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Supporting Information

Symmetrization of Cationic Hydrogen Bridges of Protonated Sponges Induced by Solvent and Counteranion Interactions as Revealed by NMR Spectroscopy

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(A) Syntheses of 1-chlorobenzotriazole and of 2-chloro-1,3,5-trinitrobenzene (picryl chloride)

1-Chlorobenzotriazole. According to Ref. 1 Benzotriazole (15 g, 0.12 mol) was dissolved in 100 ml acetic acid (50% in H_2O). Under stirring at room temperature 150 ml of a sodium hypochlorite solution (6%) were added. After 20 min. the solution was diluted with 100 ml of water. The precipitated solid was collected and dissolved in methylene chloride and the solution was dried over anhydrous magnesium sulphate. Concentration of the methylene chloride solution and addition of hexane to the cloud point, followed by cooling produced 1-chlorobenzotriazole (14.78 g, 80%), mp 105-106°C. MS [40°, EI 80 eV]: m/z 155 (28.1%, M^+ ^{37}Cl); 153 (76.1%, M^+ ^{35}Cl); 127 (12.0%, M^+-N_2); 125 (33%, M^+-N_2); 90 (100%, M^+-Cl-N_2).

2-Chloro-1,3,5-trinitro-benzene (picryl chloride). According to Ref. 2. $POCl_3$ (6 ml), picric acid (2.68 g, 11.7 mmol) and pyridine (1.05 ml) were mixed and heated under reflux (bp 112°C) for 1,5 hours. The reaction mixture was poured on ice, and the crystals, which precipitated were filtered out. Recrystallization from methanol yielded 2-chloro-1,3,5-trinitro-benzene (1.96 g, 0.8 mmol), light yellow needles, mp 79-81°C. MS [90°, EI 80 eV]: m/z 249 (28.8%, M^+ ^{37}Cl), 247 (87.15%, M^+ ^{35}Cl); 111 (28.2%, M^+-3(NO_2)); 109 (84.9%, M^+-3(NO_2)); 74 (100%, M^+- Cl-3(NO_2)).

(B) Spectra of $10H^+$ in different solvents.

Figure S1. NMR spectra of a solution of **$10H^+$** $BARF^-$ (0.02 M) in CD_2Cl_2.

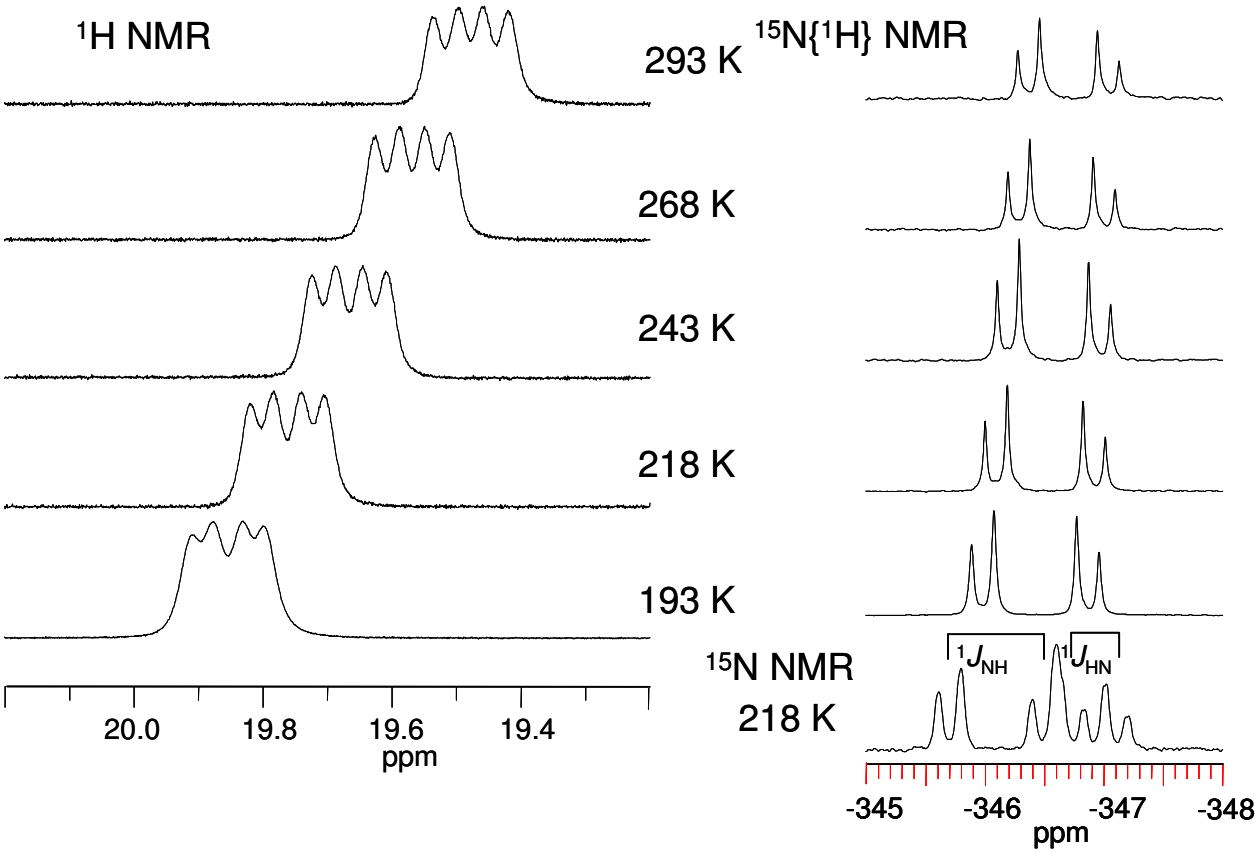


Figure S2. NMR spectra of a saturated solution of **10H**$^+$ BARF$^-$ in toluene-d_8.

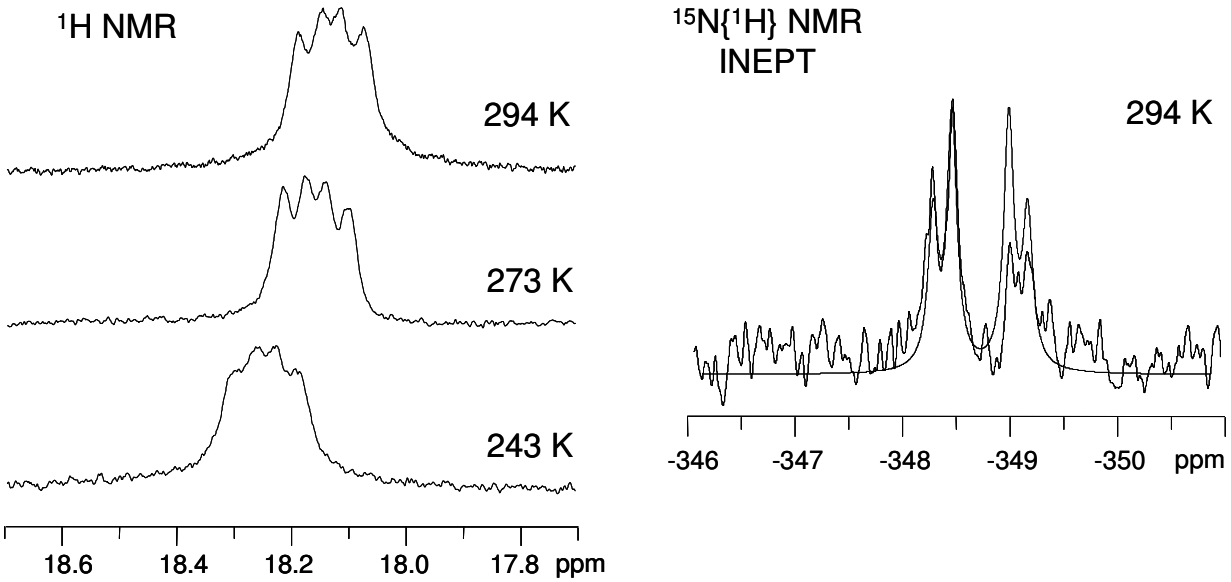


Figure S3. NMR spectra of a solution of **10** (0.02 M) in CD_2Cl_2 in the presence of an excess of trifluoroacetic acid (0.05 M). (a) $^{15}N\{^1H\}$ NMR spectra at different temperatures. (b) Corresponding low-field ^1H NMR signals. (c) Expansion of (b).

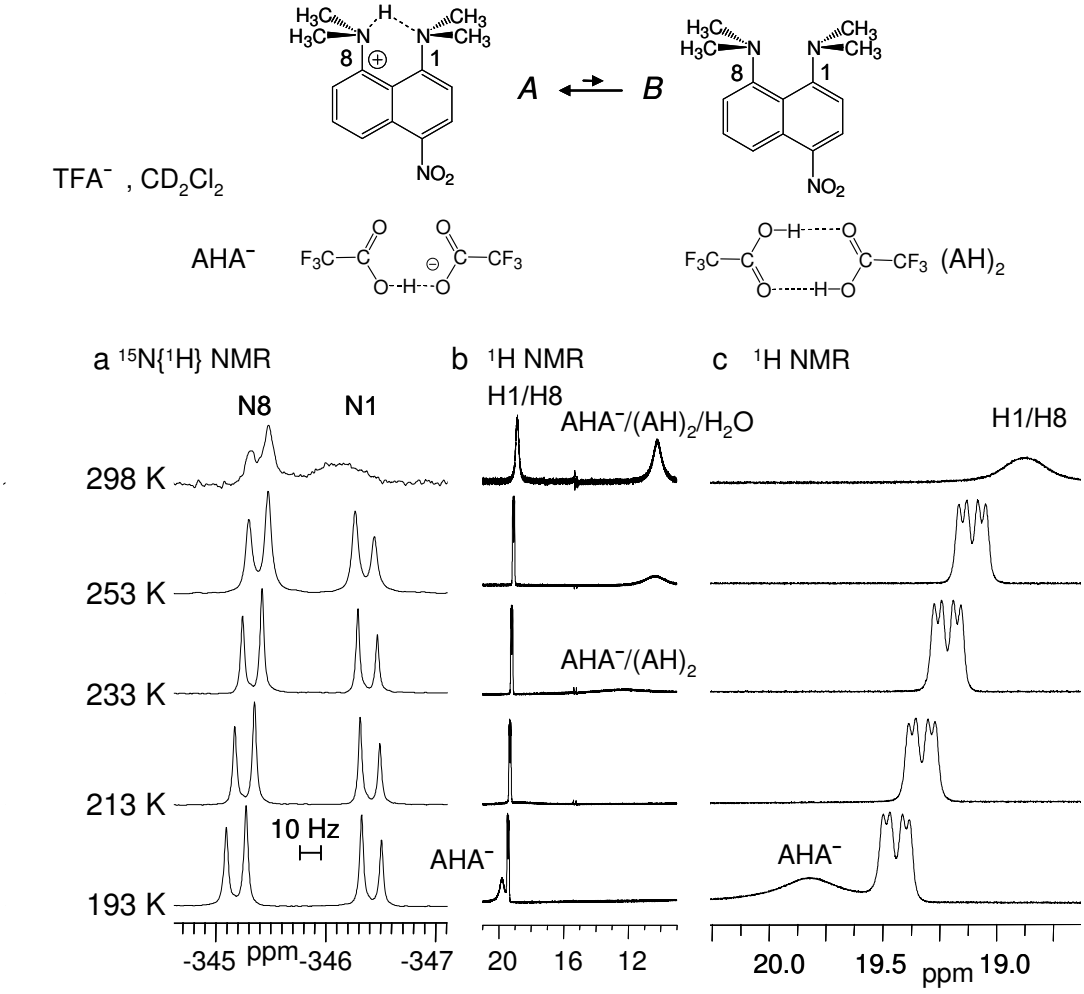
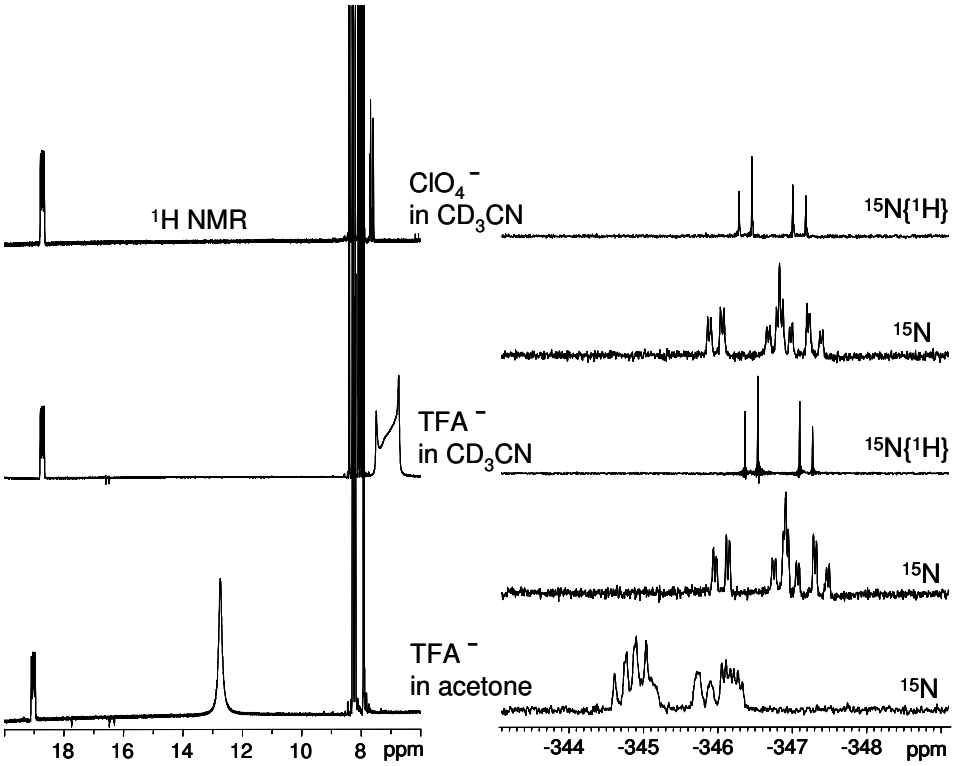
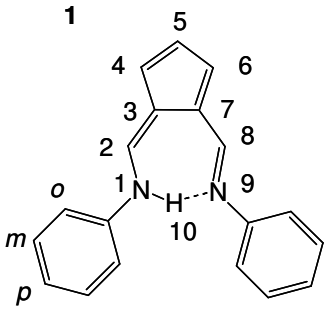


Figure S4. NMR spectra of solutions of $\mathbf{10H^+}$ (0.02 M) in different solvents in the presence of different counteranions at 293 K.



(C) Tables of ^{1}H chemical shifts and coupling constants of 1, 10, 10H$^+$.

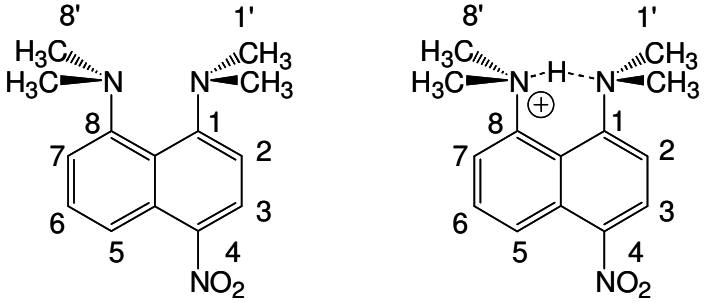
Table S1a. ^{1}H NMR parameters of **1** in $CDCl_3$ and toluene-d_8



Compound	Ref.	Solvent	T /K	H2	H4	H5	H6	H8	H10	H_o	H_m	H_p
1	3,4	$CDCl_3$	RT	8.29	7.08	6.48	7.08	8.29	15.63	7.28	7.42	7.20
1	Here	toluene-d_8	RT	7.84	6.94	6.54	6.94	7.84	15.48	6.90	7.02	6.85

Table S1b. ^{1}H NMR parameters of **10H$^+$** and of **10** for different counteranions, solvents and temperatures.

10 **10H⁺**



	Ref.	Counter -ion	Solvent	*T* /K	δ_H/ppm							
					NHN	CH3(1)	CH3(8)	H2	H3	H5	H6	H7
10H⁺	here	TFA^-	CD_3CN	293	18.73	3.07	3.17	8.01	8.29	8.40	7.92	8.09
10H⁺	here	ClO_4^-	CD_3CN	293	18.73	3.08	3.19	8.02	8.28	8.39	7.92	8.10
10H⁺	here	TFA^-	acetone-d_6	293	19.15	3.33	3.46	8.33	8.40*	8.40*	8.03	8.40*
10H⁺	here	$BARF^-$	CD_2Cl_2	293	19.48	3.09	3.19	7.86	8.32	8.58	7.95	7.91
10H⁺	here	$BARF^-$	CD_2Cl_2	268	19.57	3.08	3.18	7.86	8.32	8.56	7.94	7.90
10H⁺	here	$BARF^-$	CD_2Cl_2	243	19.67	3.06	3.17	7.86	8.31	8.54	7.93	7.90
10H⁺	here	$BARF^-$	CD_2Cl_2	218	19.76	3.05	3.17	7.86	8.30	8.52	7.91*	7.89*
10H⁺	here	$BARF^-$	CD_2Cl_2	193	19.85	3.03	3.15	7.85	8.29	8.48	7.90*	7.88*
10H⁺	here	$BARF^-$	CDF_3/CDF_2Cl (3:1)	RT	19.70	3.08	3.19	7.85	8.30	8.64	7.93	7.9*
10H⁺	here	$BARF^-$	CDF_3/CDF_2Cl (3:1)	193	20.21	3.11	3.21	7.87	8.29	8.56	7.9*	7.9*
10H⁺	here	$BARF^-$	CDF_3/CDF_2Cl (3:1)	158	20.36	3.10	3.20	7.88	8.27	8.53	7.9*	7.9*
10H⁺	here	$BARF^-$	CDF_3/CDF_2Cl (3:1)	130	20.46	3.09	3.19	7.9*	8.24	8.49	7.9*	7.9*
10H⁺	here	$BARF^-$	toluene-d_8	294	18.13	1.72		6.27#	6.38#	7.82#	6.8*	6.8*
10H⁺	here	$BARF^-$	toluene-d_8	273	18.16	1.66		6.19#	6.29#	7.76#	6.8*	6.8*
10H⁺	here	$BARF^-$	toluene-d_8	243	18.26	1.68		6.10#	6.19#	7.69#	6.8*	6.8*
10H⁺	here	TFA^-	CD_2Cl_2	293	18.86	3.14	3.28	7.87	8.30	8.53	7.92	7.96
10H⁺	here	TFA^-	CD_2Cl_2	273	18.99	3.12	3.27	7.88	8.30	8.52	7.92	7.96
10H⁺	here	TFA^-	CD_2Cl_2	253	19.09	3.10	3.25	7.89	8.29	8.51	7.92	7.96
10H⁺	here	TFA^-	CD_2Cl_2	233	19.20	3.08	3.24	7.88	8.29	8.50	7.92	7.96
10H⁺	here	TFA^-	CD_2Cl_2	213	19.32	3.06	3.22	7.87	8.29	8.49	7.91	7.95
10H⁺	here	TFA^-	CD_2Cl_2	193	19.43	3.03	3.20	7.86	8.28	8.47	7.90	7.94
10H⁺	5	ClO_4^-	DMSO	RT	18.40	3.12	3.26	8.26	8.46	8.31	8.00	8.34
10	here	-	CD_2Cl_2	RT	-	3.00#	2.78#	6.72	8.28	8.35	7.48	6.96

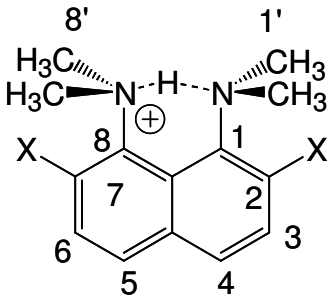
10	here	-	CD_2Cl_2	268	-	2.99[#]	2.76[#]	6.69	8.29	8.36	7.48	6.94
10	here	-	CD_2Cl_2	243	-	2.99[#]	2.74[#]	6.67	8.30	8.36	7.47	6.92
10	here	-	CD_2Cl_2	218	-	3.08 2.89[#&]	2.87 2.56[#&]	6.65	8.30	8.36	7.46	6.90
10	here	-	CD_2Cl_2	193	-	3.09 2.88[#&]	2.84 2.53[#&]	6.62	8.31	8.36	7.45	6.87
10	here	-	CDF_3/ CDF_2Cl (3:1)	RT	-	3.08[#]	2.87[#]	6.81	8.46[#]	8.36[#]	7.55	6.81
10	here	-	CDF_3/ CDF_2Cl (3:1)	193	-	3.16 2.97[#&]	2.94 2.63[#&]	6.71	8.50[#]	8.42[#]	7.53	6.71
10	here	-	CDF_3/ CDF_2Cl (3:1)	158	-	3.18 2.97[#&]	2.95 2.64[#&]	6.71	8.53[#]	8.44[#]	7.55	6.71
10	here	-	CDF_3/ CDF_2Cl (3:1)	130	-	3.21 2.98[#&]	2.94 2.64[#&]	6.69	8.54[#]	8.46[#]	7.56	6.69
10	here	-	toluene- d_8	RT	-	2.28[#]	2.24[#]	6.07	8.60	8.08	7.18	6.53
10	here	-	toluene- d_8	273	-	2.24[#]	2.21[#]	6.02	8.65	8.09	7.17	6.51
10	here	-	toluene- d_8	243	-	2.16*	2.16*	5.94	8.75	8.13	7.17	6.46
10	35	-	DMSO	RT	-	2.98	2.75	6.82	8.27	8.26	7.50	6.97

* estimated value (not resolved multiplet or overlapping lines), [#] assignment can be reversed.

[&] a dynamic process freezes out at lower temperature.

(D) Indirect determination of coupling constants J_{NN} of NHN hydrogen bonds which are symmetric or which are subject to a degenerate proton tautomerism

We have described the procedures to detect the coupling constants J_{NN} for symmetric DMAN and $DMANH^+$ in the Supporting Information of Ref. 6 and in Ref. 4. Using this method, ^{13}C nuclei adjacent to the $^{15}NH^{15}N$ hydrogen bonds were observed at natural abundance. The resulting spin systems observed are of the ABX type. By signal simulation the spectral parameters of **5** and of **5H$^+$** assembled in Table S2 and S3 were published previously in Supporting Information of Ref. 6. Here, we include also in Tables S4 to S5 the corresponding parameters of **8**, **8H$^+$**,**9** and **9H$^+$**.



5H$^+$ X=H
8H$^+$ X=Cl
9H$^+$ X=Br

Table S2. Observable parameters from $^{13}C\{^1H\}$ for C1 and CH_3 atoms for **5H**$^+$ in CD_3CN at room temperature at different magnetic fields.

Carbon nucleus	^{1}H Larmor frequency /MHz	$\Delta\nu^A$/Hz	$\Delta\nu^B$/Hz	$\Delta\nu^C$/Hz
C1	250	19.15	6.41	0.60
	500	19.35	6.40	1.12
	750	19.68	6.34	1.48
CH_3	250	18.17	4.72	~0.3
	500	18.30	4.74	~0.5

Table S3. NMR data of DMAN **5** and its protonated form **5H**$^+$ in CD_3CN at room temperature, obtained directly from the spectra or indirectly from the simulation.

	5	**5H**$^+$ $HClO_4$
δN /ppm vs CH_3NO_2	-336.8	-346.7
δH /ppm	-	+18.6
J(C1-N1) = J(C8-N8) /Hz	-11.1	-7.4 (± 0.5)[a]
J(C1-N8) = J(C8-N1) /Hz	0 (± 0.5)	+1 (± 0.5)[a]
J(C1'-N1) = J(C8'-N8) /Hz	-8.3	-5.8 (± 0.5)[b]
J(C1'-N8) = J(C8'-N1) /Hz	0.8	+1 (± 0.5)[b]
J(H1'-H') = J(H8'-H') /Hz	-	+2.6
J(N1-H') = J(N8-H') /Hz	-	-30.4
J(N1-N8) /Hz	0 (± 0.5)	+8.7 (± 0.5)[a,b]
$\lvert\Delta^{15}N\{^{13}C1\}\rvert$ /ppb	-	26 (± 8)[ac]
$\lvert\Delta^{15}N\{^{13}C1'\}\rvert$ /ppb	-	16 (± 8)[bc]
δC1 /ppm	151.7	145.3
δCH_3 /ppm	44.7	46.7

a - results obtained from the analysis of the C1 signal
b - results obtained from the analysis of the C1' signal
c – corrigendum: the values in ppb of the isotope effects published in Ref. 6 have to be multiplied by a factor of 10.

Table S4. Observable parameters from $^{13}C\{^{1}H\}$ for C1 and CH_3 atoms for **8H$^+$** and **9H$^+$** in CD_3CN at room temperature at different magnetic fields.

Compound	Carbon nucleus	^{1}H Larmor frequency /MHz	$\Delta\nu^A$/Hz	$\Delta\nu^B$/Hz	$\Delta\nu^C$/Hz
8H$^+$	C1	250	19.46	7.93	0.70
		500	19.68	7.91	1.46
	CH_3	250	17.9	~4.5	~0.5
		500	18.0	~4.5	~1
9H$^+$	C1	250	19.36	8.10	0.77
		500	19.56	8.07	1.56
	CH_3	250	17.60	5.00	~0.3
		500	17.72	4.99	~0.6

Table S5. NMR data of proton sponges **8** and **9** and their protonated forms **8H$^+$** and **9H$^+$**in CD_3CN at room temperature, obtained directly from the spectra or indirectly from the simulation

	8	**8H$^+$** $HClO_4$	**9**	**9H$^+$** $HClO_4$
δN /ppm vs CH_3NO_2	-361.3	-349.6	-359.7	-349.1
δH /ppm	-	20.2	-	20.3
J(C1-N1) = J(C8-N8) /Hz	-15.7	-8.9 (± 0.5)[a]	-16.2	-9.0 (± 0.5)[a]
J(C1-N8) = J(C8-N1) /Hz	0	+1 (± 0.5)[a]	0	+1 (± 0.5)[a]
J(C1'-N1) = J(C8'-N8) /Hz	-10.6	-5.5 (± 1)[b]	-10.9	-6.0 (± 0.5)[b]
J(C1'-N8) = J(C8'-N1) /Hz	0	+1 (± 1)[b]	0	+1 (± 0.5)[b]
J(H1'-H') = J(H8'-H') /Hz	-	+2.6	-	+2.6
J(N1-H') = J(N8-H') /Hz	-	-28.0	-	-27.6
J(N1-N8) /Hz	0 (± 0.5)	+8.3 (± 0.5)[a,b]	0 (± 0.5)	+8.2 (± 0.5)[a,b]
$\lvert\Delta^{15}N\{^{13}C1\}\rvert$ /ppb	-	30 (±8)[a]	-	32 (± 8)[a]
$\lvert\Delta^{15}N\{^{13}C1'\}\rvert$ /ppb	-	20 (± 10)[b]	-	14 (± 6)[b]
δC1	146.6	138.5	148.0	139.8
δCH_3	43.7	43.0	43.7	43.1

a - results obtained from the analysis of the C1 signal
b - results obtained from the analysis of the C1' signal

(E) Theoretical Section

The NHN chelates and proton sponges of interest in this study are subject to a fast proton tautomerism between two forms **a** and **b.**

$$[\text{N-H}\cdots\text{N}] \equiv \mathbf{a} \varnothing \mathbf{b} \equiv [\text{N}\cdots\text{H-N}] \quad (1)$$

Any NMR parameter V measured is then averaged over both forms, i.e.

$$V = x_a V_a + x_b V_b = \frac{1}{1+K_{ab}} V_a + \frac{K_{ab}}{1+K_{ab}} V_b,\ K_{ab} = \frac{x_b}{x_a},\ V = J_{\text{NH}}, J_{\text{HN}}, J_{\text{NN}}, \delta. \quad (2)$$

where K_{ab} represents the equilibrium constant of tautomerism and x_a and x_b the mole fractions of the two tautomers. V_a and V_b represent the intrinsic NMR parameters in both forms. For cases where the chemical shifts and heavy atom couplings in both forms are similar it follows that

$$J_{\text{NN}} \cong (J_{\text{NN}})_a \cong (J_{\text{NN}})_b,\ \delta_{\text{H}} \cong (\delta_{\text{H}})_a \cong (\delta_{\text{H}})_b, \quad (3)$$

i.e. that the observed values are not affected by the tautomerism as they correspond to the intrinsic values.

By contrast, the case of the nitrogen-hydrogen coupling constants is different. It follows from eq (2) that

$$J_{\text{NH}} = \frac{1}{1+K_{ab}} (J_{\text{NH}})_a + \frac{K_{ab}}{1+K_{ab}} (J_{\text{NH}})_b,\ J_{\text{HN}} = \frac{1}{1+K_{ab}} (J_{\text{HN}})_a + \frac{K_{ab}}{1+K_{ab}} (J_{\text{HN}})_b \quad (4)$$

$(J_{\text{HN}})_a$ and $(J_{\text{NH}})_b$ correspond to coupling constants across hydrogen bonds and have to be considered when deriving equilibrium constants from the averaged values. If we assume again that the hydrogen bond geometries in both tautomeric forms are similar we can write

$$(J_{\text{NH}})_a = (J_{\text{HN}})_b = {}^{1}J_{\text{NH}},\ (J_{\text{HN}})_a = (J_{\text{NH}})_b = {}^{1h}J_{\text{HN}}. \quad (5)$$

It follows then that

$$J_{\text{NH}} + J_{\text{HN}} = {}^{1}J_{\text{NH}} + {}^{1\text{h}}J_{\text{NH}}. \quad (6)$$

Thus, the averaged sum is again independent of the equilibrium constant of tautomerism.

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