Tetrahedron Letters,Vol.27,No.47,pp 5719-5722,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

PROTONATION OF 1,2,4,5-TETRAKIS(DIMETHYLAMINO)BENZENE

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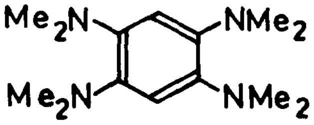
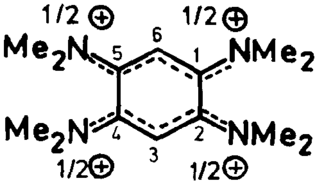
Abstract: 1,2,4,5-Tetrakis(dimethylamino)benzene (1) forms diprotonated salts like the bis(tetrafluoroborate) 3 and the dibromide 4. For 4-dihydrate an X-ray structure revealed the presence of 'bifurcated hydrogen bonds'. 1 and the protonated species derived therefrom are discussed with regard to the sterical requirements of 'proton sponges'.

Recently we reported about the synthesis of 1,2,4,5-tetrakis(dimethylamino)benzene (1) [1)]. As a very strong two-electron donor 1 forms with electron acceptors in a 1:2 ratio charge-transfer complexes in which the unusual diamagnetic dication 2 is present. The structure of 2 has been determined by X-ray analysis [1)].



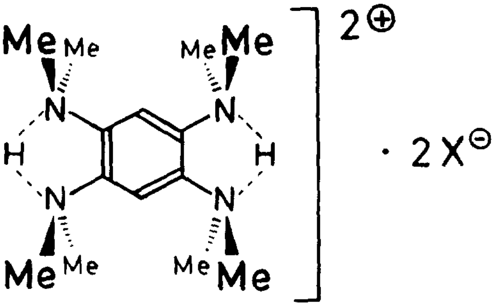
1



2

Due to its two pairs of adjacent dimethylamino groups, 1 also was of interest in connection with recent work of our group on new 'proton sponges' [2,3)]. The strong basicity of 'proton sponges' results from the destabilizing lone-pair repulsion in the free bases and from the formation of especially strong N---H---N hydrogen bonds in their protonated salts [2-4)]. For geometrical reasons both effects are expected to be considerably reduced in 1 as compared to 4,5-bis(dimethylamino)fluorene [2)] and 4,5-bis(dimethylamino)phenanthrene [3)]: the nitrogen-nitrogen distance is longer, the lone-pairs are not pointing at each other, and the formation of a short and linear N---H---N hydrogen bond seems not nearly possible. Nevertheless, the protonation of 1 and the structure determination of its protonated species were of interest, even if to countercheck the sterical requirements so far accepted for 'proton sponge' properties.

Like proper 'proton sponges', 1 with excess acid undergoes only monoprotonation for each of the two sets of two adjacent dimethylamino groups. For example, when to 1 in ether aqueous hydrogen tetrafluoroborate is added crystals precipitate which after recrystallization from methanol give correct elemental analyses for the bis(tetrafluoroborate) of 1: m.p. 290 - 291°C; ^{1}H-NMR (360 MHz, [D_6]dimethylsulfoxide, 303 K): $\delta = 2.86$ (s, 24 H), 7.36 (br. s, 2 H), 10.38 (br. s, 2 H). The data obtained are in accordance with the general structure 3. As compared to real 'proton sponges' the downfield shift of the hydrogen-bonded protons in 1 is considerably smaller indicating a relatively weak hydrogen bond.



3: X = BF_4; 4: X = Br

More evidence regarding the detailed structure of diprotonated 1 was obtained when aqueous hydrogen bromide (48%) was added to a concentrated solution of 1 in ether. The precipitate was recrystallized from methanol (m.p. 226 - 227°C); by elemental analysis the formation of a dihydrate of 4 was established. In ^{1}H-NMR (360 MHz, [D_6]dimethylsulfoxide, 323 K) the singlets for the 24 methyl protons ($\delta = 2.84$) and for the two aromatic protons ($\delta = 7.15$) correspond to those of 3; the hydrogen-bonded protons, due to an exchange process with water, show resonance however at $\delta = 4.0$.

For the crystals of 4-dihydrate an X-ray structure analysis could be solved: Monoclinic crystals with $\underline{a} = 620.8(1)$, $\underline{b} = 795.4(2)$, $\underline{c} = 2058.4(3)$ pm, $\beta = 98.38(1)^0$; space group $P2_1/c$, $Z = 2$, $D_x = 1.467$ g cm^{-3}. Intensity data were collected using graphite-monochromated Mo-K_α radiation (Enraf-Nonius CAD4). Up to $\sin\theta/\lambda = 6.80$ nm^{-1} 2543 reflections were measured out of which 1667 reflections with $I \geq 1.96\sigma(I)$ were graded as observed. The solution was possible using direct methods (MULTAN); full matrix least-squares refinement using anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen led after absorption correction to a convergence at R = 0.035.

Figure 1 shows the $\underline{\underline{4}}$-dication in a view perpendicular to the ring plane (A) and in a side-view (B). Bond-lengths and bond-angles are given in Figure 1A. The most remarkable feature of the structure applies to the geometry of the hydrogen bonds. The nitrogen atoms are nearly coplanar with the aromatic ring (Figure 1B); this leads to a rather short N···N distance of 271.6 pm which in the case of a linear arrangement would be suitable for a strong hydrogen bond. The intrinsic N(1)-H valence direction prevents, how=

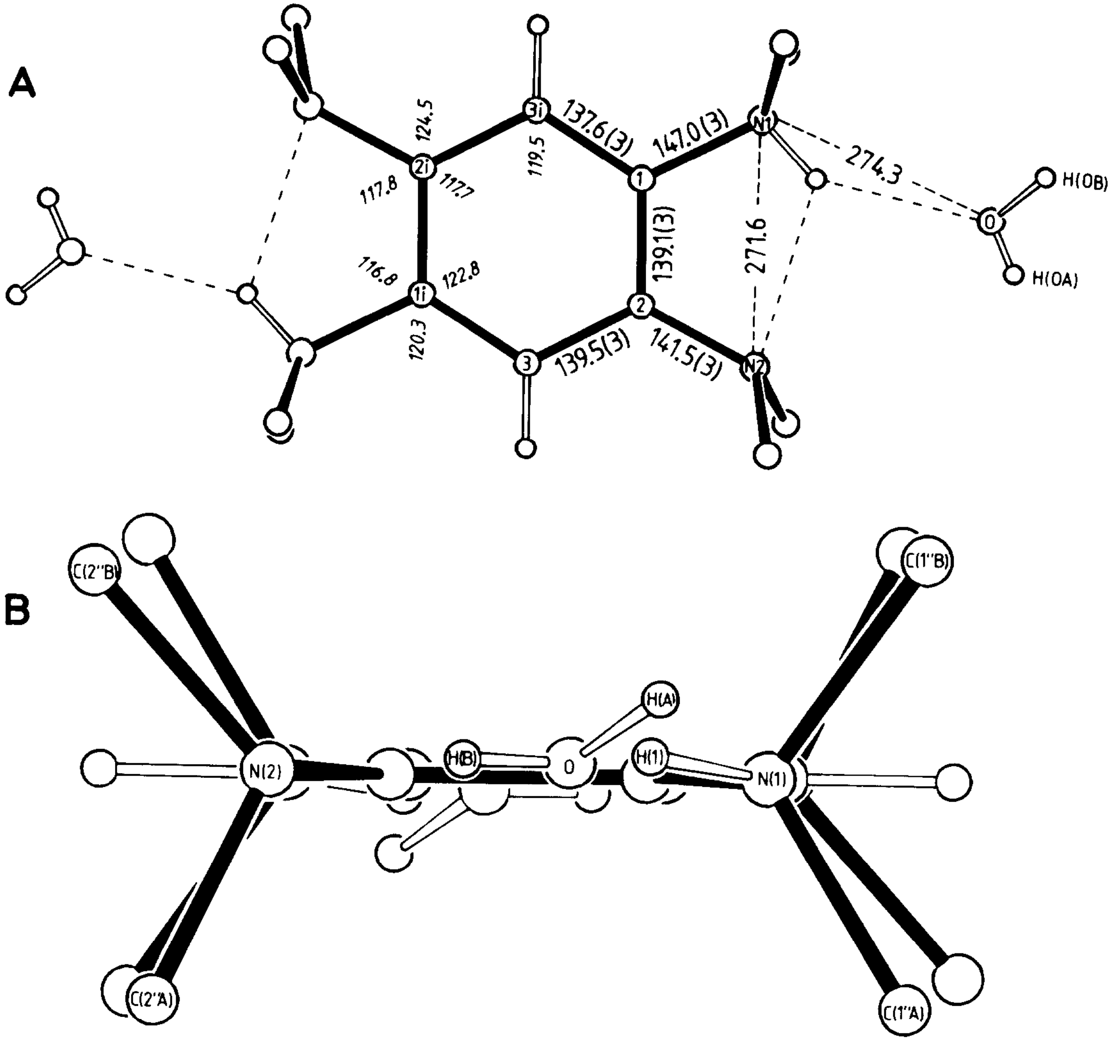


Figure 1. Structure of the $\underline{\underline{1}}$-Dication in $\underline{\underline{4}}$-Dihydrate in a View Perpendicular to the Ring Plane (A) and in a Side-View (B).

ever, a linear N---H---N arrangement; actually, the hydrogen bond is bent outwards with an angle of 119°. This leads to a 'bifurcated hydrogen bond' with the participation of the oxygen of a water molecule. The bridging hydrogen has a position very close to the plane through the atoms N(1), N(2) and O to which it is linked. 'Bifurcated hydrogen bonds' have been discussed for systems with similar geometrical arrangements $^{5)}$.

In the crystal lattice the dications formed by protonation of 1 are arranged in stacks along the a-axis of the crystal. Perpendicular to these stacks the bromide ions and the water molecules form spirals in the direction of the b-axis. Within these spirals bromide ions and water molecules are linked together by weak O-H···Br hydrogen bonds with H···Br-distances of 240 pm.

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(Received in Germany 5 September 1986)