2-Amino-1,3-dimethylimidazolium 2,2-Dimethyl-4,6-dioxo-1,3-dioxanide. First Structural Characterisation of the Anion of Meldrum's Acid [1]

Norbert Kuhn, Ahmed Al-Sheikh, and Manfred Steimann

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Reprint requests to Prof. Dr. N. Kuhn. E-mail: norbert.kuhn@uni-tuebingen.de

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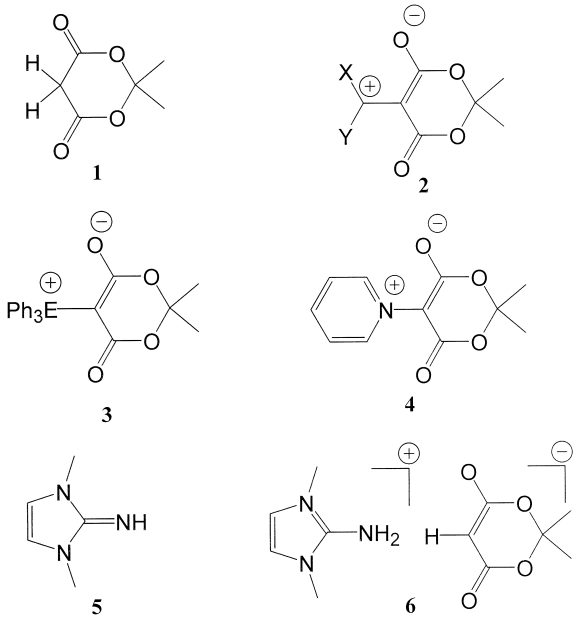
2-Amino-1,3-dimethylimidazolium 2,2-dimethyl-4,6-dioxo-1,3-dioxanide (**6**) has been obtained from the reaction of 2,2-dimethyl-4,6-dioxo-1,3-dioxan (**1**, "Meldrum's acid") and 2-imino-1,3-dimethylimidazoline (**5**) in excellent yield. The unit cell of **6** contains two crystallographically independent anions lying on crystallographic mirror planes. The structure of the anion is compared with that of compound **1**.

Key words: Heterocycles, Imidazole, Dioxan, Hydrogen Bonding, Crystal Structure



Scheme 1.

Introduction

Meldrum's acid (**1**) has been widely used in organic synthesis [2] starting with its discovery [3] and correct assignment [4]. From its crystal structure analysis [5] supported by solid state NMR experiments [6], the presence of an enol type structure could be excluded despite the pronounced ability of the six-membered ring to bear a negative charge.

The tendency of Meldrum's acid fragments to form betaine structures has been proved in numerous organic derivatives (**2**, see *e.g.* [7–10]) and, more recently, in the ylidic adducts **3** (E = As, Sb, Bi) and **4** of group 15 elements [1, 11]. Surprisingly, the structure of the Meldrum's acid anion itself has not been published though it plays an important role as an intermediate in preparative organic chemistry [2]. We therefore report on the synthesis and crystal structure of its 2-amino-1,3-dimethylimidazolium salt.

Synthesis and Crystal Structure of 2-Amino-1,3-dimethylimidazolium 2,2-Dimethyl-4,6-dioxo-1,3-dioxanide

Owing to its acidic nature, Meldrums's acid is easily deprotonated. Reaction of **1** with the strong ylide type base **5** [12] gives 2-amino-1,3-dimethylimidazolium 2,2-dimethyl-4,6-dioxo-1,3-dioxanide (**6**) as colourless stable crystals in excellent yield.

We have determined the crystal structure of **6** to get more insight into the bonding of the Meldrum's acid anion (Tables 1–2, Fig. 1). **6** crystallises in the orthorhombic space group *Pnma*. The unit cell contains two crystallographically independent anions lying on crystallographic mirror planes.

There are only small differences in the geometry of the anions A and B (see Table 2, the values for A are used in the following discussion). On comparison with the structure of **1** [5], significant shortening of the endocyclic C–C bonds and elongation of the exocyclic and endocyclic C–O carboxylate bonds is detected for the anion [C(6)–C(7) 1.4006(13), C(7)–O(1) 1.2347(13), C(7)–O(2) 1.3850(12) Å], while the other C–O bond lengths of the dioxan ring remain nearly un-

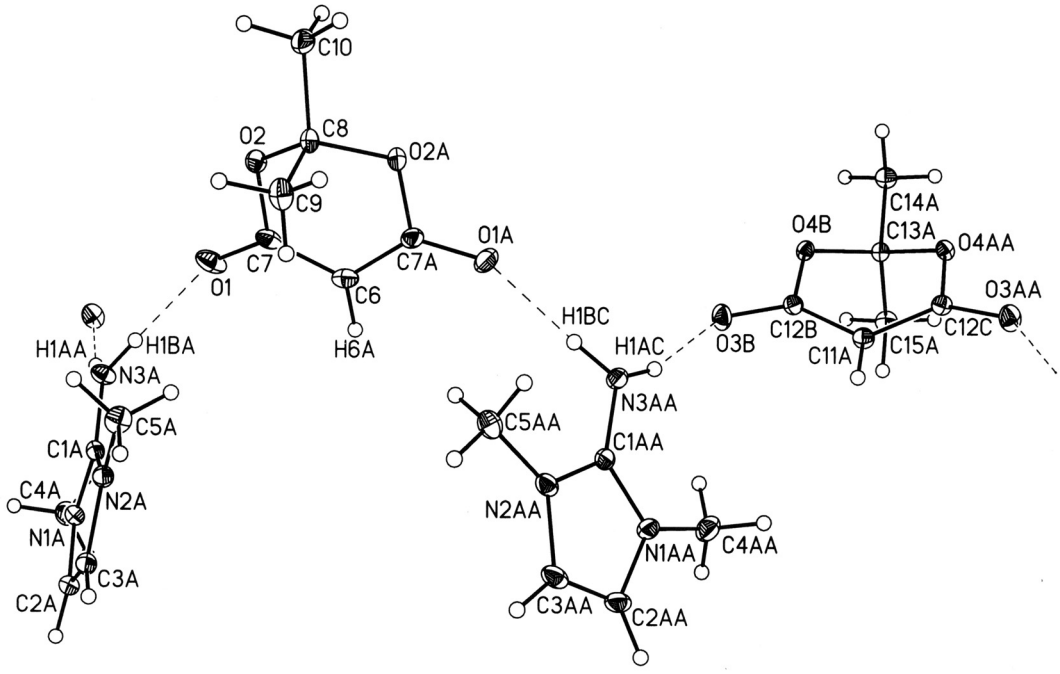


Fig. 1. View of $C_{11}H_{17}N_3O_4$ (**6**) in the crystal.

Table 1. Crystal data and structure refinement for $C_{11}H_{17}N_3O_4$ (**6**).

Empirical formula	$C_{11}H_{17}N_3O_4$
Formula weight	255.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Pnma*
Unit cell dimensions	a = 9.9070(15) Å
	b = 16.064(3) Å
	c = 15.981(3) Å
Volume	2543.5(8) Å^3
Z	8
Density (calculated)	1.333 Mg/m^3
Absorption coefficient	0.103 mm^{-1}
F(000)	1088
Crystal size	0.35 × 0.45 × 0.35 mm^3
Theta range for data collection	2.42 to 27.52°
Index ranges	$-12 \leq h \leq 12$, $-20 \leq k \leq 20$, $-20 \leq l \leq 20$
Reflections collected	22234
Independent reflections	3035 [R(int) = 0.0296]
Completeness to theta = 27.52°	100.0%
Absorption correction	empirical
Max., and min. transmission	0.2672 and 0.2351
Refinement method	full–matrix least–squares on F^2
Data/restraints/parameters	3035/0/250
Goodness–of–fit on F^2	1.877
Final R indices [$I > 2$sigma(I)]	$R1$ = 0.0345, $wR2$ = 0.0880
R indices (all data)	$R1$ = 0.0376, $wR2$ = 0.0921
Extinction coefficient	0.0211(16)
Largest diff. peak and hole	0.306 and −0.188 e · Å^{-3}

Table 2. Selected bond lengths [Å] and angles [°] for $C_{11}H_{17}N_3O_4$ (**6**).

Anion A		Anion B	
O(1)–C(7)	1.235(1)	O(3)–C(12)	1.236(1)
O(2)–C(7)	1.385(1)	O(4)–C(12)	1.382(1)
O(2)–C(8)	1.430(1)	O(4)–C(13)	1.432(1)
C(6)–C(7)	1.401(1)	C(11)–C(12)	1.404(1)
C(8)–C(10)	1.514(2)	C(13)–C(14)	1.515(2)
C(8)–C(9)	1.521(2)	C(13)–C(15)	1.517(2)
C(7)–O(2)–C(8)	116.4(1)	C(12)–O(4)–C(13)	116.3(1)
C(7)#1–C(6)–C(7)	121.4(1)	C(12)–C(11)–C(12)#1	121.4(1)
O(1)–C(7)–O(2)	114.4(1)	O(3)–C(12)–O(4)	114.9(1)
O(1)–C(7)–C(6)	128.3(1)	O(3)–C(12)–C(11)	128.1(1)
O(2)–C(7)–C(6)	117.3(1)	O(4)–C(12)–C(11)	116.9(1)
O(2)#1–C(8)–O(2)	110.9(1)	O(4)#1–C(13)–O(4)	110.8(1)
C(10)–C(8)–C(9)	113.0(1)	C(14)–C(13)–C(15)	112.0(1)
Cation			
N(1)–C(1)	1.3439(13)	C(1)–N(1)–C(2)	108.28(9)
N(1)–C(2)	1.3959(14)	C(1)–N(2)–C(3)	108.48(9)
N(2)–C(1)	1.3439(13)	N(3)–C(1)–N(1)	126.65(9)
N(2)–C(3)	1.3971(13)	N(3)–C(1)–N(2)	125.09(9)
N(3)–C(1)	1.3362(12)	N(1)–C(1)–N(2)	108.19(8)
C(2)–C(3)	1.3360(19)	C(3)–C(2)–N(1)	107.74(9)
		C(2)–C(3)–N(2)	107.31(9)

Symmetry transformations used to generate equivalent atoms: #1 x, $-y + 1/2$, z.

changed [O(2)–C(8) 1.4303(10) Å]. The folding angles along the endocyclic dioxygen axis are in the expected range [O(2)C(8)O(2A)/O(2)C(7)C(7A)O(2A) 43.8, O(4)C(13)O(4A)/O(4)C(12)C(12A)O(4A) 45.0°].

The structure of the cation (Table 2) is close to that observed for its chloride salt [12], in which isolated ions have been found. Therefore, the isolated cation may be regarded as an immonium ion more than an ammonium species (for MO calculations see [13]). In contrast to its chloride salt, the cation in **6** contains a pyramidal NH_2 substituent apparently as a consequence of the hydrogen bonding mentioned below [C(1)–N(3)–H(1a) 119.5, C(1)–N(3)–H(1b) 117.7, H(1a)–N(3)–H(1b) 118.2°]. These bonds also may cause the nonplanar arrangement of the five-membered ring and the CNH_2 fragment [H(1a)N(3)H(1b)/N(1)C(1)N(2) 23.0°].

The anions are connected to the cations *via* N–H–O hydrogen bonds incorporating the exocyclic nitrogen and oxygen atoms [N(3aa)–H(1ac) 0.844, N(3aa)–H(1bc) 0.893, O(1a)–H(1bc) 1.917, O(3b)–H(1ac) 2.002 Å; N(3aa)–H(1bc)–O(1a) 172.1, N(3aa)–H(1ac)–O(3b) 163.6, H(1bc)–O(1a)–C(7a) 152.8, H(1ac)–O(3b)–C(12b) 137.9°] thus forming a wave-like polymeric structure. As expected, the bond lengths and angles indicate a strong interaction compared with the hydrogen bonding in **1**. Apparently, neither the endocyclic oxygen atoms nor C(6)–H and C(11)–H are part of hydrogen bonds.

Concluding remarks

As expected, the enolate nature of the anion of **6** causes on comparison with the structure of **1** a shortening of the endocyclic C–C distances accompanied by elongated exocyclic C–O bonds. The presence of the hydrogen bonds seems to be of minor influence on the enolate structure as revealed by comparison with the pyridinium compound **4** (d C=C 1.411(1), 1.354(1), C–O 1.225(1), 1.227(1) Å [11]). In summary, the betaine nature in the structures of **3** [1] and the known organic adducts of type **2** [7–10] is clearly confirmed by our results. We are continuing our investigations on inorganic Meldrum's acid derivatives and will report on selenium and tellurium containing adducts [14] in due course.

Experimental Section

All experiments were performed in purified solvents under argon. 2-Imino-1,3-dimethylimidazoline (**5**) has been prepared according to a published procedure [12].

2-Amino-1,3-dimethylimidazolium 2,2-dimethyl-4,6-dioxo-1,3-dioxanide (**6**)

A solution of 0.56 g (5 mmol) of **5** and 0.72 g (5 mmol) of **1** in 20 ml of acetonitrile was stirred for 3 h at 20 °C. The solvent was removed *in vacuo*. The residue was recrystallised from dichloromethane/diethylether to give 1.25 g (98%) **6**, colourless crystals, m.p. 141 °C. – ^{1}H NMR ($CDCl_3$); cation: δ = 3.51 (s, 6 H, Me), 6.50 (s, 2 H, 4,5-H), 8.49 (s, 2 H, NH_2); anion: δ = 1.54 (s, 6 H, Me); 3.85 (s, 1 H, 5-H). – ^{13}C NMR ($CDCl_3$), cation: δ = 33.6 (Me), 116.5 (C4,5), 147.5 (C2); anion: δ = 26.1 (Me), 64.7 (C5), 102.6 (C2), 169.4 (C4,6). – Analysis for $C_{11}H_{17}N_3O_4$ 255.27): calcd. C 51.76, H 6.71, N 16.46; found C 51.54, H 6.50, N 16.49.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 208115 for compound **6**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

Acknowledgements

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