Lengthening of the N–H Bond in N–H···N Hydrogen Bonds. Preliminary Structural Data and Implications of the Bond Valence Concept

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For N–H···N hydrogen bonds, the dependence of the N–H length on the H···N distance is studied using neutron diffraction data; this dependence is the same for both charged and uncharged N–H donors; geometry predictions for strong hydrogen bonds and values for the shortest possible N···N and N···O separations are deduced on the basis of the bond valence concept.

It is an inherent property of X–H···Y hydrogen bonds that the covalent X–H bond is lengthened compared to a 'free' X–H group.[1] However, this effect is not easy to explore experimentally: if the correlation between the X–H length and the H···Y separation is to be quantified, then precise H-atom positions must be known for a large number of independent X–H···Y interactions. The accuracy of H positions determined with X-ray diffraction methods is unacceptably low and neutron diffraction data must be used although the quantity of available neutron data is very limited. Only for the abundant O–H···O and N–H···O interactions, the X–H lengthening was previously described from neutron data,[2] whereas for all other types of hydrogen bonds, accurate analysis was not possible owing to lack of structural data.

Recently, however, there is renewed interest in X–H bond lengthening: substantially more and better data have become available for O–H···O bonds,[3] and originating from different starting points, its relevance for theoretical consideration was made clear.[4–6] Even for the weak C–H···O interactions, slight C–H bond lengthening was reported.[7] The current intense interest in N–H···N hydrogen bonds, particularly in the context of strong hydrogen bonding[8] and 'proton sponges',[9] suggests an examination of the N–H lengthening in this type of homonuclear hydrogen bonds from the presently available neutron data.‡

To perform this study, two-centre N–H···N hydrogen bonds in high-quality neutron diffraction studies were retrieved§ from the Cambridge Structural Database[10] (31 bonds from 24 structures). Chemically, the obtained data sample is very non-homogeneous.¶ Within the data set, the mean hydrogen bond length of 2.00(3) Å is associated with a mean N–H bond length of 1.028(3) Å, Table 1.

The correlation of N–H with H···N is shown in Fig. 1. The scatter of data points is large, but some important features are still clearly visible: (*a*) The correlation is smooth with no indication of discontinuities or sudden changes of slope, and continues to fall even for long H···N distances > 2.0 Å, showing the long range nature of the hydrogen bond. (*b*) For all donor types, the data points are scattered around the same regression line. N–H···N hydrogen bonds with the 'strong' N^+–H donors have on average shorter H···N separations than those with 'weak' pyramidal N–H donors, Table 1, but they obey the same functional relationship N–H = *f* (H···N). In the interval H···N = 2.0–2.1 Å, the data for all donor types neatly overlap. In N–H···N bonds with a given H···N distance, the covalent N–H bond length is always the same (or, at least, very similar||), irrespective of the charge and the hybridisation state of N. This is an important observation and contradicts the view that hydrogen bonds with cation donors, N^+–H···N, are fundamentally different from those with neutral N–H donors. This behaviour exactly parallels that of O–H···O hydrogen bonds,[3a] where a common functional relationship was observed for all types of O–H donors, including H_3O^+.

Table 1 Mean H···N and N–H distances (Å) in the data sample[a]

Donor	*n*	Mean H···N	Mean N–H
All	31	2.00(3)	1.028(3)
N^+–H	7	1.91(8)	1.036(11)
N–H trigonal	19	1.96(2)	1.028(3)
N–H pyramidal	4	2.26(7)	1.019(2)
S=N–H	1[b]	2.36	1.008

[a] Standard errors of the mean values are given in parentheses. [b] The single S=N–H donor is from dimethylsulfone diimine.[13]

If N–H and H···N separations are taken as quantities of the same kind, they may be drawn on a common axis (as was suggested by Bürgi and Dunitz[5]). This yields the symmetric picture shown in Fig. 2. Unfortunately, the central region is unpopulated because no neutron data is available for short N–H···N bonds,** although these are well known to exist (for example in the so-called 'proton-sponges'[9] and other protonated diamines[8]). For strong N–H···N bonds, data points are expected to be placed on a continuous curve which is smooth at the midpoint.

To calculate the geometry of the 'missing' strong hydrogen bonds, the valence model of the hydrogen bond[4] was applied, which very nicely described the related data for O–H···O interactions.[3a] Here, the N–H and H···N bonds are assigned 'valences' *s*, which are a function of only the bond distances; the sum of valences at H must be 1. Using the approximation $s = e^{(r_0-r)/b}$, where r_0 is the bond length of 'free' N–H and *b* is a constant, one readily obtains an approximation for the function N–H = *f*(H···N) as: $r_1 = r_0 - b\ln\{1 - e^{[(r_0-r_2)/b]}\}$. In a least-squares fit against the data from Fig. 1, values of $r_0 = 0.996$ and $b = 0.381$ Å are obtained.†† This function is drawn as a solid line in Fig. 2; in neutron diffraction studies of strong N–H···N bonds, the interatomic distances should be found on or very close to this line. From the above numerical data, one can calculate the shortest possible N···N approach in a hydrogen bond, *i.e.* that which occurs in the symmetric bond N···H···N. Taking $s_1 = s_2 = 0.5$, one obtains $r_1 = r_2 = 1.260$ Å, and $(N\cdots N)_{min} = 2.520$ Å. This is very close to the shortest value observed from X-ray data in proton sponges [2.527 Å given in ref. 9(*b*)], indicating excellent validity of the valence model.

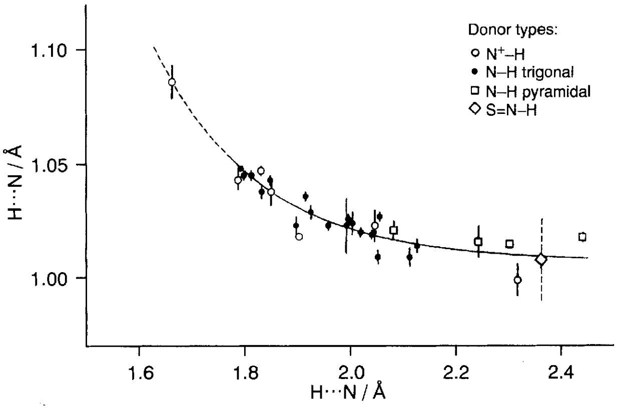

Fig. 1 Lengthening of the N–H bond in 31 two-centre N–H···N hydrogen bonds. All chemical types of N–H donors and N acceptors were considered. The vertical error bars represent the standard uncertainties of the N–H bond length given in the original publications. The solid line is only a guide to the eye.

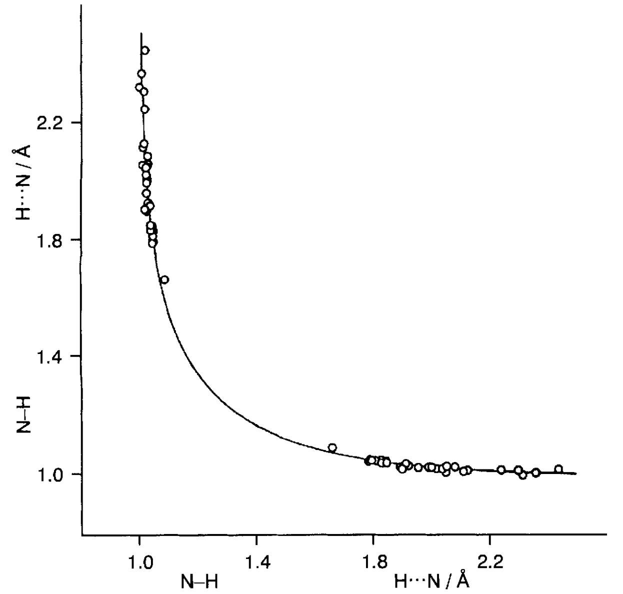

Fig. 2 Lengthening of the N–H bond in 31 two-centre N–H···N hydrogen bonds. Following Bügi and Dunitz,[5] the N–H and H···N separations are drawn on a common axis. The theoretical line is a fit against the bond valence model,[3a,4] $r_1 = r_0 - b \ln \{1 - e^{[(r_0 - r_2)/b]}\}$, with $r_0 = 0.996$, $b = 0.381$ Å.

The above results have implications for the heteronuclear N–H···O and O–H···N hydrogen bonds, for which the strong ('low-barrier') species and the proton transfer properties are currently under discussion,[8,11] particularly in the context of enzymatic reaction.[12] Also, for these bonds, the shortest possible approach is characterized by $s_1 = s_2 = 0.5$. Since the parameters r_0 and b have different values for O–H and N–H [for O–H: r_0 *ca.* 0.927 and b *ca.* 0.395 Å, ref. 3(*a*)], this does not represent a centred hydrogen bond. Instead, the corresponding geometry has N···H = 1.260, O···H = 1.201 and N···O = 2.461 Å, *i.e.* the H atom is closer to the O than to the N atom.[‡‡] The geometrically centred N–H–O bond is calculated to have $r_1 = r_2 = 1.232$ Å, $s_{NH} = 0.538$, $s_{OH} = 0.462$. Since S_{NH} is greater than S_{OH}, it is of the type N–H···O. The N···O separation of 2.464 Å is only marginally longer than for the case with $s_1 = s_2 = 0.5$.

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Footnotes

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‡ An attempt to correlate N–H with H···N from X-ray diffraction data was recently shown for the $[N–H···N]^+$ system by Llamas-Saiz *et al.*[9b] leaving the authors unsatisfied because of the extremely broad scatter of the data points [Fig. 3 of Ref. 9(*b*)].

§ Cambridge Structural Database[10] (CSD), August 1994 update with 126353 entries. Retrieved were error-free organic neutron structures with $R \leq 0.06$, no further constraints on the chemical nature, only N–H···N hydrogen bonds with no additional contact < 2.6 Å of H to a hydrogen bond acceptor. This yielded 31 N–H···N bonds in 24 crystal structures. Reference codes in the CSD: ADENOS01, AMCLPY11, AMXBPM10, ANILPC, ARGIND11, CADKEX01, CBOATZ02, CBOHAZ02, CYCHHZ01, CYGUAN01, CYTOSH, DMSDIM01, FORMAO01, HARMID03, HDRZHO11, IMAZOL06, IMAZOL13, LHISTD13, MATCQI09, MEADEN02, MELAMI04, PYCBZN01, TRAZOL02, TRAZOL03.

¶ The data sample consists of a more or less arbitrary mixture of high- and low-temperature data of different compound classes. The standard errors of the individual N–H bond lengths vary by over one decade from about 0.001 to almost 0.02 Å; see the error bars in Fig. 1. The individual N–H bond lengths are affected by thermal vibration artifacts[1] to different degrees (those measured at low temperature to a smaller degree than those measured at room temp., and those from rigidly confined N–H groups to a smaller degree than those from N–H groups that may rotate). Furthermore, some minor influence of contacts to second-nearest acceptor atoms > 2.6 Å must be expected.[3a] These limitations parallel the situation in earlier studies of O–H···O bonds.[2] Unfortunately, the present amount of data does not allow restriction to a set of low- or room-temperature data with homogeneous accuracy. The drawbacks of the data set impose preliminarity of the results, and suggest further investigation if better data become available.

|| Regarding the scatter of data points, a possible bond length difference between different N–H donor types is estimated to be ≤0.003 Å.

** The shortest bond in the data set is from PYCBZN01, N–H = 1.086, H···N = 1.658, N···N = 2.739 Å, ref. 14.

†† The value $r_o = 0.996$ Å is too short compared with the gas phase values of, for example, free NH_3, 1.012 Å (ref. 15). This parallels results for O–H···O bonds, where the valence model with the same mathematical approximation of s fits the data excellently in the central region of strong and moderate hydrogen bonds, whereas the obtained r_o values are too short.[3a,b] In the present case, the model presumably is a very accurate approximation for strong hydrogen bonds, but is only qualitatively valid for long bonds H···N > 2.2 Å.

‡‡ The shortest N–H–O bond reported so far has an N···O separation of 2.465(5) Å, and an H position closer to O than to N, ref. 11.

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