Synthesis and Structure of a Zwitterionic Imidazolium 1,3-Dioxanide [1]

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{Bis(methylthio)methylene}-2,2-dimethyl-4,6-dioxo-1,3-dioxane (**7**) reacts with *cis*-1,2-diamino-1,2-dicyanoethene to give 2,2-dimethyl-4,6-dioxo-5-{2-(4,5-dicyano)} imidazolio-1,3-dioxan-5-yl-imidazolium ylide (**8**) as a stable crystalline solid in good yield. The crystal structure of **8** × C_3H_6OS is discussed.

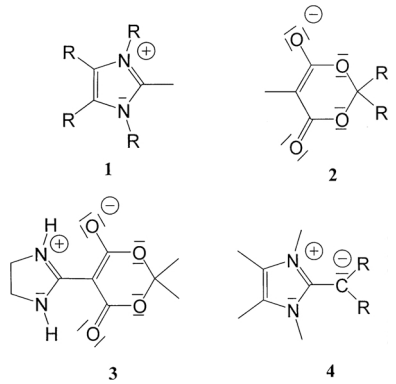
Key words: Betaines, Heterocycles, Crystal Structure

Introduction

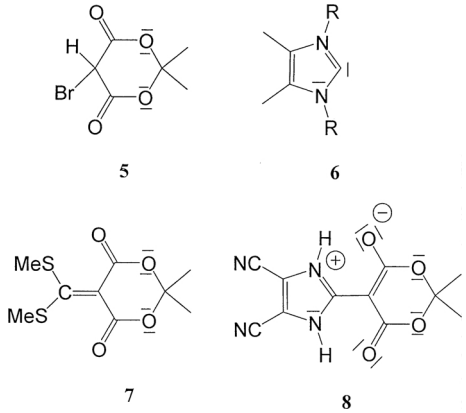
There has been much interest in conjugated 1,1-endiamines in the past years [2] starting with the pioneering work of Gompper [3]. Stabilisation of betaine structures is best achieved by heteroatom containing fragments like imidazolium (**1**) and 1,3-dioxanide (**2**) rings [4]. Recently, Westrup gave an excellent overview of the influence of intramolecular hydrogen bonds on the planarisation of *push-pull* ethylenes including the betaine compound **3** [5]. Because of our interest in the chemistry of imidazolium ylides **4** [6 – 9] we investigated the synthesis and structure of a zwitterionic imidazolium 1,3-dioxanide.

Synthesis and Structure of 2,2-Dimethyl-4,6-dioxo-5-{2-(4,5-dicyano)}imidazolio-1,3-dioxan-5-yl-imidazolium Ylide (8)

Zwitterionic derivatives of Meldrum's acid are easily obtained by bromide substitution in **5** as reported recently [1, 10]. Owing to their high basicity [11], 2,3-dihydroimidazol-2-ylidenes (**6**, R = Me, Et, *iso*-Pr [12]) cause deprotonation of **5** to give imidazolium salts exclusively [13]. We therefore used the method of Huang [14] reacting **7** with *cis*-1,2-diamino-1,2-dicyanoethylene from which we obtained **8** as stable colourless crystals in good yield.



Scheme 1.



Scheme 2.

The crystal structure of **8** × C_2H_6OS (Table 1 – 2, Fig. 1) reveals the presence of dimeric betaine solvate units connected via hydrogen bonds. In **8**, the heterocyclic ring fragments are nearly coplanar the twist angle between the planes N(1)C(1)N(2) and C(6)C(8)C(7) being 5.9°. The length of the central olefinic bond [C(1)-C(8) 1.4178(18) Å] is intermediate between the range of typical single and double bonds. The structures of the imidazolium and dioxanide rings (for details see Table 2) agree well with that of isolated imidazolium [15] and 1,3-dioxanide [16] ions thus confirming the zwitterionic nature of the compound. The N-H-O distances and angles [N(1)-H(1) 0.801(2), O(1)-H(1) 2.240(2) Å, N(1)-H(1)-O(1) 119.7(1)°; N(2)-H(2) 0.911(1), O(2)-H(2) 2.236(2) Å, N(2)-H(2)-O(2) 114.0(1) Å] are at the upper and lower end expected for intramolecular hydrogen bonds, respectively. Interestingly, the hydrogen bonds to the solvent molecule [O(5)-H(2) 1.853 Å, N(2)-H(2)-

Table 1. Crystal data and structure refinement for **8** * C_2H_6OS.

Empirical formula	$C_{13}H_{14}N_4O_5S$
Formula weight	338.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2/c$
Unit cell dimensions	$a = 12.7858(18)$ Å
	$b = 5.2218(10)$ Å
	$\beta = 103.000(11)^\circ$
	$c = 23.628(3)$ Å
Volume	1537.1(4) Å^3
Z	4
Density (calculated)	1.462 Mg/m^3
Absorption coefficient	0.242 mm^{-1}
$F(000)$	704
Crystal size	$0.35 \times 0.45 \times 0.45$ mm^3
Theta range for data collection	2.12 to 27.50°
Index ranges	$-16 \leq h \leq 0$, $-6 \leq k \leq 6$,
	$-29 \leq l \leq 30$
Reflections collected	6642
Independent reflections	3537$[R(int) = 0.0662]$
Completeness to $\theta = 27.50^\circ$	99.9%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3537 / 0 / 259
Goodness-of-fit on F^2	1.920
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0446$, $wR2 = 0.1139$
R Indices (all data)	$R1 = 0.0544$, $wR2 = 0.1240$
Extinction coefficient	0.005(3)
Largest diff. peak and hole	0.419 and -0.586 e.Å^{-3}

O(5) 152.7(1)Å] and the "intermolecular" hydrogen bonds of the central four-membered ring unit [H(1)-O(1A) 2.069(1) Å, O(1)-H(1)-O(1A) 83.8(1), H(1)-O(1)-H(1A) 96.2(1) Å] are significantly shorter than the intramolecular ones.

Over all, structural data of **8** clearly confirm its zwitterionic nature. The marked charge separation of the central olefinic bond is also indicated by the extreme shift difference of its carbon atoms in the ^{13}C NMR spectrum [$\delta = 71.6$ ($C5_M$), 148.5 ($C2_I$)].

Concluding remarks

With the presentation of structural and spectroscopic properties of the imidazolium dioxanide **8** we confirm the results of Westrup on *push-pull* ethylenes reported recently [5]. Though there is only a minor difference in the length of the central olefinic bonds and their adjacent atoms in **3** and **8**, the ^{13}C NMR shifts of $C5_M$ (δ **3** 65.4, **8** 71.6) indicate a less effective charge separation in **8** presumably as a consequence of the low donor capacity of the intrinsic 4,5-dicyanoimidazol-2-ylidene.

Table 2. Bond lengths [Å] and angles [°] for **8** * C_2H_6OS.

N(1)-C(1)	1.354(2)	O(3)-C(9)	1.437(2)
N(1)-C(2)	1.377(2)	O(4)-C(7)	1.360(2)
N(2)-C(1)	1.353(2)	O(4)-C(9)	1.438(2)
N(2)-C(3)	1.380(2)	C(1)-C(8)	1.418(2)
N(3)-C(4)	1.151(2)	C(2)-C(3)	1.361(2)
N(4)-C(5)	1.143(3)	C(2)-C(4)	1.423(2)
O(1)-C(7)	1.223(2)	C(3)-C(5)	1.428(2)
O(2)-C(6)	1.219(2)	C(6)-C(8)	1.433(2)
O(3)-C(6)	1.369(2)	C(7)-C(8)	1.432(2)
C(1)-N(1)-C(2)	109.3(1)	C(2)-C(3)-N(2)	107.4(1)
C(1)-N(2)-C(3)	109.0(1)	N(3)-C(4)-C(2)	177.3(2)
C(6)-O(3)-C(9)	118.1(1)	N(4)-C(5)-C(3)	178.0(2)
C(7)-O(4)-C(9)	117.7(1)	O(3)-C(6)-C(8)	116.5(1)
N(2)-C(1)-N(1)	107.2(1)	O(4)-C(7)-C(8)	116.7(1)
N(2)-C(1)-C(8)	126.5(1)	C(1)-C(8)-C(7)	119.4(1)
N(1)-C(1)-C(8)	126.3(1)	C(1)-C(8)-C(6)	119.4(1)
C(3)-C(2)-N(1)	107.1(1)	C(7)-C(8)-C(6)	121.0 (1)

Symmetry transformations used to generate equivalent atoms.

Experimental Section

All experiments were performed in purified solvents under argon. 5-Bis(methylthio)methylene-2,2-dimethyl-4,6-dioxo-1,3-dioxane (**7**) was prepared according to a published procedure [17]. Crystals of **8** $\times$ C_2H_6OS have been obtained by slow evaporation of a DMSO solution of **8**.

*$C_{11}H_8N_4O_4$ (**8**)*

A mixture of 1.24 g (5 mmol) of **7** and 0.54 g (5 mmol) of *cis*-1,2-diamino-1,2-dicyanoethene in 30 ml of ethanol was refluxed for 8 h. The solid precipitated after cooling was separated and recrystallised from dimethyl sulfoxide/dichloromethane to give 0.90 g (69%) of **8** as colourless crystals, m.p. 209 °C. – ^{1}H-NMR (DMSO-d_6): $\delta = 1.51$ (s, 6 H, Me), 12.2 (s, 2 H, NH). – ^{13}C-NMR (DMSO-d_6): $\delta = 26.4$ (Me), 71.6 ($C5_M$), 103.2 ($C2_M$), 109.2 (CN), 111.2 ($C4,5_I$), 148.5 ($C2_I$), 163.3 (CO). – IR (KBr): ν(CN) = 2244, ν(CO) = 1635 cm^{-1}. – MS (FAB, negative mode, 3-nitrobenzylic alcohol as matrix): *m/z* (%) = 259 (45, [M - H]$^-$), 153 (100, [M - Me_2CO, CO_2]$^-$) and further fragments. – Analysis for $C_{11}H_8N_4O_4$ (260.21): calcd. C 50.77, H 3.10, N 21.23; found C 50.68, H 3.18, N 21.73.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 212020 for compound **8** $\times$ C_2H_6OS. 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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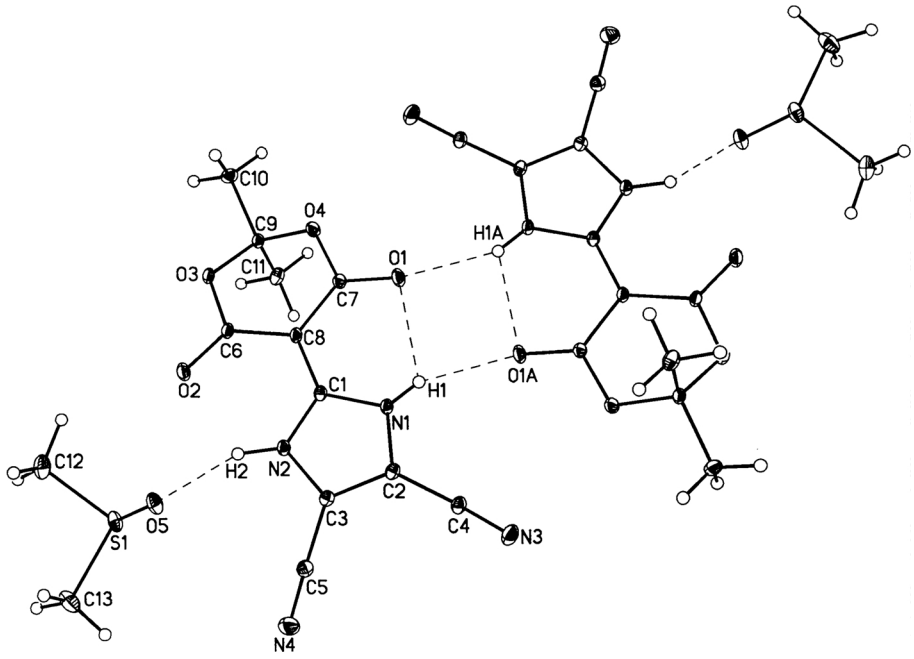

Fig. 1. View of the molecule of **8** $\times$ C_2H_6OS in the crystal. Ellipsoids of thermal vibration represent 20% probability.

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