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1,4-DIMETHYL-3,6-DIOXO-1,2,4,5-TETRAZIN-1-IUM-5(4H)-ID, A NEW SIX-MEMBERED HETEROCYCLIC BETAINE

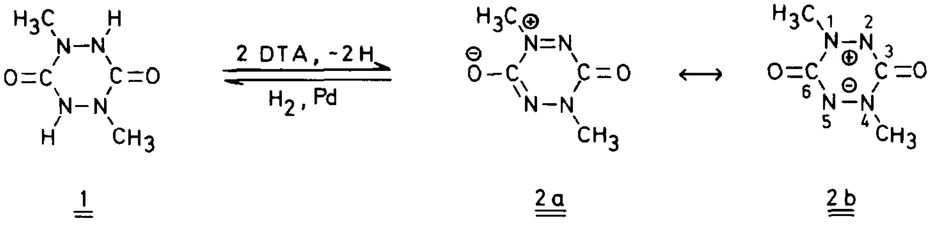
Franz A. Neugebauer*, Hans Fischer and Claus Krieger

Max-Planck-Institut für medizinische Forschung
Abteilung Organische Chemie
Jahnstr. 29, D-6900 Heidelberg, West Germany

Abstract: The preparation, the spectroscopic characterization, the crystal structure and chemical reactions of the new six-membered heterocyclic betaine 2 are reported; 2 is a representative of a possibly large group of yet unkonwn betaines of the general structure 8.

Dehydrogenation of the colourless 1,4-disubstituted 1,2,4,5-tetrahydro-1,2,4,5-tetrazin-3,6-diones[1], e.g. with atmospheric oxygen in the presence of base or with di-p-tolylaminyl [DTA, from tetra-p-tolylhydrazine in dioxane at 60°C] leads to the formation of extraordinarily deeply coloured solutions.

Starting from 1 we could now isolate the blue compound 2, as black plates from dioxane [49%, by dehydrogenation with DTA, m.p. 146°C (dec.); UV/VIS (dioxane): λ_{max} (lg ε) = 603 (3.49), 571 (3.50), 227 nm (4.23)]. Reduction of 2 (1 mole H_2, Pd) gave back the initial reactant 1. The low solubility of 2 in nonpolar organic solvents as well as the low field shift of the methyl proton resonance [$CDCl_3$; 1: δ = 3.11 ppm; 2: δ = 4.08 ppm] and the shift of the carbonyl vibration ν (C=O) to lower frequency [$CHCl_3$; 1:1690 cm^{-1};



2: 1659 cm $^{-1}$] indicate a betaine constitution. These spectroscopic data in solution suggest a resonance structure 2a with the positive charge at the methyl substituted nitrogen and the negative charge at the oxygen, in analogy to known six-membered heterocyclic betaines[2].

The crystal structure of 2 (Fig.) was determined by X-ray structure analysis[3]. In crystal 2 has C_i symmetry. The six-membered heterocycle is planar (deviations from the least squares plane < 1 pm). The remarkably short C-O distance (121.5 pm) corresponds to a neat C=O double bond like in aldehydes and ketones (121.5 pm) or in the reference compound 3 [1] (122.4 pm, 1,2,4,5-tetramethyl-1,2,4,5-tetrahydro-1,2,4,5-tetrazin-3,6-dione), whereas in betaines like pyridinium-3-olates the C-O bond length is found to be about 128 pm [4]. In comparison with 3 the betaine 2 shows as only significant difference a considerably shorter N-N distance (2: 131.0 pm; 3: 141.1 pm) which comes near to the distance of a N=N double bond (125 pm). 2 has a remarkably

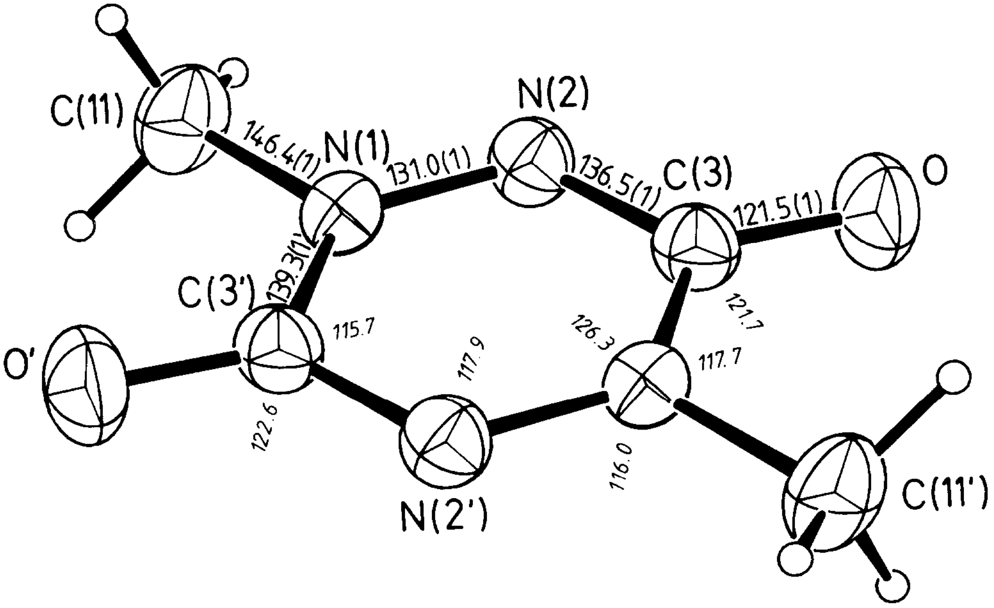
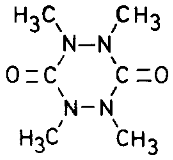


Fig. Structure of the betaine 2

high density (D_x = 1.60 g/cm^3; **3**: D_x = 1.29 g/cm^3) which results apparently from the planar ring arrangement and optimal packing.



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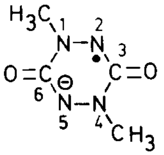
The crystal structure of the betaine **2** reminds one of a quinonoid system. Actually **2** shows such properties. For example, **2** and its precursor **1** comproportionate in the presence of base to give a persistent radical anion **4** [ESR (dimethyl sulfoxide): $g = 2.0039$; $a(H_{CH_3}) = 6.40$ (6H), $a(N_{1,4}) = 6.40$, $a(N_{2,5}) = 5.58$ G], whereas in acidic solution the corresponding radical cation **5** is immediately formed [ESR (CF_3COOH): $g = 2.0039$; $a(H_{CH_3}) = 7.38$ (6H), $a(N_{1,4}) = 7.09$, $a(N_{2,5}) = 5.29$ G]. The betaine itself is protonated in acidic solution. The blue **2** dissolves in water or weak acids with red [monoprotonation **6**; UV/VIS (HCOOH): λ_{max} (lg ε) = 524 nm (3.56)] and in 70% perchloric acid with yellow colour [probably diprotonation **7**; UV/VIS (70% $HClO_4$): λ_{max} (lg ε) = 464 (3.47), 217 nm (4.13)].



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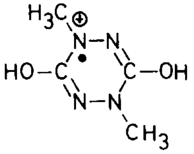

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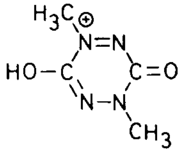

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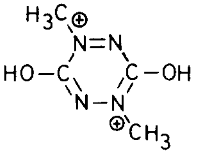

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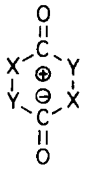
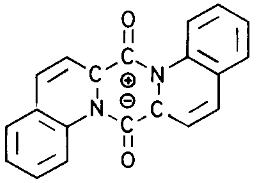


8 X: N, CR
Y: NR,O,S



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2 is a representative of a possibly large group of yet unknown betaines of the general structure **8**. In addition to the shown X and Y variations in **8**

also the carbonyl groups can be formally replaced by other functions, e. g. C=S, C=NR. The betaine **9** mentioned in the literature[5] could be regarded as first example of the series **8**; but restudies of the compound gave evidence of a di-2-quinolinylethanedione constitution[6,7].

References and Notes

1. F. A. Neugebauer and H. Fischer, Liebigs Ann. Chem. 1981, 387 and unpublished results.

2. C. A. Ramsden, Adv. Heterocycl. Chem. 26, 1 (1980).

3. Black plates from dioxane; space group $P2_1/n$, a = 680.2(1), b = 558.9(1), c = 834.7(1) pm; ß = 111.53(1); Z = 2; 775 measured, 528 [$I \geqslant 1.96\ \sigma\ (I)$] observed reflexions; R = 0.045. Further details of the crystal structure investigation can be obtained from the Cambridge Crystallographic Data Centre and from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, West Germany, by quoting the depository number CSD 50497, the name of the authors, and the journal citation.

4. A. R. Katritzky, C. A. Ramsden, Z. Zakaria, R. L. Harlow and S. H. Simonsen, J. Chem. Soc. Perkin Trans. I 1980, 1870.

5. B. R. Brown and D. L. Hammick, J. Chem. Soc. 1950, 628; C. A. Ramsden, Adv. Heterocycl. Chem. 26, 104 (1980).

6. C. A. Buehler and J. O. Harris, J. Am. Chem. Soc. 72, 5015 (1950).

7. D. R. Davies and H. M. Powell, Nature 168, 386 (1951).

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