Structure of a novel protonated oxadiazine: an unusual heterocycle from the cycloaddition of a ketone with nitriles

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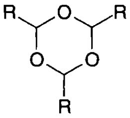
An X-ray crystal structure identifies the novel 6-membered heterocycle 3 containing two nitrogens, an oxygen, a dipositive charge and π-electron delocalisation over 5 ring atoms and 2 exocyclic nitrogens.

Aldehydes are known to undergo self condensation reactions catalysed by acids to yield cyclic acetals like the trimer **1**.[1] Similarly nitriles can be trimerized with acids (*e.g.* HCl) to give triazines[2] (*e.g.* **2**), mixed triazines resulting from mixtures of different nitriles.[3] Here we report that 2 equiv. of 1,1-dimethylcyanamide ($N{\equiv}CNMe_2$) add to acetone in the presence of strong acid to give the novel dication **3** (R = NMe_2) rather than the anticipated product **4**. The structure and a mechanism for formation of **3** are described.

Equimolar $NCNMe_2$ and acetone were treated with more than 2 equiv. of CF_3SO_3H (23 °C, 30 min), and then diethyl ether was added, and the mixture cooled for several hours to 4 °C. A crystalline precipitate, shown by analysis to be $[C_9H_{20}N_4O_1](CF_3SO_3)_2$, consistent with two dimethylcyanamides condensed with one acetone molecule, was the only product formed.† Its IR spectrum in Nujol shows two strong stretches at ν 1742 and 1689 cm^{-1}.

Fig. 1 shows a PLUTON drawing for the X-ray structure‡ of **3** and selected bond lengths and angles. The crystallographic results establish the structure as **3** rather than **4**. The ring heteroatoms could be distinguished from one another and are assigned as shown. The 6-membered heterocycle is planar (σ = 0.017 Å) with atoms O(21), C(24), C(241) on a mirror plane. The interatomic distances C(22)–N(23) and C(22)–N(221) suggest double bond character with both C(22) and N(23) having sp^2 orbitals available [N(221)–C(22)–N(23), 126.6(3)°; N(221)–C(22)–O(21), 112.6(3)°]. Hydrogen atoms, including the two associated with the positive charges on N(23) and its symmetry related nitrogen atom, were found in the final full-matrix least-squares refinement and were refined. There was no refinable hydrogen atom on O(21). The intermolecular distance between the heterocyclic cation and the triflate anion, N(23)–O(12) = 2.79 Å [H(23)···O(12) = 1.88 Å], and the related angle [N(23)–H(23)–O(12), 163.4°] are consistent with a hydrogen bond contact.

While the 6-membered ring is not aromatic, with one sp^3 carbon present, the O(21)–C(22) bond lengths (1.352 Å) are indicative of appreciable π-electron delocalisation through resonance hybrid structures **3a–c** [*cf.* C–O bond lengths in furan (1.368 Å) *vs.* dialkyl ethers (1.41 Å)]. Thus π-electron density is delocalised over 5 of the 6 ring atoms while the positive charges are localised on the endocyclic nitrogen atoms.



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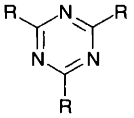

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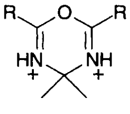

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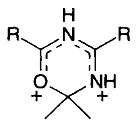


4

In considering the reaction mechanism, we anticipated that the known acid-promoted dimerization of nitriles would precede cycloaddition and protonation to give structure **4** (Scheme 1).

The unexpected crystallographic finding that the observed product is **3** rather than **4** suggests that the reaction may instead be analogous to the known formation of amidals, in which two moles of nitrile add to 1 mole of aldehyde.[4] Similarly the formation of **3** requires addition of dimethylcyanamide to acidified acetone, followed by cyclisation and protonation (Scheme 2).

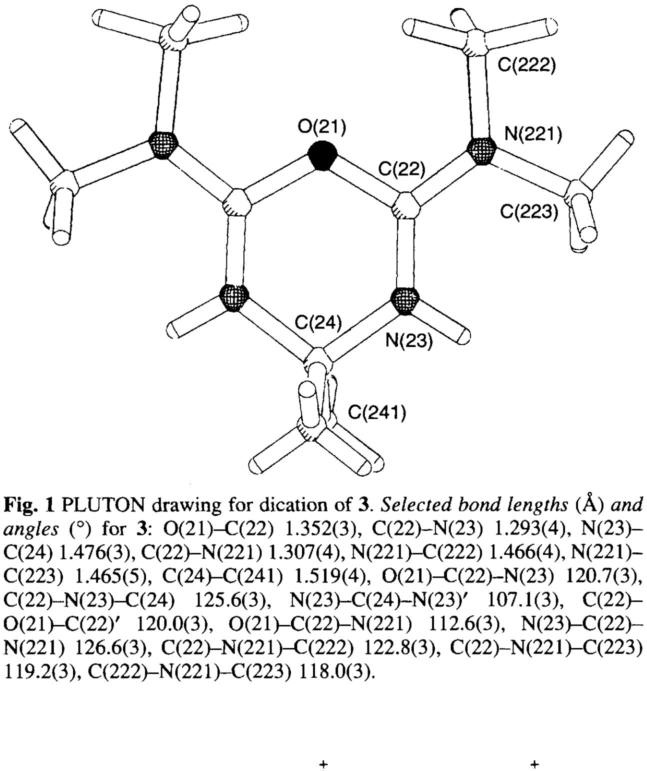
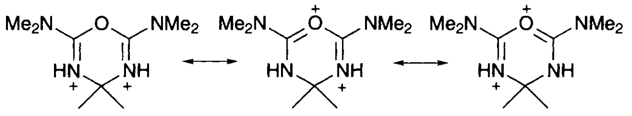
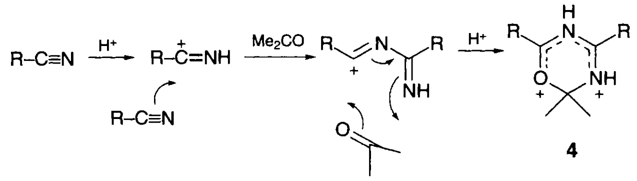


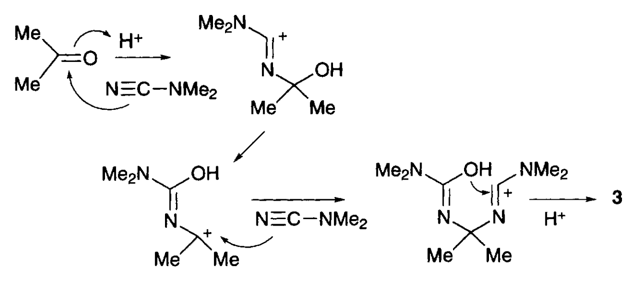
Fig. 1 PLUTON drawing for dication of **3**. *Selected bond lengths* (Å) *and angles* (°) for **3**: O(21)–C(22) 1.352(3), C(22)–N(23) 1.293(4), N(23)–C(24) 1.476(3), C(22)–N(221) 1.307(4), N(221)–C(222) 1.466(4), N(221)–C(223) 1.465(5), C(24)–C(241) 1.519(4), O(21)–C(22)–N(23) 120.7(3), C(22)–N(23)–C(24) 125.6(3), N(23)–C(24)–N(23)′ 107.1(3), C(22)–O(21)–C(22)′ 120.0(3), O(21)–C(22)–N(221) 112.6(3), N(23)–C(22)–N(221) 126.6(3), C(22)–N(221)–C(222) 122.8(3), C(22)–N(221)–C(223) 119.2(3), C(222)–N(221)–C(223) 118.0(3).



3a **3b** **3c**



Scheme 1



Scheme 2

Surprisingly this is the first reported structure for a heterocyclic 1,3,5-oxadiazine, unexpectedly stable as the dication, which has unknown chemical and biological properties.

Footnotes

† Anal. Calcd. for $C_{11}H_{20}F_6N_4O_7S_2$: C, 26.48; H, 4.01; N, 11.23%. Found: C, 25.55; H, 4.09; N, 11.18%

‡ *Crystal data* for $C_{11}H_{20}F_6N_4O_7S_2$, MW = 498.43, T = 293(2) K, λ = 0.71073 Å, monoclinic, $C2/c$, a = 13.070(3), b = 8.6046(9), c = 19.107 (7) Å, β = 107.94(1)°, Z = 4, ρ_{calc} = 1.619 mg m^{-3}, μ = 0.356 mm^{-1}, $F(000)$ = 1024, independent reflections 1891, parameters 177, $R_1[(I > 2s(I)]$ = 0.0375, wR_2 = 0.0884. Atomic coordinates bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/137.

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