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A Semi-Empirical Potential Function for the Hydrogen Atom in the N(sp^3)–H$\cdots$O Hydrogen Bond

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The forces acting on a hydrogen atom in equilibrium in a hydrogen bond of type N(sp^3)–H$\cdots$O are determined with the use of a known potential for the nitrogen–hydrogen bond, and the assumption that the force field consists of only three forces, namely a H$\cdots$O attractive force, $\mathbf{F}_{\rm HO}$, a N–H stretching restoring force $\mathbf{F}_{\rm NH}$ and a N–H bending restoring force, $\mathbf{F}_{\rm CNH}$. With crystal-structure data for the α-ammonium group in 12 α-amino acids a relationship is set up between $\mathbf{F}_{\rm HO}$ and the distance between the hydrogen and the oxygen atoms, leading to – by integration – the potential function for the H$\cdots$O interaction. In addition the forces $\mathbf{F}_{\rm CNH}$ are correlated with the distortions in the ammonium groups and force constants are obtained for the C–N–H bend, which are in good agreement with spectroscopic values.

Introduction

During the last two decades an appreciable amount of information concerning the geometrical parameters of hydrogen bonds in crystalline material has been obtained with the techniques of neutron diffraction analysis. The occurence of hydrogen bonds is widespread, ranging from inorganic materials where the major bonding forces are of electrostatic nature to organic material where van der Waals forces are often dominant. Because neutron sources are scarce and expensive the distribution of information is equally broad, and the goal of most of the studies has been to resolve particular problems, which were inaccessible before the advent of powerful neutron sources.

In the same period attempts have been made to obtain a coherent picture of the behaviour of the hydrogen atom in the hydrogen bond centred around a search for and a refinement of potential functions which enable one to predict the atomic positions and thermal-motion parameters for a wider range of hydrogen bonds. On one hand electrostatic potentials have been used, for example by Baur (1972) in the study of hydroxides and hydrates, and on the other hand the Lippincott–Schroeder potential (Schroeder & Lippincott, 1957), which assumes the interactions to be of mainly covalent nature, has been used, for example by Zigan (1972, 1974) to predict the vibration direction and frequencies in hydroxides and by Chidambaram, Balasubramanian & Ramachandran (1970) to describe the distributions of bond lengths in N–H$\cdots$O hydrogen bonds. It has however – because of the limited amount of homogeneous data – been difficult to construct semi-empirical potentials, and it is only with the advent of series of related compounds that such potentials have possibly become obtainable.

When molecules are bound together by various types of forces to form regular arrays the result is invariably a distortion of the molecule compared to the idealized 'free state', and these distortions can therefore be a valuable source of information concerning the intermolecular interactions. To render this information usable at least two conditions have to be fulfilled. First the relative distortions of the atoms or groups involved in the interactions must be big and the atomic positions must be known with high precision. This can be fulfilled for hydrogen atoms involved in hydrogen bonds. Secondly the nature of the atomic bonds must be known, as this will be the starting point for an evaluation of the intermolecular interactions. This too is fulfilled for the hydrogen atom, where several potentials for the stretching of the bond have been suggested. We shall in the following use the potential suggested by Lippincott (1953). For the bending of bonds we will assume, when necessary, that this is governed by a harmonic potential. In addition we will restrict the discussion to two-atom interactions and we will assume that all the hydrogen bonds used can be described in these terms. It must be pointed out that the choice of interatomic potentials is not a crucial point, as the other potentials are related to this starting set. As long as we succeed in forming a set of potentials, which adequately describes our observations, the main goal is achieved.

Among the molecular residues containing hydrogen atoms capable of forming hydrogen bonds only a few can be used because of the scarcity of data. In the following data from a series of studies of α-amino acids are used in an attempt to construct a potential function for the hydrogen atom in the N–H$\cdots$O hydrogen bonds, where N is sp^3 hybridized. This system has several advantages. All the bonds are of the asymmetric type with the hydrogen atom nearest to the nitrogen atom and they are all quite weak, so that the potential can be assumed to be continuous and slowly variable with interatomic distance. In addition, the hydrogen atoms belong to three-dimensional groups, the α-ammonium groups, so that the distortion within a molecular unit can be studied. To simplify the treatment we will assume that bonds involving the carbon atom, which is bound to the α-ammonium group, are not affected by the formation of hydrogen bonds. The oxygen atoms belong in most cases to carboxyl groups, and it should then be subsequently possible from a study of the orientations and distortions of the carboxyl groups to get an estimate of this potential. The oxygen atom does however in general participate in several hydrogen bonds, and this could well complicate the treatment.

Generally the dynamics of atomic interactions are best observed by spectroscopic methods, and we cannot hope to obtain from the study of the static structure values for forces or energies of a comparable quality. On the other hand, as we are basing our considerations on directly observable distortions and average thermal motion in real three-dimensional space, this should facilitate the treatment in cases where we are interested in very specific interactions in complex systems.

Formalism

The potential governing the position and motion of the hydrogen atom has a minimum at the equilibrium position, and, expressed in terms of forces acting on the hydrogen atom, this means that the sum of the forces at this position, $\sum_i \mathbf{F}_i$, is zero. The equilibrium position is – with some modifications – observable by diffraction techniques, and if some of the forces are known this supplies us with a series of relationships, if a sufficient number of assumptions are introduced.

Fig. 1 depicts a hydrogen bond of the type C–N–H···O indicating the forces that might act on the hydrogen atom in the equilibrium position, an attractive force, $\mathbf{F}_{HO}$, between the hydrogen atom and the oxygen atom, and two restoring forces, $\mathbf{F}_{NH}$ and $\mathbf{F}_{CNH}$, for the stretch and the bend of the covalent nitrogen–hydrogen bond, respectively. It is assumed, that the forces $\mathbf{F}_{NH}$ and $\mathbf{F}_{HO}$ are collinear with the bond directions, and that $\mathbf{F}_{CNH}$ is orthogonal to $\mathbf{F}_{NH}$.

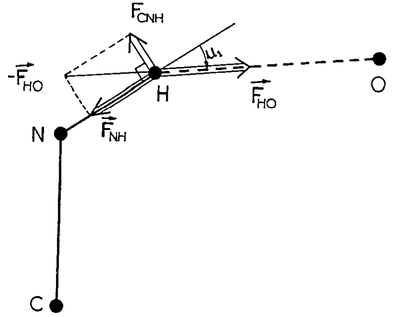

Fig. 1. The force field for the hydrogen atom in equilibrium. $\mathbf{F}_{NH}+\mathbf{F}_{HO}+\mathbf{F}_{CNH}=\mathbf{0}$. It is assumed that $\mathbf{F}_{HO}$ points toward the oxygen atom and that $\mathbf{F}_{CNH}$ is orthogonal to $\mathbf{F}_{NH}$. The angle u_1 is indicated.

We then get for the numeric values

$$\begin{aligned} F_{HO} &= F_{NH}/\cos u_1 \\ F_{CNH} &= F_{NH} \tan u_1 \\ 0 &\le u_1 \,. \end{aligned} \quad (1)$$

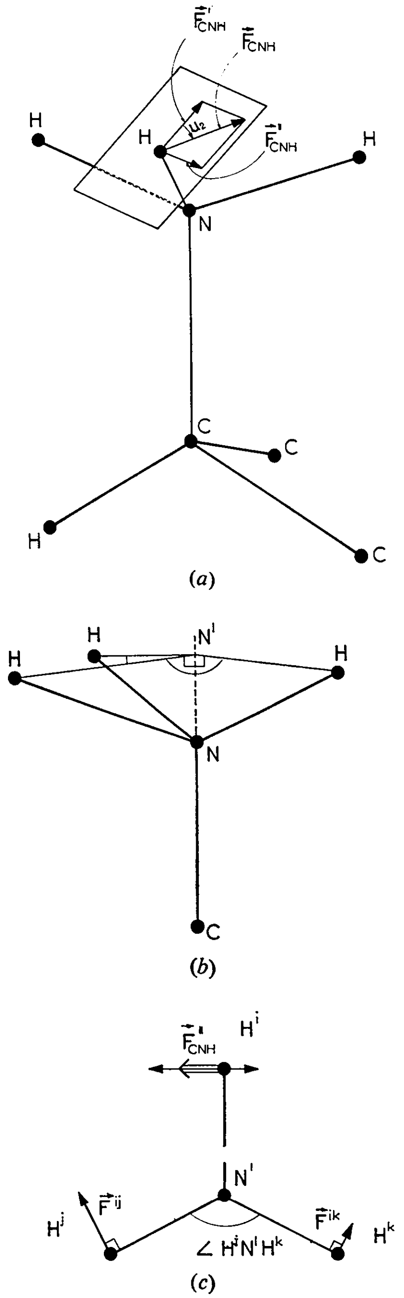

Fig. 2. Three views of the ammonium group involved in hydrogen bonding. (a) The division of $\mathbf{F}_{CNH}$ into two components, $\mathbf{F}_{CNH}=\mathbf{F}'_{CNH}+\mathbf{F}''_{CNH}$, both of which lie in a plane orthogonal to the nitrogen–hydrogen axis. The angle u_2 is indicated. (b) Definition of the point N′ which is the projection of the hydrogen atoms on the carbon–nitrogen axis. (c) Plane containing the three hydrogen atoms and N′. Some of the bending forces $\mathbf{F}^{ij}$ are indicated, and the sum for atom $\mathbf{H}^i$ is shown.

Now, if a sufficient number of hydrogen bonds are available covering the range of possible distances, r_{HO}, between the hydrogen and the oxygen atoms, and if F_{NH} is known, then a relationship between F_{HO} and r_{HO} can be established as

$$F_{HO} = f(r_{HO})\,.$$

Taking into account that $\partial V'(r_{HO})/\partial r_{HO} = -F_{HO}$ we then obtain the two-atom potential $V'(r_{HO})$ as

$$V'(r_{HO}) = \int_{r^n_{HO}}^{r_{HO}} f(r_{HO})\,dr_{HO} \qquad (2)$$

where r^n_{HO} is the non-hydrogen-bonded distance, corresponding to the approximate sum of the van der Waals radii of the atoms involved.

The force $\mathbf{F}_{CNH}$ can now in a similar manner be related to the observed angular distortions. Fig. 2(*a*) shows the division of $\mathbf{F}_{CNH}$ into two components for the case of an ammonium group. The two components are chosen to be $\mathbf{F}'_{CNH}$, which lies in the plane formed by atoms H, N and C, and $\mathbf{F}''_{CNH}$, which is orthogonal to this plane. The values of the two components are then given by

$$F'_{CNH} = F_{CNH}\cos u_2 = F_{NH}\cos u_2 \tan u_1$$
$$F''_{CNH} = F_{CNH}\sin u_2 = F_{NH}\sin u_2 \tan u_1 \qquad (3)$$

where u_2 is measured from the vector orthogonal to the N–H axis pointing towards the C–N axis.

F'_{CNH} can now be related to the distortion of the angle $\angle$CNH, and as above the potential can be determined. In this case F'_{CNH} will take either a positive or negative value; the value of $\angle$CNH corresponding to zero force is the equilibrium value when no hydrogen bonding takes place, and the distortion potential for this value we will assume to be zero.

F''_{CNH} can be related to the distortions in the angles $\angle$HN′H indicated in Fig. 2(*b*). The hydrogen-atom positions are projected onto the axis C–N, producing the point of projection N′. The angle $\angle$HN′H is related to angle $\angle$HNH, and by this choice of angles describing the distortions of the ammonium group the correlation between the parameters is minimized.

In this last case we will assume that the potential is harmonic and that the restoring force for angle $\angle H^iN'H^j$ is $F^{ij} = -k'_{HN'H}(\angle H^iN'H^j - 120°) = -k'_{HN'H}\Delta^{ij}$. We then get, by addition for the restoring force on atom H^i, $F''_{CNH} = -k'_{HN'H}(\Delta^{ik} - \Delta^{ij})$, where H^i, H^j and H^k are shown on Fig. 2(*c*), which is a view of the ammonium group seen in the direction N–C. Now, if $H^jN'H^k$ is 120°, then the angular deviation from the equilibrium position for H^i is $\Delta^{ik} = -\Delta^{ij}$, and we get $F''_{CNH} = -2k'_{HN'H}\Delta^{ik}$, so for comparison of the force constants in the two orthogonal bends and for the calculation of the potential energy we will therefore in the general case use

$$F''_{CNH} = -k_{HN'H}(\Delta^{ik} - \Delta^{ij})/2\,. \qquad (4)$$

A plot of F''_{CNH} against $(\Delta^{ik} - \Delta^{ij})/2$ will then reveal whether our assumption of harmonic forces is reasonable and if so, supply us with a force constant.

The forces $\mathbf{F}''_{CNH}$ might result in a total moment on the ammonium group along the C–N axis. However for reasons given below we assume this moment to be small, and it is therefore neglected.

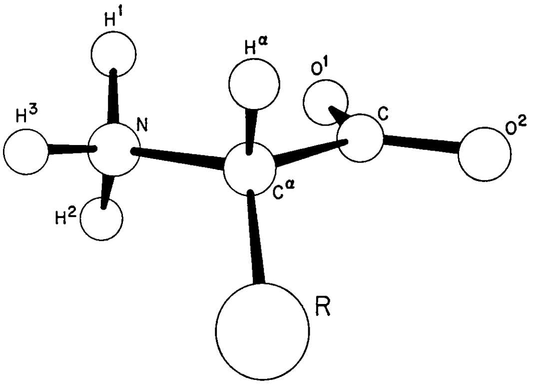

Fig. 3. The general shape of an L-α-amino acid. *R* indicates a small organic residual, ranging from an aliphatic chain to a phenol group. The molecule is shown in the zwitterion form, which is the form found in crystals of the neutral compound.

Table 1. *Some crystallographic data*

X stands for non-hydrogen atoms, H for hydrogen atoms. $R = \sum|F_{obs} - F_{calc}|/\sum F_{obs}$, where *F* is the structure amplitude, and the standard deviations indicated are mean values.

Compound	*R* value	σ(X–H) (Å)	σ($\angle$X–X–H) (°)	σ($\angle$H–X–H) (°)	Reference
L-Alanine	0·022	0·003	0·2	0·2	Lehmann, Koetzle & Hamilton (1972*a*)
L-Asparagine.H_2O	0·026	0·002	0·1	0·2	Verbist, Lehmann, Koetzle & Hamilton (1972)
L-Cystine.2HCl	0·034	0·003	0·2	0·3	Jones, Bernal, Frey & Koetzle (1974)
L-Glutamic acid	0·026	0·004	0·2	0·3	Lehmann, Koetzle & Hamilton (1972*b*)
L-Glutamine	0·032	0·005	0·3	0·4	Koetzle, Frey, Lehmann & Hamilton (1973)
α-Glysine	0·032	0·002	0·1	0·2	Jönsson & Kvick (1972)
L-Lysine.HCl.$2H_2O$	0·030	0·004	0·3	0·4	Koetzle, Lehmann, Verbist & Hamilton (1972)
L-Serine.H_2O	0·039	0·006	0·3	0·4	Frey, Lehmann, Koetzle & Hamilton (1973)
DL-Serine	0·020	0·002	0·1	0·1	
L-Tyrosine	0·026	0·004	0·2	0·3	Frey, Koetzle, Lehmann & Hamilton (1973)
L-Tyrosine.HCl	0·041	0·005	0·3	0·4	
L-Valine.HCl	0·031	0·005	0·3	0·4	Koetzle, Golic, Lehmann, Verbist & Hamilton (1973)

Source of data

The structural parameters used for this analysis are taken from a series of neutron diffraction studies of amino acids carried out at Brookhaven National Laboratory (Koetzle & Lehmann, 1974). The general shape of an L-α-amino acid is given in Fig. 3, and some information concerning the quality of the data is listed in Table 1. This includes the conventional crystallographic R value for the final refinement and the mean standard deviations, which are used in this analysis for all bonds of a given type within one structure. The 12 structures included are the ones for which final refinement of structural parameters has been carried out leading to standard deviations for the X–H bonds of less than 0·01 Å, as bond distances with higher standard deviations are of little use in this type of study. A comparative study of diffraction results on L-asparagine monohydrate (Ramanadham, Sikka & Chidambaram, 1972; Verbist, Lehmann, Koetzle & Hamilton, 1972) showed that the standard deviations were underestimated at least by a factor 1·3, and this factor is therefore applied whenever the standard deviations are used.

Not all hydrogen bonds are of the type N–H···O. However, hydrogen bonds of other types are included to increase the amount of data describing the distortions of the ammonium groups. All bonds are of the single-bond type where the hydrogen atom is connected to one hydrogen-bond acceptor, and only in one case is there an indication of two acceptors, namely for the H^1 atom in α-glycine (Jönsson & Kvick, 1972). This bond is therefore included in the plots, but not in the calculation of F_{HO}.

The observed bond lengths are foreshortened because of the thermal motion, but the effect is relatively small for hydrogen-bonded atoms. A comparison among various types of corrections suggested by Busing & Levy (1964) indicated that the so-called 'minimum correction' gave the best result for non-bonded hydrogen atoms in L-lysine hydrochloride dihydrate (Koetzle, Lehmann, Verbist & Hamilton, 1972), and this was therefore used in most of the studies. The corrections are in the range 0·001 to 0·01 Å with a mean value of 0·004 Å, and this value has been added to all nitrogen–hydrogen bond lengths involved. No correction has been made to other bond distances and angles.

Table 2. *Table showing distances, angles and related forces in the hydrogen bond and in the ammonium group*

The order of the hydrogen atoms is always H^1, H^2, H^3. Δ is $\Delta^{ik} - \Delta^{ij}$ (4) and the forces are in kcal/mole/Å.

Numbers in parentheses in this table and throughout the paper are standard deviations in units of the last digit.

Compound	H···X	r_{NH} (Å)	r_{HX} (Å)	∠N–H···X°	∠C–N–H°	Δ	F_{HO}	F'_{CNH}	F''_{CNH}
L-Alanine	O^1	1·029	1·861	160·9	111·3	2·9	18·7 (37)	−2·6	−5·3
	O^2	1·047	1·780	168·1	109·4	1·3	34·2 (33)	6·2	−2·6
	O^2	1·031	1·828	163·7	109·1	−4·2	20·4 (36)	2·9	4·8
L-Asparagine.H_2O	O^1	1·040	1·833	156·9	111·2	−4·7	29·4 (25)	−3·8	10·4
	O^w	1·030	1·946	145·8	112·3	3·1	22·8 (28)	−6·5	−10·6
	O^{δ}	1·039	1·782	168·1	110·1	1·6	26·7 (23)	0·6	−5·3
L-Cystine.2HCl	Cl	1·034	2·262	156·9	114·0	−1·5		−8·6	2·2
	Cl	1·045	2·100	167·4	109·9	2·3		4·8	−4·8
	Cl	1·025	2·270	151·1	112·9	−0·8		−6·6	3·6
L-Glutamic acid	O^2	1·038	1·845	167·8	110·8	0·4	26·1 (46)	4·9	−2·1
	O^2	1·038	1·868	166·9	110·1	0	26·0 (46)	3·9	−4·0
	$O^{\varepsilon 1}$	1·027	1·896	174·1	112·3	0·4	15·9 (48)	−0·7	1·5
L-Glutamine	O^2	1·040	1·854	163·3	111·2	1·7	28·4 (57)	−4·4	−6·5
	$O^{\varepsilon 1}$	1·023	1·941	167·3	111·0	−0·1	11·3 (61)	1·3	2·1
	O^2	1·045	1·752	164·2	108·1	−1·6	32·8 (58)	8·4	−1·1
α-Glycine	O^2	1·025	2·121	154·0	110·4	−1·0	15·2 (27)	6·5	0·6
	O^1	1·054	1·728	169·3	112·1	−3·0	39·3 (20)	−6·1	3·2
	O^2	1·037	1·832	168·5	111·7	3·9	24·7 (23)	−3·0	−3·8
L-Lysine.HCl.$2H_2O$	O^w	1·034	1·836	158·5	109·1	−3·7	24·0 (48)	1·3	8·4
	Cl	1·028	2·196	172·0	111·3	−1·2		−0·2	−2·3
	O^2	1·059	1·740	173·4	112·3	4·9	43·7 (43)	1·4	−4·5
L-Serine.H_2O	O^w	1·023	2·130	132·3	109·3	−8·8	18·6 (105)	7·0	11·4
	O^2	1·026	1·901	168·1	113·2	0·8	15·5 (72)	−1·8	−2·6
	O^2	1·035	1·804	153·4	108·6	7·9	26·0 (76)	10·2	−4·7
DL-Serine	O^{γ}	1·037	1·787	157·4	107·7	−3·2	26·4 (24)	4·9	8·5
	O^2	1·045	1·844	168·8	113·0	−2·8	32·0 (23)	−5·8	−1·1
	O^2	1·041	1·814	160·7	108·8	6·1	29·6 (23)	8·8	−3·3
L-Tyrosine	O^{η}	1·015	2·120	129·8	112·0	−0·6	6·7 (76)	−4·8	−1·7
	O^2	1·048	1·789	169·7	109·4	−0·7	34·8 (43)	5·9	0·1
	O^2	1·037	1·853	172·7	110·9	1·3	24·5 (46)	−1·9	2·3
L-Tyrosine.HCl	Cl	1·007	2·378	144·5	113·3	−1·5		1·8	−0·1
	Cl	1·017	2·471	161·8	110·8	0·6		1·4	1·6
	Cl	1·020	2·505	137·4	109·4	0·8		6·9	−4·6
L-Valine.HCl	Cl	1·030	2·356	169·4	112·5	−4·5		−3·3	−1·2
	Cl	1·041	2·161	168·1	110·1	5·5		4·3	−3·5
	Cl	1·031	2·263	154·5	109·6	−0·9		8·4	0·0

The potential used for the N–H bond is the one suggested by Lippincott (1953):

$$V(r_{\mathrm{NH}})=D\{1-\exp\,[-n(r_{\mathrm{NH}}-r^0_{\mathrm{NH}})^2/2r_{\mathrm{NH}}]\} \quad (5)$$

where D is the dissociation energy, r^0_{NH} is the equilibrium distance and n is related to the force constant k by $n=kr^0_{\mathrm{NH}}/D$. The values chosen are (Schroeder & Lippincott, 1957)

$$\begin{aligned} D &= 104 \text{ kcal/mole} \\ r^0_{\mathrm{NH}} &= 1{\cdot}014 \text{ Å} \\ n &= 9{\cdot}3 \text{ Å}^{-1}\,. \end{aligned}$$

The restoring force, F_{NH}, for the hydrogen atom in the hydrogen bond is then given by $F_{\mathrm{NH}}=-\mathrm{d}V(r_{\mathrm{NH}})/\mathrm{d}r_{\mathrm{NH}}$, and F_{HO} and F_{CNH} are then determined using (1). As the directions of $\mathbf{F}_{\mathrm{NH}}$ and $\mathbf{F}_{\mathrm{HO}}$ are known we get $\mathbf{F}_{\mathrm{CNH}}$ from $\mathbf{F}_{\mathrm{CNH}}=-\mathbf{F}_{\mathrm{NH}}-\mathbf{F}_{\mathrm{HO}}$. Finally $\mathbf{F}'_{\mathrm{CNH}}$ and $\mathbf{F}''_{\mathrm{CNH}}$ can be obtained from (3). Table 2 summarized the forces found as well as other pertinent information concerning the hydrogen bonds.

Because the changes of r_{NH} from the equilibrium distance r^0_{NH} are small compared to the standard deviations of r_{NH}, $\sigma(r_{\mathrm{NH}})$, the errors in F_{NH} and the related quantities are very big. For F_{HO} the standard deviations are estimated as $\sigma(F_{\mathrm{HO}})=(\mathrm{d}F_{\mathrm{NH}}/\mathrm{d}r_{\mathrm{NH}})\sigma(r_{\mathrm{NH}})/\cos u_1\times 1{\cdot}3$, where the factor 1·3 is explained above. For F''_{CNH} another approach is used. These forces can result in a non-zero moment $\mathbf{M}=\sum\mathbf{F}''_{\mathrm{CNH}}\times\mathbf{r}_{\mathrm{N'H}}\simeq\mathbf{e}_{\mathrm{CN}}r_{\mathrm{N'H}}\sum F''_{\mathrm{CNH}}$, where $\mathbf{e}_{\mathrm{CN}}$ is a unit vector along the C–N axis, and N′ is defined in Fig. 2(*b*). The expected moment is small. If we describe the torsional potential for the ammonium group as $V(\alpha)=V_0/2\times(1-\cos 3\alpha)$ where α is the angle of rotation around $\mathbf{e}_{\mathrm{CN}}$, then a typical value for V_0 is probably in the range 2 to 3 kcal/mole as determined for methyl groups in L-valine hydrochloride (Koetzle, Golic, Lehmann, Verbist & Hamilton, 1974) by diffraction techniques and ethane (Lide, 1958) by infrared studies. We can assume the equilibrium position to be a staggered configuration with respect to the C–N axis as this is the mean value observed for 12 ammonium groups in α-amino acids (Hamilton, Frey, Golic, Koetzle, Lehmann & Verbist, 1972), with a mean deviation from this orientation of 9°. On average, we can then expect a torsional moment not much bigger than $\frac{3}{2}\times 3\times\sin 27^\circ=2$ kcal/mole/rad, or, as $r_{\mathrm{N'H}}$ is approximately 1 Å, that $\sum F''_{\mathrm{CNH}}$ takes this value. From Table 2 it is clear that the observed sums are larger, and they must therefore arise mainly from the errors in F''_{CNH}. The mean value of this sum for the 12 groups is 0·5 kcal/mole/Å and the variance is 25·2 (kcal/mole/Å)^2. As the sum consists of three components the variance for one component should be approximately a third of this value, leading to a $\sigma(F''_{\mathrm{CNH}})$ of 2·9 kcal/mole/Å, in good agreement with $\sigma(F_{\mathrm{HO}})$, which takes a mean of 4·5 kcal/mole/Å, when we take into consideration that following (1) we would expect $\sigma(F_{\mathrm{CNH}})$ to be less than $\sigma(F_{\mathrm{HO}})$. For F'_{CNH} we expect the standard deviations to be of the same order of magnitude.

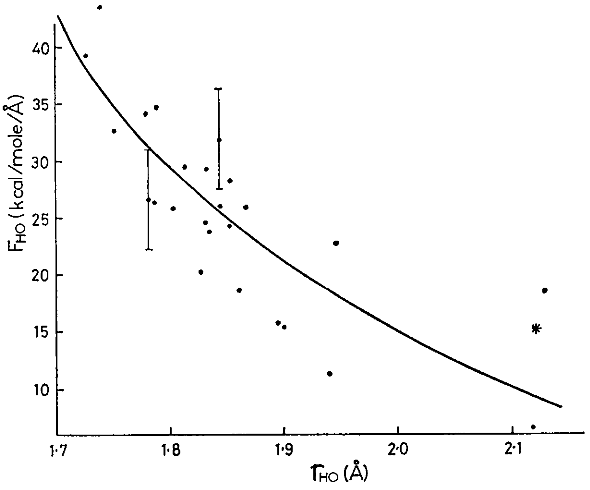

Fig. 4. The forces F_{HO} plotted against r_{HO}. The solid curve represents the calculated relationship (6). Points for which the observed and calculated force differ by more than $2\sigma(F_{\mathrm{HO}})$ are indicated by error bars of size $\pm 2\sigma(F_{\mathrm{HO}})$.

Results

In Fig. 4 is shown the relationship between F_{HO} and r_{HO}. As expected the attractive force increases with decreasing distance. The inverse relationship is nearly linear, and to get an analytical description of the behaviour three types of functions, $F_{\mathrm{HO}}{}^{\mathrm{calc}}=f_i$, were tried

$$\begin{aligned} f_1 &= k\exp\,(-\gamma r^m_{\mathrm{HO}}) \\ f_2 &= k/(r_{\mathrm{HO}}-\varrho)^m \\ f_3 &= -k\log_e\,[\gamma(r_{\mathrm{HO}}-\varrho)]\,. \end{aligned}$$

In all cases the quantity $\Delta=\sum(F^{\mathrm{obs}}_{\mathrm{HO}}-F^{\mathrm{calc}}_{\mathrm{HO}})^2/\mathrm{var}\,(F^{\mathrm{obs}}_{\mathrm{HO}})$ was minimized by stepwise variation of γ, ϱ and m and calculation of k. The error in k, $\sigma(k)$, therefore reflects the compounded errors from using a given set of γ, ϱ and m.

Table 3. *Parameters and goodness-of-fit for three types of functions describing the relationship between* F_{HO} *and* r_{HO}

Units for k are combinations of kcal/mole and Å.

	γ (Å^{-1})	ϱ (Å)	k	$\sigma(k)$	Goodness-of-fit
$k[\exp\,(-\gamma\times r_{\mathrm{HO}})-\exp\,(-\gamma\times 2{\cdot}4)]$	2·62		4·2 × 10^3	0·1 × 10^3	1·259
$k[1/(r_{\mathrm{HO}}-\varrho)-1/(2{\cdot}4-\varrho)]$		1·22	34	1	1·249
$-k\log_e\,[(r_{\mathrm{HO}}-\varrho)/(2{\cdot}40-\varrho)]$		1·58	22·5	0·7	1·237

It was found that $m=1$ gave the best agreement, and that f_3 gave the best fit with a goodness-of-fit, $\sqrt{\Delta/(n-1)}$, where n is the number of observations, of 1·218. The differences among the three functions were however small with virtually identical values for $F_{\text{HO}}^{\text{calc}}$ in the range for r_{HO} of 1·75 to 1·95 Å.

As the hydrogen-bond force F_{HO} is expected to approach zero for values of r_{HO} near the sum of the van der Waals radii for hydrogen and oxygen and as very few observations are available in this range, an additional assumption was introduced, namely that $F_{\text{HO}}=0$ for $r_{\text{HO}}^{n}=2·4$ Å, the upper limit for which an interaction of hydrogen and oxygen is considered to be a hydrogen bond [Baur (1972) using the criterion of Hamilton & Ibers, (1968) but with a modified value for the van der Waals radius of hydrogen]. The result of calculations including this constraint is given in Table 3. Again f_3 is found to give the best agreement, but the differences among the calculated values for F_{HO} in the range of interest are very small, mainly because the relationship is nearly linear and the deviation from linearity is too small to give a hint towards the best choice of function.

The function f_3 is used in the present calculations and its behaviour is given in Fig. 4. Points for which the disagreement between $F_{\text{HO}}^{\text{obs}}$ and $F_{\text{HO}}^{\text{calc}}$ is bigger than $2\sigma(F_{\text{HO}})$ are indicated by error bars of size $\pm 2\sigma(F_{\text{HO}})$. One point coming from the hydrogen bond involving H^1 in α-glycine was not included in the calculations for reasons given above and is indicated by an asterisk.

Ideally the goodness-of-fit should be 1·0, but it is found to be around 1·2, indicating the standard deviations on F_{HO} to be underestimated. This could well be the case as these values are derived from standard deviations on bond lengths, the magnitude of which are possibly underestimated as discussed above.

Using expression (2), we now get for the potential

$$V'(r_{\text{HO}}) = -22·5(r'_{\text{HO}} \log_e 1·22 r'_{\text{HO}} - r'_{\text{HO}} + 0·82) \text{ kcal/mole} \quad (6)$$

where

$$r'_{\text{HO}} = r_{\text{HO}} - 1·58 \,.$$

An estimate of the error can be obtained from

$$\text{Var}(V') \cong \left(\frac{\delta V'}{\delta r_{\text{HO}}}\right)^2 \text{Var}(r_{\text{HO}}) + \left(\frac{\delta V'}{\delta k}\right)^2 \text{Var}(k)$$
$$= F_{\text{HO}}^2 \text{Var}(r_{\text{HO}}) + V'^2(r_{\text{HO}})[\sigma(k)/k]^2 .$$

For a typical case of $r_{\text{HO}}=1·8$ Å and $\sigma(r_{\text{HO}})=0·004$ Å we get $V'=7·0$ kcal/mole and $\sigma(V')=0·3$ kcal/mole. This error must be taken as a minimal estimate. If a similar calculation is carried out using a sum of van der Waals radii of 2·5 Å then a potential is found which differs from (6) by 0·1 to 0·9 kcal/mole in the range from 2·0 to 1·8 Å for r_{HO}.

This potential function can now, in conjunction with the potential for the nitrogen–hydrogen bond, expression (5), be used to give an estimate of the relationship

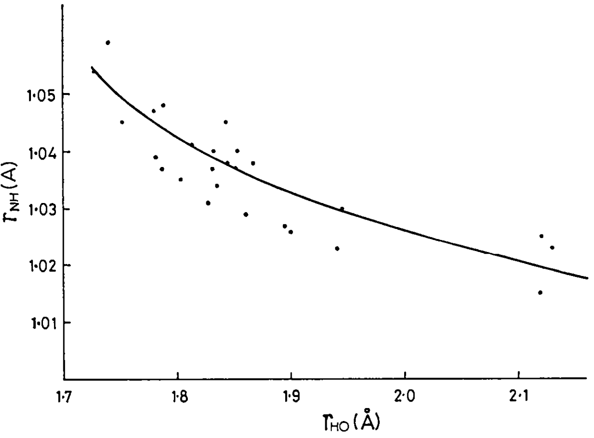

Fig. 5. Relationship between r_{NH} and r_{HO} as found using (4) and (6) assuming the bond angle, ∠NH···O, to be 162°. The points given are the 26 hydrogen bonds used in this study.

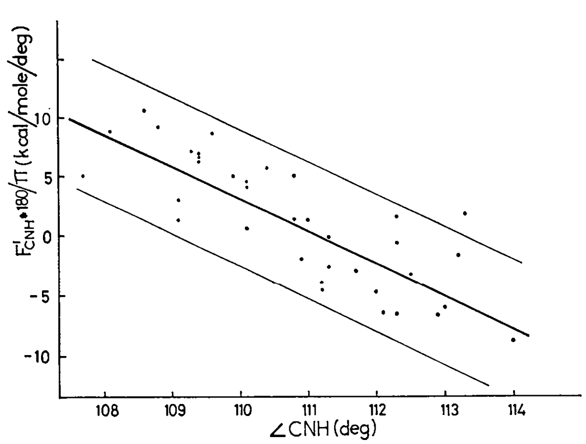

Fig. 6. Relationship between angular distortion for angle ∠CNH and force F'_{CNH}. The dark line represents a linear least-squares fit, the lighter lines are at distances of $\pm 2\sigma(F'_{\text{CNH}}) \sim \pm 6 \times \pi/180$ kcal/mol/deg.

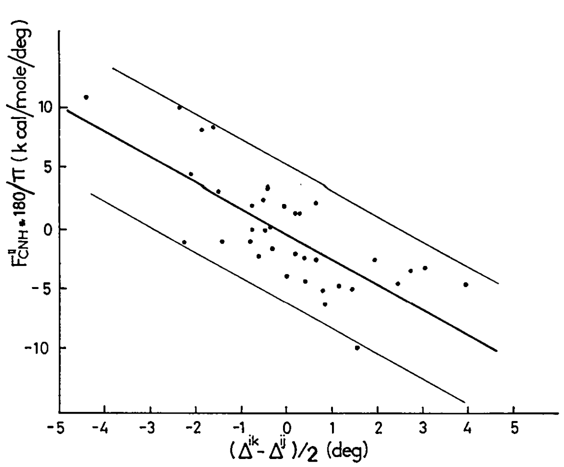

Fig. 7. The force F''_{CHN} as a function of $(\Delta^{ik}-\Delta^{ij})/2$. The three lines have the same meaning as in Fig. 6.

between r_{NH} and r_{HO}. A calculated relationship must however be treated with some caution, as it is sensitive to the angle $\angle \mathrm{NH}\cdots\mathrm{O}$, which lies in the range 130 to 180°. For the data used here the mean value is 162°, and the curve is obtained by minimizing $V(r_{\mathrm{NH}})+V'(r_{\mathrm{HO}})$ for a series of values of r_{NO}, the distance between nitrogen and oxygen, and for angle $\angle\mathrm{NHO}$ fixed at 162°. Fig. 5 shows the observed points $(r_{\mathrm{HO}}, r_{\mathrm{NH}})$ and the calculated curve. As the observed values for r_{NH} are expected to be underestimated by 0·004 Å the curve is shifted by this amount in the negative direction. The total energy for $r_{\mathrm{HO}}=1\cdot8$ Å is found to be $-6\cdot5$ kcal/mole.

Figs. 6 and 7 show plots of the observed restoring forces F'_{CNH} and F''_{CNH} on the hydrogen atom *versus* the two orthogonal distortions defined earlier.

On the plots as well as in the calculation the forces are measured in kcal/mol/deg. This is obtained by multiplication of F'_{CNH} and F''_{CNH} by $r_{\mathrm{NH}}\times\pi/180$ and $r_{\mathrm{NH}}\sin(\angle\mathrm{CNH})\times\pi/180$, respectively. Although the scatter of points is quite appreciable there is a clear indication of a systematic relationship, which we will assume arises from a harmonic potential. The force constants k_{CNH} defined by $F'_{\mathrm{CNH}}=-k_{\mathrm{CNH}}(\angle\mathrm{CNH}-\angle\mathrm{CNH}_0)$ (Fig. 6), where $\angle\mathrm{CNH}_0$ is the equilibrium position and $k_{\mathrm{HN'H}}$ defined by (4) (Fig. 7) are then obtained by linear least-squares fit. All points were given the same standard deviation, and to obtain a goodness-of-fit of one the standard deviations were chosen to be $3\cdot2\times\pi/180$ and $3\cdot1\times\pi/180$ kcal/mole/deg for F'_{CNH} and F''_{CNH}, respectively, in good agreement with the estimate of 2·9 kcal/mol/Å obtained earlier. The force constants were then found to be

$$k_{\mathrm{CNH}}=0\cdot048\ (6)\ \mathrm{kcal/mol/deg^2}$$
$$k_{\mathrm{HN'H}}=0\cdot037\ (6)\ \mathrm{kcal/mol/deg^2}\,.$$

The ratio between a distortion in angles $\angle\mathrm{HN'H}$ and $\angle\mathrm{HNH}$ is

$$\cos(\angle\mathrm{HNH}/2)/[\cos(\angle\mathrm{HN'H}/2)\sin(\angle\mathrm{CNH})]=1\cdot2,$$

so if the force constant is expressed in terms of angle $\angle\mathrm{HNH}$ we get

$$k_{\mathrm{HNH}}=1\cdot2k_{\mathrm{HN'H}}=0\cdot44\ (7)\ \mathrm{kcal/mole/deg}\,.$$

Destrade, Garrigou-Lagrange & Forel (1971) have studied the force field for α-glycine and found for the normal vibration $\delta_a(\mathrm{NH_3})=(\angle\mathrm{H}^i\mathrm{NH}^k-\angle\mathrm{H}^i\mathrm{NH}^j)/\sqrt{2}$ a force constant of 0·555 mdyn Å/rad² or 0·0244 kcal/mole/deg². The non-normalized coordinate used in defining k_{HNH} is $(\Delta^{ik}-\Delta^{ij})/2=(\mathrm{H}^i\mathrm{NH}^k-\mathrm{H}^i\mathrm{NH}^j)/2=\delta_a(\mathrm{NH_3})/\sqrt{2}$, so their observation predicts a value $k_{\mathrm{HNH}}=0\cdot0244\sqrt{2}=0\cdot034$ kcal/mole/deg², in reasonable agreement with our observation.

The bend of angle $\angle\mathrm{CNH}$ can be compared with the normal coordinate $\delta_s(\mathrm{NH_3})=(\angle\mathrm{CNH}^i+\angle\mathrm{CNH}^j+\angle\mathrm{CNH}^k-\angle\mathrm{H}^i\mathrm{NH}^j-\angle\mathrm{H}^j\mathrm{NH}^k-\angle\mathrm{H}^k\mathrm{NH}^i)/\sqrt{6}$, but because the angle $\angle\mathrm{H}^i\mathrm{N'H}^j$ is chosen instead of angle $\angle\mathrm{H}^i\mathrm{NH}^j$ our normal coordinate would reduce to a sum of the first three terms, *i.e.* $\delta_s=(\angle\mathrm{CNH}^i+\angle\mathrm{CNH}^j+\angle\mathrm{CNH}^k)/\sqrt{3}=3\angle\mathrm{CNH}/\sqrt{3}$. So $\angle\mathrm{CNH}=\delta_s/\sqrt{3}$, and a denormalization factor of $\sqrt{3}$ is therefore appropriate. The force constant for this normal mode is observed to be 0·584 mdyn Å/rad² or 0·0256 kcal/mole/deg² and the expected value for k_{CNH} would then be $0\cdot0256\sqrt{3}=0\cdot044$ kcal/mole/deg², again in satisfactory agreement with the observation.

The intersection of the least-squares line in Fig. 6 with $F'_{\mathrm{CNH}}=0$ supplies us with the equilibrium angle $\angle\mathrm{CNH}_0$ which is 111°. This is in good agreement with *ab initio* calculations on ethane (Newton, Lathan, Hehre & Pople, 1970) which gave $\angle\mathrm{CCH}=110\cdot7°$.

The intersection for the least-squares line in Fig. 7 with $F''_{\mathrm{CNH}}=0$ has a value of 0·4 (3), which does not deviate significantly from 0. This is not surprising when we take into account that the abscissae values are differences between distortions, and we therefore should expect a distortion which is symmetric around zero. It would however have been disquietening if a small value had not been observed.

In addition to the least-squares line given in Figs. 6 and 7 the confidence limits are given in terms of two additional lines for each figure at distances $\pm2\sigma(F_{\mathrm{CNH}})=\pm6\times\pi/180$ kcal/mole/deg. Only very few points fall outside this range. In Fig. 6 a slightly unusual feature is observed. For $\angle\mathrm{CNH}>\angle\mathrm{CNH}_0$ the maximum force observed is in general not greater than $7\times\pi/180$ kcal/mole/deg whereas values up to $12\times\pi/180$ kcal/mol/deg are found for $\angle\mathrm{CNH}<\angle\mathrm{CNH}_0$. This can be understood if we consider the total effect of the two types of distortion. When the hydrogen atom is pulled towards the carbon–nitrogen axis, *i.e.* $\angle\mathrm{CNH}$ is increased, then the strain can be partly released by a rotation of the ammonium group around the axis whereby the hydrogen atom escapes, whereas a stress on the hydrogen atom in a direction away from the axis will only result in little or no rotation and no release. What we observe is therefore not necessarily a deviation from the harmonic approximation, but merely a dispersion of the forces in some special cases. Indeed, a deviation from the harmonic approximation would normally give a hardening of the force, resulting in large restoring forces.

The mean distortion for both $\angle\mathrm{CNH}$ and $(\Delta^{ik}-\Delta^{ij})/2$ is 1·3°. A typical value for the energies involved in the distortions of the ammonium group is therefore $\frac{1}{2}k_{\mathrm{CNH}}(\angle\mathrm{CNH}-\angle\mathrm{CNH}_0)^2+\frac{1}{2}k_{\mathrm{HN'H}}(\Delta^{ik}-\Delta^{ij})^2/4=0\cdot07\ (1)$ kcal/mole. These deviations can be neglected when energy estimates of hydrogen bonds are made. It is however an interesting fact that we can estimate energies of this small size.

Conclusion

It has been shown that knowledge of the distortions of a series of ammonium groups involved in hydrogen bonding can be applied to construct potential functions for the hydrogen atom in the hydrogen bond as well as potentials for the angular distortions when a simple force field for the hydrogen atom is used in conjunction with a known potential for the nitrogen–hydrogen bond stretch. This should then make it possible to predict hydrogen-atom positions as well as thermal-motion parameters, and studies of this type are now in progress.

The results are of limited accuracy mainly because the starting point, the restoring stretching force for the hydrogen atom, is based on differences in bond lengths that never take values greater than twenty times their standard deviations, and there is no hope of achievement of higher accuracy in the near future, as these standard deviations are of the same order of magnitude as the known errors arising from limitations in our model. It is thus necessary either to possess a large amount of information or to seek systems where the starting forces are better known.

It must however be kept in mind that if the obtained potentials are used to predict hydrogen-atom positions, the starting point for the analysis, then the outcome should have the same precision as our starting material.

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