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A 1:2 Host–Guest Complex of Diaza-15-crown-5 with Picric Acid

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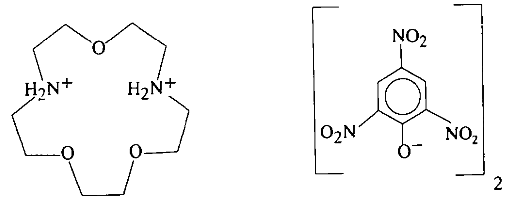
Abstract

In $C_{10}H_{24}N_2O_3^{2+}.2C_6H_2N_3O_7^-$, the crown ether, 1,4,10-trioxa-7,13-diazacyclopentadecane (diaza-15-crown-5), exists as a dication by accepting protons from two 2,4,6-trinitrophenol (picric acid) molecules. The crown ether shows disorder due to the two uniangular conformations at C3 and C4. The anions are stacked between the dications and are connected to them by N—H···O hydrogen bonds to form columns of interleaved ions. The crystal structure is stabilized by N—H···O and C—H···O hydrogen bonds.

Comment

The interaction between crown ethers and neutral organic molecules has been reviewed by several authors (Vogtle, Sieger & Muller, 1981; Watson, Galloy, Grossie, Vogtle & Muller, 1984; Goldberg, 1984). Replacement of ether O atoms by —NH— groups provides sites that can act as either electron or proton donors; such diaza-crown ether molecules form stable complexes with neutral organic molecules containing proton donors and have been found useful in selectively precipitating some polyhydroxy guests from mixtures of oligohydroxy phenols (Watson, Nagl & Eduok, 1989). It is well known that picric acid (PicH) forms charge-transfer complexes, but little has been reported on its complexes with crown ethers. We have investigated the reaction of PicH with diaza-15-crown-5 and obtained single crystals of the title complex, (I), in which the host–guest ratio is 1:2, as is the case for many crown ether complexes with organic compounds. The structural results are presented in Fig. 1 and Tables 1, 2 and 3.



(I)

The crown ether ring shows disorder of atoms C3 and C4. Such disorder is common in 15-crown-5 molecules because of the two uniangular conformations at C3 and C4 (Wei, Tinant, Declercq, Van Meerssche & Dale, 1988; Rogers, 1988). The *gauche* O—C—C—O torsion angle sequences in the ether ring are + + − − for C3*A* and C4*A* and + + + − − for C3*B* and C4*B*; the disordered region occupies a corner in each conformation. The forced *gauche* angles are −82.3 (4) (C5—O2—C4*A*—C3*A*) and 84.3 (6)° (C2—O1—C3*B*—C4*B*), which are (always) greater than 70° as a result of non-bonded H···H repulsion (Rogers, Kurihara & Benning, 1987). The ether has near mirror symmetry with the mirror plane passing through atom O3 and the C3—C4 bond and adopts a sofa-like conformation; all non-H atoms except O1, O2, C3 and C4 lie approximately in one plane [the mean deviation is 0.182 (3) Å and the maximum is 0.554 (3) Å for C9]. Atoms O1, O2, C3 and C4 lie well above this plane. Both N1 and N2 have acquired additional protons from the two PicH molecules and hence the crown exists as a dication. The two anions sit on either side of the dication.

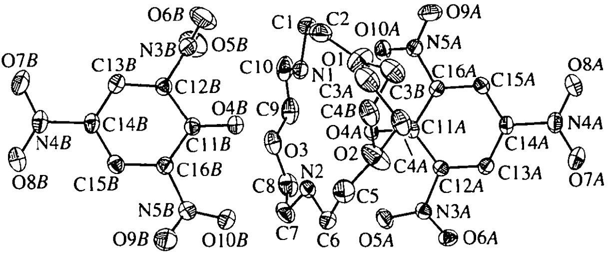


Fig. 1. Displacement ellipsoid plot (30% probability) of the title compound with the numbering scheme; H atoms are excluded for clarity.

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The two independent Pic anions (Pic-*A* and Pic-*B*) are individually planar and the dihedral angle between them is 35.44 (7)°. The three nitro groups attached to each of them have different orientations with respect to the C_6 ring; the angles made by the nitro groups in Pic-*A* are 45.4 (1), 25.7 (2) and 46.4 (1)° (for the O5*A*—N3*A*—O6*A*, O7*A*—N4*A*—O8*A* and O9*A*—N5*A*—O10*A* groups, respectively) and the corresponding angles in Pic-*B* are 92.3 (2), 10.1 (1) and 21.1 (1)°.

The crystal contains columns of Pic anions sandwiched between the dications, to which they are connected by hydrogen bonds (Fig. 2). Two parallel picrate anions are stacked between each pair of dications. The interplanar distances, 3.554 (8) Å between parallel Pic-*A* residues and 3.345 (7) Å between parallel Pic-*B* residues, are typical of distances found in π complexes of PicH (Van Staveren *et al.*, 1984; Banerjee & Brown, 1985; Colquhoun, Doughty, Stoddart, Slawin & Williams, 1986). In the title complex, the molecular columns lie parallel to one another in the (111) planes and are perpendicular to $(20\bar{1})$.

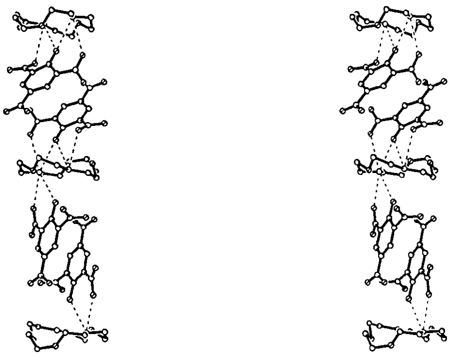

Fig. 2. Stereoview of one column of the complex. N—H···O bonds are shown as dashed lines.

There are seven N—H···O hydrogen bonds (Table 3) between the dication and the anions [six three-centre and one two-centre (Taylor, Kennard & Versichel, 1984)]; O5*B* is not involved in N—H···O bonding due to the perpendicular orientation of the nitro group relative to the phenyl plane of Pic-*B*. A number of C—H···O bonds within the limits suggested by Taylor & Kennard (1982) are also present, as are two notably short contacts, which link anions in neighbouring columns [N5*B*···O9*A*^{i} 2.857 (2) and O6*A*···O7*A*^{ii} 2.900 (3) Å; symmetry codes: (i) $x, y, 1+z$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$].

Experimental

Equimolar amounts of diaza-15-crown-5 and picric acid were dissolved in warm methanol. The resulting solution was filtered immediately and then refluxed for 7 h. After cooling, slow evaporation at room temperature for several days yielded yellow crystals of the 1:2 host–guest complex suitable for X-ray structure determination.

Crystal data

$C_{10}H_{24}N_2O_3^{2+}.2C_6H_2N_3O_7^-$
$M_r = 676.52$
Monoclinic
$P2_1/c$
$a = 17.832\,(2)$ Å
$b = 15.088\,(1)$ Å
$c = 11.023\,(1)$ Å
$\beta = 103.26\,(1)°$
$V = 2886.7\,(5)$ Å^3
$Z = 4$
$D_x = 1.557$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–25°$
$\mu = 0.136$ mm^{-1}
$T = 293\,(2)$ K
Rectangular prism
$0.54 \times 0.48 \times 0.22$ mm
Yellow

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
8154 measured reflections
6584 independent reflections
4144 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0183$

$\theta_{\rm max} = 27.5°$
$h = -23 \rightarrow 22$
$k = -19 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections monitored every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0466$
$wR(F^2) = 0.1343$
$S = 0.981$
6584 reflections
527 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	$U_{\rm eq}$
O1	0.18509 (10)	0.53058 (12)	0.0154 (2)	0.0835 (6)
O2	0.27933 (14)	0.64816 (12)	0.1813 (2)	0.0943 (7)
O3	0.31885 (9)	0.35190 (11)	0.3598 (2)	0.0664 (4)
N1	0.21766 (11)	0.37668 (12)	0.1447 (2)	0.0548 (5)
N2	0.32234 (10)	0.53252 (12)	0.37599 (15)	0.0459 (4)
C1	0.14959 (15)	0.3855 (2)	0.0379 (2)	0.0683 (7)
C2	0.12281 (14)	0.4783 (2)	0.0279 (3)	0.0723 (7)
C3*A*†	0.1637 (3)	0.6225 (3)	0.0420 (5)	0.0709 (11)
C3*B*†	0.1827 (5)	0.6217 (5)	−0.0180 (6)	0.0709 (11)
C4*A*†	0.2363 (2)	0.6765 (3)	0.0680 (4)	0.0634 (9)
C4*B*†	0.1873 (4)	0.6659 (4)	0.1020 (6)	0.0634 (9)
C5	0.2697 (2)	0.6763 (2)	0.2980 (2)	0.0635 (6)
C6	0.32990 (13)	0.6308 (2)	0.3933 (2)	0.0551 (5)
C7	0.37094 (14)	0.4777 (2)	0.4770 (2)	0.0638 (6)
C8	0.38921 (15)	0.3908 (2)	0.4268 (3)	0.0722 (7)
C9	0.3275 (2)	0.2931 (2)	0.2638 (3)	0.0739 (8)
C10	0.2511 (2)	0.2850 (2)	0.1756 (3)	0.0779 (8)
O4*A*	0.36029 (7)	0.47077 (8)	0.14752 (11)	0.0442 (3)
O5*A*	0.47303 (9)	0.55278 (13)	0.30993 (13)	0.0730 (5)
O6*A*	0.56411 (7)	0.60596 (10)	0.23557 (13)	0.0515 (3)

O7A	0.49954 (11)	0.74054 (12)	−0.1670 (2)	0.0829 (5)
O8A	0.42254 (12)	0.67164 (14)	−0.3136 (2)	0.0917 (6)
O9A	0.25887 (10)	0.44259 (12)	−0.2153 (2)	0.0796 (5)
O10A	0.30517 (10)	0.36763 (9)	−0.05142 (14)	0.0620 (4)
N3A	0.49817 (8)	0.57874 (11)	0.22224 (14)	0.0432 (4)
N4A	0.45177 (11)	0.68303 (11)	−0.2038 (2)	0.0554 (4)
N5A	0.30161 (9)	0.43546 (11)	−0.1131 (2)	0.0463 (4)
C11A	0.38537 (9)	0.51399 (11)	0.0683 (2)	0.0356 (4)
C12A	0.44931 (9)	0.57565 (11)	0.0971 (2)	0.0373 (4)
C13A	0.47007 (11)	0.62982 (12)	0.0104 (2)	0.0411 (4)
C14A	0.43018 (11)	0.62571 (12)	−0.1121 (2)	0.0417 (4)
C15A	0.37273 (11)	0.56318 (12)	−0.1511 (2)	0.0400 (4)
C16A	0.35395 (9)	0.50784 (11)	−0.0648 (2)	0.0371 (4)
O4B	0.16754 (7)	0.46299 (9)	0.36442 (12)	0.0493 (3)
O5B	0.09757 (14)	0.26761 (14)	0.2840 (2)	0.1028 (7)
O6B	0.01837 (13)	0.3665 (2)	0.2013 (2)	0.1029 (7)
O7B	−0.07771 (10)	0.31715 (12)	0.6340 (2)	0.0784 (5)
O8B	−0.01325 (10)	0.3982 (2)	0.7816 (2)	0.0834 (6)
O9B	0.15835 (10)	0.61045 (11)	0.6773 (2)	0.0746 (5)
O10B	0.23247 (9)	0.57259 (12)	0.55921 (15)	0.0713 (5)
N3B	0.06052 (11)	0.33249 (14)	0.2911 (2)	0.0578 (5)
N4B	−0.02474 (10)	0.36783 (13)	0.6767 (2)	0.0551 (4)
N5B	0.17542 (10)	0.56119 (12)	0.6003 (2)	0.0496 (4)
C11B	0.12620 (10)	0.44426 (12)	0.4392 (2)	0.0388 (4)
C12B	0.06820 (10)	0.37556 (12)	0.4115 (2)	0.0419 (4)
C13B	0.02044 (11)	0.34946 (14)	0.4846 (2)	0.0458 (4)
C14B	0.02623 (10)	0.39262 (13)	0.5972 (2)	0.0436 (4)
C15B	0.07782 (10)	0.46043 (13)	0.6327 (2)	0.0424 (4)
C16B	0.12562 (10)	0.48600 (12)	0.5565 (2)	0.0410 (4)

† C3*A*, C3*B*, C4*A* and C4*B* are disordered (see below).

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.395 (3)	N3A—C12A	1.453 (2)
O1—C3A	1.485 (5)	N4A—C14A	1.448 (2)
O1—C3B	1.421 (8)	N5A—C16A	1.456 (2)
O2—C4A	1.376 (4)	C11A—C16A	1.448 (2)
O2—C4B	1.694 (7)	C11A—C12A	1.449 (2)
O2—C5	1.402 (3)	C12A—C13A	1.372 (2)
O3—C9	1.416 (3)	C13A—C14A	1.376 (3)
O3—C8	1.428 (3)	C14A—C15A	1.386 (3)
N1—C1	1.490 (3)	C15A—C16A	1.365 (2)
N1—C10	1.514 (3)	O4B—C11B	1.258 (2)
N2—C7	1.494 (3)	O5B—N3B	1.194 (3)
N2—C6	1.497 (3)	O6B—N3B	1.211 (3)
C1—C2	1.475 (4)	O7B—N4B	1.223 (2)
C3A—C4A	1.500 (7)	O8B—N4B	1.217 (2)
C3B—C4B	1.468 (10)	O9B—N5B	1.218 (2)
C5—C6	1.487 (4)	O10B—N5B	1.217 (2)
C7—C8	1.488 (4)	N3B—C12B	1.456 (3)
C9—C10	1.486 (4)	N4B—C14B	1.448 (2)
O4A—C11A	1.252 (2)	N5B—C16B	1.453 (2)
O5A—N3A	1.220 (2)	C11B—C16B	1.440 (3)
O6A—N3A	1.222 (2)	C11B—C12B	1.446 (3)
O7A—N4A	1.218 (2)	C12B—C13B	1.358 (3)
O8A—N4A	1.215 (2)	C13B—C14B	1.385 (3)
O9A—N5A	1.212 (2)	C14B—C15B	1.371 (3)
O10A—N5A	1.222 (2)	C15B—C16B	1.382 (2)
C2—O1—C3B	126.5 (4)	O2—C5—C6	106.7 (2)
C2—O1—C3A	105.2 (3)	C5—C6—N2	109.7 (2)
C4A—O2—C5	125.4 (3)	C8—C7—N2	110.5 (2)
C5—O2—C4B	96.8 (3)	O3—C8—C7	108.3 (2)
C9—O3—C8	114.2 (2)	O3—C9—C10	107.5 (2)
C1—N1—C10	117.8 (2)	C9—C10—N1	109.1 (2)
C7—N2—C6	115.7 (2)	O4A—C11A—C16A	123.8 (2)
C2—C1—N1	109.6 (2)	O4A—C11A—C12A	124.8 (2)
O1—C2—C1	107.0 (2)	C16A—C11A—C12A	111.43 (14)
O1—C3A—C4A	107.2 (4)	O4B—C11B—C16B	128.0 (2)
O1—C3B—C4B	102.3 (5)	O4B—C11B—C12B	121.4 (2)
O2—C4A—C3A	106.4 (3)	C16B—C11B—C12B	110.55 (15)
C3B—C4B—O2	104.0 (5)		
C10—N1—C1—C2	176.5 (2)	C4A—O2—C5—C6	−178.3 (3)
C3A—O1—C2—C1	−164.2 (3)	C4B—O2—C5—C6	154.9 (3)
C3B—O1—C2—C1	168.5 (4)	O2—C5—C6—N2	−57.3 (3)
N1—C1—C2—O1	56.9 (3)	C7—N2—C6—C5	−170.8 (2)
C2—O1—C3A—C4A	163.2 (3)	C6—N2—C7—C8	−152.3 (2)
C2—O1—C3B—C4B	84.3 (6)	C9—O3—C8—C7	153.1 (2)
C5—O2—C4A—C3A	−82.3 (4)	N2—C7—C8—O3	−51.2 (3)
O1—C3A—C4A—O2	−70.3 (4)	C8—O3—C9—C10	−159.3 (2)
O1—C3B—C4B—O2	71.2 (6)	O3—C9—C10—N1	47.6 (3)
C5—O2—C4B—C3B	−168.2 (4)	C1—N1—C10—C9	167.3 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···O4B	0.88 (3)	2.19 (3)	3.059 (3)	173 (2)
N1—H2N1···O4A	0.92 (3)	2.05 (3)	2.907 (2)	155 (2)
N1—H2N1···O10A	0.92 (3)	2.45 (3)	2.945 (3)	114 (2)
N2—H1N2···O4B	0.88 (2)	2.07 (2)	2.928 (2)	169 (2)
N2—H1N2···O10B	0.88 (2)	2.50 (2)	2.915 (3)	110 (2)
N2—H2N2···O4A	0.96 (3)	1.95 (3)	2.907 (2)	173 (2)
N2—H2N2···O5A	0.96 (3)	2.50 (2)	2.957 (3)	109 (2)
C1—H1A···O10A	0.98 (3)	2.51 (3)	3.161 (3)	124 (2)
C1—H1B···O6B	0.90 (3)	2.66 (3)	3.277 (4)	127 (2)
C6—H6A···O5A	0.98 (3)	2.43 (2)	3.134 (3)	128 (2)
C6—H6B···O10B	1.02 (3)	2.28 (3)	2.931 (3)	121 (2)
C7—H7B···O10B	0.93 (3)	2.54 (2)	3.161 (3)	125 (2)
C9—H9A···O4A	0.96 (3)	2.47 (2)	3.085 (3)	122 (2)
C10—H10A···O5B	0.96 (3)	2.41 (3)	3.240 (5)	144 (2)
C2—H2A···O8B^{i}	0.98 (2)	2.58 (2)	3.420 (3)	143 (2)
C6—H6B···O8A^{ii}	1.02 (3)	2.58 (2)	3.331 (3)	131 (2)
C7—H7A···O5A^{iii}	1.03 (3)	2.60 (3)	3.236 (3)	120 (2)
C9—H9B···O6A^{iv}	1.02 (3)	2.62 (3)	3.421 (3)	135 (2)
C9—H9B···O10A^{v}	1.02 (3)	2.41 (3)	3.249 (3)	139 (2)

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

Atoms C3 and C4 showed large displacement parameters and an unusual C3—C4 bond length and hence were each split over alternate sites *A* and *B*; a single occupancy parameter was refined [0.585 (5) for set *A*, 0.415 (3) for *B*]. Attempts were made to restrain the bonds around the disordered atoms, but the refinement did not converge; hence the final refinement was carried out without any positional restraints but with U_{ij}(C3*A*) = U_{ij}(C3*B*) and U_{ij}(C4*A*) = U_{ij}(C4*B*). This led to good convergence and better *R* values but the O2—C4*B* distance [1.694 (7) Å] deviates from the normal value. H atoms, except those attached to C3*A*, C4*A*, C3*B* and C4*B*, were located from difference maps and refined isotropically; H atoms at the disordered positions were fixed geometrically and allowed to ride on their respective parent atoms.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93. Geometrical calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1223). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Aminopyrazine-2-carboxylic Acid

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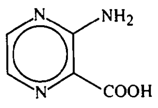
Abstract

3-Aminopyrazine-2-carboxylic acid, $C_5H_5N_3O_2$, displays an extensive network of intra- and intermolecular hydrogen bonds which are undoubtedly responsible for the modest values of the displacement parameters. H-atom transfer to the ring N atoms did not occur and the carboxy and amino H atoms are ordered. The virtually planar molecules lie very nearly in planes parallel to $(10\bar{2})$ and are stacked along the *a* direction with separations of 3.324 (2) Å indicating π–π interactions.

Comment

As pyridinium pamoate afforded numerous hydrogen-bonding possibilities (Blackburn, Dobson & Gerkin, 1996), so too does the title compound, (I). Its structure was therefore of interest and was found to exhibit extensive hydrogen bonding.



(I)

An *ORTEP*II diagram (Johnson, 1976) of (I) showing the atomic numbering scheme is presented in Fig. 1 and a stereoview of a portion of the structure, including a unit cell and with hydrogen bonds depicted, is given in Fig. 2. In the structure of (I), both intra- and intermolecular hydrogen bonds are significant (Fig. 2, Table 3). The following points may be noted: (i) each N and O atom is involved in at least one substantial hydrogen bond, (ii) the H1 and H3 atoms are involved in bifurcated hydrogen bonds, each of which comprises one intramolecular and one intermolecular bond, and (iii) each molecule participates in six intermolecular as well as in two intramolecular hydrogen bonds. The extensive hydrogen-bonding network is undoubtedly responsible for the modest size of the displacement parameters in this structure.

In contrast to the case of pyridinium pamoate (Blackburn *et al.*, 1996), H-atom transfer does not occur in the present case. The carboxy H atom is ordered, as are the amino H atoms. This behavior is, however, similar to that reported for pyrazine-2-carboxylic acid (Takusagawa, Higuchi, Shimada, Tamura & Sasada, 1974), in which the carboxy H atom is retained and is ordered, and the acceptor atom is a ring N atom.

Excluding atoms within hydrogen bonds, only the approach of the C6 and $H2^i$ atoms [symmetry code: (i) $-1+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$] falls short of the corresponding sum of the van der Waals radii (Bondi, 1964), by as much as 0.1 Å. Although the approaches of the H5 and H6 atoms to neighboring O1 and O2 atoms are seen prominently in Fig. 2, they are of normal value.

The pyrazine core is planar, the average distance of its atoms from the best least-squares plane through them being 0.002 Å, with a mean e.s.d. of 0.002 Å. The angle between the core plane and the carboxy group plane is 1.60 (7)°, that between the core plane and the amino group plane is 3 (2)° and that between the carboxy and amino planes is 2 (2)°. The molecule as a whole is thus virtually planar. Moreover, all the molecules lie in planes parallel to $(10\bar{2})$ to within a dihedral angle of $\sim 5°$. [Strictly, there are two equally occupied orientations of the pyrazine core planes, the dihedral angle between them being 10.02 (6)°, and along any chain of hydrogen-bonded molecules within one plane, the pyrazine core planes alternate between these two orientations.] Each plane of molecules is separated by ~ 1.34 Å from the nearer of the two adjacent planes of