

## A Simple Point Charge Model for the Hydrogen Bonds of the Type $N \cdots H-O$

NADA SALAJ

*Institute of Theoretical Physics, Vanadisvägen 9, S-113 46 Stockholm, Sweden*

A simple point charge model suggested in an earlier paper, including electrostatic, repulsive, and dispersive interactions, has been applied to the intermolecular hydrogen bonds of type  $N \cdots H-O$  and  $N-H \cdots O$  between hydroxylamine molecules. According to the model used  $N-H \cdots O$  bond distance is found to be shorter (2.84 Å) than  $N \cdots H-O$  bond distance (3.15 Å).

The continued studies of the intermolecular hydrogen bonds have been extended to the hydrogen bonds of the type  $N \cdots H-O$ , *i.e.* to hydrogen bonds containing a nitrogen atom. The point charge model previously described is used and the detailed description given in the earlier paper<sup>1</sup> will not be repeated here.

The point charge model has been suggested for the intermolecular hydrogen bonds of the type



where A and B stand for groups of atoms and where the hydrogen atom, H, is supposed to be fixed to the group of atoms A, while the distance between  $A-H$  and B can be varied.

To each atom a point charge is assigned and put equal to the charge of its nucleus minus the quantum mechanically calculated total net atomic population<sup>2</sup> on the actual atom. The quantum mechanical calculations have been performed separately on the two groups of atoms,  $A-H$  and B, *i.e.* the charge distribution of the whole system  $A-H \cdots B$  is assumed to be unchanged (or changed only slightly) with the varying distance between  $A-H$  and B. Negative charges (proportional to overlap populations<sup>2</sup>) are placed midway between the atoms, where covalent bonds are supposed to exist, giving the right total charge to the group of atoms, *i.e.* to  $A-H$  and B separately. The charges describing lone pair electrons are placed so as to fit the geometry of and to give the right (*i.e.* experimental) dipole moment to the group of atoms, *i.e.* to the molecule or ion ( $A-H$  and B in this case). The charge distribution in  $A-H$  and in B being thus known, the pure electrostatic interaction of the

whole system  $A-H\cdots B$  can be calculated for various distances between  $A-H$  and  $B$ .

The dispersive and repulsive interactions are taken into account only between the hydrogen atom,  $H$ , and the nearest atom to it, say  $D$ , from the group of atoms  $B$ . The potential energy,  $V(r_{DH})$ , due to these interactions is assumed to be of the form

$$V(r_{DH}) = a_{DH} \exp(-b_{DH}r_{DH}) - (c_{DH}/r_{DH}^6) \quad (1)$$

where  $a_{DH}$ ,  $b_{DH}$ , and  $c_{DH}$  are parameters dependent on the chemical character of the atom  $D$  and also on the actual charges on atoms  $H$  and  $D$ .

As stated in the beginning of this paper the hydrogen bonds of the type  $N\cdots H-O$  are to be considered here, *i.e.* atom  $D$  is a nitrogen atom. The parameters  $a_{NH}$ ,  $b_{NH}$ , and  $c_{NH}$  are determined as follows. The expression

$$c_{NH} = \frac{\frac{3}{2}(e\hbar/\sqrt{m}) \alpha_N \alpha_H}{\sqrt{\alpha_N/N_N + \sqrt{\alpha_H/N_H}}} \quad (2)$$

given by Pitzer<sup>3</sup> has been adopted and the assumptions for  $\alpha_N$  and  $\alpha_H$  have been made in accordance with the previous article,<sup>1</sup> *i.e.*

$$\alpha_H = \text{const.} \times (1 - Q_H) \quad (3)$$

where  $Q_H$  is the point charge assigned to the hydrogen atom of the hydrogen bond under consideration, and

$$\alpha_N = \text{const.} \quad (4)$$

The values of  $c_{NN}=1807.9 \text{ \AA}^6 \text{ kcal/mole}^3$  and  $c_{HH}=45.2 \text{ \AA}^6 \text{ kcal/mole}^4$  give, using eqn. (2) and assuming  $N_N=\text{const.}$  and  $N_H=\text{const.} \times (1 - Q_H)$ , the following value for  $c_{NH}$  when  $Q_H=0$ :

$$c_{NH} = 284.9 \text{ \AA}^6 \text{ kcal/mole} \quad (5)$$

and when  $Q_H$  is different from zero:

$$c_{NH}' = c_{NH}(1 - Q_H) \quad (6)$$

Eqn. (17) in my earlier paper<sup>1</sup> has been used to calculate  $b_{NN}$  under the assumption that the van der Waals radius of nitrogen is  $1.6 \text{ \AA}$ .  $b_{NN}$  has been found to be  $4.96 \text{ \AA}^{-1}$ . This implies  $b_{NH}$  equal to  $4.34 \text{ \AA}^{-1}$ , as  $b_{NH} = \frac{1}{2}(b_{NN} + b_{HH})$  and  $b_{HH}$  is  $3.73 \text{ \AA}^{-1}$ .

As the theoretical value of  $a_{NH}$  is very uncertain<sup>5</sup> this parameter is preferably determined by adjusting it to the experimentally found results. The crystal structure of ammonium monohydrate,<sup>6</sup>  $NH_3 \cdot H_2O$ , where the short bond of  $2.78 \text{ \AA}$  between  $O$  and  $N$  is assumed to be of the type  $O-H\cdots N$ , has been used for the determination of  $a_{NH}$ . Fig. 1 gives the assumed relative positions of  $NH_3$  and  $H_2O$ , while Table 1 gives the charge distributions<sup>7,8</sup> used for the  $NH_3$  and  $H_2O$  molecules. Minimizing the total energy (which is the sum of the repulsive and dispersive parts given by eqn. (1) and the total electrostatic energy) at the  $r_{NH}=2.78 \text{ \AA}$  gives

$$a_{NH} = 1.53 \times 10^4 \text{ kcal/mole} \quad (7)$$

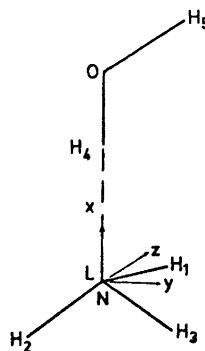
Table 1.  $x$ ,  $y$ ,  $z$  are the position coordinates in Å of the point charges in ammonium monohydrate,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , as shown in Fig. 1,  $Q$  is the strength of the corresponding point charges in  $e^+$ , where  $e^+ = 4.8 \times 10^{-10}$  e.s.u.  $D_1$ ,  $D_2$ ,  $D_3$ , and  $D_4$  are the point charges given in order to take care of the dipole moments of the further water molecules in the crystal.  $n$ 's stand for negative charges in covalent bonds while  $L$ 's stand for the lone pair electrons.

The name of the point charge	$x$ (Å)	$y$ (Å)	$z$ (Å)	$Q$
N	0.0	0.0	0.0	2.33
H <sub>1</sub>	-0.381	0.0	0.940	0.45
H <sub>2</sub>	-0.381	-0.814	-0.470	0.45
H <sub>3</sub>	-0.381	0.814	-0.470	0.45
$n_1$	-0.191	0.0	0.470	-0.56
$n_2$	-0.191	-0.407	-0.235	-0.56
$n_3$	-0.191	0.407	-0.235	-0.56
L <sub>1</sub>	0.058	0.0	0.0	-2.00
O	$d$	0.0	0.0	4.12
H <sub>4</sub>	$d-0.960$	0.0	0.0	0.28
H <sub>5</sub>	$d+0.248$	0.803	0.464	0.28
$n_4$	$d-0.480$	0.0	0.0	-0.34
$n_5$	$d+0.124$	0.402	0.242	-0.34
L <sub>2</sub>	$d+0.039$	-0.090	0.054	-2.00
L <sub>3</sub>	$d+0.039$	0.002	-0.105	-2.00
D <sub>1</sub>	$d+0.779$	2.394	1.302	1.93
D <sub>2</sub>	$d+0.657$	2.256	1.382	-1.93
D <sub>3</sub>	$d+0.779$	-2.256	1.302	1.93
D <sub>4</sub>	$d+0.657$	-2.394	1.382	-1.93

The energy of the hydrogen bond  $\text{O}-\text{H} \cdots \text{N}$  of this hydrate was found to be 10.0 kcal/mole.

The parameters  $a_{\text{NH}}$ ,  $b_{\text{NH}}$ , and  $c_{\text{NH}}$  determined in the described manner have been used to calculate a possible hydrogen bond distance between two hydroxylamine molecules,  $\text{NH}_2\text{OH}$ . Table 2 gives the point charge distribution in one  $\text{NH}_2\text{OH}$ -molecule.<sup>9</sup> Since no experimental value of the dipole

Fig. 1. The assumed relative positions of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in ammonium monohydrate,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , crystal (cf. Table 1).



**Table 2.**  $x$ ,  $y$ ,  $z$  are the position coordinates in Å of the point charges in hydroxylamine,  $\text{NH}_2\text{OH}$ .  $Q$  is the strength of the corresponding point charges in  $e^+$ , where  $e^+ = 4.8 \times 10^{-10}$  e.s.u. The  $n$ 's stand for negative charges in covalent bonds, while  $L$ 's stand for lone pair electrons. These charges have been taken from a population analysis on a SCF calculation which used Gaussian type functions as basis. The basis set consisted of seven  $s$  and three  $p$  functions on N and O, and three  $s$  and one  $p$  functions on each of the hydrogens.<sup>a</sup>

The name of the point charge	$x$ (Å)	$y$ (Å)	$z$ (Å)	$Q$
N	0.0	0.0	0.0	2.72
H <sub>1</sub>	0.842	-0.561	-0.271	0.41
n <sub>1</sub>	0.421	-0.280	-0.135	-0.60
H <sub>2</sub>	-0.842	-0.561	-0.271	0.41
n <sub>2</sub>	-0.421	-0.280	-0.135	-0.60
O	0.0	0.0	1.460	4.06
n <sub>3</sub>	0.0	0.0	0.730	-0.32
H <sub>3</sub>	0.0	0.936	1.676	0.50
n <sub>4</sub>	0.0	0.468	1.568	-0.58
L <sub>1</sub>	0.0	0.054	-0.022	-2.00
L <sub>2</sub>	+0.092	-0.051	1.499	-2.00
L <sub>3</sub>	-0.092	-0.051	1.499	-2.00

moment of this molecule seems to have been published, the value was estimated in the following way. The lone pair electrons on nitrogen were assumed to have approximately the same position as in the  $\text{NH}_3$ -molecule and the lone pair electrons on oxygen the same positions as in the  $\text{H}_2\text{O}$ -molecule (see Table 1). Then the dipole moment was calculated to be around 2 Debye. As it is not known how the two  $\text{NH}_2\text{OH}$ -molecules are hydrogen bonded to each other the following assumption was made about the  $\text{N}\cdots\text{H}-\text{O}$  bond. The nitrogen atom and its lone pair electrons in one molecule are assumed to be on the same line as the oxygen atom and the hydrogen atom nearest to this oxygen in the second molecule (see Fig. 2). All atoms are in the same plane except the pairs of hydrogen atoms nearest to the nitrogen atoms which are symmetrically out of the plane. If the position coordinates of one  $\text{NH}_2\text{OH}$ -molecule (1) are those given by Table 2 then the position coordinates of the second molecule (2) are given in accordance with the above description to be

$$\left. \begin{aligned} x' &= x \\ y' &= -0.9877 y + 0.1572 (z - 1.460) + 0.9265 d \\ z' &= 0.1572 y + 0.9877 (z - 1.460) - 0.3750 d \end{aligned} \right\} \quad (8)$$

where  $d$  is the distance in Å between the atoms  $\text{N}_1$  and  $\text{O}_2$  (see Fig. 2). The equilibrium distance,  $d_{\text{eq}}$ , between  $\text{N}_1$  and  $\text{O}_2$  is found to be 3.15 Å. The energy of this hydrogen bond,  $\text{N}_1\cdots\text{H}-\text{O}_2$  is found to be around 0.7 kcal/mole. This energy differs very much from the energy obtained for the hydrogen bond in  $\text{NH}_3\cdots\text{H}_2\text{O}$ . The smallness of the energy in the  $\text{NH}_2\text{OH}$ -case is primarily due to the more positively charged N and H nearest to oxygen in  $\text{NH}_2\text{OH}$

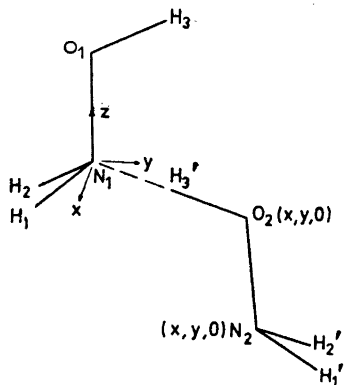


Fig. 2. The approximate relative positions of two hydroxylamine molecules in case a hydrogen bond of the type  $N \cdots H-O$  is assumed (see the text).

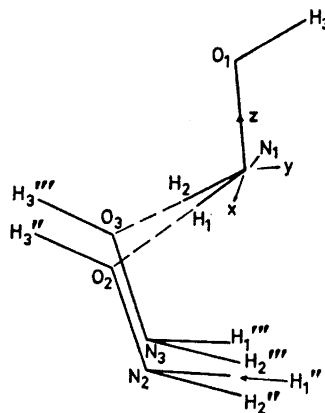


Fig. 3. The approximate relative positions of three hydroxylamine molecules in case a hydrogen bond of the type  $N-H \cdots O$  is assumed (see the text).

than in  $NH_3 \cdot H_2O$ , which means a more repulsive electrostatic interaction which also results in a rather long bond between  $N_1$  and  $O_2$ .

In the discussion above it has been pointed out that it is not known in which way the  $NH_2OH$ -molecules are hydrogen bonded. This is the reason why another possibility of hydrogen bonding has been assumed in the following way. The nitrogen atom,  $N_1$ , and one of the hydrogen atoms,  $H_1$ , nearest to  $N_1$  in one  $NH_2OH$ -molecule are assumed to be almost on the same line as the oxygen atom,  $O_2$ , and one pair of its lone pair electrons,  $L_2''$ , in the second  $NH_2OH$ -molecule. There is also a third  $NH_2OH$ -molecule (see Fig. 3) which is the mirror image of the second one in the  $yz$ -plane.  $N_1$ ,  $O_1$ , and  $H_3$  are all in the same  $yz$ -plane,  $N_2$ ,  $O_2$ , and  $H_3''$  are also in the same plane which is parallel with the  $yz$ -plane. This means a hydrogen bond of the type  $N-H \cdots O$  has been assumed. If the position coordinates of the first mentioned  $NH_2OH$ -molecule (1) are given by Table 2, then the position coordinates of the second molecule (2) are given in accordance with the above description to be

$$\left. \begin{aligned} x'' &= -x + 0.8039 d \\ y'' &= -0.9796 y + 0.1232 (z - 1.460) - 0.5356 d \\ z'' &= 0.1232 y + 0.9796 (z - 1.460) - 0.2587 d \end{aligned} \right\} \quad (9)$$

and those of the third one (3) are given to be

$$\left. \begin{aligned} x''' &= -x - 0.8039 d \\ y''' &= y'' \\ z''' &= z'' \end{aligned} \right\} \quad (10)$$

where  $d$  is the distance in Å between  $N_1$  and  $O_2$  but also between  $N_1$  and  $O_3$  (see Fig. 2). The parameters  $a_{OH}$ ,  $b_{OH}$  and  $c_{OH}$  used in the previous paper<sup>1</sup> have been used in this case again [ $a_{OH}=0.5 \times 10^4$  kcal/mole,  $b_{OH}=4.16$  Å<sup>-1</sup>,  $c_{OH}=90.4$  Å<sup>6</sup> kcal/mole]. The equilibrium distance,  $d_{eq}$ , is obtained with these values to be 2.84 Å, while the energy of this bond, N—H···O is found to be around 2.7 kcal/mole.

Summarizing, this would mean that N—H···O bond distance would be 2.84 Å while the corresponding N···H—O distance would be 3.15 Å under the above assumptions on the relative positions of the molecules. This result suggests alternative b) discussed by Meyers and Lipscomb,<sup>10</sup> where the corresponding types of distances are supposed to be 2.74 Å and 3.07 Å.

*Acknowledgement.* This investigation has been supported by grants from the *Swedish Natural Science Research Council*. The data machine computations have been supported by *Kungl. Statskontoret*. The author is indebted to Professor Inga Fischer-Hjalmars for having suggested the subject treated here and for her valuable help during preparation of this paper. Thanks are due to Mr. L. Norén for assistance in the numerical computations. The author is grateful to Dr. B. Roos and Civ.Ing. Per Siegbahn for making their SCF calculation on hydroxylamine available.

#### REFERENCES

1. Salaj, N. *Acta Chem. Scand.* **23** (1969) 1534.
2. Mulliken, R. S. *J. Chem. Phys.* **23** (1955) 1833.
3. Pitzer, K. S. *Advan. Chem. Phys.* **2** (1959) 59.
4. Scott, R. A. and Scheraga, H. A. *J. Chem. Phys.* **42** (1965) 2209.
5. Mason, E. A. and Rice, W. E. *J. Chem. Phys.* **22** (1954) 522.
6. Olovsson, I. and Tampleton, D. H. *Acta Cryst.* **12** (1959) 827.
7. Duncan, A. B. F. *J. Chem. Phys.* **27** (1957) 423.
8. Kaplan, H. *J. Chem. Phys.* **26** (1957) 1704.
9. Roos, B. and Siegbahn, P. *Private communication*.
10. Meyers, E. A. and Lipscomb, W. N. *Acta Cryst.* **8** (1955) 583.

Received September 12, 1969.