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Molecular structure and vibrational and chemical shift assignments of 6-(2-hydroxyethyl)-2,3,4-triphenyl-2,6-dihydro-7*H*-pyrazolo-[3,4-*d*]pyridazin-7-one by DFT and *ab initio* HF calculations

Sibel Demir [a,*], Muharrem Dinçer [a], Emine Şahan [b], Elif Korkusuz [b], İsmail Yıldırım [b]

[a] Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit, Samsun, Turkey
[b] Department of Chemistry, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey

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ABSTRACT

The molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO) ^{1}H and ^{13}C chemical shift values and several thermodynamic parameters of 6-(2-hydroxyethyl)-2,3,4-triphenyl-2,6-dihydro-7*H*-pyrazolo[3,4-*d*]pyridazin-7-one in the ground state have been calculated by using the Hartree–Fock (HF) and density functional methods (B3LYP) with 6–31G(d) basis set. The results of the optimised molecular structure are presented and compared with the experimental X-ray diffraction. The calculated results show that the optimised geometries can well reproduce the crystal structural parameters and the theoretical vibrational frequencies, and ^{1}H and ^{13}C NMR chemical shift values show good agreement with experimental data. The computed vibrational frequencies are used to determine the types of molecular motions associated with each of the experimental bands observed. To determine conformational flexibility, molecular energy profile of the title compound was obtained by semi-empirical (AM1) with respect to selected degree of torsional freedom, which were varied from −180° to +180° in steps of 10°. Besides, molecular electrostatic potential (MEP), frontier molecular orbitals (FMO), and thermodynamic properties were performed at HF and DFT levels of theory.

1. Introduction

The title compound, is a derivative of 7*H*-pyrazolo[3,4-*d*]pyridazin-7-one, which are reported as very important organic compounds because they are widely used as pharmaceuticals and agrochemicals. Their excellent control activities on various plant diseases are studied [1,2]. Pyrazoles are important compounds that have many derivatives with a wide range of interesting properties, such as anti-hyperglycaemic, analgesic, antiinflammatory, antipyretic, anti-bacterial, hypoglycaemic and sedative–hypnotic activity. They were also reported to have non-nucleoside HIV-1 reverse transcriptase inhibitory activity [3,4]. Pyrazolo[3,4-*d*]pyridazine derivative was obtained from cyclization of 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic acid or -acid chloride with 2-hydroxyethyl hydrazine. The title compound is a novel compound synthesized firstly in our laboratories by us. The possible biological properties of the pyrazol, pyridazinone [5,6], and pyrazolo-pyridazinone [7,8] derivatives make it attractive to study these compounds.

In this study, we present results of a detailed investigation of the synthesis and structure characterization of 6-(2-hydroxyethyl)-2,3,4-triphenyl-2,6-dihydro-7*H*-pyrazolo[3,4-*d*]pyridazin-7-one using single crystal X-ray, IR, NMR and quantum chemical methods, besides elemental analysis. The geometrical parameters, fundamental frequencies and GIAO ^{1}H and ^{13}C NMR chemical shift values of the title compound in the ground state were calculated using the Hartree–Fock (HF) and DFT (B3LYP) methods with the 6–31G(d) basis set. These calculations are valuable for providing insight into molecular parameters and the vibrational and NMR spectra. The aim of this work is to explore the molecular dynamics and the structural parameters that govern the chemical behaviour, and to compare predictions made from theory with experimental observations.

2. Experimental

2.1. Synthesis

Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. Microanalysis was performed using a Leco-932 CHNS-O Elemental Analyzer. The ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance III 400 MHz spectrometer and the chemical shifts are expressed in ppm relatively to TMS.

* Corresponding author. Tel.: +90 03623121919/5260; fax: +90 03624576081.
E-mail addresses: sibeld@omu.edu.tr, sibdemir@hotmail.com (S. Demir).

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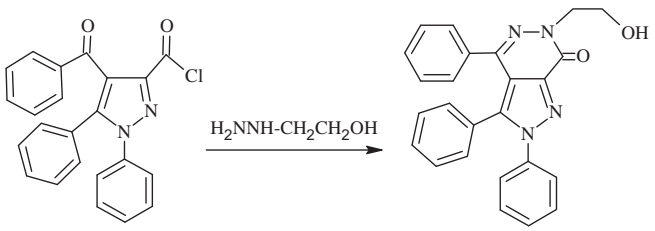

Scheme 1. Synthesis scheme of the title compound.

When necessary to identify all C- and H-atoms, complementary NMR experiments (HETCOR, and Exchange with D_2O) were performed. IR spectra of the compound were recorded in the range of 400–4000 cm^{-1} region with a Shimadzu FT-IR 8400 spectrophotometer. Solvents were dried by refluxing with the appropriate drying agents and distilled before use. All other reagents were purchased from Merck, Fluka, Aldrich and used without further purification. The starting material was prepared according to the literature procedure that described by Ziegler and co-workers [9] and by Akçamur and co-workers [10,11]. The 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic acid chloride (0.20 g, 0.52 mmol) and 2-hydroxyethyl hydrazine (0.07 mL, 1.04 mmol) were refluxed in xylene for 5 h. The solvent was evaporated, then the oily residue was treated with diethyl ether and the formed crude product was recrystallized from toluene. (Scheme 1) (yield: 0.16 g, 76%; m.p. 195 °C). IR (ATR, ν, cm^{-1}): 3460 (O—H), 3065 (aromatic C—H), 2951, 2912 (aliph. C—H), 2000–1750 (overtone or combination bands), 1662 (C=O), 1593–1446 (phenyl, pyridazine and pyrazole rings C⋯C, C⋯N), 1225 (C—O). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.43–6.85 (m, 15H, ArH), 4.58 (t, 2H, CH_2—OH), 4.12 (t, 2H, N—CH_2), 2.73 (b, s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156.86 (C_7=O), 144.46 (C_{7a}), 142.65 (C_4), 140.16 (C_3) 138.89 (C_9), 133.98, 130.43, 129.09, 128.99, 128.89, 128.66, 128.45, 128.16, 127.85, 127.74, 126.03 (arom. C's), 116.68 (C_{3a}), 62.41 (CH_2—OH), 52.80 (N—CH_2). Analysis calculated for $C_{25}H_{20}N_4O_2$ (408.45 g/mol): C 73.51, H 4.94, N 13.72%; found: C 73.25, H 4.73, N 13.89%.

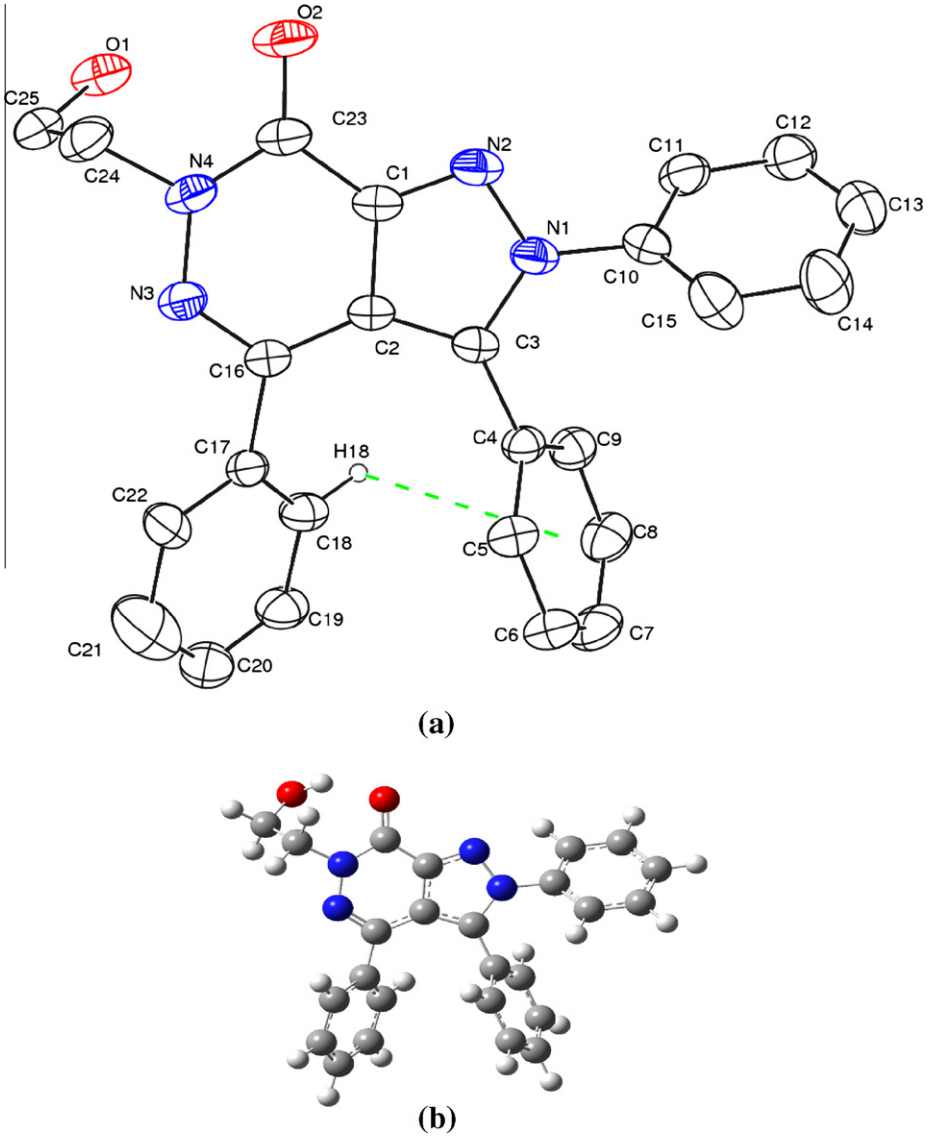

Fig. 1. (a) The molecular structure of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the %40 probability level and H atoms are shown as small spheres of arbitrary radii. (b) The theoretical geometric structure of the title compound.