Probing the Conformational Space and Molecular Structure of 5,10,15,20-Tetraphenyl-21H,23H-Porphyrin - Reference Point for Tetraphenylporphyrin Metal Complexes

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Content

Table S1. Cell parameters of the H_2TPP crystal.

References	CCDC Refcode	*T*, K	Density	Molecular volume, A^3	Z	Spacegroup	R_f, %	polymorph	θ_{av}
[8]	TPHPOR10	293	1.28	3189.0	4.0	I-42d	10.80	tetragon	78.1
[9]	TPHPOR01	293	1.28	798.7	1.0	P-1	5.60	triclinic	60.9
[10]	TPHPOR04	293	1.28	800.1	1.0	P-1	4.37	triclinic	62.1
[11]	TPHPOR14	293	1.27	801.3	1.0	P-1	4.90	triclinic	62.3
[12]	TPHPOR16	293	1.29	790.3	1.0	P-1	3.67	triclinic	62.2
[13]	TPHPOR11	100	1.31	778.8	1.0	P-1	4.90	triclinic	59.7
[14]	TPHPOR12	100	1.32	776.3	1.0	P-1	4.49	triclinic	60.0
[15]	TPHPOR13	120	1.31	778.6	1.0	P-1	5.47	triclinic	59.9
[16]	TPHPOR15	133	1.31	779.8	1.0	P-1	4.12	triclinic	59.9

Table S2. Conditions of GED/MS experiment.

nozzle-to-film distance, mm	338	598
number of recorded films	6	6
primary electrons beam current, μA	1.51	0.95
wavelength of electrons, Å	0.04114(4)	0.04174(4)
temperature of effusion cell, K	657(5)	657(5)
exposure time, s	85	82
residual gas pressure, Torr:		
- in the diffraction chamber	$1.3\cdot10^{-6}$	$1.8\cdot10^{-6}$
- in the mass-spectrometric block	$4.0\cdot10^{-7}$	$4.0\cdot10^{-7}$
scattering angles range/step, $Å^{-1}$	3.5-28.3/0.1	1.4-16.1/0.1
ionization voltage, V	50	50

Table S3. Experimental and theoretical vibrational amplitudes l_{exp}, l_{theor} and corrections r_{h1}-r_a for H_2TPP (B97D start model C_{2v} R_f=4.37%).

Group of amplitudes for distances in a range, Å	Labels from the Fig. S3	Labels from the Fig. 3	l_{exp}	l_{theor}	r_{h1}-r_a
0.0-1.2	-	C-H (ave)	0.088(7)	0.076	0.0010
	11,59	N-H	0.083(7)	0.072	0.0017
1.2-1.8	14,17	N_1-C_{a1}	0.061(2)	0.051	0.0039
	7,11	N_2-C_{a2}	0.059(2)	0.049	0.0004
	3,7	C_{a2}-C_m	0.060(2)	0.050	0.0000
	3,13	C_{a1}-C_m	0.061(2)	0.050	0.0000
	15,29	C_{a1}-C_{b1}	0.065(2)	0.054	-0.0011
	7,23	C_{a2}-C_{b2}	0.062(2)	0.052	0.0002
	23,24	C_{b2}-C_{b2}	0.057(2)	0.047	-0.0003
	29,30	C_{b1}-C_{b1}	0.055(2)	0.045	-0.0050
	33,40	C_1-C_2'	0.060(2)	0.050	0.0008
1.8-2.6	15,16	C_{a1}...C_{a1}	0.056(5)	0.057	0.0065
	15,30	C_{a1}…C_{b1}	0.058(5)	0.059	0.0007
	8,23	C_{a2}…C_{b2}	0.058(5)	0.059	0.0048
	4,18	N_1…C_m	0.069(6)	0.070	0.0109
	16,32	C_{a1}…C_1	0.076(7)	0.077	0.0025
2.6-3.2	34,54	C_1…C_4	0.073(9)	0.074	0.0100
	12,18	N_1…N_2	0.134(16)	0.137	0.0194
	7,17	C_{a2}…N_1	0.099(12)	0.101	0.0180
3.2-4.0	24,39	C_{b2}...C_2	0.247(25)	0.253	0.0316
	3,43	C_m...C_3	0.080(9)	0.082	0.0160
4.0-5.4	11,12	N_2…N_2	0.144(9)	0.132	0.0295
	30,45	C_{b1}...C_3	0.281(17)	0.258	0.0041
5.4-6.7	29,45	C_{b1}...C_3	0.302(26)	0.292	0.0163
	4,8	C_{a2}…C_m	0.117(10)	0.113	0.0451
6.7-8.0	4,39	C_m….C_2	0.270(23)	0.262	0.0402
	13,33	C_{a1}...C_1	0.138(20)	0.129	0.0642
8.0-10.0	38,42	C_2…C_2	0.499(72)	0.465	0.0230
	3,49	C_m…C_2	0.303(42)	0.283	0.0626
10.0-11.3	5,54	C_m…C_4	0.220(54)	0.210	0.1758
	49,51	C_3…C_4	0.608(78)	0.554	0.0915
11.3-20.0	26,51	C_{b2}…C_4	0.242(120)	0.217	0.1746
	44,52	C_3'…C_4	0.362(180)	0.326	0.2956

Table S4. Quantum chemical macrocyclic core parameters (bond length and valence angles: Å, deg.) of the H_2TPP conformers by B97D/cc-pVTZ and B3LYP/cc-pVTZ.

Parameter	B97D				B3LYP			
	C_{2h}(1)	C_{2h}(2)	C_{2v}	D_2	C_{2h}(1)	C_{2h}(2)	C_{2v}	D_2
N_1-C_{a1}	1.367	1.367	1.367	1.367	1.362	1.362	1.362	1.362
N_2-C_{a2}	1.377	1.376	1.376	1.376	1.372	1.372	1.372	1.371
C_{a1}-C_{b1}	1.459	1.459	1.459	1.459	1.456	1.456	1.456	1.456
C_{a2}-C_{b2}	1.433	1.433	1.433	1.434	1.430	1.430	1.430	1.430
C_{b1}-C_{b1}	1.356	1.356	1.357	1.356	1.348	1.348	1.348	1.348
C_{b2}-C_{b2}	1.371	1.372	1.372	1.372	1.364	1.364	1.364	1.364
C_m-C_{a1}	1.412	1.413	1.413	1.412	1.406	1.406	1.406	1.405
C_m-C_{a2}	1.406	1.406	1.406	1.405	1.399	1.399	1.399	1.398
C_m-C_1	1.493	1.493	1.491	1.494	1.497	1.497	1.497	1.498
C_1-C_2	1.404	1.404	1.405	1.404	1.397	1.396	1.397	1.396
C_2-C_3	1.396	1.396	1.396	1.397	1.390	1.390	1.390	1.390
C_3-C_4	1.398	1.398	1.398	1.398	1.390	1.390	1.390	1.390
N_2-H (2)	1.014	1.014	1.013	1.014	1.010	1.010	1.010	1.010
C_b-H ave	1.081	1.081	1.081	1.081	1.076	1.076	1.076	1.076
C_{ph}-H ave	1.086	1.087	1.086	1.087	1.082	1.082	1.082	1.082
N-C_{a1}-C_{b1}	110.9	110.9	110.9	110.9	110.7	110.7	110.7	110.7
N-C_{a2}-C_{b2}	106.6	106.5	106.5	106.5	106.4	106.4	106.4	106.4
C_{a1}-C_{b1}-C_{b1}	106.3	106.3	106.3	106.3	106.4	106.4	106.4	106.4
C_{a2}-C_{b2}-C_{b2}	108.1	108.1	108.1	108.1	108.2	108.2	108.2	108.2
C_{a1}-N-C_{a1}	105.6	105.5	105.6	105.6	105.8	105.8	105.8	105.8
C_{a2}-N-C_{a2}	110.6	110.7	110.7	110.7	110.7	110.8	110.8	110.8
C_{a1}-C_m-C_{a2}	125.5	125.6	125.4	125.6	125.4	125.4	125.3	125.4

Table S5. Quantum chemical macrocyclic core parameters of the H_2TPP conformers by B97D/cc-pVTZ and B3LYP/cc-pVTZ, calculated root-mean-square deviation RMSD (P_{C2v},$P_{i\ conf.}$) between parameters, calculated relative to C_{2v} structure for C_2, $C_{2h}(1)$, $C_{2h}(2)$, D_2.

	B97D/cc-pVTZ				B3LYP/cc-pVTZ			
	$C_{2h}(1)$	$C_{2h}(2)$	C_{2v}	D_2	$C_{2h}(1)$	$C_{2h}(2)$	C_{2v}	D_2
RMSD bonded parameters	0.00045	0.00043	0.0	0.00073	0.00018	0.00024	0.0	0.00050
N_1-X	2.05	2.05	2.04	2.04	2.04	2.04	2.04	2.04
N_2-X	2.11	2.11	2.11	2.11	2.10	2.10	2.10	2.10
C_m-C_m	6.94	6.94	6.94	6.93	6.91	6.91	6.91	6.91
N_1-N_1	4.09	4.09	4.09	4.09	4.08	4.07	4.07	4.07
N_2-N_2	4.23	4.23	4.23	4.22	4.20	4.20	4.21	4.20
Ca_2-C_m–C_1-C_2	64.3	64.5	61.5	67.0	74.2	75.5	72.6	79.8
C_{b1}-C_{b1}-C_{a1}-N_1	0.7	0.3	1.0	0.7	0.4	0.2	0.5	0.3
C_{b2}-C_{b2}-C_{a2}-N_2	0.3	0.8	0.5	0.7	0.2	0.4	0.2	0.3
C_{a1}-N_1-N_1-C_{a1}	180.0	180.0	170.7	178.9	180.0	180.0	175.3	179.5
C_{a2}-N_2-N_2-C_{a2}	180.0	180.0	171.7	179.9	180.0	180.0	175.8	180.0
C_{a1}-N_1-N_2-C_{a2}	2.6	2.4	7.0	0.4	1.7	1.2	3.5	0.2
C_{b1}-C_{a1}-N_1-X	179.7	171.6	170.0	179.7	179.9	175.6	174.8	179.9
C_{b2}-C_{a2}-N_2-X	170.5	179.7	171.1	179.7	173.8	179.9	175.3	179.9
C_m-C_m-C_m-C_m	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.2
C_{b1}-C_{b1}-C_{b1}-C_{b1}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
C_{b2}-C_{b2}-C_{b2}-C_{b2}	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.4

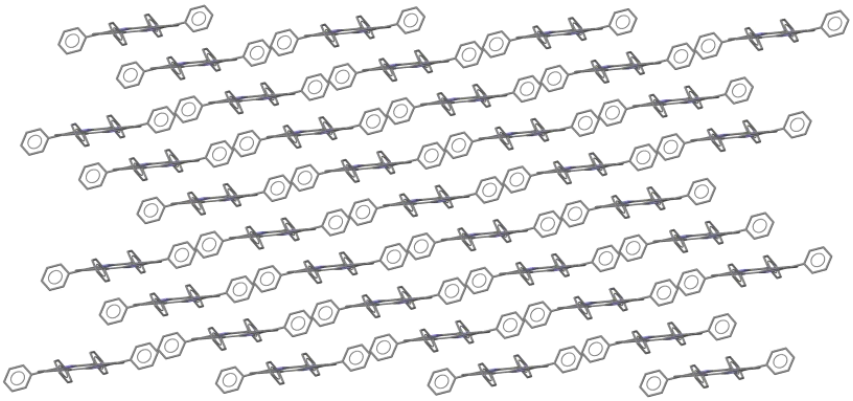

Fig. S1. Crystal structure of H_2TPP corresponded to the triclinic syngonia

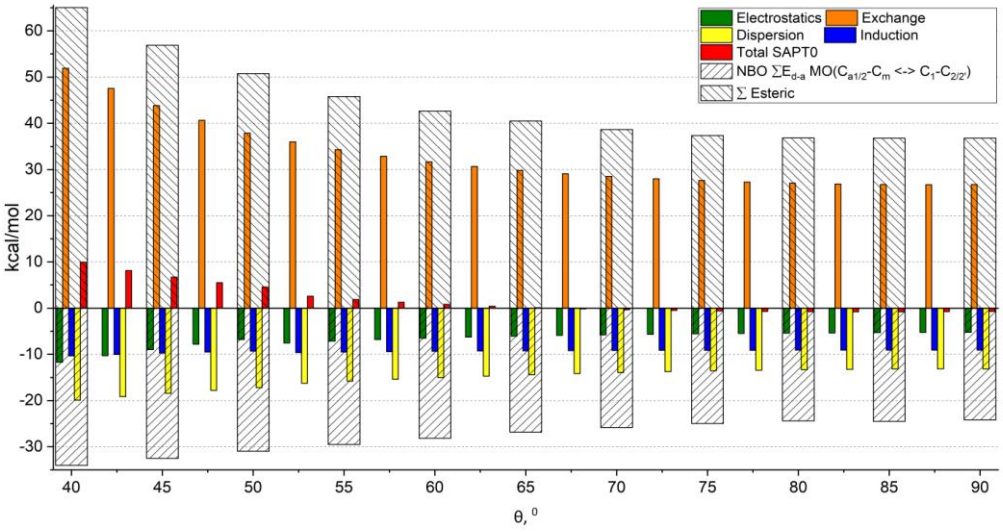

Fig. S2. Results of NBO analysis and SAPT0 methods. Decrease in steric repulsion energy when the torsion angle changes from θ =50º to 90º (graphs ΣE_{steric} (NBO) and ΣE_{exch} (SAPT0)). Method SAPT0 decomposes the total interaction energy into physically significant components: electrostatic (E_{elst}), exchange (E_{exch} - a consequence of the Pauli principle, repulsion between electrons with parallel spins), inductive (E_{ind}) and dispersive (E_{disp}).

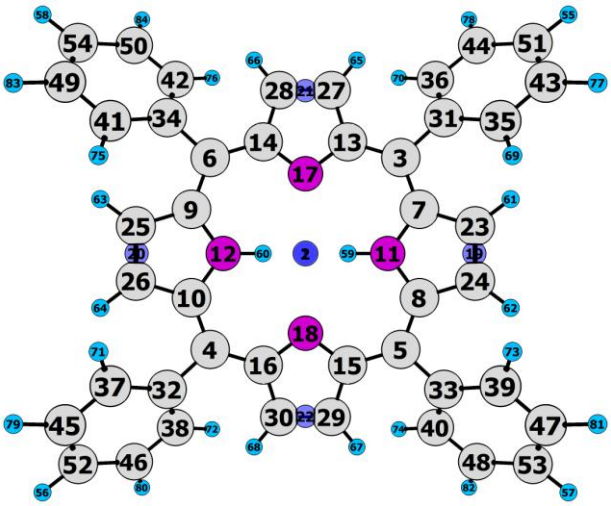

Fig. S3. Atom labeling to the Table S3.

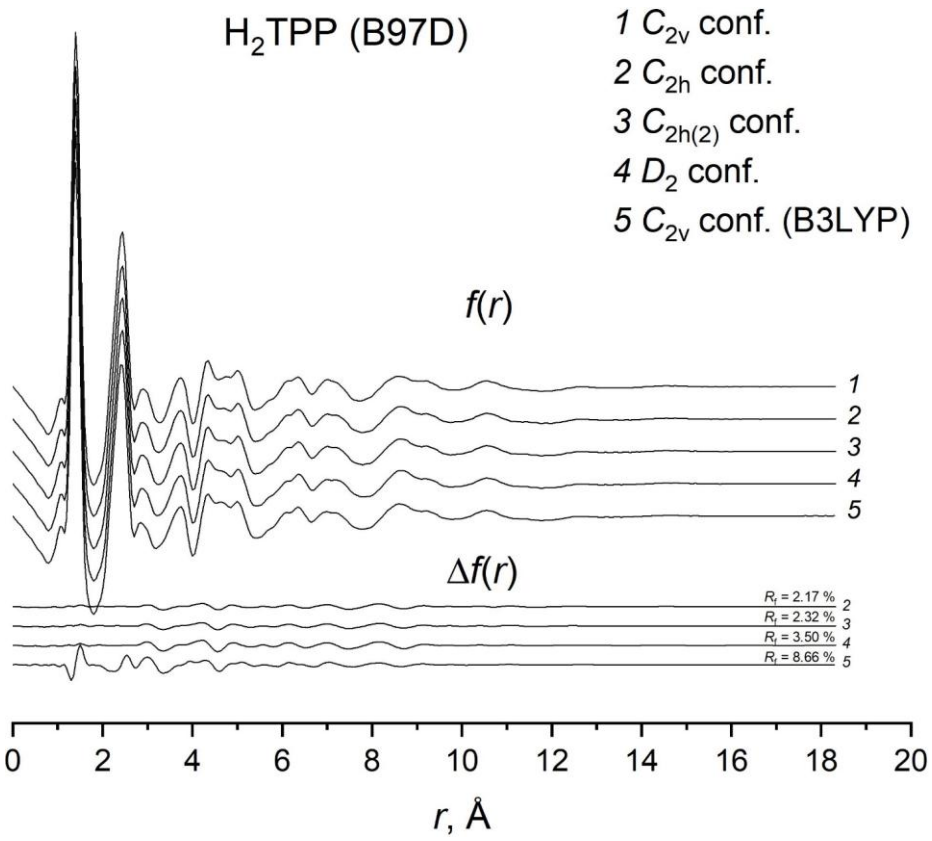

Fig. S4. Comparison of theoretical B97D/cc-pVTZ radial distribution functions $f(r)$ of H_2TPP. $\Delta f(r) = f(r)_1 - f(r)_j$ (j: 2,3,4,5,6).

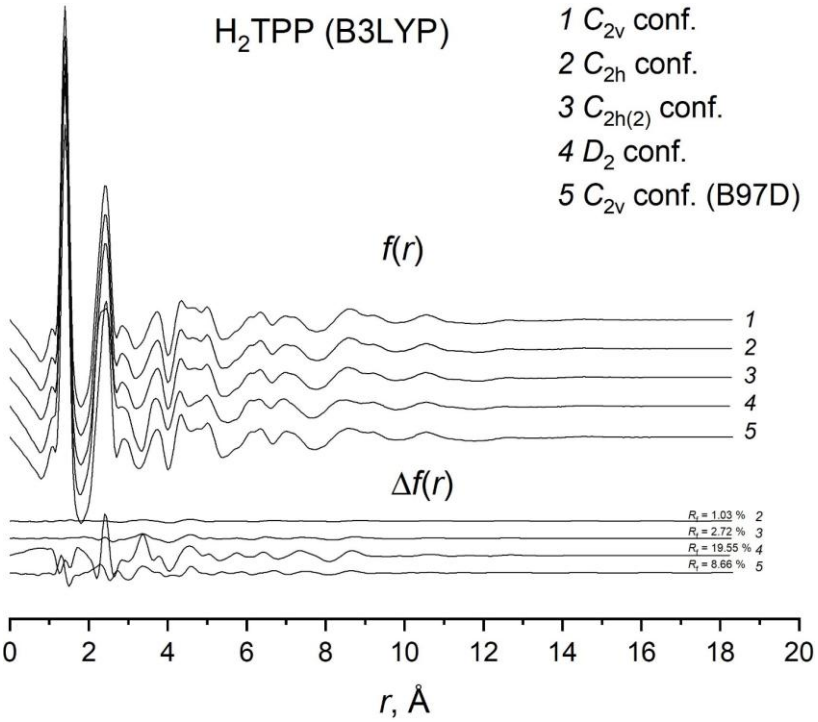

Fig. S5. Comparison of theoretical B3LYP/cc-pVTZ radial distribution functions $f(r)$ of H_2TPP. $\Delta f(r) = f(r)_1 - f(r)_j$ (j: 2,3,4,5,6).

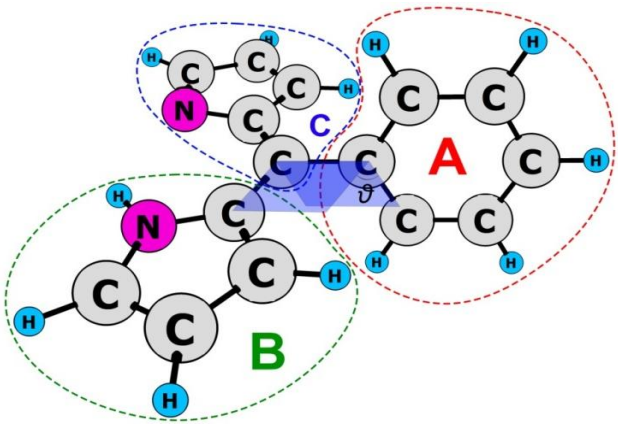

Fig. S6. C_6H_5-C_5NH_3-C_4NH_4 fragment being considered F/I-SAPT0/aug-cc-pVTZ calculations. The system is divided into three subsystems: **A**(C_6H_5-)and **B**(C_4NH_4) the strength of the interaction which we want to assess, as well as the link **C**(-C_5NH_3-).