A Strong Symmetrical N–H–N Bond. A 120 K Neutron Diffraction Study of Hydrogen Diquinuclidinone Perchlorate

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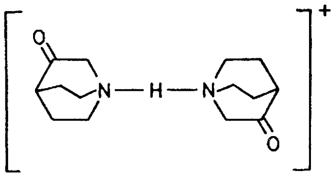
Neutron diffraction studies provide evidence for the existence of the hydrogen diquinuclidinone homoconjugated cation containing a very short and symmetrical linear N–H–N hydrogen bond [$N \cdots N = 2.635(2)$ Å and $N–H = 1.317(1)$ Å].

The main interest of acid salts with $[B \cdot H \cdot B]^+$ or $[A \cdot H \cdot A]^-$ homoconjugated cations and anions is that some of them contain the shortest known and possibly symmetrical hydrogen bonds between oxygen atoms. Heterocyclic bases also may form hydrogen bonds with their conjugate cations to give formally symmetrical $[B \cdot H \cdot B]^+$ cations and thus these are possible systems which may contain strong and symmetrical N–H–N bonds. However, it is generally thought that N–H–N



(1)

hydrogen bonds are not as strong as F–H–F or O–H–O hydrogen bonds and, before this study, a symmetrical case had not been observed.

The present paper is concerned with the symmetrical hydrogen bond involving two nitrogen atoms in the $[B{\cdot}H{\cdot}B]^+$ cation (**1**). One of the main points of interest in this neutron diffraction study was to determine the location of the bridging proton and its relation to the form of the proton potential function. Quinuclidin-3-one hemiperchlorate was selected for this study amongst similar salts since its i.r. spectrum indicated a very strong N–H–N bond at low temperature (90 K).[1] Other recent neutron diffraction studies have included the related systems $[NH_2py{\cdot}H{\cdot}pyNH_2]^+$ and $[py{\cdot}H{\cdot}py]^+$ (py = pyridine).[2,3]

Crystal data: $C_{14}H_{23}ClO_6N_2$, $M = 350.5$, monoclinic, space group *C*2/*c*, $a = 15.921(13)$, $b = 7.214(7)$, $c = 14.322(12)$ Å and $\beta = 98.68(2)°$, $U = 1626.17$ Å^3, $Z = 4$; $\mu = 1.52$ cm^{-1} ($\lambda = 0.8405$ Å). The single crystal used in this study (6.25 × 4.55 × 1.25 mm) was placed in a closed-cycle helium refrigerator on the D_9 four-circle diffractometer at the high-flux-beam reactor of the Laue-Langevin Institute, Grenoble.[4] Two octants of reciprocal space and portions of two additional octants (3200 reflections) were collected at 120 K to $\sin\theta/\lambda = 0.70$. Data reduction was carried out with the minimum $\sigma(I)/I$ method[5] and the data were corrected for absorption effects and the Lorentz factor. Averaging of all equivalent data yielded 2188 independent reflections. The structure was solved by application of the program MULTAN.† Disorder of the perchlorate anion was immediately recognized. Refinement by full-matrix least-squares methods of all atomic positional parameters and anisotropic thermal parameters (with half-weighted perchlorate atoms) led to a final *R* factor of 0.069, $R_w = 0.057$.‡ The scattering lengths used in the refinements were taken from Bacon.[6]

The crystal structure consists of discrete homoconjugated hydrogen-diquinuclidinone cations and perchlorate anions. The perchlorate groups are disordered across the crystallographic two-fold symmetry axis. The homoconjugated cation (Figure 1) lies on a crystallographic inversion centre with N–N and N–H distances respectively of 2.635(2) and 1.317(1) Å.

Therefore the salt corresponds exactly to a type A basic salt according to Speakman's classification.[7] The analogy with corresponding O–H–O systems is borne out further by the close similarity of their i.r. spectra, which exhibit broad, intense absorptions and transmission windows in the region below *ca.* 1000 cm^{-1}.

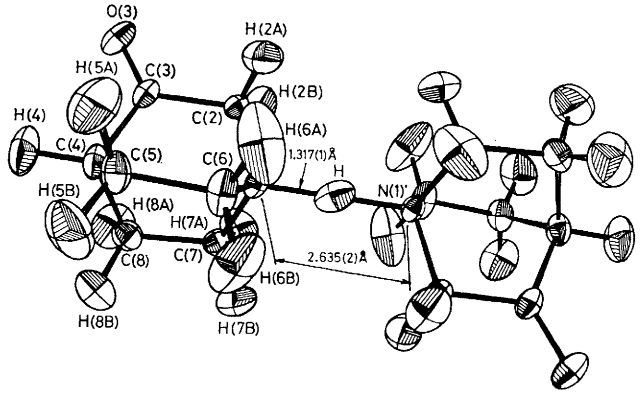


Figure 1. Structure of the symmetrical hydrogen diquinuclidinone cation (**1**).

The bridging hydrogen atom appears to be located on the crystallographic symmetric centre but, of course, our results do not preclude a disordered arrangement with two closely spaced sites for the hydrogen. There is, however, no indication of this as would be suggested by a high thermal motion of the central hydrogen atom. The largest principal axis of the thermal ellipsoid of the H atom makes an angle of 150° with the N ··· N direction and the root-mean-square displacement along the hydrogen bond axis is 0.19 Å.

This very short N–H–N hydrogen bond is to our knowledge the shortest and the first centrosymmetric hydrogen bond observed to date for a $[B{\cdot}H{\cdot}B]^+$ cation involving nitrogen bases. However, the N–N distance approaches that of 2.637(3) Å in the asymmetric N–H ··· N bond observed in 9-ethylguanine hemihydrochloride.[8] In this context, it is interesting that, although *ab initio* studies of the related species $NH_4^+{\cdot}NH_3$ have shown that proton transfer occurs through a contraction of the N–N distances to 2.60 Å, the minimum-energy geometry for this complex is found for larger N–N separations (2.71 and 2.78 Å) and a double-minimum energy well.[9] Additional investigations including a vibrational spectroscopic study are in progress, and the full study will be reported later.

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† The computer programs used in this study were the following: data reduction and absorption correction, DATAPH; structure solution by direct methods, MULTAN (J. P. Leclerq, G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr., Sect. A.*, 1973, **29**, 231); least-squares refinements, ORXFLS3; fourier summation, FORDAP; error analysis of distances and angles, ORFFE; structure plotting, ORTEP II.

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