

Hydrogen Bond Studies

43.* Calculations of the Electrostatic Energy in Hydrazinium Hydrogenoxalate, $N_2H_5HC_2O_4$

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The electrostatic energy for different orientations of the $-NH_2$ and $-NH_3^+$ groups of the $N_2H_5^+$ ion in $N_2H_5HC_2O_4$ has been calculated using a simple point charge model. The conformation of minimum electrostatic energy has been determined. This conformation is in agreement with the results obtained from neutron diffraction studies of the compound. An estimate of the energy barrier associated with the reorientation of the $-NH_3^+$ group about the N-N axis has also been made, resulting in a value of 7.5 kcal/mol. A reorientation of the $-NH_2$ group alone is not possible. In all cases a potential energy of the Lennard-Jones type has been added to the electrostatic energy, to account for the van der Waals forces present.

Hydrazinium hydrogenoxalate, $N_2H_5HC_2O_4$, has recently been studied by a series of complementary techniques at this Institute. The crystal structure has been determined by X-ray¹ and neutron diffraction methods.² Infrared spectroscopic studies of the compound together with its deuterated analogue, $N_2D_5DC_2O_4$, have given symmetry information supporting the choice of space group in the structure determinations.³ Proton magnetic resonance spectra at different temperatures have been used to study the dynamical properties of the compound.⁴

In the present work the electrostatic energy of $N_2H_5HC_2O_4$ has been calculated for different orientations of the $-NH_2$ and $-NH_3^+$ groups of the $N_2H_5^+$ ion to determine the conformation of minimum electrostatic energy. A simple point charge model for the distribution of electric charges has been used. Baur⁵ has found that the orientations of water molecules in a number of hydrogen-bonded hydrates can be quite accurately determined by this method. Similar calculations have also been made earlier for $LiN_2H_5SO_4$.⁶

It is also of interest to make a theoretical estimate of the energy barriers associated with the reorientation of the $-NH_2$ and $-NH_3^+$ groups. These

* Part 42. *Acta Chem. Scand.* 25 (1971) 101.

values can then be compared with the experimental results obtained from the PMR studies.

A purely electrostatic model cannot be expected to give the correct conformation in all situations as the van der Waals forces are neglected (*cf.* Ref. 7). Accordingly, in the present calculations, a potential energy of the Lennard-Jones type has been added to the electrostatic terms.

Crystals of hydrazinium hydrogenoxalate are monoclinic, space group $P2_1/m$, with four formula units in a cell of dimensions: $a=3.580$, $b=13.321$, $c=5.097$ Å, $\beta=102.62^\circ$. Fig. 1 shows the crystal structure, in particular the bonding coordination around the hydrazinium ion as determined by neutron diffraction. For discussion of the hydrogen bonds present, see Ref. 2.

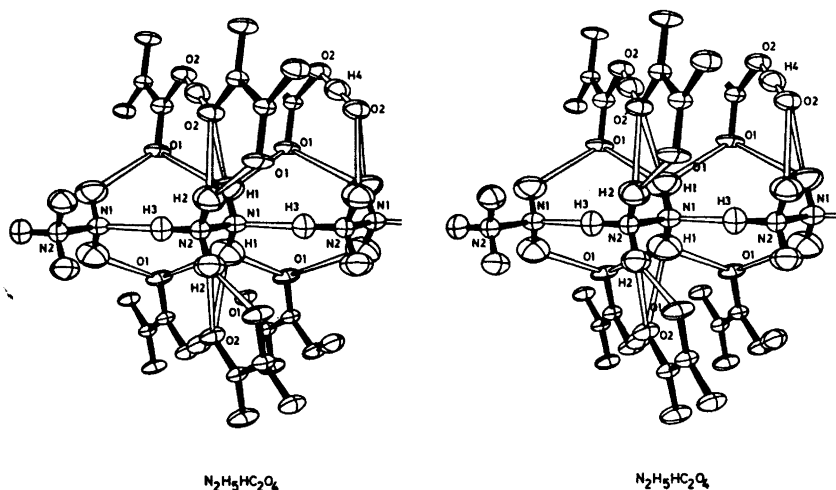


Fig. 1. A stereoscopic drawing, showing the bonding arrangement around an $N_2H_5^+$ ion in $N_2H_5HC_2O_4$. The atoms are represented by ellipsoids, corresponding to the anisotropic temperature coefficients in Ref. 2, scaled to enclose 50 % probability.

THE CALCULATIONS

The electrostatic energy of the compound was calculated for different angles of rotation of the $-NH_2$ and $-NH_3^+$ groups about the N—N axis of the hydrazinium ion. The electric charges were chosen as point charges, placed at the centre of the atoms. The charges were chosen by consideration of the electronegativities of the atoms and the interatomic distances within the ions. The magnitude of the electrostatic energy is directly dependent upon this choice of charges. However, as pointed out by Baur,⁵ the positions of the maxima and minima in the electrostatic energy are insensitive to small variations in the choice of electric charges on the atoms. The atomic coordinates taken from the neutron diffraction study and the charges are given in Table 1. The calculations were made using a slightly modified version of the program MANIOC written by Baur.⁵ For convenience the following values for the

Table 1. Atomic coordinates and electric charges.

| Atom | Charge (atomic units) | <i>x</i> | <i>y</i> | <i>z</i> |
|------|--------------------------|----------|----------|----------|
| C | 0.10 | 0.6189 | 0.0246 | 0.6279 |
| N(1) | -1.00 | 0.2930 | 0.2500 | 0.0804 |
| N(2) | -0.50 | 0.1029 | 0.2500 | 0.3020 |
| O(1) | -0.45 | 0.5873 | 0.1155 | 0.6658 |
| O(2) | -0.50 | 0.8375 | -0.0364 | 0.7847 |
| H(1) | 0.50 | 0.2068 | 0.1876 | -0.0238 |
| H(2) | 0.50 | 0.1998 | 0.1877 | 0.4121 |
| H(3) | 0.50 | -0.1913 | 0.2500 | 0.2305 |
| H(4) | 0.70 | 0.0000 | 0.0000 | 0.0000 |

bond lengths and angles in the $N_2H_5^+$ ion were used: $N-H=1.02$ Å, $N-N-H=109.5^\circ$, $H-N-H=109.5^\circ$. The experimentally determined values are: $N-H=1.00-1.04$ Å, $N-N-H=105.6-110.0^\circ$, $H-N-H=109.0-113.0^\circ$.²

The $-NH_2$ group was rotated around the $N-N$ axis through 360° in steps of 30° . For each orientation of the $-NH_2$ group the $-NH_3^+$ group was rotated 120° in steps of 30° . Near the minimum points of the curves, describing the variation of the electrostatic energy, calculations were made for steps of 3° .

It should be noted that the symmetry operations within the crystal have the effect of applying a given reorientation to all symmetry equivalent groups.

Two series of calculations were made:

1. All $-NH_2$ and $-NH_3^+$ groups in the crystal were allowed to rotate.
2. All $-NH_2$ groups were set to their experimentally determined orientations. Every second $-NH_3^+$ group in the hydrogen-bonded chains was allowed to rotate. The other $-NH_3^+$ groups were set to their experimentally determined orientations.

In all cases a potential energy of the Lennard-Jones type was added to the electrostatic energy. The potential energy function has the following form:

$$V(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{r_{ij}^0}{r_{ij}} \right)^{12} - \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right]$$

where

$$r_{ij}^0 = 0.8909 [r_{VDW}(i) + r_{VDW}(j)]$$

and

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$$

The parameters r_{VDW} and ε were chosen in accordance with earlier works of this type.^{6,7} The values are given in Table 2.

RESULTS

1. All $-NH_2$ and $-NH_3^+$ groups in the structure reorient simultaneously. The results of the calculations are illustrated in Figs. 2 and 3. In Fig. 2a the electrostatic energy is plotted *versus* the angle of rotation of the $-NH_2$ group.

The four different curves correspond to different orientations of the $-\text{NH}_3^+$ group. The variation of the van der Waals energy is illustrated in Fig. 2b.

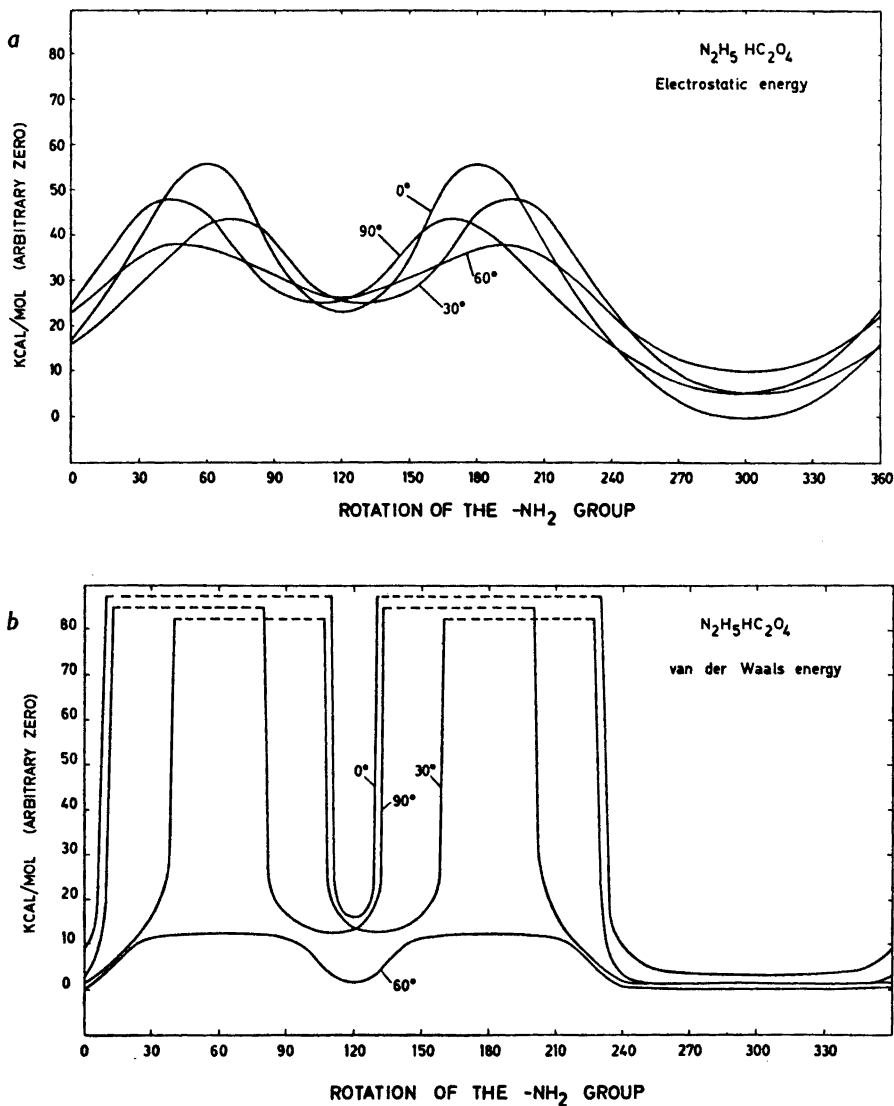


Fig. 2. a. The electrostatic energy for different orientations of the $-\text{NH}_2$ group with respect to the N-N axis. b. The corresponding van der Waals energy. The four curves correspond to different orientations of the $-\text{NH}_3^+$ group. The experimentally determined orientation of the $-\text{NH}_3^+$ group corresponds to the angle 300° in the figure. The curves denoted by 0° correspond to the experimentally determined position of the $-\text{NH}_3^+$ group.

Table 2. Constants used in the Lennard-Jones 12-6 potential.

| Atom | r_{VDW} (Å) | ϵ (kcal/mol) |
|------|----------------------|-----------------------|
| O | 1.4 | 0.054 |
| N | 1.5 | 0.054 |
| H | 1.2 | 0.020 |

All $-\text{NH}_2$ and $-\text{NH}_3^+$ groups in the crystal were allowed to rotate simultaneously. The minimum point on the curve of lowest energy at a rotation angle of 300° for the $-\text{NH}_2$ group (Fig. 2) corresponds to the experimentally determined orientations of the $-\text{NH}_2$ and $-\text{NH}_3^+$ groups. The curves denoted by 0° in Fig. 2 correspond to the experimentally determined orientation of the $-\text{NH}_3^+$ group. The van der Waals energy has its minimum for an orientation 60° from the experimentally determined position for the $-\text{NH}_3^+$ group. The difference in van der Waals energy between this minimum point and the experimentally determined position is 3.2 kcal/mol. However, on summing the electrostatic and van der Waals energies, the total energy has its minimum for the experimentally determined orientation of the N_2H_5^+ ion.

From Figs. 2a and 2b it is clear that a reorientation of the $-\text{NH}_2$ group alone is not possible. A coupled reorientation of the $-\text{NH}_2$ and $-\text{NH}_3^+$ groups is more plausible, but the energy barrier is still rather high.

The $-\text{NH}_3^+$ group, on the other hand, can change its orientation without having to overcome high energy barriers. Fig. 3 shows the variation of the electrostatic energy with the angle of rotation of the $-\text{NH}_3^+$ group. The position of the $-\text{NH}_2$ group is set to the experimentally determined orientation. The sum of the electrostatic and van der Waals energies (= total energy) is also shown in Fig. 3. The minimum points are separated by barriers of 7.1 kcal/mol.

2. *One $-\text{NH}_3^+$ group is allowed to reorient.* The program used for the calculations does not allow the reorientation of a single group of atoms in the structure. Groups related by symmetry operations including translations must

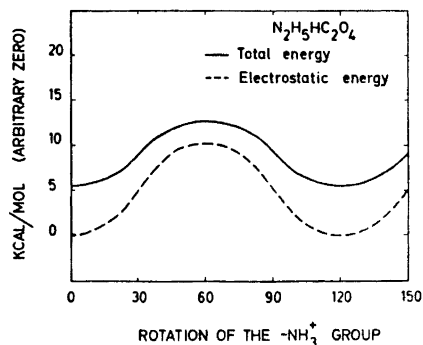


Fig. 3. The electrostatic energy and the sum of the electrostatic and van der Waals energies for different orientations of the $-\text{NH}_3^+$ group. The $-\text{NH}_2$ group is set to the experimentally determined orientation. The experimentally determined orientation of the $-\text{NH}_3^+$ group corresponds to the angle 0° (or 120°), in the figure.

undergo the same reorientation. Therefore, in order to estimate the height of the barrier when only one $-\text{NH}_3^+$ group is allowed to rotate, a series of calculations were made in which every second $-\text{NH}_3^+$ group in a hydrogen-bonded chain was allowed to rotate. The orientations of the other $-\text{NH}_3^+$ groups and all $-\text{NH}_2$ groups were not changed. The ultimate result was little different from that of the previous calculation. A barrier height of 7.5 kcal/mol was obtained in this case. This energy barrier is due mainly to interactions with atoms outside the N_2H_5^+ ion. The internal energy barrier calculated from electrostatic and van der Waals interactions within a single N_2H_5^+ ion, using the same point charge model, is only about 0.8 kcal/mol.

In a recent PMR study of $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4^4$ it was found that the second moment decreased rapidly in the region 210–280°K. This effect was interpreted as resulting from the onset of reorientation of the $-\text{NH}_3^+$ group about the N–N axis. An estimate of the energy barrier associated with this reorientation based on PMR data gave a value of 8.1 kcal/mol, which is in good agreement with the results obtained here.

Acknowledgements. This work has been supported by grants from the *Swedish Natural Science Research Council*, which are hereby gratefully acknowledged.

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Received June 4, 1970.