

Supplementary Material of B821127B

Theoretical Study of Proton Encircling Modes in Proton Sponges with Tetraamido/Diamino Quaternized Macrocycles: The Role of π -Conjugated and Aliphatic Bridges

Nan Jiang, Jing Ma*

School of Chemistry and Chemical Engineering, Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of MOE, Nanjing University, Nanjing, 210093, People's Republic of China
E-mail: majing@nju.edu.cn, Fax: 86-25-83596131, Tel: 86-25-83597408

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Table S1. Hartree-Fock RHF→UHF stability tests for tetraamido/diamino quaternized macrocyclic complexes with proton.

System	Stability of wave function	
	HF	B3LYP
1a (phenyl)	no	yes
1b (pyridine)	no	yes
2a (furan)	no	yes
2b (thiophene)	no	yes
3a (butadienyl)	no	yes
3b (ethylene)	no	yes
4 (propyl)	yes	yes
5 (butyl)	yes	yes

Table S2. The difference (kcal/mol) in electronic energies and enthalpies between the protonated and unprotonated macrocycles.

	ΔE^a	ΔH^b
1a (phenyl)	137.9	132.0
1b (pyridine)	136.0	130.1
2a (furan)	130.5	125.2
2b (thiophene)	125.1	119.5
3a (butadienyl)	129.4	123.4
3b (ethylene)	145.8	139.5
4 (propyl)	149.0	145.3
5 (butyl)	143.5	138.5

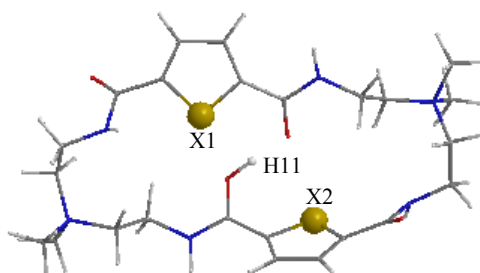
^aThe electronic energies are computed at MP2/6-31G(*d,p*) //B3LYP/6-31G(*d,p*) level.

^bThe Enthalpies are computed at B3LYP/6-31G(*d,p*)+ZPE level.

Table S3. The activation barriers, ΔE_A , (in units of kcal/mol) of proton transfer in O–H···O \rightleftharpoons O···H–O hydrogen bonds.

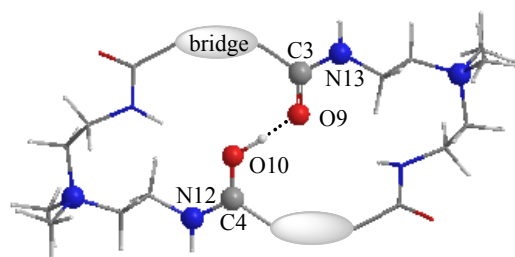
	B3LYP/6-31G(<i>d,p</i>)		MP2/6-31G(<i>d,p</i>) //B3LYP/6-31G(<i>d,p</i>)	
	ΔE_A	ΔE_A +ZPE	ΔE_A	ΔE_A +ZPE
1a (phenyl)	−0.22	−1.48	0.31	0.24
1b (pyridine)	−0.21	−1.44	0.39	0.33
2a (furan)	−0.95	−1.54	1.07	0.23
2b (thiophene)	−1.30	−1.20	3.20	2.65
3a (butadienyl)	−0.78	−1.41	1.82	0.77
3b (ethylene)	−1.02	−1.87	0.23	0.16
5 (butyl)	−0.73	−0.82	0.29	0.20

Table S4. Calculated NBO atomic charges at the MP2/6-31G(*d,p*)/B3LYP/6-31G(*d,p*) level on the encircled proton and the hetero atoms in the aromatic rings in the aromatic ring-bridged macrocycles.



	NBO charges			Interatomic distance	
	X1	X2	H11	$r_{X1 \cdots H11}$	$r_{X2 \cdots H11}$
Proton-trapped minima					
1a (phenyl)	-0.14	-0.12	0.60	2.73	2.62
1b (pyridine)	-0.48	-0.47	0.61	2.70	2.53
2a (furan)	-0.54	-0.53	0.60	2.51	2.40
2b (thiophene)	0.47	0.56	0.60	2.85	2.69
Transition states of proton transfer					
1a (phenyl)	-0.13	-0.13	0.60	2.68	2.68
1b (pyridine)	-0.47	-0.47	0.61	2.62	2.62
2a (furan)	-0.53	-0.53	0.60	2.46	2.46
2b (thiophene)	0.52	0.52	0.59	2.74	2.74

Table S5. Selected interatomic distances (Å) and angles (°) in the hydrogen bond frameworks in tetraamido/diamino macrocycles containing π -conjugated or aliphatic bridges. The corresponding geometric parameters of transition states of proton transfer are also given. The calculations are carried out at B3LYP/6-31G(*d,p*) level.



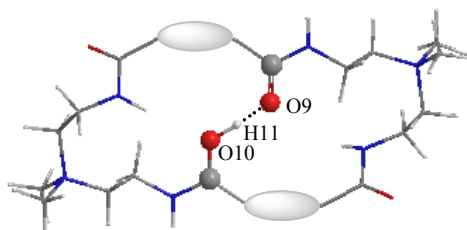
	π -Conjugated bridge						Aliphatic bridge	
	1a (phenyl)	1b (pyridine)	2a (furan)	2b (thiophene)	3a (butadienyl)	3b (ethylene)	4 (propyl) ^a	5 (butyl)
Proton-trapped minima								
$r_{C3=O9}$	1.261	1.251	1.256	1.253	1.259	1.257	1.267	1.263
$r_{C4=O10}$	1.286	1.275	1.285	1.301	1.298	1.284	1.267	1.274
r_{C3-N13}	1.351	1.352	1.354	1.351	1.352	1.352	1.336	1.340
r_{C4-N12}	1.338	1.336	1.340	1.332	1.333	1.329	1.336	1.333
$\angle O9-C3-N13$	119.4	120.4	120.9	120.6	121.2	119.0	117.8	119.4
$\angle O10-C4-N12$	116.6	117.7	117.8	117.6	117.9	115.8	117.8	118.3
Transition states of proton transfer								
$r_{C3=O9}$	1.273	1.262	1.269	1.274	1.278	1.274	--	1.272
$r_{C4=O10}$	1.273	1.262	1.269	1.274	1.278	1.274	--	1.272
r_{C3-N13}	1.344	1.344	1.344	1.342	1.342	1.350	--	1.335
r_{C4-N12}	1.344	1.344	1.344	1.342	1.342	1.350	--	1.335
$\angle O9-C3-N13$	118.0	119.1	119.4	119.2	120.5	118.0	--	118.6
$\angle O10-C4-N12$	118.0	119.1	119.4	119.1	120.5	118.0	--	118.6

^a In the propyl-containing macrocycle **4**, there is only a single-minimum for proton binding.

Table S6. Contributions from individual subsystems to the strength of hydrogen bonds, obtained from the energy-based fragmentation method at MP2/6–31G(*d,p*) level.

	Sub1 (Sub3)	Sub2 (Sub4)
1a	18.9	−5.4
1b	18.4	−5.3
2a	18.2	−5.2
2b	16.6	−5.1
3a	17.8	−5.1
3b	21.5	−4.7
4	25.2	−4.8
5	20.4	−4.7

Table S7. NBO charges on the oxygen and hydrogen atoms involved in the hydrogen bonding interactions.^a The Coulombic interaction energies (kcal/mol) between H⋯O are also listed in the last column.



	NBO charges			Coulombic interaction ^b
	O9	H11	O10	
1a (phenyl)	−0.83	0.60	−0.79	−118.7
1b (pyridine)	−0.79	0.61	−0.76	−113.5
2a (furan)	−0.79	0.60	−0.77	−109.5
2b (thiophene)	−0.81	0.60	−0.77	−99.7
3a (butadienyl)	−0.83	0.59	−0.77	−101.1
3b (ethylene)	−0.80	0.60	−0.78	−124.6
4 (propyl)	−0.80	0.59	−0.80	−130.2
5 (butyl)	−0.81	0.60	−0.79	−120.5

^a The calculations are carried out at MP2/6-31G(*d,p*)/B3LYP/6-31G(*d,p*) level.

^bThe interatomic Coulombic interaction energies are calculated by

$$E^{Coulomb} = 330.26q_{O9}q_{H11} / r_{O9\cdots H11}$$

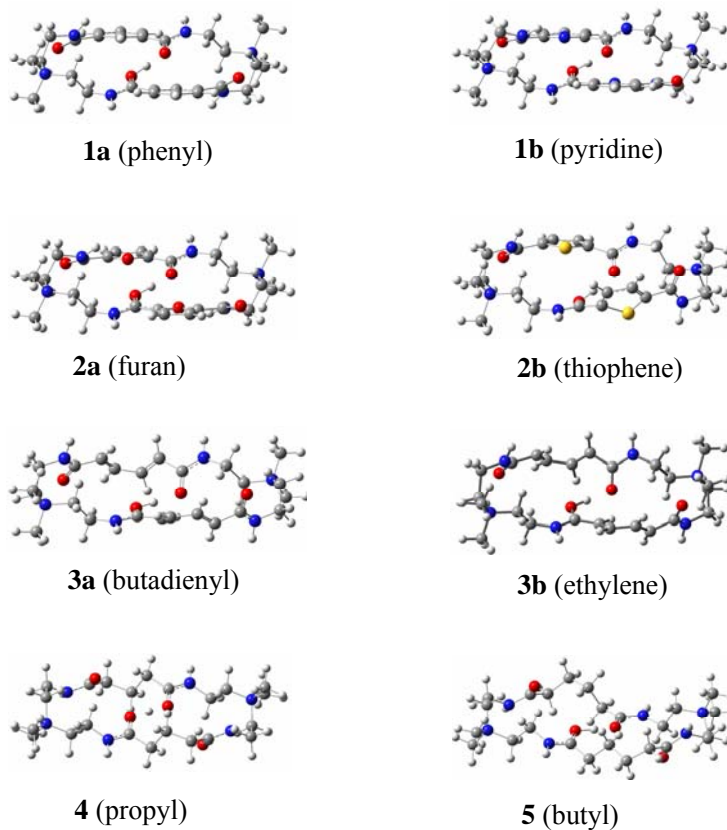
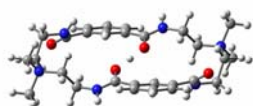
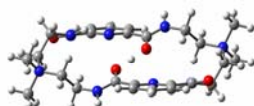


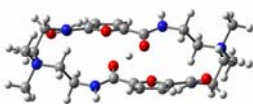
Fig. S1 Side view of B3LYP/6-31G(*d,p*) optimized structures of the complexes formed by proton and tetraamido/diamino quaternized macrocyclic analogues **1a** (phenyl), **1b** (pyridine), **2a** (furan), **2b** (thiophene), **3a** (butadienyl), **3b** (ethylene), **4** (propyl), and **5** (butyl).



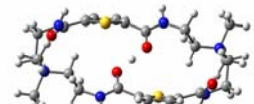
1a-TS (phenyl)



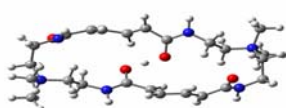
1b-TS (pyridine)



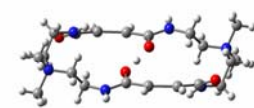
2a-TS (furan)



2b-TS (thiophene)



3a-TS (butadienyl)



3b-TS (ethylene)



5-TS (butyl)

Fig. S2 Side view of the transition states of proton transfer in macrocyclic analogues **1a** (phenyl), **1b** (pyridine), **2a** (furan), **2b** (thiophene), **3a** (butadienyl), **3b** (ethylene), and **5** (butyl). The structural optimization are carried out at B3LYP/6-31G(*d,p*) level, and there is only a single-minimum for proton binding in propyl-containing **4**.