

## Study of geometrical parameters in N-H...N type of hydrogen bonds

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**Abstract.** Geometrical parameters associated with N-H...N types of hydrogen bonds have been analysed using crystal structure data on nucleic acids, amino acids and related compounds. Histograms depicting the frequency distribution of N-H...N length ( $l$ ) and H-N...N angle ( $\theta$ ) have been drawn and conclusions on the favoured geometry of such bonds have been arrived at. The distribution of  $l$  shows a pronounced maximum in the range between 2.9 Å and 3.0 Å with an overall average of 2.98 Å. The  $\theta$  distribution shows a pronounced maximum for the hydrogen bond angle in the range 0°-10°, with a rapid fall-off in frequency for nonlinear hydrogen bonds. The frequency shows a  $\cos^6\theta$  dependence as compared to  $\cos^2\theta$  dependence term used earlier to predict the angular dependence of hydrogen bond potential energy in proteins and polypeptides.

**Keywords.** N-H...N hydrogen bond; geometrical parameters; hydrogen bond length distribution; hydrogen bond angle distribution; potential function.

### 1. Introduction

It is now widely accepted that hydrogen bonds play vital roles in the stabilisation of biopolymer structures. Extensive data on N-H...N types of hydrogen bonds are available in the case of nucleic acids, amino acids and related compounds. Detailed studies on various types of hydrogen bonding including N-H...N type are available in literature (Hamilton and Ibers 1968, Murthy and Rao, 1968, 1970; Pimental and McClellan 1960; Donohue 1957; Wells 1962; Robertson 1953; Kollman and Allen 1972; Olovsson and Jonesson 1975 and Joester and Schaad 1974). Discussion on these types of hydrogen bonds are cited (Donohue 1967). A systematic analysis of the hydrogen bond parameters of N-H...N type of hydrogen bond does not seem to have been presented in literature. The reasons might be the lack of crystallographic data needed for the statistical analysis. In recent years, very accurate x-ray and neutron diffraction data have become available. It is possible with the present data to analyse the geometrical behaviour of these bonds. Keeping in view the importance of the hydrogen bond para-

meters (the hydrogen bond length,  $N \cdots N$  ( $l$ ) and the hydrogen bond angle,  $H-N \cdots \hat{N}(\theta)$ ) in the evaluation of the minimum energy conformation of nucleic acids and proteins, we have tried to analyse these parameters from the geometrical viewpoint. The results are reported in this paper.

## 2. Results

In our present study, data have been collected from 60 structures and as such we have 92 cases for the analysis. The study can be considered to be statistically significant because of the availability of quite a good number of examples. The aim of the analysis is to explore patterns in the distribution of hydrogen bond-parameters  $l$  and  $\theta$ .

### 2.1. The hydrogen bond length

The values of this parameter have been given in table 1. The histogram showing the distribution of length is given in figure 1 and numerical values are given in

Table 1. Distribution of the geometrical parameter associated with  $N-H \cdots N$  types of hydrogen bonds in crystal structures of nucleic, amino acids and related compounds.

Compound	Space groups	$N \cdots N$ ( $l$ ) (in Å)	$H-\hat{N} \cdots N$ ( $\theta$ ) (in degrees)	References
Carbohydrazide	$P2_1/c$	3.068 2.950	28.6 20.1	Damino <i>et al</i> 1972
Ethyl amino ethanol	$P2_1$	2.720	38.0	Glusker <i>et al</i> 1972
Ethylguanine	$P4_12_12$	2.846 2.776 3.272	10.0 7.0 46.0	Destro <i>et al</i> 1974
Aldeninato chlorobis cobalt bromide $H_2O$	$I2/a$	3.130 2.850	34.0 32.0	Kristenmacher 1974
Isonicotinic acid hydrazide	$P2_12_12_1$	2.967 3.094	12.0 12.0	Bhat <i>et al</i> 1974
Thiadiazine dioxide	$Pbca$	3.261 3.368 3.044	37.5 35.6 8.7	Foces <i>et al</i> 1975
Adeninium hemi- sulphate, $H_2O$	$P\bar{1}$	2.948 2.951	18.2 22.8	Langer <i>et al</i> 1978
Adenine $HBr$ , $\frac{1}{2} H_2O$	$P1$	2.948	10.2	Langer and Huml 1978
Formyl-morpholino pyridine thio-semi carbazone	$P2_1/c$	2.998	9.7	Brown and Agrawal 1978
Stizolamine	$C2/c$	2.730	33.7	Veno. <i>et al</i> 1978
Amino-ethoxy carbonyl triazole	$P2_1/c$	3.034	6.7	Parkanyi 1977 <i>et al</i>
Methyl cytosine	$P\bar{1}$	3.038	8.7	Ross and Kristenmacher 1977

Table 1. (Contd.)

Compound	Space groups	N...N (1) (in Å)	H-N...N ( $\theta$ ) (in degrees)	References
Adenyl-propionyl tryptamine H <sub>2</sub> O	P $\bar{1}$	3.012 3.064	7.6 24.7	Ohki <i>et al</i> 1977
$\beta$ -alanyl-L-histidine	C2	2.885	1.3	Itoh <i>et al</i> 1977
Dimethyl-diacetyl- pyridyl-dihydro- pyridine	P2 <sub>1</sub> /c	2.972	3.9	Krajewski <i>et al</i> 1977
Methyl adenosine	P2 <sub>1</sub> /c	2.969 3.074	10.5 4.6	Edwards <i>et al</i> 1977
Dimethyl triazeno phenyl carboxamide	P2 <sub>1</sub> /c	2.709	20.9	Brown <i>et al</i> 1976
Trihydrazino triazine	Cc	2.827	8.9	Brown <i>et al</i> 1976
Methylamino triazole carbonitrile H <sub>2</sub> O	P $\bar{1}$	2.875	27.9	Kalman <i>et al</i> 1976
Purin-glycine H <sub>2</sub> O	P2 <sub>1</sub> /c	2.737	28.3	Parthasarathy <i>et al</i> 1976.
Amino-acetophenone	P2 <sub>1</sub> /a	3.217	18.6	Haisa <i>et al</i> 1976
Tri-aminotriazine	P2 <sub>1</sub>	3.116 3.033 3.086	3.3 3.4 9.2	Varghese <i>et al</i> 1977
Pyridyl-dihydro- tetrazine	P $\bar{1}$	2.782 2.721	19.7 19.2	Caira <i>et al</i> 1976
Methyl adenosine	P2 <sub>1</sub>	2.999 3.003 2.950 2.994	31.4 2.5 13.0 7.7	Pruisiner and Sunderlingam 1976
Amino pynazine	P2 <sub>1</sub> /c	3.080 3.059	4.5 9.2	Chao <i>et al</i> 1976.
2-Amino pyrimidine	Pcab	3.117 3.073	12.9 8.4	Otterson and Hope 1979
Formycin B	P2 <sub>1</sub>	3.003	10.0	Scheinbeim and Schempp 1976
Carbano hydrazide	P2 <sub>1</sub> /c	2.933 3.034	19.6 24.6	Koyama <i>et al</i> 1976
Adenine phosphate	P2 <sub>1</sub> /c	2.979	22.4	Langer 1979
Methyl-furoxan carboxamide	C2/c	3.044	37.5	Calleri <i>et al</i> 1975
Ethylguanine $\frac{1}{2}$ HCl	P $\bar{1}$	2.960 3.041	4.9 2.8	Mandel and Marsh 1975
Amino pyridine	Cc	3.123	8.6	Chao <i>et al</i> 1975
Amino thiazolo- thiadiazine-dioxide H <sub>2</sub> O	P2 <sub>1</sub> /c	3.113 2.983	6.3 22.9	Foces <i>et al</i> 1975
Mercapto purine copper I		2.932 2.938	6.2 8.8	Caira and Nassimbeni 1975
Aminomethyl pyridine	Pbca	3.001	4.2	Nahringbauer and Kvick 1977
Amino-dihydro dimethoxynaptho- thiazole	Pbca	3.093	11.1	Ekstrand and Van der Helm 1977
Theophylline	Pnma	2.962	6.3	Nakao <i>et al</i> 1977
N-acetyl histidine methyl amide	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	2.955	13.2	Harada and Ithaka 1977

Table 1. (Contd.)

Compound	Space groups	N...N (l) (in Å)	H-N...N ( $\theta$ ) (in degrees)	References
Formyl amino trizoline thione	Pna 2 <sub>1</sub>	3.130	47.5	Gors <i>et al</i> 1979
Isopyridin adenosine	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	2.863	17.3	Sprang <i>et al</i> 1978
Methylcytosine $\frac{1}{2}$ H <sub>2</sub> O	Pba 2	2.872	29.2	Srikrishnan <i>et al</i> 1978
Methyl adenine copper II dichloride dihydrate	C2/m	2.984	3.8	Slitten and Rund 1975
Diamino ethylpurine ethanol water	P2 <sub>1</sub> /c	2.960 2.953 2.988 3.060 2.981 2.894	13.5 25.8 9.4 9.4 10.0 18.1	Scarborough <i>et al</i> 1977
Adenyl propionyl tyramine 2H <sub>2</sub> O	P2 <sub>1</sub> /c	3.000	13.4	Ohki <i>et al</i> 1977
Phenyl phospho diamidate	Pbca	3.197	9.5	Bullen and Dann 1973
L (+) Histidine	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	2.785	24.7	Maddin <i>et al</i> 1972
Hexamethylene tetramine	C2/c	3.320 0.031	28.0 10.9	Mark <i>et al</i> 1978
Rifampicin	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	2.711	17.7	Gadret <i>et al</i> 1975
Butylthio carbonyl pyridine	P2 <sub>1</sub> /c	2.925	21.8	Clolleter <i>et al</i> 1973
Adenine HCl, $\frac{1}{2}$ H <sub>2</sub> O	P2 <sub>1</sub> /c	2.920	14.2	Kristenmacher and Shigematsa 1974
Pyrazolo pyrimidine thione	P2 <sub>1</sub> /c	2.866	7.9	Gadret <i>et al</i> 1974
Djaquobis copper II	P $\bar{1}$	3.075 3.403	17.8 13.3	Chiesi <i>et al</i> 1971
Amino furozo-thiadiazine dioxide	P2 <sub>1</sub> /c	3.040	20.0	Foces <i>et al</i> 1975
Formyl pyridine thio-semi carbazone	P2 <sub>1</sub> /c	2.610 2.958	57.1 5.9	Restivo and Palenik 1970
Inosine	P2 <sub>1</sub>	2.923	20.0	Munns and Tollin 1970
Thiocarbohydrazide	P2 <sub>1</sub> /c	3.044	17.8	Braibanti <i>et al</i> 1969
Ammonium hexacyano heptatrienide	P2 <sub>1</sub> /c	2.909 2.961 2.978	7.5 11.5 8.5	Edmonds <i>et al</i> 1970
Isoguanine sulphate H <sub>2</sub> O	A2/a	2.989	9.9	Subramaniam and Marsh 1971
Anilino-oxophenyl dihydroxo pyrazolo	P2 <sub>1</sub> /c	3.009	8.9	Smith 1969
Di-ammonium-amido thiophosphate	P $\bar{1}$	3.040	25.1	Mootz and Goldmann 1969

table 2. A pronounced maximum is observed in the range 2.8 Å–2.9 Å. The average value is 2.98 Å with an average deviation of 0.1 Å. Of the 92 examples considered 32 lie in the range 2.9 Å to 3.0 Å and 29 lie in the range 3.0 Å to

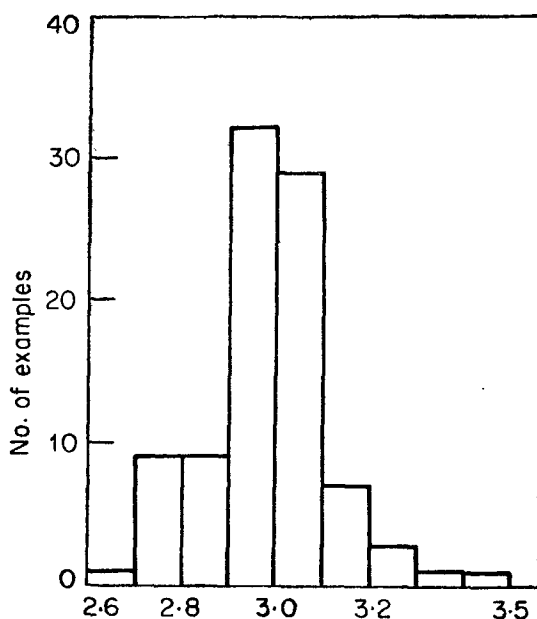


Figure 1. Histogram showing the distribution of the hydrogen bond length ( $N \cdots N$ ).

Table 2. Distribution of the hydrogen bond length ( $N \cdots N$ )

Range for $l$ (in Å)	No. of examples
2.6-2.7	1
2.7-2.8	9
2.8-2.9	9
2.9-3.0	32
3.0-3.1	29
3.1-3.2	7
3.2-3.3	3
3.3-3.4	1
3.4-3.5	1
Total	92

3.1 Å. The distribution in the range between 2.8 Å and 3.0 Å can be considered to be quite uniform and a fall-off in frequency is observed only after 3.0 Å. There is only one example (formyl pyridine thiosemicarbazone) where the length of one of the hydrogen bonds is 2.61 Å. This bond length is very short and is perhaps the weakest hydrogen bond reported so far. The other hydrogen bond length in the structure is fairly good ( $l = 2.958$  Å).

The histogram shows a rapid fall-off after 3.1 Å and it is easy to see that the number of examples lying in the ranges between 3.3 Å and 3.4 Å and between 3.4 Å and 3.5 Å has reduced to 1 in both these classes. This implies that for structures where  $2.6 > l > 3.4$ , one has to be cautious about treating them as hydrogen bonds.

It is to be noted here that in order to assess whether a particular hydrogen bond length is reasonable or not one should also take into account the dependence of  $l$  on  $\theta$  which is discussed in § 2.3 below.

## 2.2. Hydrogen bond angle ( $\theta$ )

The values of  $\theta$  for various cases are given in table 1. Of the 60 structures totalling 92 cases considered for the analysis, positions of hydrogen atoms have been reported in all of them. It has been found from the reports on these structures that different methods have been adopted for the location of hydrogen positions. In some cases positions have been obtained from difference Fourier maps and in some cases by geometrical considerations. In the present study we have used the coordinates given by the authors and as such we have not given any preference of one method over the other.

The histogram showing the distribution of hydrogen bond angle is depicted in figure 2 and numerical values are given in table 3. The histogram shows a maximum in the range  $0^\circ$ – $10^\circ$  with a mean value of  $16^\circ$ . The frequency decreases rapidly with  $\theta$  for  $\theta > 20^\circ$ . Of the 92 cases studied, 27 lie in the range between  $10^\circ$  and  $20^\circ$ . There are 26 cases where  $\theta$  is greater than  $20^\circ$ . The maximum observed  $\theta$  value is  $57^\circ$ . Thus one finds a wider spread in  $\theta$  values compared to  $l$  and non-linear N-H...N bonds occur quite abundantly.

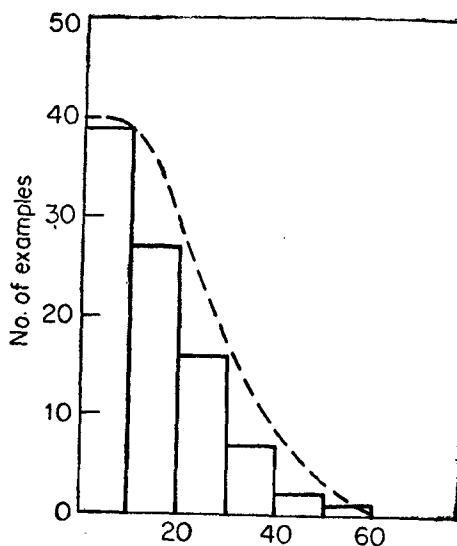


Figure 2. Histogram showing the distribution of the hydrogen bond angle  $\theta$  (H-N...N).

Table 3. Distribution of the hydrogen bond angle ( $\widehat{\text{H-N}} \cdots \text{N}$ )

Range for $\theta$ (in degrees)	No. of examples
0-10	39
10-20	27
20-30	16
30-40	7
40-50	2
50-60	1
TOTAL	92

The idea of angular dependence of hydrogen bond seems to have come from the "quantum mechanical" nature of the hydrogen bond which involves the lone pair electrons on the acceptor atom. There is only one lone pair in case of N-H...N type of hydrogen bond which should favour linear hydrogen bond. However crystal structure reports show a number of non-linear hydrogen bonds. One of the possible explanations for the non-linearity can be that the original  $sp^2$  hybridised orbitals are distorted because of the interaction of  $1s$  orbital of the hydrogen of the donor NH group. The other explanation can be thought in terms of intermolecular interactions between the donor, the hydrogen, the acceptor and other atoms in the hydrogen bonded complex. For a particular hydrogen bonded case, the minimum energy conformation will depend upon the positioning of the atoms in the donor and acceptor molecules. Hence one can conclude that the non-linearity is due to both local and long range intermolecular interactions.

Potential energy functions for N-H...O bond have been extensively studied (Lippincott and Schroeder 1955; Murthy and Rao 1970; Bratoz 1967 and Balasubramaniam *et al* 1970). Similar studies on N-H...N bonds have been lacking. The main idea in semi-empirical potential function has been to fix the optimum length from observed data in crystals and the absolute energy from thermodynamic data. A similar approach has also been put forth (McGuire *et al* 1972) for the angular dependence of hydrogen bond with a damping using a method similar to that described earlier (Lovenberg 1944). The potential function (Lippincott and Schroeder 1955 and Schroeder and Lippincott 1957) for systems of the type (X-H...Y i.e. O-H...O, N-H...O, N-H...N, etc.) has been modified (Moulton and Kromhout 1956, Ramachandran and Sasisekharan 1968) to include angular terms. As applied to the N-H...N bonds, these modifications suggest a  $\cos^2 \theta$  dependence for the hydrogen bond energies. We find that the frequency of observation decrease much faster than what is predicted by  $\cos^2 \theta$  dependence. In fact, the observations fit in very nicely with a  $\cos^6 \theta$  dependence (shown in figure 2 by dotted lines). On the basis of the analysis done here it is possible to propose an empirical potential function for N-H...N type of hydrogen bond. Such a function should have a minimum hydrogen bond energy for

$l = 2.98 \text{ \AA}$  and an angular dependence of the form  $\cos^6 \theta$ . The work is in progress and is expected to be presented in due course.

### 2.3. Correlation between $l$ and $\theta$

At this stage it is pertinent to ask if there is any correlation between the hydrogen bond length and angle. Such a correlation has been noticed earlier for N-H  $\cdots$  O bonds (Ramakrishnan and Prasad 1971). In this connection it may be mentioned that the near value of  $l$  for those hydrogen bonds which have  $\theta > 20^\circ$  is  $2.99 \text{ \AA}$  whereas the overall average is  $2.98 \text{ \AA}$ . There are cases of stizolamine chloride (Veno *et al* 1978) ( $l = 2.73 \text{ \AA}$ ,  $\theta = 33.7^\circ$ ), formyl pyridine thiosemicarbazone (Restivo and Polenik 1970) ( $l = 2.61 \text{ \AA}$ ,  $\theta = 57.1^\circ$ ) where lower values of length have higher values of angles. In the case of structures of triamino triazine (Varghese *et al* 1977) ( $l = 3.033 \text{ \AA}$ ,  $\theta = 3.4^\circ$ ), ethyl guanine  $\frac{1}{2}$  HCl (Mandel and Marsh 1975) ( $l = 3.041 \text{ \AA}$ ,  $\theta = 2.8^\circ$ ), methyl copper II dichloride dihydrate (Slitten *et al* 1975) ( $l = 2.984 \text{ \AA}$ ,  $\theta = 3.8^\circ$ ), diamino ethyl purine ethanol water (Scarborough *et al* 1977) ( $l = 3.060 \text{ \AA}$ ,  $\theta = 5.3^\circ$ ), the trend of variation of length with the angle is in the reverse way. That is while the length is larger, the angle is smaller. It can be observed from table 1 that in nearly 20% of the cases the trend is somewhat similar to what has been observed in N-H  $\cdots$  O type of hydrogen bond (Ramakrishnan and Prasad 1971) wherein the hydrogen bonds with large values of  $\theta$  tend to have a larger hydrogen bond length. Therefore, from the present data it is not possible to categorically establish that for N-H  $\cdots$  N type of hydrogen bond, the greater the angle, the larger will be the length and vice versa. This observation is reflected in the two-dimensional plot of  $l$  vs  $\theta$  in figure 3. It can be very well seen from figure that distribution is more clustered around  $\theta$  between  $10^\circ$  and  $30^\circ$  in the range of  $l$  varying from  $2.9 \text{ \AA}$  to  $3.1 \text{ \AA}$  and under this range for both  $l$  and  $\theta$ , the distribution can be said to be a random one. There are only two cases where the angle is larger than  $40^\circ$  and only one case where the

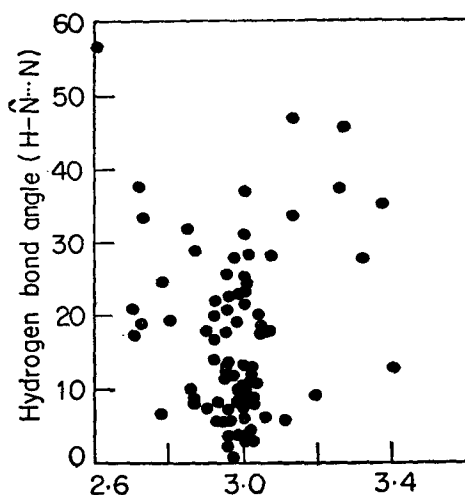


Figure 3. Two-dimensional plot of hydrogen bond length ( $l$ ) and hydrogen angle ( $\theta$ ).



angle is even larger than 50°. In the latter case it has been clearly stated by the authors (Restivo and Palenik 1970) that the hydrogen bond is the weakest one.

### 3. Conclusions

The conclusions drawn from our study on the N-H...N type of hydrogen bond are that the geometrical parameters for this bond lie in the range 2.9 Å to 3.1 Å for the bond length and 0° to 20° for the bond angle. The distribution is unlike N-H...O hydrogen bonds which have the most probable distribution in the range 2.8 Å to 2.9 Å for  $l$  and 0° to 10° for the angle  $\theta$  (see figures 2a and 3a of Ramakrishnan and Prasad 1971). The corresponding average values for the bond lengths in N-H...O and N-H...N are 2.89 Å and 2.98 Å, respectively. This suggests the fact that hydrogen bond lengths in the N-H...N bond are larger compared to N-H...O bond. From this analysis one can fairly well decide whether a particular bond is a hydrogen-bonded one or just the van der Waal's contact distance especially in ambiguous cases.

This analysis provides the ground work necessary for proposing empirical hydrogen bond potential function.

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