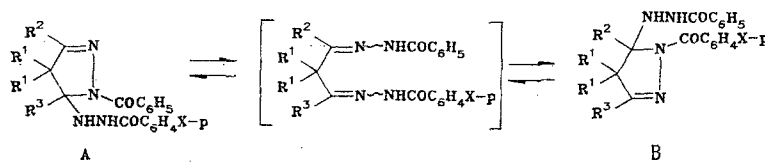


RING-RING TAUTOMERISM OF 1-ACYL-5-ACETYLHYDRAZINO-2-PYRAZOLINES

K. N. Zelenin, M. Yu. Malov, I. P. Bezhan,
V. A. Khrustalev, and S. I. Yakimovich

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The existence of bis-acylhydrazones of 1,3-dioxo compounds in the form of the corresponding 1-acyl-5-acylhydrazino-2-pyrazolines [1] anticipates the existence of an $A \rightleftharpoons B$ tautomerism. We are offering the confirmation of this fact by using the derivatives I and II as an example.



I $R^1=X=H$, $R^2=CH_3$, $R^3=C_2H_5$; II $R^1=R^2=R^3=CH_3$; $X=Cl$

Compound I was prepared with a yield of 65% by refluxing benzhydrazide with 2,4-hexanedione in benzene mp 133-135° (from ethanol). All signals in the NMR spectra are double; it is therefore difficult to attribute them to a given form. PMR spectrum (acetone- D_6): 0.91 and 1.01 (t, 3H, $J = 7.5$ Hz, β - CH_3); 1.85 (s) and 1.88 (t, 3H, $J = 1.0$ Hz, CH_3); 2.31 (qu, 2H, $J = 7.5$ Hz, α - CH_2); 2.81 and 3.19 ($J_{AB} = 19.0$ Hz), 2.98, and 3.08 (2H, $J_{AB} = 19.0$, $J = 1.0$ Hz, 4-H); 6.26 (d, 1H, $J = 5.5$ Hz, NH); 9.20 and 9.69 (d, 1H, $J = 5.5$ Hz, NHCO), 7.1-8.0 ppm (m, 10H, H_{arom}). The position of the equilibrium $A \rightleftharpoons B$ in the solutions is reached slowly at room temperature; however, it is established rapidly at 100° or in the presence of catalytic amounts of trifluoroacetic acid; the ratio of the forms at equilibrium (about 3:2) is practically independent of the nature of the solvent. The ^{13}C NMR spectrum ($CDCl_3$) contains the following signals: 7.8 and 10.2 (β - CH_3); 15.8 and 22.4 (CH_3); 23.5 and 26.9 (α - CH_2); 45.1 and 46.5 ($C(4)$); 86.8 and 87.5 ($C(5)$); 155.2 and 169.7 ($C=N$); 166.9, 167.9, and 168.1 ($C=O$); 129.0-135.0 ppm (C_{arom}).

Compound II was prepared by the procedure given in [2]. Due to the similarity between the structures A and B only some signals of the tautomers are resolved in the NMR spectra, the amounts of which present in different solvents are the same. PMR spectrum (acetone- D_6): 1.15 and 1.27 (s, 6H, 4- CH_3); 1.55, 1.58, 1.92, 1.93 (s, 6H, CH_3); 5.65 (broad s, 1H, NH); 9.31 and 9.50 (d, 1H, $J = 11.0$ Hz, NHCO); 7.0-8.0 ppm (m, 9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$): 15.9 and 16.2 (4- CH_3); 18.1 and 18.8 (CH_3); 52.2 ($C(4)$); 87.6 ($C(5)$); 163.0 and 164.0 ($C=N$); 164.8, 165.9, 167.8, and 169.2 ($C=O$); 126.0-138.0 ppm (C_{arom}).

The existence of the $A \rightleftharpoons B$ tautomerism is confirmed indirectly by published data on the oxidation and mass spectra of compound II and some of its analogs, to which a linear structure has been wrongly attributed [2]. The phenomenon studied represents a new case of the rare ring-ring tautomerism [3-5].

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S. M. Kirov Military Medical Academy, Leningrad 194175. Translated from *Khimiya Geterotsiklicheskich Soedinenii*, No. 7, pp. 1000-1001, July, 1985. Original article submitted January 21, 1985.