Lengthening of the Covalent X−H Bond in Heteronuclear Hydrogen Bonds Quantified from Organic and Organometallic Neutron Crystal Structures

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The lengthening of the covalent X−H bond in heteronuclear hydrogen bonds is quantified from neutron crystal structures for combinations of the donors N−H and O−H with the acceptors O, N, S, and Cl$^-$. For N−H···O hydrogen bonds, only high-precision low-temperature crystal structures are used. For the other hydrogen bond types, there are too few neutron crystal structures available to allow restriction to low-temperature data. For all donor/acceptor combinations studied, systematic lengthening of the X−H bond due to the hydrogen bond interaction is definitely confirmed, and this includes the relatively weak sulfur acceptors. The experimental data are discussed in the frame of the valence model of the hydrogen bond, and on this basis, the geometries of a number of hydrogen bonds are predicted for which only X-ray crystal structures have been published.

I. Introduction

It is an inherent characteristic of X−H···Y hydrogen bonds that the covalent X−H bond is elongated compared to an undisturbed X−H group. Experimentally, this effect can be best quantified in single-crystal neutron diffraction studies, whereas X-ray diffraction data are unsuitable.[1] For the best examined example, the homonuclear O−H···O hydrogen bonds, a correlation of the O−H with the H···O distance has been described from neutron crystal structures already in 1955[2] and was subsequenty refined by several groups of authors.[3−6] Restriction to accurate low-temperature neutron crystal structures considerably improves the quality of the correlation.[6] In essence, it is observed that with shortening H···O separation, the O−H bond length continuously increases until the point is reached where the proton is equally shared between the oxygen atoms, O···H···O. This latter "symmetric hydrogen bond" represents the shortest possible hydrogen bond between two oxygen atoms. In the solid state, it is associated with a well-defined O···O separation of 2.39−2.40 Å. With larger O···O separations, the proton resides closer to one of the two oxygen atoms than to the other. In "normal" O−H···O hydrogen bonds, such as formed between water or alcohol molecules, the O−H and H···O distances are very different, and the O−H bond is lengthened only by a few hundreds of an angstrom compared to the relaxed state. Very short hydrogen bonds are stably formed in charged species, such as O$^+$−H···O or O−H···O$^-$, and in arrangements where the oxygen atoms are connected by π-conjugated double bonds ("resonance-assisted hydrogen bonding").[7,8] Chemically or structurally different types of O−H···O hydrogen bonds normally have different average hydrogen bond distances, but obey the same dependence of O−H on H···O.[5,8] The correlation curve O−H versus H···O can be regarded as the reaction path for proton transfer between two oxygen atoms; in this view, each individual hydrogen bond found in a crystal structure represents a snapshot of the proton-transfer process, which is "frozen" in the crystal by the particular environment.[9]

Despite the far-reaching relevance of the X−H lengthening in X−H···Y hydrogen bonds, the effect is well investigated only for X = Y = O. For all other hydrogen bond types, only relatively rough or preliminary statistical analyses have been published, if such studies are available at all. For the homonuclear N−H···N hydrogen bonds, a short statistical study based on neutron crystal structures has been published,[10] which is complemented by solid-state NMR data.[11] The structural information, however, does not cover the entire range of possible hydrogen bond distances. For the very important heteronuclear hydrogen bonds N−H···O, early neutron crystal structures have been briefly analyzed,[3,12] but (to the best knowledge of the author) the analysis has never been refined in the following. The lengthening of the N−H bond in some types of N−H···Cl$^-$ hydrogen bonds has been documented from neutron crystal structures in the general context of halide anion acceptors.[13] Finally, a slight lengthening of the C−H bond in the weak C−H···O hydrogen bonds has become apparent in an analysis of amino acid neutron crystal structures[14] and more recently for a small number of terminal alkynes.[15,16] For the many other hydrogen bond types known, the correlations of the X−H with the H···Y distances have not yet been analyzed.

The current lack of information on X−H versus H···Y distance dependencies in heteronuclear hydrogen bonds calls for a comprehensive crystal correlation study.[9] In the present work, the experimental correlation of the N−H and H···O distances in N−H···O hydrogen bonds is documented for low-temperature neutron crystal structures of the highest available quality. This yields insights going substantially beyond the previous studies, which were based on less accurate room-temperature experiments.[3,12] Furthermore, the elongation of the X−H bond in O−H···N, O−H···S, N−H···S, O−H···Cl$^-$, and N−H···Cl$^-$ hydrogen bonds is characterized from neutron crystal structures. For the latter cases, there are too few crystal structures available to allow restriction to low-temperature experiments. The experimental data will be discussed in the frame of the valence model of the hydrogen bond, and

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implications of this model will be presented for hydrogen bond types for which no neutron crystal structures have been determined as yet.

II. N−H···O and O−H···N Hydrogen Bonds: Structural Data

Accuracy of the Data. Low-temperature (<150 K) single-crystal neutron crystal structures containing N−H···O hydrogen bonds were compiled, and the geometry of each hydrogen bond was individually inspected (for quality criteria and technical procedures, see Appendix II). In crystal structures of this kind, standard uncertainties of N−H bond lengths are typically in the range 0.0005−0.002 Å, with some exceptions in the range 0.002−0.008 Å. Apart from the stochastic uncertainty, N−H bond lengths determined by diffraction experiments are biased by thermal vibration effects (shortening due to R−N−H bending vibrations and molecular librations, lengthening due to N−H stretching vibrations in an anharmonic potential). At room temperature, bias from thermal vibration effects on the N−H bond length can be larger than the lengthening due to hydrogen bonding: this is the main reason for the excessive data scatter in some earlier studies. At low temperatures, shortening and lengthening vibrational effects tend to cancel,[17,18] but some residual bias of a few thousandths of an angstrom must still be expected.

In N−H···O hydrogen bonds, the N−H bond is lengthened by several hundredths of an angstrom. This means that the effects discussed in this section are larger by at least an order of magnitude than the bias and the stochastic uncertainties occurring in the data sample.

Two-Center N−H···O Hydrogen Bonds. In the first step of the analysis, only N−H···O hydrogen bonds are considered where the O atom is the *only* acceptor within a distance of 2.7 Å from the donor H atom. "Three-center" (or "bifurcated") hydrogen bonds were excluded, in which the donor forms a contact H···X < 2.7 Å with a second O or N atom. The reason is that in three-center hydrogen bonds, the donor experiences bond lengthening by *both* H···X interactions,[19] which means a considerable complication. The data sample obtained consists of 43 two-center hydrogen bonds in 21 crystal structures. Chemically, the sample is highly heterogeneous, i.e., composed of different types of N−H donors [$-NH_3^+$, $>NH_2^+$, $-N(sp^2)H_2$, $-N(sp^3)H_2$, $>N(sp^2)-H$] and of O atom acceptors [C=O, CO_2^-, C−OH, P−OH, $P-O^-$, H_2O, H_2O_2, C−O−C]. For these 43 hydrogen bonds, the scatter plot of N−H against H···O is shown in Figure 1a. The mean H···O distance of 1.86(2) Å is associated with a mean N−H bond length of 1.028(3) Å, Table 1.

The correlation of N−H with H···O in Figure 1a is very sharp when compared with the previous publications,[3,12] which have been based on room-temperature crystal structures and where no distinction has been made between two-center and multi-center hydrogen bonds. Within the data sample, the H···O distances range from 1.6 to 2.25 Å, leading to variation of N−H by ca. 0.08 Å between the shortest and longest hydrogen bonds. The correlation is smooth with no discontinuities or sudden changes of the slope and continues falling even for long H···O distances > 2.0 Å. Relevant numerical values are given in Table 1.

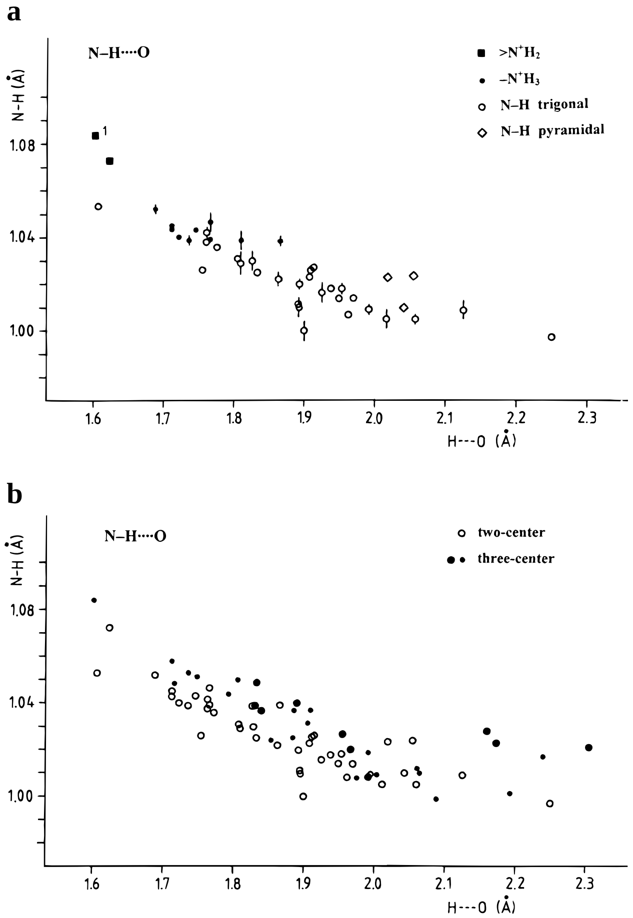


Figure 1. Lengthening of the N−H bond in 43 two-center N−H···O hydrogen bonds (low-temperature crystal structures). All chemical types of N−H donors and O acceptors are considered. (a) 43 two-center hydrogen bonds. Different donor types are labeled with different symbols. Error bars of the N−H bond length are drawn if they are larger than the central graphical symbols. A single data point of a three-center hydrogen bond has been included because it represents the shortest hydrogen bond in the sample (marked **1**, crystal structure shown in Figure 2). (b) 71 two-center and three-center O hydrogen bonds. Open spheres: two-center hydrogen bonds with no minor components < 2.7 Å. Small dots: three-center hydrogen bonds with minor components between 2.4 and 2.7 Å. Large black dots: three-center hydrogen bonds with short minor components H···O < 2.4 Å.

TABLE 1: Two-Center N−H···O Hydrogen Bonds: Mean N−H, H···O, and N···O Distances (Å) Based on Low-Temperature Neutron Crystal Structures

	n	N−H	H···O	N···O
hydrogen bond distances				
H···O < 1.7 Å	4	1.065(7)	1.63(2)	2.69(2)
1.7 < H···O < 1.8 Å	11	1.040(2)	1.748(7)	2.773(8)
1.8 < H···O < 1.9 Å	10	1.026(3)	1.85(1)	2.87(1)
1.9 < H···O < 2.0 Å	11	1.016(2)	1.939(9)	2.927(9)
2.0 < H···O < 2.1 Å	5	1.013(4)	2.038(9)	3.00(1)
2.1 < H···O	2	1.003(−)	2.19(−)	3.11(−)
all	43	1.028(3)	1.86(2)	2.87(2)
donor types				
$>NH_2^+$	2	1.078(−)	1.61(−)	2.69(−)
$-NH_3^+$	10	1.043(1)	1.76(2)	2.78(2)
$-N(sp^2)H_2$	28	1.020(2)	1.90(2)	2.90(2)
$-N(sp^3)H_2$	3	1.019(−)	2.04(−)	3.00(−)

In the correlation plot, data points for all chemical types of N−H donors appear to be scattered around a common regression function. Hydrogen bonds with the stronger N^+-H donors are on the average shorter than those formed by uncharged N−H, but they obey the same relation N−H = *f*(H···O). Therefore, covalent N^+-H bonds are *on the average* longer than N^0-H (Table 1, bottom), but if N^+-H and N^0-H form hydrogen bonds with the same H···O distance, their covalent bond length is the same (within a few 0.001 Å; see scatter and error bars of data points). This contradicts the view that N^+-H bonds are

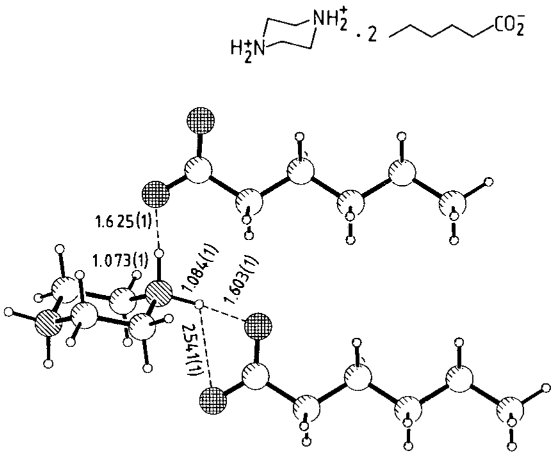
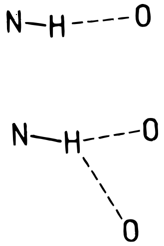


Figure 2. The shortest N−H···O hydrogen bonds in the data set: piperazinium hexaonate, structure published by Luo et al.[20] The N···O separations are 2.680(1) and 2.694(1) Å for the hydrogen bonds with H···O = 1.603 and 1.625 Å, respectively.

CHART 1



"inherently" longer than N^0−H. The general behavior of the correlation in Figure 1a exactly parallels the behavior for the homonuclear hydrogen bonds O−H···O and N−H···N, where common functional relations X−H = *f*(H···X) have also been observed for all types of O−H and N−H, respectively.[5,10]

The structural data shown in Figure 1a do not cover the whole distance range of N−H···O hydrogen bonds. The shortest hydrogen bonds in the data set are found in piperazinium hexaonate,[20] where both the donor and the acceptor are charged groups, Figure 2 [H···O = 1.603(1), N···O = 2.680(1), N−H = 1.084(1) Å]. Appreciably shorter N−H···O hydrogen bonds are known to exist in many charged systems N^+−H···O^-. Particularly short are the hydrogen bonds in phenolate salts of protonated amines, for which N···O separations < 2.55 Å are not unusual (see section VI).[21]

Three-Center N−H···O Hydrogen Bonds. It is well-known that hydrogen bonds experience numerous effects from their environment,[1] so that, in principle, interactions with all neighboring atoms must be considered as potential secondary effects on the N−H bond length. This includes interactions with all second-, third- fourth-, etc.-nearest hydrogen bond donors and acceptors, with ions, but also through-bond influences of the carrier molecules.[8] It cannot be expected that all these possible influences can be characterized in a relatively small structural data sample, but it can be pointed at least at the strongest one: that is, three-center hydrogen bonding.

In a three-center hydrogen bond, the donor X−H interacts with two acceptors simultaneously (i.e., it is bonded to the three atoms X, Y_1, and Y_2).[1] Normally, one of the two interactions is stronger than the other one and is called the "major component" of the three-center bond, and the weaker interaction is called the "minor component". It is easy to conceive that, in this type of hydrogen bond, the major component causes relatively large lengthening of X−H, and the minor component causes some slight lengthening in addition, as is sketched in Chart 1. To show this effect, the correlation plot of the N−H with the H···O distance is drawn in Figure 1b for two-center hydrogen bonds *and* major components of multicenter hydrogen bonds (open spheres, two-center bonds; small and large black dots, multicenter bonds with with minor components < 2.4 and 2.4−2.7 Å, respectively). It is obvious that, on the average, the black symbols are scattered "higher" than the open spheres and show additional lengthening by the minor components. The additional lengthening amounts to about 0.01 Å or more if the major component is only relatively weak (right end of the plot), whereas it is only marginal if the major component is strong (left end of the plot). These observations parallel findings on O−H···O hydrogen bonds.

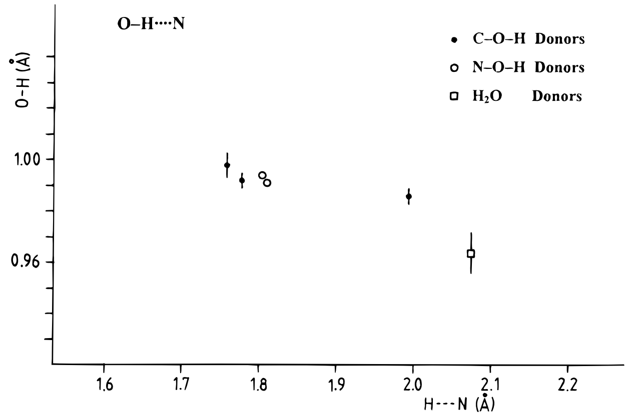


Figure 3. Lengthening of the O−H bond in 6 O−H···N hydrogen bonds (mixed room and low-temperature data). Different donor types are marked with different symbols.

For minor components in the distance range 2.7−3.0 Å, additional lengthening of N−H must also be anticipated, but is not apparent with the given scatter and quantity of the data (not shown in Figure 1b). Because of the chemical heterogeneity and the small number of the analyzed crystal structures, it was not attempted to quantify the effect further.

O−H···N Hydrogen Bonds. Only very few neutron crystal structures with O−H···N hydrogen bonds have been published. The correlation of the O−H and H···N distances is shown in Figure 3 for six two-center hydrogen bonds [mean distances: O−H = 0.987(5), H···N = 1.87(5), and O···N = 2.84(5) Å]. This very small data set cannot serve much more than showing that the lengthening effect of H···N on O−H as such does exist. From X-ray diffraction experiments, it is known that O−H···N hydrogen bonds can be much shorter than those in the neutron diffraction data set, which is limited to H···N > 1.76 Å (see section VI).

N−H···O and O−H···N Hydrogen Bonds Treated in Common. If O−H and H···O separations are taken as quantities of the same kind, they may be drawn on a common axis.[9] Analogously, N−H and H···N separations can be drawn on a common axis. In consequence the distance correlations of N−H···O and O−H···N hydrogen bonds can be presented in a common diagram, Figure 4. The obtained correlation parallels related pictures for homonuclear hydrogen bonds.[5,9] It is very unfortunate that no neutron diffraction data for short N−H···O and O−H···N hydrogen bonds are available, although such interactions are well-known to exist. Therefore, it would be very desirable to peform relevant neutron diffraction experiments on suitable compounds. In principle, one must expect that the data points for N−H···O and O−H···N hydrogen bonds meet without discontinuity at a midpoint corresponding to the

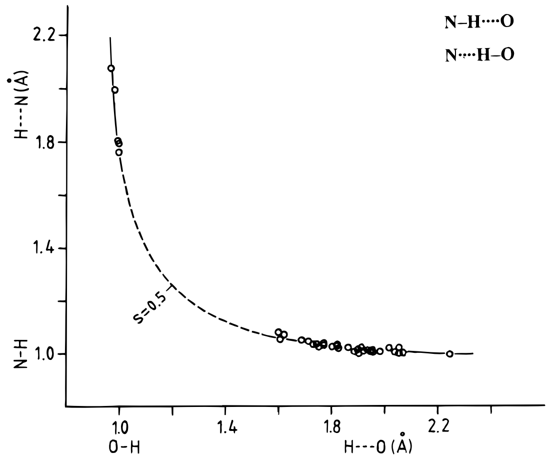


Figure 4. Lengthening of the N−H bond in N−H···O hydrogen bonds (data as in Figure 1a) and of the O−H bond in O−H···N hydrogen bonds (data as in Figure 3) drawn in a common diagram. The theoretical line is a fit against the valence model of the hydrogen bond, eq 6 with parameters given in Table 4.

situation where the proton is equally shared between N and O. The theoretical curve shown in Figure 4 is derived from the valence model of the hydrogen bond (section V).

III. O−H···S and N−H···S Hydrogen Bonds: Structural Data

Accuracy of the Data. The number of neutron crystal structures containing O−H···S and N−H···S hydrogen bonds is much smaller than for N−H···O hydrogen bonds. Therefore, restriction to low-temperature crystal structures is not feasible, and room-temperature structures of reasonable quality have to be included (typical X−H standard uncertainties: 0.005−0.010 Å). Hydrogen bonds with standard uncertainties of X−H larger than 0.01 Å were generally not tolerated, with the exception of the chemically very important example shown in Figure 6b.

O−H···S Hydrogen Bonds. The geometry of O−H···S hydrogen bonds has only recently been analyzed comprehensively by Allen and co-workers.[22] Since the covalent O−H bond has been out of the focus of that study, the correlation of the O−H and H···S distances is shown in Figure 5a; numerical values are given in Table 2 ($n = 18$, mixed room-temperature and low-temperature crystal structures).

In Figure 5a, two distinct kinds of data points can be recognized. Those clustered in the H···S range 2.2−2.5 Å represent “normal” intermolecular O−H···S hydrogen bonds.[22] In this region, a correlation of O−H and H···S can be clearly seen; for the shortest hydrogen bonds, the O−H bond is elongated by ca. 0.03 Å compared to the longest hydrogen bonds. Clearly separate from this cluster, there are two data points with much shorter H···S distances (slightly above 1.9 Å) and correspondingly longer covalent O−H bonds. The two points represent the two compounds MCPROP01[23] and BABCOW01,[24] which are shown in Figure 6a,b, respectively. These O−H···S hydrogen bonds are intramolecular and of a type that allows charge flow through suitably polarizeable π-bond systems (“resonance assisted hydrogen bonding”[25]). This matter was only recently discussed in a short communication:[26] for the example of the monothio-β-diketones in the enol tautomeric form (Chart 2) it could be shown from X-ray crystal structures that, within the cyclic hydrogen bond arrangement, the formal single bonds d_1 and d_3 are systematically shortened and the formal double bonds d_2 and d_4 are systematically lengthened. The arrangement as a whole forms a resonant cycle that facilitates the formation of unusually strong O−H···S hydrogen bonds. Note that in the exemplary case shown in Figure 6a, the formal C=C and C−C bonds have almost equal lengths; that is, they exhibit very pronounced π-bond delocalization. The “bond orders” (“valences”) of H···S in resonance-assisted hydrogen bonds are up to 0.2, whereas the bond order of O−H is reduced to almost 0.8; see section V.

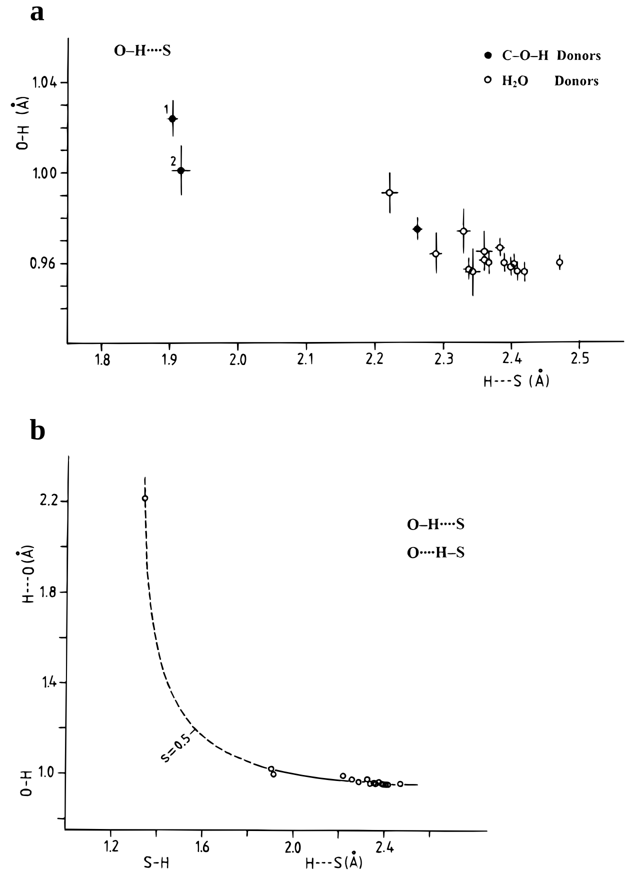


Figure 5. (a) Lengthening of the O−H bond in 18 O−H···S hydrogen bonds (mixed room and low-temperature crystal structures). Different donor types are marked with different symbols. The two data points at very short H···S distances correspond to compounds MCPROP01, **1**, and BABCOW01, **2** (crystal structures shown in Figure 6). (b) Lengthening of the O−H bond in O−H···S hydrogen bonds and of the S−H bond in S−H···O hydrogen bonds (single data point from ref 27) drawn in a common diagram. The theoretical line is a fit against the valence model of the hydrogen bond, eq 6 with parameters given in Table 4.

O−H···S and S−H···O Hydrogen Bonds Treated in Common. Similar to N/O−H···O/N hydrogen bonds (Figure 4), the bond distance correlations of O−H···S and S−H···O hydrogen bonds can be drawn in a common diagram. Since only a single neutron diffraction example of an S−H···O hydrogen bond has been published [*N*-acetyl-L-cysteine,[27] H···O = 2.216(2), S−H = 1.338(2) Å], only a sparsely populated plot is obtained, Figure 5b. Unlike for N−H···O and O−H···N hydrogen bonds, there is no X-ray diffraction evidence for very short O−H···S and S−H···O hydrogen bonds. Therefore, the theoretical line based on the valence model (section V) is to a large degree hypothetical.

N−H···S Hydrogen Bonds. Only very few neutron crystal structures containing N−H···S hydrogen bonds have been published, Figure 7 ($n = 8$, mixed room-temperature and low-temperature crystal structures). The H···S distances range from

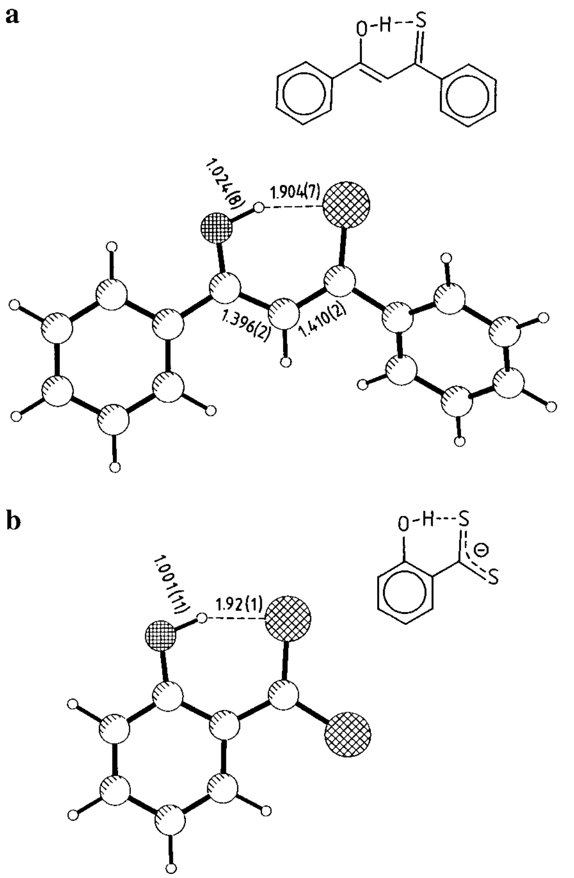
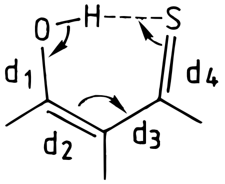


Figure 6. The two shortest O−H···S hydrogen bonds in the data sample. Both represent resonance-assisted O−H···S hydrogen bonds.[26] (a) 1-Mercapto-1,3-diphenylprop-1-ene-3-thione, structure published by Power et al. (O···S = 2.865(5) Å).[23] (b) The anion in 2,6-dimethylpiperidinium dithiosalicylate, structure published by van Roey and Kerr (O···S = 2.860 Å).[24]

TABLE 2: O−H···S Hydrogen Bonds: Mean O−H, H···S, and O···S Distances (Å), Based on Room- and Low-Temperature Neutron Crystal Structures

	n	O−H	H···S	O···S
1.9 < H···S < 2.0 Å	2	1.01(−)	1.91(−)	2.86(3)
2.2 < H···S < 2.3 Å	3	0.98(−)	2.26(−)	3.22(−)
2.3 < H···S < 2.4 Å	9	0.962(2)	2.363(8)	3.310(10)
2.4 < H···S < 2.5 Å	4	0.958(1)	2.425(16)	3.358(8)
all	18	0.964(4)	2.369(4)	3.26(4)

CHART 2



2.27 to 2.75 Å, which is the normal range as described in a much larger set of X-ray crystal structures.[22] There is no X-ray evidence for the occurrence of substantially shorter N−H···S hydrogen bonds (although they might occur, in principle). A correlation of N−H and H···S distances is obvious from Figure 7, but detailed analysis does not seem to be justified [mean distances: N−H = 1.020(4), H···S = 2.48(6), N···S = 3.44(4) Å].

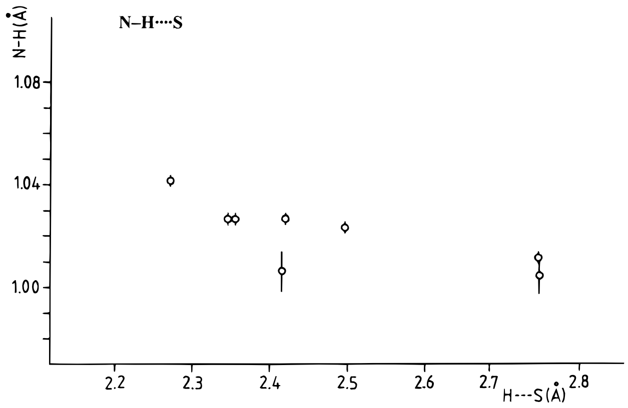


Figure 7. Lengthening of the N−H bond in 8 N−H···S hydrogen bonds (mixed room- and low-temperature crystal structures).

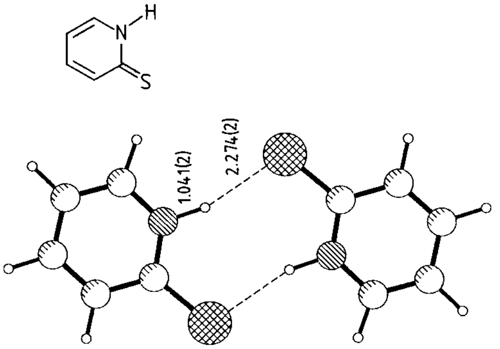


Figure 8. The shortest N−H···S hydrogen bond in the data sample: 2-thiopyridone, structure published by Ohms et al. (N···S = 3.287(2) Å).[28]

It is of interest to look at the shortest N−H···S hydrogen bond in the sample, which is found in 2-thiopyridone,[28] Figure 8. In this compound, molecular dimers are formed that are linked by a cyclic motif of mutual N−H···S═C hydrogen bonds. This motif is the structural analogue to the well-known N−H···O═C amide dimer, which is a classical example for cooperative hydrogen bonding.[1] Significant cooperativity is suggested also for the hydrogen bonds of 2-thiopyridone and possibly is the reason for the short hydrogen bond distance.

S−H···N Hydrogen Bonds. S−H···N hydrogen bonds occur in crystals only very rarely, and not a single relevant neutron crystal structure has been published as yet. An interesting X-ray crystal structure can be found in ref 29.

IV. Hydrogen Bonds to Halide Ions: Structural Data

Accuracy of the Data. As for X−H···S hydrogen bonds, the number of neutron crystal structures containing X−H···Hal$^-$ hydrogen bonds is only small. Therefore, room-temperature crystal structures have to be included in the analysis. Hydrogen bonds with standard uncertainties > 0.01 Å of the X−H bond length were excluded with the exception of the unusual crystal structure shown in Figure 10.

No example of an N−H···F$^-$, O−H···F$^-$, or O−H···I$^-$ hydrogen bond is contained in the neutron diffraction subset of the CSD.

N−H···Cl$^-$ Hydrogen Bonds. The lengthening of the N−H bond in N−H···Cl$^-$ hydrogen bonds is shown in Figure 9a; numerical values are given in Table 3. As for the other heteronuclear hydrogen bonds, it is observed that all donor types obey the same dependence of N−H on H···Cl$^-$. This can be best seen in the interval 2.2 < H···Cl$^-$ < 2.3 Å. The shortest hydrogen bonds in the sample are formed in chloroacetiminium chloride with the relatively unusual donor ═$\mathrm{NH_2^+}$, Figure 10.[30] As a byproduct of this study, bending of donor C−N−H angles

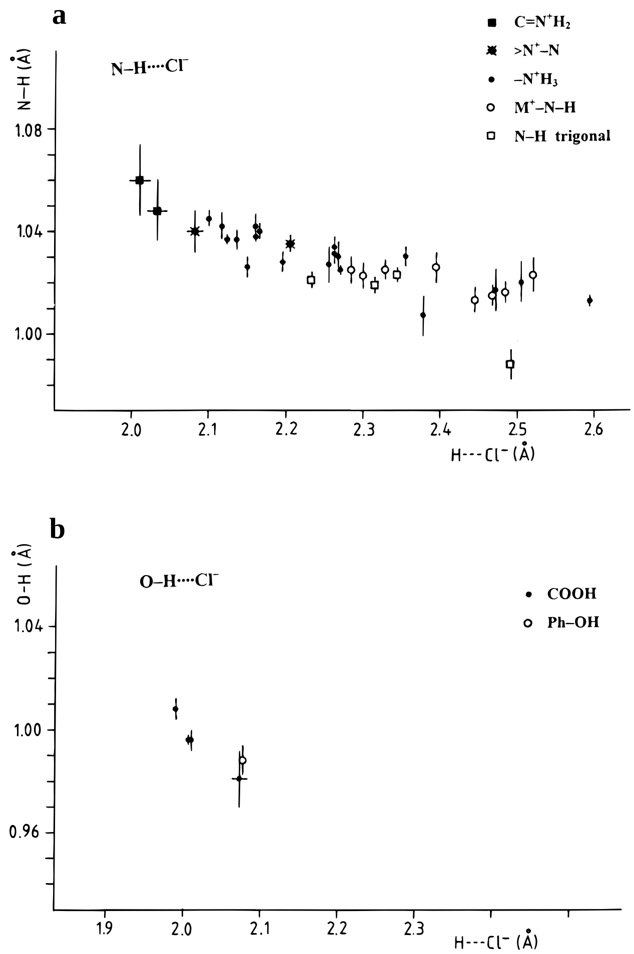


Figure 9. (a) Lengthening of the N–H bond in 39 N–H···Cl⁻ hydrogen bonds (mixed room- and low-temperature crystal structures). (b) Lengthening of the O–H bond in 5 O–H···Cl⁻ hydrogen bonds (mixed room- and low-temperature crystal structures).

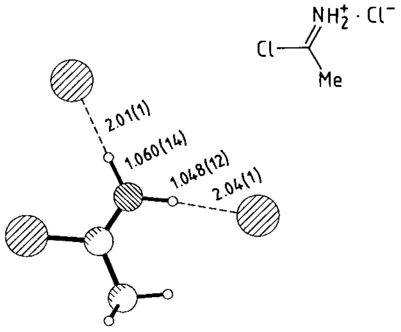


Figure 10. The shortest N–H···Cl⁻ hydrogen bonds in the data sample: chloroacetiminium chloride, structure published by Williams et al.[30] The N···Cl⁻ distances are 3.072 and 3.081 Å for the hydrogen bonds with H···Cl⁻ = 2.01 and 2.04 Å, respectively.

is discussed in Appendix I for ammonium groups engaged in N–H···Cl⁻ hydrogen bonds.

O–H···Cl⁻ Hydrogen Bonds. Neutron diffraction data of O–H···Cl⁻ hydrogen bonds are dominated by water donors. For these, covalent geometries are so heavily affected by thermal vibration artifacts[31] that they were excluded from the present study. The remaining set consists of only five hydrogen bonds, Figure 9b [mean distances: O–H = 0.994(5), H···Cl⁻ = 2.03(2), O···Cl⁻ = 3.02(1) Å]. It is known from X-ray diffraction studies that much shorter O–H···Cl⁻ hydrogen bonds exist than those shown in Figure 9b (see section VI).

TABLE 3: N–H···Cl⁻ Hydrogen Bonds: Mean N–H, H···Cl⁻, and N···Cl⁻ Distances (Å) Based on Room- and Low-Temperature Neutron Crystal Structures

	n	N–H	H···Cl⁻	N···Cl⁻
hydrogen bond distances				
2.0 < H···Cl⁻ < 2.1 Å	3	1.049(–)	2.04(–)	3.09(–)
2.1 < H··Cl⁻ < 2.2 Å	10	1.038(2)	2.147(9)	3.172(9)
2.2 < H···Cl⁻ < 2.3 Å	10	1.030(2)	2.261(8)	3.22(1)
2.3 < H···Cl⁻ < 2.4 Å	7	1.022(3)	2.35(1)	3.30(2)
2.4 < H···Cl⁻ < 2.6 Å	9	1.014(4)	2.50(1)	3.29(2)
all	39	1.028(2)	2.29(2)	3.25(2)
donor types				
$=NH_2^+$	2	1.054(–)	2.02(–)	3.08(–)
$>NH^+$	2	1.037(–)	2.14(–)	3.15(–)
$-NH_3^+$	21	1.031(2)	2.26(3)	3.22(2)
peptide >NH	1	1.033(–)	2.30(–)	3.30(–)
$M^+-N(sp^3)H_2$	9	1.021(2)	2.41(3)	3.37(3)
$-N(sp^2)H_2$	4	1.013(8)	2.35(5)	3.29(5)

Hydrogen Bonds to Br⁻ and I⁻ Ions. There is only a single neutron crystal structure archived in the CSD which contains an N–H···Br⁻ hydrogen bond: iminodiacetic acid hydrobromide [$>N^+H_2$ donor, N–H = 1.026(4), H···Br⁻ = 2.285(4), N···Br⁻ = 3.288(1) Å].[32] This structure also contains the only example in the CSD of an O–H···Br⁻ hydrogen bond [COOH donor, O–H = 0.978(4), H···Br⁻ = 2.264(4), O···Br⁻ = 3.211(2) Å].

Also for N–H···I⁻ hydrogen bonding, there is only one neutron crystal structure found in the CSD: phase II of anilinium iodide [donor NH_3^+, $n = 3$, mean distances: N–H = 1.030(5), H···I⁻ = 2.53(2), N···I⁻ = 3.521(2) Å].[33]

V. Valence Model of the Hydrogen Bond

General. The experimental data shown here (and in studies on homonuclear hydrogen bonds)[5,8,10] indicate that in X–H···Y hydrogen bonds the X–H bond length is determined mainly by the H···Y distance (or, in multicenter hydrogen bonds, by all H···Y_i distances). This behavior is predicted by a very simple model based on a stringent relation of bond distances and "bond orders" and an additional bond order conservation rule. Therefore, it is worthwhile to look at this model more closely.

In the purely empirical bond valence (bond order) model,[34] bonds between atom pairs are assigned formal "valences" or "bond orders", *s*, which are functions of *only* the bond distances, *r*, and the atom types involved. The rule of bond order conservation requires that at any atom type the valence sum is constant in all bonding situations. Different expressions $s = f(r)$ have been proposed, but most commonly used is Pauling's exponential model function[35]

$$s = \exp[(r_0 - r)/b] \tag{1}$$

where r_0 is the length of a single bond with $s = 1$, and b is a constant which has different values for different atom pairs. Typically, b is around 0.37 Å.

In X–H···Y hydrogen bonds, the H atom is bonded to the two atoms X and Y with bond valences s_{XH} and $s_{H\cdots Y}$. In multicenter hydrogen bonds, the donor H atom is bonded to more than one acceptor atom, and each of these bonds has its own valence. To satisfy the rule of bond order conservation at H,

$$\sum s = 1 \tag{2}$$

one has to sum over all atoms bonding with the hydrogen atom. Because eq 1 falls fast with increasing distance [for H···O =

TABLE 4: Numerical Values of r_0 and b (Å) in Eq 1 Obtained by Fit against Neutron Diffraction Data

			O−H		N−H		S−H		Cl−H		
H-bond type	n_{data}	temp[a]	$r_{0,\mathrm{OH}}$	b_{OH}	$r_{0,\mathrm{NH}}$	b_{NH}	$r_{0,\mathrm{SH}}$	b_{SH}	$r_{0,\mathrm{ClH}}$	b_{ClH}	ref
homonuclear hydrogen bonds											
O−H···O, all types	80	LT	0.928	0.393							5
O−H···O, all types			0.925	0.397[b]							8
$\mathrm{O_{Water}}$−H···O	93	all	0.911	0.403							6
$\mathrm{O_{Hydroxy}}$−H···O	69	LT	0.934	0.388							this work
N−H···N	32	all			0.996	0.381					10
heteronuclear hydrogen bonds											
N−H···O, O−H···N	49	LT[c]	0.942	0.371	0.992	0.385					this work
O−H···S, S−H···O	19	all	0.944	0.369			1.33[d]	0.342			this work
N−H···S	8	all			1.00	0.37	1.33[d]	0.35			this work
N−H···$\mathrm{Cl^-}$	39	all			0.997	0.378			1.27[e]	0.388	this work

[a] Temperature. LT: low temperature < 150 K. [b] The authors used a different expression of eq 1. Their values were transformed to the form used in this work. [c] LT for the 43 N−H···O hydrogen bonds, mixed LT and RT data for the 6 O−H···N hydrogen bonds. [d] Assumption based on the only available neutron value for r_{SH} in a hydrogen bond, 1.338(2) Å.[27] [e] Gas-phase value.[35]

TABLE 5: Valences s and Theoretical X−H Bond Lengths (Å) in N−H···O and O−H···N Hydrogen Bonds [Eq 6, Table 4][a]

	N−H···O		O−H···N	
H···Y	$s_{\mathrm{H\cdots O}}$	N−H	$s_{\mathrm{H\cdots N}}$	O−H
1.20	0.50	1.258		
1.30	0.38	1.177	0.45	1.163
1.40	0.29	1.124	0.35	1.100
1.50	0.22	1.089	0.27	1.057
1.60	0.170	1.064	0.21	1.028
1.70	0.130	1.045	0.159	1.006
1.80	0.099	1.032	0.123	0.991
2.00	0.058	1.015	0.073	0.970
2.20	0.034		0.043	
2.50	0.015		0.020	
3.00	0.004		0.005	

[a] Because of the uncertainty of r_0, the calculation of X−H bond lengths in very long hydrogen bonds is very uncertain, and only values for s are given.

3.0 Å, $s \approx 0.004$, Table 5], and because the validity of (eq 1) at long distances is unproven, the summation is usually stopped at relatively short distances. For a two-center hydrogen bond, eq 2 simply becomes

$$s_{\mathrm{XH}} + s_{\mathrm{H\cdots Y}} = 1 \tag{3}$$

The simplest hydrogen bonds are homonuclear two-center bonds, X−H···X. For these, eq 3 leads to a very simple expression for the dependence of the X−H on the H···X bond distance:

$$r_{\mathrm{XH}} = r_0 - b \ln\{1 - \exp[(r_0 - r_{\mathrm{H\cdots X}})/b]\} \tag{4}$$

In the shortest possible homonuclear hydrogen bond, the hydrogen atom is equally bonded to both atoms X with $s = 0.5$ and $r = r_0 - b \ln {}^1/_2$. Assuming linearity, this determines the shortest possible X···X approach in a hydrogen bond:

$$(\mathrm{X\cdots X})_{\min} = 2(r_0 - b \ln {}^1/_2) \tag{5}$$

The parameters r_0 and b are in practice obtained by fitting eq 2 [or expressions derived from it] against experimental data of the kind shown in Figure 4. It turns out, unfortunately, that the results are to some degree sample-dependent. Recently published values listed in Table 4. The slight discrepancies are of relevance mainly for long hydrogen bonds; for short and very short hydrogen bonds, eq 4 describes the experimental data satisfactorily with all published values of r_0 and b.

For heteronuclear hydrogen bonds, X−H···Y, the expressions 1 describing the relevant valences contain a total of four adjustable parameters: $s_{\mathrm{XH}} = \exp[(r_{0,\mathrm{XH}} - r_{\mathrm{XH}})/b_{\mathrm{XH}}]$ and $s_{\mathrm{H\cdots Y}} = \exp[(r_{\mathrm{o,YH}} - r_{\mathrm{H\cdots Y}})/b_{\mathrm{YH}}]$. The dependence of the X−H on the H···Y bond distance then becomes

$$r_{\mathrm{XH}} = r_{0,\mathrm{XH}} - b_{\mathrm{XH}} \ln\{1 - \exp[(r_{0,\mathrm{YH}} - r_{\mathrm{H\cdots Y}})/b_{\mathrm{YH}}]\} \tag{6}$$

In principle, one could in eq 6 use parameters of r_0 and b obtained from homonuclear hydrogen bonds, but it is more advisable to determine these parameters by fitting eq 2 or 6 against structural data of X−H···Y and Y−H···X hydrogen bonds.

If only the elongation of X−H compared to an undisturbed bond is of interest, i.e., $\Delta r_{\mathrm{XH}} = r_{\mathrm{XH}} - r_{0,\mathrm{XH}}$, and not not the absolute value, one can use

$$\Delta r_{\mathrm{XH}} = - b_{\mathrm{XH}} \ln\{1 - \exp[(r_{0,\mathrm{YH}} - r_{\mathrm{H\cdots Y}})/b_{\mathrm{YH}}]\} \tag{7}$$

which does not require knowledge of $r_{0,\mathrm{XH}}$.

Although one should not expect that the simple exponential function 1 can describe experimental results over the whole range of $s = 0$ to $s = 1$ (deviations have actually been reported),[36] eqs 4−7 are normally well suited for semiquantitative calculations. In many instances, they even describe low-temperature neutron diffraction data within the experimental uncertainties. It should also be noted that the complete independence of bond lengths from bond angles, which contradicts chemical intuition, is not in perfect agreement with structural results reported for inorganic crystal structures, pointing at limitations of the model.[36]

N−H···O and O−H···N Hydrogen Bonds. According to the valence model of the hydrogen bond, the experimental data in Figure 4 should follow eq 6. If the published values of r_0 and b for O−H and N−H are used,[5,10] however, the obtained theoretical curve falls slightly but noticeably too steep at long H···Y distances. This is not really surprising because some sample-dependence of the adjustable parameters is well-known. Therefore, a new least-squares fit of eq 3 against the data in Figure 4 was performed [quantity minimized: $\sum(1 - \sum s)^2$]. The parameters obtained are given in Table 4; the corresponding curve is shown in Figure 4. The values r_0 and b for N−H differ only marginally from those obtained from homonuclear N−H···N hydrogen bonds.[10] More significant are the deviations of the values for O−H bonds from those obtained from O−H···O hydrogen bonds.[5,6,8] In Table 5, the theoretical X−H bond lengths are given for some H···Y bond distances.

The hypothetical hydrogen bond where the proton is equally shared between the two heteronuclei, N···H···O, is characterized by $s_{N\cdots H} = s_{H\cdots O} = 0.5$. The bond distances predicted by eq 6 are N···H = 1.259 and H···O = 1.199 Å; that is, the proton is closer to the O than to the N atom. Assuming linearity, the N···O distance is 2.458 Å; this should be a good approximation for the shortest observable N···O separation in a hydrogen bond. The geometrically centered hydrogen bond is calculated to have N···H = H···O distances of 1.230 Å and N···O = 2.460 Å. Since for this geometry $s_{N\cdots H} = 0.539$ and $s_{H\cdots O} = 0.460$, the hydrogen bond is of the type N−H···O.

The central region of Figure 4 is not populated with experimental data, although short N/O−H···O/N hydrogen bonds are known to exist. Good experience with O−H···O hydrogen bonds lets one assume that the theoretical curve is valid also in this region (within about 0.02 Å), but definite conclusions cannot be drawn unless relevant neutron crystal structures are determined.

O−H···S Hydrogen Bonds. The number of neutron crystal structures containing O−H···S and S−H···O hydrogen bonds is so small that a fit of eq 6 to the experimental data can be performed only with reservations. In particular, it is not feasible to vary $r_{0,SH}$ in a fitting procedure, and a constant value must be used. Assuming that the S−H bond in the only available neutron crystal structure, 1.338(2) Å,[27] is only slightly elongated compared to $r_{0,SH}$, a tentative value of $r_{0,SH} = 1.33$ Å is selected. The least-squares fit of eq 6 against the data shown in Figure 5b leads to the values given in Table 4. Using the obtained parameters, it is calculated that in O−H···S hydrogen bonds of the normal distance range $2.2 <$ H···S < 2.5 Å the valences $s_{H\cdots S}$ vary between about 0.08 and 0.03, whereas in resonance-assisted O−H···S hydrogen bonds, $s_{H\cdots S}$ can be close to 0.2.

Even though there is no experimental evidence for the existence of stable very short O···H···S hydrogen bonds, the geometry of such a hypothetical interaction can be predicted. If a proton is equally shared by an O and an S atom, i.e., $s_{O\cdots H} = s_{H\cdots S} = 0.5$, the bond distances are O···H = 1.199 Å and H···S = 1.567 Å. For a linear hydrogen bond, this means $(O\cdots S)_{min} = 2.77$ Å.

N−H···S Hydrogen Bonds. The number of neutron-determined N−H···S hydrogen bonds (Figure 7) obviously is too small for reliably determining *b* and r_0. Only in order to check consistency, a corresponding fit of eq 6 against the eight experimental data was performed. The obtained values of $r_{0,NH}$, b_{NH}, and b_{SH} are consistent with those obtained from N/O−H···O/N and O/S−H···S/O hydrogen bonds, Table 4.

N−H···Cl⁻ Hydrogen Bonds. In a fit of eq 6 against the data shown in Figure 9a, the gas-phase value of $r_{0,ClH}$, 1.27 Å,[37] has to be used. This yields the numerical values given in Table 4 and the theoretical curve shown in Figure 11. The obtained parameters can in principle be used to calculate Cl−H distances in bichloride ions, Cl−H···Cl⁻. In a hypothetical centrosymmetric bichloride ion, this leads to $r_{ClH} = 1.54$ and $(Cl\cdots Cl)^{-}_{min} = 3.08$ Å. Real bichloride ions are noncentrosymmetric with somewhat longer Cl···Cl separations.[13]

O−H···O Hydrogen Bonds. It is unsatisfactory that the numerical values for r_0 and *b* in eq 1 are sample-dependent, Table 4. To see if the discrepancies are, possibly, due to different fitting procedures, low-temperature neutron crystal structures containing O−H···O hydrogen bonds were again retrieved from the CSD. If all kinds of donors and acceptors are included, a fit of eq 4 against the data reproduces the published values[5] of r_0 and *b* within 0.002 Å. If water donors are excluded from the data set (because their geometry is most heavily affected by thermal vibration artifacts),[31] significantly different values are obtained: $r_{0,OH} = 0.934$ and $b_{OH} = 0.388$ Å, Table 4. This sample dependence should be considered when eq 4 or (6) is used to calculate O−H distances in practice.

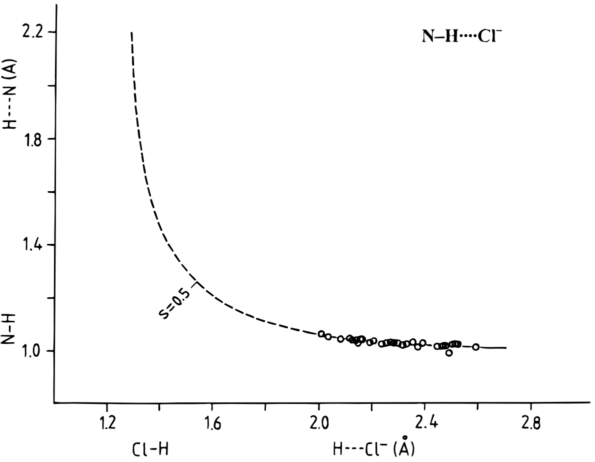


Figure 11. Lengthening of the N−H bond in N−H···Cl⁻ hydrogen bonds (data as in Figure 9a). The theoretical line is a fit against the valence model of the hydrogen bond, eq 6, with parameters given in Table 4.

TABLE 6: Approximate Valences $s_{H\cdots O}$ and Bond Lengthening $\Delta r_{CH} = r_{CH} - r_{0,CH}$ in C−H···O Hydrogen Bonds (Eq 7, $b_{CH} \approx 0.37$, $b_{OH} = 0.942$, $r_{0,OH} = 0.371$ Å)

H···O (Å)	$s_{H\cdots O}$	Δr_{CH} (Å)
1.9	0.076	0.029
2.0	0.058	0.022
2.1	0.044	0.017
2.2	0.034	0.013
2.4	0.020	0.007
2.6	0.011	0.004

C−H···O Hydrogen Bonds. For the long C−H···O hydrogen bonds,[38,39] C−H elongations are small and the validity of eq 1 is probably only very approximate. Therefore, it is advisable not to use eq 6 to calculate absolute values of r_{CH}, but only to estimate elongations $\Delta r_{CH} = r_{CH} - r_{0,CH}$ from eq 7. Assuming that $b_{CH} \approx 0.37$ Å,[34] eq 7, yields the values of $s_{H\cdots O}$ and Δr_{CH} as listed in Table 6. These values are in good agreement with experimental data on Cα−H···O contacts in amino acids (H···O in the range 2.2−2.8 Å).[14] The shortest known C−H···O hydrogen bonds have H···O separations around and slightly below 2.0 Å,[39,40] and C−H bond lengthening Δr_{CH} around 0.025 Å is expected.

VI. Calculating X−H Distances in Some Short Heteronuclear Hydrogen Bonds

There are entire classes of short heteronuclear hydrogen bonds, for which no neutron diffraction studies have been performed as yet. It is tempting to use eq 6 and the data in Table 4 to calculate theoretical geometries for some important exampes with published X-ray crystal structures. This is performed by shifting the H atom in the X-ray crystal structure along the X−H vector to a distance at which eq 6 is fulfilled.

N−H···O Hydrogen Bonds. The shortest N−H···O hydrogen bonds in Figure 1 have H···O distances slightly longer than 1.6 Å. In X-ray crystal structures, significantly shorter N−H···O hydrogen bonds are frequently observed, mostly with N^+−H donors. An interesting example is 4,4′-bipyridinium squarate,[41] Figure 12a. Using eq 6, theoretical H···O and N−H distances of 1.522 and 1.082 Å, respectively, are obtained (experimental N···O = 2.593 Å). Of greater biological importance are related

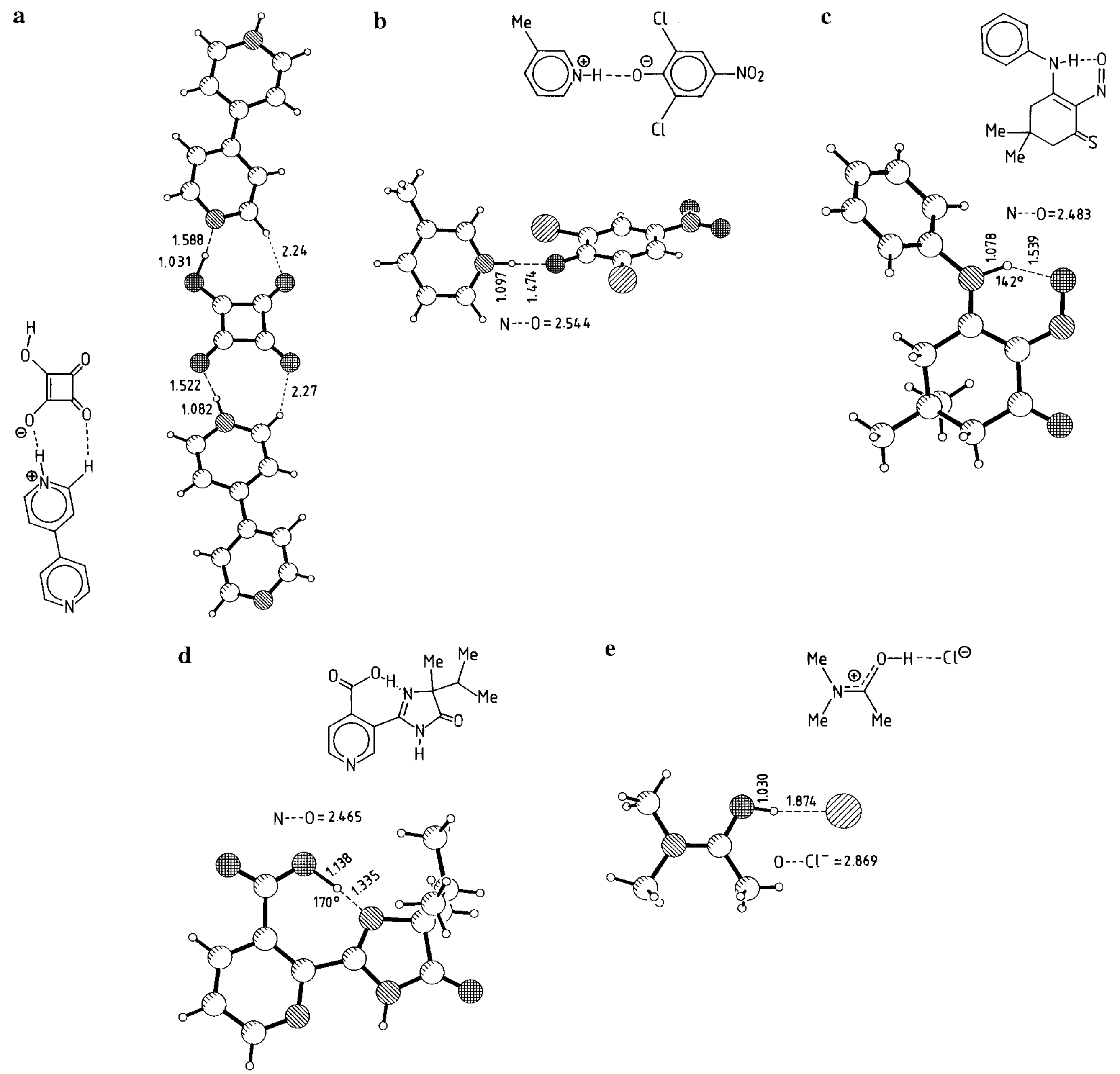


Figure 12. Examples for X-ray crystal structures exhibiting short heteronuclear hydrogen bonds. The X−H and H···Y distances given are theoretical values based on eq 6. (a) 4,4′-Bipyridinium squarate at 183 K, structure published by Reetz et al.;[41] note the short C−H···O contacts, which are indicative of weak hydrogen bonds.[39] (b) 3-Methylpyridinium 2,6-dichloro-4-nitrophenolate, structure published by Majerz et al.[42] (c) Compound BUWFUU, structure published by Gilli et al.[43] (d) Compound JAZCOC01, structure published by Camilleri et al.[44] (e) *N,N*-dimethylacetamide hydrochloride, structure published by Benedetti et al.[45]

N^+−H···O^- hydrogen bonds involving protonated bases as occurring in polypeptides and nucleotides. Particularly short N^+−H···O^- hydrogen bonds are observed with phenolate acceptors,[21] such as in 3-methylpyridinium 2,6-dichloro-4-nitrophenolate,[42] Figure 12b. In this compound, the experimental N^+···O^- distance is 2.544(4) Å, and the theoretical H···O and N−H distances are 1.474 and 1.097 Å, respectively. A very short *intra*molecular N−H···O hydrogen bond has been found in the uncharged compound 5,5-dimethyl-2-nitroso-3-phenylamino-2-cyclohexen-1-one,[43] Figure 12c, with an experimental N···O distance of 2.483(3) Å. The theoretical H···O and N−H distances are 1.539 and 1.078 Å, respectively.

O−H···N Hydrogen Bonds. Short O−H···N hydrogen bonds often occur in compounds where the pK_a values of O−H and N^+−H are very similar. Then, proton transfer is easy, and the systems can be found in both states O−H···N and O^-···H−N^+. A good example is the binary system pyridine−pentachlorophenole;[21] depending on substituents, these molecules can cocrystallize as uncharged species linked by short hydrogen bonds O−H···N or as salts linked by hydrogen bonds O^-···H−N^+. In the example of 4,4′-bipyridinium squarate, Figure 12a, there are even both kinds of short hydrogen bonds in one crystal structure.[41] For the O−H···N hydrogen bond in this compound, the theoretical H···N and O−H distances are 1.588 and 1.031 Å, respectively (O···N = 2.615 Å).

The far shortest of the published O−H···N hydrogen bonds is intramolecular[44] and occurs in a situation that is clearly suggestive of resonance-assisted hydrogen bonding, Figure 12d. The theoretical H···N and O−H distances are 1.335 and 1.138 Å, respectively. Note that the O···N separation of 2.465 Å comes close to the theoretical shortest possible value of 2.458 Å.

O−H···Cl⁻ Hydrogen Bonds. The shortest $O-H\cdots Cl^-$ hydrogen bonds known are formed by charged donors such as N^+-O-H, P^+-O-H, As^+-O-H or $C{=}O^+-H$.[31] For none of these cases has a neutron diffraction study been performed as yet. As a typical example, the X-ray crystal structure of *N,N*-dimethylacetamide hydrochloride is shown in Figure 12e ($O\cdots Cl^- = 2.869$ Å).[45] The theoretical $H\cdots Cl^-$ and $O-H$ distances are 1.874 and 1.030 Å, respectively (for $r_{0,OH} = 0.942$, $b_{OH} = 0.371$ Å).

VII. Summary and Conclusions

Structural Data. The elongation of the $X-H$ bond in heteronuclear $X-H\cdots Y$ hydrogen bonds is characterized for the first time for sulfur acceptors and the cases $O-H\cdots N$ and $O-H\cdots Cl^-$. For $N-H\cdots O$ hydrogen bonds, restriction to crystal structures determined at low temperatures improves data quality considerably compared to earlier studies. Published reports on discontinuous behavior at certain "critical" hydrogen bond distances are clearly disfavored.

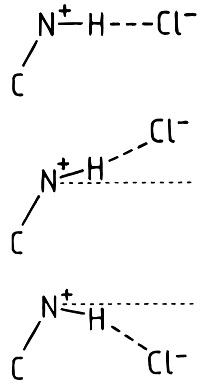
For $N-H\cdots O$ hydrogen bonds, it is observed that for all types of $N-H$ donors the dependence of $N-H$ on the $H\cdots O$ distance follows the same relation $r_{NH} = f(r_{H\cdots O})$. Stronger donors form shorter hydrogen bonds, on the average, than weaker donors, but the dependence of $N-H$ on $H\cdots O$ is the same. The existence of slightly different relations $r_{NH} = f(r_{H\cdots O})$ for different $N-H$ donor types can never be definitely excluded (and would not be chemically unreasonable), but in view of the scatter of data points and the error bars in Figure 1a, it seems that the maximal offset between such different relations is <0.01 Å. Analogous observations are made for $O-H\cdots S$ and $N-H\cdots Cl^-$ hydrogen bonds. This is in line with observations on the homonuclear hydrogen bonds $O-H\cdots O$ and $N-H\cdots N$, where common relations $r_{XH} = f(r_{H\cdots X})$ have also been found for all types of $O-H$ and $N-H$ donors, respectively.[5,8,10]

Of the $X-H\cdots Y$ hydrogen bond types studied, lengthening of the $X-H$ bond is definitely confirmed for *all* pairs X, Y. This includes hydrogen bonds to sulfur acceptors, which are normally considered as weak. In a previous study, $X-H$ bond lengthening has even been found for short $C-H\cdots O$ contacts.[14] This supports unitary views of the hydrogen bond phenomenon and disproves several reports that for particular "weak" donor/acceptor combinations hydrogen bonds are formed without elongation of the $X-H$ bond. Typically, these earlier findings of a constant $X-H$ bond length have been based either on data of too low accuracy or on data samples that were too small for analysis of statistical significance.

Data such as for $N-H\cdots O$ hydrogen bonds in Figure 1a and for $O-H\cdots N$ hydrogen bonds in Figure 3 can be readily shown in one diagram, Figure 4. The obtained figure can be taken as a picture of the proton transfer reaction path between X and Y. Only for $O-H\cdots O$ hydrogen bonds is this diagram populated with experimental data over the whole distance range.[5,9] For all other hydrogen bond types, the central part, i.e., for the region of strong and very strong hydrogen bonds, is unpopulated. This is unfortunate for the pair N/O (and also for N/N)[10] because, for this combination, very short hydrogen bonds are known to exist stably in the solid state. For the pairs O/S, N/S, O/Cl, and N/Cl, no structural evidence from single crystals is known (as yet) for stable hydrogen bonds with $X-H$ and $H\cdots Y$ distances of similar lengths.

It is of importance that in hydrogen bonds to chloride ions, $X-H$ bond lengthening is only moderate even for charged donors such as in $N^+-H\cdots Cl^-$ ("salt bridges"). In $N-H\cdots Y$ hydrogen bonds, the mean $N-H$ bond length is 1.028(3) Å for $X = O$, 1.028(3) Å for $X = N$,[10] 1.028(2) Å for $X = Cl^-$, and 1.020(4) Å for $X = S$. This implies that the lengthening of $X-H$ is not governed by the electrostatic energy in the hydrogen bond, which is much larger for hydrogen bonds between ionic than between uncharged partners. The same implication follows from the observation that for $N-H\cdots O$ hydrogen bonds of equal distance $N-H$ is equal irrespective if N is charged or not.

CHART 3



Valence (Bond Order) Model. According to this model, the $X-H$ and $H\cdots Y$ interactions in a hydrogen bond are of the same nature and are fully characterized by "bond orders" or "valences". These are strict functions of the bond distances, irrespective of charges and angles. In addition, the sum of valences at any atom type is conserved in all bonding situations. The relevance of this apparently simplistic description of hydrogen bonds is supported by the experimental data shown above. The theoretical funtion $r_{XH} = f(r_{H\cdots Y})$ as given in eq 6 can be excellently fitted against the experimental data. The model allows extrapolation of the experimental $X-H/H\cdots Y$ relation to regions for which experimental data are currently not available.

Numerical values for the parameters r_0 and b in eq 1 are now available for a number of homonuclear and heteronuclear hydrogen bonds, Table 4. It is somewhat disquieting that the values obtained in fitting procedures are clearly sample-dependent: for example, the data for the O/H atom pair are slightly different from those obtained from $O-H\cdots N$ and $O-H\cdots O$ hydrogen bonds, and for the latter case, it matters if water molecules are included in the sample or not. If the "truth" of the model is to be assessed, it must be considered that eq 1 is a function with only two adjustable parameters, so that some slight deviations of model and experiments can be taken calmly. In view of the simplicity of the model, the quality of the fits to the data is rather astonishing.

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Appendix I

Bending of the Covalent C−N⁺−H Angle of Primary Ammonium Groups. Bending of donor $R-X-H$ angles in hydrogen bonds is far less well documented than the elongation of the $X-H$ bond. In principle, it is obvious that the angular position of the hydrogen bond acceptor with respect to the $R-X$ bond must have an effect on the $R-X-H$ angle as illustrated in Chart 3. For large $R-X\cdots Y$ angles, the $R-X-H$ angle is opened, and for small $R-X\cdots Y$ angles, it is narrowed. This effect has been quantified from neutron diffraction data for water

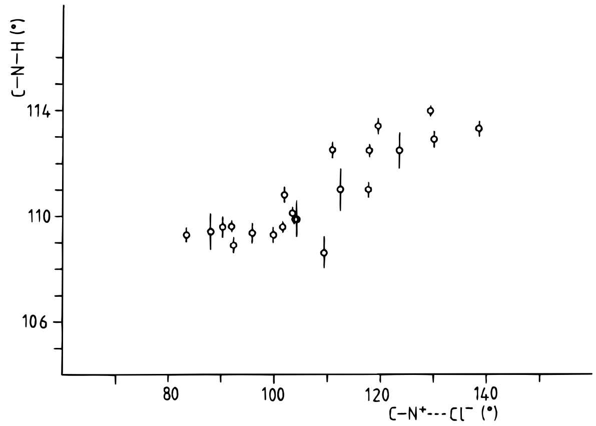

Figure 13. Bending of the covalent C−N−H angle in 28 N−H···Cl⁻ hydrogen bonds donated by primary ammonium groups.

TABLE 7: Bending of the Covalent C−N$^+$−H Angle in N$^+$−H···Cl$^-$ Hydrogen Bonds Donated by Primary Ammonium Groups

C−N$^+$···Cl$^-$ angle (deg)	*n*	mean C−N$^+$···Cl$^-$ (deg)	mean C−N$^+$−H (deg)
80−100	7	92(2)	109.4(1)
100−120	15	110(2)	111.0(3)
120−140	6	130(2)	113.2(2)
all	28	110(2)	111.0(3)

donors[4,31] and for hydroxyl groups.[31] The bending effect on R−X−H is heavily affected by secondary effects such as multicenter hydrogen bonding. Since it is not in the focus of the present study, it is shown for only one of the discussed hydrogen bond types, that is, N$^+$−H···Cl$^-$ hydrogen bonds; Figure 13 and Table 7. The variation of C−N$^+$···Cl$^-$ angles in the range of ca. 80−140° causes corresponding variation of the C−N$^+$−H angles from ca. 109 to 113°.

Appendix II

Data Retrieval. All database searches were performed on SGI workstations using the single-crystal neutron diffraction subset of the Cambridge Structural Database[46] (CSD) (January 1998 update with 175 093 entries). Standard uncertainties of bond lengths and angles were retrieved from the original publications. All subsequent numerical calculations were performed using in-house programs.

To obtain high-precision data on N−H···O hydrogen bonds, ordered and error-free neutron crystal structures with $T < 150$ K and $R < 0.06$ were considered and hydrogen bonds were retrieved to an upper limit of H···O = 3.0 Å (angle at H > 90°). No distinction was made between H and D. If the same crystal structure has been determined at several temperatures, only the structure at the lowest temperature was considered. Of structures that were determined independently by different authors, only the one with the lowest *R*-value was used. Thirty-one relevant crystal structures were found (CSD entry codes: ACANIL02, ADENOS01, AEPHOS02, ALOXAN11, ASPARM06, BZAMID02, CBOHAZ02, CENHAE02, CYACHZ01, CYTOSM04, CYURAC12, DQOLAC20, FACETA01, FORAMO01, GAMBUT02, GLYCIN16, GLYGLY04, LARGPH04, METURA01, NRURAM11, PARBAC03, POBDEP, PSULHZ11, PUTRDP11, PYRIDO04, QUICNA02, UREAXX12, UREXPO11, UROXAL01, URPRBN01, ZUGQEX).

For retrieval of the other heteronuclear hydrogen bond types, the small numbers of relevant crystal structures did not allow restriction to low-temperature data. Even the permissive quality criteria $T < 300$ K and $R < 0.08$ yielded only relatively few hits. O−H···N hydrogen bonds: five crystal structures (ADENOS01, AHXGLP, FORAMO01, GLOXIM11, JAPKOA). O−H···S hydrogen bonds: six crystal structures (BABCOW01, COKHAL, HYTPRD01, MCPROP01, NACTMO02), which were combined with neutron diffraction data from three inorganic hydrates[47a,b,c] that were found compiled in an organic structure report.[48] N−H···S hydrogen bonds: four crystal structures (NALCYS02, PYRIDS02, THACEM01, THIOUR04). N−H···Cl$^-$ hydrogen bonds: 14 crystal structures (ACNITR20, AMBONC01, AMBXPT10, CYGUAN01, CYSTCL02, ETDCOH11, GLCICH01, GLYHCL, HISTCM12, LTYRHC10, LYSCLH11, OPHDAH01, PYRXCL10, VALEHC11). O−H···Cl$^-$ hydrogen bonds, no water donors considered: 5 crystal structures (CYSTCL02, GLYHCL, LGLUTA, LTYRHC10, VALEHC11).

For (C)O−H···O hydrogen bonds, 25 low-temperature crystal structures with $T < 150$ K and $R < 0.06$ were considered (ABINOR04, ABINOS02, ACETAC04, ADENOS01, BUVSEQ03, DHNAPH17, DQOLAC20, FERROCA12, FUDVUV02, KACBEV01, KECYBU12, KHDFRM12, MEPRNL10, MERYOL03, NAHMAL01, NALCYS02, NHOXAL14, NRURAM11, SIGHOF, SUBRAC01, SUCACB03, TEPHTH04, UROXAL01, VUYYUJ, XYLOSE03).

No hydrogen bonds with uncertainties of bond lengths ≥0.01 Å were tolerated, with the exception of two chemically important cases (shown in Figures 6b and 10).

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