

4,10-DINITRO-2,6,8,12-TETRAOXA-4,10-DIAZATETRACYCLO[5.5.0.0^{5,9}.0^{3,11}]DODECANE

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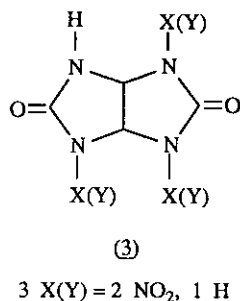
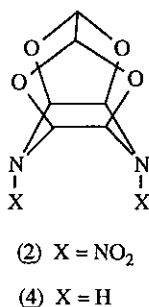
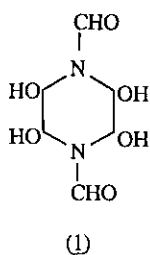
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Abstract - Glyoxal condensed with 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine in the presence of sulfuric and nitric acids to give the title compound.

We wish to report 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (2) as the first example of a dioxazepane and the densest dinitramine (including dinitramides) composed of C, H, N, and O atoms that is known.

In the presence of sulfuric and nitric acids 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (1) (obtained from a base catalyzed reaction between formamide and glyoxal)¹ and glyoxal condensed to give the di-N-nitro derivative (2) (92%) of a tetraoxadiazaisowurtzetane. An X-ray crystallographic examination confirmed the structure (2),² and revealed an exceptionally high density of 2.03 at 100 °K. A density of 1.99 at 25 °C was obtained by the flotation method. The highest recorded density, 1.94, for a dinitramine or dinitramide was assigned to an unspecified derivative (3) (Dingu) of glycoluril. The exceptionally high density of the dinitramine (2) was partially attributed to its caged structure.

When the reaction was carried out in the absence of nitric acid, in an attempt to obtain the secondary amine (4), an intractable dark tar was obtained.



EXPERIMENTAL

Instruments included Pye-Unicam SP-200 IR, Varian A-60 and T-60 NMR Spectrometers. Elemental analyses were provided by Galbraith Laboratories, Knoxville, Tennessee; oxygen content was determined by the Unterzaucher Method.

A mixture of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine **1** (4.0 g, 0.02 mol) and trimeric glyoxal as a dihydrate (2.1 g, 0.01 mol) was added to concentrated sulfuric acid (25 ml) at 0 °C. As it was stirred at 10-15 °C for 5 h the reaction mixture became light brown in color. It was cooled to 0 °C and treated with the dropwise addition of nitric acid (100%, 25 ml). Stirring was resumed for 2 h at 0-10 °C and then for 45 h at 25 °C. After the mixture was poured on-to ice a colorless solid precipitated. It was isolated and washed with ice-water and with aqueous ethanol to give the title compound **2**, 4.8 g (92%) as a colorless solid, mp > 250 °C (dec on heating in a flame) (acetone). Ir (KBr): 1590 s, 1380, 1285 s, 1250, 1180, 1130 s, 1115, 1055, 1020, 900 s, 875, 770, 755, and 655 cm⁻¹; nmr ((CD₃)₂CO): δ 7.08 (s) and 5.95 (s); ¹³C nmr ((CD₃)₂CO): δ 102.65 and 82.68. Ei-ms (%): 170 (26) (M⁺ - 2 NO₂), 115 (18), 96 (96), 87 (88), 69 (58), 59 (100), 46 (40). Anal. Calcd for C₆H₆N₄O₈: C, 27.49; H, 2.31; N, 21.37; O, 48.83. Found: C, 28.13; H, 2.35; N, 21.41; O, 46.56.

ACKNOWLEDGMENT

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REFERENCES

- 1 A. C. Currie, A. H. Dinwoodie, G. Fort, and J. M. C. Thompson, J. Chem. Soc.(C), 1967, 491.
- 2 Personal communication from Professor E. D. Stevens. The X-ray crystallographic analysis will be published elsewhere.

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