THREE-DIMENSIONAL STRUCTURE OF 2-PYRAZOLINES FROM THE RESULTS OF A STUDY OF THE $^{13}C-^{13}C$ SPIN-SPIN COUPLING CONSTANTS (SSCC)

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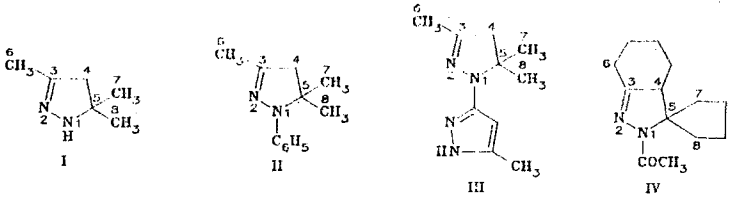
2-Pyrazolines are products of the incomplete reduction of pyrazole and are widely used in preparative organic synthesis [1]. The question of the three-dimensional and electronic structures of this class of compounds has been investigated by means of the extensive application of physicochemical methods. In most studies it was concluded that the pyrazoline ring has an almost planar structure that is stabilized to a significant extent by orbital interaction of the $2p_z$ electrons of the $N_{(1)}$ atom with the π system of the azomethine group in both the ground and excited states of the molecules [2-4]. Nevertheless, data from an x-ray diffraction analysis provide evidence for substantial deviation of the $C_{(4)}$ (−0.053 Å) and $C_{(5)}$ (+ 0.052 Å) atoms from the plane of the pyrazoline ring [5].

Below we present the $^{13}C-^{13}C$ spin-spin coupling constants (SSCC) in hertz for four representatives of this series with various substituents attached to the nitrogen atom and two carbon substituents attached to the $C_{(5)}$ atom.



I II III IV

I $^1J_{57}=^1J_{58}=38{,}0$; $^1J_{45}=37{,}5$; $^1J_{36}=52{,}3$; II $^1J_{57}=^1J_{58}=38{,}4$; $^1J_{54}=38{,}1$; $^1J_{36}=52{,}1$; III $^1J_{57}=^1J_{58}=38{,}4$; $^1J_{45}=37{,}6$; $^1J_{36}=52{,}3$; IV $^1J_{57}=^1J_{58}=36{,}5$; $^1J_{45}=38{,}3$; $^1J_{34}=39{,}4$ **Hz.**

In the case of a nonplanar structure of the pyrazoline ring, which is characterized by a hybridization of the $N_{(1)}$ atom that is intermediate between sp^3 and sp^2 [2], one should expect manifestation of the effect of the unshared electron pair of this atom, which leads to a substantial difference in the $^1J_{57}$ and $^1J_{58}$ constants similar to that which occurs in a number of oximes [6-8]. It is apparent from the data presented above that the values of the constants under discussion coincide with the accuracy of their experimental measurement (±0.2 Hz) for all of the investigated pyrazolines; this constitutes evidence for a virtually planar structure of the pyrazoline ring, regardless of the nature of the substituent attached to the $N_{(1)}$ atom.

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