The Structure of 1,6-Diazabicyclo[4.4.4]tetradecane and of its Inside Protonated Ion

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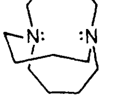
1,6-Diazabicyclo[4.4.4]tetradecane (**1**) and its inside-protonated ion (**4**) are essentially isostructural with effective D_3 symmetry; the N,N′ distance contracts by 0.28 Å on protonation, giving the shortest known N–H:N hydrogen bond (2.53 Å).

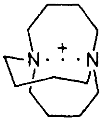
We have described the preparation[1,2] and remarkable properties[1,3] of 1,6-diazabicyclo[4.4.4]tetradecane (**1**). Diamine (**1**) is oxidised[4] very easily to stable radical cation and dication salts (**2**) and (**3**), and it was argued[1,4] that this was due to lone pair–lone pair interaction within a preferred *in,in* conformation for (**1**). We were also able to isolate both outside- and inside-protonated salts of (**1**), and the latter, (**4**), showed spectroscopic evidence for a strong intrabridgehead hydrogen bond.[3] We now report *X*-ray structures for (**1**) and (**4**) (as a chloride salt).

Diamine (**1**) is an air-sensitive, volatile, waxy solid and it was not easy to obtain crystals suitable for structure determination. Satisfactory crystals were eventually grown by very slow vacuum sublimation at 0 °C. Crystals cooled below this temperature showed a destructive phase change resulting in fragmentation of the crystal. Diffraction measurements were therefore made at room temperature. *Crystal data* for (**1**): $C_{12}H_{24}N_2$, $M = 196.3$, monoclinic, space group $C2/c$, $a = 12.266(7)$, $b = 11.817(8)$, $c = 8.520(5)$ Å, $\beta = 92.64(5)°$, $Z = 4$, $U = 1233.6(1.3)$ Å^3, $D_c = 1.06$ g cm^{-3}, $F(000) = 440$, Mo-K_α X-radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 0.5$ cm^{-1}. The structure was solved by direct methods and refined to a current R of 0.048 for a total of 838 unique observed $[I > 2\sigma(I)]$ data measured in the range $4 < 2\theta < 50°$ on a Nicolet P3m diffractometer.†

Crystals of (**4**)·Cl were grown by slow diffusion of diethyl ether into an ethanol solution and similarly subjected to *X*-ray diffraction study† at room temperature. *Crystal data* for (**4**)·Cl: $C_{12}H_{25}ClN_2$, $M = 232.8$, monoclinic, space group, $C2/c$, $a = 8.233(4)$, $b = 14.261(7)$, $c = 10.671(5)$ Å, $\beta = 90.05(4)°$, $Z = 4$, $U = 1253(1)$ Å^3, $D_c = 1.23$ g cm^{-3}, $F(000) = 512$, Mo-K_α X-radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 2.8$ cm^{-1}. As for (**1**), structure solution was by direct methods, all atoms including hydrogens being located on difference electron density syntheses. Refinement led to a current R of 0.037 for 678 unique, observed data in the range $4 < 2\theta < 50°$.



(1)



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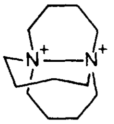

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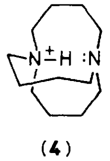
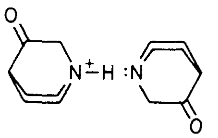
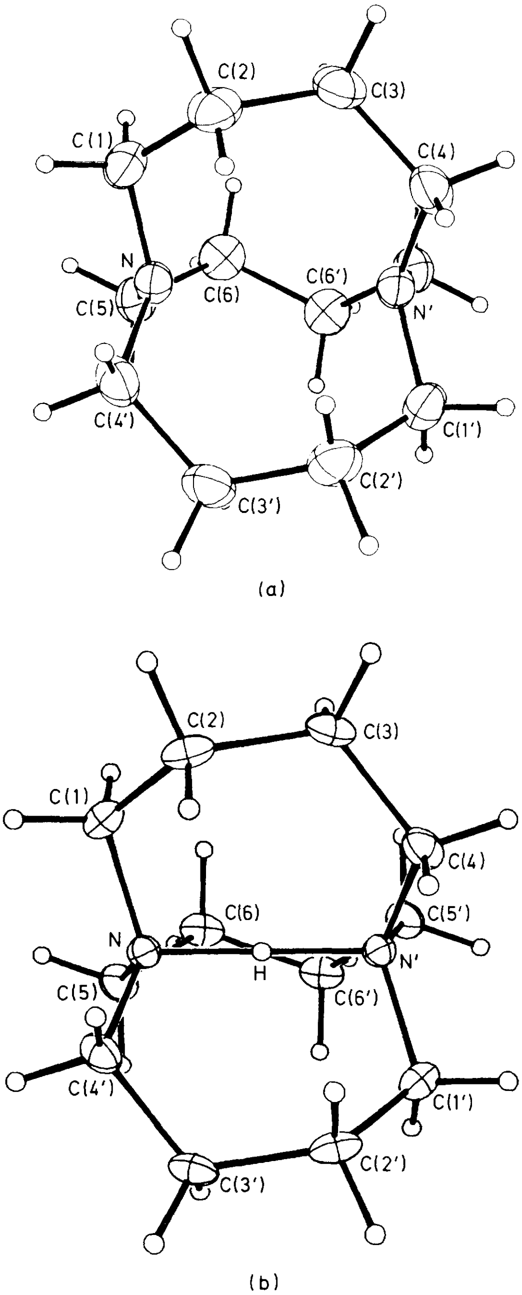


(4)



(5)

In their respective crystal structures (**1**) and (**4**) each occupy



(a)

(b)

Figure 1. Molecular structures of (**1**), (a) and (**4**), (b) viewed along the crystallographic two-fold axis.

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† The atomic co-ordinates for the structures reported here are available on request from The Director, Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Important data from the *X*-ray structure determination of compounds (**1**) and (**4**)·Cl.

Interatomic distances/Å	(1)	(4)·Cl
N–C	1.443(3)[a]	1.485(3)
C–C[b]	1.521(4)	1.523(3)
N. . . .N′	2.806(3)	2.526(3)
Bond angles/°		
C–N–C	115.5(2)	113.5(2)
C–C–C	116.3(2)	115.8(2)
N–C–C	114.1(2)	112.4(2)
Torsion angles/°		
C–N–C–C	79.8(2) −141.0(2)	77.1(3) −151.3(2)
N–C–C–C	68.2(2)	66.7(2)
C–C–C–C	90.1(2)	81.9(3)

[a] Estimated standard deviation in the least significant digit is given in parentheses here and throughout. [b] The two types of C–C bond are not significantly different in length.

sites of crystallographic two-fold symmetry as illustrated in Figure 1. Both (**1**) and (**4**) show D_3 symmetry to within experimental error in the solid state. Important geometric features of (**1**) and (**4**) averaged over the molecular symmetry are listed in Table 1.

The structures of (**1**) and (**4**) can be viewed as a compromise between the conformational demands of the $[CH_2]_4$ bridges which seek to impose a [4.4.4]propellane structure[5] with an intrabridgehead N,N′ distance of *ca.* 1.5 Å, and the effects of the four-electron lone-pair interaction in (**1**) and the hydrogen bond in (**4**) which impose much larger N,N′ distances. It is interesting that the hydrogen bond in (**4**) permits more relief of this conformational pressure than the lone-pair interaction in (**1**) so that the N,N′ distance contracts by 0.28 Å on inserting a proton. On going from (**1**) to (**4**), the N_2C_4 rings become more chair-like with a 10° rotation of one NR_3 moiety relative to the other and the bond angles and dihedral angles relax towards normal values, as can be seen from Table 1. There is a marked lengthening in N–C bond length on protonation of (**1**) which is presumably associated with partial sp^2 character of the bridgehead nitrogen atoms in (**1**). Force-field calculations[6] for (**1**) at the experimental geometries of (**1**) and (**4**) show a 22 kJ mol^{-1} decrease in strain energy on going from (**1**) to (**4**) when the N. . . .N′ interactions are excluded. It is interesting that the barriers to interconversion of enantiomeric D_3 structures in solution increase in the order (**1**), 46 ± 1.5; (**4**), 53 ± 1.5; (**3**), 73 ± 2 kJ mol^{-1}.

The conformational pressure of the $[CH_2]_4$ bridges results in (**4**) having an N,N′ distance 0.1 Å shorter than any previously recorded N^+–H:N system. Neutron diffraction data[7] for the 3-quinuclidone dimer cation (**5**) gave an N,N′ distance of 2.635 Å with the hydrogen midway between the nitrogens. Does (**4**) have a symmetrical (single-minimum) hydrogen bond? The *X*-ray data cannot answer this definitely, but least squares refinement of the bridging hydrogen led to physically unreasonable thermal parameters unless it was constrained to lie on the crystallographic two-fold axis. However the electron density maximum associated with this hydrogen is noticeably elongated along the N,N′ axis. Other evidence on this point is discussed in the following communication.[8]

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