

Computational Study of Protein Splicing: entire reaction pathway for C-terminal Splice and Intein scission

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Figure 1: Energy profile in kcal/mol for all reaction pathways characterized along the present work: the three pathways of Asn-Thr dipeptide and the Large model. In order to test the validity of B3LYP DFT functional, the energy of all stationary points were recalculated at the B3LYP/6-31+G(d) optimized geometries with two other DFT functionals (B3PW91 and B3P86) and MP2 ab-initio method. The 6-311++G(d,p) basis set was used for all calculations.

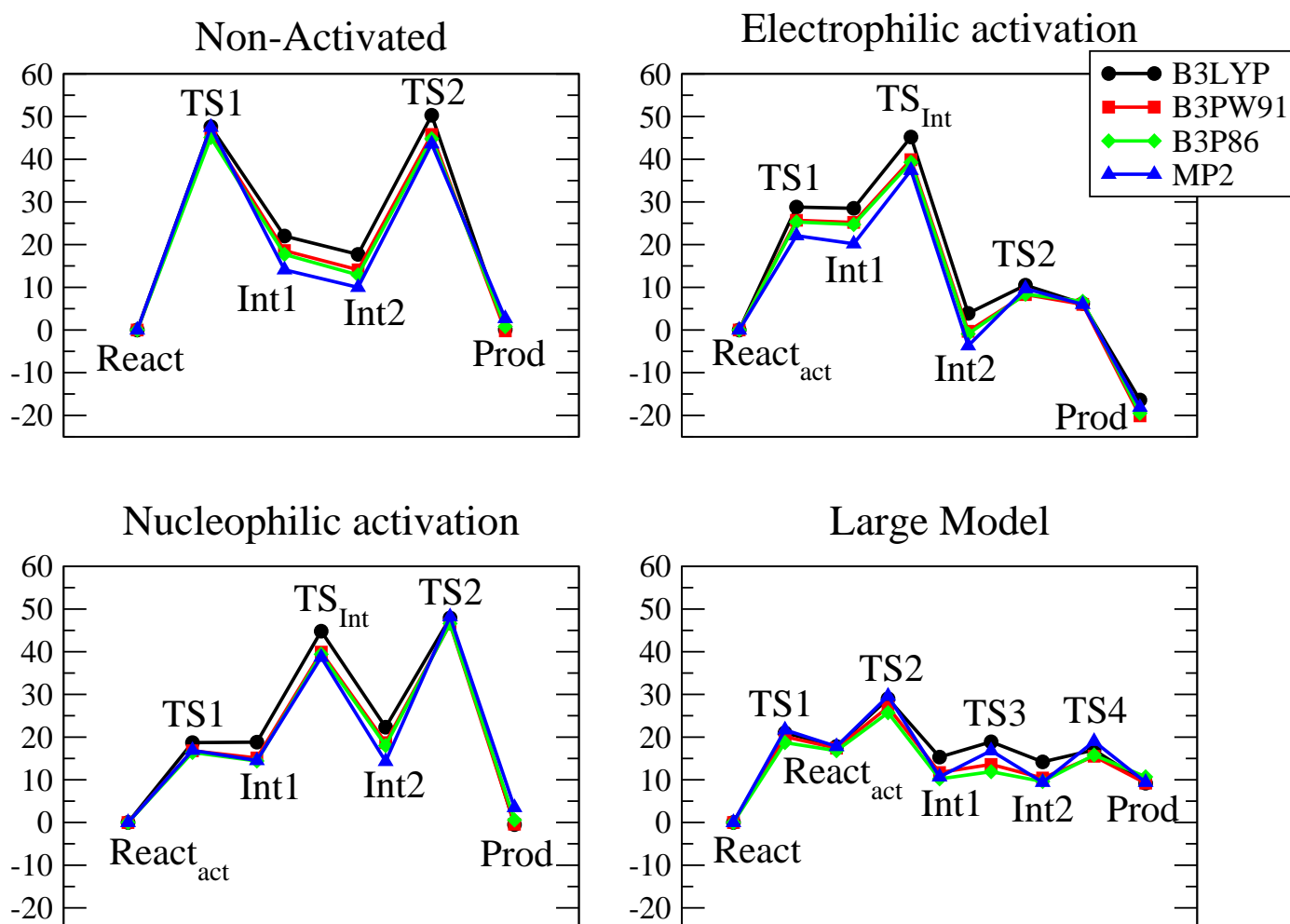


Table I: Electronic energy values in kcal/mol for all reaction pathways characterized along the present work: the three pathways of Asn-Thr dipeptide and the Large model. In order to test the validity of B3LYP DFT functional, the energy of all stationary points were recalculated at the B3LYP/6-31+G(d) optimized geometries with two other DFT functionals (B3PW91 and B3P86) and MP2 ab-initio method. The 6-311++G(d,p) basis set was used for all calculations.

	B3LYP	B3PW91	B3P86	MP2
Non-activated Reaction				
React	0.0	0.0	0.0	0.0
TS1	47.6	46.0	45.1	47.5
Int1	22.0	18.6	17.7	14.1
Int2	17.7	14.1	12.9	10.0
TS2	50.3	45.8	44.8	43.6
Prod	0.1	-0.2	0.8	2.7
Electrophilic activation				
<i>React^{elec}_{act}</i>	0.0	0.0	0.0	0.0
TS1	28.8	25.7	25.3	22.1
Int1	28.5	25.2	24.7	20.2
<i>TS_{Int}</i>	45.2	39.9	39.3	37.4
Int2	3.9	-0.3	-0.9	-3.7
TS2	10.5	8.3	8.4	9.7
Prod1	6.2	6.0	6.7	6.0
Prod2	-16.4	-20.1	-19.5	-18.1
Nucleophilic activation				
<i>React^{nuct}_{act}</i>	0.0	0.0	0.0	0.0
TS1	18.7	16.8	16.4	16.9
Int1	18.8	15.1	14.4	14.5
<i>TS_{Int}</i>	44.8	39.9	39.4	38.7
Int2	22.3	18.7	18.0	14.3
TS2	47.9	46.5	46.6	48.2
Prod	-0.5	-0.4	0.6	3.5
Large model				
React	0.0	0.0	0.0	0.0
TS1	21.0	20.1	18.7	21.7
<i>React_{act}</i>	17.8	17.4	16.8	17.8
TS2	29.0	27.0	25.7	29.6
Int1	15.3	11.7	10.2	10.7
TS3	18.9	13.6	11.9	16.8
Int2	14.2	10.4	9.6	9.4
TS4	17.0	15.5	15.8	19.0
Prod	9.2	9.2	10.7	9.4