(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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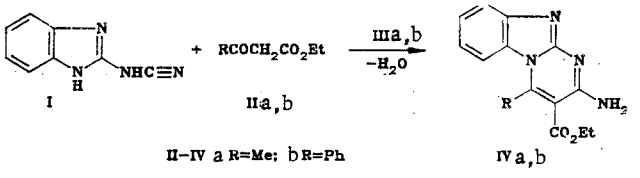
A new method has been developed for the synthesis of functionalized pyrimido[1,2-a]-benzimidazoles. It has been found that 2-benzimidazolylcyanamide (I) reacts with acylacetate esters (II) to form 2-amino-3-ethoxycarbonylpyrimido[1,2-a]benzimidazoles (IV). The reaction is catalyzed by $Ni(RCOCHCO_2Et)_2$ 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].)



I IIa,b IIa,b

II–IV a R=Me; b R=Ph IVa,b

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

2-Amino-4-methyl-3-ethoxycarbonylpyrimido[1,2-a]benzimidazole (IVa). 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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was distilled off, and the residue was washed with 1:1 ether–pentane and 25% NH_4OH solution. Yield 0.351 g (63%). mp 245-246°C (from EtOH). IR spectrum (KBr): 3400 (NH), 3300-2800 (NH, CH), 1690 (CO), 1645 cm^{-1} (C=N). PMR spectrum (DMSO-D_6): 7.95 (1H, d, 9-H), 7.55 (1H, d, 6-H), 7.50-7.20 (3H, m, 8-H and NH_2), 7.14 (1H, t, 7-H), 4.38 (2H, q, OCH_2), 3.00 (3H, s, CH_3), 1.33 ppm (3H, t, $OCH_2\underline{CH_3}$). Mass spectrum, m/z: 270 $[M]^{+\cdot}$.

2-Amino-4-phenyl-3-ethoxycarbonylpyrimido[1,2-a]benzimidazole (IVb) was synthesized analogously to compound IVa by heating a mixture of compounds I, IIb, and IIIb. Ether was added to the cooled mixture, and the residue was filtered off and treated as in the case of compound IVa. The mixture was placed on a 20 × 3 cm column of Silpearl silica gel (eluent 20:1 chloroform–alcohol) and the fraction with R_f 0.2 was collected. The solvent was distilled off to yield 0.398 g (62%) of IVb, mp 304-305°C (from EtOH). Mass spectrum, m/z: 332 $[M]^{+\cdot}$.

3-(N-Benzoyldiamino)methylidenepentane-2,4-dione. A mixture of 4 mmoles of benzoylcyanamide, 0.4 mmoles of nickel acetylacetonate, and 16 mmoles of acetylacetone was heated at 140°C for 10 min. Excess acetylacetone was distilled off, and the residue was recrystallized from EtOH to yield 0.886 g (90%) of 3-(N-benzoyldiamino)methylidenepentane-2,4-dione, mp 127-128°C.

The elemental composition of the synthesized compounds agreed with the calculated composition.

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