Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI)

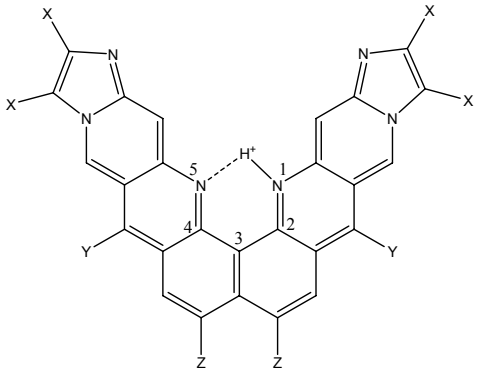
for

Polycyclic Croissant–like Organic Compounds are Powerful Superbases in the Gas Phase and Acetonitrile – A DFT Study

Nena Peran[a] and Zvonimir B. Maksić*[a]

Quantum Organic Chemistry Group, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Zagreb, Croatia. E-mail: zmaksic@spider.irb.hr

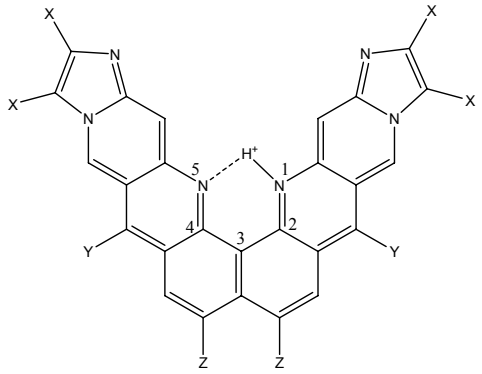
Table S1. Some geometric parameters and numbering of atoms pertaining the H^+–bridge in conjugate acids compared to those in initial bases.



	r_1(N1-H^+)[a]	r_2(N5---H^+)[a]	r_3(N1---N5)[b]	r_3(N1---N5)[b]	ϕ(N1-H^+---N5)[a]	ϕ_1[a,c]	ϕ_2[b,d]
1a	1.037	1.754	2.634	2.722	139.9	0.0	13.0
1b	1.035	1.759	2.636	2.722	139.8	0.4	12.5
1c	1.036	1.750	2.630	2.724	140.0	0.5	9.6
1d	1.036	1.759	2.637	2.729	139.9	1.4	11.4
1e	1.039	1.722	2.611	2.706	140.8	0.0	18.5
1f	1.040	1.729	2.617	2.714	140.6	0.1	15.7
1g	1.043	1.692	2.592	2.701	141.7	0.3	18.1
1h	1.039	1.716	2.600	2.710	140.0	5.2	22.2
1i	1.041	1.688	2.579	2.662	140.7	0.4	22.2
1j	1.042	1.679	2.572	2.649	140.8	4.4	19.4
1k	1.042	1.685	2.579	2.695	141.0	4.4	28.8
1l	1.041	1.689	2.581	2.696	140.8	3.1	25.4
1m	1.042	1.675	2.573	2.762	141.3	9.6	28.4

[a]in a protonated base, [b]in a neutral base [c]ϕ_1 and ϕ_1 are dihedral $N_5C_4C_3N_1$ angles in protonated and neutral bases, respectively.

Table S2. Selected angles at the protonation site.



	C2-N1---H^{+a}	C4-N5---H^{+a}	C2-C3-C4^{a}	C2-C3-C4^{b}	N1-C2-C3^{a}	N1-C2-C3^{b}
1a	112.6	103.3	123.7	124.2	120.6	120.6
1b	112.6	103.3	123.8	124.2	120.6	120.6
1c	112.6	103.3	123.6	124.4	120.6	120.8
1d	112.6	103.2	123.7	124.4	120.7	120.8
1e	112.4	103.8	123.9	123.8	119.9	119.8
1f	112.5	103.6	123.8	124.1	120.1	120.1
1g	112.3	104.1	123.9	123.9	119.4	119.5
1h	112.3	103.7	121.7	121.5	121.3	120.4
1i	112.2	104.1	121.1	120.7	121.3	120.8
1j	112.1	104.0	120.7	120.1	121.5	121.1
1k	112.2	104.0	121.9	121.4	120.7	119.6
1l	112.4	104.1	121.6	121.4	121.0	120.0
1m	112.3	103.6	122.2	121.7	120.0	119.4

[a]in a protonated base, [b]in a neutral base

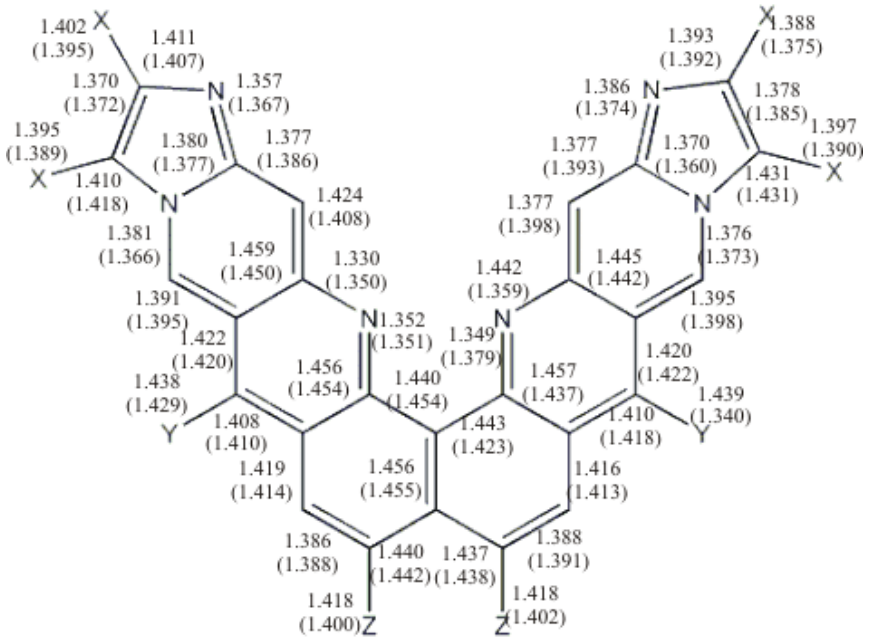


Figure S1. Bond distances for molecule **1k** and **1kH**$^+$ (in parenthesis). (X=Y=Z=NMe_2)

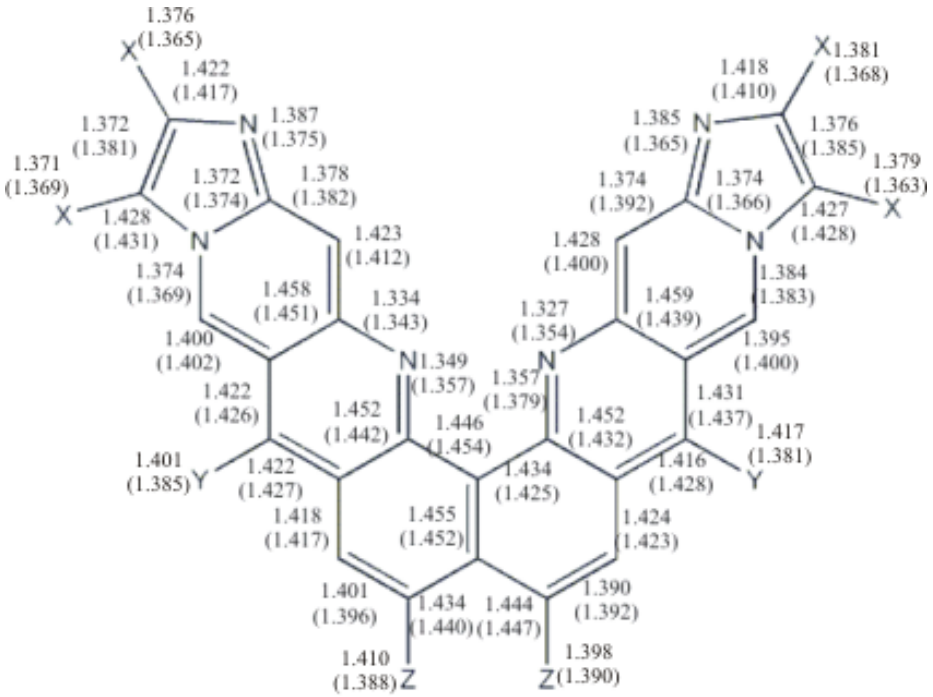
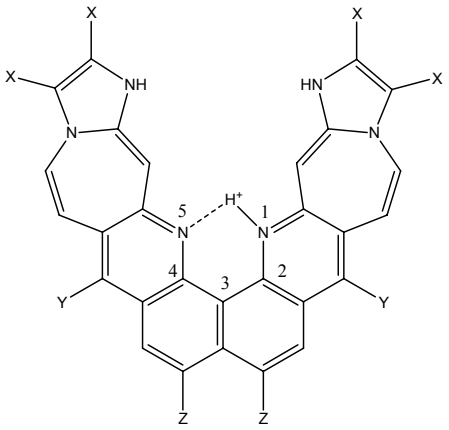


Figure S2. Bond distances for molecule **1m** and **1mH**$^+$ (in parenthesis).
(X=Y=Z=N=$P(NMe_2)_3$)

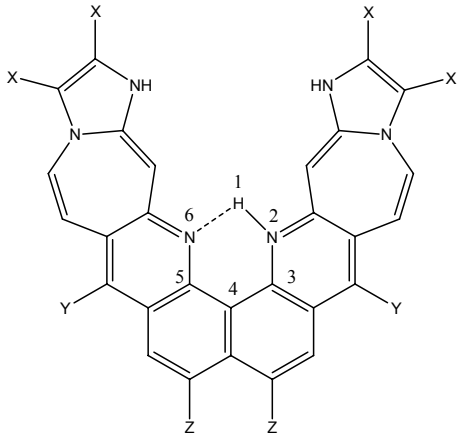
Table S3. Some geometric parameters and numbering of atoms pertaining the H^+–bridge in conjugate acids compared to those in initial bases.



	r_1(N1-H^+)[a]	r_2(N5---H^+)[a]	r_3(N1---N5)[a]	r_3(N1---N5)[b]	ϕ(N1-H^+---N5)[a]	ϕ_1[a,c]	ϕ_2[b,d]
2a	1.044	1.770	2.664	2.769	141.1	4.2	15.9
2b	1.044	1.767	2.662	2.774	141.1	4.4	14.0
2c	1.044	1.754	2.652	2.776	141.4	0.3	18.0
2d	1.039	1.805	2.687	2.801	140.2	6.6	19.4
2e	1.046	1.724	2.625	2.756	141.6	9.0	23.6
2f	1.045	1.735	2.634	2.747	141.5	5.6	18.5
2g	1.047	1.709	2.616	2.739	142.1	6.6	20.6
2h	1.046	1.731	2.628	2.737	141.1	9.8	25.4
2i	1.048	1.709	2.614	2.698	141.7	5.2	22.1
2j	1.049	1.703	2.612	2.689	142.2	2.6	18.1
2k	1.047	1.692	2.598	2.714	141.8	5.8	27.2
2l	1.045	1.703	2.603	2.703	141.4	9.2	24.2
2m	1.044	1.705	2.604	2.806	141.5	7.4	33.8

[a]in a protonated base, [b]in a neutral base [c]ϕ_1 and ϕ_1 are dihedral $N_5C_4C_3N_1$ angles in protonated and neutral bases, respectively.

Table S4. Selected angles at the protonation site.



	C2-N1-H^{+a}	C4-N5---H^{+a}	C2-C3-C4^{a}	C2-C3-C4^{b}	N1-C2-C3^{a}	N1-C2-C3^{b}
2a	111.7	101.9	124.2	124.8	120.6	120.6
2b	111.7	101.9	124.2	125.0	120.5	120.8
2c	111.8	102.2	124.0	124.6	120.4	120.5
2d	112.1	101.6	124.3	124.8	120.9	120.7
2e	112.0	102.3	124.0	124.0	119.3	119.5
2f	112.0	102.5	124.0	124.4	119.8	119.9
2g	112.0	102.8	124.1	124.3	119.2	119.4
2h	111.5	102.0	122.1	121.9	121.1	120.4
2i	111.3	102.3	121.7	121.3	121.2	120.8
2j	111.3	102.4	121.4	121.1	121.4	121.3
2k	112.0	102.9	122.0	121.6	120.4	119.3
2l	112.0	102.6	122.0	121.9	120.4	119.8
2m	112.2	102.8	121.8	123.0	120.6	118.9

[a]in a protonated base, [b]in a neutral base

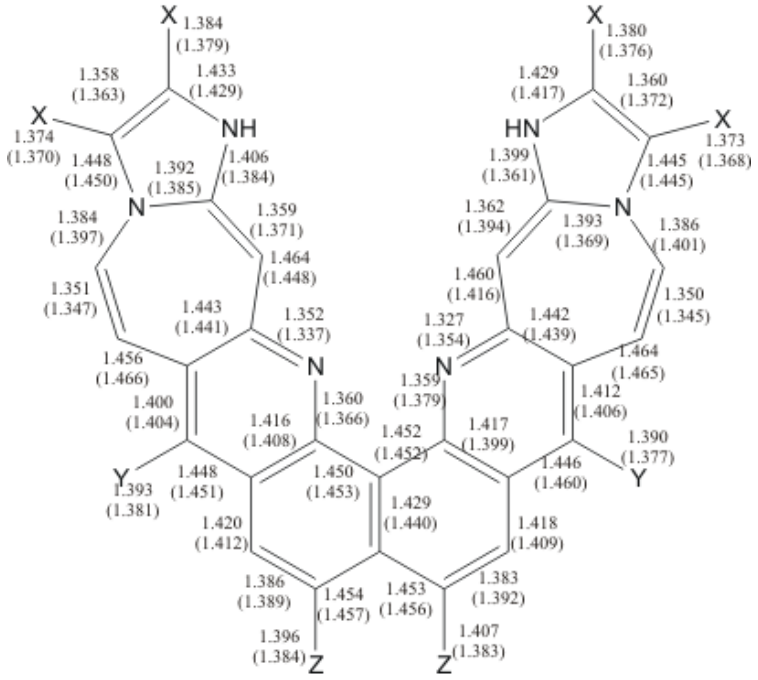


Figure S3. Bond distances for molecule **2m** and **2mH**$^+$ (in parenthesis). ($X=Y=Z=N=P(NMe_2)_3$)

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