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CRYSTAL STRUCTURE AND NMR SPECTROSCOPIC CHARACTERIZATION OF 1,5-BIS(2-HYDROXY-3-METHOXYBENZYLIDENE)CARBONOHYDRAZIDE

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Abstract. The solid-state structure of a symmetrical carbohydrazone, namely 1,5-bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide was determined by X-ray single crystal diffraction method. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters a= 10.1198(6), b= 22.7847(11), c= 15.1738(10) Å, β= 100.458(6)°, Z= 4, V= 3440.6(3) Å^3, R_1= 0.0540. Crystal structure of **1** is defined by two crystallographic independent molecules, which are bonded *via* N–H···O hydrogen bond. The organic molecules are as keto tautomers with respect to the carbamide fragment, and adopt the *anti* conformation. 1D and 2D NMR experiments have argued on the presence of the title compound in DMSO-d_6 solution mostly as keto tautomer in *syn* conformation, and enol-imino form when considering *o*-vanillin residue.

Keywords: carbohydrazide, *o*-vanillin, *syn-anti* isomer, X-ray diffraction, NMR spectroscopy.

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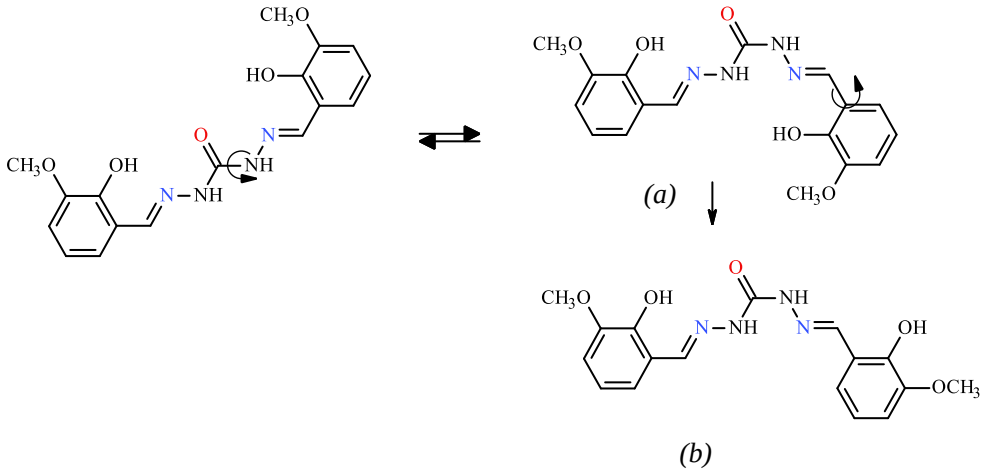
Introduction

Due to its two terminal amino groups, carbohydrazide can serve as a precursor for the synthesis of ditopic polydentate Schiff base ligands through an easy condensation reaction with appropriate aldehydes/ketones, containing pyridine, carboxylate, oxime functional groups. Endowed by conformational and tautomeric flexibility, these ligand systems displayed rich coordination flexibility towards both *d*- and *f*-block ion metals [1-7]. *Via* the condensation reaction of carbohydrazide with 2-hydroxybenzaldehyde results 1,5-bis(salicylidene)carbohydrazide, a chelating agent that has been reported to generate a number of coordination compounds, ranging from mono- to polynuclear ones, with both discrete and polymeric structures [8-16].

1,5-Bis(2-hydroxy-3-methoxybenzylidene) carbonohydrazide (**1**), formed by the reaction between 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) and carbohydrazide, looks as a promising ligand due to several potential N,O-coordination sites, as it contains additional donor atoms placed in suitable positions, the fact that could lead to increasing of its topicity. Indeed, it proved its proficiency in construction of dinuclear and nonanuclear dysprosium clusters [17,18]. The ligand also imposed asymmetrical coordination with ONO and ONN chelating compartments generating discrete and polymeric ensembles based on asymmetrical dinuclear Mo(VI) building blocks [19]. Depending on the reaction conditions, this compound may adopt different geometric configurations *syn* or *anti*, related to rotation around simple C-N bond in the amide C(O)-NH fragment (Scheme 1).

The aim of this study was to prove the formation of a distinct new solid form of a known compound, 1,5-bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (**1**), and to follow the supramolecular organization within the crystal by means of intermolecular weak bonds. Herein, the molecular and crystal structures of **1** are presented, that showed a solvatomorphus with a conformation different from the one reported in the literature, which crystallizes as a *syn* conformer [20]. The relative stabilities of the obtained crystalline form and its conversion were investigated through a number of solution NMR experiments and the obtained results were compared with the available NMR data for *syn*-1,5-bis(2-hydroxy-3-methoxybenzylidene) carbonohydrazide and its congeners.



Scheme 1. The s*yn* (left) and *anti* (right) isomers of 1,5-bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide obtained by rotating around the C-N bond *(a)*; *anti* isomer of 1,5-bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide rotated through the C9-C10 bond *(b)*.

Experimental

Materials

Carbohydrazide, *o*-vanillin and solvents were commercially purchased (Aldrich) and used without any further purification.

Synthesis

The 1,5-bis(2-hydroxy-3-methoxy benzylidene)carbonohydrazide was synthesized according to the method reported in the literature [17]. Crystals suitable for the X-ray study of **1** were obtained as the by-product of its reaction with $Mn(NO_3)_2 \cdot 4H_2O$ in a molar ratio of 1:2 in methanol, according to the following: to a MeOH solution (10 mL) containing $Mn(NO_3)_2 \cdot 4H_2O$ (0.063 g, 0.25 mmol) was added 1,5-bis(2-hydroxy-3-methoxybenzylidene) carbonohydrazide (0.045 g, 0.115 mmol) and the solution was stirred for 1 h at room temperature. The obtained clear solution was filtered and the filtrate was allowed to stand at room temperature for crystallization. After 1 week, colourless rectangular crystals of **1** were filtered off, washed with ethanol, and dried in air.

Physical measurements

X-ray single crystal diffraction analysis was performed at 293 K on a Rigaku XtaLAB Synergy-S diffractometer operating with Mo-Kα (λ= 0.71073 Å) micro-focus sealed X-ray tube. The structure of the compound was solved by direct methods and refined by least squares in the anisotropic full-matrix approximation for nonhydrogen atoms (SHELX-97) [21]. The positions of the hydrogen atoms were calculated geometrically and isotropically refined in the rigidbody model with U_{eff}= 1.2U_{equiv} or 1.5U_{equiv} of the corresponding atoms (C, N, and O). Supplementary X-ray crystallographic data in CIF format have been deposited with the CCDC with the reference number 2255087.

Solution-state NMR spectra were recorded on a Bruker Avance 400 spectrometer equipped with an inverse probe and *z*-gradient accessories and operating at constant magnetic field of 9.4 T. Samples were measured in 5 mm tubes at 298 K with dimethyl sulfoxide-d_6 (DMSO-d_6) as a solvent. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual non-deuterated solvent peak (2.50 ppm for ^{1}H and 40.00 ppm for ^{13}C). The 1D (^{1}H, ^{13}C and DEPT-135) and 2D homo- (^{1}H/^{1}H NOESY) and heteronuclear (^{1}H/^{13}C gHSQC, ^{1}H/^{13}C HMBC and (^{1}H/^{15}N HMQC) NMR experiments were performed through standard pulse sequences. Data analysis was performed using Bruker TOPSPIN software. The minimum-energy stereo-structure for the examined *anti* conformer of **1** have been obtained by using molecular modelling with energy minimization software, namely PERCH NMR TOOLS (version 2014.1).

Results and discussion

Reaction of 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) and carbohydrazide in ethanol in the molar ratio 2:1 under reflux yields 1,5-bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide as a white powder. The crystals of **1** were obtained in an attempt to synthesize its corresponding manganese(II) coordination compound.

X-ray crystallographic study

Compound **1** crystallizes in the monoclinic space group $P2_1/n$. The experimental and structure refinement characteristics are given in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The geometric parameters of intermolecular hydrogen bonds are given in Table 3.

Table 1

Crystal data and details of data collection for 1.

Parameter	*Value*
Empirical formula	$C_{17}H_{18}N_4O_5$
M	358.35
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	10.1198(6)
b, Å	22.7847(11)
c, Å	15.1738(10)
β, deg	100.458(6)
V, Å^3	3440.6(3)
Z	8
ρ_{calcd}, g·cm^{-3}	1.384
Crystal size, mm^3	0.50×0.08×0.03
Reflections collected/independent reflections (R_{int})	26978/6073 [*R(int)*= 0.0883]
Reflections with $I > 2\sigma(I)$	4100
Completeness, %	99.7
Number of refined parameters	511
GOF	1.003
Final *R* indices ($I > 2\sigma(I)$)	R_1= 0.0540, wR_2= 0.1485
R indices (all data)	R_1= 0.0837, wR_2= 0.1674

Table 2

Selected bond lengths (Å) and bond angles (°) for 1.

Bond	*Bond length, Å*	*Bond length, Å*
	A	B
C(1)–N(1)	1.270(3)	1.281(3)
N(1)–N(2)	1.375(2)	1.372(2)
N(2)–C(8)	1.366(3)	1.358(3)
C(8)–O(3)	1.221(2)	1.228(2)
C(8)–N(3)	1.353(3)	1.354(3)
N(3)–N(4)	1.374(2)	1.373(3)
N(4)–C(9)	1.286(2)	1.267(3)
Bond angle	*Bond angle value, °*	*Bond angle value, °*
	A	B
C(1)-N(1)-N(2)	119.5(2)	118.6(2)
N(1)-N(2)-C(8)	115.0(2)	117.5(2)
N(2)-C(8)-O(3)	122.6(2)	123.7(2)
N(2)-C(8)-N(3)	116.3(2)	115.0(2)
O(3)-C(8)-N(3)	121.0(2)	121.4(2)
C(8)-N(3)-N(4)	122.5(2)	120.6(2)
N(3)-N(4)-C(9)	115.6(2)	117.0(2)

Table 3

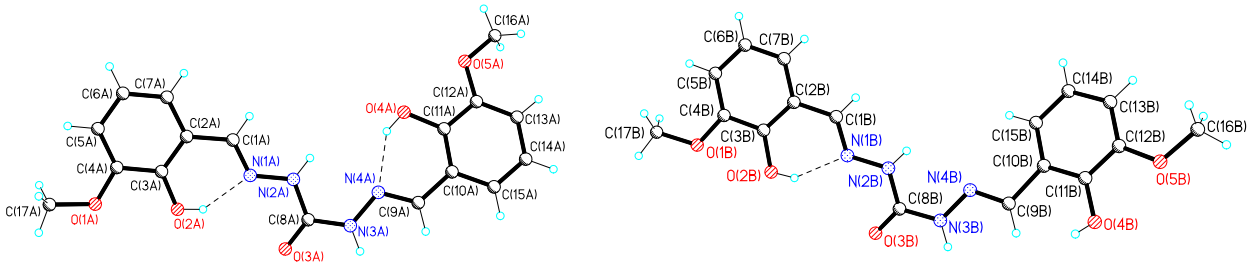
Geometric parameters of intra- and intermolecular hydrogen bonds in the structures of 1.

D–H···A	*D–H, Å*	*H···A, Å*	*D···A, Å*	*DHA, °*	*Symmetry transformations used to A*
N(2A)–H(1N)···O(3B)	0.86	2.49	3.119(2)	131	*x*+1, *y*, *z*
N(3A)–H(2N)···O(3B)	0.86	2.18	2.971(2)	153	-*x*, -*y*+1, -*z*+1
N(2B) –H(3N)···O(3A)	0.86	2.11	2.881(2)	150	*x*, *y*, *z*
N(3B)–H(4N)···O(4A)	0.86	2.21	2.936(2)	143	*x*-1, *y*, *z*
O(2A)–H(1OA)···N(1A)	0.82	1.88	2.591(2)	144	*x*, *y*, *z*
O(4A)–H(4OA)···N(4A)	0.82	1.95	2.669(2)	146	*x*, *y*, *z*
O(2B)–H(1OB)···N(1B)	0.82	1.87	2.585(2)	144	*x*, *y*, *z*
O(4B)–H(4B)···O(2B)	0.88	2.18	3.063(5)	173	-*x*, -*y*+1, -*z*+1
O(4C)–H(4C)···N(4B)	0.82	1.92	2.637(5)	146	*x*, *y*, *z*
C(1A)–H(1A)···O(3B)	0.93	2.60	3.306(3)	133	*x*+1, *y*, *z*
C(16A)–H(16A)···O(4B)	0.96	2.55	3.280(6)	133	*x*+1, *y*, *z*
C(1B)–H(1B)···O(3A)	0.93	2.40	3.164(3)	139	*x*, *y*, *z*
C(7B)–H(7B)···O(2A)	0.93	2.54	3.462(3)	169	*x*, *y*, *z*
C(9B)–H(9B)···O(5A)	0.93	2.61	3.426(3)	147	*x*-1, *y*, *z*
C(16C)–H(16C)···O(1A)	0.96	2.21	3.016(10)	141	*x*+1/2, -*y*+1/2, *z*+1/2

The asymmetric unit of compound **1** comprises two crystallographic independent molecules: A shown in Figure 1*(a)* and B shown in Figure 1*(b)*. In B, molecule one of the *o*-vanillin ring is disordered over two positions with occupancy coefficients 0.56 and 0.44, noted as B and C respectively. The molecular structure with the atomic-labelling scheme is shown in Figure 1*(a,b)*. The three molecules are stabilized as keto tautomers with respect to the central keto group, which is confirmed by the corresponding bond lengths (Table 2). The examination of the molecular configuration in compound **1** revealed that within the crystal, the carbonohydrazide segments of molecules all adopt the identical conformation, specifically the *anti* conformation (Scheme 1, right). The corresponding torsion angles O3-C8-N3-N4 equals 168.6(2)° in all molecules. Molecules A and C are stabilized by two intramolecular O-H···N hydrogen bonds, with $S^1_1(6)$ graph set, while in molecule B there is only one intramolecular hydrogen bond of this type (Table 3, Figure 1*(a,b)*). The crystal packing is supported by a number of intermolecular hydrogen bonds of the type N-H···O, O-H···O and C-H···O, which bind molecules of both the same and different type (A···B, B···A, B···B, C···A) (Table 3). These H-bonds unite molecules in supramolecular parallel ribbons running along *a* crystallographic axis, Figure 2. The intermolecular N-H···O and O-H···O hydrogen bonds form $D^1_1(2)$, $C^2_2(8)$ and $C^2_2(13)$ graph sets.

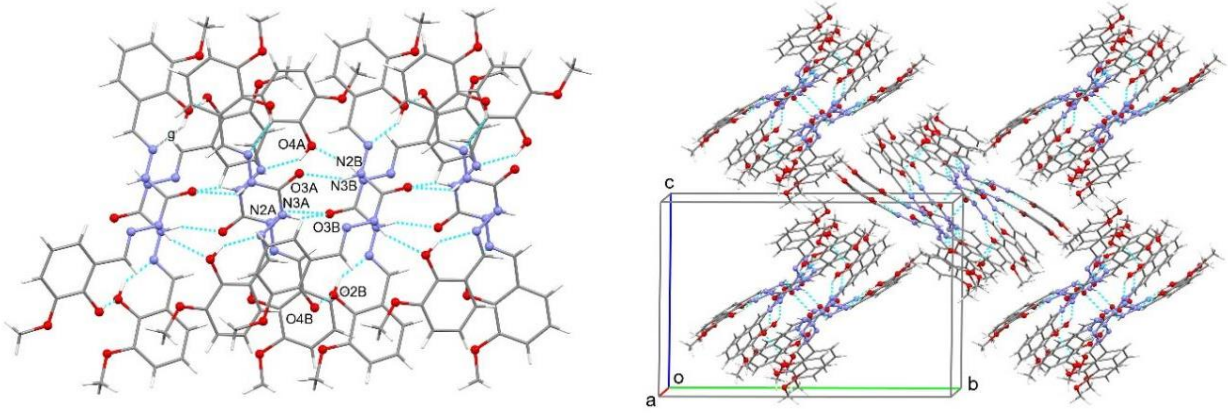
NMR characterization

The ^{1}H and ^{13}C NMR profile of compound **1** is close to the reported NMR data of 1,5-bis(2-hydroxy-3-methoxybenzylidene) carbonohydrazide [17,20]. It should be mentioned that, according to the results of Sow M.M., *et al.* 1,5-bis(2-hydroxy-3-methoxybenzylidene) carbonohydrazide exists both in crystal structure (as a methanol 0.47 solvate) and in DMSO-d_6 solution as the same *syn* conformer bearing carbamide fragment in the keto form and *o*-vanillin fragment in the enol-imino form [20]. Similar parallels also regarding the structure characterization in solid state and in solution, were reported for the related to **1** symmetrical disubstituted carbohydrazides, namely 1,5-bis(2,3-dihydroxybenzylidene)carbohydrazide [22] and 1,5-bis(salicylidene)carbohydrazide [23].



(a) ***(b)***

Figure 1. Structure of crystallographic independent molecules A *(a)* and B *(b)*.



(a) ***(b)***

Figure 2. Supramolecular hydrogen bonded ribbon in 1 *(a)*; packing of parallel ribbons in the crystal 1 *(b)*.

Interestingly, Kuo, C.-J. *et al.* presented ^{1}H NMR characteristics close to those shown here for 1,5-bis(2-hydroxy-3-methoxybenzylidene) carbonohydrazide in DMSO-d_6 solution, while preparing it as a ligand for synthesis of dysprosium complexes, and ligand switching from *syn* to *anti* upon complexation has been noted: in crystals of dinuclear dysprosium complex the ligand *anti* conformation was the preferred one [17]. To the authors' knowledge, a few works regarding the NMR characteristics obtained in solution for *anti* conformers of carbohydrazones are reported in literature [24,25]. On the other hand, the related ligand, based on thiocarbohydrazide, 1,5-bis(2-hydroxy-3-methoxybenzylidene) thiocarbonohydrazide was found in the solid state also in the form of the *anti* conformer [26]. It should be mentioned that some distinctions were found at the chemical shift assignment in the description of the ^{1}H and ^{13}C NMR spectral data for **1** [17,20] that could be explained by the absence of the 2D heterocorrelation techniques (HETCOR) NMR amongst the used methods. Thus, aimed at definitive structural elucidation for compound **1** in solution, combined NMR experiments: one-dimensional [^{1}H, ^{13}C and distortioneless enhancement by polarization transfer (DEPT) and two-dimensional gradient-selected heteronuclear single quantum coherence (gHSQC), gradient selected heteronuclear multiple bond correlation (gHMBC), and nuclear Overhauser effect spectroscopy (NOESY)] have been carried out. Chemical shifts of the protonated nitrogen nuclei are presented for the first time. As discussed, in the solid-state compound **1** exists as the *anti* conformer in the keto tautomeric form regarding carbamide and as an enol-imino tautomer with respect to the aldehyde fragments. At the same time, according to the liquid NMR spectral data, in DMSO-d_6 solution the dominant form is the *syn* conformation (Table 4, [17,20]). Both ^{1}H and ^{13}C NMR spectra of the compound under investigation **1** comprised one set of signals; this observation along with the values of chemical shifts have demonstrated that in DMSO-d_6 solution exists one prevailing, symmetrical, tautomeric form: the keto form regarding the central carbamide fragment and the enol-imino form when considering *o*-vanillin residues (Scheme 1; *syn* conformer; Figures S1-S3, included in Supplementary material). Nonetheless, the presence of *anti* conformers in solution cannot be excluded, as suggested by the data proved by the gHSQC technique.

Table 4

The ^{1}H and ^{13}C chemical shifts for 1 in DMSO-d_6 at 298 K.

Atom[a]	δ_H, *ppm*	δ_C, *ppm*	δ_N[c], *ppm*
C(1), C(9)	8.44	143.33	
C(2), C(10)		148.37	
C(3, C(11)		146.74	
C(4), C(12)		148.08	
C(5), C(13)	6.99	113.67	
C(6), C(14)	6.83	119.31	
C(7), C(15)	7.30	120.16	
C(8)		152.30	
C(16), C(17)	3.81	56.35	
O(2)H, O(4)H	≈ 10.27[b]		
N(2)H, N(3)H	10.85		153

[a] *For atom numbering see Figure 1.*
[b] *Very broad signals with low S/N.*
[c] *^{15}N chemical shifts are reported relative to liquid ammonia.*

The ^{1}H and ^{13}C chemical shifts in the NMR spectra of compound **1** supplement the published data [17,20], serving as an evidence of a correct assignment of the nuclei under discussion. For instance, the signals of the *o*-vanillin protons H-5/H-13 – H-7/H-15 were exactly assigned by using the heteronuclear ^{1}H/^{13}C gHSQC experiment: the signal at δ 7.30 ppm is described in [20] as characterizing the N2H, N3H nuclei (cross peak at δ 7.30/120.16 ppm in the ^{1}H/^{13}C HSQC spectrum, Figure S4, from Supplementary material). The signal of methine carbon nuclei in [20] was omitted (cross peak at δ 8.44/143.33 ppm in the ^{1}H/^{13}C HSQC spectrum, Figure S4), while resonance at δ 11.00 ppm has been ascribed to hydroxyl protons (N2H, N3H, two protons resonating at 10.85 ppm correlate with amide nitrogen nucleus at 153 ppm in ^{1}H/^{15}N HMQC spectrum, Figure S5). In the ^{1}H spectrum of the title compound the downfield signals characterizing -OH and -NH protons are separated (δ 10.27 ppm and 10.85 ppm, respectively), whilst in the molecules of analogous 1,5-bis(salicylidene)carbohydrazide these protons were found resonating at the same frequency (δ 10.86 ppm) [23]. Strong deshielding of these protons is the consequence of hydrogen-bond formation, which was confirmed by acquiring ^{1}H NMR spectra at different temperatures (Figure S6). The upfield shift of these signals caused by an increase in temperature is well-documented for protons involved in hydrogen bonds. The signals of the afore-discussed aromatic H-7/H-15 protons at δ 7.30 ppm change their shape too, as a result

of temperature augment, thus also demonstrating their participation in hydrogen intermolecular bonds, as also shown for packing motifs in crystal structure (Figures 2 and S6).

The signal at δ 8.44 ppm assigned to azomethine proton was not temperature dependent, proving the absence of *syn*–*anti* conformational isomerization. A conclusive evidence for the existence of the keto form of carbamide moiety in compound **1** has been proved by chemical shifts in the spectra, as well as NOESY correlations between azomethine protons at δ 8.44 ppm and amide -NH protons at δ 10.85 ppm (Figure S7). From the ^{13}C NMR spectra that were registered at two temperatures, a supplementary confirmation has been offered, regarding the nuclei of the atoms participating in the hydrogen bonding. Thus, in the ^{13}C NMR spectra recorded at 298 K and 348 K, the shape of the signals at δ 143.33 ppm and 120.16 ppm changed, corresponding to the azomethine and the carbon bearing the H-7/H-15 protons (Figure S8). These data corroborate both the above-discussed results of ^{1}H solution NMR experiments (Figure S6) and the found hydrogen bonds in the crystal structure of **1** (Figure 2). It should be mentioned, that the signal of azomethine carbon at δ 143.33 ppm is well-recognized by the typical line broadening caused by large quadrupole moment of ^{14}N [27] (N(1), N(4) nuclei).

Upon analysis of the ^{1}H/^{13}C gHSQC spectrum, the following hetero-correlations has been ascertained: each H-6/H-14 and H-5/H-13 protons presented two cross peaks of different intensity: δ 6.83/119.31 and δ 6.99/113.67 ppm, respectively – intense correlations and δ 6.83/113.67 and δ 6.99/119.31 ppm – "mutual" less intense correlations, as well. These data can serve as a demonstration on the presence of the *anti* conformer(s) in solution (Figure S4). Integration of the peaks under discussion in the ^{1}H/^{13}C gHSQC spectrum pointed to a cca 10:1 ratio of *syn*-*anti* conformers in the studied solution. As a result of molecular modelling studies obtained with PERCH NMR TOOLS (minimum-energy stereo structure depicted in Figure S10, Supplementary material), the ^{1}H and ^{13}C chemical shifts for an *anti* conformer of **1** have been calculated. The computed values partially suit experimental data, supporting to some extent the above-mentioned considerations on the co-existence of the isomers in solution. Results of the liquid state NMR investigations presented in this paper, complete the literature data reported for the *syn*-conformer of **1** [17,20], being in accordance with the described ^{1}H and ^{13}C chemical shifts of its congener-1,5-bis(salicylidene)carbohydrazide [23].

Conclusions

It has been proven for the first time that in the solid state the described 1,5-bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (1) can adopt *anti*-keto-tautomeric forms, taking into account the carbamide part of the molecule, and differs from the previously reported *syn*-keto-tautomeric forms [20,22,23]. In the crystal, molecules form supramolecular ribbons due to N-H···O and O-H···O intermolecular hydrogen bonds.

Full assignment for the proton, carbon and protonated nitrogen nuclei in **1** is presented for the first time, by use of combined 1D and 2D ^{1}H/^{13}C and ^{1}H/^{15}N NMR HETCOR techniques. The solution NMR data support the presence of the title compound in DMSO-d_6 solution as a mixture of *syn* and *anti* conformers of **1**, at a *cca.* 10:1 ratio, containing carbamide fragment in the keto form and *o*-vanillin moiety in the enol-imino form. Thus, NMR studies proved evidence on the switching of **1** from *anti* to *syn* conformation in DMSO-d_6 solution.

Funding

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Supplementary information

Supplementary data are available free of charge at http://cjm.ichem.md as PDF file.

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