Electronic Supplementary Information:

Excited state potential energy surfaces of N-phenylpyrrole upon twisting: Reference values and comparison between BSE/*GW* and TD-DFT

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PES FOR THE TD-DFT, BSE/EVGW, AND CC METHODS

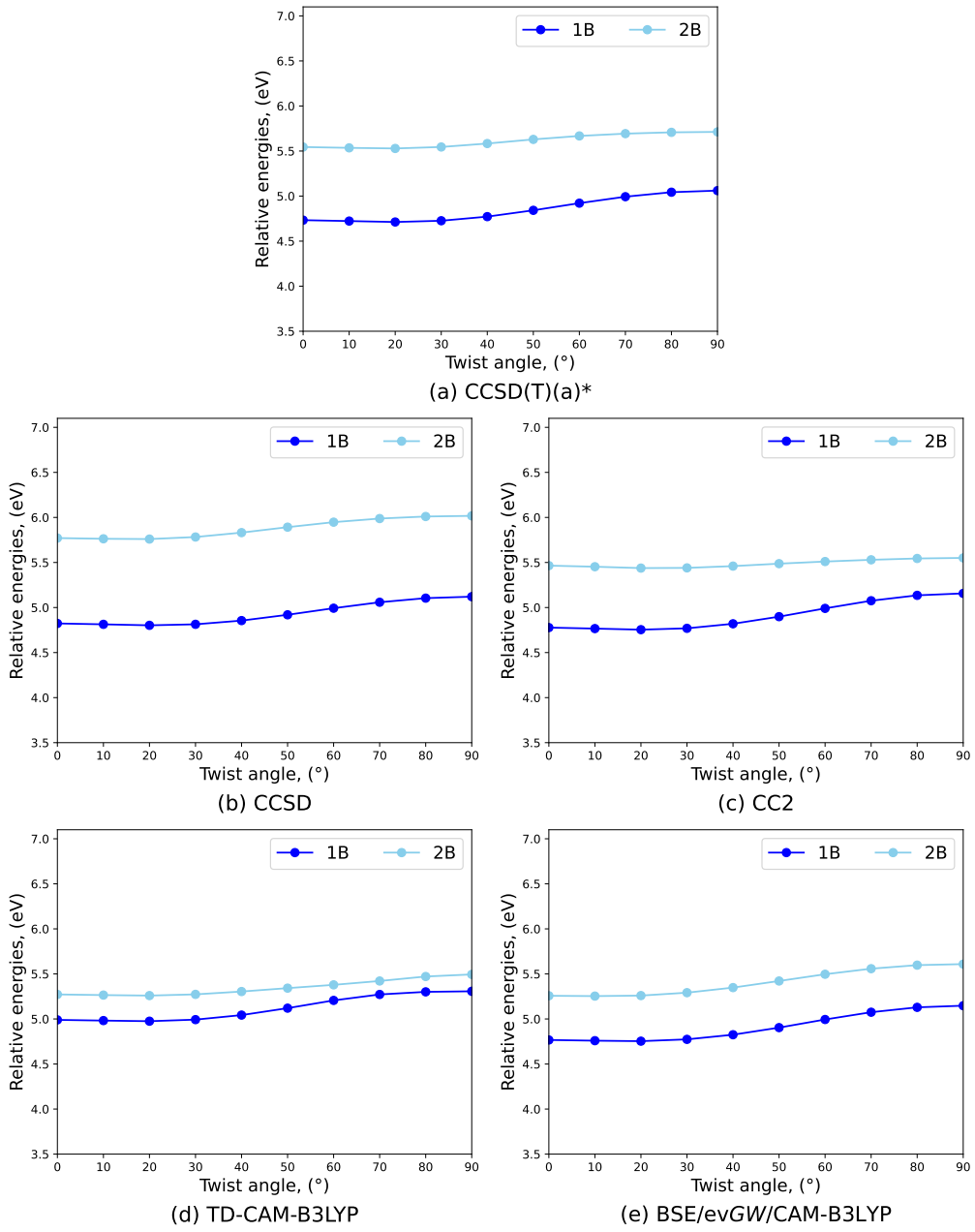

FIG. S1. PES for the 1B and 2B ES of N-PP calculated at the (a) CCSD(T)(a)*, (b) CCSD, (c) CC2, (d) TD-CAM-B3LYP, and (e) BSE/evGW/CAM-B3LYP levels of theory with the cc-pVTZ atomic basis set. The GS energy of the planar molecule was used as a reference to calculate the relative energies. In the case of the BSE/evGW calculations, the GS energy is calculated at CAM-B3LYP level.

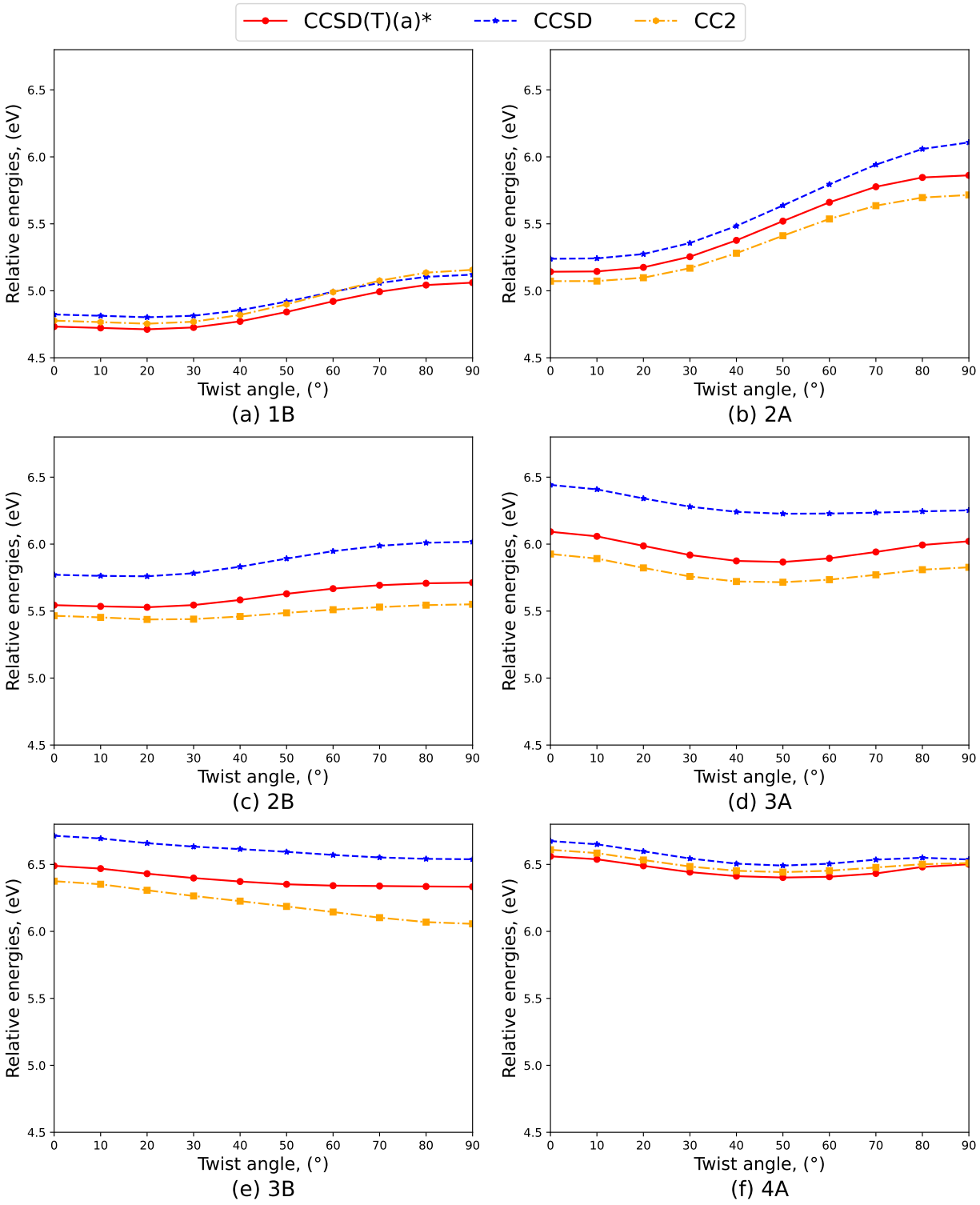

FIG. S2. PES for the (a) 1B, (b) 2A, (c) 2B, (d) 3A, (e) 3B, and (f) 4A states of N-PP determined at CCSD(T)(a)*, CCSD, and CC2 levels. The GS energy of the untwisted geometry was used as a reference for the calculation of relative energies.

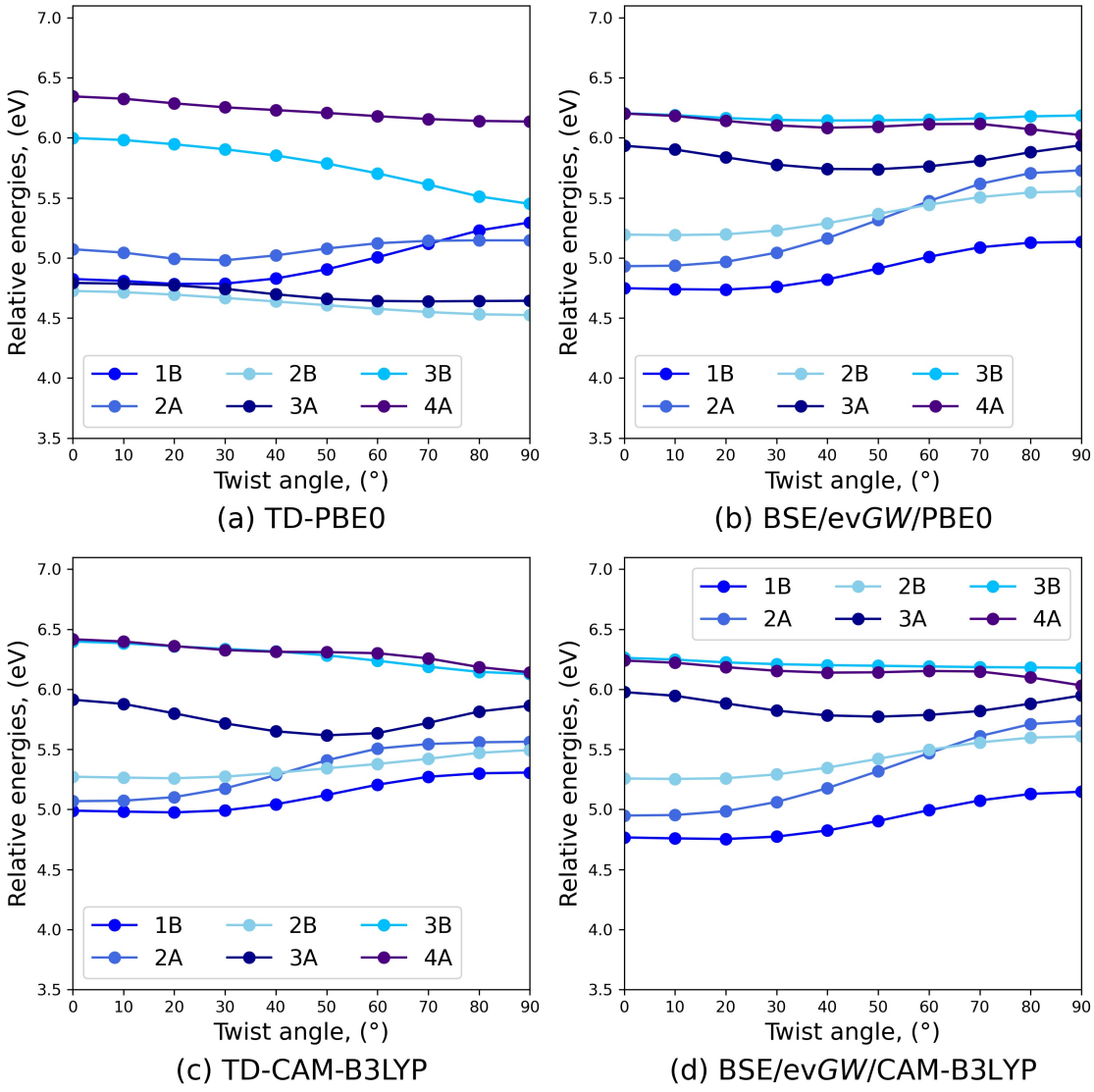

FIG. S3. PES for the six lowest ES of N-PP calculated at the (a) TD-PBE0, (b) BSE/evGW/PBE0, (c) TD-CAM-B3LYP, and (d) BSE/evGW/CAM-B3LYP levels of theory with the cc-pVTZ atomic basis set. Relative energies use the GS energy of the planar molecule as a reference. In the case of the BSE/evGW calculations, the GS energy is calculated at the corresponding DFT level.

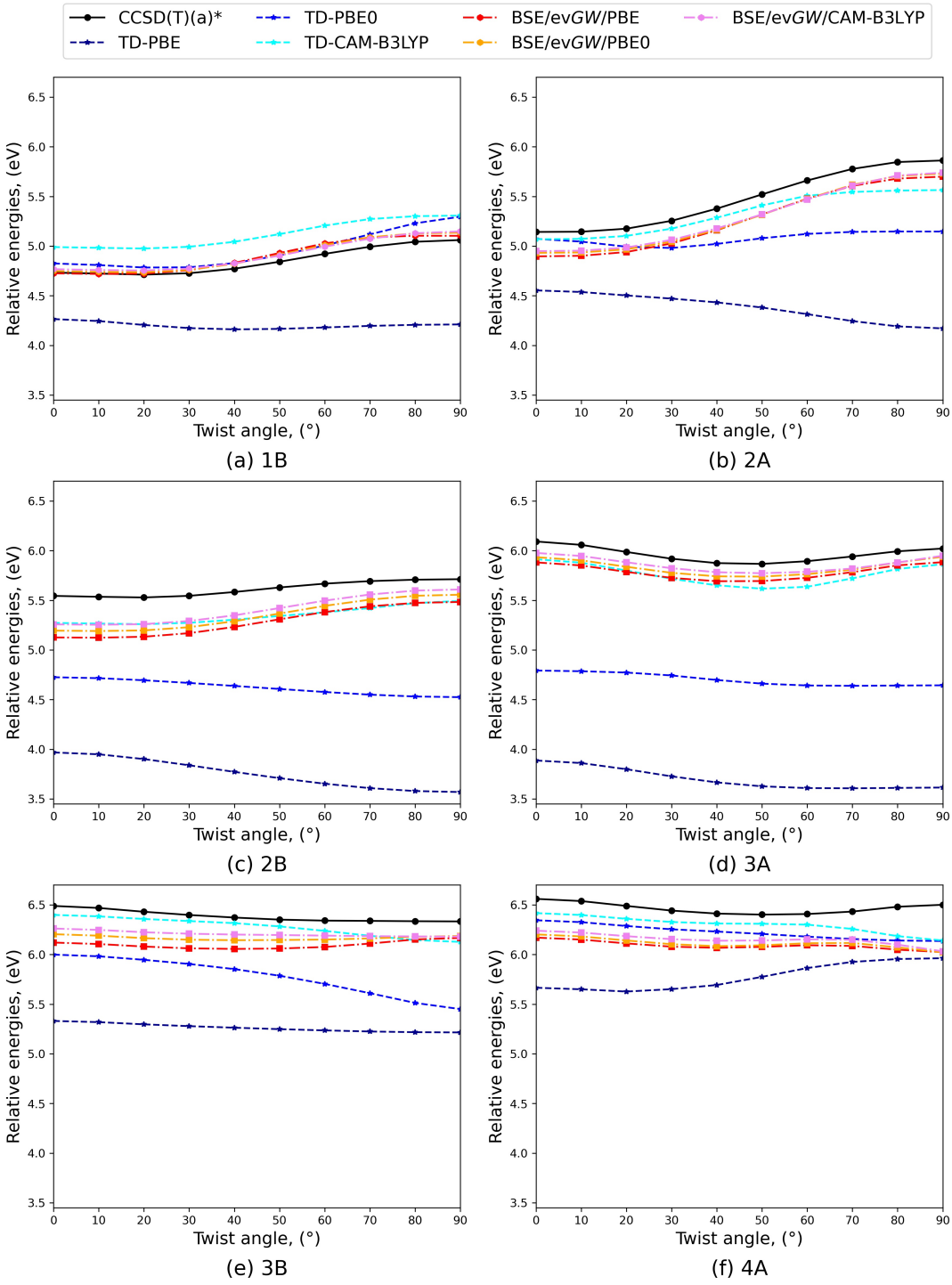

FIG. S4. PES for the (a) 1B, (b) 2A, (c) 2B, (d) 3A, (e) 3B, and (f) 4A states of N-PP determined at TD-DFT and BSE/evGW levels with the PBE, PBE0, and CAM-B3LYP functionals compared to the CCSD(T)(a)* reference. As a reference for the calculation of relative energies, the GS energy of the untwisted geometry was used (for BSE/evGW - the GS energy obtained with corresponding DFT functional).

RELATIVE ENERGIES AND DIFFERENCES BETWEEN CC METHODS

TABLE S1. Calculated relative energies (ΔE_{rel}) for the 1B state of N-PP using CCSD(T)(a)*, CCSD, and CC2 levels of theory. The differences (ΔE_{diff}) between the last two methods and the CCSD(T)(a)* reference as well as MAE values are also listed. Calculations have been done with the cc-pVTZ atomic basis set. The GS energy of the untwisted molecule is used as a reference to calculate relative energies. All values are in eV.

(°)	$\boldsymbol{\Delta E_{\mathrm{rel}}}$			$\boldsymbol{\Delta E_{\mathrm{diff}}}$ [a]	
	CCSD(T)(a)*	**CCSD**	**CC2**	**CCSD**	**CC2**
			1B		
0	4.733	4.823	4.777	0.090	0.045
10	4.723	4.814	4.766	0.091	0.043
20	4.712	4.802	4.754	0.090	0.042
30	4.726	4.814	4.769	0.087	0.043
40	4.772	4.855	4.820	0.083	0.048
50	4.842	4.919	4.899	0.077	0.057
60	4.921	4.992	4.991	0.071	0.069
70	4.993	5.059	5.076	0.065	0.082
80	5.043	5.104	5.135	0.061	0.092
90	5.061	5.121	5.157	0.060	0.096
MAE [b]				**0.078**	**0.062**

[a] $\Delta E_{\mathrm{diff}}^{\mathrm{Method}} = \Delta E_{\mathrm{rel}}^{\mathrm{Method}} - \Delta E_{\mathrm{rel}}^{\mathrm{CCSD(T)(a)*}}$

[b] $\mathrm{MAE} = \frac{\sum_{i=1}^{10} |\Delta E_{\mathrm{rel}}^{\mathrm{Method}} - \Delta E_{\mathrm{rel}}^{\mathrm{CCSD(T)(a)*}}|}{10}$

TABLE S2. Theoretical relative energies (in eV) for the 2A state of N-PP using CCSD(T)(a)*, CCSD, and CC2 levels of theory.[a]

(°)	ΔE_{rel}			ΔE_{diff}	
	CCSD(T)(a)*	**CCSD**	**CC2**	**CCSD**	**CC2**
			2A		
0	5.142	5.239	5.072	0.097	-0.070
10	5.144	5.242	5.073	0.098	-0.072
20	5.175	5.274	5.098	0.099	-0.077
30	5.254	5.357	5.169	0.102	-0.086
40	5.377	5.484	5.281	0.107	-0.096
50	5.520	5.637	5.411	0.117	-0.109
60	5.660	5.795	5.537	0.134	-0.124
70	5.777	5.942	5.636	0.165	-0.141
80	5.846	6.059	5.696	0.213	-0.150
90	5.862	6.108	5.715	0.246	-0.147
MAE				**0.138**	**0.107**

[a] See caption of Table S1 for more info.

TABLE S3. Theoretical relative energies (in eV) for the 2B state of N-PP using CCSD(T)(a)*, CCSD, and CC2 levels of theory.[a]

(°)	ΔE_{rel}			ΔE_{diff}	
	CCSD(T)(a)*	**CCSD**	**CC2**	**CCSD**	**CC2**
			2B		
0	5.544	5.771	5.465	0.227	-0.079
10	5.535	5.763	5.453	0.228	-0.082
20	5.529	5.760	5.438	0.231	-0.091
30	5.545	5.783	5.440	0.238	-0.105
40	5.583	5.831	5.460	0.248	-0.124
50	5.629	5.892	5.487	0.263	-0.142
60	5.668	5.948	5.510	0.280	-0.157
70	5.693	5.988	5.530	0.294	-0.163
80	5.708	6.010	5.545	0.303	-0.163
90	5.712	6.018	5.551	0.305	-0.162
MAE				**0.262**	**0.127**

[a] See caption of Table S1 for more info.

TABLE S4. Theoretical relative energies (in eV) for the 3A state of N-PP using CCSD(T)(a)*, CCSD, and CC2 levels of theory.[a]

(°)	ΔE_{rel}			ΔE_{diff}	
	CCSD(T)(a)*	**CCSD**	**CC2**	**CCSD**	**CC2**
			3A		
0	6.092	6.442	5.926	0.350	-0.166
10	6.058	6.409	5.892	0.351	-0.166
20	5.987	6.341	5.823	0.354	-0.164
30	5.918	6.279	5.759	0.361	-0.160
40	5.875	6.241	5.721	0.366	-0.154
50	5.866	6.227	5.716	0.361	-0.151
60	5.894	6.228	5.735	0.334	-0.159
70	5.941	6.235	5.771	0.294	-0.171
80	5.993	6.245	5.809	0.251	-0.184
90	6.021	6.252	5.827	0.231	-0.194
MAE				**0.325**	**0.167**

[a] See caption of Table S1 for more info.

TABLE S5. Theoretical relative energies (in eV) for the 3B state of N-PP using CCSD(T)(a)*, CCSD, and CC2 levels of theory.[a]

(°)	ΔE_{rel}			ΔE_{diff}	
	CCSD(T)(a)*	**CCSD**	**CC2**	**CCSD**	**CC2**
			3B		
0	6.489	6.714	6.375	0.224	-0.115
10	6.469	6.694	6.352	0.225	-0.117
20	6.431	6.659	6.307	0.228	-0.124
30	6.398	6.633	6.264	0.234	-0.134
40	6.372	6.614	6.226	0.242	-0.146
50	6.352	6.594	6.186	0.242	-0.165
60	6.341	6.571	6.144	0.229	-0.197
70	6.339	6.552	6.103	0.213	-0.236
80	6.335	6.542	6.069	0.206	-0.266
90	6.333	6.538	6.056	0.205	-0.277
MAE				**0.225**	**0.178**

[a] See caption of Table S1 for more info.

TABLE S6. Theoretical relative energies (in eV) for the 4A state of N-PP using CCSD(T)(a)*, CCSD, and CC2 levels of theory.[a]

(°)	ΔE_{rel}			ΔE_{diff}	
	CCSD(T)(a)*	**CCSD**	**CC2**	**CCSD**	**CC2**
			4A		
0	6.561	6.675	6.609	0.114	0.049
10	6.538	6.650	6.585	0.112	0.046
20	6.490	6.598	6.533	0.108	0.043
30	6.442	6.544	6.484	0.102	0.042
40	6.412	6.505	6.452	0.093	0.040
50	6.402	6.491	6.442	0.089	0.040
60	6.408	6.505	6.453	0.098	0.045
70	6.432	6.536	6.477	0.103	0.045
80	6.481	6.550	6.502	0.069	0.020
90	6.501	6.537	6.510	0.035	0.009
MAE				**0.092**	**0.038**

[a] See caption of Table S1 for more info.

TABLE S7. CCSD and CC2 MAE values for each of six states (collected from the previous Tables) and their total MAE (MAE_{tot}).

State	**CCSD**	**CC2**
1B	0.078	0.062
2A	0.138	0.107
2B	0.262	0.127
3A	0.325	0.167
3B	0.225	0.178
4A	0.092	0.038
$\mathbf{MAE_{tot}}$	**0.187**	**0.113**

RELATIVE ENERGIES AND DIFFERENCES BETWEEN TD-DFT METHODS

TABLE S8. Calculated relative energies (ΔE_{rel}) for the 1B state of N-PP using TD-DFT with the PBE, PBE0, and CAM-B3LYP exchange-correlation functionals. The differences (ΔE_{diff}) with the CCSD(T)(a)* reference and MAE values are also listed. Calculations have been done with the cc-pVTZ atomic basis set. The GS energy of the untwisted molecule is used as a reference to calculate relative energies. All values are in eV.[a]

(°)	ΔE_{rel}				ΔE_{diff}		
	CCSD(T)(a)*	TD-DFT					
		PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				1B			
0	4.733	4.264	4.825	4.990	-0.468	0.092	0.257
10	4.723	4.245	4.809	4.982	-0.478	0.086	0.259
20	4.712	4.205	4.784	4.975	-0.507	0.071	0.263
30	4.726	4.174	4.786	4.993	-0.553	0.060	0.266
40	4.772	4.161	4.829	5.043	-0.611	0.057	0.271
50	4.842	4.166	4.906	5.120	-0.676	0.064	0.278
60	4.921	4.180	5.006	5.206	-0.741	0.084	0.285
70	4.993	4.196	5.118	5.272	-0.797	0.125	0.279
80	5.043	4.207	5.229	5.301	-0.836	0.186	0.258
90	5.061	4.211	5.296	5.307	-0.850	0.235	0.246
MAE					**0.652**	**0.106**	**0.266**

[a] See caption of Table S1 for more info.

TABLE S9. Theoretical relative energies (in eV) for the 2A state of N-PP at the TD-DFT level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
	CCSD(T)(a)*	TD-DFT					
		PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				2A			
0	5.142	4.553	5.073	5.069	-0.589	-0.070	-0.073
10	5.144	4.537	5.045	5.073	-0.607	-0.100	-0.072
20	5.175	4.503	4.993	5.102	-0.672	-0.181	-0.073
30	5.254	4.471	4.981	5.175	-0.784	-0.274	-0.079
40	5.377	4.433	5.021	5.285	-0.944	-0.355	-0.091
50	5.520	4.381	5.079	5.409	-1.139	-0.442	-0.111
60	5.660	4.314	5.122	5.507	-1.346	-0.538	-0.154
70	5.777	4.245	5.143	5.545	-1.532	-0.634	-0.232
80	5.846	4.191	5.147	5.559	-1.655	-0.699	-0.287
90	5.862	4.171	5.146	5.564	-1.691	-0.716	-0.298
MAE					**1.096**	**0.401**	**0.147**

[a] See caption of Table S8 for more info.

TABLE S10. Theoretical relative energies (in eV) for the 2B state of N-PP at the TD-DFT level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
	CCSD(T)(a)*	TD-DFT					
		PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				2B			
0	5.544	3.967	4.725	5.272	-1.577	-0.819	-0.272
10	5.535	3.949	4.716	5.265	-1.587	-0.820	-0.270
20	5.529	3.901	4.694	5.260	-1.628	-0.834	-0.269
30	5.545	3.838	4.667	5.273	-1.707	-0.878	-0.272
40	5.583	3.772	4.637	5.305	-1.811	-0.946	-0.279
50	5.629	3.708	4.607	5.342	-1.921	-1.022	-0.287
60	5.668	3.652	4.576	5.379	-2.015	-1.091	-0.289
70	5.693	3.608	4.550	5.422	-2.085	-1.144	-0.272
80	5.708	3.579	4.531	5.471	-2.129	-1.177	-0.236
90	5.712	3.569	4.524	5.494	-2.144	-1.188	-0.218
MAE					**1.860**	**0.992**	**0.266**

[a] See caption of Table S8 for more info.

TABLE S11. Theoretical relative energies (in eV) for the 3A state of N-PP at the TD-DFT level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
		TD-DFT					
	CCSD(T)(a)*	PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				3A			
0	6.092	3.886	4.792	5.914	-2.206	-1.300	-0.179
10	6.058	3.861	4.785	5.879	-2.198	-1.273	-0.180
20	5.987	3.798	4.772	5.800	-2.188	-1.215	-0.187
30	5.918	3.727	4.743	5.716	-2.192	-1.175	-0.202
40	5.875	3.666	4.697	5.651	-2.209	-1.177	-0.224
50	5.866	3.626	4.660	5.617	-2.240	-1.206	-0.250
60	5.894	3.609	4.642	5.636	-2.285	-1.252	-0.258
70	5.941	3.606	4.638	5.721	-2.335	-1.303	-0.221
80	5.993	3.611	4.642	5.816	-2.383	-1.352	-0.178
90	6.021	3.614	4.644	5.864	-2.407	-1.378	-0.158
MAE					**2.264**	**1.263**	**0.204**

[a] See caption of Table S8 for more info.

TABLE S12. Theoretical relative energies (in eV) for the 3B state of N-PP at the TD-DFT level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
		TD-DFT					
	CCSD(T)(a)*	PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				3B			
0	6.489	5.331	5.999	6.399	-1.158	-0.490	-0.090
10	6.469	5.319	5.982	6.384	-1.150	-0.487	-0.085
20	6.431	5.297	5.946	6.358	-1.134	-0.484	-0.073
30	6.398	5.279	5.905	6.337	-1.120	-0.493	-0.061
40	6.372	5.263	5.853	6.316	-1.109	-0.519	-0.056
50	6.352	5.248	5.786	6.283	-1.103	-0.565	-0.069
60	6.341	5.236	5.704	6.238	-1.106	-0.637	-0.103
70	6.339	5.225	5.610	6.189	-1.114	-0.728	-0.150
80	6.335	5.218	5.513	6.146	-1.118	-0.823	-0.190
90	6.333	5.215	5.450	6.127	-1.118	-0.883	-0.206
MAE					**1.123**	**0.611**	**0.108**

[a] See caption of Table S8 for more info.

TABLE S13. Theoretical relative energies (in eV) for the 4A state of N-PP at the TD-DFT level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
		TD-DFT					
	CCSD(T)(a)*	**PBE**	**PBE0**	**CAM-B3LYP**	**PBE**	**PBE0**	**CAM-B3LYP**
				4A			
0	6.561	5.665	6.345	6.417	-0.895	-0.215	-0.144
10	6.538	5.650	6.326	6.398	-0.889	-0.212	-0.140
20	6.490	5.627	6.287	6.360	-0.863	-0.202	-0.130
30	6.442	5.651	6.254	6.327	-0.791	-0.188	-0.115
40	6.412	5.693	6.231	6.312	-0.719	-0.181	-0.100
50	6.402	5.775	6.208	6.310	-0.627	-0.194	-0.092
60	6.408	5.864	6.180	6.301	-0.544	-0.227	-0.107
70	6.432	5.925	6.156	6.258	-0.507	-0.276	-0.175
80	6.481	5.955	6.141	6.185	-0.526	-0.340	-0.296
90	6.501	5.963	6.136	6.141	-0.538	-0.365	-0.360
MAE					**0.690**	**0.240**	**0.166**

[a] See caption of Table S8 for more info.

TABLE S14. MAE values for each of six states (collected from the previous Tables) and their total MAE (MAE_{tot}) for the TD-DFT levels of theory.

State	**TD-DFT**		
	PBE	**PBE0**	**CAM-B3LYP**
1B	0.652	0.106	0.266
2A	1.096	0.401	0.147
2B	1.860	0.992	0.266
3A	2.264	1.263	0.204
3B	1.123	0.611	0.108
4A	0.690	0.240	0.166
MAE_{tot}	**1.281**	**0.602**	**0.193**

RELATIVE ENERGIES AND DIFFERENCES BETWEEN BSE/EVGW METHODS

TABLE S15. Calculated relative energies (ΔE_{rel}) for the 1B state of N-PP using the BSE/evGW level of theory with the PBE, PBE0, and CAM-B3LYP results as a starting point. The differences (ΔE_{diff}) with the CCSD(T)(a)* reference and MAE values are also listed. Calculations have been done with the cc-pVTZ atomic basis set. The DFT GS energy of the untwisted molecule is used as a reference to calculate relative energies. All values are in eV.[a]

	ΔE_{rel}				ΔE_{diff}		
(°)	CCSD(T)(a)*	BSE/evGW					
		PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				1B			
0	4.733	4.725	4.748	4.767	-0.008	0.015	0.034
10	4.723	4.719	4.740	4.759	-0.004	0.017	0.036
20	4.712	4.722	4.736	4.754	0.009	0.024	0.041
30	4.726	4.756	4.760	4.774	0.030	0.034	0.047
40	4.772	4.830	4.821	4.825	0.058	0.050	0.053
50	4.842	4.930	4.912	4.904	0.088	0.070	0.062
60	4.921	5.027	5.010	4.994	0.105	0.089	0.073
70	4.993	5.087	5.089	5.075	0.094	0.095	0.082
80	5.043	5.104	5.127	5.129	0.061	0.084	0.086
90	5.061	5.103	5.135	5.147	0.042	0.074	0.086
MAE					**0.050**	**0.055**	**0.060**

[a] See caption of Table S1 for more info.

TABLE S16. Theoretical relative energies (in eV) for the 2A state of N-PP using the BSE/evGW level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
		BSE/evGW					
	CCSD(T)(a)*	**PBE**	**PBE0**	**CAM-B3LYP**	**PBE**	**PBE0**	**CAM-B3LYP**
				2A			
0	5.142	4.896	4.932	4.949	-0.246	-0.211	-0.193
10	5.144	4.902	4.935	4.953	-0.242	-0.209	-0.191
20	5.175	4.940	4.967	4.985	-0.235	-0.208	-0.190
30	5.254	5.026	5.044	5.062	-0.228	-0.210	-0.192
40	5.377	5.159	5.164	5.177	-0.218	-0.212	-0.199
50	5.520	5.318	5.315	5.319	-0.202	-0.205	-0.201
60	5.660	5.477	5.474	5.469	-0.183	-0.186	-0.191
70	5.777	5.606	5.617	5.610	-0.171	-0.160	-0.166
80	5.846	5.680	5.706	5.711	-0.167	-0.140	-0.136
90	5.862	5.699	5.730	5.739	-0.163	-0.132	-0.123
MAE					**0.205**	**0.187**	**0.178**

[a] See caption of Table S15 for more info.

TABLE S17. Theoretical relative energies (in eV) for the 2B state of N-PP using the BSE/evGW level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
		BSE/evGW					
	CCSD(T)(a)*	**PBE**	**PBE0**	**CAM-B3LYP**	**PBE**	**PBE0**	**CAM-B3LYP**
				2B			
0	5.544	5.126	5.194	5.258	-0.419	-0.350	-0.287
10	5.535	5.123	5.191	5.254	-0.412	-0.345	-0.282
20	5.529	5.133	5.197	5.260	-0.396	-0.332	-0.269
30	5.545	5.169	5.229	5.292	-0.376	-0.316	-0.253
40	5.583	5.232	5.289	5.348	-0.351	-0.294	-0.235
50	5.629	5.308	5.366	5.422	-0.321	-0.263	-0.208
60	5.668	5.381	5.444	5.496	-0.286	-0.224	-0.171
70	5.693	5.439	5.507	5.558	-0.254	-0.187	-0.135
80	5.708	5.474	5.545	5.597	-0.234	-0.162	-0.110
90	5.712	5.483	5.556	5.609	-0.229	-0.156	-0.103
MAE					**0.328**	**0.263**	**0.205**

[a] See caption of Table S15 for more info.

TABLE S18. Theoretical relative energies (in eV) for the 3A state of N-PP using the BSE/evGW level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
	CCSD(T)(a)*	BSE/evGW					
		PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				3A			
0	6.092	5.882	5.934	5.977	-0.211	-0.158	-0.115
10	6.058	5.851	5.903	5.946	-0.207	-0.156	-0.112
20	5.987	5.786	5.837	5.883	-0.200	-0.149	-0.104
30	5.918	5.725	5.777	5.823	-0.193	-0.142	-0.096
40	5.875	5.692	5.741	5.783	-0.182	-0.134	-0.092
50	5.866	5.694	5.739	5.772	-0.173	-0.128	-0.094
60	5.894	5.726	5.763	5.787	-0.167	-0.131	-0.107
70	5.941	5.783	5.808	5.820	-0.158	-0.133	-0.122
80	5.993	5.852	5.881	5.881	-0.142	-0.113	-0.113
90	6.021	5.884	5.939	5.949	-0.137	-0.082	-0.072
MAE					**0.177**	**0.133**	**0.103**

[a] See caption of Table S15 for more info.

TABLE S19. Theoretical relative energies (in eV) for the 3B state of N-PP using the BSE/evGW level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
	CCSD(T)(a)*	BSE/evGW					
		PBE	PBE0	CAM-B3LYP	PBE	PBE0	CAM-B3LYP
				3B			
0	6.489	6.121	6.205	6.262	-0.369	-0.285	-0.228
10	6.469	6.106	6.190	6.248	-0.363	-0.279	-0.221
20	6.431	6.080	6.165	6.224	-0.350	-0.266	-0.206
30	6.398	6.062	6.149	6.210	-0.336	-0.249	-0.189
40	6.372	6.056	6.144	6.201	-0.316	-0.228	-0.171
50	6.352	6.060	6.146	6.196	-0.291	-0.206	-0.155
60	6.341	6.076	6.151	6.190	-0.265	-0.191	-0.151
70	6.339	6.110	6.162	6.185	-0.228	-0.177	-0.154
80	6.335	6.152	6.179	6.182	-0.184	-0.156	-0.153
90	6.333	6.167	6.186	6.179	-0.166	-0.147	-0.154
MAE					**0.287**	**0.218**	**0.178**

[a] See caption of Table S15 for more info.

TABLE S20. Theoretical relative energies (in eV) for the 4A state of N-PP using the BSE/evGW level of theory. [a]

(°)	ΔE_{rel}				ΔE_{diff}		
		BSE/evGW					
	CCSD(T)(a)*	**PBE**	**PBE0**	**CAM-B3LYP**	**PBE**	**PBE0**	**CAM-B3LYP**
				4A			
0	6.561	6.170	6.202	6.240	-0.390	-0.358	-0.321
10	6.538	6.151	6.182	6.221	-0.388	-0.356	-0.317
20	6.490	6.112	6.141	6.185	-0.378	-0.348	-0.305
30	6.442	6.079	6.104	6.154	-0.363	-0.339	-0.288
40	6.412	6.067	6.084	6.139	-0.345	-0.328	-0.273
50	6.402	6.077	6.093	6.142	-0.325	-0.309	-0.260
60	6.408	6.093	6.114	6.153	-0.314	-0.294	-0.255
70	6.432	6.087	6.116	6.149	-0.346	-0.316	-0.284
80	6.481	6.049	6.072	6.099	-0.432	-0.409	-0.382
90	6.501	6.024	6.022	6.032	-0.477	-0.479	-0.469
MAE					**0.376**	**0.354**	**0.315**

[a] See caption of Table S15 for more info.

TABLE S21. MAE values for each of six states (collected from the previous Tables) and their total MAE ($\mathrm{MAE_{tot}}$) for the BSE/evGW level of theory.

State	BSE/evGW		
	PBE	**PBE0**	**CAM-B3LYP**
1B	0.050	0.055	0.060
2A	0.205	0.187	0.178
2B	0.328	0.263	0.205
3A	0.177	0.133	0.103
3B	0.287	0.218	0.178
4A	0.376	0.354	0.315
$\mathbf{MAE_{tot}}$	**0.237**	**0.202**	**0.173**

CARTESIAN COORDINATES

The ground state structures with the twist angle between the pyrrole and phenyl rings going from 0° to 90° by 10° steps are given below and were optimized at the CCSD/cc-pVDZ level of theory. These optimizations were done constraining the twist angles and thus, the 0° and 90° structures have C_{2v} symmetry, while the others fall into the C_2 point group. These optimizations were done using the Gaussian 16 program.

0° twist angle

C	-0.000000	0.000000	0.417890
C	1.213735	0.000000	1.136307
C	-1.213735	-0.000000	1.136307
C	0.000000	0.000000	3.254275
C	1.208212	0.000000	2.539696
C	-1.208212	0.000000	2.539696
C	1.125937	-0.000000	-1.824346
C	-1.125937	-0.000000	-1.824346
C	0.719250	-0.000000	-3.144059
C	-0.719250	-0.000000	-3.144059
N	-0.000000	-0.000000	-1.006958
H	2.172065	0.000000	0.612546
H	-2.172065	-0.000000	0.612546
H	2.164613	0.000000	3.074171
H	-2.164613	0.000000	3.074171
H	0.000000	0.000000	4.349127
H	2.131171	-0.000000	-1.411202
H	-2.131171	-0.000000	-1.411202
H	1.380756	-0.000000	-4.011330
H	-1.380756	-0.000000	-4.011330

10° twist angle

C	-0.000000	-0.000000	0.418083
C	1.214458	0.002784	1.134608
C	-1.214458	-0.002784	1.134608
C	0.000000	-0.000000	3.251886
C	1.208903	-0.000989	2.538048
C	-1.208903	0.000989	2.538048
C	1.109613	-0.193034	-1.822150
C	-1.109613	0.193034	-1.822150
C	0.708305	-0.125100	-3.142170
C	-0.708305	0.125100	-3.142170
N	-0.000000	0.000000	-1.006054
H	2.170773	0.029161	0.607029
H	-2.170773	-0.029161	0.607029
H	2.164819	0.002684	3.073387
H	-2.164819	-0.002684	3.073387
H	0.000000	-0.000000	4.346770
H	2.092417	-0.399237	-1.405402
H	-2.092417	0.399237	-1.405402
H	1.358075	-0.247167	-4.009743
H	-1.358075	0.247167	-4.009743

20° twist angle

C	-0.000000	-0.000000	0.418679
C	1.216052	0.004582	1.130900
C	-1.216052	-0.004582	1.130900
C	-0.000000	-0.000000	3.246534
C	1.210508	-0.002749	2.534469
C	-1.210508	0.002749	2.534469
C	1.060484	-0.381466	-1.817352
C	-1.060484	0.381466	-1.817352
C	0.675917	-0.246043	-3.138052
C	-0.675917	0.246043	-3.138052
N	-0.000000	0.000000	-1.004199
H	2.168103	0.043392	0.594738
H	-2.168103	-0.043392	0.594738
H	2.165289	0.002323	3.071829
H	-2.165289	-0.002323	3.071829
H	-0.000000	-0.000000	4.341498
H	1.984871	-0.767540	-1.392502
H	-1.984871	0.767540	-1.392502
H	1.292347	-0.482606	-4.006336
H	-1.292347	0.482606	-4.006336

30° twist angle

C	0.000000	-0.000000	0.419693
C	1.217688	0.005372	1.127234
C	-1.217688	-0.005372	1.127234
C	0.000000	-0.000000	3.240950
C	1.212335	-0.004706	2.531003
C	-1.212335	0.004706	2.531003
C	0.979097	-0.559538	-1.812558
C	-0.979097	0.559538	-1.812558
C	0.623158	-0.359286	-3.134042
C	-0.623158	0.359286	-3.134042
N	-0.000000	0.000000	-1.002653
H	2.165387	0.044618	0.581852
H	-2.165387	-0.044618	0.581852
H	2.165818	-0.000105	3.070657
H	-2.165818	0.000105	3.070657
H	0.000000	-0.000000	4.336022
H	1.820554	-1.098069	-1.379099
H	-1.820554	1.098069	-1.379099
H	1.187784	-0.699697	-4.003103
H	-1.187784	0.699697	-4.003103

40° twist angle

C	-0.000000	-0.000000	0.421104
C	1.218921	0.005384	1.124721
C	-1.218921	-0.005384	1.124721
C	-0.000000	-0.000000	3.236672
C	1.213981	-0.006185	2.528753
C	-1.213981	0.006185	2.528753
C	0.867414	-0.721342	-1.809144
C	-0.867414	0.721342	-1.809144
C	0.551599	-0.461563	-3.131413
C	-0.551599	0.461563	-3.131413
N	0.000000	0.000000	-1.002050
H	2.163027	0.038948	0.571688
H	-2.163027	-0.038948	0.571688
H	2.166295	-0.002878	3.070440
H	-2.166295	0.002878	3.070440
H	-0.000000	-0.000000	4.331860

H	1.606416	-1.390165	-1.368804
H	-1.606416	1.390165	-1.368804
H	1.048509	-0.893748	-4.001084
H	-1.048509	0.893748	-4.001084

50° twist angle

C	-0.000000	-0.000000	0.422794
C	1.219644	0.004836	1.123610
C	-1.219644	-0.004836	1.123610
C	-0.000000	-0.000000	3.234130
C	1.215286	-0.006739	2.527934
C	-1.215286	0.006739	2.527934
C	0.728707	-0.861478	-1.807422
C	-0.728707	0.861478	-1.807422
C	0.463304	-0.549926	-3.130417
C	-0.463304	0.549926	-3.130417
N	0.000000	0.000000	-1.002437
H	2.161130	0.030911	0.565198
H	-2.161130	-0.030911	0.565198
H	2.166680	-0.004754	3.071189
H	-2.166680	0.004754	3.071189
H	-0.000000	-0.000000	4.329430
H	1.347150	-1.641121	-1.362649
H	-1.347150	1.641121	-1.362649
H	0.878688	-1.060414	-4.000452
H	-0.878688	1.060414	-4.000452

60° twist angle

C	-0.000000	-0.000000	0.424540
C	1.219957	0.003912	1.123571
C	-1.219957	-0.003912	1.123571
C	-0.000000	-0.000000	3.233024
C	1.216242	-0.006187	2.528171
C	-1.216242	0.006187	2.528171
C	0.567295	-0.975347	-1.807020
C	-0.567295	0.975347	-1.807020
C	0.360783	-0.621784	-3.130628
C	-0.360783	0.621784	-3.130628
N	0.000000	-0.000000	-1.003474
H	2.159729	0.022850	0.561850
H	-2.159729	-0.022850	0.561850
H	2.166971	-0.005145	3.072529
H	-2.166971	0.005145	3.072529
H	-0.000000	-0.000000	4.328421
H	1.048104	-1.845651	-1.359961
H	-1.048104	1.845651	-1.359961
H	0.682980	-1.195476	-4.000817
H	-0.682980	1.195476	-4.000817

70° twist angle

C	-0.000000	-0.000000	0.426066
C	1.220036	0.002734	1.124028
C	-1.220036	-0.002734	1.124028
C	-0.000000	-0.000000	3.232738
C	1.216897	-0.004661	2.528848
C	-1.216897	0.004661	2.528848
C	0.388251	-1.059315	-1.807282
C	-0.388251	1.059315	-1.807282

C	0.247027	-0.674907	-3.131354
C	-0.247027	0.674907	-3.131354
N	0.000000	-0.000000	-1.004662
H	2.158768	0.015185	0.560425
H	-2.158768	-0.015185	0.560425
H	2.167180	-0.004159	3.073932
H	-2.167180	0.004159	3.073932
H	-0.000000	-0.000000	4.328211
H	0.717093	-1.997220	-1.359248
H	-0.717093	1.997220	-1.359248
H	0.466951	-1.295033	-4.001575
H	-0.466951	1.295033	-4.001575

80° twist angle

C	-0.000000	-0.000000	0.427106
C	1.220027	0.001403	1.124489
C	-1.220027	-0.001403	1.124489
C	-0.000000	-0.000000	3.232753
C	1.217285	-0.002485	2.529448
C	-1.217285	0.002485	2.529448
C	0.197174	-1.110753	-1.807651
C	-0.197174	1.110753	-1.807651
C	0.125499	-0.707535	-3.132012
C	-0.125499	0.707535	-3.132012
N	0.000000	0.000000	-1.005563
H	2.158189	0.007619	0.559905
H	-2.158189	-0.007619	0.559905
H	2.167311	-0.002282	3.074942
H	-2.167311	0.002282	3.074942
H	-0.000000	-0.000000	4.328274
H	0.364091	-2.090334	-1.359240
H	-0.364091	2.090334	-1.359240
H	0.237009	-1.356027	-4.002215
H	-0.237009	1.356027	-4.002215

90° twist angle

C	0.000000	-0.000000	0.427641
C	1.220016	-0.000000	1.124835
C	-1.220016	-0.000000	1.124835
C	0.000000	-0.000000	3.232951
C	1.217414	-0.000000	2.529843
C	-1.217414	-0.000000	2.529843
C	-0.000000	1.128076	-1.807642
C	-0.000000	-1.128076	-1.807642
C	-0.000000	0.718539	-3.132102
C	-0.000000	-0.718539	-3.132102
N	-0.000000	0.000000	-1.005731
H	2.157995	-0.000000	0.559945
H	-2.157995	-0.000000	0.559945
H	2.167358	-0.000000	3.075466
H	-2.167358	-0.000000	3.075466
H	0.000000	-0.000000	4.328488
H	-0.000000	2.121723	-1.359135
H	-0.000000	-2.121723	-1.359135
H	-0.000000	1.376583	-4.002285
H	-0.000000	-1.376583	-4.002285