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MESOIONIC COMPOUNDS WITH A BRIDGED NITROGEN ATOM.

8.* INVESTIGATION OF THE STRUCTURES OF CONDENSED THIAZOLE DERIVATIVES BY PMR SPECTROSCOPY

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K. V. Fedotov, and N. N. Romanov

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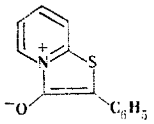
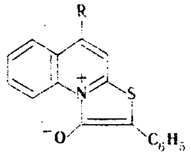
The structures of thiazolopyridinium, thiazoloquinolinium, and thiazolopyrimidinium oxides were studied by PMR spectroscopy with the aid of a lanthanide shift reagent [Eu(DPM)$_3$].

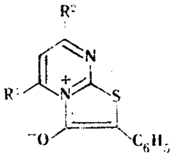
In a previous communication [1] we described the synthesis of a number of condensed thiazole derivatives that have mesoionic structures. In order to perform conformational analysis and confirm the structures we investigated the PMR spectra of I-VIII (Table 1).



I



II, III

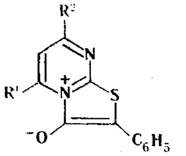


IV–VIII

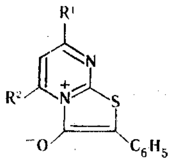
II R=H; III R=CH$_3$; IV R^1=R^2=H; V R^1=H, R^2=CH$_3$; VI R^1=H, R^2=C$_6$H$_5$; VII R^1=R^2=CH$_3$; VIII R^1=CH$_3$, R^2=CF$_3$

A characteristic feature of these spectra is the appreciable paramagnetic shift of the signal of the aromatic proton or the CH$_3$ group in the vicinity of the oxygen atom. Thus in the spectrum of product I the signal of the proton in the 5 position is shifted almost 1 ppm to the weak-field side relative to the signals of the other aromatic protons. This fact can be explained not only by the effect of the electron-acceptor quaternary nitrogen atom but also by the unbonded coupling of this proton with the unshared electron pairs of the oxygen atom, which bears a negative charge (compare this with the analogous effects of the carbonyl oxygen atom [2]). This shift is manifested particularly clearly in the spectra of II and III, in which the proton in the 9 position is even closer to the oxygen atom. The chemical shift of the 9-H signal reaches 10.35 ppm in this case.

It follows from the method used to prepare them [1] that IV-VIII can have one of the alternative structures



A



B

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*See [1] for Communication 7.

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