NMR Study of Solvation Effects on the Geometry of Proton-Bound Homodimers of Increasing Size

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Table S1. The proton affinities of selected bases at ε = 108.94 at the 311++g(3df,2p) level.

Base	DFT functional and the Polarizable Continuum Model		
	B3LYP, PCM-SMD	B97D3, PCM	B97D3, PCM-SMD
pyridine	605	617	723
4-chloro-pyridine	595	607	714
quinoline	607	620	727
acridine	614	628	736

Table S2. The N...N distance in the proton-bound homodimer of pyridine calculated in the gas phase and polar solvents at different approximations.

DFT Functional	Basis set	Solvation model, ε	N...N, Å
B3LYP	6-31g	Gas phase	2.608735
B3LYP	6-31g	PCM, ε = 108.94	2.650268
B3LYP	6-31g(d,p)	Gas phase	2.663657
B3LYP	6-31g(d,p)	PCM, ε = 1.43	2.673460
B3LYP	6-31g(d,p)	PCM, ε = 108.94	2.711993
B3LYP	6-31g(d,p)	PCM-SMD, ε = 108.94	2.734824

B97D3	6-31g(d,p)	Gas phase	2.633379
B97D3	6-31g(d,p)	PCM, ε = 108.94	2.734824
B3LYP	6-311++g(d,p)	Gas phase	2.687368
B3LYP	6-311++g(d,p)	PCM, ε = 108.94	2.739689
B3LYP	6-311++g(3df,2p)	Gas phase	2.692473
B3LYP	6-311++g(3df,2p)	PCM, ε = 108.94	2.747587
B3LYP	6-311++g(3df,2p)	PCM-SMD, ε = 108.94	2.767025

Table S3. The N...N distance in the proton-bound complexes calculated in the gas phase and the PCM approximation at ε = 108.94.

Complex	DFT Functional	Basis set	Solvation model, ε	Distance, Å
pyridine...phenol N...H-O	B3LYP	6-311++G(3df,2p)	Gas phase	N...O=2.833347
			PCM, ε = 108.94	N...O=2.754762
pyridine...N-phenylaniline N...H-N	B3LYP	6-31	Gas phase	N...N=3.048903
			PCM, ε = 108.94	N...N=2.990875
$[H_3N...H...NH_3]^+$ N...H...N	B3LYP	6-31	Gas phase	N...N=2.611854
			PCM, ε = 108.94	N...N=2.593117
[pyridine-H...N,N-diphenylaniline]$^+$ N-H...N	B3LYP	6-31	Gas phase	N...N=2.721726
			PCM, ε = 108.94	N...N=3.119706
$[(CH_3)_3N-H...N(CH_3)_3]^+$ N-H...N	B3LYP	6-31	Gas phase	N...N=2.673737
			PCM, ε = 108.94	N...N=2.715264
$[(CH_3)(CN)_2N-H...N(CN)_2(CH_3)]^+$ N-H...N	B3LYP	6-31	Gas phase	N...N=2.799408
			PCM, ε = 108.94	N...N=3.336273

XRD Measurements

1. Structure of protonated dimer of acridine tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate ([BArF]$^-$) with toluene solvent molecule.

Crystal Data: $C_{72}H_{47}BF_{24}N_2$ (M =1406.93 g/mol): monoclinic, space group C2/c (no. 15), a = 24.307(4) Å, b = 18.043(3) Å, c = 19.611(4) Å, β = 133.202(3)°, V = 6269.3(19) Å^3, Z = 4, T = 100 K, μ(MoKα) = 0.136 mm^{-1}, *Dcalc* = 1.491 g/cm^3, 19268 reflections measured (3.08° ≤ 2Θ ≤ 56.56°), 7703 unique (R_{int} = 0.0371, R_{sigma} = 0.0515) which were used in all calculations. The final R_1 was 0.0584 (>2sigma(I)) and wR_2 was 0.1708 (all data).

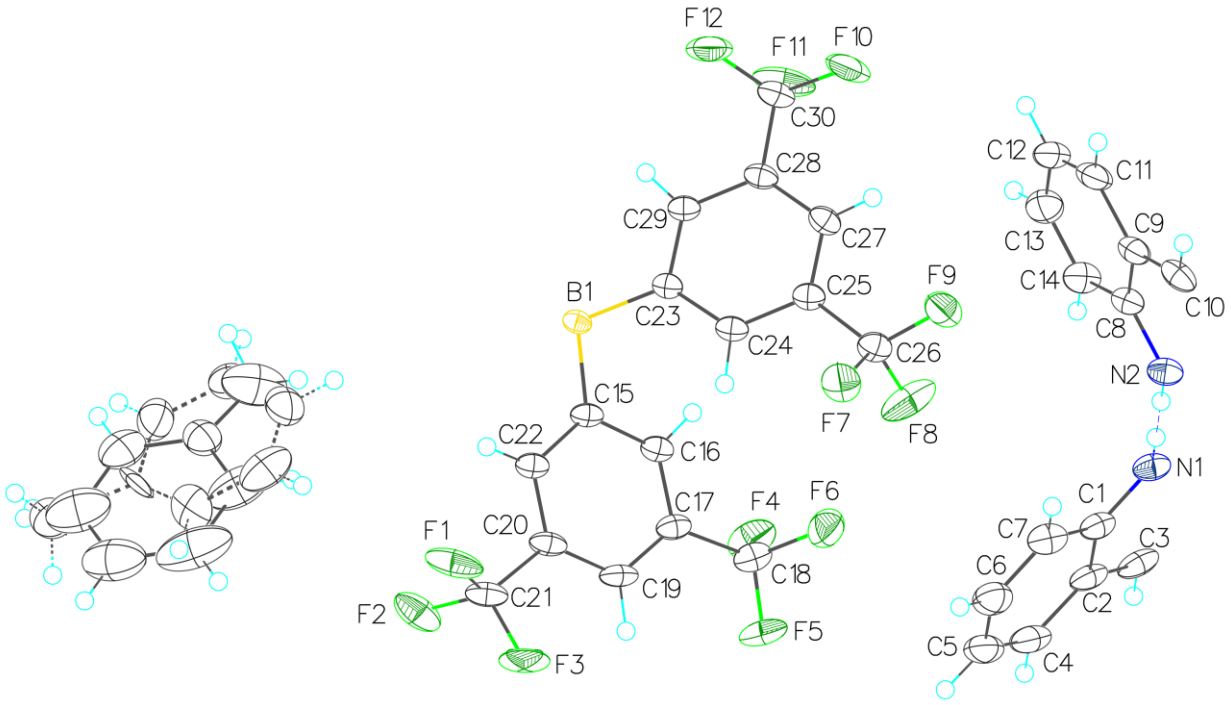

Figure S1. Structure of independent part of the unit cell of salt with toluene solvent molecule. Atoms are represented by thermal displacement ellipsoids (ρ = 50%).

2. Structure of protonated acridine tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate ([BArF]$^-$) with $CHCl_3$ solvent molecule.

Crystal Data: $C_{60}H_{33}BCl_6F_{24}N_2$ (M =1461.39 g/mol): monoclinic, space group C2/c (no. 15), a = 23.4747(14) Å, b = 18.1680(10) Å, c = 17.2650(18) Å, β = 124.4790(10)°, V = 6069.8(8) Å^3, Z = 4, T = 100 K, μ(MoKα) = 0.399 mm^{-1}, *Dcalc* = 1.599 g/cm^3, 19909 reflections measured (3.08° ≤ 2Θ ≤ 58°), 8066 unique (R_{int} = 0.0231, R_{sigma} = 0.0313) which were used in all calculations. The final R_1 was 0.0699 (>2sigma(I)) and wR_2 was 0.2147 (all data).

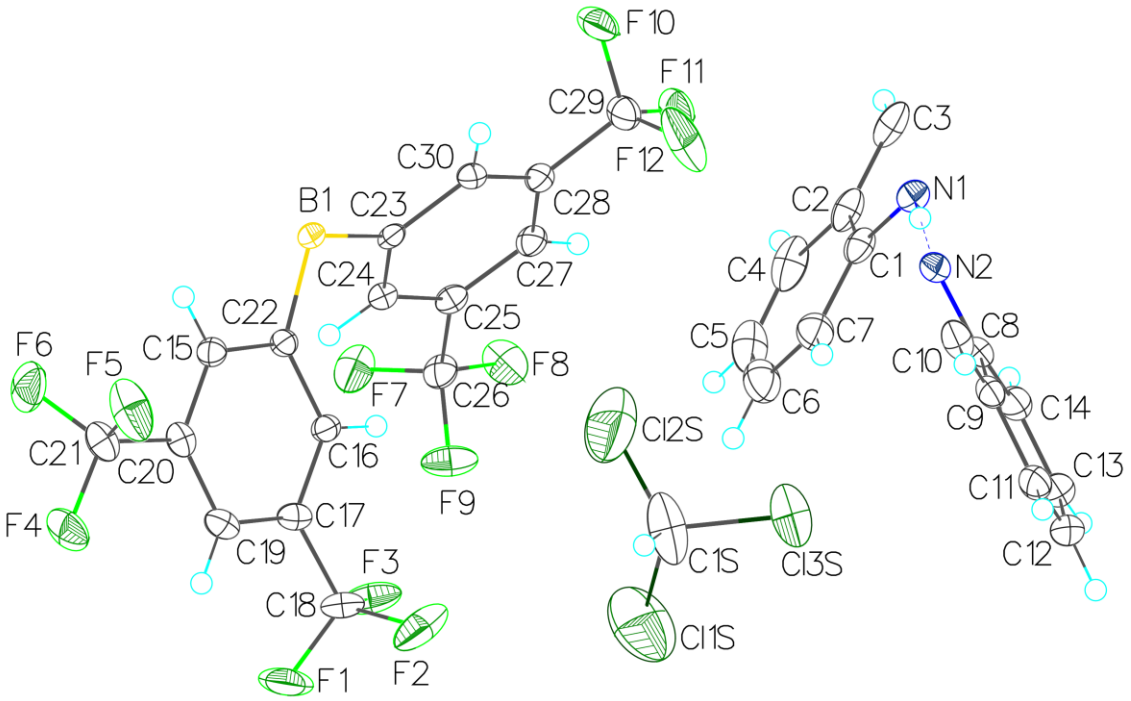

Figure S2. Structure of independent part of the unit cell of salt with $CHCl_3$ solvent molecule. Atoms are represented by thermal displacement ellipsoids (ρ = 50%).