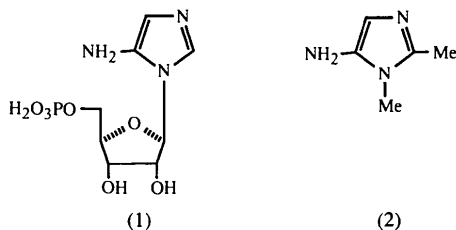


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5-Amino-1,2-dimethylimidazole

RICHARD H. JONES, AILEEN P. LOTHIAN AND
CHRISTOPHER A. RAMSDEN

Department of Chemistry, Keele University, Keele, Staffordshire ST5 5BG, England. E-mail: cha35@cc.keele.ac.uk

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Abstract

The determination of the structure of the title compound, C₅H₉N₃, provides the first geometrical data for 5-amino-4-unsubstituted imidazoles. The amino group is planar and inclined at 45(3)° to the plane of the imidazole ring. The N3—C4 bond is slightly longer than that in imidazole and significantly longer than those in 5-nitroimidazoles. There is intermolecular hydrogen bonding between the amino substituents and the ring N atoms at position 3.

Comment

5-Aminoribonucleotide (AIR), (1), is an intermediate in the biosynthesis of purine ribonucleotides and thiamin (Mueller, Meyer, Rudolph, Davisson & Stubbe, 1994). Until recently, simple 5-aminoimidazoles were regarded as too unstable to be isolated and the properties of this fundamental heterocyclic system, including its structural features, remained unexplored (Lythgoe & Ramsden, 1994). In earlier studies we have described the preparation and isolation of several 5-amino-4-unsubstituted imidazoles (Al-Shaar, Gilmour, Lythgoe, McClenaghan & Ramsden, 1992; Al-Shaar, Chambers *et al.*, 1992; Humphries & Ramsden, 1995). We now report the molecular structure of the title compound, (2), and compare the results with those previously calculated (Al-Shaar, Gilmour *et al.*, 1992) using the semi-empirical AM1 method (Dewar, Zoebisch, Healy & Stewart, 1985).

Fig. 1 shows a perspective view of (2). A comparison of the bond lengths with those in antibacterial 1,2-dialkyl-5-nitroimidazoles (Blaton, Peeters & De Ranter, 1979*a,b*; Goldberg, 1982; Chasseaud, Henrick, Matthews, Scott & Wood, 1984; De Bondt, Blaton, Peeters & De Ranter, 1991; Germain, Declercq, Van Meerseche & Koch, 1977) shows that most bond lengths are similar. There is one significant difference: the N3—C4 bond in the 5-nitroimidazoles varies between 1.343 and 1.367 Å (average 1.356 Å) whereas in the 5-aminoimidazole (2) it is 1.400(4) Å. The significantly shorter N3—C4 bond lengths in the nitroimidazoles, which are slightly shorter than the mean value for imidazoles (1.377 Å) found in the Cambridge Structural Database (Allen *et al.*, 1987), can be rationalized in terms of partial double-bond character resulting from resonance between the nitro substituent and N1. In the amino derivative (2), resonance between ring and substituent is not favoured. The amino N atom is displaced 0.044(6) Å from the plane of the imidazole ring and the N6—H6*a*—H6*b* plane is inclined at 45(3)° to the ring plane. This results in a structure which has bond lengths closer to those of imidazole (N3—C4 1.375 Å; McMullan, Epstein, Ruble & Craven, 1979). With one exception, the ring bond lengths in the crystal structure of (2) are 0.02–0.06 Å shorter than the values calculated by the AM1 method, and, as suggested in our earlier paper (Al-Shaar, Gilmour *et al.*, 1992), we believe that this is a result of the AM1 method overestimating the core-repulsion energies for multi-nitrogen heterocycles. Interestingly, the exception is the N3—C4 bond length which is calculated (1.388 Å) to be 0.012 Å shorter than observed [1.400(4) Å]. The reason for this difference is not clear.

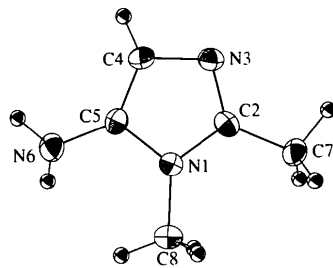


Fig. 1. Structure of (2) showing 50% probability displacement ellipsoids. H atoms are shown as circles of arbitrary radii.

Within the crystal there is evidence of intermolecular hydrogen bonding between N3 and the amino group [H6b...N3 2.04 (4) Å] (Table 3) and this interaction may influence the N3—C4 bond. A weaker intermolecular interaction is observed between N6 and H4 (Table 3).

Experimental

The title compound was prepared by catalytic reduction of 1,2-dimethyl-5-nitroimidazole (Al-Shaar, Gilmour *et al.*, 1992). Crystals suitable for X-ray analysis were obtained from 1,2-dioxane solution and kept under argon at 273 K.

Crystal data

C₅H₉N₃
M_r = 111.15
 Orthorhombic
*P*2₁2₁2₁
a = 5.892 (3) Å
b = 8.480 (3) Å
c = 11.509 (9) Å
V = 575.0 (6) Å³
Z = 4
D_x = 1.284 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 206 reflections
 θ = 2–20°
 μ = 0.085 mm⁻¹
T = 120 K
 Plate
 0.22 × 0.16 × 0.04 mm
 Yellow

Data collection

Enraf–Nonius FAST TV area-detector diffractometer
 Data collection: *MADNES* (Pflugrath & Messerschmidt, 1990)
 Absorption correction: none
 2527 measured reflections

904 independent reflections
 484 observed reflections
 $[I > 2\sigma(I)]$
R_{int} = 0.0689
 θ_{\max} = 24.95°
h = -6 → 4
k = -9 → 9
l = -12 → 12

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.0365$
 $wR(F^2) = 0.0723$
S = 0.623
 904 reflections
 104 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0159P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.139$
 $\Delta\rho_{\max} = 0.156 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.165 \text{ e \AA}^{-3}$
 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 (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
N1	0.0189 (4)	0.4987 (3)	1.0352 (2)	0.0240 (7)
C2	0.0005 (6)	0.5661 (4)	0.9274 (3)	0.0239 (8)
N3	0.1620 (4)	0.5155 (3)	0.8570 (3)	0.0261 (7)
C4	0.2933 (6)	0.4120 (4)	0.9238 (3)	0.0270 (9)
C5	0.2094 (5)	0.4017 (4)	1.0334 (3)	0.0230 (8)
N6	0.2700 (5)	0.3119 (3)	1.1306 (3)	0.0298 (8)
C7	-0.1765 (7)	0.6848 (4)	0.8987 (3)	0.0298 (10)
C8	-0.1284 (7)	0.5249 (5)	1.1357 (4)	0.0353 (11)

Table 2. Selected geometric parameters (Å, °)

N1—C2	1.370 (4)	C2—C7	1.486 (5)
N1—C5	1.391 (3)	N3—C4	1.400 (4)
N1—C8	1.463 (5)	C4—C5	1.358 (5)
C2—N3	1.321 (4)	C5—N6	1.400 (4)
C2—N1—C5	107.3 (3)	C2—N3—C4	105.4 (3)
C2—N1—C8	127.3 (3)	C5—C4—N3	110.4 (3)
C5—N1—C8	125.4 (3)	C4—C5—N1	105.6 (3)
N3—C2—N1	111.2 (3)	C4—C5—N6	133.2 (3)
N3—C2—C7	126.1 (3)	N1—C5—N6	121.0 (3)
N1—C2—C7	122.7 (3)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N6—H6b...N3 ⁱ	0.99 (4)	2.04 (4)	3.015 (5)	171 (3)
C4—H4...N6 ⁱⁱ	0.91 (3)	2.60 (3)	3.448 (5)	154 (3)

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

Data were collected on a Delft Instruments FAST TV area-detector diffractometer. The orientation matrix and unit-cell parameters were determined using *MADONL* software (the small-molecule version of *MADNES*; Pflugrath & Messerschmidt, 1990). Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2). The structure was solved by direct methods. Refinement was by full-matrix least squares on *F*². H atoms were located in difference Fourier maps and included in the refinement. The displacement parameters of the H atoms attached to the same atom were equivalenced. Owing to the small contribution of anomalous scattering it did not prove possible to determine the absolute structure of the compound [Flack (1983) parameter = 1.56 (559)].

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1990). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, least-squares-planes data, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1207). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Photochromic Zwitterionic Viologen: 4,4'-Bipyridinium-1,1'-bis(2-ethylsulfonate) Monohydrate

LORI A. VERMEULEN^a AND PAUL D. ROBINSON^{b*}

^aDepartment of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA, and

^bDepartment of Geology, Southern Illinois University, Carbondale, IL 62901, USA. E-mail: robinson@geo.siu.edu

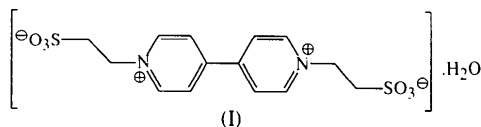
(Received 14 September 1995; accepted 9 October 1995)

Abstract

The structural analysis of the title compound, C₁₄H₁₆N₂O₆S₂·H₂O, shows that the packing of the zwitterionic molecule in the crystal is such that the anionic sulfonate groups are located between the dicationic bipyridinium groups of adjacent molecules. Hydrogen bonds between a water molecule and the sulfonate groups link adjacent molecules into infinite molecular chains. The bipyridinium portions of adjacent molecules are not parallel, but form an angle of 58.0(1)° with respect to one another, forming a wedge within which the anionic groups are located.

Comment

The viologens (1,1'-dialkylbipyridinium compounds) have been well studied because of their herbicidal properties (Summers, 1980) and their potential use as electron acceptors in photochemical redox systems (e.g. Meyer, 1989; Turro & Kavarnos, 1986). In addition, some of these compounds have photochromic properties in the solid state (Vermeulen & Thompson, 1992; Nakato, Kuroda & Kato, 1992; Kamogawa & Suzuki, 1987; Nagamura & Sakai, 1986). There is great interest, therefore, in their use in electrochromic display or photoelectrochromic memory systems (Kamogawa & Ono, 1991; Nagamura, Isoda, Sakai & Ogawa, 1990). Their molecular orientation in such a system is an important property to be controlled. Directional dependence of optical response is an important factor to be considered and has not yet been studied to any great extent. We have grown large single crystals (average 5 × 5 × 2 mm) of the title compound, (I). These crystals are photochromic and exhibit a directional dependence in their optical response. The crystal structure of (I) is reported here. The photochemistry will be presented in a subsequent paper.



In previous reports, the packing of viologen crystals in the solid state has been described as a stacking of planar bipyridinium dication and anionic counterions. In some cases, adjacent bipyridinium planes are parallel and the anions are located precisely between adjacent groups (Argay & Kálmán, 1995; Poojary, Vermeulen, Vicenzi, Clearfield & Thompson, 1994). In other cases, adjacent bipyridinium planes are not parallel but form a wedge that encompasses the counterion (Russell & Wallwork, 1972). The anions have close contacts between the N and neighboring C atoms of the pyridyl rings and are directed towards this cationic center rather than towards the centroid of the rings. In the bipyridinium halides, this interaction is described as charge transfer in nature and is responsible for the colors of the halide salts. In all cases, there are no close contacts between adjacent bipyridinium groups because of charge–charge repulsion of the cationic centers.

Fig. 1 shows the molecular structure of (I) along with the atom-numbering scheme, while Fig. 2 shows the packing of the molecules in the crystal. Note that the zwitterion lies on an inversion center and the water molecule on a twofold axis. Adjacent molecules are connected *via* a hydrogen-bonding interaction between a water molecule and the sulfonate anions. The resulting molecular chains propagate infinitely in the [001] direction. The hydrogen-bond geometry is given in Table 2. Bipyridinium planes of adjacent