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TRIALKYLAMMONIUM-TRIALKYLAMINE-TETRAPHENYLBORATES $[R_3N^{\oplus}\text{-}H\cdots NR_3][B^{\ominus}(C_6H_5)_4]$ WITH PROTOTYPE $N^{\oplus}\text{-}H\cdots N$ HYDROGEN BRIDGES [1,2]

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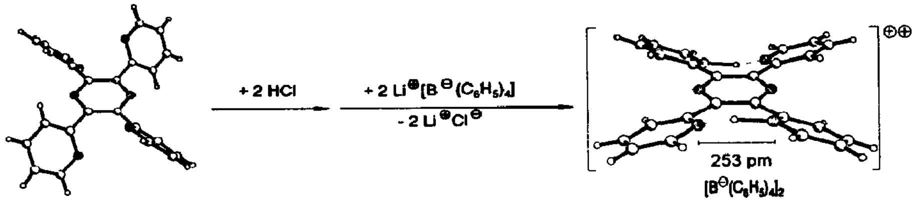
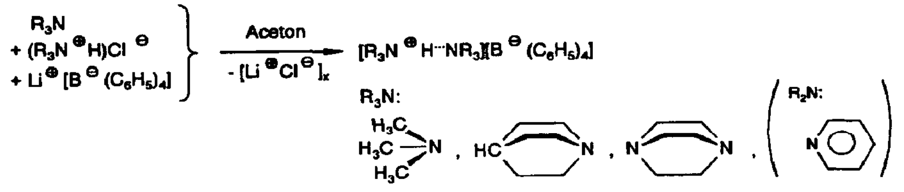
Abstract: Protonation of trialkylamines in the presence of the non-protonable anion tetraphenylborate allows to crystallize $[R_3N^{\oplus}\text{-}H\cdots NR_3]$ salts with trimethylamine, quinuclidine, diazabicyclooctane or pyridine. Their single crystal structures are rationalized by SCF and force-field calculations.

Protonation of organic bases to salts containing the non-protonable anion tetraphenylborate enforces unusual intra- and intermolecular interactions such as the planarization of the colourless tetrapyridylpyrazine to its mimetically yellow-coloured dication salt:[3,4]



(1)

From acetone solutions of trialkylamines or pyridine, their hydrochlorides and lithium tetraphenylborate, the title salts - including those from different amines - can be crystallized: [2]



$$\left.\begin{array}{l} R_3N \\ +\ (R_3N^{\oplus}H)Cl^{\ominus} \\ +\ Li^{\oplus}[B^{\ominus}(C_6H_5)_4] \end{array}\right\} \xrightarrow[-\,[Li^{\oplus}Cl^{\ominus}]_x]{\text{Aceton}} [R_3N^{\oplus}H\cdots NR_3][B^{\ominus}(C_6H_5)_4]$$

(2)

These compounds[5] are represented here by tetraphenylborate[7] salts of trimethylammonium-trimethylamine- and quinuclidinium-quinuclidine-cations (Figure 1), which due to their identical subunits contain prototype $N^{\oplus}\text{-}H\cdots N$ hydrogen bridges and, therefore, allow to approximate their molecular dynamics (Figure 2).

The low-temperature structures (Figure 1) exhibit hydrogen bridges $N^{\oplus}\text{-}H\cdots N$ with an N···N distance of only 264 pm; according to a search in the Cambridge Structural Database[3,5a-e] only few shorter ones are known[3,5e] such as 253 pm in diprotonated tetrapyridylpyrazine (1). The subunits $C_3N\cdots NC_3$ are in a staggered conformation and, especially for quinuclidinium-quinuclidine (Figure 1: C), the different dihedral angles ω(CN···NC) of 50° and 70° prove, in close analogy to organosilicon

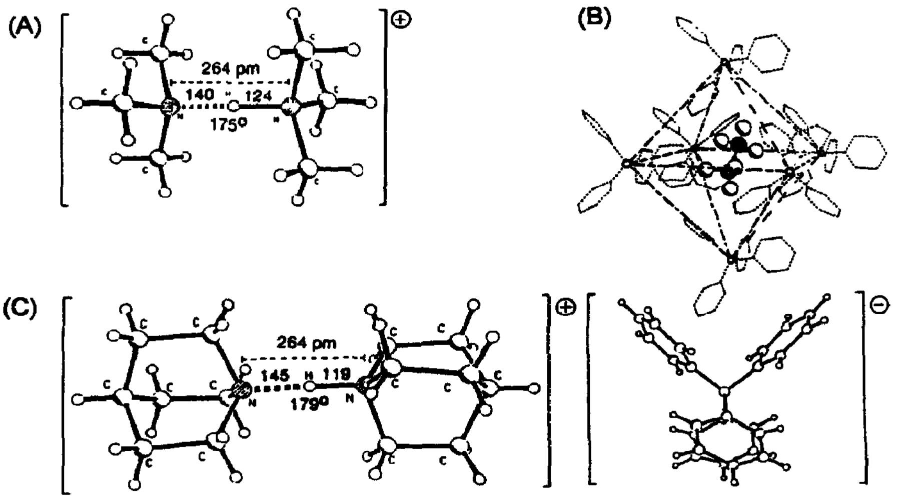


Figure 1. Molecular structures of selected[2] trialkylammonium-trialkylamine-tetraphenylborates. (A) Trimethylammonium salt in side view and (B) lattice packing within a distorted octahedron of tetraphenylborate anions (shortest nonbonding distances (pm): $C_{phenyl}\cdots C_{methyl}$ 348, 350, 354, $C_{phenyl}\cdots N$ 433, 439, 444, *and B···N 598, 617, 635). Essential distances (pm) and angles (°) for* the two independent molecules : H bridges $N(H^{\oplus})N$ 264/265 pm and 175°/173°, $(H^{\oplus})NC$, 146, 148, 149, NC, 144, 146, 150, $CN(H^{\oplus})C$ 110, 111, 112, CNC 106, 111, 114, CN···NC 51, 53, 56, 64, 68, 69/(18, 29, 39, 82, 90, 104). (C) Quinuclidinium salt: H bridge $N(H^{\oplus})N$ 264 pm and 179°, $(H^{\oplus})NC$ 149, NC 148, CN $(H^{\oplus})C$ 109, 110, 110, CNC 109, 109, 110, CC 153, NCC 110, CCC 109, ω(CN···NC) 50, 50, 52, 69, 69, 71, C···C(intramolecular) 372 - 400, (C)H···H(C)(intramolecular) 292 - 318 and anion with BC 165 and CBC 107-113.

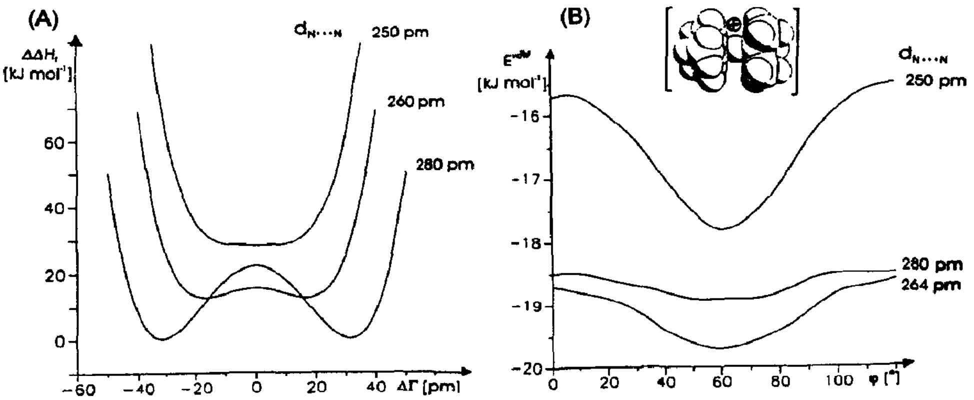


Figure 2. Distance-dependent potential calculations for trimethylammonium-trimethylamine cation based on the crystal structure data.[6] (A) Double and single minima potentials of the bridge $N^{\oplus}$-H···N for distances $d_{N\cdots N}$ varying between 280 and 250 pm, *generated by moving the $H^{\oplus}$ center along* the NN axis. All AM1 heats of formation have been calculated with total geometry optimization of the units $N(CH_3)_3$,[3] and the barrier for $d_{N\cdots N}$ = 264 pm is estimated to be about 2,5 kJ mol^{-1}.(B) MOMO potential curves for torsions φ(CN···NC) at NN distances between 280 and 250 pm with the barrier for 264 pm (Figure 1) approximated to be about 1 kJ mol^{-1}.

compounds such as $[(CH_3C)_3Si]_3Si\text{-}Si[Si(CH_3)_3]_3$, a considerable steric overcrowding: The distances C···C between the molecular halves of only 372 pm are 7 % within the van der Waals radii sum for two methyl groups $-CH_3)(H_3C-$ of 400 pm. The trimethylammonium-trimethylamine cations are enclosed within an octahedron of six anions $[B^{\ominus}(C_6H_5)_4]$ (Figure 1: B) and the rather short intermolecular distances $C_{phenyl}\cdots C_{methyl}$ of only 348 pm suggest also for the lattice packing a stabilizing van der Waals-attraction within the effective Coulombic range $B(^{\ominus})\cdots N(^{\oplus})$ estimated to be about 600 pm.

The threefold rotationally symmetric hydrogen bridge $C_3N^{\oplus}H\cdots NC_3$ of the protonated bis(trimethylamine) cation is characterized by both semiempirical AM1 [8a] and MOMO force-field calculations[8b] (Figure 2): By approaching the two subunits $(H_3C)_3N^{\oplus}\text{-}H$ and $N(CH_3)_3$ from 1000 pm to the N···N bonding distance of 264 pm (Figure 1: A), an AM1 heat of formation $\Delta\Delta H_f^{AM1} = -38$ kJ mol^{-1} results. Starting from the structure coordinates and with additional geometry-optimization, charges at the N centers of -.17 and at the $H^{\oplus}$ center of +.33 are estimated. Comparison with analogous calculations[3] for the pyridinium-pyridine cation $[H_5C_5N)^{\oplus}\text{-}H\cdots NC_5H_5]$ show a smaller $\Delta\Delta H_f^{AM1}$ value, which corresponds to the larger experimental N···N distance of 270 pm[5b] and can be traced to the smaller negative charge at the nitrogen in neutral pyridine, $q_N(H_5C_5N) = -.14$ vs. $q_N(R_3N) = -.26$. The distance-dependent AM1 calculations (Figure 2: A), suggest a change from double to single minimum only at about 250 pm and a barrier of about 2,5 kJ mol^{-1} at the experimental N,N distance of 264 pm. Additional force-field calculations[8b] (Figure 2: B, based on empirical Lennard-Jones potentials, $E^{vdW} = c\ r^{6} + d\ r^{12}$) with experimentally calibrated parameters,[8c] have been performed for torsion angles ω(CN-NC) between 0^{o} and 120^{o} in 10^{o}-steps. Despite of the rather short and, in addition, sterically overcrowded bridges $R_3N^{\oplus}\text{-}H\cdots NR_3$, low barriers of only about 1 kJ mol^{-1} result for both cations and suggest a fully activated rotation at room temperature. For the methyl derivative, the minimum of the van der Waals energy is predicted at the experimental N···N distance of 264 pm (Figure 1: A) and, the structure, therefore, should be predominantly determined by the electrostatic H bridge component.[9]

The use of non-protonable tetraphenylborate anions[3] in crystallizing H-bridged bis(alkylamino)cations $[R_3N^{\oplus}\text{-}H\cdots NR_3]$, $[R_3N^{\oplus}\text{-}H\cdots NR_2]$ and $[R_2N^{\oplus}\text{-}H\cdots NR_2]$ can be widely applied to nitrogen compounds with σ- and π-type N lone pairs and, therefore, will allow to investigate numerous novel H-bridged molecular aggregates.

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6. Crystal structures: Reflexes were recorded using a four circle diffractometer Siemens AED II with λ (MoK_α = 71.073 pm; structure solution using direct methods and difference Fourier technique (SHELXTL-Plus). **Trimethylammonium-trimethylamine-tetraphenylborate.** *Preparation*: To a solution of 50 mg (0.13 mmol) trimethylammonium-tetraphenylborate in 3 ml acetone are added 2 ml of a 33 % trimethylamine solution in ethanol. On diffusion of n-hexane from an added upper layer, colourless polyhedra grow within 3 days. *Structure*: $C_{30}H_{39}N_2B$ (MW 450.45), $a = 1393.4(1)$, $b = 1413.1(1)$, $c = 2767.6(2)$ pm, $V = 5449.44 \bullet 10^6$ pm^3 (200 K), $Z = 8$, $\rho_{calc.} = 1.098$ g/cm^3, orthorhombic, space group $P2_12_12_1$, 9040 measured reflections within $3^o < 2\Theta < 60^o$, of which 5278 are independent with $I > 2\sigma(I)$. NP = 632, R = 0.067, $R_w = 0.062$, $w = 1/\sigma^2(F) + 0.0001\ F^2$, GOOF = 2.07, Shift/Err < 0.001, rest electron density +0.53 and -0.29 e/Å^3. Extinction correction, all C, N and B centers anisotropically, H centers isotropically refined. Crystal quality has been checked by the profiles of 60 reflections within $10^o < 2\Theta < 35^o$. C1 and C2 are each 40 % disordered; the positions are refined at a fixed distance of 148 (0.5) pm using isotropic temperature factors. **Quinuclidinium-quinuclidine-tetraphenylborate.** *Preparation*: 0.5g (3.4 mmol) quinuclidinium-chloride are dissolved by heating in 50 ml isopropanol and an isopropanol solution of 1.5 g (4.6 mmol) lithiumtetraphenylborate is added. On cooling, white crystals of quinuclidinium-tetraphenylborate form, of which 50 mg (0.34 mmol) are disolved together with 120 mg (1.1 mmol) quinuclidine in 5 ml acetone. On diffusion of n-hexane from an added upper layer, colourless polyhedra grow within two days. Structure: $C_{38}H_{47}N_2B$ (MW 542.59), $a = 940.0(2)$, $b = 1788.1(2)$, $c = 1865.1(2)$ pm, $\beta = 97.47(1)^o$, $V = 3093.28 \bullet 10^6$ pm^3 (200 K), $Z = 4$, $\rho_{calc.} = 1.165$ g/cm^3, monoclinic, space group $P2_1/n$, 6063 measured reflections within $3^o < 2\Theta < 50^o$, of which 4425 are independent with $I > 2\sigma(I)$. NP = 423, R = 0.042, $R_w = 0.042$, $w = 1/\sigma^2(F) + 0.0001\ F^2$, GOOF = 2.11, Shift/Err < 0.001, rest electron density +0.22 and 0.14 e/Å^3. Extinction correction, all C, N, B centers anisotropically, H centers isotropically refined. Crystal quality has been checked by profiles of 24 reflections within $10^o < 2\Theta < 30^o$. For further structural details cf. the report submitted to the Cambridge Crystallographic Data Centre.
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