An *X*-Ray Study at 298 and 120 K of the Strong, Symmetrical NHN Bond in Hydrogen Diquinuclidin-3-one Perchlorate †

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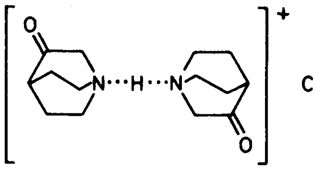
The effect of temperature on the NHN hydrogen bond in bis(quinuclidin-3-one)hydrogen(1+) perchlorate has been investigated by *X*-ray diffraction. The N ··· N distance has been found to be 2.648(9) Å at 298 K and 2.629(4) Å at 120 K. The splitting of the electron density at room temperature has been interpreted as indicating an asymmetric location for hydrogen. At 120 K the bond becomes more symmetrical, probably due to bridge shortening. The type of potential governing the proton motion is discussed and it is proposed that an energy barrier may develop during high-amplitude low-frequency hydrogen-bond vibrations.

Considerable advances have been made during the last decade in the study of very strong hydrogen-bonded compounds in the solid state. Recent review articles reflect current interest in strong hydrogen bonding in general.[1] Single-crystal diffraction has shown that very short hydrogen bonds are mostly found in symmetrical AHA^- anions in acid salts,[2,3] as in the classical example of potassium [4] or sodium [5] hydrogendifluoride. Analogous 'type A' basic salts such as salts of $H_5O_2^+$ are also known.[6,7] The vast majority of crystal studies on very strongly hydrogen-bonded compounds have dealt with OHO centres; however cations BHB^+, where B is a nitrogen-containing base, present the possibility of studying the NHN hydrogen bond in a formally symmetrical environment. The simplest system that can be envisaged is a salt of $N_2H_7^+$. Although a single-crystal diffraction study of such a compound has never been reported, analogues formed by heterocyclic bases hydrogen bonded to their conjugate cations have stimulated much crystallographic [8–18] and spectroscopic [19,20] investigation. Despite short NHN bonds in the range 2.63—2.79 Å, single-crystal studies show that, in general, the hydrogen atom is asymmetrically located in the bond. Such a wide range of NHN hydrogen-bond lengths clearly suggests the importance of slight changes in the local crystal environment. A phenomenon probably related to this is the drastic change observed in the i.r. spectra of certain BHB^+ salts on cooling,[15,20] which might indicate a change in the proton potential function with temperature.

Bis(quinuclidin-3-one)hydrogen(1+) perchlorate, $C_{14}H_{23}ClN_2O_6$ (1), has been reported to show a temperature effect in the i.r. spectrum of this type.[20] A short report of a neutron diffraction study has already been published, describing a proton-centred, short NHN bond, the first to be observed in a homonuclear complex cation of a heterocyclic base.[18]

The work described here was carried out in order to investigate the nature of the symmetrical NHN hydrogen bond by a study of the temperature effect on its geometry and proton potential function.

Experimental



(1)

Data Collection.—Fragments of the crystal of bis(quinuclidin-3-one)hydrogen(1+) perchlorate used in the neutron diffraction study of Rozière *et al.*[18] were used for *X*-ray data collection on a CAD4 diffractometer at 298 and 120 K. Different crystals were used for data collection at the two temperatures. The orientation matrix was obtained by least-squares fitting to the observed angular positions of 25 sufficiently strong, high-order reflections.

In the low-temperature experiment, cooling of the crystal was achieved using an Enraf-Nonius low-temperature cooling system with liquid nitrogen as the cryogen. This maintained the temperature around the crystal, which was mounted in a Lindemann glass capillary tube, at a steady 120 K.

The intensities of three strong reflections were monitored at regular intervals to provide a check on experimental stability and no significant variation in intensity was found. Reflections were measured using the θ—2θ scan mode for two non-equivalent octants of the Ewald sphere up to a maximum sinθ/λ of 0.75 $Å^{-1}$ for the low-temperature experiment and to a maximum of sinθ/λ of 0.66 $Å^{-1}$ for the room-temperature experiment. In this way, the intensities of 1 443 independent reflections were measured at 120 K and 690 reflections at 298 K, with $I > 3\sigma(I)$. In view of the unsatisfactory observation to parameter ratio in the latter case, a second data set was taken on the same crystal, up to sinθ/λ = 0.70 $Å^{-1}$. In order to improve counting statistics the two data sets were subsequently averaged, giving 758 independent reflections.

The data were corrected for Lorentz and polarisation effects, and for absorption. Crystal data are given in Table 1.

Structure Refinements.—Refinements were carried out using the program SHELX 76.[21] In each case the starting atomic parameters were taken from the final refinement cycle of the neutron study of Rozière *et al.*[18] For the data at 298 K, owing to correlation problems, it was difficult to refine the disordered perchlorate group, such that the resulting bond lengths had no physical significance, even with damped least-squares cycles. Ultimately, ClO_4^- was refined as a rigid group in a regular tetrahedral geometry using the DFIX option. Cl–O distances were constrained to 1.37 Å, within 0.01 Å. Application of these constraints did not change the *R* factor

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† Bis(quinuclidin-3-one)hydrogen(1+) perchlorate.

Supplementary data available (No. SUP 23921, 14 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

and led to a satisfactory convergence. The atomic parameters of the methylene and methylidyne hydrogen atoms were refined about the positions obtained from neutron diffraction using a fixed isotropic thermal parameter. The hydrogen atom in the hydrogen bond was easily located from difference-Fourier maps at the two temperatures.

During the final stages accelerated least-squares refinements were used, and a formal extinction coefficient was introduced. Finally, 25 low-angle reflections probably affected by extinction (with $F_c > F_o$) were omitted from the study at 298 K and 27 from the experiment at 120 K. Fractional co-ordinates are listed in Table 2.

The R factors were $R' = 0.0934$, $R = 0.0856$ for the room-temperature study and $R' = 0.0831$, $R = 0.0812$ for that at 120 K. The weighting scheme used was $w = 1/\sigma^2(F)$; $\sigma^2(F) = \sigma_c^2 + aF^2$, where $a = 0.007$ and 0.023 in the refinements at 120 and 298 K respectively.

Results and Discussion

General Description of the Structure.—A brief description of the structure of bis(quinuclidin-3-one)hydrogen(1+) perchlorate has already been published.[18] The *X*-ray results presented here are in agreement with this previous work. Between the neutron and *X*-ray experiments (both at 120 K), no atomic parameter disagrees in the quinuclidin-3-one unit by more than 3σ. However, for the disordered perchlorate group, agreement between the positional parameters is not as satisfactory. As already reported, the structure consists of discrete bis(quinuclidin-3-one)hydrogen(1+) cations and perchlorate anions. The hydrogen-bonded cation is shown in Figure 1. Bond lengths and angles in the ions at 120 K and at room temperature are given in Table 3.

Cooling the crystal causes a decrease in the cell volume of 3.2%. From Table 3 it may be seen that the effect of cooling on the C–C and C–N bond lengths is variable, resulting in contraction in some cases and expansion in others. The effect of temperature on the anisotropic thermal motion of the atoms is the most important factor accounting for this variation in bond length, especially when the distance at high temperature is shorter than that for the corresponding atom pair at 120 K. Riding motion may be responsible in particular for the large difference in the N(1)–C(2) distances. Nevertheless, the C–C

Table 1. Crystal data at 298 and 120 K for bis(quinuclidin-3-one)-hydrogen(1+) perchlorate *

	298 K	120 K
a/Å	16.169(3)	15.967(17)
b/Å	7.341(3)	7.237(4)
c/Å	14.363(5)	14.251(6)
β/°	99.23(2)	98.58(8)
U/Å^3	1 683	1 628
D_c/g cm^{-3}	1.38	1.43
μ/cm^{-1}	2.12	2.19

* $C_{14}H_{23}ClN_2O_6$, $M = 350.5$, monoclinic, space group $C2/c$, $Z = 4$, $F(000) = 744$, λ(Mo-K_α) = 0.710 69 Å.

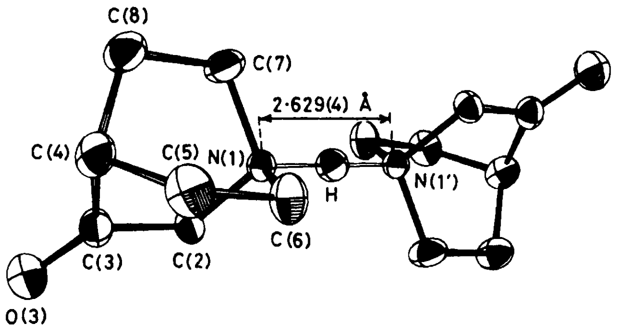


Figure 1. The bis(quinuclidin-3-one)hydrogen(1+) cation

Table 2. Fractional atomic co-ordinates (× 10^4 for non-hydrogen atoms; × 10^3 for hydrogen atoms) at 298 and 120 K for bis(quinuclidin-3-one)hydrogen(1+) perchlorate. Standard deviations in parentheses refer to the least significant figure

	298 K			120 K		
Atom	x	y	z	x	y	z
N(1)	5 743(3)	5 305(7)	513(3)	5 743(2)	5 294(4)	513(2)
C(2)	6 079(4)	7 054(9)	348(5)	6 082(2)	7 126(5)	339(2)
C(3)	6 924(4)	7 383(10)	970(5)	6 926(2)	7 407(5)	958(2)
C(4)	7 154(4)	5 776(10)	1 591(5)	7 158(2)	5 801(6)	1 608(3)
C(5)	7 177(4)	4 084(11)	991(6)	7 196(3)	4 079(7)	987(3)
C(6)	6 345(3)	3 813(9)	325(5)	6 364(2)	3 853(6)	322(3)
C(7)	5 621(5)	5 197(10)	1 517(5)	5 612(2)	5 184(7)	1 528(2)
C(8)	6 443(5)	5 598(10)	2 183(5)	6 433(2)	5 581(7)	2 194(3)
O(3)	7 319(3)	8 742(8)	933(4)	7 331(2)	8 798(4)	917(2)
Cl	−115(4)	5 245(5)	2 316(3)	−129(2)	5 261(3)	2 259(2)
O(1)	672(6)	5 475(17)	2 091(13)	687(5)	5 524(15)	1 985(9)
O(2)	−596(6)	6 736(10)	2 027(8)	−633(4)	6 772(10)	2 005(5)
O(4)	−479(7)	3 740(11)	1 858(10)	−479(7)	3 740(13)	1 678(9)
O(5)	−66(14)	5 019(19)	3 268(6)	−145(14)	4 689(27)	3 185(11)
H	−1(3)	−46(3)	−2(3)	0	0	0
H(2A)	569(2)	827(3)	40(2)	570(3)	804(8)	46(4)
H(2B)	611(2)	744(3)	−10(2)	614(3)	718(8)	−36(3)
H(4)	765(2)	623(3)	201(2)	771(3)	607(8)	203(4)
H(5A)	736(2)	271(3)	146(2)	728(4)	311(9)	136(4)
H(5B)	756(2)	413(3)	71(2)	769(4)	425(8)	59(4)
H(6A)	603(2)	239(3)	37(2)	612(4)	263(8)	40(3)
H(6B)	640(2)	416(3)	−38(2)	640(3)	412(8)	−40(4)
H(7A)	537(2)	371(3)	158(2)	537(3)	416(8)	171(4)
H(7B)	525(2)	646(3)	157(2)	519(3)	618(8)	167(4)
H(8A)	640(2)	680(3)	252(2)	635(3)	680(8)	259(4)
H(8B)	653(2)	433(3)	255(2)	658(4)	460(8)	267(4)

Table 3. Interatomic distances (Å) and angles (°) in bis(quinuclidin-3-one)hydrogen(1+) perchlorate. Standard deviations in parentheses refer to the least significant figure

	298 K	120 K		298 K	120 K
(*a*) Distances					
N(1)-C(2)	1.429(7)	1.466(4)	C(2)-H(2A)	1.10(4)	0.93(5)
N(1)-C(6)	1.518(7)	1.491(5)	C(2)-H(2B)	0.71(5)	1.02(5)
N(1)-C(7)	1.489(8)	1.494(4)	C(4)-H(4)	0.98(5)	1.01(5)
C(2)-C(3)	1.524(9)	1.511(5)	C(5)-H(5A)	1.22(4)	0.87(6)
C(3)-C(4)	1.484(9)	1.498(6)	C(5)-H(5B)	0.79(5)	1.04(6)
C(4)-C(8)	1.541(10)	1.533(5)	C(6)-H(6A)	1.17(4)	0.98(6)
C(8)-C(7)	1.536(10)	1.526(6)	C(6)-H(6B)	1.06(5)	1.06(5)
C(4)-C(5)	1.515(10)	1.535(6)	C(7)-H(7A)	1.18(4)	0.89(6)
C(5)-C(6)	1.534(9)	1.522(6)	C(7)-H(7B)	1.12(4)	1.03(5)
C(3)-O(3)	1.197(7)	1.202(4)	C(8)-H(8A)	1.01(4)	1.07(6)
			C(8)-H(8B)	1.07(4)	0.98(6)
O(1)-Cl	1.372(7)	1.428(10)	O(4)-Cl	1.369(6)	1.439(12)
O(2)-Cl	1.368(6)	1.374(7)	O(5)-Cl	1.366(7)	1.386(16)
(*b*) Angles					
C(7)-N(1)-C(2)	108.8(5)	108.7(3)	C(6)-N(1)-C(7)	108.8(5)	109.4(3)
N(1)-C(2)-C(3)	111.7(5)	110.1(3)	C(4)-C(3)-O(3)	127.3(6)	126.5(3)
C(2)-C(3)-C(4)	110.2(5)	111.9(3)	C(2)-C(3)-O(3)	122.5(6)	121.6(4)
C(3)-C(4)-C(8)	105.1(5)	106.3(3)			
C(4)-C(8)-C(7)	108.7(5)	109.2(3)	O(1)-Cl-O(2)	109.4(6)	110.2(5)
C(8)-C(7)-N(1)	110.9(5)	111.1(3)	O(1)-Cl-O(4)	109.2(6)	103.7(7)
C(8)-C(4)-C(5)	109.4(6)	109.2(4)	O(1)-Cl-O(5)	110.0(7)	116.6(10)
C(3)-C(4)-C(5)	109.4(6)	107.5(3)	O(2)-Cl-O(4)	108.7(6)	107.2(5)
C(4)-C(5)-C(6)	111.2(5)	109.9(3)	O(2)-Cl-O(5)	109.9(6)	113.3(9)
C(5)-C(6)-N(1)	108.6(5)	110.7(3)	O(4)-Cl-O(5)	109.5(6)	105.0(9)
C(6)-N(1)-C(2)	110.3(5)	109.2(3)			
(*c*) Hydrogen bonds					
N(1) ··· N(1′)	2.648(9)	2.629(4)	H ··· N(1′)	1.44(4)	1.31
N(1)-H	1.29(4)	1.31	N(1)-H-N(1′)	152(2)	180
H-H	0.68(4)				

and C-N distances obtained at 120 K, where because of the reduction in thermal motion and lower standard deviations the distances are expected to be more accurate, fall within the range expected for such single bonds.

Quinuclidin-3-one has a formal mirror plane which passes through the atoms N(1)C(2)C(3)O(3)C(4). As expected, at 120 K the distances between the corresponding atoms in the sequences C(4)-C(5)-C(6)-N(1) and C(4)-C(8)-C(7)-N(1) are similar within 1σ, whereas the atom sequence N(1)-C(2)-C(3)-O(3)-C(4) has, in general, much shorter distances, owing to the presence of the carbonyl group, Figure 2.

The perchlorate groups are disordered across the two-fold symmetry axis. Both the chlorine and oxygen atoms suffer from high-amplitude thermal motion and the difficulty in refining the room-temperature data was largely due to these problems, although even at 120 K the thermal motion of all atoms is high, especially for O(5).

The quinuclidin-3-one moieties are held together by a very short hydrogen bond, *r*(N ··· N) = 2.629 Å at 120 K. This distance is consistent with that obtained from neutron data and is the shortest N ··· N hydrogen bond yet reported for $B-H-B^+$ systems. A shorter NHN bond has been found in $[Co^{III}(CN)_6H_3]$ for which *r*(N ··· N) = 2.58 Å.[22] A very short N ··· N distance of 2.53 Å has recently been observed in protonated 1,6-diazobicyclo[4.4.4]tetradecane.[23a] In the ‘ proton sponge ’, protonated 1,8-bis(dimethylamino)naphthalene, the intramolecular N ··· N bond is 2.62(1) Å and is probably bent.[23b] A brief survey of NHN hydrogen bonds in BHB^+ systems is given in Table 4. These crystal studies show that the geometry of the NHN bond can be related to the N ··· N distance and to the environment around the bridging atoms.

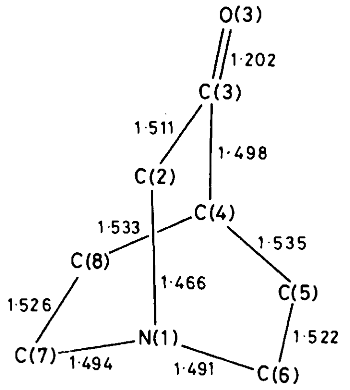
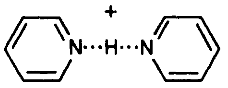
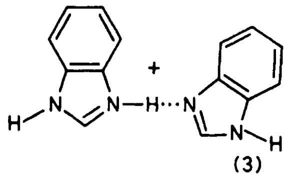
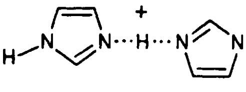
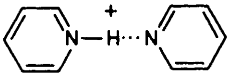
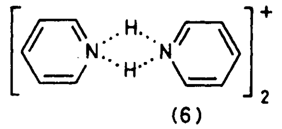
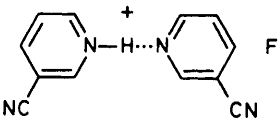
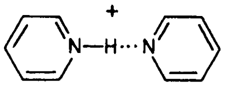
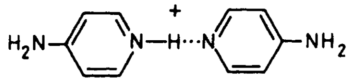
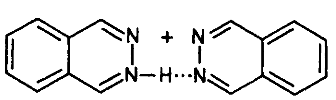
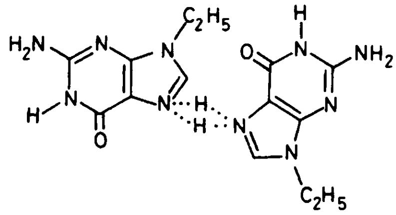


Figure 2. Bond distances (Å) in the quinuclidin-3-one unit

Effect of Temperature on the NHN *Bond*.—The principal object of this study was to evaluate the effect of temperature on the geometry of the NHN hydrogen bond. In fact, it has been found that the hydrogen-bond lengths at 298 and 120 K are 2.648(9) and 2.629(4) Å respectively, so that with the high standard deviation of the N ··· N distance at room temperature, the difference is barely significant. More information can be obtained however, on the temperature effect on the NHN bond, by comparing the difference-Fourier maps in Figure 3(*a*)—(*d*). At room temperature, Figure 3(*a*), it appears that the hydrogen is disordered as two half-atoms 0.68 Å apart, on either side of the centre of symmetry and off the N ··· N axis. This situation has already been reported for accurate *X*-ray studies of an important number of examples,

Table 4. A survey of NHN hydrogen bonds in hydrogen-bonded BHB^+ cations (bond lengths are in Å, angles in °)

Method [a] (*T*/K)	Compound [b]	$r(N\cdots N)$, $\widehat{NHN}$, $r(N-H)$, $r(H\cdots N)$	Ref.
X-Ray (r.t.) Neutron (r.t.)	 $[ZnBr_{\frac{3}{2}}Cl_{\frac{3}{2}}(py)]^-$ (2)	2.737(3), 172, 1.086, 1.658	8
X-Ray (283)	 BF_4^- (3)	2.784(4)	9
X-Ray (283)	 ClO_4^- (4)	2.73(1)	10
X-Ray (293)	 $[WBr_4(py)_2]^-$ (5)	2.73(2)	11
X-Ray (r.t.)	 $P_2S_8^{2-}$ (6)	2.655(7)	12 [c]
X-Ray (r.t.)	 $FeCl_4^-$ (7)	2.74(2), 144 1.01, 1.86	13
X-Ray (r.t.)	 $[Hpy][Fe_2OCl_6]$ (8)	2.747, 160	14
Neutron (295) *X*-Ray (193)	 ClO_4^- (9)	2.698(8), 277, 1.17, 1.52 2.697(4)	15(*a*) 15(*b*)
X-Ray (r.t.)	 ClO_4^- (10)	2.66(2), 162, 1.00, 1.69	16
X-Ray (r.t.)	 Cl^- (11)	2.637(3), 176, 0.89, 1.75 174, 1.03, 1.61	17 [c]

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[a] r.t. = Room temperature. [b] py = pyridine. [c] These authors report a delocalised H^+ atom between the nitrogen centres, with the two indicated positions only partially occupied, *i.e.* a total site occupation of unity.

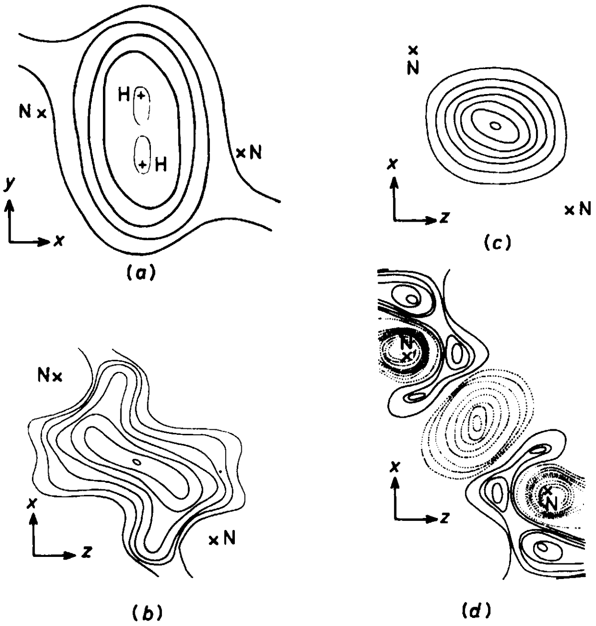

Figure 3. (*a*) *X*-Ray $F_o - F_c$ synthesis, with H omitted from F_c, from the data at 298 K showing the disordered half-hydrogen atoms. Contour interval 0.05 e Å^{-3} (*xy* plane). (*b*) *X*-Ray $F_o - F_c$ synthesis, with H omitted from F_c, from the data at 120 K. Contour interval 0.05 e Å^{-3} (*xz* plane). (*c*) Neutron $F_o - F_c$ synthesis with H omitted from F_c, using the data at 120 K from ref. 18. Contour interval 0.05 p Å^{-3} (*xz* plane). (*d*) X–N (deformation electron density) map in the region of the NHN bond in the *xz* plane. Dotted lines represent negative contours; contour interval 0.05 e Å^{-3}. Zero contour is omitted from all maps

such as hydrazinium hydrogenoxalate.[24] It is recognised that this effect is not simply due to errors in the experimental intensity data, but corresponds to a real splitting of the electron density. It is generally termed the KKM (Kroon–Kanters–McAdam) effect.[25] Careful analyses using combined neutron and *X*-ray data have been carried out in several cases, including potassium *meso*-tartrate [26] and potassium hydrogen succinate.[27] In the case of hydrazinium hydrogenoxalate, the apparent splitting of the electron density has been interpreted as indicating an asymmetrical hydrogen bond, with a statically disordered hydrogen.

In contrast, for the present case at 120 K, one single position for the proton is found for the *X*-ray data, which seems consistent with the neutron data result of Rozière *et al.*[18] at the same temperature. Nevertheless, the difference-density maps in the two experiments show some marked differences.

From the *X*-ray data the hydrogen appears delocalised with the electron density distorted and elongated in the direction of the nitrogen atoms, Figure 3(*b*). Such a smearing is not apparent from the neutron data, where the difference map shows an almost spherical proton distribution, Figure 3(*c*). A deeper insight into the electron distribution in the NHN bond can be obtained from X–N deformation maps, which show the deviation from spherical symmetry of the electron density of the hydrogen atom in the hydrogen bond. The resulting electron density map, in particular the large region of charge depletion in the centre of the bond, is strongly reminiscent of the case of the formally symmetrical, but non-centred OHO bond in hydrazinium hydrogenoxalate, Figure 3(*d*). This pattern is not found in cases where the hydrogen bond is thought to be truly symmetrical, as in sodium hydrogen diacetate.[28] Moreover, the distribution resembles that of the asymmetric hydrogen bond in $N_2H_7^+$, from recent *ab initio* calculations.[29] It therefore seems that even at 120 K the hydrogen atom in bis(quinuclidin-3-one)hydrogen(1+) perchlorate is not centred.

The Proton Potential in NHN *Hydrogen Bonds.*—This result is relevant to the long-standing debate as to the existence of the double minimum in very strongly hydrogen-bonded compounds. It is well known that from diffraction data alone it is impossible to distinguish between disorder in time or in space, so that uncertainty must remain as to the shape of the potential well. Disorder in time would produce a symmetrical double minimum, whereas disorder in space implies a slightly asymmetric potential. The idea of proton motion governed by a symmetrical double minimum has recently been questioned by Bratos,[30] who has shown that for short OHO bonds this type of well is theoretically unacceptable and can only develop from a progressive increase in the hydrogen-bond length. Closely related to this is the earlier suggestion of Hamilton and co-workers [31] that for most very short bonds the vibrational amplitude of the proton along the bond is such that, in this motion, the proton can be brought from one site to another. Similarly, 'type A' structures containing hydrogen bonds of less than 2.50 Å have been described by Speakman *et al.*[32] as having a flattened single-minimum potential function for the proton.

In the light of these arguments, the situation for bis(quinuclidin-3-one)hydrogen(1+) perchlorate can be described in terms of a hydrogen atom asymmetrically located in a wide-bottomed potential energy curve which becomes more symmetrical on cooling.

The concept of a double-minimum potential should not, however, be rejected out of hand. *Ab initio* calculations on the model system $N_2H_7^+$ have shown that, at least in the case of the NHN bond, at the geometry of lowest energy the potential is of the double-minimum type.[33] This is in contrast to the isoelectronic system $H_5O_2^+$, where the energy barrier is very low or non-existent at the equilibrium geometry.[33d,34] The consistent point emerging from the calculations on $N_2H_7^+$ is that the height of the energy barrier between the two minima depends on the inter-nitrogen distance and moreover, that the barrier increases steeply after 2.6 Å, falling in the range of commonly observed NHN hydrogen bonded lengths in hydrogen-bonded BHB$^+$ cations, Table 4.

The variation of the energy barrier with the N···N distance implies that the low-frequency vibrations involving the motion of the nitrogen atoms along the hydrogen-bond axis, in particular the symmetric stretching mode, strongly influence the barrier height. For instance, the symmetric stretching mode of bis(quinuclidin-3-one)hydrogen(1+) perchlorate has been assigned to a Raman line at 103 cm^{-1},[35] which would correspond to a maximum r.m.s. displacement of 0.03 Å. Such a variation about the equilibrium distance is sufficient to pass from a situation in which the potential barrier is absent or irrelevant to one where it affects the distribution of the energy levels. In the case of a fluctuating energy barrier it is no longer valid to discuss the vibrational spectra in terms of discrete energy levels, but rather in terms of a continuous energy level distribution. Some parallel is therefore found with Zundel's theory of easily polarisable hydrogen bonds,[36] and the above proposal can be considered as an alternative to that used by Sobczyk and co-workers [15a,37] to explain the anomalous i.r. spectra of NHN hydrogen-bonded compounds.

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References

1 (*a*) 'The Hydrogen Bond,' eds. P. Schuster, G. Zundel, and C. Sandorfy, North Holland, Amsterdam, 1976, vol. I—III; (*b*) J. Emsley, D. J. Jones, and J. Lucas, *Rev. Inorg. Chem.*, 1981, **3**, 105.
2 J. C. Speakman, *Struct. Bonding (Berlin)*, 1972, **12**, 141.
3 I. Olovsson and P-G. Jonsson, in ref. 1*a*, vol. II, ch. 8, p. 393.
4 S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, 1952, **20**, 704; J. A. Ibers, *ibid.*, 1964, **40**, 402.
5 B. L. McGraw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.
6 J. O. Lundgren and I. Olovsson, in ref. 1*a*, vol. II, ch. 10, p. 471.
7 J. M. Williams, in ref. 1*a*, vol. II, ch. 14, p. 657.
8 E. O. Schlemper and B. E. Villareal-Salinas, *J. Cryst. Mol. Struct.*, 1978, **8**, 217.
9 A. Quick and D. J. Williams, *Can. J. Chem.*, 1976, **54**, 2482.
10 A. Quick and D. J. Williams, *Can. J. Chem.*, 1976, **54**, 2465.
11 J. V. Brecic, B. Ceh, and I. Leban, *Acta Crystallogr., Sect. B*, 1979, **35**, 3028.
12 P. C. Minshall and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1378.
13 J-C. Daran, Y. Jeannin, and L. M. Martin, *Acta Crystallogr., Sect. B*, 1979, **35**, 3030.
14 M. G. B. Drew, V. McKee, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1978, 80.
15 (*a*) J. Rozière, J. M. Williams, E. Grech, Z. Malarski, and L. Sobczyk, *J. Chem. Phys.*, 1980, 72, 6117; (*b*) P. Teulon, R. Delaplane, I. Olovsson, and J. Rozière, *Acta Crystallogr., Sect. B*, in the press.
16 E. Grech, T. Glowiak, Z. Malarski, and L. Sobczyk, *Chem. Phys. Lett.*, 1980, **76**, 495.
17 G. S. Mandel and R. E. Marsh, *Acta Crystallogr., Sect. B*, 1975, **31**, 2862.
18 J. Rozière, C. Belin, and M. S. Lehmann, *J. Chem. Soc., Chem. Commun.*, 1982, 388.
19 D. H. Bonsor, B. Borah, R. L. Dean, and J. L. Wood, *Can. J. Chem.*, 1976, **54**, 2458; B. Borah and J. L. Wood, *ibid.*, p. 2470.
20 E. Grech, Z. Malarski, and L. Sobczyk, *Pol. J. Chem.*, 1978, **52**, 131.
21 G. M. Sheldrick, SHELX 76, program system for crystal structure determination, University of Cambridge, 1976.
22 R. Haser, B. Bonnet, and J. Rozière, *J. Mol. Struct.*, 1977, **40**, 177.
23 (*a*) R. W. Alder, A. G. Orpen, and R. B. Sessions, *J. Chem. Soc., Chem. Commun.*, 1983, 99; (*b*) M. R. Truter and B. L. Vickery, *J. Chem. Soc., Dalton Trans.*, 1972, 395.
24 J. O. Thomas and R. Liminga, *Acta Crystallogr., Sect. B*, 1978, **34**, 3686.
25 A. L. Macdonald, J. C. Speakman, and D. Hadzi, *J. Chem. Soc., Perkin Trans. 2*, 1972, 825.
26 M. Currie, J. C. Speakman, J. A. Kanters, and J. Kroon, *J. Chem Soc., Perkin Trans. 2*, 1975, 1549.
27 M. Currie and J. C. Speakman, *J. Chem. Soc. A*, 1970, 1923.
28 E. D. Stevens, M. S. Lehmann, and P. Coppens, *J. Am. Chem. Soc.*, 1977, **99**, 2829.
29 P. J. Desmeules and L. C. Allen, *J. Chem. Phys.*, 1980, **72**, 4731.
30 S. Bratos, *J. Chem. Phys.*, 1982, **76**, 77.
31 A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Struct.*, 1967, **1**, 283.
32 J. C. Speakman, M. S. Lehmann, J. R. Allibon, and D. Semmingsen, *Acta Crystallogr., Sect. B*, 1981, **37**, 2098.
33 (*a*) J. J. Delpuech, G. Serratrice, A. Strich, and A. Veillard, *J. Chem. Soc., Chem. Commun.*, 1972, 817; (*b*) *Mol. Phys.*, 1975, **29**, 849; (*c*) P. Merlet, S. D. Peyerimhoff, and B. J. Buenker, *J. Am. Chem. Soc.*, 1972, **94**, 8301; (*d*) S. Scheiner, *J. Phys. Chem.*, 1982, **86**, 376.
34 P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, 1970, **92**, 6101. W. P. Kraemer and G. H. F. Diercksen, *Chem. Phys. Lett.*, 1970, **5**, 463.
35 L. Sobczyk, personal communication.
36 G. Zundel, in ref. 1*a*, vol. II, ch. 15, p. 683.
37 H. Romanowski and L. Sobzcyk, *Chem. Phys. Lett.*, 1978, **58**, 73.

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