

Modelling the NMR Signatures associated with the functional conformational switch in the major light-harvesting antenna of Photosystem II in Higher Plants

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SUPPORTING INFORMATION

Effects of dihedral constraints on chlorophyll-a carbon chemical shifts

The structures of Chla602, Chla603, Chla604, Chla610, and Chla612 were taken from the LHCII structure (PDB code 1RWT) reported by Liu et al 2004. The carbon atoms were replaced with the C13 isotope and the missing hydrogen atoms were added. Whilst freezing all dihedrals along the conjugated macrocycle each structure was optimised to the DFT/wB97xD/6-31G(d) level. The C13 chemical shifts (relative to a tetramethylsilane (TMS) chemical shift standard) were computed via a GIAO/wB97xD/6-311G(2d,2p) calculation. For comparison the same NMR calculations were performed on C13-enriched planar Chla. The constrained optimisation results in significant perturbations to the C13 chemical shifts relative to the values obtained for planar chlorophyll. The rms difference between the planar and distorted values is ~2.9 ppm with a maximum deviation of +13.8 ppm for C1 in Chla612. Such differences are typically larger than the qE-associated changes being investigated. Additionally, the precise physical meaning of these non-planar distortions is unclear given the resolution (2.72Å) of the LHCII structure. For this reason all no dihedral constraints were imposed on the chlorophylls during the calculations described in the main text.

REFERENCES

Liu Z, Yan H, Wang K, Kuang T, Zhang J, Gui L, An X, Chang W (2004) Crystal structure of spinach major light-harvesting complex at 2.72 Å resolution. Nature 428: 287-292.

TABLES

TABLE S1: The calculated C13 chemical shifts (ppm) of the conjugated macrocycle of a planar Chla compared with those calculated for constrained optimised Chla602, Chla603, Chla604, Chla610 and Chla612.

Macrocycle	C13 Chemical Shift (ppm)					
	Chla	Chla602	Chla603	Chla604	Chla610	Chla612
1	157.817	157.777	158.860	158.237	157.697	171.657
2	135.261	136.122	137.691	136.054	138.394	137.357
3	144.344	146.670	145.987	140.070	142.360	154.079
4	144.573	145.400	144.727	148.693	146.643	137.743
5	107.517	105.957	107.112	105.991	107.194	105.055
6	150.075	148.975	151.332	150.838	150.149	153.499
7	135.095	135.416	136.753	138.006	135.849	140.986
8	146.072	148.105	147.385	147.604	147.184	148.405
9	143.629	144.143	145.011	142.871	143.658	145.257
10	114.489	115.025	113.398	114.506	113.924	107.140
11	146.327	147.387	147.096	146.638	147.205	146.367
12	143.969	144.366	142.221	147.548	144.887	147.349
13	133.310	132.711	131.916	134.379	132.115	135.194
14	165.712	163.006	165.123	167.971	166.350	161.655
15	103.375	103.003	103.093	107.559	103.413	111.120
16	163.270	161.146	163.159	162.625	161.066	167.750
17	47.069	51.807	49.439	50.312	48.206	45.861
18	49.754	46.218	44.586	51.245	49.360	48.344
19	171.859	173.811	173.319	174.760	175.839	175.043
20	89.404	88.443	87.998	88.790	90.803	88.099