Supplementary Information

for the paper entitled

Protein-induced geometric constraints and charge transfer in Bacteriochlorophyll-histidine complexes in LH2

by

Piotr K. Wawrzyniak, A. Alia, Roland G. Schaap, Mattijs M. Heemskerk, Huub J.M. de Groot and Francesco Buda*

Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Discussion on basis set tests and choice of exchange-correlation functional

Basis set tests were performed for the reference compounds (TMS, NH_3) in vacuum, using 6-311++G, 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) and analogous double-zeta basis sets together with the 6-31G(d,p) without diffuse functions. The results are collected in Table 1S. Addition of diffuse functions has the largest effect on the nitrogen shielding (8.0 ppm) and influences ^{13}C and ^{1}H chemical shieldings by only 1.2 ppm and 0.6 ppm, respectively. The inclusion of polarization functions has also important effects: When going from the 6-311++G basis to the 6-311++G(d,p) basis, the chemical shieldings change by 9.4 ppm for nitrogen, 5.5 ppm for carbon and 0.8 ppm for hydrogen. Addition of polarization functions in the triple-zeta basis beyond the (d,p) set results in only small changes for all the atoms. Interestingly, the smallest basis set used here, namely 6-31G(d,p), produces values for ^{15}N close to those obtained with larger triple-zeta basis sets. This coincidence, however, may be attributed to a fortuitous error cancellation rather than to the accuracy of this particular basis.

The above-mentioned triple-zeta basis sets were also tested on histidine in all four possible protonation states of its imidazole ring and the results are reported in Table 2S. Similarly to the chemical shieldings of the reference compounds, convergence is essentially reached with the 6-311++G(d,p) basis set. Also in this case the inclusion of (d,p) polarization functions into the 6-311++G basis set has important effects, particularly for the unprotonated ring nitrogens where a chemical shift change of about 30 ppm is observed.

Table 3S contains the chemical shifts for all the histidines using the B3LYP hybrid functional with the 6-311++G(d,p) basis set. These results show that the choice of this popular functional has a marginal effect on the chemical shifts when compared to BLYP.

Table 1S. Basis set influence on the DFT/BLYP computed chemical shieldings [ppm] for the reference compounds.

	NH_3		TMS	
	N	H	C	H
6-31G(d,p)	255.8	32.0	186.4	31.5
6-31++G	270.7	32.3	189.5	32.3
6-31++G(d,p)	263.8	31.4	187.6	31.4
6-31++G(2d,2p)	265.1	31.4	186.6	31.4
6-31++G(3df,3pd)	262.7	31.4	185.7	31.3
6-311++G	264.2	32.5	184.1	32.5
6-311++G(d,p)	254.8	31.8	178.6	31.7
6-311++G(2d,2p)	255.8	31.7	178.7	31.6
6-311++G(3df,3pd)	256.4	31.4	179.1	31.5

Table 2S. Histidine chemical shifts [ppm] in different protonation states calculated with DFT/BLYP and various basis sets. B1, B2, B3 and B4 refer to 6-311++G, 6-311++G(d,p), 6-311++G(2d,2p) and 6-311++G(3df,3pd) basis set, respectively. The ^{1}H and ^{13}C chemical shifts are referred to TMS, while the ^{15}N chemical shifts to NH_3.

	Positive				Neutralτ				Neutralπ				Negative			
	B1	B2	B3	B4	B1	B2	B3	B4	B1	B2	B3	B4	B1	B2	B3	B4
C	201.8	190.3	191.3	191.6	196.6	186.5	187.1	187.5	197.2	186.5	187.2	187.4	194.3	185.7	186.4	192.1
C α	65.4	64.6	64.9	66.0	64.2	63.2	63.3	64.2	64.9	64.8	65.0	65.9	65.8	64.6	64.5	65.9
C β	39.7	37.2	37.2	38.2	44.4	42.5	42.0	43.4	34.5	34.3	34.0	35.3	53.3	51.7	51.3	48.9
C γ	146.2	144.3	143.8	144.9	151.8	148.5	148.7	149.7	133.8	131.6	130.9	131.5	141.0	137.7	138.0	139.3
C δ	125.4	122.6	121.6	122.6	120.1	117.9	116.8	116.4	137.2	134.5	134.8	135.4	136.4	133.4	133.2	131.0
C ε	135.3	132.9	131.8	132.3	139.4	136.0	135.9	137.3	140.8	137.3	137.0	138.0	159.3	154.0	154.5	154.2
N	60	54	54	53	46	44	44	44	69	62	63	62	48	42	42	51
N π	220	212	213	213	331	302	302	302	198	190	190	190	320	293	293	290
N τ	195	188	188	188	182	175	176	175	332	303	302	302	323	295	294	292
H δ	7.1	7.2	7.3	7.3	6.7	6.9	6.9	6.9	6.9	7.0	7.1	7.1	6.7	7.0	7.1	6.9
H ε	7.8	8.0	8.1	8.1	7.4	7.4	7.5	7.6	7.3	7.3	7.4	7.4	7.5	7.4	7.5	7.4
H π	13.1	14.2	14.9	15.3	-	-	-	-	8.6	8.9	9.2	9.3	-	-	-	-
H τ	8.5	8.9	9.3	9.4	7.6	8.1	8.4	8.6	-	-	-	-	-	-	-	-
H (-C α)	3.9	3.7	3.9	3.8	4.2	4.0	4.1	4.1	3.8	3.5	3.6	3.5	4.2	3.9	4.0	4.4
H (-C β)	3.4	3.3	3.3	3.3	3.4	3.2	3.2	3.2	3.1	3.0	3.1	3.0	3.7	3.6	3.7	3.7
H (-C β)	3.7	3.4	3.5	3.5	2.4	2.3	2.3	2.3	3.2	3.0	3.0	3.0	2.2	2.2	2.2	2.4
H (-N)	1.8	1.7	1.7	1.7	1.4	1.3	1.4	1.5	1.4	1.2	1.3	1.4	1.7	1.7	1.8	0.8
H (-N)	2.5	2.2	2.2	2.3	0.9	0.7	0.7	0.8	2.0	1.8	1.8	1.9	0.6	0.3	0.4	0.5
H (-O)	7.8	7.2	7.4	7.5	6.3	5.8	6.1	6.2	6.4	5.8	6.0	6.2	5.4	4.9	5.2	5.4

Table 3S. Histidine chemical shifts [ppm] in different protonation states calculated with B3LYP/6-311++G(d,p). The ^{1}H and ^{13}C chemical shifts are referred to TMS, while the ^{15}N chemical shifts to NH_3.

	Positive	Neutralτ	Neutralπ	Negative
C	190.3	185.7	186.7	187.4
C α	61.1	62.1	61.8	61.4
C β	34.9	40.9	32.6	48.1
C γ	144.5	149.0	132.4	137.5
C δ	124.0	117.2	135.6	133.4
C ε	135.9	138.6	139.3	154.2
N	47.9	49.2	53.1	36.2
N π	209.6	305.9	187.1	290.2
N τ	186.1	173.8	301.9	290.8
H δ	7.3	6.9	7.1	6.9
H ε	8.1	7.4	7.4	7.3
H π	14.2	-	9.1	-
H τ	9.1	8.1	-	-
H (-C α)	3.6	3.3	3.4	3.9
H (-C β)	3.2	2.9	2.9	3.4
H (-C β)	3.4	3.0	3.0	2.1
H (-N)	1.5	0.9	1.6	0.2
H (-N)	2.2	1.6	1.0	1.5
H (-O)	7.1	5.6	5.8	5.0

Figure 1S. Comparison between experimental and DFT bond lengths in the imidazole ring of histidine. a) Positively charged histidine. The experimental values are from refs. [16,45-46]. The grey area represents the experimental range of bond lengths from different crystal structures. b) Neutral$_\pi$ and c) neutral$_\tau$ histidines. The experimental values are from refs. [16] and [47], respectively.

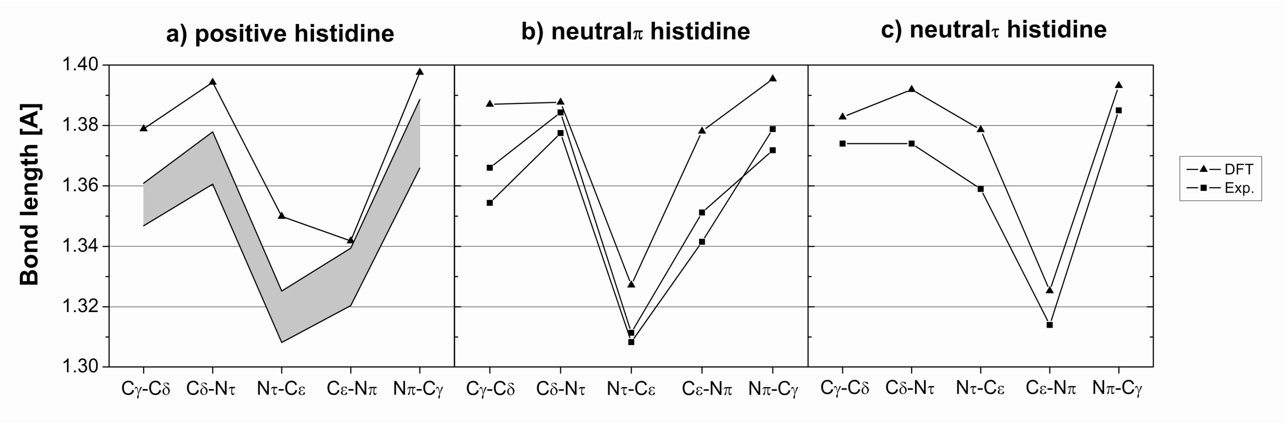

Figure 2S. Comparison between experimental and DFT chemical shifts [ppm] for a) positive histidine and b) neutral$_\tau$ histidine. The experimental values are from refs. [21,48] for histidine crystal samples.

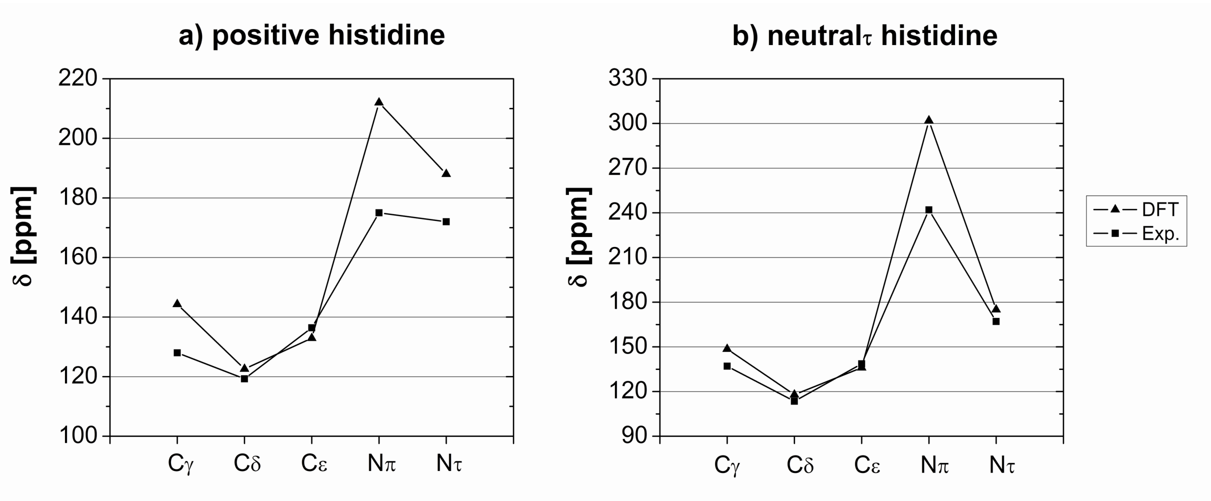

Figure 3S. Bond lengths of the histidine imidazole ring in BChl-His complex: DFT-optimized structure (triangles), DFT-partially optimized structure (squares) and X-ray structure of LH2 [27] (open circles).