

## **Photochemical Synthesis of Benzoyl Spiro[2.2]pentane**

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# 1 Supplementary Information

## 1.1.1 Quantum chemical calculations (B3PW91/6-31G\*//B3PW91/6-31G\*)

The geometry optimization were performed with the *ab initio* program package GAUSSIAN 98<sup>1</sup>, the B3PW91 hybrid functional<sup>2,3,4</sup>, and the 6-31G\* basis set. At the same level of theory, frequency calculations were carried out to characterize each structure as minimum (**21**, **22**, **15**, **12**) or transition state (**TS-21**, **TS-22**, **TS-15**, **TS-12**) and to obtain the zero-point vibrational energies.

structure	E [a.u.] <sup>[a]</sup>	E [kcal/mol]	ZPE [kcal/mol] <sup>[b]</sup>	E + ZPE [kcal/mol]	E <sub>rel</sub> [kcal/mol] <sup>[c]</sup>
<b>21</b>	- 541.8378692	- 340008.41	156.81579	- 339851.87	± 0.0
<b>TS-21</b>	- 541.8315906	- 340004.47	153.68497	- 339851.06	+ 3.9 (+ 0.8)
<b>22</b>	- 1204.7942852	- 756019.86	183.58912	- 755836.87	± 0.0
<b>TS-22</b>	- 1204.7920961	- 756018.49	181.14821	- 755837.94	+ 1.4 (- 1.1)
<b>15</b>	- 540.5962682	- 339229.29	142.91041	- 339086.65	± 0.0
<b>TS-15</b>	- 540.5803766	- 339219.32	139.23719	- 339080.35	+ 10.0 (+ 6.3)
<b>12</b>	- 1203.5534998	- 755241.26	169.80897	- 755072.05	± 0.0
<b>TS-12</b>	- 1203.5416236	- 755233.80	166.41963	- 755067.98	+ 7.5 (+ 4.1)

[a]: Electronic energy (B3PW91/6-31G\*), 1 a.u. = 627.5095 kcal/mol. [b] Zero-point vibrational energy (B3PW91/6-31G\*).

[c]: Energy relating to **21**, **22**, **15** or **12** respectively. The value in parentheses includes the zero-point vibrational energy.

<b>structure:</b>	<b>12</b>			
<b>method:</b>	B3PW91/6-31G*//B3PW91/6-31G*			
<b>cartesian coordinates:</b>	H	- .455955	3 .289255	- .339516
	O	.768159	1 .356362	-1 .981267
	C	-1 .342396	2 .802176	.062847

<sup>1</sup> Gaussian 98, Revision A.9, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

<sup>2</sup> B3PW91 = BECKES 3-parameter functional (B3) with the nonlocal correlation provided by the PERDEW-WANG 91 expression (PW91).

<sup>3</sup> A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

<sup>4</sup> J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671-6687.

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C	-1.661944	1.464061	-.562242
C	.770277	.725343	-.825877
O	-1.237228	-1.902198	1.427657
C	-.593582	.411128	-.271536
O	-1.012196	-.876208	-.861173
S	-1.848196	-1.900761	.099255
C	-1.427781	-3.401162	-.768671
O	-3.277718	-1.650470	-.031513
H	-1.759949	-3.309118	-1.803878
H	-.348680	-3.549292	-.713409
H	-1.957842	-4.215318	-.269404
C	2.014719	.277753	-.272834
H	-.482002	.264335	.806631
H	-1.786706	1.559130	-1.647799
H	-2.611041	1.081880	-.167730
C	-2.458907	3.720616	.481770
C	-1.619144	3.038064	1.526262
C	2.067855	-.609739	.831331
C	3.292982	-1.004455	1.347846
C	4.492195	-.557145	.783752
C	4.450659	.303646	-.316837
C	3.238069	.718597	-.843190
H	1.155098	-.998204	1.273060
H	3.312758	-1.678353	2.200850
H	5.445205	-.876722	1.195839
H	5.375519	.659471	-.764333
H	3.215843	1.402984	-1.686805
H	-3.480527	3.374214	.345143
H	-2.327822	4.788265	.328475
H	-.911637	3.635044	2.095042
H	-2.077269	2.231420	2.094406

**structure:****TS-12****method:**

B3PW91/6-31G\*\*/B3PW91/6-31G\*

**cartesian coordinates:**

O	.582406	2.242756	.409456
C	-1.800697	2.222514	-.150373
C	-1.470652	1.193275	-1.187016
C	.797747	1.033859	-.128654
O	-3.134396	-1.591750	-.136511
C	-.365246	.271459	-.678435
O	-.890383	-.569864	.431039
S	-1.716400	-1.909599	.011709
C	-1.470538	-2.807833	1.533460
O	-1.014402	-2.577507	-1.082500
H	-.402490	-2.982783	1.668327
H	-1.878673	-2.219219	2.356429
H	-2.009678	-3.752733	1.435709
C	2.127849	.506564	-.065308
H	-.040084	-.413221	-1.464880
H	-1.114440	1.677621	-2.105149
H	-2.358393	.597722	-1.440466
C	-2.838408	3.278066	-.194781
C	2.441325	-.806103	-.501149
C	3.744603	-1.277817	-.442712
C	4.776480	-.475949	.053224
C	4.480874	.816200	.497456

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C	3.184740	1.304251	.443651
H	1.661012	-1.464892	-.871197
H	3.958079	-2.288042	-.783969
H	5.794389	-.853714	.095890
H	5.273319	1.450039	.888724
H	2.964017	2.310101	.786668
H	-3.544482	3.262140	-1.023534
H	-2.594755	4.276535	.161442
C	-2.885829	2.172549	.856249
H	-2.670327	2.469965	1.879990
H	-3.614765	1.369869	.764318
H	-.639631	2.498917	.278791

**structure:****15****method:**

B3PW91/6-31G\*\*/B3PW91/6-31G\*

**cartesian coordinates:**

H	1.452292	-.589715	-1.171676
O	-.208152	2.589051	-.308410
C	2.314159	-.446213	-.522004
C	2.389772	.916740	.124479
C	-.128676	1.410186	.272875
C	1.184094	1.253877	1.020660
C	-1.178113	.460572	.148151
H	1.384576	2.190164	1.557967
H	2.491690	1.693539	-.644382
H	3.295215	.974088	.745983
C	3.573095	-1.154122	-.940575
C	-1.087803	-.848031	.696754
C	-2.140333	-1.739446	.567676
C	-3.310676	-1.382375	-.112122
C	-3.410338	-.101008	-.666702
C	-2.373524	.807453	-.545880
H	-.183866	-1.161581	1.209631
H	-2.046989	-2.733332	.999429
H	-4.128850	-2.090263	-.208947
H	-4.313716	.191333	-1.197126
H	-2.469071	1.802975	-.971299
H	4.523808	-.668536	-.731840
H	3.561510	-1.724986	-1.865131
C	2.776427	-1.669338	.228796
H	2.219853	-2.594666	.106830
H	3.194023	-1.529878	1.223979
H	1.036235	.478672	1.781211

**structure:****TS-15****method:**

B3PW91/6-31G\*\*/B3PW91/6-31G\*

**cartesian coordinates:**

O	.704571	-1.146299	.060348
C	2.914344	-.111149	-.116839
C	2.227471	1.132090	-.597923
C	.056058	.033459	.027954
C	.886520	1.290791	.130126
C	-1.365631	-.007513	.023467
H	.334447	2.138029	-.286358
H	2.058969	1.071158	-1.680276
H	2.860934	2.012176	-.408374
C	4.230735	-.666364	-.505881
C	-2.164240	1.166691	.105179

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C	-3.547907	1.090983	.082741
C	-4.199811	-.143041	-.011529
C	-3.431213	-1.310852	-.082161
C	-2.048240	-1.254362	-.064809
H	-1.693792	2.141210	.198117
H	-4.129977	2.007866	.145759
H	-5.285024	-.193734	-.027042
H	-3.922980	-2.278623	-.153765
H	-1.463279	-2.166641	-.125769
H	4.875447	-.053541	-1.134435
H	4.324843	-1.735220	-.685302
C	3.959718	-.231486	.929981
H	3.878535	-1.020854	1.674001
H	4.417833	.684351	1.301102
H	1.082662	1.529057	1.189464
H	1.917986	-.900324	-.011740

**structure: 21****method: B3PW91/6-31G\*\*/B3PW91/6-31G\***

<b>cartesian coordinates:</b>	H	1.811522	-.065775	-1.253166
	O	.240921	2.243880	-.090571
	C	2.542798	-.424292	-.514053
	C	2.476988	.514233	.699031
	C	-.020323	1.081252	.469671
	C	1.106163	.634449	1.386554
	C	-1.247444	.412954	.204284
	H	1.189064	1.350542	2.216619
	H	2.805635	1.515000	.391352
	H	3.196798	.172977	1.457951
	C	3.932082	-.350976	-1.153061
	C	-1.615222	-.805497	.837775
	C	-2.821260	-1.419876	.541695
	C	-3.711341	-.858634	-.380680
	C	-3.368938	.345397	-1.006572
	C	-2.168887	.974982	-.726984
	H	-.958766	-1.264160	1.571012
	H	-3.075337	-2.351699	1.041585
	H	-4.654349	-1.348771	-.604807
	H	-4.050466	.796632	-1.724070
	H	-1.915025	1.907164	-1.224813
	H	4.705156	-.699981	-.455715
	H	4.185846	.674908	-1.445637
	H	3.988334	-.978231	-2.050293
	C	2.185921	-1.869482	-.158181
	H	1.154382	-1.964301	.197485
	H	2.854028	-2.259309	.621706
	H	2.285747	-2.520820	-1.034142
	H	.806844	-.322278	1.822632

**structure: TS-21****method: B3PW91/6-31G\*\*/B3PW91/6-31G\***

<b>cartesian coordinates:</b>	O	.670994	-1.135357	.228723
	C	2.958788	-.133199	-.027011
	C	2.221488	1.040212	-.661367
	C	.029835	.026630	.044149
	C	.861697	1.287251	.000743

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C	-1.393498	-.007118	.023549
H	.321885	2.064626	-.548414
H	2.068633	.838560	-1.728701
H	2.835859	1.951079	-.588862
C	3.901443	-.873664	-.954067
C	-2.183947	1.174042	-.031005
C	-3.567774	1.104004	-.065333
C	-4.227438	-.129215	-.037900
C	-3.466500	-1.302454	.026986
C	-2.083579	-1.252511	.058913
H	-1.707263	2.149959	-.033674
H	-4.143970	2.025799	-.107705
H	-5.312653	-.174962	-.063866
H	-3.964264	-2.269526	.050862
H	-1.504752	-2.169921	.102619
H	4.744628	-.223880	-1.233154
H	3.398836	-1.179340	-1.877764
H	4.319665	-1.766082	-.475974
C	3.531645	.132981	1.352723
H	2.799295	.593140	2.023308
H	4.391258	.815068	1.275528
H	3.885830	-.791088	1.822079
H	1.010340	1.680974	1.020737
H	1.995758	-.863313	.150912

**structure:****22****method:**

B3PW91/6-31G\*//B3PW91/6-31G\*

**cartesian coordinates:**

H	1.409856	-2.790061	.377232
C	2.240514	-2.171725	-.020049
C	1.610713	-1.182119	-1.007202
C	-.732053	-1.118242	.034725
O	2.833351	2.029250	-.222717
C	.426493	-.345543	-.537535
O	.833892	.643040	.487742
S	1.387541	2.084544	-.045797
C	1.007141	3.020886	1.424277
O	.544337	2.529646	-1.154289
H	-.070953	2.997695	1.587599
H	1.542332	2.579887	2.266582
H	1.351308	4.042279	1.247104
C	-2.095962	-.667436	-.013913
H	.038583	.229192	-1.383973
H	1.255069	-1.738688	-1.885475
H	2.378997	-.486297	-1.371120
C	3.194482	-3.111272	-.763163
C	-2.452198	.600548	-.538340
C	-3.783903	.985411	-.589602
C	-4.795723	.149049	-.107702
C	-4.454222	-1.095282	.429721
C	-3.131206	-1.504089	.480061
H	-1.690160	1.286768	-.895482
H	-4.035802	1.957819	-1.005826
H	-5.834716	.463642	-.149839
H	-5.230785	-1.756459	.806686
H	-2.877780	-2.481536	.880254
H	4.035387	-2.548924	-1.189983

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H	2.691772	-3.637450	-1.583124
H	3.610575	-3.863630	-.084093
C	2.938912	-1.511062	1.169249
H	2.236824	-.953132	1.793045
H	3.711451	-.810789	.828033
H	3.422589	-2.269761	1.795491
O	-.459472	-2.185436	.756323

**structure:** TS-22**method:** B3PW91/6-31G\*\*/B3PW91/6-31G\*

<b>cartesian coordinates:</b>	O	.494245	2.222724	.560941
	C	-1.969044	2.256613	-.022431
	C	-1.594777	1.179308	-1.035865
	C	.719301	1.055299	-.040643
	O	-3.008416	-1.893543	-.141847
	C	-.436936	.286495	-.599002
	O	-.876600	-.668866	.457509
	S	-1.562699	-2.062840	-.041584
	C	-1.179518	-3.030978	1.407473
	O	-.817513	-2.572612	-1.191202
	H	-.095600	-3.086789	1.515110
	H	-1.636495	-2.555848	2.276822
	H	-1.605675	-4.024000	1.248054
	C	2.063763	.552088	-.032173
	H	-.102870	-.326656	-1.439676
	H	-1.283905	1.657502	-1.973477
	H	-2.463842	.547478	-1.264582
	C	-2.486393	3.537942	-.650036
	C	2.393431	-.729915	-.540244
	C	3.707863	-1.174397	-.533536
	C	4.733824	-.376711	-.019367
	C	4.421672	.885023	.495130
	C	3.114813	1.346873	.492915
	H	1.620295	-1.385323	-.930318
	H	3.934497	-2.160652	-.931774
	H	5.760015	-.733871	-.017760
	H	5.209225	1.516187	.900329
	H	2.882511	2.330498	.889198
	H	-3.449457	3.348474	-1.146606
	H	-1.794941	3.929089	-1.404055
	H	-2.652699	4.314374	.104081
	C	-2.782336	1.785212	1.169777
	H	-2.306657	.943270	1.676781
	H	-3.774037	1.450644	.833277
	H	-2.929223	2.596657	1.890747
	H	-.875663	2.505648	.403994