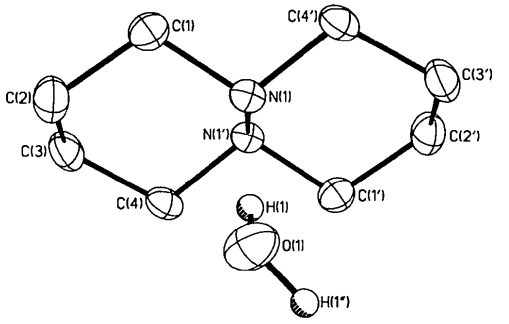


Fig. 1. Molecular structure of (1).$H_2O$ with methylene-group hydrogens omitted for clarity. Non-hydrogen atoms are drawn to enclose 50% probability density.

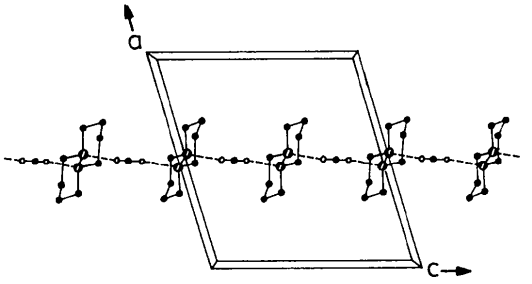


Fig. 2. Part of the crystal structure of (1).$H_2O$ viewed down the *b* axis and showing the hydrogen-bonded chain ···(1)···$H_2O$···(1)··· along the *c* axis.

107·7 (1)°, which compares favourably with other tetraalkylhydrazine structures having the N lone pairs *anti* which have N—N distances in the range 1·47–1·51 Å (Nelsen, Hollinsed & Calabrese, 1977; Nelsen, Hollinsed & Kessel, 1978; Katritzky *et al.*, 1980). In hydrazine structures having the N lone pairs in an approximately *gauche* conformation, the N—N distances are shorter, in the range 1·44–1·46 Å; they also tend to have larger C—N—C bond angles (Nelsen, Hollinsed & Calabrese, 1977; Spagna & Vaciago, 1978; Katritzky *et al.*, 1980). This difference in the N—N bond lengths between *anti* or *syn* and *gauche* hydrazines has been discussed in detail elsewhere (Nelsen, Hollinsed & Calabrese, 1977; Nelsen, 1981, 1986).

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# Structure of Histaminium Dinitrate*

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**Abstract.** $C_5H_{11}N_3^{2+}.2NO_3^-$, $M_r = 237·17$, monoclinic, $P2_1/c$, $a = 7·083$ (2), $b = 11·775$ (3), $c = 12·930$ (2) Å, $\beta = 105·13$ (2)°, $V = 1041·0$ (4) Å$^3$, $Z = 4$, $D_m = 1·52$ (1), $D_x = 1·513$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·094$ mm$^{-1}$, $F(000) = 496$, room temperature, $R = 0·058$ for 829 observed reflections.

* 4-(2-Ammonioethyl)imidazolium dinitrate.

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The side chain has an unusual conformation, the C—C—C—N torsion angle being −57·8 (5)°. The structure contains a three-dimensional network of hydrogen bonds with N(1)—H, C(2)—H, N(3)—H (imidazole) and ammonium groups of the chain acting as donors and the nitrate O atoms as acceptors.

**Introduction.** The histamine group functions as a nucleophile towards transition-metal ions in a variety of biologically important molecules, *e.g.* in the heme system and in metalloproteins, as well as in proton-transfer processes. There have been several crystal-structure determinations of histamine complexes and salts. Some of them (Veidis, Palenik, Schaffrin & Trotter, 1969; Bonnet & Jeannin, 1972; Yamane, Ashida & Kakudo, 1973; Bonnet, Jeannin & Laaouini, 1975) deal with the histaminium dication. The present study has been undertaken as part of our studies of the histamine system.

**Experimental.** Crystals from water, density by flotation, 15 reflections with $12 < 2\theta < 26°$ used to obtain lattice parameters, 1660 unique reflections up to $2\theta = 48°$ ($h$: −8→7, $k$: 0→13, $l$: 0→14) measured on a Syntex $P2_1$ diffractometer, crystal 0·3 × 0·45 × 0·45 mm, graphite-monochromated Mo $K\alpha$ radiation, profile analysis according to Lehmann & Larsen (1974), no significant intensity variations for two check reflections ($23\bar{1}$ and $2\bar{3}1$) monitored every 100 reflections, no absorption correction. Structure solved by direct methods *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), $\sum w(\Delta F)^2$ minimized in full-matrix least-squares refinement using *SHELX*76 (Sheldrick, 1976), 829 observed reflections with $I \geq 2\sigma(I)$, $w = \sigma^{-2}(F)$ from counting statistics, H-atom positions from $\Delta\rho$ map and not refined, extinction $x = 0{\cdot}00220\ (17)$, $F_c' = F_c(1-0{\cdot}0001xF_c^2/\sin\theta)$, final $R = 0{\cdot}058$, $wR = 0{\cdot}0488$, $S = 5{\cdot}593$, $|\Delta/\sigma|_{max}$ in the final refinement cycle 0·005, $\Delta\rho_{max} = 0{\cdot}32$, $\Delta\rho_{min} = -0{\cdot}23$ e Å$^{-3}$, scattering factors from *International Tables for X-ray Crystallography* (1974). Other programs used: *PLUTO*78 (Motherwell & Clegg, 1978) and those described by Jaskólski (1982), RIAD32 computer.

**Discussion.** The atomic parameters and bond lengths and angles are given in Tables 1 and 2.* Fig. 1 shows the atom-numbering scheme of the ions.

The imidazole bond lengths and angles are similar to those found in other histaminium dications (Veidis *et al.*, 1969; Bonnet & Jeannin, 1972; Bonnet *et al.*, 1975; Yamane *et al.*, 1973). A slight difference is observed for the C(2)—N(3) bond; this has a value of 1·293 (7) Å in the present structure, whereas the average value for other histaminium dications is 1·328 (5) Å. The N(1)—C(2) and C(2)—N(3) bonds in the present structure are shorter than those found in imidazolium phosphate [both 1·320 (4) Å; Blessing & McGandy, 1972] and

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| N(1) | 0·574 (1) | 0·4570 (3) | 0·3855 (4) | 0·068 (2) |
| C(2) | 0·4166 (9) | 0·3951 (7) | 0·3523 (5) | 0·069 (2) |
| N(3) | 0·4659 (7) | 0·2891 (4) | 0·3579 (3) | 0·057 (2) |
| C(4) | 0·6654 (8) | 0·2799 (4) | 0·3959 (4) | 0·047 (2) |
| C(5) | 0·7329 (8) | 0·3863 (5) | 0·4123 (5) | 0·060 (2) |
| C(6) | 0·7726 (8) | 0·1700 (5) | 0·4102 (5) | 0·071 (3) |
| C(7) | 0·7457 (9) | 0·1009 (4) | 0·5025 (5) | 0·066 (3) |
| N(8) | 0·8053 (6) | 0·1596 (4) | 0·6070 (4) | 0·062 (2) |
| N(9) | 0·3184 (9) | 0·2394 (5) | 0·0829 (4) | 0·064 (2) |
| O(1) | 0·3004 (7) | 0·3433 (4) | 0·0852 (4) | 0·098 (2) |
| O(2) | 0·4872 (6) | 0·1945 (3) | 0·1141 (3) | 0·065 (2) |
| O(3) | 0·1773 (6) | 0·1751 (4) | 0·0514 (4) | 0·090 (2) |
| N(10) | 0·1002 (9) | 0·1007 (5) | 0·2660 (4) | 0·066 (2) |
| O(4) | 0·2715 (7) | 0·0697 (3) | 0·3086 (3) | 0·078 (2) |
| O(5) | −0·0259 (7) | 0·0303 (4) | 0·2332 (4) | 0·120 (3) |
| O(6) | 0·0686 (6) | 0·2054 (4) | 0·2599 (3) | 0·083 (2) |

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with their e.s.d.'s*

| | | | |
|---|---|---|---|
| N(1)—C(2) | 1·308 (7) | C(7)—N(8) | 1·477 (6) |
| C(2)—N(3) | 1·293 (7) | N(9)—O(1) | 1·231 (5) |
| N(3)—C(4) | 1·373 (6) | N(9)—O(2) | 1·273 (6) |
| C(4)—C(5) | 1·338 (7) | N(9)—O(3) | 1·235 (6) |
| C(5)—N(1) | 1·369 (7) | N(10)—O(4) | 1·249 (6) |
| C(4)—C(6) | 1·487 (7) | N(10)—O(5) | 1·211 (5) |
| C(6)—C(7) | 1·497 (8) | N(10)—O(6) | 1·252 (6) |

| | | | |
|---|---|---|---|
| C(5)—N(1)—C(2) | 108·5 (5) | C(6)—C(7)—N(8) | 114·2 (5) |
| N(1)—C(2)—N(3) | 108·9 (5) | O(2)—N(9)—O(1) | 120·0 (6) |
| C(2)—N(3)—C(4) | 109·5 (5) | O(3)—N(9)—O(1) | 122·5 (6) |
| N(3)—C(4)—C(5) | 106·0 (5) | O(3)—N(9)—O(2) | 117·5 (5) |
| C(4)—C(5)—N(1) | 107·1 (5) | O(5)—N(10)—O(4) | 119·8 (6) |
| C(5)—C(4)—C(6) | 130·2 (5) | O(6)—N(10)—O(4) | 117·0 (5) |
| N(3)—C(4)—C(6) | 123·9 (5) | O(6)—N(10)—O(5) | 123·2 (7) |
| C(4)—C(6)—C(7) | 113·9 (5) | | |

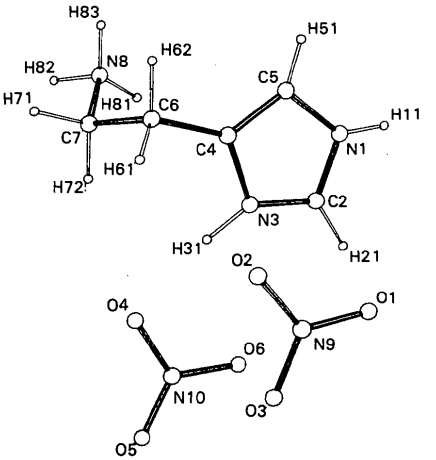


Fig. 1. A perspective view of the ions with atomic numbering scheme.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51043 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sulfate [1·323 (4) and 1·333 (4) Å, respectively; Freeman, Huq, Rosalky & Taylor, 1975]. The ring angles in the histaminium and imidazolium cations are quite similar. However, the bond lengths mentioned above are different from those found in histamine complexes [*e.g.* N(1)–C(2) 1·335 (4), 1·338 (5) Å; C(2)–N(3) 1·316 (4), 1·317 (4) Å; Wojtczak, Jaskólski & Kosturkiewicz, 1985]. The C(5)–C(4)–N(3), C(4)–N(3)–C(2) and N(3)–C(2)–N(1) ring angles of the reported structure [106·0 (5), 109·5 (5) and 108·9 (5)°, respectively] are different from average values found in histamine complexes [108·8 (2), 105·9 (2) and 110·8 (2)°, respectively; Wojtczak *et al.*, 1985, and references cited therein]. The imidazole ring is planar ($\chi^2 = 1{\cdot}81$).

The bond lengths and angles of the side chain are similar to those found in other histamine derivatives. The side chain has an unusual conformation (*gauche*), the C(4)–C(6)–C(7)–N(8) and C(5)–C(4)–C(6)–C(7) torsion angles being −57·8 (5) and 109·7 (7)°, respectively. The corresponding values in other histaminium structures vary from −178·9 (10) to −171·0 (6)° and from 26·4 (8) to −9·2 (15)°, respectively (Bonnet & Jeannin, 1972; Bonnet *et al.*, 1975; Yamane *et al.*, 1973). Only in histaminium phosphate has the opposite value of C(5)–C(4)–C(6)–C(7) been found [−100·8 (3)°; Veidis *et al.*, 1969]. The reported geometry of the side chain is similar to that found in the monodentate histaminium ligand [torsion angles of −69·4 (4) and 92·1 (4)°, respectively; Wojtczak, Jaskólski & Kosturkiewicz, 1983]. Both steric effects and hydrogen bonds could be responsible for this similarity.

The nitrate ions are planar and have a geometry [N–O distances 1·211 (5) to 1·273 (6) Å, O–N–O angles 117·0 (5) to 123·2 (7)°] similar to that found in other $NO_3^-$-containing structures.

There is a three-dimensional network of hydrogen bonds in the structure with N(1)–H, C(2)–H, N(3)–H and ammonium groups of the chain acting as donors and the nitrate O atoms as acceptors (Fig. 2, Table 3).

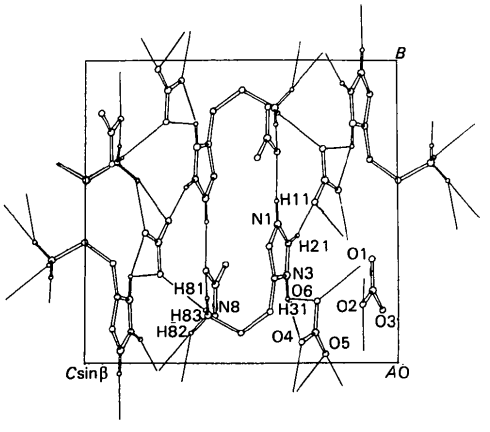


Fig. 2. Projection of the structure down the *a* axis showing hydrogen bonds.

Table 3. *Geometry of the hydrogen bonds*

| *D*–H···*A* | *D*–H (Å) | H···*A* (Å) | *D*···*A* (Å) | *D*–H···*A* (°) |
|---|---|---|---|---|
| N(1)–H(11)···O(2$^{i}$) | 0·92 | 1·91 | 2·831 (6) | 176 |
| C(2)–H(21)···O(5$^{ii}$) | 1·03 | 2·14 | 3·133 (8) | 161 |
| N(3)–H(31)···O(4) | 0·99 | 1·95 | 2·919 (6) | 166 |
| N(3)–H(31)···O(6) | 0·99 | 2·38 | 2·939 (6) | 115 |
| N(8)–H(81)···O(2$^{iii}$) | 1·00 | 1·86 | 2·853 (6) | 173 |
| N(8)–H(82)···O(4$^{iv}$) | 1·01 | 2·11 | 3·014 (6) | 147 |
| N(8)–H(82)···O(5$^{iv}$) | 1·01 | 2·40 | 3·167 (6) | 132 |
| N(8)–H(83)···O(6$^{v}$) | 1·01 | 2·30 | 2·827 (6) | 112 |

Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $1-x, -y, 1-z$; (v) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The N(1)–H group forms a hydrogen bond with O(2) and the C(2)–H group acts as a donor in a CH···O(5) bond. The N(3)–H group forms a bifurcated hydrogen bond to O(4) and O(6) of the same nitrate ion [N(10)]. The ammonium N(8)–H(81) and N(8)–H(83) groups are involved in NH···O(2)($x, \frac{1}{2}-y, \frac{1}{2}+z$) and NH···O(6)($1+x, \frac{1}{2}-y, \frac{1}{2}+z$) bonds, respectively. The third hydrogen of the ammonium group forms a bifurcated bond with O(4) and O(5) of the N(10)($1+x, \frac{1}{2}-y, \frac{1}{2}+z$) nitrate ion. The N(9) nitrate ion is involved in two hydrogen bonds, both *via* the O(2) atom. The N(10) nitrate ion forms as many as six hydrogen bonds, each O atom acting as an acceptor in two of them.

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