1-Methyl-2-(5-piperidinofuryl-2)-4,6-diphenylpyridinium Perchlorate. mp 131-133°C (dec.). UV spectrum: λ_{max} 478 nm (log ε 4.44).

1-Methyl-2-(5-morpholinofuryl-2)-4,6-diphenylpyridinium Perchlorate. mp 130-132°C (dec.). UV spectrum: λ_{max} 467 nm (log ε 4.35).

1-Methyl-4-(5-piperidinofuryl-2)-2,6-diphenylpyridinium Perchlorate. mp 152-154°C (dec.). UV spectrum: λ_{max} 480 nm (log ε 4.68).

1-Methyl-4-(5-morpholinofuryl-2)-2,6-diphenylpyridinium Perchlorate. mp 162-164°C (dec.). UV spectrum: λ_{max} 470 nm (log ε 4.53). All of the compounds were purified by recrystallization from isopropyl alcohol. The results of elemental analysis for C, H, N, and Cl, as well as the PMR spectral data were consistent with the proposed structures.

TRANSFER OF LONG-RANGE SPIN—SPIN COUPLING BETWEEN PROTONS IN 1,3-DIVINYL-6-AZAURACIL VIA A HYPERVALENT N...H BOND

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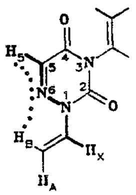
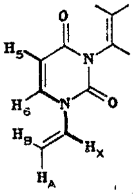
UDC 543.422.25:547.854.4:
541.553

Long-range spin—spin coupling of protons is widely used in structural investigations of organic molecules [1]. There are two main pathways for transmission of long-range spin—spin coupling in PMR spectra, namely, via a system of bonds across a stereospecific fragment, and across space in the case of spatially proximate interacting protons.

In the case of 1,3-divinyl-6-azauracil (I), we have detected the feasibility of transmission of long-range spin—spin coupling between the 5-H and B-H protons via a third different pathway. This conclusion is based on a comparison of long-range proton spin—spin-coupling between the ring and 1-vinyl group in 1,3-divinyluracil II and its 6-aza analog I. Both molecules exhibit long-range spin—spin coupling via 5 bonds, between the 5-H and X-H protons (0.55 and 0.45 Hz, respectively). This interaction is transmitted predominantly via a system of σ-bonds across a planar zig-zag-shaped fragment [1].



I



II

$^5J_{5X}$=0,55 Hz, $^6J_{5B}$=0,25 Hz; $^5J_{5X}$=0,45 Hz, $^5J_{6B}$=0,35 Hz

A similar fragment array appears in molecules I and II in the case of an s-trans(O)-conformation of the 1-vinyl group. For molecule II this conformation furthermore results in spatial proximity of the 6-H and B-H protons, which makes it possible to consider the observed interaction between these nuclei (0.35 Hz) as occurring through space.

The similarity in the electronic and three-dimensional structures of molecules I and II would be expected to be reflected in an identical character of long-range spin—spin coupling transmission across bonds, as has in fact been observed in the case of the 5-H and X-H protons. However, long-range spin—spin coupling between the 5-H and 6-H protons occurs across 6 bonds and, because of the distance separating them, these protons cannot interact through space, and is present, in fact, in only one of these compounds, namely molecule I

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(0.25 Hz). It would seem to follow, therefore, that the appearance of this long-range spin–spin coupling interaction is associated with the specific structure of molecule I. The uniqueness of this compound consists of the spatial proximity of the $N_{(6)}$ atom and the B-H proton. This results in overlap of the antibonding orbital of the $C{-}H_B$ bond and the unshared electron pair on the heteroatom, which, in turn, leads to the formation of a hypervalent N...H bond. Spin–spin interaction or coupling can apparently be transmitted via this proposed N...H hypervalent bond [2].

Thus, the main contribution to the interaction of the 5-H and B-H protons in molecule I apparently is determined by two conventional bonds, $H_{(5)}{-}C$ and $C{-}N_{(6)}$, and a hypervalent $N_{(6)}...H_{(B)}$ bond, i.e., the interaction under consideration appears to be pseudovicinal. The observed effect should be furthermore useful both in structural investigations as well as in the study of hypervalent interactions.

PMR spectra of evacuated samples were recorded on a Tesla BS-497 (100 MHz) spectrometer. The sample concentrations were 5%, the solvent $CDCl_3$.

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NEW SYNTHESIS OF FUNCTIONALLY SUBSTITUTED PYRIMIDO[1,2-a]BENZIMIDAZOLES

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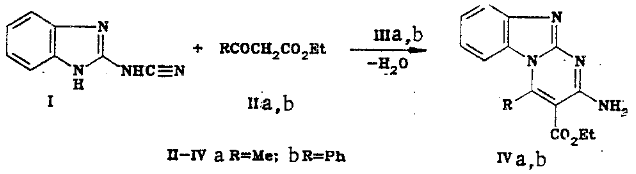
A new method has been developed for the synthesis of functionalized pyrimido[1,2-a]benzimidazoles. It has been found that 2-benzimidazolylcyanamide (I) reacts with acylacetate esters (II) to form 2-amino-3-ethoxycarbonylpyrimido[1,2-a]benzimidazoles (IV). The reaction is catalyzed by $Ni(RCOCHCO_2Et)_2$ complexes (III), which are obtained from esters II and Ni(2+) salts; the best yields of compound IV (~60%) were achieved with equimolar amounts of complexes III and cyanamide I.

In the absence of III, compound IV could not be synthesized even when acidic (TosOH) or basic (EtONa) catalysts were used. In confirming the ability of Ni(2+) complexes to catalyze the addition of β-dicarbonyl compounds to cyanamides we showed that the reaction of benzoylcyanamide with acetylacetone goes smoothly in the presence of catalytic amounts of nickel acetylacetonate to form 3-(N-benzoyldiamino)methylidenepentan-2,4-dione. (It is also known that nickel acetylacetonate catalyzes the addition of β-dicarbonyl compounds to cyanogen [1].)



Cyanamide I was synthesized by the procedure of [2]; complexes III, by the procedure of [3].

<u>2-Amino-4-methyl-3-ethoxycarbonylpyrimido[1,2-a]benzimidazole (IVa)</u>. A mixture of 2 mmoles of cyanamide I, 2 mmoles of complex IIIa, and 8 mmoles of ester IIa was heated at 140°C for 40 min. The reaction mixture was treated with 1.5 N alcoholic HCl, the solvent

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