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LETTERS TO THE EDITOR

Intramolecular Specific Interaction C–H···O in 1-Vinyl-5-pyrazolecarboxylic Acid Revealed by ^{1}H NMR Spectroscopy Data

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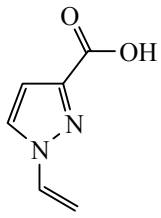
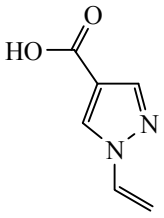
The presence of intramolecular hydrogen bond C–H¨N in 2-vinyloxy(vinylthio)pyridine and 2-vinyloxy (vinylthio)quinoline was shown earlier [1]. Structural studies of a wide series of vinylimidazoles on the basis of ^{1}H and ^{13}C NMR spectroscopy revealed the presence of intramolecular specific interactions (ISI) C–H···N in some molecules [2–4]. By the ^{1}H and ^{13}C NMR spectra data, the intramolecular specific interactions, namely, the weak hydrogen bonds of the C–H···O type between vinyl α-proton and carbonyl oxygen atom occur also in 1-vinyl-2-formylimidazole and 1-vinyl-2-formylbenzimidazole [5].

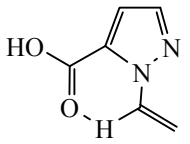
In the present work we analyzed the ^{1}H NMR spectra of 1-vinyl-3-pyrazolecarboxylic **I**, 1-vinyl-4-pyrazolecarboxylic **II**, and 1-vinyl-5-pyrazolecarboxylic acids **III**. The similar C–H···O interaction was found only in compound **III**.



I



II



III

According to the ^{1}H NMR spectra, the intramolecular bond between vinyl α-proton and *p*-electrons of carbonyl oxygen atom (C–H···O=C–OH) exists in compound **III**. As a result the α-proton signal is shifted downfield (to 8.05 ppm) in comparison with compounds **I** and **II**. The peak of the vinyl α-proton in compounds **I** and **II** appears in a stronger field owing to the impossibility of its deshielding by the carbonyl group.

1-Vinyl-3-pyrazolecarboxylic acid (I). A mixture of 8.3 g of ethyl 1-vinyl-3-pyrazolecarboxylate [6], 4 g of sodium hydroxide, and 20 ml of water was stirred for 5 h at room temperature. Then this mixture was extracted with diethyl ether. The aqueous layer was neutralized with hydrochloric acid. The precipitated crystals were filtered off. Yield 62.1 g (45%), mp 89°C (benzene). IR spectrum, ν, cm^{-1}: 1530 (ring), 1645 (C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.94 d.d (1H, CH=CH_2, *J* 8.9 and 1.2 Hz), 5.71 d.d (1H, CH=CH_2, *J* 15.7 and 1.2 Hz), 6.73 d (1H, 4-H, *J* 2.4 Hz), 7.21 d.d (1H, C*H*=CH$_2$, *J* 15.7 and 8.9 Hz), 7.94 d (1H, 5-H, *J* 2.4 Hz), 12.20 br.s (1H, COOH). Found, %: C 52.39; H 4.14; N 20.44. $C_6H_6N_2O_2$. Calculated, %: C 52.17; H 4.35; N 20.29.

1-Vinyl-5-pyrazolecarboxylic acid (III) was

prepared similarly from 8.3 g of ethyl 1-vinyl-5-pyrazolecarboxylate [6], 4 g of sodium hydroxide, and 20 ml of water. Yield 66.24 g (48%), mp 85°C (benzene). IR spectrum, ν, cm^{-1}: 1520 (ring), 1645 (C=C), 1720 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.90 d.d (1H, CH=CH_2, *J* 8.8 and 1.2 Hz), 5.79 d.d (1H, CH=CH_2, *J* 15.4 and 1.2 Hz), 6.85 d (1H, 4-H, *J* 1.9 Hz), 7.52 d (1H, 3-H, *J* 1.9 Hz), 8.05 d.d (1H, C*H*=CH_2, *J* 15.4 and 8.8 Hz), 12.70 br.s (1H, COOH). Found, %: C 52.34; H 4.21; N 20.38. $C_6H_6N_2O_2$. Calculated, %: C 52.17; H 4.35; N 20.29.

1-Vinyl-4-pyrazolecarboxylic acid (II). A mixture of 8.7 g of 1-(2-chloroethyl)-4-pyrazolecarboxylic acid [7], 9 g of potassium hydroxide, 50 ml of water, and 0.01 g of hydroquinone was refluxed for 2 h at 100°C. After cooling, the solution was neutralized with hydrochloric acid. Crystalline precipitate was filtered off and dried. Yield 124.2 g (90%), mp 207–209°C (isopropyl alcohol–water, 8:2). IR spectrum, ν, cm^{-1}: 1550 (ring), 1650 (C=C), 1670 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.93 d (1H, CH=CH_2, *J* 8.8 Hz), 5.72 d (1H, CH=CH_2, *J* 15.8 Hz), 7.18 d (1H, C*H*=CH_2, *J* 15.8 and 8.8 Hz), 7.80 s (1H, 3-H), 8.39 s (1H, 5H), 11.5 br.s (1H, COOH). Found, %: C 52.38; H 4.58; N 20.49. $C_6H_6N_2O_2$. Calculated, %: C 52.17; H 4.35; N 20.29.

The IR spectra were taken on a Specord 75-UR instrument (thin layer). The ^1H and ^{13}C NMR spectra were registered on a spectrometer Varian Mercury (300 MHz) in DMSO-d_6.

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