Supplementary Information

Paracyclophanes as Model Compounds for Strongly Interacting π-Systems,

Part 2: *Mono*–hydroxy[2.2]paracyclophane

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The supporting information contains a comparison of the excited state twist potential computed at different levels, mass spectrum, solution phase UV/Vis spectra, a hole burning spectrum (SHB), a list of peaks observed in the REMPI spectra and Cartesian coordinates of the most important stationary points of the computations.
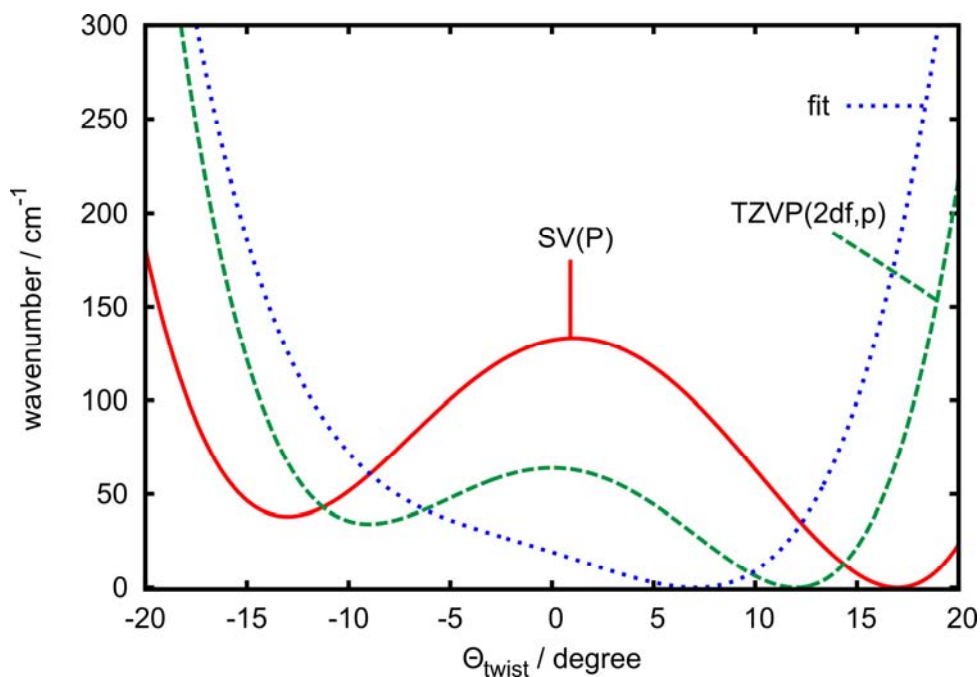

Figure S1: The potential energy curves of the excited sate of MHPC as a function of the twist coordinate at different levels of theory. The SV(P) [TZV(2df,p)] curve is the curve, obtained by optimizing the structure of the molecule for given θ_{twist} values at the SCS-CC2/SV(P) [SCS-CC2/TZV(2df,p)] level. The fitted curve is a fourth order polynomial that provides relative term energies and intensities fitting best to the corresponding experimental values.
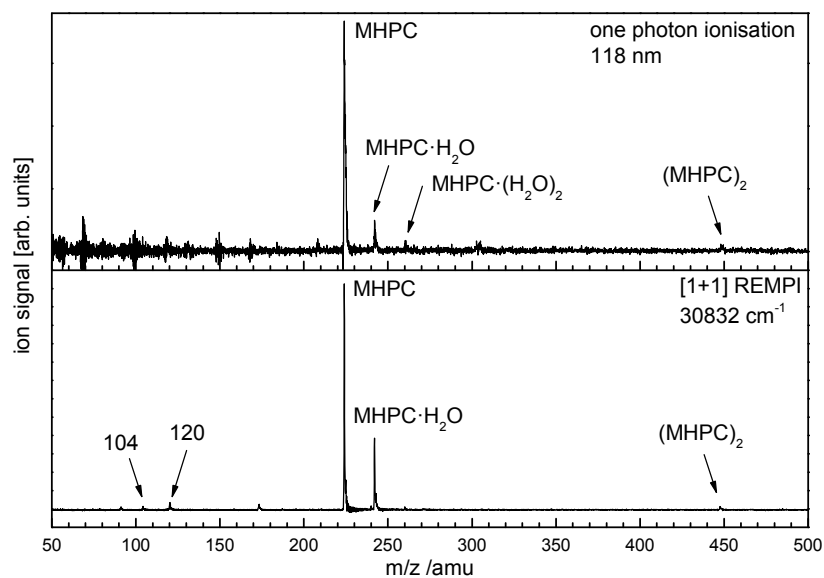
Figure S2: Mass spectra of MHPC using one-photon ionisation at 118 nm (upper trace) and [1+1] ionisation through the T^3 band (lower trace). The mass spectrum at 118 nm was obtained by focusing the third harmonic of a Nd:YAG laser at 355 nm into a cell filled with 23 mbar of xenon. The VUV light was focused into the ionisation region by a 100 mm MgF_2 lens mounted at the exit of the cell. A small signal due water clusters is visible, but no significant fragmentation of MHPC is evident. The signals at m/z = 104 and m/z = 120 originate from dissociative photoionization of the unsymmetric cyclophane and correspond to substituted benzene ($\cdot CH_2\text{-}C_6H_4\text{-}CH_2\cdot$) and phenol ($\cdot CH_2\text{-}C_6H_3OH\text{-}CH_2\cdot$) subunits. Their low intensity indicates that higher order photon processes are not important.
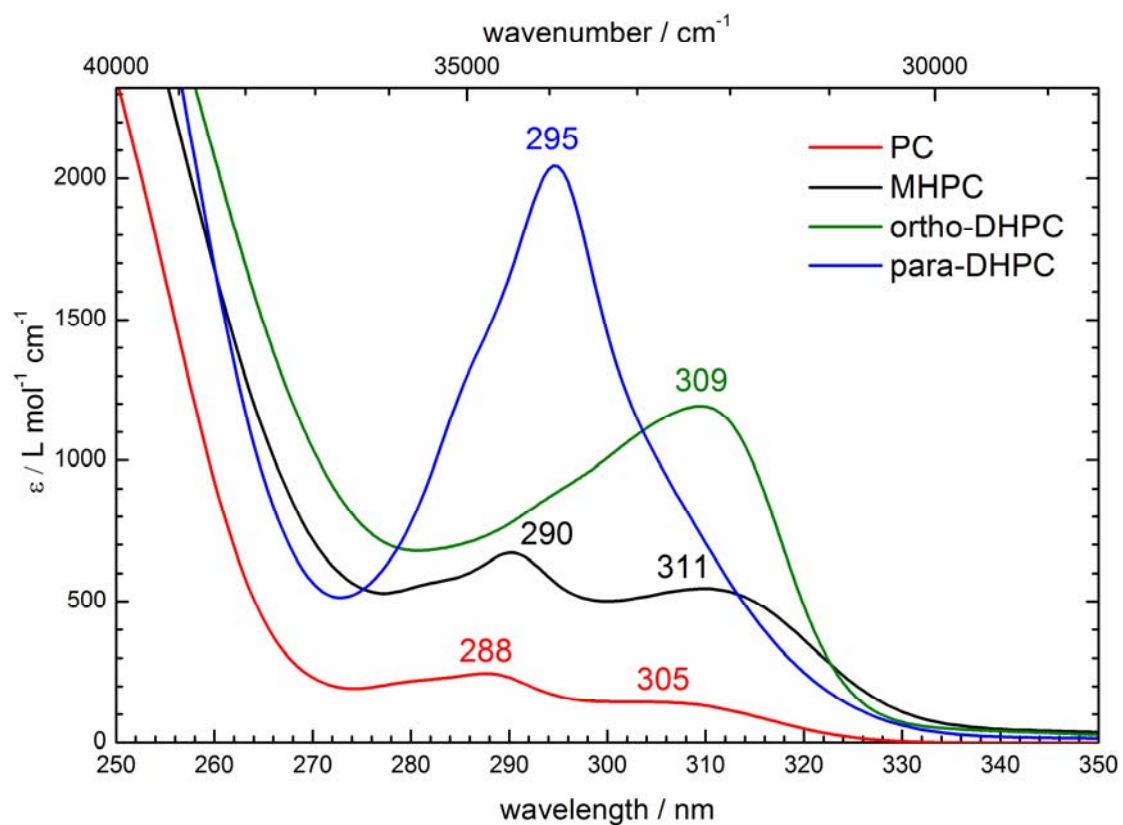
Figure S3: UV/Vis spectra of hydroxyl-substituted [2.2]paracyclophanes, recorded in CH_2Cl_2. As visible the onset of the spectrum as well as the absorption maximum depend strongly on the substitution pattern.
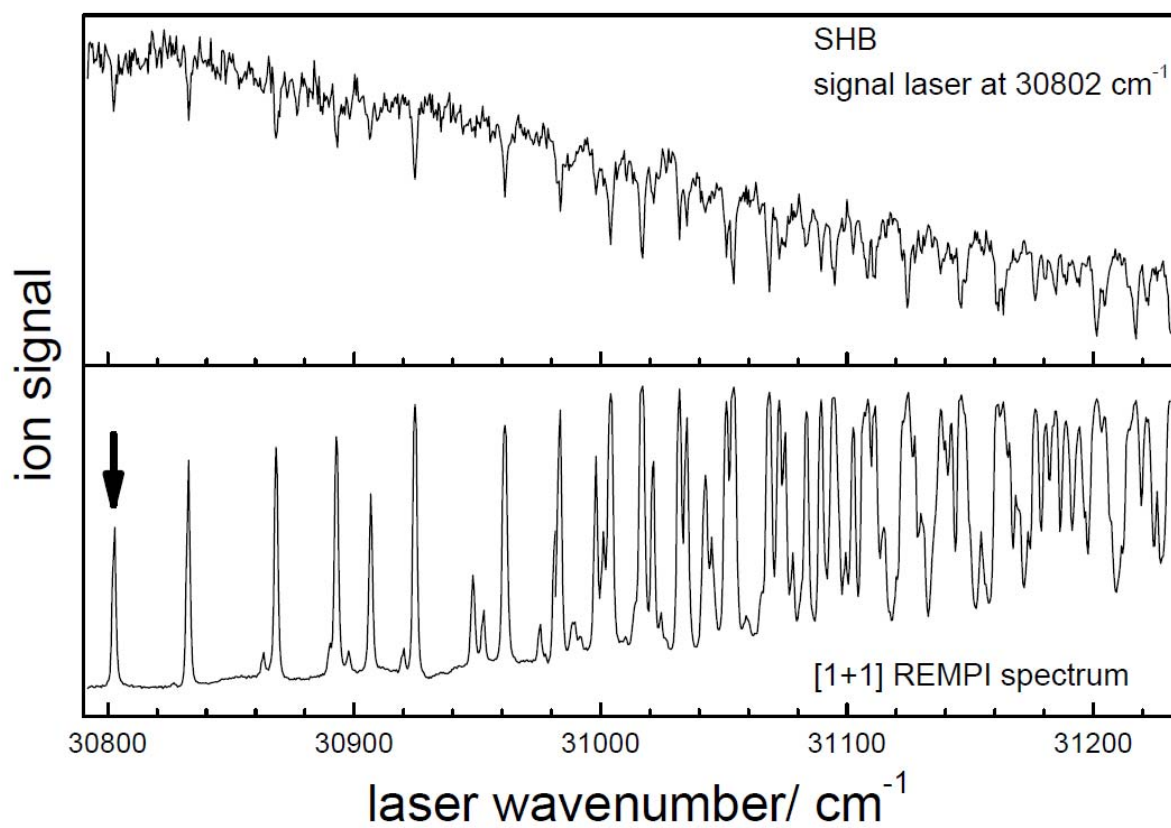
Figure S4: SHB-spectrum of MHPC. The signal laser was set on the peak marked with an arrow, assigned to the twist mode fundamental in the excited state. As visible, the most intense peaks originate all from the same isomer.

Table S1: Parameters for the calculated and fitted one dimensional potential energy curve of the electronically excited state of MHPC as a function of θ_{twist}. θ_1 and θ_2 represent the local minima of the potential energy curves, E_0 is the energy at $\theta_{twist}=0°$, while E_2 is the energy at θ_2. The potential energy is represented by a fourth order polynomial of θ_{twist} with the expansion coefficients a_0 to a_4.

	SV(P)	TZV(2df,p)	fit
θ_1 (degree)	16	11	7.1
θ_2 (degree)	-13	-10	-
E_0 (cm^{-1})	132	64	19.0
E_2 (cm^{-1})	38	34	-
a_0	132	64	19.0
a_1	2.087534	-1.59058	-3.391260
a_2	-0.969547	-0.840616	-0.050240
a_3	-0.01507549	-0.0002282	0.00229112
a_4	0.00223629	0.00378674	0.00266640

Table S2: Term wavenumbers of the excited state with respect to the $v'=0$ level, where v' represents the quantum number of the twist vibration, and intensities of the transitions to these states from the ground state. Results from the calculated potential energy curves at the SCS-CC2/SV(P) and SCS-CC2/TZV(2df,p) level are compared with those of the fitted potential energy curve and the corresponding experimental values. The standard deviation of the difference between the calculated and experimental wavenumbers, σ, is also shown.

v	wavenumber (cm^{-1})				Intensity (%)			
	SV(P)	TZV(2df,p)	fit	expt.	SV(P)	TZV(2df,p)	fit	expt
0	0	0	0.0	0	0	0	1.4	2
1	36	28	29.8	30	88	80	16.4	20
2	57	46	60.4	60	0	13	33.4	31
3	86	73	95.5	96	10	5	29.1	23
4	103	104	134.2	134	1	0	14.8	16
5	126	141	176.0	176	1	0	4.8	8
σ	26.8	23.9	0.3					

Table S3:   List of all peaks observed in the REMPI spectra of MHPC

Absolute band position / cm^{-1}	Relative band position / cm^{-1}	Intensity	Assignment
30772		w	0_0^0
30802	30	s	T
30832	60	s	T^2
30863	91	w	S
30868	96	s	T^3
30893	121	s	ST
30906	134	m	T^4
30920	148	w	
30924	152	s	ST^2
30948	176	m	T^5
30952	180	w	S^2
30961	189	s	ST^3
30975	203	w	B
30981	209	m	
30983	211	s	S^2T
30998	226	m	ST^4
31001	229	w	
31004	232	s	BT
31016	244	s	S^2T^2
31021	249	m	
31032	260	s	
31035	263	m	BT^2
31043	271	W	
31045	273	w	
31051	279	m	
31054	282	s	S^2T^3
31060	288	w	BS
31068	296	s	BT^3
31072	300	m	
31075	303	m	
31083	311	m	
31089	317	m	
31094	322	s	BST
31102	330	m	
31108	336	s	BT^4
31111	339	s	
31115	343	w	
31124	352	s	BST^2
31130	358	w	
31138	366	m	
31146	374	s	BT^5
31161	389	s	BST^3

31163	391	s	
31169	397	w	B^2
31176	404	s	
31180	408	m	
31184	412	m	
31188	416	w	
31194	422	w	
31201	429	s	B^2T
31204	432	m	
31216	444	s	
31221	449	m	
31231	459	m	B^2T^2
31237	465	w	
31243	471	w	
31245	473	w	
31253	481	s	
31258	486	m	
31262	490	w	B^2S
31267	495	m	B^2T^3
31268	496	m	
31271	499	m	
31281	509	m	
31285	513	w	
31291	519	w	B^2ST
31294	522	w	
31301	529	w	
31304	532	m	B^2T^4
31308	536	s	
31311	539	m	
31319	547	m	
31322	550	s	B^2ST^2
31326	554	w	
31333	561	w	
31337	565	m	
31346	574	m	B^2T^5
31349	577	w	
31352	580	w	
31361	589	s	B^2ST^3
31363	591	s	
31369	597	w	B^3
31374	602	m	
31378	606	w	
31383	611	m	
31388	616	m	
31400	628	m	B^3T
31415	643	s	

31430	658	s	B^3T^2
31438	666	w	
31441	669	w	
31443	671	w	
31453	681	s	
31460	688	w	B^3S
31466	694	m	B^3T^3
31470	698	s	
31482	710	w	
31485	713	m	
31491	719	s	B^3ST
31493	721	m	
31506	734	m	B^3T^4
31521	749	s	B^3ST^2
31535	763	m	
31545	773	m	
31549	777	m	B^3T^5
31562	790	s	B^3ST^3
31588	816	m	
31591	819	m	
31599	827	m	

Table S4: Cartesian coordinates (x, y, z) for the most important points. These points are a) the ground state minimum energy structure and b) the two minima and the maximum along the twist coordinate in the electronically excited state. The data given in figures 2 and 3 as well as tables 1 and of the main paper were computed using the TZV(2df,p) basis set. For computations of zero point vibrational energies the SV(P) basis set was used.

Ground state (global minimum), SCS-MP2, TZV(2df,p) basis set

2.41605499975078	-1.47439549229383	-1.65117714365664	c
2.11107321529098	0.97632269579099	-2.58956692089128	c
2.65463481421225	2.95743966584108	-0.93157568559473	c
2.95653515146017	2.54754115558829	1.65516172779681	c
2.72001400312869	0.10808910027957	2.63511026776604	c
2.69866857343568	-1.90121749069439	0.92341710367751	c
0.71321838466997	1.38496218688493	-5.03886275006491	c
-2.12637294149195	0.43846914772197	-4.87151018309160	c
-2.98933694205179	0.21377154675394	-2.16310972853298	c
-3.08727788786271	2.35980064235329	-0.62626662353772	c
-2.81194050575391	2.15369166900314	1.97746958817609	c
-2.45531953478362	-0.20354159813463	3.11836890353271	c
-2.93338377085634	-2.34526691826350	1.64385165792214	c
-3.19852076475397	-2.13793171703583	-0.97113636604743	c
-1.10479440343999	-0.35526383035800	5.61926964389436	c
1.89900821828433	-0.37939671117137	5.31634865751486	c
2.07640891095543	-3.41583807817604	-3.33227778992529	o
2.55672330948704	4.88418100251107	-1.63354757590801	h
-3.09372462240170	4.22329127823162	-1.48915978588643	h
2.60156010896288	-3.82982937448532	1.62996089932109	h
-3.30926106894721	-3.83874054822732	-2.11389036951479	h
-2.85511215011059	-4.20852785623572	2.50528164823533	h
3.10525207304922	4.15216003559363	2.92509453342935	h
2.69597885449077	1.03323043094897	6.59520245734568	h
2.59718737082326	-2.22392117012239	5.93220083484520	h
-2.62463550541380	3.85785077765518	3.10597681421946	h
-3.30273234535951	1.76103216231317	-5.94008503507723	h
-2.27076144381463	-1.40515628788012	-5.78574835845340	h
-1.66931673509513	-2.04907423450025	6.65927449332832	h
-1.62094749071982	1.27461364110166	6.77863529533799	h
0.72342562136644	3.40783138412679	-5.45756319370445	h
1.62292470055730	0.41866536826484	-6.62094808667593	h
2.12497721949505	-4.99121788235027	-2.40817526668428	h

Ground state, SCS-CC2, SV(P) basis set

2.25457780894598	-1.66924327350980	-1.60377790726541	c
2.22483209369380	0.80424522580629	-2.59156899945472	c
2.96112974380445	2.75591896330621	-0.95062349611536	c
3.20095533676926	2.35528288633418	1.66424227251591	c
2.70227104469129	-0.04574711492491	2.68570644824410	c
2.48044070634151	-2.08587793853257	0.99608493342504	c
0.89228900054093	1.28154109630491	-5.07597476956030	c

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-2.02282753138768     0.59133423614881    -4.92917024686286    c
-2.92832026659256     0.43678274001852    -2.21831082848178    c
-2.80818934532140     2.59182338470895    -0.66400989497213    c
-2.58132053349006     2.35412162896555     1.95720933428995    c
-2.49862148450192    -0.04481317135464     3.10499734990126    c
-3.18592016806519    -2.13345895762894     1.60593547077693    c
-3.40795533882676    -1.89551915550346    -1.02812686660133    c
-1.19008259369259    -0.34801442208575     5.62716983733726    c
 1.82093056815648    -0.40357335356482     5.37986623436015    c
 1.72083120337703    -3.57924326471155    -3.26361925884520    o
 3.07117139942443     4.69479031510999    -1.68979405473316    h
-2.60563341822778     4.46883119226162    -1.53146957788576    h
 2.17929789338270    -4.00438414092048     1.73968714481313    h
-3.69107244376761    -3.59395868555898    -2.18865516378220    h
-3.31791247827080    -4.01761646515995     2.47479425512001    h
 3.50223268934840     3.97638892545390     2.92626237060855    h
 2.62919918535382     1.08863596137048     6.60002472587989    h
 2.51647370918179    -2.23133928674186     6.12007264628918    h
-2.22547483006045     4.04836282464570     3.10448811809053    h
-3.09783593328615     2.02222853637635    -6.01442172533552    h
-2.33381969325500    -1.25165056193205    -5.85769182273177    h
-1.82554625880622    -2.10875363139171     6.55879149805613    h
-1.72059326902737     1.22967708303060     6.89213063771098    h
 1.09659896861322     3.30816052132768    -5.54759531262716    h
 1.75587944625453     0.19434753347376    -6.63800261449063    h
 1.60736018577127    -5.16745371993626    -2.32942270974180    h
```

Excited state 1 (local minimum, θ_{twist} = -10°), SCS-CC2, TZV(2df,p)

```
 2.40742179444909    -1.63421045539069    -1.67892479561058    c
 1.94960672855365     0.82145130548223    -2.63398221120769    c
 2.28865694613203     2.88126774388242    -0.95608205967967    c
 2.50075485474779     2.43354914974865     1.66128879196947    c
 2.51332597562381    -0.06152873653738     2.63922646410410    c
 2.74152977608787    -2.09483868683722     0.93511596984446    c
 0.70726945647638     1.22351514719546    -5.16599578611488    c
-2.19178774447416     0.63823098722232    -4.90985255280209    c
-2.84730974908819     0.41033014675742    -2.14315580370651    c
-3.08298567039155     2.57624338269988    -0.59704948814208    c
-2.76631397991977     2.32874844718679     2.03178899766879    c
-2.32438682442425    -0.04890341580632     3.15844450733725    c
-2.64527778600250    -2.23957649386901     1.66413907145205    c
-2.85973733617829    -1.98638278836523    -0.97066714950182    c
-1.09212881687329    -0.22526644298261     5.72140393992336    c
 1.84219417672806    -0.55348271340716     5.36491243073271    c
 2.35924432892203    -3.57217547359228    -3.38178751075083    o
 2.16336312431363     4.79711974438213    -1.67306891062177    h
-3.30114296295842     4.43212555950313    -1.44349272901703    h
 2.92079448803015    -4.02093715235009     1.62521797434096    h
-2.86230550694063    -3.66317339749207    -2.15637454033441    h
-2.53050624013402    -4.09957792393034     2.52343198757590    h
 2.53828632154399     4.01506268779808     2.97042863031584    h
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```
   2.84862527951025     0.74396912155672     6.62443713512667  h
   2.41011678963496    -2.47466344424140     5.87805512668651  h
  -2.72694564439493     4.00938676643380     3.21268899064412  h
  -3.30354972806693     2.12334220645559    -5.82922905812276  h
  -2.61750203323926    -1.14406598214153    -5.86604104866566  h
  -1.85620903194758    -1.80895955657026     6.81494426299947  h
  -1.46725744554464     1.50454882156338     6.79039192967790  h
   0.98748026545603     3.19341540002526    -5.72698014767284  h
   1.54356078641133     0.03010240979397    -6.62987420226122  h
   2.57332282452052    -5.14104166313857    -2.45733455309196  h
```

Excited state 2 (global minimum, θ_{twist} = +11°), SCS-CC2, TZV(2df,p)

```
  -0.83406085681275     5.24513563514652    -0.53062031864460  c
  -2.02580662521018     2.67638046320201    -0.23845300914424  c
  -2.20691713303977     1.46451238985649     2.14973806588154  c
  -2.66170354159879     1.21632386047087    -2.40691412740050  c
  -2.47529538088191    -1.18943824014331     2.38417187055402  c
  -2.79310765762682    -1.43410975214400    -2.19650080215593  c
  -2.46975821966851    -2.67143824932265     0.16509859185419  c
  -1.69657321230204    -5.40823616821238     0.25559547042162  c
   1.97057564503301     4.92009098509368    -1.45869331831096  c
   2.73585269348060     2.19747366185951    -1.08136934055398  c
   3.04791432813678     1.23165274295429     1.37816067739019  c
   2.68111318248174     0.49018066139827    -3.11569233258408  c
   2.95087959958933    -1.38222943817655     1.85544094705903  c
   2.44816507509112    -2.11504100094717    -2.62978904900526  c
   2.39458437197584    -3.05122532440848    -0.13847160526495  c
   1.26831873745206    -5.60695265086050     0.43266807911626  c
  -1.92476123968725     2.93967838788487     4.24207803081830  o
  -1.94631143911116     1.83893564679541     5.70913266656298  h
  -2.81543938596514     2.12828236388176    -4.23636673418900  h
  -2.47092756237242    -2.06964281787694     4.24033931715209  h
  -3.02554584504952    -2.58110069845048    -3.88388101204306  h
  -0.86134367662873     6.24093788856145     1.27506979103521  h
  -1.90192318313125     6.38811112281631    -1.88830964797427  h
  -2.56840623522514    -6.37757704635326     1.86538165136654  h
  -2.34542964640565    -6.35678682908782    -1.46347160274847  h
   3.20368224704176     6.21089666607568    -0.41267262956592  h
   2.12172676626349     5.40531515533765    -3.46219620413725  h
   1.82711379614598    -6.19806018380193     2.33355179054366  h
   1.94493270224207    -7.04815400399648    -0.88836507631210  h
   3.21193941548579     2.54554434596479     2.94877547585680  h
   2.58022269518926     1.18964353217275    -5.04100491495606  h
   3.07866214056971    -2.08719156233473     3.77769614871040  h
   2.18178840083967    -3.42156430593215    -4.19338202431430  h
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Excited state (θ_{twist} = 0°), SCS-CC2, TZV(2df,p)

```
  -1.17649534210604     5.22452658600047     0.16122573494133     c
  -1.39861363052699     2.69409597873468     1.44763942080262     c
   0.61703814577330     1.65887566536595     2.87567552476823     c
```

-3.49437231389494	1.09726982005453	0.93950369893726	c
0.79991492277024	-0.96319774252101	3.37515428791191	c
-3.27095733418332	-1.52851836756321	1.32175979102360	c
-1.03285584460787	-2.59822745108054	2.34071762498246	c
-0.43145726294784	-5.35049792474601	1.92973190838201	c
0.05258172281808	4.85428228067171	-2.52432405674383	c
0.62562213618917	2.08709187639224	-2.90576104726670	c
2.85631913644682	1.03637911811845	-1.89540347289766	c
-1.21561752171765	0.43701984469858	-3.90105577866229	c
3.09651126279201	-1.58121666340866	-1.50459753707762	c
-1.02724644171320	-2.17043302446997	-3.40987735371915	c
1.02372107888619	-3.17336546338684	-2.03440551613837	c
0.81011234779263	-5.71042268750436	-0.75539652097043	c
2.47336207583837	3.28212773321250	3.62948138013547	o
3.77400735829604	2.29802760526625	4.46738239368863	h
-5.17535677420954	1.88282676075765	0.06860054957252	h
2.44631162993116	-1.71537425244897	4.34625998638311	h
-4.78689903748408	-2.78110721937352	0.73088246072275	h
-0.02929029340834	6.51856844283704	1.28677491075159	h
-3.05940847143472	6.06055625152907	-0.02696431336115	h
0.85231229169536	-6.02656189335897	3.40508022481165	h
-2.15897346498914	-6.48187029806441	2.05003032460604	h
1.78755592573360	5.97215940451134	-2.65161864598291	h
-1.23183598962199	5.53156059174824	-3.99747693826735	h
2.67799870884648	-6.57967645800165	-0.56401292535805	h
-0.35438542256870	-6.98969966246198	-1.88852549879641	h
4.34858864529125	2.30070154115159	-1.26847436249949	h
-2.86483634483766	1.19112868716206	-4.85945741251434	h
4.78306866430739	-2.34854522042048	-0.62347176544346	h
-2.54409292249092	-3.42764148026191	-3.99292165874652	h

Excited state 1 (local minimum, θ_{twist} = -10°), SCS-CC2, SV(P)

2.73199772400946	-0.74147455740904	-1.79934335838902	c
1.51460089125543	1.48283091419301	-2.69552597390379	c
1.21073697992987	3.51385770596907	-0.95416751815156	c
1.67550585073822	3.13264452377789	1.65771857469614	c
2.49656251169213	0.73828707300904	2.58019215707444	c
3.31933987664858	-1.09408717640264	0.80300294131970	c
0.08600211300693	1.45218946023136	-5.17151692774696	c
-2.36902618648819	-0.18456500474596	-4.85873061157957	c
-2.87734158722432	-0.59559964172597	-2.07158136226474	c
-3.77983119839226	1.40271810584105	-0.52124122433296	c
-3.34022678381189	1.31672610444545	2.11234218245980	c
-2.12801656879612	-0.78376230562479	3.25708804205226	c
-1.73792526660336	-2.98279933577153	1.76766025070939	c
-2.10696828687771	-2.86880934538861	-0.87282015349647	c
-0.80685723469969	-0.49912762654571	5.77806341879160	c
2.08395295778831	0.00884496478856	5.31551151514674	c
3.22607147551910	-2.56611771954589	-3.55015036502345	o
0.47439159078653	5.33215170382029	-1.62753810993849	h
-4.61608172747785	3.09616798848377	-1.38223448983772	h

4.13435512951165	-2.89330777480831	1.44582654994372	h
-1.58716064252575	-4.49724148691631	-2.05180330200089	h
-1.01338847756250	-4.71880349603802	2.64731768834153	h
1.25096082124100	4.64951648581671	3.01154330682884	h
2.76838475724930	1.50556420352170	6.61062749617591	h
3.19332666789501	-1.71241699155669	5.74121607664326	h
-3.84062836212003	2.95547099139332	3.28771559305895	h
-3.99222892165811	0.74336403037841	-5.80443172034517	h
-2.09248589356324	-2.03723621885023	-5.78466742136749	h
-1.06515508462141	-2.20034971442428	6.97365401805926	h
-1.64675264866042	1.10902334978008	6.81853589480827	h
-0.41926400139861	3.42039969986395	-5.66384673697101	h
1.26059661743838	0.70520214273666	-6.73057284277301	h
3.97638081674729	-4.02384493831666	-2.69734004395382	h

Excited state 2 (global minimum, θ_{twist} = +11°), SCS-CC2, SV(P)

-0.20796522066982	5.26629451812537	-0.79190569804725	c
-1.50017993361240	2.77091810142853	-1.29920920294440	c
-3.01094801374131	1.55125309629794	0.58250298716420	c
-0.88151975833372	1.31959777276668	-3.50117979640216	c
-3.44831551244423	-1.11191678003590	0.57249148456118	c
-1.15892630822980	-1.34543813747353	-3.43675506504659	c
-2.23489602533550	-2.61112103721142	-1.30252156382596	c
-1.66842075221104	-5.36649416355034	-0.81465873173680	c
2.67014183530865	4.81201136141988	-0.21893176684136	c
3.01886029590957	2.08306612911363	0.57384784350190	c
1.87143433433364	1.19604624753561	2.81617027414801	c
4.01300272045025	0.28808626216733	-1.12917906743164	c
1.39334716069838	-1.40245301858213	3.18686792839333	c
3.45095515212551	-2.30218446737670	-0.80668725819464	c
1.98243955730077	-3.14932179319477	1.25693584392680	c
0.57821067959228	-5.63764601101580	1.11763585193690	c
-3.88465196772002	3.01128061459982	2.50803700728856	o
-4.75939883916978	1.92677876981114	3.72408872180625	h
0.00884292132121	2.24458870186120	-5.13078682943421	h
-4.57136753663248	-1.99517344150700	2.08189778367123	h
-0.43692646947935	-2.49025723447110	-5.01306268264961	h
-1.11801774529107	6.19099230103843	0.84086010795333	h
-0.41999531226291	6.56156227438168	-2.42665422257897	h
-3.36085053547384	-6.37146424011475	-0.09211189542122	h
-1.14500588994770	-6.28126950757119	-2.62130845738870	h
3.32589978776132	6.14605863333733	1.25593517890858	h
3.81585030676385	5.18225359337662	-1.92796504230377	h
-0.15866705510562	-6.12098166497426	3.01395637818062	h
1.83382529961912	-7.20741546977760	0.53326170739391	h
1.18339633676290	2.56938114955651	4.21395095630551	h
5.02858363145813	0.91985588200055	-2.82491657657205	h
0.38591775627817	-2.03965692803973	4.88600851136427	h
4.04991583681620	-3.66641824426513	-2.25582111014700	h