

Pyrazolo[1,2-*a*]1,2,3-triazinium-4-olate

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The title mesomeric betaine **1** is formed by a novel thermal cyclisation method; its X-ray crystal structure, that of its 3-bromo derivative, and its reactions with acids, bases and electrophiles are reported.

As part of our continuing studies of the preparative applications of pyrolytic reactions of aminomethylene Meldrum's acid derivatives,¹⁻³ we report here the synthesis, structure and chemical properties of pyrazolo[1,2-*a*]1,2,3-triazinium-4-olate **1**, the parent member of a novel series of heterocyclic mesomeric betaines.^{4,5}

We have found that two isomeric products are obtained by flash vacuum pyrolysis (FVP) of the *N*-pyrazolyl derivative **2**[†] (readily obtained by reaction of *N*-aminopyrazole⁶ with

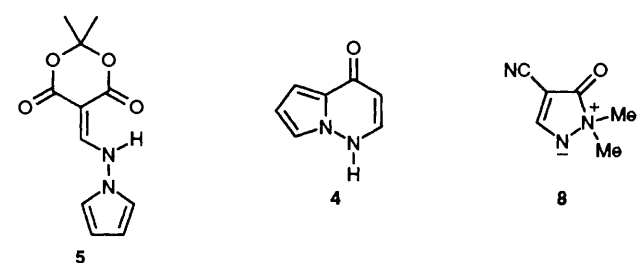
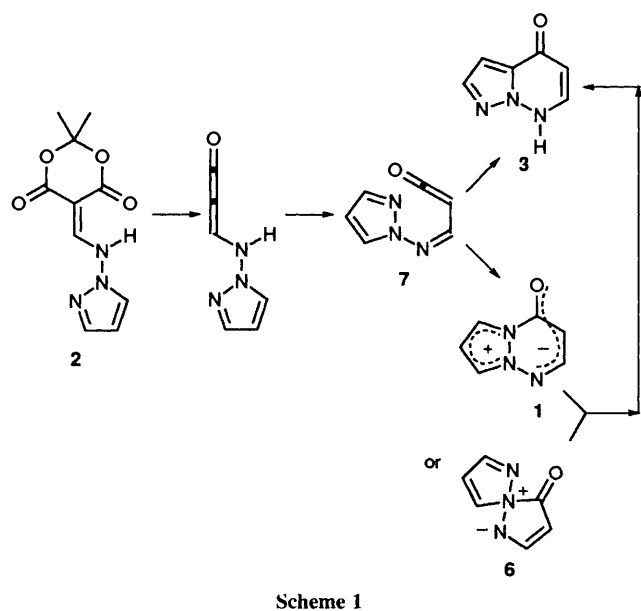
methoxymethylene Meldrum's acid²) in the range 450–700 °C (Scheme 1). The relative proportion of these products is strongly temperature dependent (Fig. 1). The major product at high temperatures was readily identified as the pyrazolopyridazinone **3**; an analogous pyrrolopyridazinone **4** is formed by pyrolysis of the *N*-aminopyrrole derivative **5**. The major isomer at lower temperatures was readily converted to **3** by pyrolysis (see below), but the spectroscopic data did not allow unambiguous discrimination between the betaine structures **1** and **6**. Either of these compounds could be formed by collapse of the key iminoketene intermediate **7**: there is some precedent for the spiro-compound **6** from the work of Chuche *et al.*, who obtained betaines (e.g. **8**) by cyclisation of dialkylhydrazonoketenes obtained from enaminoesters.⁷

[†] All new compounds were characterised by their spectra and by elemental analysis.

However, an X-ray crystal structure determination (Fig. 2) revealed that the unknown compound was in fact the pyrazolotriaziniumolate **1**.[‡]

The optimum conditions for the isolation of **1** proved to be pyrolysis at 500 °C (8×10^{-5} Torr—mercury diffusion pump; 1 Torr \approx 133.3 Pa) using a sublimation temperature of 80–85 °C. Yields of 50–55% were obtained reproducibly on a 2.5 mmol scale. These conditions provide a simple and convenient three-step route from pyrazole to the parent betaine system **1**; only highly substituted examples of this system have been previously synthesized.⁴

Our initial studies of the chemistry of the mesomeric betaine **1** are summarised in Scheme 2. It proved to have high thermal stability, and is unaffected by either sublimation at 100 °C or by FVP at 500 °C. At 700 °C **1** was transformed quantitatively into the 'thermodynamic' isomer **3**, which suggests that it can



exist in equilibrium with the ketene **7** at high temperatures. The electron-rich nature of the six-membered ring is confirmed by rapid deuterium exchange at the 3-position using [²H]trifluoroacetic acid, and by electrophilic substitution using *N*-bromosuccinimide in chloroform (room temp. over-

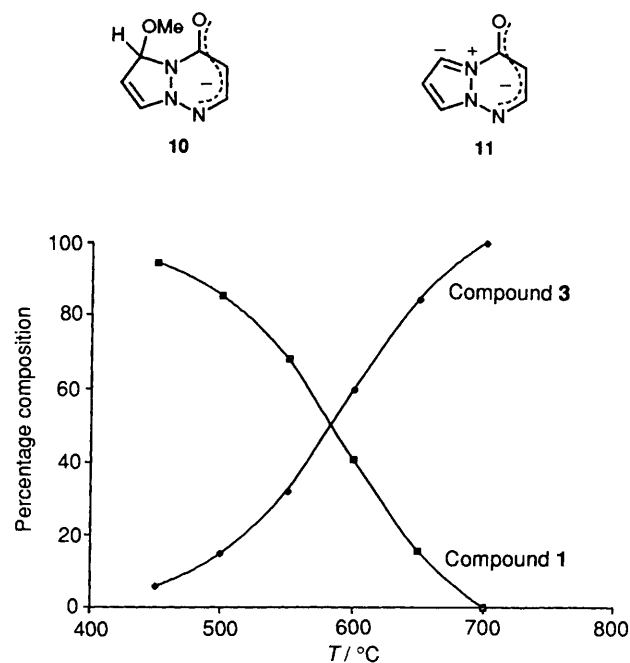
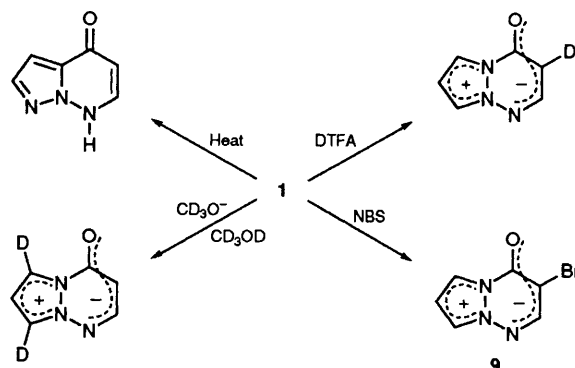


Fig. 1 Temperature dependence of the formation of **1** and **3** by flash vacuum pyrolysis of **2**

[‡] Crystal data for $C_6H_5N_3O \cdot C_3H_6O$, **1**, $M = 193.20$, triclinic, space group $P\bar{1}$, $a = 5.633(5)$, $b = 8.221(3)$, $c = 9.958(9)$ Å, $\alpha = 110.10(3)$, $\beta = 95.12(3)$, $\gamma = 92.74(3)^\circ$, $V = 430$ Å³ [from 2θ values of 16 reflections measured at $\pm\omega$ ($2\theta = 20$ – 24° , $\lambda = 0.71073$ Å), $T = 298$ K], $Z = 2$, $D_c = 1.492$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.102$ mm⁻¹. A colourless lath ($0.02 \times 0.08 \times 0.43$ mm) was mounted on a Stoe Stadi-4 four-circle diffractometer. Data collection using Mo-K α X-radiation ($\lambda = 0.71073$ Å), ω - 2θ scans and the learnt-profile method⁸ yielded 1219 reflections ($2\theta_{\text{max}} 45^\circ$), 830 unique ($R_{\text{int}} 0.05$), of which 641 with $F \geq 4\sigma(F)$ were used in all calculations. Following solution by automatic direct methods,⁹ the structure was refined by full-matrix least-squares analysis (on F^2), with anisotropic thermal parameters for all non-H atoms. The CH₃- groups of the acetone solvate were treated as rigid entities while other H atoms were included in fixed, calculated positions.¹⁰ At final convergence, $R = 0.0885$, $wR = 0.0928$, $S = 1.370$ for 133 parameters and the final ΔF synthesis showed no feature outwith ± 0.38 e Å⁻³. The high residuals are attributed to the unfavourable morphology of the crystal and to the presence of the acetone solvent in the crystal lattice.

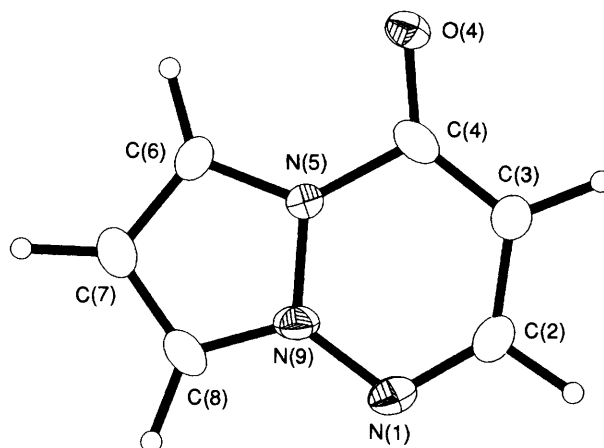


Fig. 2 ORTEP diagram of the mesomeric betaine **1**

night, 94% yield). The X-ray crystal structure of the resulting bromo-compound **9** (Fig. 3) confirms the site of reaction but

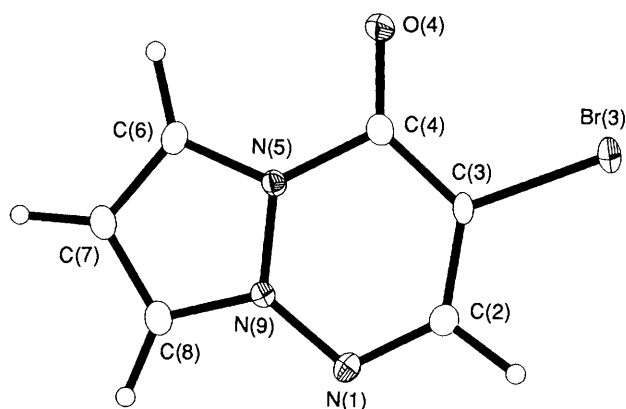


Fig. 3 ORTEP diagram of one of the two independent molecules of **9** in the asymmetric unit

§ *Crystal data* for $C_6H_4BrN_3O$, **9**, $M = 214.02$, triclinic, space group $P\bar{1}$, $a = 6.792(7)$, $b = 7.639(16)$, $c = 14.041(15)$ Å, $\alpha = 102.83(8)$, $\beta = 92.26(7)$, $\gamma = 101.18(9)^\circ$, $V = 694$ Å³ [from 2 θ values of 14 reflections measured at $\pm\omega$ ($2\theta = 30$ – 32° , $\lambda = 0.71073$ Å), $T = 150.0(1)$ K], $Z = 4$, $D_c = 2.047$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 5.797$ mm⁻¹. A colourless tablet ($0.58 \times 0.54 \times 0.12$ mm) was mounted on a Stöe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.¹³ Data collection using Mo-K α X-radiation ($\lambda = 0.71073$ Å) and ω - 2θ scans gave 2490 reflections ($2\theta_{\text{max}} 45^\circ$, ψ -scan-based absorption correction, 7% decay correction), 1764 unique ($R_{\text{int}} 0.017$), of which 1589 with $F \geq 4\sigma(F)$ were used in all calculations. Following solution by automatic direct methods,⁹ the structure was refined by full-matrix least-squares analysis (on F^2), with anisotropic thermal parameters for all non-H atoms: H atoms were included in fixed, calculated positions with a common U_{iso} of $0.0307(12)$ Å². At final convergence, $R = 0.0356$, $wR = 0.0484$, $S = 1.055$ for 201 parameters and the final ΔF synthesis showed no feature above 0.86 e Å⁻³.

Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the geometry is otherwise similar to that of the parent compound (*cf.* ref. 11). Surprisingly, methoxide ion did not add to the five-membered ring to give a pseudobase (*e.g.* **10**) but instead deuterium exchange was observed at the 6- and 8-positions, presumably *via* ylide-like intermediates *e.g.* **11** (*cf.* ref. 12).

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