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## Oximo-Nitron Tautomerism in Nitrophospholene Oximes

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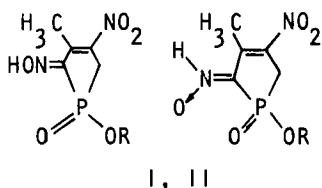
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# OXIMO-NITRON TAUTOMERISM IN NITROPHOSPHOLENE OXIMES

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Oxime-nitron tautomerism in various organic substances is widely discussed. However, only the oxime form has been established experimentally<sup>1,2</sup>. The existence of oxime tautomer in the solution of 1-alkoxy-2-oximino-3-methyl-4-nitro-3-phospholene-1-oxides (I, II) was confirmed spectrometrically. The x-ray structural analysis unexpectedly exposed the form of NH-nitron in crystals of substances I and II. It is the first experimental proof of the coexistence of oxime and nitron tautomeric forms. There are several factors that can stabilize the thermodynamically less



R = CH<sub>3</sub> (I), C<sub>2</sub>H<sub>4</sub>Cl (II)

preferable NH-nitron, like O'-atom conjugation with exo- and endocyclic unsaturated bonds of nitro-diene system, or extraordinary molecular packing with intermolecular contact distance (P=O)O...  
 ...O(O-NH=) 2.60-2.70 Å. The detection of NH-nitron in crystals of sulphurcontaining structural analogue of I and II 2-oximino-3-methyl-4-nitro-3-thiylene-1,1-dioxide allows to suppose that the existence of the nitron form is based upon the combination of electronattracting nitro- and heteroatomic groups in heterocyclopentenes as well as rigid fixation of molecular geometry.

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