

Anion Radical of Mutagenic 3-methyl-5-nitropyridazine-1,2-dioxide

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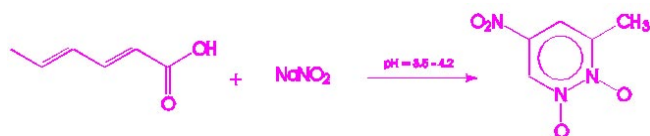
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Abstract

The mixture of sorbic acid and nitrite, both used as food additives, exhibits mutagenicity in a weak acidic milieu. The formed 3-methyl-5-nitropyridazine-1,2-dioxide was studied with cyclic voltammetry and EPR spectroscopy.

Keywords: EPR, voltammetry, radical, mutagenicity

The mixture of two food additives, sorbic acid and nitrite, exhibits mutagenicity in a weak acidic milieu. The strongest mutagenic species in the mixture was identified [1] and has been believed [2] to be 2-methyl-1,4-dinitropyrrrole [75142-42-6]. The X-ray structure analysis revealed that the compound is 3-methyl-5-nitropyridazine-1,2-dioxide [3] (**1**).



The deuteration [1] of **1** should yield 3-methyl-5-nitropyridazine-1,2-dioxide-6-*d* (**2**) since the methylation [1] produces 3,6-dimethyl-5-nitropyridazine-1,2-dioxide (**3**) (X-ray [3]).

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Cyclic voltammetry (DMF/0.1 M TBAPF₆, stationary Hg-electrode, 0.2 V/s) shows a reversible one-electron peak at -0.68 V (SCE) as the first stage of reduction of **1**. The compounds **2** and **3** behave similarly. The anion radicals of **1**, **2**, and **3** were generated *in situ* by the potential controlled electrolysis at Pt-electrode (net) in the same solu-

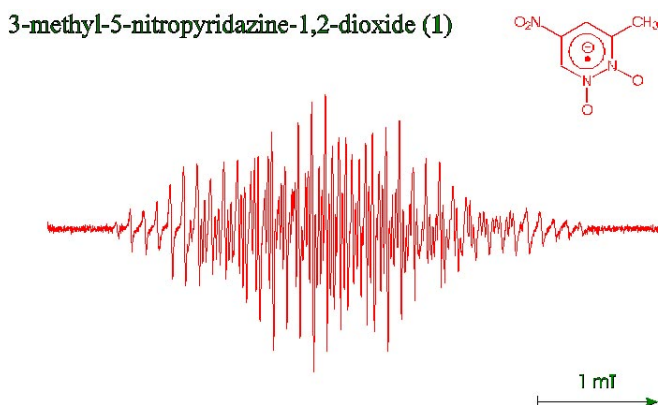


Figure 1. EPR of radical anion of 3-methyl-5-nitropyridazine-1,2-dioxide (**1**) in DMF/0.1 M TBAPF₆

Table 1. Parameters of EPR spectra of anion radicals of 3-methyl-5-nitropyridazine-1,2-dioxides.

	a^N/mT	a^N/mT	a^N/mT	$a^{\text{H}}_{\text{CH}_3}/\text{mT}$	a^{H}/mT	a/mT	$\Delta B_{\text{pp}}/\text{mT}$	g-factor
1	0.565	0.536	0.203	0.107	0.411	H: 0.303	0.014	2.00544
2	0.565	0.536	0.203	0.107	0.411	D: 0.048	0.013	2.00549
3	0.580	0.555	0.179	0.122	0.425	CH₃: 0.257	0.015	2.00554

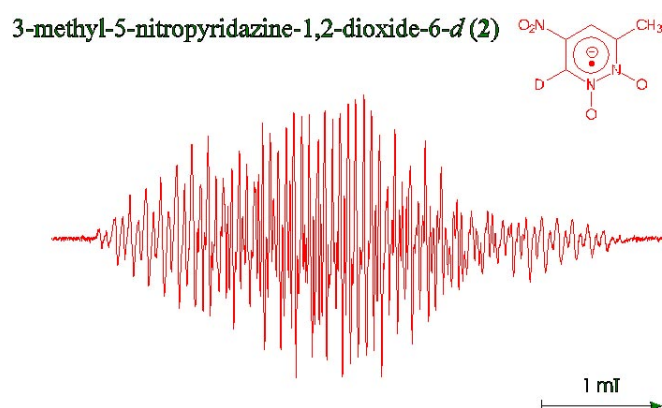


Figure 2. EPR of radical anion of 3-methyl-5-nitropyridazine-1,2-dioxide-6-*d* (2) in DMF/0.1 M TBAPF₆.

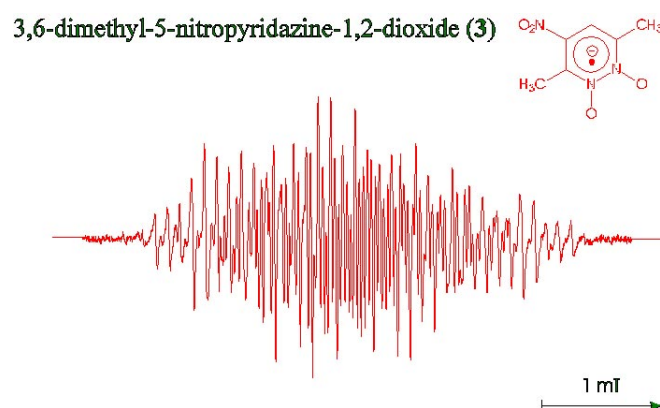


Figure 3. EPR of radical anion of 3,6-dimethyl-5-nitropyridazine-1,2-dioxide (3) in DMF/0.1 M TBAPF₆.

tion. The EPR spectra are shown in Figures 1, 2, and 3 and their parameters in Table 1. The obvious asymmetric pattern of HFS reflects a cumulative dependence of the linewidth on the components of the ¹⁴N-nuclear spin quantum numbers.

References

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2. Hartman, P. E. *Environmental Mutagenesis* **1983**, *5*, 217.
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