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Structure and Thermal Motion of 2-Amino-1-methyl-4-imidazolecarbaldehyde

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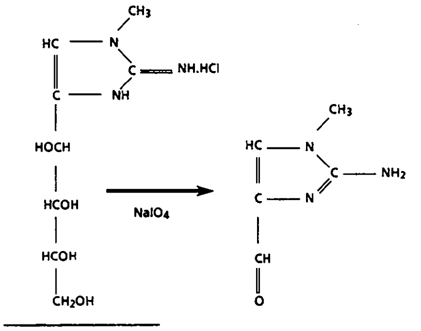
Abstract. $C_5H_7N_3O$, $M_r = 125\cdot1$, monoclinic, $P2_1/a$, $a = 7\cdot885\,(1)$, $b = 10\cdot217\,(1)$, $c = 8\cdot181\,(1)$ Å, $\beta = 116\cdot39\,(1)^\circ$, $V = 590\cdot4\,(1)$ Å^3, $Z = 4$, $D_m = 1\cdot40$, $D_x = 1\cdot41$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot10$ mm^{-1}, $F(000) = 264$, room temperature, final $R = 0\cdot07$ for 973 observed reflections. The double bonds on the imidazole ring are delocalized and the positive charges are located on C(4), C(1), C(5) and the two H atoms of the amino group. The configuration in the crystals and in the isolated molecule is planar. A least-squares fit of the thermal parameters to a rigid-body model gives good agreement, $R = 5\cdot1\%$. The molecules are linked by van der Waals forces, together with intermolecular hydrogen bonds between the N atom of the amino group and N(1) of the imidazole group and the O atom of the carbonyl group.

Introduction. This is one of a series of newly synthesized 1-methylimidazole derivatives that we are investigating. We have previously determined the crystal structure of 2-amino-3-methyl-5-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)imidazolium chloride (I) (Vega, López-Castro & Márquez, 1988). The title compound (II) has been synthesized in the Organic Chemistry Department of Seville University by Professor Fernandez-Bolaños and co-workers by oxidation with $NaIO_4$ of (I).



(I) (II)

The compounds have been studied by UV, IR and NMR (Alaiz-Barragan, 1987). The crystal structure of the title compound (II) was determined in order to establish possible correlations between the UV, IR and NMR spectroscopy data and X-ray single-crystal structural data. The resolution of the structure confirms the molecular conformation and the canonical form that contributes more to the structure, as shown by the spectroscopic data.

Experimental. Crystals appear as colourless prisms. Specimen size $0\cdot20 \times 0\cdot25 \times 0\cdot18$ mm. Enraf–Nonius CAD-4 diffractometer with graphite monochromator and Mo $K\alpha$ radiation. Cell dimensions from 2θ angles for 25 reflections ($6 < \theta < 14^\circ$), $\omega/2\theta$ mode, $2\theta_{\max} = 60^\circ$ ($-11 < h < 11$, $k \le 14$, $l \le 11$). From 1690 independent reflections measured, only 973 were considered as observed, $R_{\text{int}} = 0\cdot011$ from merging 48 equivalent reflections, $I > 2\sigma(I)$; Lp correction, absorption ignored; two check reflections (031, $0\bar{3}\bar{1}$) every 5400 s showed no unusual variation; direct methods, *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); full-matrix least-squares refinement based on F, anisotropic temperature factors for the non-hydrogen atoms; difference Fourier synthesis revealed H atoms; refined with isotropic temperature factors. Further least-squares refinement including all parameters of H atoms gave $R = 0\cdot07$ ($wR = 0\cdot07$); weighting scheme based on statistical count criterion $w = 1/\sigma^2(F)$. $(\Delta/\sigma)_{\max} = 0\cdot035$ for non-hydrogen atoms and $0\cdot48$ for the H atoms, $S = 1\cdot44$ for 110 refined parameters. 8·8 reflections/parameter. Final difference synthesis showed $\Delta\rho = +0\cdot3$ e Å^{-3}. Neutral-atom scattering factors used (*International Tables for X-ray Crystallography*, 1974). Crystallographic programs of *XRAY*70 system (Stewart, Kundell & Baldwin, 1970) were used.

Discussion. Table 1 gives the atomic coordinates and Table 2 the bond lengths and angles.* A view of the molecule with the atom numbering is shown in Fig. 1.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters and the rigid-body movement tensor have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51052 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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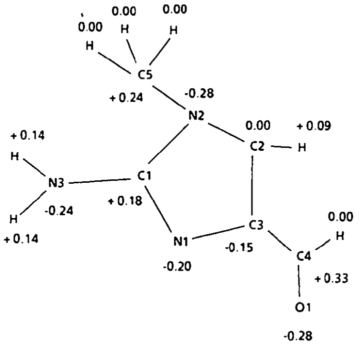
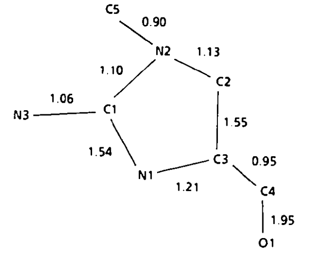
The molecule is planar and the substituents C(4), C(5) and N(3) are 0·002 (5), −0·049 (5) and 0·064 (4) Å out the imidazole plane.

The three bond lengths C(1)—N [mean value 1·354 (5) Å] are shorter than C(2)—N(2) = 1·361 (5) and C(3)—N(1) = 1·385 (4) Å; their values are intermediate between a double bond (1·265 Å) and a single bond (1·470 Å). The value of the C(2)—C(3) bond length of 1·371 Å is also intermediate between a double-bond (1·330 Å) and a single-bond C—C (1·541 Å). This result indicates a delocalization of the double bonds on the imidazole ring. In order to verify this assumption semiempirical MNDO calculations (Dewar & Phiel, 1977) were performed.

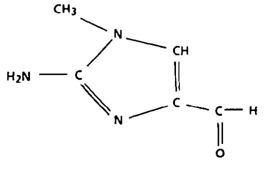
The atomic charges for the molecule are:



where we can observe the positive charges located on C(4), C(1) and C(5), and the two H atoms of the amino group. The Wilberg indices:



were obtained from the calculated bond lengths and give us rather good information about the bond orders in the molecule. The results indicate a large contribution of the following canonical form to the structure:



Thermal motion. The experimental atomic thermal parameters have been analysed in terms of molecular rigid-body translations and rotations (Schomaker & Trueblood, 1968). A least-squares fit of the thermal parameters to a rigid-body behaviour gives a good agreement ($R = 5\cdot1\%$). The **T**, **L** and **S** tensors obtained have been deposited.* The moment-of-inertia values for the two molecular in-plane (Y and Z) principal directions (see Fig. 1) are $74\cdot37 \times 10^{-46}$ and $21\cdot86 \times 10^{-46}$ respectively, and $95\cdot63 \times 10^{-46}$ kg m^{-2} for the third perpendicular direction (X). The librational ellipsoid is oriented in the following way: the first librational principal direction forms an angle of 7·2° with the least-inertia molecular principal axis Z and 3·7° with the molecular plane. The second and third principal directions form angles of 17·9 and 71·7° with the molecular plane respectively, and the corresponding eigenvalues are 36·8, 7·3 and 6·3 deg^2. Both the inertia and the libration tensors are close to a revolution ellipsoid, the largest librational movement taking place

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

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j\cos(\mathbf{a}_i,\mathbf{a}_j).$$

	x	y	z	$U_{\rm eq}$
O1	0·8917 (5)	0·3265 (3)	0·8820 (4)	59 (1)
C2	0·8461 (6)	0·1409 (3)	0·4887 (5)	44 (1)
C1	0·8823 (5)	0·3248 (3)	0·3684 (5)	37 (1)
C5	0·8456 (6)	0·1199 (4)	0·1810 (5)	46 (2)
N2	0·8548 (4)	0·1919 (3)	0·3389 (4)	37 (1)
N1	0·8915 (4)	0·3594 (3)	0·5280 (4)	40 (1)
C3	0·8676 (5)	0·2438 (3)	0·6039 (5)	38 (1)
C4	0·8676 (6)	0·2348 (4)	0·7786 (6)	45 (2)
N3	0·8893 (6)	0·4078 (3)	0·2415 (5)	49 (1)

Table 2. *Bond distances* (Å) *and angles* (°)

O1—C4	1·219 (5)	C1—N3	1·360 (5)
C2—N2	1·361 (5)	C5—N2	1·459 (5)
C2—C3	1·371 (5)	N1—C3	1·385 (4)
C1—N2	1·379 (4)	C3—C4	1·432 (6)
C1—N1	1·323 (5)		
N2—C2—C3	106·5 (3)	C2—N2—C1	106·6 (2)
N1—C1—N3	125·6 (3)	C1—N1—C3	104·7 (2)
N2—C1—N3	122·4 (3)	C2—C3—N1	110·2 (3)
N2—C1—N1	111·8 (2)	N1—C3—C4	124·1 (3)
C1—N2—C5	126·3 (3)	C2—C3—C4	125·5 (3)
C2—N2—C5	126·9 (2)	O1—C4—C3	125·0 (3)

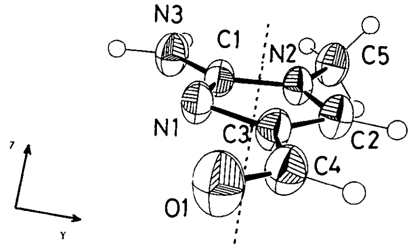


Fig. 1. *ORTEP* drawing (Johnson, 1965) of asymmetric unit of the structure along [100] with the atomic numbering scheme. The dashed line is the molecular in-plane least-inertia principal axis (Z direction). The Y direction is the corresponding molecular in-plane direction perpendicular to Z.

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* See deposition footnote.

approximately about the axis of least moment-of-inertia.

From the diffraction data it is possible to obtain a rough estimate of an average librational frequency assuming a single independent frequency for the librations about each principal axis of inertia (Cruickshank, 1958):

$$\bar{\theta}_i^2 = (h/8\pi^2\nu_i I_i)\coth(h\nu_i/2k_BT)$$

where $\bar{\theta}_i^2$ is the mean-square librational displacement about the principal axis i, h and k_B are Planck's and Boltzmann's constants, I_i is the corresponding inertia moment and T is the absolute temperature. The resulting frequencies are 2·3, 2·4 and 2·1 THz respectively, showing that, on average, the largest librational movement about the least-inertia axis is due to modes of lower frequency.

Crystal packing. Crystal-energy packing calculations have been carried out with empirical atom–atom potential functions which account for both van der Waals and electrostatic interactions. The results of an energy minimization process show that the molecules tend to readjust within the unit cell in order to increase the short contact distances, giving additional evidence for the presence of hydrogen bonds for two short contacts $N(3)—H\cdots O(1)(x, y, z-1) = 3{\cdot}065\ (6)$ and $N(3)—H\cdots N(1)(-x+2, -y+1, -z+1) = 3{\cdot}049\ (4)$ Å.

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5β-(1-Pentyl)-2,3,3aβ,4,5,7aα-hexahydroindene-4β-carboxanilide

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Abstract. $C_{21}H_{29}NO$, $M_r = 311{\cdot}47$, monoclinic, $P2_1/c$, $a = 9{\cdot}678\ (7)$, $b = 19{\cdot}883\ (11)$, $c = 9{\cdot}901\ (4)$ Å, $\beta = 97{\cdot}26\ (5)°$, $V = 1890{\cdot}0\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}094$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}06$ mm^{-1}, $F(000) = 680$, $T = 298$ K, final $R = 0{\cdot}061$ for 1447 unique observed reflections. The ring fusion is *trans* and the pentyl and carboxanilide substituents are oriented in *cis* positions. The five-membered ring exhibits a twist conformation and the six-membered ring has a half-chair conformation. The molecules are held together by hydrogen bonds.

Introduction. The intramolecular Diels–Alder (IMDA) reaction is a highly useful tool in synthetic organic chemistry, which has become increasingly important in recent years (Ciganek, 1984; Fallis, 1984). Stereochemical aspects play a central role in these synthetic applications, as well as in many theoretical studies dealing with IMDA reactions.

The title compound was prepared in connection with an NMR study of the stereochemistry involved in the IMDA reaction in non-activated systems (Kaltia, Matikainen & Hase, 1988; Matikainen, Kaltia & Hase,

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