-3.377131	-0.057488
16	1	0	-1.196165	0.944839	-1.802885
17	1	0	-1.188274	3.444476	-1.812463
18	1	0	-0.000285	4.702189	0.000041
19	1	0	1.187820	3.444606	1.812558
20	1	0	1.195985	0.944973	1.802979
21	6	0	2.540275	-0.725712	-0.086112
22	6	0	3.548351	-1.033185	0.853679
23	6	0	2.812559	0.229293	-1.090813
24	6	0	4.797726	-0.392086	0.798836
25	1	0	3.338949	-1.765125	1.642458
26	6	0	4.062213	0.865299	-1.147801
27	1	0	2.040170	0.468050	-1.829258
28	6	0	5.057545	0.560299	-0.201555
29	1	0	5.566835	-0.633746	1.540513
30	1	0	4.260656	1.601007	-1.934711
31	1	0	6.030308	1.061552	-0.244830
32	6	0	-2.540195	-0.725863	0.086104
33	6	0	-3.548164	-1.033202	-0.853849
34	6	0	-2.812582	0.229024	1.090887
35	6	0	-4.797560	-0.392144	-0.799030
36	1	0	-3.338659	-1.765000	-1.642733
37	6	0	-4.062259	0.864988	1.147850
38	1	0	-2.040260	0.467713	1.829426
39	6	0	-5.057501	0.560083	0.201481
40	1	0	-5.566587	-0.633705	-1.540825
41	1	0	-4.260788	1.600589	1.934839
42	1	0	-6.030279	1.061310	0.244733

7. 1,2,4-triphenylbenzene

1	6	0	1.575633	-1.901845	-0.173799
2	6	0	2.075298	-0.585921	-0.055739
3	6	0	1.149065	0.473580	0.046296
4	6	0	-0.243941	0.253406	0.023352
5	6	0	-0.735402	-1.075046	-0.108894
6	6	0	0.193864	-2.135373	-0.200616
7	1	0	2.273643	-2.739190	-0.284613
8	1	0	1.516533	1.494908	0.201880
9	1	0	-0.183232	-3.155547	-0.336716
10	6	0	-2.188387	-1.376789	-0.191847
11	6	0	-2.754813	-2.373998	0.632436
12	6	0	-3.019981	-0.697245	-1.110177
13	6	0	-4.123977	-2.678970	0.548635

14	1	0	-2.117845	-2.895211	1.356482
15	6	0	-4.386173	-1.005797	-1.196234
16	1	0	-2.587279	0.070523	-1.760309
17	6	0	-4.943818	-1.994540	-0.365150
18	1	0	-4.551381	-3.448257	1.200916
19	1	0	-5.017957	-0.474303	-1.916092
20	1	0	-6.011174	-2.230761	-0.430754
21	6	0	-1.154291	1.417867	0.188535
22	6	0	-0.997451	2.561564	-0.624873
23	6	0	-2.166547	1.414818	1.174109
24	6	0	-1.840136	3.674641	-0.464564
25	1	0	-0.222268	2.564404	-1.399987
26	6	0	-3.004409	2.528709	1.336632
27	1	0	-2.288784	0.535861	1.815899
28	6	0	-2.847043	3.660558	0.515976
29	1	0	-1.712959	4.551379	-1.108858
30	1	0	-3.781971	2.514608	2.108015
31	1	0	-3.504899	4.527055	0.641514
32	6	0	3.534481	-0.321097	-0.026743
33	6	0	4.080806	0.777280	-0.728204
34	6	0	4.406064	-1.161021	0.702395
35	6	0	5.461572	1.029795	-0.699956
36	1	0	3.418256	1.419939	-1.318608
37	6	0	5.787222	-0.910046	0.727826
38	1	0	3.991320	-1.999369	1.273048
39	6	0	6.319826	0.186502	0.027376
40	1	0	5.870010	1.881035	-1.255188
41	1	0	6.448308	-1.566050	1.304318
42	1	0	7.396899	0.382792	0.048420

8. 1,3,5-triphenylbenzene

1	6	0	0.000924	-1.404252	0.000001
2	6	0	-1.227247	-0.710978	-0.040579
3	6	0	-1.215217	0.700161	-0.044288
4	6	0	-0.000932	1.417799	-0.000001
5	6	0	1.214298	0.701760	0.044288
6	6	0	1.228182	-0.709361	0.040581
7	1	0	0.001649	-2.500354	0.000004
8	1	0	-2.161179	1.246627	-0.133259
9	1	0	2.159542	1.249466	0.133253
10	6	0	2.513068	-1.450461	0.102057
11	6	0	3.619976	-1.034225	-0.671203
12	6	0	2.653520	-2.584726	0.932761
13	6	0	4.836194	-1.733452	-0.614431
14	1	0	3.514260	-0.171501	-1.338430
15	6	0	3.869115	-3.285426	0.986849
16	1	0	1.810910	-2.900104	1.558113
17	6	0	4.964678	-2.862083	0.214071
18	1	0	5.682601	-1.402592	-1.225866
19	1	0	3.964515	-4.158078	1.641892
20	1	0	5.912879	-3.408062	0.257538
21	6	0	-0.001911	2.902139	0.000000
22	6	0	-0.936460	3.621982	0.777734
23	6	0	0.931688	3.623217	-0.777732
24	6	0	-0.938290	5.026005	0.776412
25	1	0	-1.647463	3.073592	1.405672
26	6	0	0.931664	5.027241	-0.776408
27	1	0	1.643413	3.075766	-1.405672
28	6	0	-0.003780	5.733522	0.000002
29	1	0	-1.664282	5.569286	1.390814
30	1	0	1.656937	5.571480	-1.390810
31	1	0	-0.004503	6.828537	0.000003
32	6	0	-2.511154	-1.453763	-0.102058
33	6	0	-3.618631	-1.038946	0.671150
34	6	0	-2.650091	-2.588254	-0.932709
35	6	0	-4.833928	-1.739773	0.614375
36	1	0	-3.514072	-0.176054	1.338342
37	6	0	-3.864760	-3.290555	-0.986797
38	1	0	-1.807050	-2.902558	-1.558022

39	6	0	-4.960904	-2.868614	-0.214075
40	1	0	-5.680786	-1.409994	1.225768
41	1	0	-3.958991	-4.163366	-1.641798
42	1	0	-5.908385	-3.415841	-0.257542

9. 1,2,4,5-tetraphenylbenzene

1	6	0	-1.236979	0.710293	-0.033240
2	6	0	0.000010	1.386903	-0.064437
3	6	0	1.236996	0.710269	-0.033279
4	6	0	1.236980	-0.710302	0.033253
5	6	0	-0.000014	-1.386912	0.064448
6	6	0	-1.236992	-0.710279	0.033279
7	1	0	0.000015	2.477832	-0.177991
8	1	0	-0.000022	-2.477844	0.177986
9	6	0	2.491445	-1.501668	0.124280
10	6	0	3.480568	-1.188361	1.083593
11	6	0	2.698241	-2.604260	-0.733853
12	6	0	4.650251	-1.957949	1.176441
13	1	0	3.323625	-0.341702	1.760288
14	6	0	3.872073	-3.371313	-0.642978
15	1	0	1.940251	-2.844096	-1.488577
16	6	0	4.852161	-3.049196	0.311658
17	1	0	5.406351	-1.706910	1.928192
18	1	0	4.023153	-4.218140	-1.321214
19	1	0	5.767744	-3.645823	0.383024
20	6	0	2.491467	1.501617	-0.124304
21	6	0	2.698179	2.604303	0.733734
22	6	0	3.480681	1.188220	-1.083496
23	6	0	3.872002	3.371363	0.642871
24	1	0	1.940134	2.844194	1.488384
25	6	0	4.650356	1.957825	-1.176336
26	1	0	3.323817	0.341499	-1.760123
27	6	0	4.852171	3.049169	-0.311657
28	1	0	4.023016	4.218249	1.321048
29	1	0	5.406517	1.706724	-1.928004
30	1	0	5.767754	3.645799	-0.383014
31	6	0	-2.491488	-1.501616	0.124214
32	6	0	-2.698332	-2.604014	-0.734157
33	6	0	-3.480535	-1.188554	1.083685
34	6	0	-3.872161	-3.371086	-0.643391
35	1	0	-1.940378	-2.843681	-1.488971
36	6	0	-4.650212	-1.958165	1.176427
37	1	0	-3.323530	-0.342082	1.760592
38	6	0	-4.852186	-3.049194	0.311383
39	1	0	-4.023284	-4.217751	-1.321820
40	1	0	-5.406257	-1.707322	1.928298
41	1	0	-5.767771	-3.645830	0.382664
42	6	0	-2.491461	1.501649	-0.124189
43	6	0	-3.480757	1.188246	-1.083292
44	6	0	-2.698049	2.604401	0.733791
45	6	0	-4.650424	1.957869	-1.176055
46	1	0	-3.323954	0.341498	-1.759900
47	6	0	-3.871868	3.371485	0.643005
48	1	0	-1.939902	2.844336	1.488325
49	6	0	-4.852141	3.049252	-0.311398
50	1	0	-5.406664	1.706757	-1.927641
51	1	0	-4.022790	4.218428	1.321133
52	1	0	-5.767717	3.645899	-0.382692