



Derivatives of 1-phenyl-3-methylpyrazol-2-in-5-thione and their oxygen analogues in the crystalline phase and their tautomeric transformations in solutions and in the gas phase

Galina A. Chmutova^a, Olga N. Kataeva^{b,*}, Hubertus Ahlbrecht^c, Almira R. Kurbangalieva^a, Alexander I. Movchan^a, Albert T.H. Lenstra^d, Herman J. Geise^d, Igor A. Litvinov^b

^aKazan State University, Kremlevskaya 18, Kazan 420008, Russia

^bA.E. Arbutov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, A.E. Arbutov str. 8, Kazan 420088, Russia

^cInstitut für Organische Chemie, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392, Germany

^dUniversity of Antwerpen (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Antwerpen (Wilrijk), Belgium

Received 20 October 2000; revised 31 January 2001; accepted 31 January 2001

Abstract

1-Phenyl-3-methylpyrazol-2-in-5-thione, crystallised from methanol, was shown to exist in the tautomeric NH-form, stabilised by intermolecular NH...S hydrogen bonds. In solutions, however, the molecule is found predominantly as the SH-tautomer, accompanied (in low-polar solvents) by a small amount of the CH-tautomer.

1-Phenyl-3-methyl-4-benzoylpyrazol-2-in-5-thione occurs in the crystal as well as in solution in the SH-tautomeric form, stabilised by an intramolecular SH...O bridge. In dimethylsulfoxide solution indications were found for an additional SH-tautomer in a conformation lacking the intramolecular H-bridge.

The structure of 1-phenyl-3-methylpyrazol-2-in-5-one was redetermined by X-ray single crystal diffraction at 120°K in order to obtain more accurate geometry and hydrogen bonding parameters. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiopyrazolones and pyrazolones; Tautomerism; X-ray single crystal diffraction; Ab initio calculations

1. Introduction

1-Phenyl-3-methylpyrazol-2-in-5-thione (**1**) and 1-phenyl-3-methyl-4-benzoyl-pyrazol-2-in-5-thione (**2**) are the nearest structural analogues of 1-phenyl-3-methylpyrazol-2-in-5-one (**3**) and 1-phenyl-3-methyl-4-benzoylpyrazol-2-in-5-one (**4**) which are widely used in pharmacology, in the dyeing industry and as metal extracting agents [1–3]. Thioanalogues

of pyrazolinones, hereinafter referred to as thiopyrazolones, would be expected to have high biological and chemical activity. Whereas oxygen containing compounds **3** and **4** have been studied extensively both in solutions [4–8] and in the crystalline phase [9–14], their thioanalogues **1** and **2** are hardly explored. As numerous as are the structural data on pyrazolones in the crystalline phase deposited in the Cambridge Structural Database [15], there is a single entry [16] on their thioderivatives.

As the reactivity and useful properties of thiopyrazolones are determined to a great extent by their

* Corresponding author. Tel./Fax: +7-8432-767424.

E-mail address: kataeva@kfti.knc.ru (O.N. Kataeva).