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On the structures of 5-(4-, 3- and 2-methoxyphenylazo)-3-cyano-1ethyl-6-hydroxy-4-methyl-2-pyridone: An experimental and theoretical study

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ABSTRACT

In this work, a combined experimental and theoretical study on the structures of methoxy substituted 5phenylazo-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridones has been reported. The dyes under the investigation have been thoroughly characterized. X-ray single-crystal analysis shows that 5-(4methoxyphenylazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone crystallizes in the hydrazone form. Quantum chemical calculations of energies, geometrical structure and vibrational wavenumbers of the investigated dyes have been performed using density functional theory. The optimized geometrical parameters obtained by density functional theory calculations are in good conformity with the singlecrystal data. The fundamental vibrational wavenumbers, as well as their intensities have been calculated and a good agreement between observed and scaled calculated wavenumbers has been achieved. Stability of the molecule arising from hyperconjugative interactions and charge delocalization has been analyzed using natural bond orbital analysis. Vibrational, nuclear magnetic resonance and natural bond orbital analysis confirm that the prepared dyes exist in the hydrazone tautomeric form in the solid state and dimethyl sulfoxide solution.

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1. Introduction

Azo dyes represent a large group of colored organic compounds and have been the subject of substantial interest due to their physicochemical features and widespread commercial application. Besides their traditional role in textile dyeing, cosmetics, leather and food industries [1], azo dyes have been recently used in biological and medical studies [2], optical recording [3], dye-sensitized solar cells [4] and high technology products and innovations [5]. Disperse dyes having pyridone as a coupling component have gained a great significance in the dyestuff industry as a result of their excellent coloration features, simplicity of preparation, good light and wash fastness properties [1].

Azo-hydrazone tautomerism occurs in azo dyes bearing groups with labile proton conjugated with azo linkage. Because the tautomers differ in physical and optical properties, their functional and structural characterization has been of considerable controversy,

0143-7208/\$ - see front matter © 2014 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2014.01.007 and different approaches regarding this topic can be found in the literature [6-9]. Arylazo pyridone dyes under investigation in this paper contain hydroxy group in the *ortho* position to the azo bridge enabling intramolecular proton transfer and, thus, possibility for existence of azo and hydrazone tautomers (Scheme 1). Numerous investigations have been conducted regarding the tautomeric structure of azo pyridone dyes in the solid state and solutions using a variety of spectroscopic methods. The spectral data generally lead to the conclusion that the tautomeric equilibrium of azo pyridone dyes is in favor of the hydrazone tautomeric form in the solid state and, depending on the dye structure and used solvent, the equilibrium is predominantly in the favor of the hydrazone form in different solvents [10-12].

The molecular-level structure and supramolecular interactions in the solid state of azo dyes can be investigated employing singlecrystal X-ray diffraction technique. This method is useful for investigation of azo dye tautomerism, because it provides structural characterization of individual tautomers existing in the solid state and, moreover, reveals molecular packing modes. The detailed knowledge of the crystal structure of tautomers is crucial for understanding the difference in their physicochemical behavior. On







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Scheme 1. Azo-hydrazone tautomerism in studied arylazo pyridone dyes, X = 4-OMe (1), 3-OMe (2) and 2-OMe (3).

the other hand, quantum chemical calculations are suitable for investigation of geometry and the relative stabilities of distinct tautomers, as well as the charge transfer through the molecule and the possibility for the intramolecular hydrogen bonds. DFT calculations are often combined with X-ray crystallography because they complement each other and provide a better insight into effects controlling the predominance of one tautomer over the other [13–15].

Despite the commercial significance of pyridone based dyes, only several papers concerning their crystal structures have been published so far [16–19]. A general characteristic of these dyes is crystallization in the hydrazone form. Hydrogen bonding and π – π stacking interactions are further responsible for the formation of layered structures. Different dihedral angles between planes of pyridone and phenyl rings, as well as different packing arrangements are observed with a subtle change of functional groups in the phenyl ring [17]. It is also found that alteration of *N*-alkyl chains in pyridone ring results in dissimilar crystal packings [19].

In this study, three dyes with a methoxy group in different positions (*o*-, *m*- and *p*-) of phenyl moiety and the same 3-cyano-1ethyl-6-hydroxy-4-methyl-2-pyridone coupling component have been synthesized (Scheme 1). Single-crystal structure of 5-(4methoxyphenylazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2pyridone (1) has been reported. Quantum chemical calculations of energies have been carried out in order to compare the energies of the single-crystals and energy-minimized structures, as well as energies of azo and hydrazone tautomers. In addition, the harmonic vibrational frequencies, ¹H and ¹³C chemical shifts have been calculated in order to be compared with experimental data.

2. Experimental part

2.1. Materials and measurement

All reagents were purchased from either Aldrich, Fluka and Merck and were used without any further purification. The melting points were determined in capillary tubes on an automated melting point system Stuart SMP30. The IR spectra were acquired using a Bomem MB-Series 100 Fourier Transformation-infrared (FT-IR) spectrophotometer in the form of KBr pellets. The ¹³C and ¹H spectra were taken on a Varian Gemini 2000 (50 Hz and 200 Hz respectively) in deuterated dimethyl sulfoxide (DMSO-d₆) with tetramethylsilane (TMS) as an internal standard. All spectral measurements were carried out at room temperature (25 °C). Electrospray ionization mass spectra (ESI-MS) were recorded on an LCQ Advantage ion trap in acetonitrile. Elemental analysis was performed using a Vario EL III elemental analyzer. The ultraviolet–visible (UV–Vis) absorption spectra were recorded on a Schimadzu 1700 spectrophotometer in the region 200–700 nm.

2.2. Synthesis

All investigated arylazo pyridone dyes were synthesized from the corresponding diazonium salt and 3-cyano-1-ethyl-6-hydroxy4-methyl-2-pyridone following the modified procedure from the literature [20]. *N*-ethyl cyanoacetamide was obtained from ethyl cyanoacetate and ethylamine [21] and was further used in the reaction with ethyl acetoacetate for preparation of 3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone [22]. The azo colorants under the study were characterized by melting point, FT-IR, UV–Vis, ¹H NMR, ¹³C NMR spectra. elemental analysis and ESI-MS spectra.

2.2.1. 5-(4-Methoxyphenylazo)-3-cyano-1-ethyl-6-hydroxy-4methyl-2-pyridone (1)

4-Anisidine (1.23 g, 10.0 mmol) was dissolved in concentrated hydrochloric acid (2.5 mL) and cooled to -5 °C. Sodium nitrite (0.76 g, 11.0 mmol) was dissolved in cold water (4 mL) and added dropwise in the solution of 4-anisidine. The mixture was stirred 1 h and diazonium salt was obtained. 3-Cyano-1-ethyl-6-hydroxy-4methyl-2-pyridone (1.78 g, 10 mmol) was dissolved in the potassium hydroxide (0.56 g, 10.0 mmol) water (4 mL) solution and cooled to -5 °C. Diazonium salt was added dropwise to a vigorously stirred pyridone solution for 0.5 h and the mixture was additionally stirred for 3 h. The temperature of the reaction mixture was maintained at 0-5 °C. The red solid was filtrated, washed with water and dried. The crude product was recrystallized from chloroform. Red crystalline solid; yield: 2.28 g (73%); m.p. 215.6-217.2 °C; FT-IR (KBr, v/cm⁻¹): 3433 (NH on hydrazone form), 2223 (CN), 1672, 1627 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSOd₆): 1.13 (3H, t, J = 7.0 Hz, CH₃-CH₂), 2.50 (3H, s, CH₃), 3.80 (3H, s, OCH₃), 3.89 (2H, q, J = 7.0 Hz, CH₃-CH₂), 7.06 (2H, d, J = 9.0 Hz, Ar-H), 7.71 (2H, d, I = 9.0 Hz, Ar–H), $1\overline{4.81}$ (1H, s, NH hydrazone); ¹³C NMR (50 MHz, DMSO-d₆): 161.8 (Py), 161.2 (Py), 160.6 (Py), 158.9 (Ar), 134.8 (Ar), 122.9 (Py), 119.5 (Ar), 115.4 (Ar), 115.3 (CN), 99.6 (Py), 55.8 (OCH₃), 34.5 (CH₃CH₂), 16.6 (CH₃), 12.9 (CH₃CH₂); Anal. Calcd for C₁₆H₁₆N₄O₃ (312.33): C, 61.53; H, 5.16; N, 17.94. Found: C, 61.39; H, 5.10; N, 17.82; ESI-MS (negative): m/z 311.2 [M-H]⁻, Uv-Vis (EtOH) (λ_{max}/nm (log ε)): 460.0 (4.19), 273.5 (3.62).

2.2.2. 5-(3-Methoxyphenylazo)-3-cyano-1-ethyl-6-hydroxy-4methyl-2-pyridone (**2**) and 5-(2-methoxyphenylazo)-3-cyano-1ethyl-6-hydroxy-4-methyl-2-pyridone (**3**)

The synthesis of the compounds **2** and **3** were the same as for compound **1** using corresponding anisidine. Compound **2**: Dark orange powder; yield: 2.09 g (67%); m.p. 211.0–211.5 °C; FT-IR (KBr, ν/cm^{-1}): 3434 (NH on hydrazone form), 2223 (CN), 1676, 1628 (C= O on heterocyclic); ¹H NMR (200 MHz, DMSO-d₆): 1.14 (3H, t, *J* = 7.1 Hz, CH₃–CH₂), 2.50 (3H, s, CH₃), 3.81 (3H, s, OCH₃), 3.88 (2H, q, *J* = 7.5 Hz, CH₃–CH₂), 6.87 (1H, d, *J* = 8.4 Hz, Ar–H), 7.27–7.44 (3H, m, Ar–H), 14.54 (1H, s, NH hydrazone); ¹³C NMR (50 MHz, DMSO-d₆): 161.0 (Py), 160.6 (Py), 160.1 (Py), 159.4 (Ar), 142.7 (Ar), 131.0 (Py), 123.3 (Ar), 115.3 (CN), 113.0 (Ar), 109.9 (Ar), 103.2 (Ar), 101.1 (Py), 55.6 (OCH₃), 34.6 (CH₃CH₂), 16.7 (CH₃), 12.9 (CH₃CH₂); Anal. Calcd for C₁₆H₁₆N₄O₃ (312.33): C, 61.53; H, 5.16; N, 17.94. Found: C, 61.64; H, 5.08; N, 17.86; ESI-MS (negative): *m/z* 311.3 [M-H]⁻, Uv–Vis (EtOH) (λ_{max}/nm (log ε)): 436.0 (4.37), 276.0 (3.85).

Compound **3**: Orange-red powder; yield: 1.81 g (58%); m.p. 271.1–273.3 °C; FT-IR (KBr, ν/cm^{-1}): 3441 (NH on hydrazone form), 2223 (CN), 1676, 1624 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-d₆): 1.13 (3H, t, *J* = 7.0 Hz, CH₃–CH₂), 2.51 (3H, s, CH₃), 3.89 (2H, q, *J* = 6.7 Hz, CH₃–<u>CH₂</u>), 3.99 (3H, s, OCH₃), 7.12 (1H, t, *J* = 6.7 Hz, Ar–H), 7.26 (1H, t, *J* = 6.7 Hz, Ar–H), 7.47 (1H, d, *J* = 7.8 Hz, Ar–H), 7.85 (1H, d, *J* = 7.8 Hz, Ar–H), 14.95 (1H, s, NH hydrazone); ¹³C NMR (50 MHz, DMSO-d₆): 161.4 (Py), 160.9 (Py), 160.0 (Py), 149.0 (Ar), 142.3 (Ar), 131.0 (Ar), 128.2 (Py), 122.1 (Ar), 121.5 (Ar), 115.7 (CN), 112.6 (Ar), 101.0 (Py), 56.6 (OCH₃), 34.5 (CH₃CH₂), 16.5 (CH₃), 12.9 (CH₃CH₂); Anal. Calcd for C₁₆H₁₆N₄O₃ (312.33): C, 61.53; H, 5.16; N, 17.94. Found: C, 61.42; H, 5.19; N, 17.85;

ESI-MS (negative): m/z 311.3 [M-H]⁻, Uv–Vis (EtOH) (λ_{max} /nm (log ε)): 454.5 (4.53), 277.5 (3.85).

2.3. X-ray crystallography

Single crystals of compound 1 suitable for X-ray diffraction measurement were grown from chloroform by slow evaporation in a refrigerator for three weeks. Room temperature (20 °C) singlecrystal X-ray diffraction data were collected on an Oxford Gemini S diffractometer equipped with a sapphire 3 CCD detector, using monochromatized Cu K α radiation ($\lambda = 1.5418$ Å). A multi-scan correction for absorption was applied. The structure was solved by direct methods (SIR97) [23] and refined on F^2 by full-matrix least-squares using the programs SHELXL97 [24] and WinGX [25]. All non-hydrogen atoms were refined anisotropically. Positions of H atoms bonded to C atoms were calculated at ideal positions and refined by the riding model with $U_{iso} = 1.5U_{eq}(C)$ for methyl, and $U_{\rm iso} = 1.2U_{\rm ed}(C)$ for remaining H atoms. H₂ atom connected to N1 was found in ΔF map and freely refined with isotropic displacement parameter. The figures were produced with Mercury [26]. Crystal data and refinement results are listed in Table 1, while selected bond distances and angles are given in Table 2.

2.4. Computational studies

All the density function theory (DFT) calculations were performed using Gaussian 09 Revision D.01 program package [27] on the B3LYP [28], M06 and M06-2X [29] level of theory with the default convergence criteria and without any constraint on the geometry.

In the present work all the possible isomers of **1** are generated and fully optimized at the DFT B3LYP/6-311++G(d,p) level. 24 stable isomers of **1** are obtained. Two most stable isomers, pyridine-2,6-dione and 2-hydroxy-6-pyridone are used for further geometry and energy studies. The harmonic vibrational frequencies were derived from the numerical values of these second derivatives and used to obtain the Gibbs energy contributions at 298.15 K and standard pressure. Structural parameters (bond lengths) were extracted directly from the data files following the geometry optimizations. Because of well known lack to underestimate the

Table 1

Crv	/stal	data	and	structure	refinement	for	compound	1.
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Empirical formula	C16H16N4O2
$M/g \text{ mol}^{-1}$	312 33
Crystal system	Orthorhombic
Space group	P2,2,2,
a/Å	7 5800(8)
h/Å	10 1990(8)
c/Å	19.753(2)
$\alpha / ^{\circ}$	90
βļ°	90
$\gamma / ^{\circ}$	90
V/Å ³	1527.1(2)
Ζ	4
$\rho_c/\mathrm{g}~\mathrm{cm}^{-3}$	1.359
μ/mm^{-1}	0.800
F(000)	656
θ range for data collection/°	4.48-70.06
Range of h, k, l	$-8 \leq h \leq 9$, $-12 \leq k \leq 9$, $-20 \leq l \leq 23$
Reflections collected	3777
Independent reflections (R_{int})	2511(0.0216)
Data/restraints/parameters	2511/0/212
S	1.044
<i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0464, wR_2 = 0.1217$
R indices (all data)	$R_1 = 0.0558, wR_2 = 0.1309$
Flack parameter	0.0(4)
$\Delta ho_{ m max}$, $\Delta ho_{ m min}/ m e$ Å $^{-3}$	0.246, -0.196

Table 2

Selected bond distances and angles for compound 1.

Bond distances/Å			
C5-N1	1.411(3)	C11-02	1.212(3)
C8-N2	1.331(3)	C11-N4	1.396(3)
C8–C9	1.429(4)	C12-03	1.230(3)
C8-C12	1.461(4)	C12-N4	1.380(3)
C9-C10	1.354(4)	N1-N2	1.294(3)
C10-C11	1.470(4)		
Bond angles/°			
C5-N1-N2	120.0(2)	C8-N2-N1	121.2(2)

activation energy [30], the B3LYP method was not able to locate 2hydroxy-6-pyridone isomers which exist as vary shallow minima on the potential the energy surface. To resolve that problem DFT M06 and M06-2X calculations with 6-311++G(d,p) basis set are carried out to compare the energy differences between single-point energy of the single-crystal structure of **1** and energies of the fully optimized structures for both pyridine-2,6-dione and 2-hydroxy-6pyridone isomers for all investigated compounds.

The harmonic frequencies were calculated by B3LYP method using 6-311++G(d,p) basis set and then scaled by 0.9668 [31]. The assignments of the calculated wavenumbers were aided by the animation option of Gauss View 5.0 graphical interface from Gaussian programs, which gave a visual presentation of the shape of the vibrational modes [32].

The nuclear magnetic resonance (NMR) chemical shifts calculations were performed using Gauge-Invariant Atomic Orbital (GIAO) method [33] at B3LYP/6-311++G(d,p) level with SMD model [34] for simulation of solvent (DMSO). The ¹H and ¹³C isotropic chemical shifts were referenced to the corresponding values for TMS, which were calculated at the same level of theory.

The natural bonding orbitals (NBO) calculations [35] were performed using NBO 3.1 program as implemented in the Gaussian 09 [27] package at the B3LYP/6-311G(d,p) level in order to understand various second order interactions between the filled and vacant orbitals of the investigated molecule, which is a measure of the intramolecular delocalization and hyperconjugation.

3. Results and discussion

3.1. Synthesis

Azo dyes 1–3 having the same pyridone skeleton are prepared via classical coupling reactions between 3-cyano-1-ethyl-6hydroxy-4-methyl-2-pyridone and diazonium salts of the corresponding anisidine. Coupling reactions are performed under the alkaline conditions and pure azo pyridone dyes are obtained after recrystallization in a good yield. Dye 1 has been reported earlier in order to study azo-hydrazone tautomerism [36], but without analytical and experimental data. Dyes 2 and 3 have not been registered in the literature so far. The FT-IR spectra of the compounds clearly show the existence of the hydrazone form in the solid state. This is concluded on the basis of the two intense carbonyl bands in each spectrum appearing within the region $1627 - 1676 \text{ cm}^{-1}$. The vibrations in the region $3431 - 3440 \text{ cm}^{-1}$ are assigned to the imino group of hydrazone unit. The aromatic C-H stretching vibrations are observed in the region 2919–3071 cm⁻¹, while the aliphatic C–H stretching vibrations are found between 2850 and 2980 cm⁻¹. The band at 2223 cm⁻¹ in FT-IR is assigned to C≡N stretching vibrations. The data obtained from NMR spectra also strongly suggest the existence of the hydrazone tautomer of all three dyes in DMSO-d₆ solution. The ¹H NMR shifts assigned to the N-H proton of the hydrazone form are within the range 14.54-14.95 ppm. This is in accordance with chemical shifts of the imino group in DMSO-d₆ for analogous pyridone azo dyes reported by Peng et al. (δ 14.30–16.09) [37] and Alimmari et al. (δ 14.27–14.93) [38]. Comparing the ¹H NMR spectra of the compounds 1-3, one can notice that the chemical shift of NH group for o-substituted dye is slightly larger than for *m*- and *p*-substituted compounds. This is the reflection of intramolecular hydrogen bond formed between the hydrazone hydrogen atom and the oxygen atom of methoxy group in *ortho* position to the hydrazone unit. In the present study, signals for two carbons of carbonyl groups, expected in hydrazone form, are observed at 160-160.6 and 160.6-161.2 ppm, respectively, in ¹³C NMR spectra for the molecules **1–3**. Peng et al. [37] have reported that chemical shifts of the phenyl carbon atoms connected to the azo group in azo and hydrazone form of the arylazo pyridone dyes differ for \sim 14 ppm. It is, also, reported that these shifts for hydrazone form are the range 134.1–140.7, which match with shifts of the same carbon atoms of 1-3, proving the presence of hydrazone form. The signals at 122.9-131.0 ppm are assigned to carbons of hydrazone C=N group and agree with literature data.

UV–Vis absorption spectra of the dyes **1–3** in ethanol are given in Fig. 1. Strong absorption bands at 460.0, 436.0 and 454.5 nm for **1–3**, respectively, are ascribed to $\pi - \pi^*$ transitions between pyridone ring and phenyl ring in hydrazone form. Weak bands appearing at 273.5–277.5 nm correspond to $n-\pi^*$ transitions between the phenyl ring and middle hydrazone unit [19]. Methoxy group exerts positive mesomeric effect in *para* and *ortho* positions and causes a batochromic shift of the longest wavelength when compared with *meta* substituted dye where only positive inductive effect is present. *Ortho* substituted dye show a small hypsochromic shift with respect to *para* substituted dye due to the steric effect preventing pyridone and phenyl rings lying in the same plane and, thus, inhibiting effective delocalization.

3.2. Crystal structure of azo dye 1

Compound **1** crystallizes in orthorhombic space group $P_{2_12_12_1}$, with 4 molecules per unit cell. The molecular structure of **1** with the atomic-numbering scheme is shown in Fig. 2. The main structural feature of **1** is its planarity, with the expected exception of terminal CH₃ group from the ethyl radical. The maximal deviation from least-squares plane through skeletal C, N and O atoms is 0.207 Å for



Fig. 1. UV-Vis spectra of the investigated compounds 1-3.



Fig. 2. ORTEP-like representation of compound **1** with the atomic-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is shown as a dashed line.

the C1 atom from the methoxy group. The dihedral angle between benzene (C2–C7) and the pyridone (N4, C8–C12) ring is only 3.3°.

The investigated dye **1** crystallizes in the hydrazone form. This can be deduced from the position of the hydrogen atom on N1 rather than O3 and from the bond lengths of C12–O3 (1.230 (3) Å) and C8–N2 (1.331 (3) Å) exhibiting a double bond character. Another indicator supporting the hydrazone tautomer of **1** is a noticeable difference between N1–C5 (1.411 (3) Å) and N2–C8 (1.331 (3) (Å)) bond lengths expected for this tautomer. The N1–N2 bond amounts 1.294 (3) Å, which is shorter than N–N single bond but not short enough to be regarded as a double bond, indicating extended delocalization of electron density from electron donating methoxy group to pyridone ring through the hydrazone unit. This may be one of the reasons for planarity of the molecule.

Comparing the averaged bond lengths of the compound **1** with the bond distances of the compounds having the same pyridone backbone described in literature (**4–6**, Scheme 2) the significant difference is noticed for the C5–N1–N2–C8 fragment [17,19]. Due to the presence of nitro group in *ortho* position in the phenyl moiety of these compounds, shortening of N1–N2 bond and elongations of the C5–N1 and N2–C8 bonds are observed for the compound **1**. A possible explanation may be the withdrawing nature of the nitro group having the opposite effect to the charge transfer present in the investigated compound **1**, as well as the presence of an additional intramolecular hydrogen bond formed between nitro group and NH group. The steric hindrance of nitro group in C.I. Disperse Yellow 119 (**4**) is responsible for the noticeable different dihedral angle between pyridone and phenyl rings (16.9°) with respect to the investigated compound **1**, as expected.

According to the observed hydrazone form, an intramolecular and short N–H···O hydrogen bond of the S(6) type, with N···O distance of 2.602(3) Å is noticed (Table 3). This hydrogen bond completes pseudo six-membered ring whose presence may be another reason for the planarity of the molecule. Some authors suggest that this intramolecular hydrogen bond contributes to stabilization of the hydrazone form in the solid state [17,18].

In the solid state, molecules are held together by a complex system of hydrogen bonds, $\pi-\pi$ and van der Waals interactions making first a 2D layered structure and then a 3D framework. On one hand, there is one series of corrupted, herringbone-like layers approximately parallel to the *bc*-plane (Fig. 3(a)). Inside the individual segments of this layer all molecules are oriented in the same way and connected by C–H···N/O hydrogen bonding interactions (Fig. 3(b)). The following short contacts: C1–H1A···O3, C3–H3···O2 and C6–H6···N3 (Table 3) are found in these layers. On the other hand, when the packing is projected onto *bc*-plane another set of



Scheme 2. Molecular structures of the compounds having the same pyridone backbone described in the literature.

highly corrupted layers oriented perpendicular to the *c*-axis, with partially overlapped aromatic rings is visible (Fig. 4(a)). Among these layers possible hydrogen bonding contacts involve two out of three methyl groups: C1–H1B···O2, C1–H1C···O2 and C13–H13C···N1 (Table 3). Practically all short contacts around C1H₃ methyl group are concentrated in one hemisphere explaining why, as described above, C1 atom deviates from the mean-plane of the skeleton atoms. Within these layers the molecules are stacked together by parallel-displaced π – π interactions, with details shown in Fig. 4(b). The dihedral angle between mean-planes of the benzene and pyridone ring from adjacent molecules is 10.6°. As a consequence, C···C distances vary from 3.532(4) Å for C10···C4 to 4.117(4) Å for C12···C7 contacts. These values indicate moderate to weak π – π interactions.

3.3. Optimized geometry

In the present work all the possible isomers of **1** are generated and fully optimized at DFT-B3LYP/6-311++G(d,p). 24 stable isomers (the four tautomers with corresponding number of rotational conformers, Scheme 3) of **1** are obtained. The Gibbs energy and the statistical Boltzmann distribution weighted values at 298.15 K and standard pressure of all isomers are presented in Table S1. The optimized geometries of all isomers are confirmed to be located at the local true minima on the potential energy surface, as they do not contain imaginary frequencies.

The results show that two most stable geometries belong to pyridine-2,6-dione (**I-a**) and 2-hydroxy-6-pyridone (**II-b**) isomer (Fig. 5). The obtained results are consistent with the previous report concerning 5-arylazo-6-hydroxy-4-phenyl-3-cyano-2-pyridones [38]. The Gibbs energies and statistical Boltzmann distribution weights show that in the solid state only pyridine-2,6-dione (**I-a**) isomer is present, whereas hydroxy-6-pyridone (**II-b**) could be present in no more than 0.0002%, and all other isomers are untraceable. In accordance to that, in the further calculations only these two isomers for all investigated compounds are used for the geometry and energy studies.

The optimized geometries for the geometry studies of **1**–**3** have been obtained using the B3LYP, M06 and M06-2X methods with 6-311G++(d,p) basis set (Table S2). All methods agree that the most stable geometry belongs to pyridine-2,6-dione (**I-a**) isomer. The most stable geometries of pyridine-2,6-dione isomers of compounds **1**–**3** are shown in Figs. S1–S3 and calculated bond lengths are listed in Table S3 along with the experimental data for **1**. The optimized bond lengths for compounds **1**–**3** are correlated with data determined by X-ray for compound **1**. The results show a very good agreement between experimental and calculated bond lengths of all heavy atoms for all used DFT methods ($R^2 > 0.985$). The relations for the bond lengths between calculated and experimental values and the corresponding R^2 and RMSD values are presented in Table 4.

The results for the Gibbs energies determined with M06 and M06-2X methods summarized in Table 5, demonstrate a large

energy gap between the single-crystal and energy-minimized structures in the same hydrazone form (157.20 and 158.05 kcal mol⁻¹ for **1**), which may be the reflection of the energy compensation for the formation of hydrogen bonding and $\pi - \pi$ stacking between molecules. These results are according to the previously reported results for compounds 4 and 5 (Scheme 2) [17]. The results also indicate that the pyridine-2,6-dione isomer is more thermally stable than the 2-hydroxy-6-pyridone isomer for **1** with the energy gaps of 8.68 and 6.21 kcal mol⁻¹, which may be regarded as theoretical support for the crystallization in the hydrazone form for 1. Results for compounds 2 and **3** show an additional increase of the energy gap (8.27 and 7.11 and 15.84 and 7.61 kcal mol⁻¹) between pyridine-2,6-dione and 2-hydroxy-6-pyridone isomers. The largest energy gap observed and difference in the energy of two conformers with different orientation of o-methoxyphenyl group around Ph-N bond of 6.61 and 5.84 kcal mol⁻¹ (correspondingly to the used DFT models) for ortho substituted dye may be attributed to an additional stabilization of the hydrazone form through formation of the intramolecular hydrogen bond between methoxy and imino group, which is not present in *m*- and *p*-substituted dyes.

All shown results are consistent with the aforementioned tendency between the energy-minimized pyridine-2,6-dione and 2hydroxy-6-pyridone isomers. In summary, both, the geometry and energy studies, demonstrate the existence of the hydrazone form for this family of azo dyes in the solid state [16–18].

3.4. Vibrational and NMR analysis

The harmonic vibrational frequencies for the azo dye **1** have been calculated by using DFT method at 6-311++G(d,p) level. In order to compare the theoretical results using the experimental values, a scaling factor of 0.9668 is applied to all of the calculated frequencies. Experimental and scaled theoretical spectra for the qualitative comparison are shown in Fig. S4. Some of the characteristic frequencies for the title compounds are given in Table S4. The broad band at 3433 cm⁻¹ in FT-IR spectrum assigned to N–H stretching vibration shows deviation of 273 cm⁻¹ with scaled frequency value at 3160 cm⁻¹ by DFT method. This deviation may be due to the presence of

Iable 5					
Geometry of possible	hydrogen	bonds	for	compound	1.

Table 2

D—H…A	d(D—H)/ Å	d(H…A)/ Å	d(D…A)/ Å	∠(DHA)/°	Symmetry code
N1-H2…O3	0.97(4)	1.82(4)	2.602(3)	136(3)	
C1-H1A…O3	0.96	2.656	3.461(4)	142	-x + 1/2, -y, z + 1/2
C1-H1B…O2	0.96	2.763	3.402(4)	125	-x + 1/2, -y + 1,
					z + 1/2
C1-H1C…O2	0.96	2.888	3.817(4)	163	-x, y + 1/2, -z + 3/2
C3-H302	0.93	2.493	3.420(3)	174	-x + 1/2, -y, z + 1/2
C6-H6…N3	0.93	2.543	3.386(4)	151	<i>x</i> , <i>y</i> + 1,+ <i>z</i>
C13-H13C…N1	0.96	2.588	3.530(4)	167	-x, y - 1/2, -z + 3/2



Fig. 3. Crystal packing of compound 1: (a) space filling model viewed along *b*-axis; (b) projection showing intralayer C-H…N/O hydrogen bonding interactions as thin lines.

intramolecular hydrogen N1–H2···O3 bonding (1.767 Å). While the C=O and C=N stretching vibrations were seen at 1672, 1627 cm⁻¹ and 1398 cm⁻¹, respectively, the same bands were calculated as 1676, 1612 cm⁻¹ and 1386 cm⁻¹, respectively, *i.e.* there is a very good agreement between experimental and calculated data. These stretching modes are also consistent with those reported in the literature [39].

A powerful way to predict and interpret the structure of azohydrazone tautomers is to combine computer simulation with NMR methods. The experimental and theoretical values for ¹H and ¹³C NMR of the **1–3** are given in Tables S5 and S6.

The ¹H NMR spectra of dyes **1–3** measured in DMSO-d₆ at room temperature show a characteristic singlet for the CH₃ group at the 4-position at 2.5 ppm, with calculated chemical shift values at 2.57–2.61. Two signals, triplet and quartet, at 1.13–1.14 and 3.88–3.99 ppm mark the ethyl hydrogens (Table S5). The chemical shift values for ethyl hydrogen atoms (with respect to TMS) are 1.26–1.27 and 4.17–4.26 ppm in DMSO solution. The experimental peaks of aromatic hydrogen atoms are found at 7.06–8.38 ppm and correlate well with calculated chemical shifts. The hydrogen atom of –NH group appears at chemical shift of 14.54–14.95 ppm, with theoretical peaks at 14.56–14.76 ppm. These results suggest that dyes **1–3** exist in the hydrazone tautomeric form in DMSO solution.

In the ¹³C NMR spectra for the dyes **1–3**, the two carbon atoms (C11 and C12) of the carbonyl groups resonate at 160–160.6 and 160.6–161.2 ppm, respectively, and show good agreement with computed values at 168.66–169.07 and 168.97–169.76 ppm. The carbon atom of C=N group has peak at 122.9–130.25 ppm with respect to TMS in experimental ¹³C NMR spectra for dyes **1–3**, which matches well with the theoretically calculated chemical shift at 129.32–131 ppm. These signals characteristic for carbonyl groups and C=N group again suggest that dyes **1–3** exist in hydrazone tautomeric form. The calculated chemical shifts in ¹³C NMR spectra show excellent agreement with the experimental data (Table S6).

3.5. Natural bond orbital (NBO) analysis

NBO analysis has been performed on **1** in order to elucidate intramolecular charge transfer (ICT), rehybridization and delocalization of electron density within the molecule. The important interactions between occupied Lewis type (bonding or lone pair) NBO orbitals and unoccupied (antibonding or Rydberg) non Lewis NBO orbitals of investigated dye **1** are given in Table S7.

The natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding, and it also provides a convenient basis for investigating charge transfer in molecular systems. The larger the E(2) value, the more intensive is the interaction between electron donors and electron acceptors.

The intramolecular interactions for dye **1** are formed by the orbital overlap between bonding N–N, C–C, C–N, C–H and C=N, C=O antibonding orbitals which results in an ICT causing stabilization of the system.

The intramolecular hyperconjugative interaction of $\sigma(N1-N2)$ distributes to $\sigma^*(N1-C5)$, N2-C8, C8-C9 and C4-C5, leading to stabilization of 0.9-2 kcal mol⁻¹, as shown in Table S7.

The $\pi \to \pi^*$ interactions of $\pi(N1-C5)$ with $\pi^*(N2-C8, C3-C4)$ and C6–C7) lead to stabilization of 6.8–32.7 kcal mol⁻¹, as shown in Table S7. The same kind of interaction is calculated among $\pi(N2-C8)$ with $\pi^*(N1-C5, N2-C8, C9-C10)$ and C12–O3) with stabilization of 6.7–18 kcal mol⁻¹. This $\pi \to \pi^*$ interaction shows that there is charge transfer through the molecule. It can be said that there is an electron–donor interaction of OCH₃ group to the molecule, LP(2) O2 \to LP(1)C2, as well as electron–acceptor interaction of CN group through $\pi(C9-C10) \to \pi^*(N3-C14)$, with values of *E*(2) 57.1 and 19.61, respectively.

The interaction energy, related to the resonance in the molecule, is electron withdrawing to the ring through $\sigma^*(N4-C11, C10-C11$ and N4-C12, C8-C12) bond from the lone pairs LP(2)O2 and LP(2) O3 which leads to moderate stabilization energy of 13-



Fig. 4. (a) Projection of compound **1** onto the *bc*-plane showing intra- and interlayer C–H…N/O hydrogen bonding interactions as thin lines. (b) Details of π - π stacking interactions (Centroids, Cg, are shown as white spheres of arbitrary radii).

28 kcal mol⁻¹ (Table S7). These interactions confirm the existence of charge transfer in the **1.** The most important interaction energies of LP(1)N4 $\rightarrow \pi^*$ (C11–O2) and LP(1)N4 $\rightarrow \pi^*$ (C12–O3) are 47.37 and 65.38 kcal mol⁻¹, respectively.

The intramolecular N–H···O hydrogen bond is formed by the orbital overlap between the lone pairs of electrons LP(O) and $\sigma^*(N-H)$ which results in ICT causing stabilization of the H-bonded systems. Therefore, hydrogen bonding interaction leads to an increase in electron density (ED) of the N–H antibonding orbital. The increase of the population of C=O antibonding orbital weakens the C=O bond. NBO analysis of azo dye **1** makes clear evidence of the formation of a strong H-bond interactions between the LP(O) and $\sigma^*(N-H)$ antibonding orbital. The stabilization energies E(2) associated with hyperconjugative interaction LP(1)O3 $\rightarrow \sigma^*(N1-H2)$, and LP(2) O3 $\rightarrow \sigma^*(N1-H2)$ are obtained as 3.89 and 12.5 kcal mol⁻¹, respectively (Table S7), which quantify the extend of intramolecular hydrogen bonding, causing additional stabilization of the hydrazone tautomer.

4. Conclusion

Three methoxy substituted 5-phenylazo-3-cyano-1-ethyl-6hvdroxy-4-methyl-2-pyridones have been synthesized and thoroughly characterized. According to the spectral data, dyes exist in the hydrazone form in the solid state and in DMSO- d_6 . X-ray singlecrystal analysis of 5-(4-methoxyphenylazo)-3-cyano-1-ethyl-6hydroxy-4-methyl-2-pyridone revealed that this dye crystallizes in hydrazone form. The main structural feature of the molecule is planarity. In the solid state, molecules are held together by a complex system of hydrogen bonds, $\pi - \pi$ and van der Waals interactions creating parallel zigzag pseudo-chains along the *b*-axis. DFT calculations of the compounds **1–3** show that the most stable geometry belongs to the hydrazone form. The results also indicate that the hydrazone form is more thermally stable than the azo form. A large energy gap between the single-crystal and energyminimized structures in the same hydrazone form is observed for the dye **1** (157.20 and 158.05 kcal mol^{-1} determined with M06 and M06-2X methods, respectively) which is due to supramolecular



Scheme 3. Possible tautomers of the investigated compound 1.



Fig. 5. The most stable geometries of 1 (hydrazone (I-a) and azo (II-b) tautomer).

Table 4

Correlation equations between calculated and experimental bond lengths.

Compound	B3LYP method	M06 method	M06-2X method
1	$d_{\text{cal.}} = 0.9896 d_{\text{exp.}} + 0.0202$	$d_{\text{cal.}} = 0.9789 d_{\text{exp.}} + 0.0283$	$d_{\text{cal.}} = 1.0100 d_{\text{exp.}} - 0.0121$
	($R^2 = 0.9883$, RMSD = 0.0098)	($R^2 = 0.9869$, RMSD = 0.0103)	($R^2 = 0.9883$, RMSD = 0.0100)
2	$d_{\rm cal.} = 0.9910 d_{\rm exp.} + 0.0188$	$d_{cal.} = 0.9825 d_{exp.} + 0.0234$	$d_{\text{cal.}} = 1.0143 d_{\text{exp.}} - 0.0179$
	($R^2 = 0.9892$, RMSD = 0.0094)	($R^2 = 0.9865$, RMSD = 0.0105)	($R^2 = 0.9878$, RMSD = 0.0103)
3	$d_{cal.} = 0.9913 d_{exp.} + 0.0186$	$d_{\text{cal.}} = 0.9817 d_{\text{exp.}} + 0.0246$	$d_{\text{cal.}} = 1.0127 d_{\text{exp.}} - 0.0156$
	($R^2 = 0.9878$, RMSD = 0.0101)	($R^2 = 0.9860$, RMSD = 0.0107)	($R^2 = 0.9875$, RMSD = 0.0104)

Table 5

Calculated Gibbs energy (ΔG in a.u.) and dipole moment (*p* in D) for the investigated compounds **1–3** on M06 and M06-2X (in brackets) models.

Structure	Compound						
	1		2		3		
	ΔG	р	ΔG	р	ΔG	р	
The single-crystal structure in the hydrazone form	-1063.0712 (-1063.3555)	9.40 (9.09)	_	_	_	_	
The energy-minimized structure in the pyridine-2,6-dione form	-1063.3217 (-1063.6073)	9.31 (10.05)	-1063.3225 (-1063.6088)	8.38 (6.97)	-1063.3231 (-1063.6085)	10.25 (10.08)	
The energy-minimized structure in the 2-hydroxy-6-pyridone form	-1063.3079 (-1063.5974)	9.32 (10.50)	-1063.3093 (-1063.5974)	8.43 (7.27)	-1063.2984 (-1063.5964)	9.40 (10.54)	

interactions in the solid state. The harmonic vibrational frequencies and NMR calculations provide chemical shifts that are consistent with experimental data. The NBO calculations confirm the existence of charge transfer in the molecule **1** and intramolecular hydrogen bonding causing additional stabilization of the hydrazone tautomer. It can be concluded that both experimental and theoretical data support the existence of the hydrazone tautomer of the dyes **1–3** in the solid state and DMSO solution.

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Appendix B. Supplementary data

CCDC reference number 966964 for **1** at 291 K contains supplementary crystallographic data for this paper. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.dyepig. 2014.01.007.

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