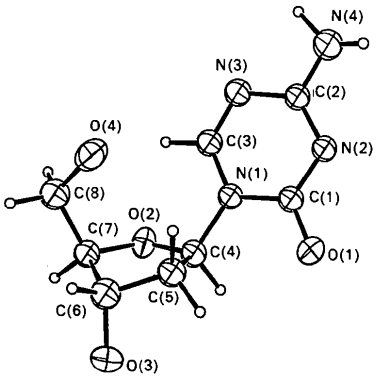

Fig. 1. Molecular structure for decitabine showing 50% probability thermal ellipsoids for the non-H atoms, and the atom-numbering scheme. H atoms on O(3) and O(4) were not located.

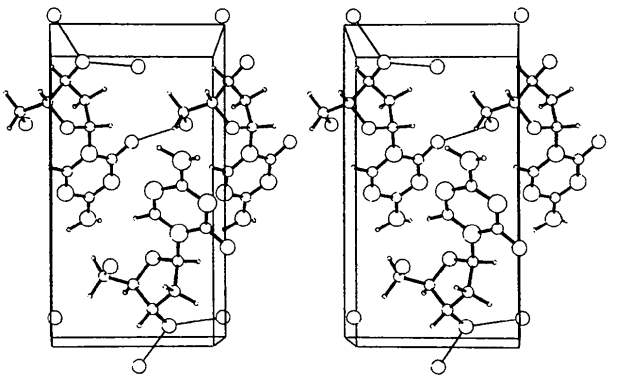

Fig. 2. Stereoscopic view of the unit-cell contents of decitabine monohydrate. Short O···O contacts involved in H bonding are shown by thin connecting lines.

lengths, arising from the small size of the data set, precludes detailed comparison with related systems.

The packing of the molecules is shown in Fig. 2. There appears to be an intermolecular H bond between O(4) and O(1) at $(x, y-1, z)$; the O···O distance is 2·747 (12) Å. The single water molecule, which appears to be crucial for non-hygroscopic crystal formation, is involved in H bonding to two O(3) atoms from different molecules; O(5)···O(3) is 2·717 (11) Å and O(5)···O(3) at $(-x, \frac{1}{2}+y, 1-z)$ is 2·676 (11) Å. The single H atom attached to the water O atom, which was located in a difference Fourier map, refined satisfactorily giving a O(5)—H(5) distance of 0·79 (8) Å. It does not lie along the short O(5)···O(3) vectors listed above, but lies along the vector to O(1) at $(x, y, 1+z)$; this O···O vector is 2·897 (9) Å in length. It is curious that no H atoms corresponding to the second water H, or attached to O(3) and O(4), could be located even though all other H atoms gave significant peaks in difference Fourier maps.

We thank the SERC for financial support and the University of Leicester Computer Centre for use of computing facilities.

References

BEN-HATTAR, J. & JIRICNY, J. (1986). *J. Org. Chem.* **51**, 3211–3213.

CLEGG, W. & SHELDRICK, G. M. (1984). *Z. Kristallogr.* **167**, 23–27.

MOMPARLER, R. L. (1985). *Pharmacol. Ther.* **30**, 287–299.

MOMPARLER, R. L., RIVARD, G. E. & GYGER, M. (1985). *Pharmacol. Ther.* **30**, 277–286.

PISKALA, A. & SORM, F. (1978). *Nucleic Acid Chemistry*, Vol. 1, edited by L. TOWNSEND & R. TIPSON, pp. 443–449. New York: Wiley.

PISKALA, A., SYNACKOVA, M., TOMANKOVA, H., FIEDLER, P. & ZIZKOWSKY, V. (1978). *Nucleic Acids Res.* **4**, s109–s113.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

SRIVASTAVA, P. C., ROBBINS, R. K., TAKUSAGAWA, F. & BERMAN, H. M. (1981). *J. Heterocycl. Chem.* **18**, 1659–1662.

Acta Cryst. (1991). C**47**, 1420–1423

Structure of Diprotonated DL-Histidinium Dinitrate

BY S. ASATH BAHADUR AND R. K. RAJARAM

School of Physics, Madurai Kamaraj University, Madurai-625 021, *India*

AND M. NETHAJI

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, *India*

(*Received* 29 *June* 1990; *accepted* 9 *October* 1990)

Abstract. $C_6H_{11}N_3O_2^{2+}.2NO_3^-$, $M_r = 281{\cdot}18$, monoclinic, $P2_1/a$, $a = 8{\cdot}370\ (2)$, $b = 14{\cdot}973\ (3)$, $c = 9{\cdot}342\ (2)$ Å, $\beta = 100{\cdot}69\ (2)°$, $V = 1150\ (1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}622$ (flotation), $D_x = 1{\cdot}623$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}62$ cm^{-1}, $F(000) = 584$, $T = 293$ K, $R = 0{\cdot}035$, $wR = 0{\cdot}037$ for 1104

0108-2701/91/071420-04$03.00

unique reflections with $I > 3\sigma(I)$. In addition to the usual amino NH_3^+ group, the carboxylate group and the imidazole ring of the histidine molecule are protonated. Hence this compound is diprotonated. One O atom of one of the nitrate groups is distorted.

Introduction. The molecular stereochemistry of the amino acid histidine has been the subject of several crystal structure analyses: L-histidine hydrochloride monohydrate (Donohue, Lavine & Rollett, 1956; Donohue & Caron, 1964; Oda & Koyama, 1972), DL-histidine hydrochloride dihydrate (Bennett, Davidson, Harding & Morelle, 1970), orthorhombic L-histidine (Madden, McGandy, Seeman, Harding & Hoy, 1972), DL-histidine (Edington & Harding, 1974), L-histidine hydrochloride (Kistenmacher & Sorrell, 1973). From the present study we hope to establish how the conformation and perhaps bond lengths or angles vary from one environment to another. In contrast to the variety of conformations found for metal–histidine complexes (Cadlin & Harding, 1970) and histidine hydrochloride compounds (Bennett *et al.*, 1970), these free-base histidines are shown to have remarkably uniform conformational angles, bond distances and valence angles. Similarly, the conformation, bond lengths and bond angles of the title compound are related to those of diprotonated L-histidine dihydrochloride.

Experimental. The title compound was crystallized in aqueous solution from DL-histidine and nitric acid (1:2 stoichiometric ratio). Colourless needle-type crystals elongated along **a** were grown. Cell dimensions were determined by least-squares refinement of the observed Bragg angles of 17 strong reflections in the range $7{\cdot}36 > \theta > 14{\cdot}85°$. 1443 reflections in the hemisphere with index range $-8 \le h \le 8$, $0 \le k \le 15$, $0 \le l \le 9$, $2\theta < 22{\cdot}0°$, were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation and ω–2θ-scan mode. The crystal size used was $0{\cdot}4 \times 0{\cdot}3 \times 0{\cdot}1$ mm. Three standard reflections ($0\bar{6}4$, $00\bar{6}$, 412) were monitored every 85 reflections and no significant differences in the intensities were noted. No absorption correction was applied. The systematic absences *hkl*: *h*0*l*, $h = 2n + 1$ and 0*k*0: $k = 2n + 1$ for this compound are consistent with the space group $P2_1/a$. The structure determination was initially carried out by direct methods (*SHELXS*86, Sheldrick, 1986). Initially, the imidazole ring of the histidine molecule and nitrate groups were identified. Then Fourier and difference Fourier syntheses were carried out to identify the primary amine and carboxylate groups. The scale factor, positional and anisotropic thermal parameters for non-H atoms, and isotropic thermal parameters for H atoms, were refined using full-matrix least-squares techniques (*SHELX*76, Sheldrick, 1976). The unweighted R factor converged to 0·047, the maximum shift/e.s.d. was 0·02. At this stage the equivalent isotropic thermal parameters for one of the O atoms of one of the nitrate groups were found to be very high (0·169 Å^2). Subsequently, a Fourier synthesis was computed with the final parameters. Two different peaks of slightly differing peak heights were located above and below the nitrate plane, revealing a disordered O atom. Two O atoms with site-occupancy factors (s.o.f.'s) 0·45 and 0·55 were added instead of the O atom with high U_{eq}. Positional and anisotropic thermal parameters of all non-H atoms and s.o.f.'s of the disordered O atoms were refined (*SHELX*76); the function minimized was $w\Delta(F)$ with $\Delta F = |F_o| - |F_c|$ and $w = 3{\cdot}2715/[\sigma^2(F) + 0{\cdot}000109F^2]$. This resulted in a final $R = 0{\cdot}035$ and $wR = 0{\cdot}037$. The s.o.f.'s of these disordered O atoms are 0·42 and 0·58. This disordered model is significantly different from the earlier model as shown by a significance level of less than 0·005 in a Hamilton significance test (Hamilton, 1965). The maximum shift/e.s.d. is 0·001. The final difference Fourier map showed maximum and minimum peaks of 0·196 and $-0{\cdot}189$ e Å^{-3}, respectively. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). All computations were carried out on a Cyber 180/830A.

Discussion. The structure of diprotonated DL-histidinium dinitrate is shown in Fig. 1, together with its numbering scheme. Positional parameters and U_{eq} values of the anisotropic temperature factors for non-H atoms are given in Table 1.* The dimensions of one of the nitrate groups are normal and as expected. The second nitrate group is disordered.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53629 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

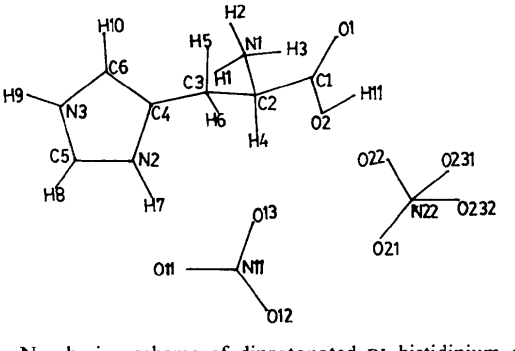

Fig. 1. Numbering scheme of diprotonated DL-histidinium dinitrate.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

$U_{eq} = (1/3)[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$.

	x	y	z	U_{eq}
N(11)	0·0886 (3)	0·8812 (2)	0·2022 (2)	45·8 (5)
O(11)	0·0770 (3)	0·9594 (1)	0·2440 (2)	60·0 (5)
O(12)	0·0143 (2)	0·8200 (1)	0·2521 (2)	58·0 (5)
O(13)	0·1728 (2)	0·8638 (1)	0·1097 (2)	62·5 (5)
N(22)	0·1549 (4)	0·8547 (2)	0·6890 (3)	62·2 (7)
O(21)	0·1649 (3)	0·9024 (2)	0·5823 (2)	76·5 (6)
O(22)	0·0243 (3)	0·8421 (2)	0·7244 (3)	86·1 (7)
O(231)*	0·2778 (12)	0·8034 (6)	0·7084 (10)	96·3 (26)
O(232)†	0·2800 (9)	0·8371 (4)	0·7855 (7)	93·0 (17)
N(1)	0·3226 (3)	0·5938 (2)	0·4388 (2)	53·3 (6)
N(2)	0·1745 (3)	0·6765 (1)	0·0486 (2)	50·3 (6)
N(3)	0·2696 (3)	0·5702 (2)	−0·0606 (2)	53·9 (6)
O(1)	0·1096 (3)	0·5818 (1)	0·6153 (2)	71·1 (6)
O(2)	−0·0658 (3)	0·6743 (2)	0·4856 (3)	110·5 (8)
C(1)	0·0691 (3)	0·6287 (2)	0·5128 (3)	50·4 (7)
C(2)	0·1637 (3)	0·6377 (2)	0·3915 (3)	40·3 (6)
C(3)	0·0678 (3)	0·5973 (2)	0·2509 (3)	50·4 (7)
C(4)	0·1495 (3)	0·6002 (2)	0·1226 (3)	41·5 (6)
C(5)	0·2473 (4)	0·6562 (2)	−0·0612 (3)	56·7 (6)
C(6)	0·2102 (3)	0·5341 (2)	0·0526 (3)	49·8 (7)

* S.o.f. 0·42.
† S.o.f. 0·58.

The disordered O atoms, O(231) and O(232), are out of the N(22)–O(21)–O(22) plane by 0·474 and −0·348 Å, respectively. The angle between the N(22)–O(21)–O(22) and N(22)–O(231)–O(232) planes is 69·6°. The geometry of the nitrate groups is presented in Table 2. It is well known that histidine, like other amino acids, generally exists in the crystal as a zwitterion with the proton on the carboxylic acid function moving to the N atom of the primary amine (Madden, McGandy & Seeman, 1972; Madden, McGandy, Seeman, Harding & Hoy, 1972). The monoprotonated histidine moiety (Donohue & Caron, 1964; Bennett *et al.*, 1970) is protonated at the imidazole ring as well as at the primary-amine N atom. In addition to this atom, protons were observed in the carboxylate group and imidazole ring of the title compound, as in L-histidine dihydrochloride (Kistenmacher & Sorrell, 1974). The hydrogen bonds, in this case, play an important role in the conformational properties of histidine.

The distances and angles involving heavy atoms are listed in Table 2. In general, bond lengths in the diprotonated histidine cation are in good agreement with the values found in both the mono- and diprotonated cations. The bond lengths in the present work compare well with the dication in histidine dihydrochloride, except for the C(1)—C(2) bond length. There are, as anticipated, highly significant differences in the C(1)—O(1) and C(1)—O(2) bond lengths arising out of the protonation of the carboxylate group.

The conformations of the histidine moiety are generally different (Table 2), chiefly around the bonds C(2)—C(3) and C(3)—C(4). The imidazole

Table 2. *Bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and hydrogen-bond geometry* (Å, °)

Histidine moiety

N(1)—C(2)	1·476 (3)	C(4)—N(2)—C(5)	109·6 (2)
N(2)—C(4)	1·372 (3)	C(5)—N(3)—C(6)	108·9 (2)
N(2)—C(5)	1·322 (4)	O(1)—C(1)—O(2)	121·6 (3)
N(3)—C(5)	1·300 (4)	O(1)—C(1)—C(2)	123·4 (3)
N(3)—C(6)	1·362 (4)	O(2)—C(1)—C(2)	111·4 (2)
C(1)—O(1)	1·185 (3)	N(1)—C(2)—C(1)	107·8 (2)
C(1)—O(2)	1·304 (4)	N(1)—C(2)—C(3)	112·4 (2)
C(1)—C(2)	1·504 (4)	C(1)—C(2)—C(3)	110·2 (2)
C(2)—C(3)	1·531 (3)	C(2)—C(3)—C(4)	115·7 (2)
C(3)—C(4)	1·486 (4)	N(2)—C(4)—C(3)	124·6 (2)
C(4)—C(6)	1·338 (4)	N(2)—C(4)—C(6)	105·2 (2)
		C(3)—C(4)—C(6)	130·2 (2)
		N(2)—C(5)—N(3)	108·1 (2)
		N(3)—C(6)—C(5)	108·2 (2)

Nitrate group (ordered)

N(11)—O(11)	1·243 (3)	O(11)—N(11)—O(12)	120·1 (2)
N(11)—O(12)	1·246 (3)	O(12)—N(11)—O(13)	119·6 (2)
N(11)—O(13)	1·240 (3)	O(11)—N(11)—O(13)	120·3 (2)

Nitrate group (disordered)

N(22)—O(21)	1·241 (4)	O(21)—N(22)—O(22)	120·4 (3)
N(22)—O(22)	1·246 (3)	O(22)—N(22)—O(231)	127·8 (5)
N(22)—O(321)	1·270 (10)	O(21)—N(22)—O(231)	106·8 (5)
N(22)—O(232)	1·277 (7)	O(22)—N(22)—O(232)	115·9 (4)
		O(21)—N(22)—O(232)	121·2 (4)

Torsion angles

	Present work	L-Histidine dihydrochloride	L-Histidine hydrochloride monohydrate
N(2)—C(4)—C(3)—C(2)	−70·545	−75·10	−120·3
C(4)—C(3)—C(2)—C(1)	−178·819	−174·30	−52·8
N(1)—C(2)—C(1)—O(2)	173·042	−27·10	−1·7
N(1)—C(2)—C(3)—C(4)	−58·565	–	–

Hydrogen bonds and angles

	N—H	H—O	N—H···O	Angle
N(1)—H(1)···O(12)	0·906 (2)	2·009	2·885[i]	162·21
N(1)—H(2)···O(22)*	0·941 (2)	2·112	3·306[i]	166·89
N(1)—H(2)···O(21)*	0·941 (2)	2·428	2·930[i]	113·26
N(1)—H(3)···O(21)	0·892 (2)	1·996	2·876[ii]	168·69
N(2)—H(7)···O(13)	0·827 (2)	2·068	2·863[iii]	161·11
N(3)—H(9)···O(11)	0·830 (2)	2·028	2·856[iv]	175·28
O(2)—H(11)···O(21)*	0·746 (2)	2·276	2·824[v]	131·23
O(2)—H(11)···O(231)*	0·746 (2)	1·987	2·667[v]	151·62

Symmetry code: (i) $\frac{1}{2}+x, \frac{3}{2}-y, z$; (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$; (iii) x, y, z; (iv) $\frac{1}{2}-x, -\frac{1}{2}+y, -z$; (v) $-\frac{1}{2}+x, \frac{3}{2}-y, z$.

* Bifurcated hydrogen bonds.

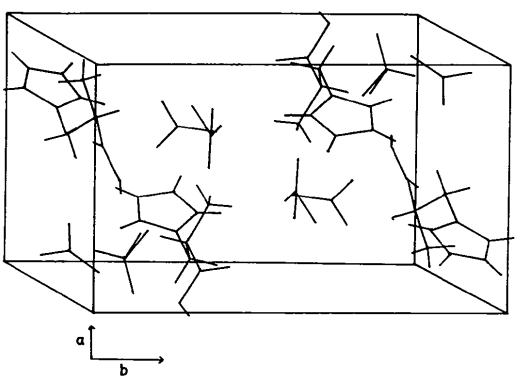

Fig. 2. Unit-cell packing of DL-histidinium dinitrate.

ring is planar. The atom N(2), *cis* with respect to C(2) and C(4) and *trans* with respect to C(1), confirms the DL-form of the histidine moiety in the present work (Bennett *et al.*, 1970). The C(3)—C(2) conformation is such that C(1) is *trans* with respect to C(4) and N(1) is *gauche*.

The bond angles involving heavy atoms in the title compound are comparable with those in histidine dihydrochloride and histidine hydrochloride monohydrate. There are, in general, three single bonds in the histidine moiety which permit conformational freedom: C(4)—C(3), C(3)—C(2) and C(2)—C(1). A comparison of the torsion angles about these bonds in the histidine molecule in title compound, and in L-histidine dihydrochloride and L-histidine hydrochloride monohydrate, is given in Table 2. The difference in the torsion angle C(4)—C(3)—C(2)—C(1) of about 4·5° between the present work and L-histidine dihydrochloride is consistent with an 'open' conformation; the molecular conformation in L-histidine dihydrochloride monohydrate is 'closed' with the torsion angle about C(2)—C(3) equal to −52·8° (Oda & Koyama, 1972).

The crystal-packing diagram of DL-histidinium dinitrate is shown in Fig. 2. Ribbons of histidine cations, each straddling a glide plane, lie essentially in parallel channels along the crystallographic *a* axis. The head-to-tail alignment of the molecules is stabilized by a series of hydrogen bonds [N(1)—H(1)···O(12), N(2)—H(7)···O(22), N(1)—H(2)···O(21) *etc.*] running approximately parallel to **b**. The hydrogen-bond distances and their angles are given in Table 2. All protons attached to N and O atoms are involved in hydrogen bonding. However, there seems to be a bifurcated hydrogen bond between the carboxylate O(2) atom and two O atoms [O(21) and O(231)] of the same nitrate group. The thermal parameters of O(231), O(2) and H(11) involved in this hydrogen bond are relatively high (0·0963, 0·1105 and 0·16 Å^2, respectively). Similarly there is one more bifurcated hydrogen bond between the amino-group N atom and two O atoms [O(21) and O(22)] of the same nitrate group.

The authors thank Professors K. S. Chandrasekaran and H. Manohar for their keen interest and encouragement.

References

BENNETT, I., DAVIDSON, A. G. H., HARDING, M. M. & MORELLE, I. (1970). *Acta Cryst.* **B26**, 1722–1729.

CADLIN, R. & HARDING, M. M. (1970). *J. Chem. Soc. A*, pp. 384–394.

DONOHUE, J. & CARON, A. (1964). *Acta Cryst.* **17**, 1178–1180.

DONOHUE, J., LAVINE, L. R. & ROLLETT, J. S. (1956). *Acta Cryst.* **9**, 655–662.

EDINGTON, P. & HARDING, M. M. (1974). *Acta Cryst.* **B30**, 204–206.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

KISTENMACHER, T. J. & SORRELL, T. (1973). *Cryst. Struct. Commun.* **2**, 673–679.

KISTENMACHER, T. J. & SORRELL, T. (1974). *J. Cryst. Mol. Struct.* **4**, 419–432.

MADDEN, J. J., MCGANDY, E. L. & SEEMAN, N. C. (1972). *Acta Cryst.* **B28**, 2377–2382.

MADDEN, J. J., MCGANDY, E. L., SEEMAN, N. C., HARDING, M. M. & HOY, A. (1972). *Acta Cryst.* **B28**, 2382–2389.

ODA, K. & KOYAMA, H. (1972). *Acta Cryst.* **B28**, 639–642.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1991). C**47**, 1423–1426

Structure of a *p*-Bromobenzoyl Derivative of Amyrinol*

BY A. C. GOMES,† G. BISWAS,† A. K. BARUA,‡ S. RAY‡ AND A. BANERJEE†§

Biophysics Department and Chemistry Department, Bose Institute, Calcutta-700 054, *India*

AND Y. IITAKA

University of Tokyo, Bunkyo-ku, Tokyo 113, *Japan*

(*Received* 16 *June* 1990; *accepted* 12 *October* 1990)

Abstract. 5,6,9,9-Tetramethyl-10-oxatricyclo-[6.2.2.0^{1,6}]dodec-2-yl *p*-bromobenzoate, $C_{22}H_{29}BrO_3$, $M_r = 420·9$, orthorhombic, $P2_12_12_1$, $a = 7·038$ (1), $b = 23·924$ (2), $c = 24·84$ (1) Å, $V = 4182·5$ Å^3, $Z = 8$, $D_x = 1·336$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 26·2$ cm^{-1}, $F(000) = 1760$, $T = 288$ K, final $R = 0·053$ for 2830 reflections. The compound crystallizes with two molecules in the asymmetric unit where each molecule has two cyclohexane rings of which one is

* This paper was presented at the National Seminar on Crystallography, BARC, India, December 1989.

† Biophysics Department.

‡ Chemistry Department.

§ To whom correspondence should be addressed.

0108-2701/91/071423-04$03.00