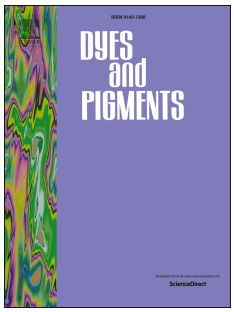
Accepted Manuscript



The possible tautomerism of the potential rotary switch 2-(2-(2-Hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione

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The possible tautomerism of the potential rotary switch 2-(2-(2-Hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione

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Abstract:

The title compound is potentially tautomeric and its tautomerism was studied by means of molecular spectroscopy (^{1}H and ^{13}C NMR and UV-Vis) in DMSO as well as by quantum chemical calculations (M06-2X/TZVP). The detailed assignment of the NMR signals supported by the theoretical calculations clearly shows that the previous interpretation, available in the literature, about the coexistence of two tautomeric forms is not correct. The compound exists as major and minor isomer of a single tautomeric form. In addition, a 2-methoxy derivative (the OH group replaced by a methoxy group) is also investigated and show similar trends.

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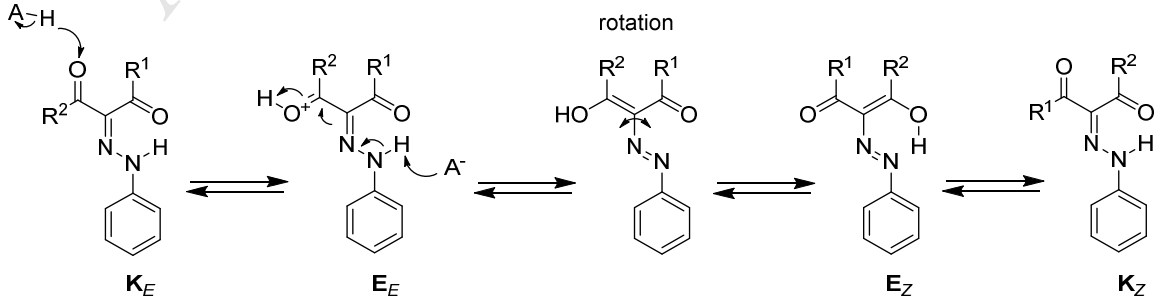
Key words: rotary switch, tautomerism, hydrazone, NMR, UV-Vis spectroscopy, DFT

Introduction:

The switch is one of the simplest components of an electrical circuit. In molecular electronics this term is used to assign any molecular "structure" able to reversibly shift between two or more stable states in response to environmental stimuli such as changes in pH, light, temperature, electric current, microenvironment, or in the presence of an ion [1–6]. Virtually, every single molecule changes its behaviour when acted upon by external stimuli, but its use as a molecular switch is possible only if these changes are reproducible, reversible and can be explicitly controlled [7]. Most of the existing switches [7–12], are based on primary processes like photochromism, host-guest interactions, protonation/deprotonation, oxidation/reduction or a combination of them. Tautomerism could be an additional elemental process, because, on one side, the change in the tautomeric state is accomplished by a fast proton transfer reaction between two or more structures, each of them with different properties. The practically unlimited number of *on*/*off* cycles and, hence, high fatigue resistance, can be the obvious advantage over the other existing primary mechanisms [13]. Real or potentially switchable tautomeric systems have been classified as tautomeric tweezers, tautomeric cavities, proton cranes and rotary switches [14]. The analysis of the advantages/disadvantages of the first three of these classes leads to clear conclusion that a real switching is possible only when a suitable mediator is structurally implemented in the tautomeric molecule. In such a case the addition of acid/base/ions in solution or suitable irradiation could lead to indirect change in the position of the tautomeric equilibrium in a controlled and reproducible manner. The mediating unit (arm, crane [15,16] or cavity [17,18]) plays the role of an antenna transferring the signal from the external stimuli to the tautomeric backbone, which responses to the changes by altering its tautomeric state. Of course, a very careful selection of the tautomeric backbone and thoughtful design of the antenna are required [14].

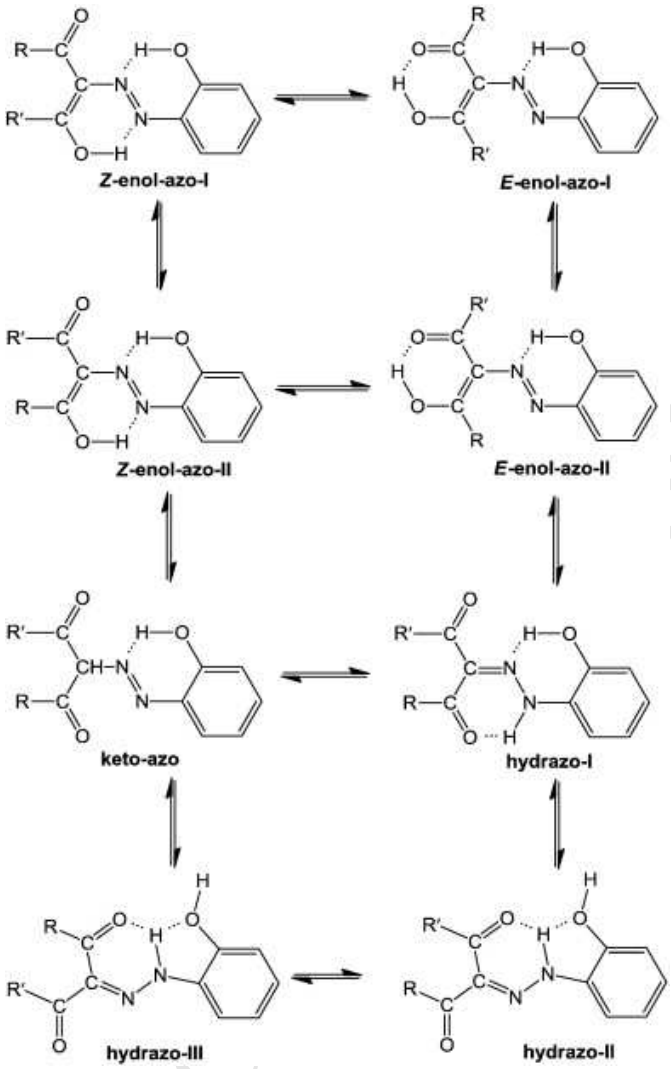
It is known [19] that 1,2,3-tricarbonyl-2-aryl-hydrazones exist in solution as an equilibrated mixture of intra-molecularly H-bonded *E/Z* isomers ($\mathbf{K}_E$ and $\mathbf{K}_Z$, Scheme 1). The for/backward isomerization proceeds through keto-enol tautomerization followed by rotation around a C–N single bond, giving a name "rotary switches". Actually this may be considered as a molecular motor consisting a stator (aromatic unit) and a rotor (β-diketone part) connected by an axle. The position of the isomerization equilibrium can be altered by catalytic amounts of acid and base, albeit the process does not proceed to full completion. The similar hydrogen bond accepting capability of the two carbonyl groups, providing insufficient impetus to drive the equilibrium to full extent in either direction, makes such design not ideal for molecular switch related applications[20]. Substantial improvement was achieved by Aprahamian and co-workers [20–22], who replaced one of the carbonyl groups (R_1CO) with a pyridyl group, a much stronger hydrogen bond acceptor. This modified rotor has led to systems having an appreciable bias in favour of the $\mathbf{K}_E$. The basic nature of the pyridyl nitrogen atom allows its hydrogen bond accepting ability to be switched off using acid input, which in turn makes the $\mathbf{K}_Z$ isomer the sole configuration upon protonation. Modifications of the stator, i.e. replacement of the 1-phenyl/1-naphthyl ring with an 8-quinolinyl one leads to a tristable switch [21,22], controlled by addition of acid, base and Zn^{2+}. A very recent application has shown that such molecular rotors can be used not only for switching, but also as a molecule with robotic arms, which deliver cargo from one part of the molecule to another [23].



Scheme 1. Sketch of possible mechanism for the acid-catalyzed tautomerization in *E/Z* switching process of 1,2,3-tricarbonyl-2-arylhydrazones ($R^1 \neq R^2$).

The title molecule **1**, belonging to a series of arylhydrazones of β-diketones, where an additional tautomeric functionality is added in the stator, is an interesting example for potential action as a rotary switch, This system has been studied by Mahmudov et al [24,25] by means of IR spectroscopy and NMR and the authors have pointed out that a tautomeric mixture between Z-enol-azo-II and hydrazo-III forms (Scheme 2) exists in methanol and dimethyl sulfoxide (DMSO) solutions. If so, compound **1** differs substantially from the rotary switches described above, which exist as a mixture of isomers of the **K**-tautomeric form, and, therefore, can be counted as a real tautomeric switching system. On the other side it is not likely that the implementation of the OH group in the stator could lead to additional tautomerism due to aromatic reasons [26] and the added group, due to its ability to form hydrogen bonding, could either facilitate the tautomeric proton transfer in the rotor as an accelerator or to hamper it like a brake. Therefore, critically analyzing the existing results and providing new experimental and theoretical data we would like in this communication to explain the effect of the additional OH group in the stator of **1** on the tautomeric properties of this system. The discussion is facilitated by using a model compound **2**, where the OH group is replaced by a methoxy group. The aim of the present paper is, based on UV-VIS measurements, a complete assignment of all ^{1}H and ^{13}C NMR resonances and NMR studies, including deuterium isotope effects on ^{13}C chemical shifts, and finally on DFT calculations, to elucidate the structure, the predominant tautomeric forms and barriers to rotation around vital bonds. This system is a powerful system

to elucidate tautomerism and factors determining preferred tautomers as well as the influence of solvent and specific solvent interactions.



Scheme 2. Sketch of the tautomeric forms of the compounds investigated by Mahmudov at al. [24]. The other substituents in the aromatic ring are omitted for simplicity. (Reprinted from Journal of Molecular Liquids, 162, K.T.Mahmudov, R.A.Rahimov, M.B.Babanly, P.Q. Hasanov, F.G.Pashaev, A.G.Gasanov, M.N.Kopylovich, A.J.L.Pombeiro, Tautomery and acid–base properties of some azoderivatives of benzoylacetone, 84-88, Copyright (2011), with permission from Elsevier).

Results and discussion

It is well-known that the azo-hydrazo tautomerism [26–28] is solvent dependent even when the proton is transferred through an intramolecular hydrogen bond [29]. Therefore the change in the absorption spectra, when the solvent is changed, is the first sign of existence of a tautomeric equilibrium. In the case of **1** the spectra are virtually the same in a number of solvents (from benzene to acetonitrile, see Figure S1), showing an absorption maximum at 420 nm. As seen from Figure 1, in diluted solutions (Figure S2) of alcohols and especially in strong proton acceptor solvents like DMSO and dimethyl formamide an additional red shifted band appears.

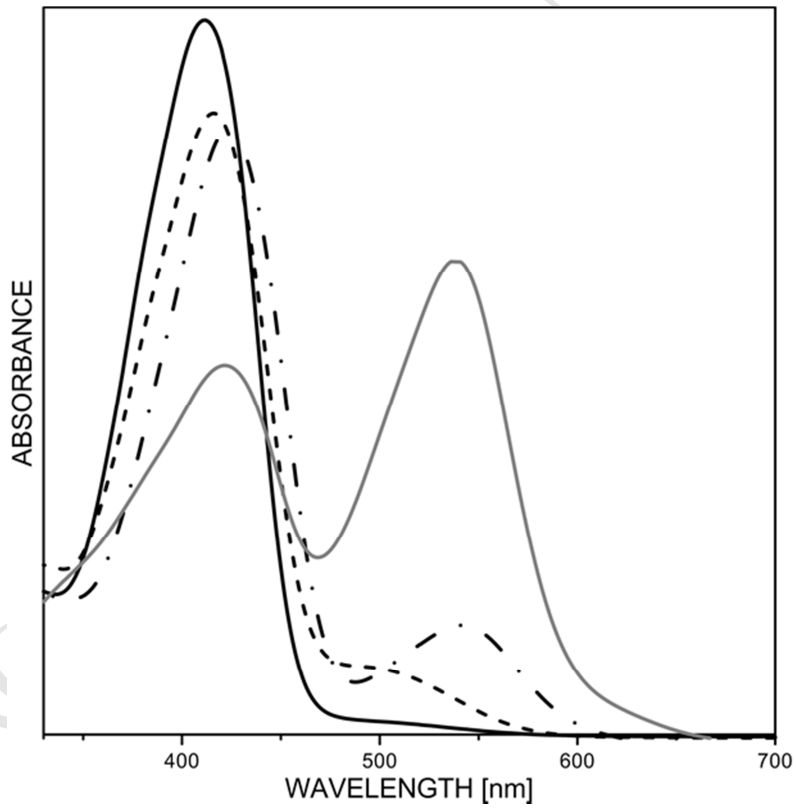


Figure 1. Absorption spectra of **1** in acetonitrile (——), ethanol (-----), DMSO (-.-.-) and DMF (——) with the same concentration.

The origin of the long-wavelength band can be explained having in mind the deprotonation of the phenols, especially such with strong electron acceptor substituents, in solution [30–32]. As seen from Figure 2 the addition of acid in DMSO leads to disappearance of the band at 540 nm, while the deprotonation with base strengthens it. The same effect is observed in ethanol (Figure S3).

The spectra of **2** are solvent and concentration independent and no additional band is seen in the solvents listed in Figure 1. The deprotonation of **2** in DMSO occurs in stronger basicity of the solution and the deprotonation band is shifted only by ~ 60 nm.

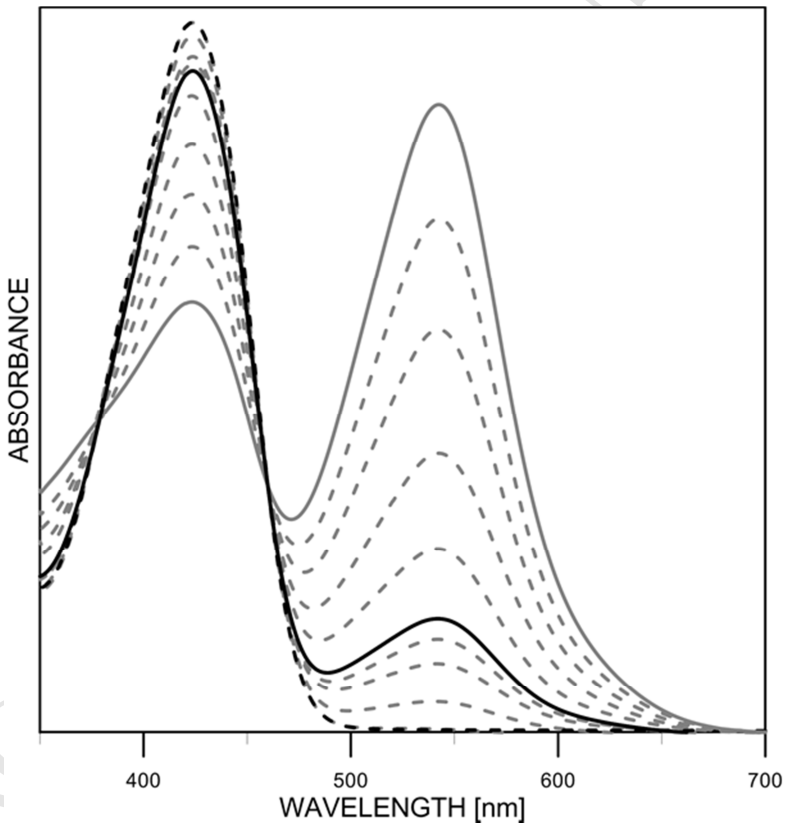


Figure 2. Absorption spectra of **1** in DMSO upon acid and base addition (—— without acid/base addition; - - - - final spectrum upon acid addition (2.16 equivalents H_2SO_4); —— final spectrum upon base addition (21.6 equivalents NaOH)).

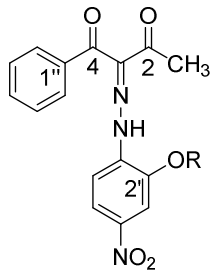
These UV-Vis spectral data show that there are no evidences for tautomeric equilibrium in **1** in the used solvents (no spectral changes upon changing solvent) and the compound most probably exists as a mixture of neutral and deprotonated form depending on the solvent and concentration.

Both compounds **1** and **2** have been investigated by NMR in a series of solvents. The most important solvent is DMSO-d_6 as this refers directly to the study of Mahmudow et al. [24], but other solvents have been also used although the compounds are not very soluble in non-polar solvents.

Yao [33] in the synthesis of the phenyl derivative found only one product and assigned this to a hydrazone with a the NH forming a hydrogen bond to the $CH_3C{=}O$ group based on the its NH chemical shift of 14.70 ppm. He made a comparison between the derivative of acetylacetone (NH chemical shift 14.68 ppm) and that of dibenzoylmethane (NH chemical shift 13.40 ppm) to make this assignment. However, from both the ^{1}H and ^{13}C NMR spectra of **1** and **2** in DMSO-d_6 (Figures S4-S8), it is obvious that two species are present in different ratios in the following called major and minor form. A comparison of data for **1** and **2** indicates very similar structures. The assignments are based on ^{1}H and ^{13}C NMR spectra, HMBC spectra (including one-bond correlations) and NOESY spectra. ^{1}H and ^{13}C chemical shift and HMBC correlations are given in Tables 1 and 2. Numbers and a few assignments have previously been given in original work of Mahmudov at al. [24]. The ^{13}C data also not based on a full assignment were given in the same paper.

The NH and phenolic OH chemical shifts for the major species in DMSO-d_6 are found at 14.14 ppm and 11.52 ppm (the assignment of NH and OH resonances are based on isotope

substitution, see below). These are for the NH resonance rather different from the minor species (11.70 ppm) and OH resonance of the minor species (11.34 ppm).



Scheme 3. Numbering of the carbon atoms in **1** (R=H) and **2** (R=CH_3).

Table 1. ^{1}H and ^{13}C chemical shifts of the major form of **1** and **2** in DMSO-d_6.

Compound	**1**	**1**	**1**	**1**	**2**	**2**
Carbons	^{1}H chemical shift	^{13}C chemical shift	One bond correlation	HMBC correlation	^{1}H chemical shift	^{13}C chemical shift
1	2.51	30.67	Obs.	C-3(s), C-2(s)	2.51	30.19
2	-	198.08				197.80
3	-	135.66				135.83
4	-	191.95				191.45
1´	-	136.25				136.48
2´	-	145.99				146.92
3´	7.70	110.60	Obs.	C-5'(s), C-4´(w), C-2´(w)	7.55	107.11
4´	-	143.78				143.44
5´	7.72	116.78	Obs.	C-3´(s), C-1´(w), C-4´(w)	7.90	118.03
6´	7.11	114.08	Obs.	C-1´(w) ,C-2´(s), C-3´(w), C-4´(w)	7.26	113.59

1”	-	137.96				137.24
2”	7.89	130.75	Obs.	C-4”(s)	7.90	130.33
3”	7.54	128.50		C-1”(s), C-3”(s)	7.55	128.11
4”	7.66	133.10		C-2”(s)	7.67	132.84
NH	14.14	-		C-6´(s),C-3(s) and C-2´(w)	14.11	-
OH	11.52	-		-	-	-

Table 2. ^{1}H and ^{13}C chemical shifts of the minor form of **1** and **2** in DMSO-d_6.

Compound	**1**	**1**	**1**	**1**	**2**	**2**
Carbons	^{1}H chemical shift	^{13}C chemical shift	One bond correlation	L.R. correlation	^{1}H chemical shift	^{13}C chemical shift
1	2.56	25.92	Obs.	C-3(s), C-2(s)	2.57	25.47
2	-	196.83				196.53
3	-	139.28				139.68
4	-	193.17				192.73
1´	-	136.51				136.86
2´	-	145.50				146.67
3´	7.70	110.49			7.87	106.94
4´	-	143.23				142.80
5´	7.81	116.83	Obs.		8.00	117.98
6´	7.75	114.25	Obs.	C-2´(s),C-4´(s)	7.84	113.59
1”	-	137.56				137.24
2”	7.71	129.08[a]			7.72	128.68[a]
3”	7.52	128.93[a]	Obs.	C-1”(s)	7.51	128.49[a]
4”	7.65	133.99		C-2” (w), C-	7.66	133.66

				3”(w)		
NH	11.70	-		C-1´(s), C-3(m), C-6´(w)		-
OH	11.34	-				-

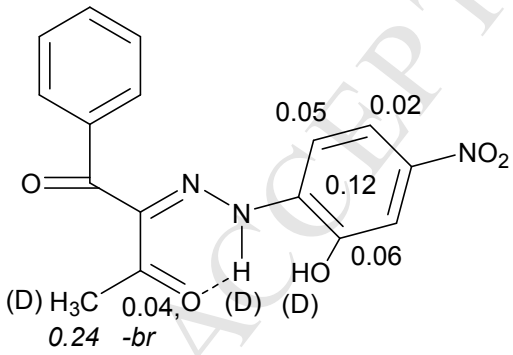
a. May be interchanged

It has been possible to isolate an almost pure form of **1** (NMR spectra in non-polar solvents, Figures S9-S10), which turned out to be the major form. In case of **2** a small amount of almost pure minor form was isolated. Dissolving **1** or the minor form of **2** in DMSO, acetonitrile-d_3 or tetrahydrofuran-d_8 and recording the NMR spectra within 10 min led to an equilibrium mixture as seen in the NMR spectra and with a higher content of the minor form than seen when dissolving the compound in a nonpolar solvent (see below). Something similar was seen with DMF-d_7 (Figure S11). However, dissolving the compounds in toluene-d_8 or $CDCl_3$ led only to a very slow conversion (days) into the equilibrium mixture.

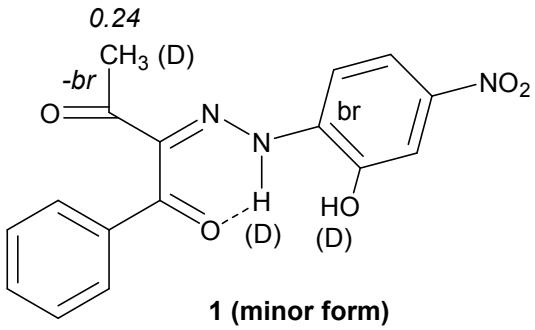
Deuteriation is one of the effective tools to study complex tautomeric systems [34]. A brief summary is given below: In case of an equilibrium, fast on the NMR time scale, only averaged NMR signals are seen. With respect to deuterium isotope effects these will be averaged too, but in case of equilibrium large effects may be seen [35]. Deuteriation is achieved by dissolving the compounds in CH_3OD and subsequent evaporation. Deuteriation was repeated with different content of deuterium to determine the signs of the isotope effects. Deuteriation of **1** and **2** will primarily take place at the OH and NH hydrogens but may also take place at the $CH_3C{=}O$ group. Deuterium substitution may lead to isotope splittings provided the exchange of the label is slow on the NMR time scale. This can usually be judged from the broadness of the XH resonance.

Isotope effects in **1** both the OH of the major and the minor form and the NH resonance of the minor form merge into two broad signals at 11.64 and 11.50 ppm upon deuteriation. The NH resonance of the major form is reduced to 33%. The remaining resonances are reduced to the same extent. The isotope effects are summarized in Scheme 4. It is seen that effects due to deuteriation of the OH group of **1** are not seen due to exchange. The observed effects are due to deuteriation at the NH groups and those effects are similar to effects observed for a derivative of acetylacetone [36] and also to a couple of fluorosubstituted derivatives [37]. The effects due to deuteriation at the methyl group is only seen at the nearby C=O carbon (see Scheme 3). The observed isotope effects are consistent with the major form. For the minor form only one isotope effect is seen as a broadening of C-1` (Schemes 3-4).

Deuteriation would happen at the enolic OH and this would lead to large deuterium isotope effects at the C=O carbons [38], if any enol-azo form (Scheme 2) was present, but this is clearly not seen. OH groups like these are less prone the exchange so this could not be the reason for not seeing such large isotope effects. The mentioned forms can be excluded from consideration.



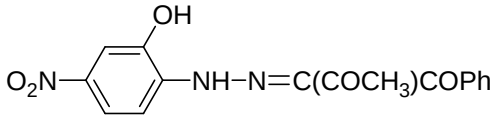
1 (major form)



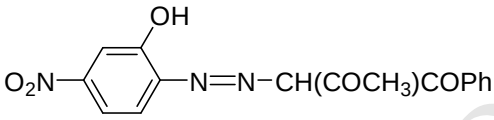
1 (minor form)

Scheme 4. Deuteriium isotope effects on ^{13}C chemical shifts. Numbers in italics are due to deuteriation at the methyl group. DMSO molecules are left out for simplicity.

The apparent contradiction between the UV-Vis data (single neutral compound) and NMR results (two neutral components) can be explained by the theoretical calculations, performed in DMSO as media. As seen from Scheme 5 the title compound could exist as seven neutral and three zwitterionic tautomers. Taking the OH group in the phenyl ring as a starting point, structures **I**-**IV** could be attributed to the enol-like tautomer, while the rest are keto-like ones. Each of them exists as a large number of possible conformers (see Scheme S1 for an example), but after the performed lengthy calculations the most stable isomer of each tautomer are presented in Table 3.



I



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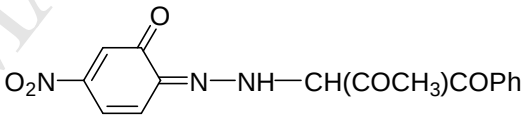

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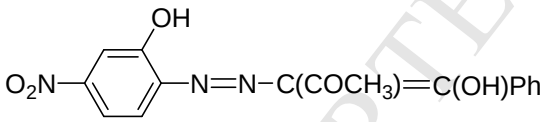
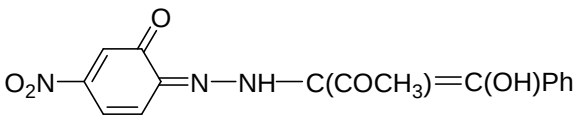
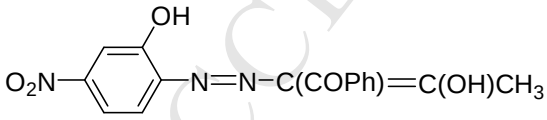


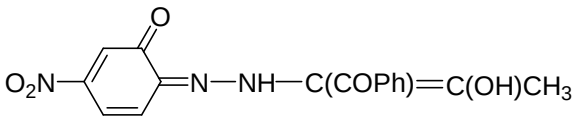
III



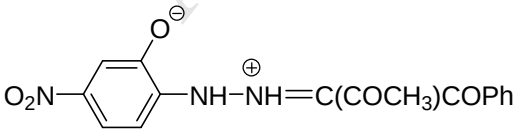
VI



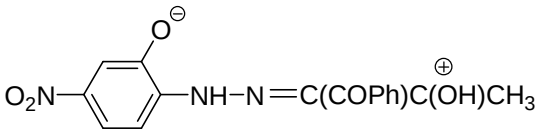
IV



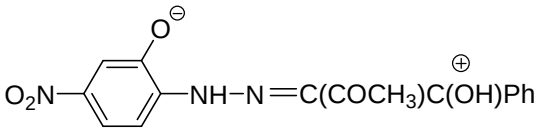
VII



VIII



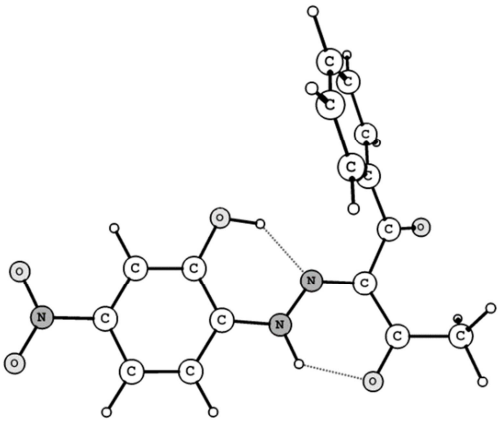
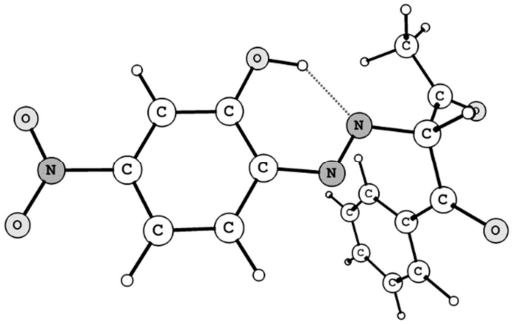
IX

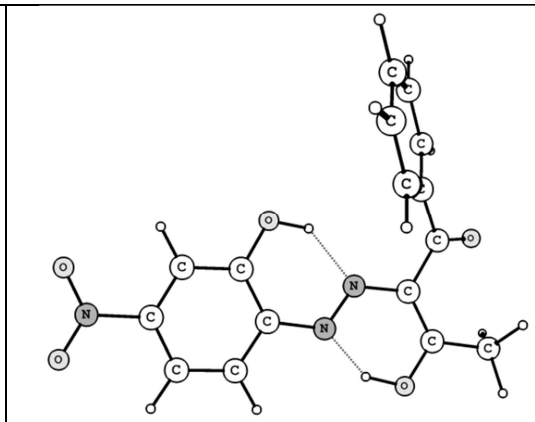
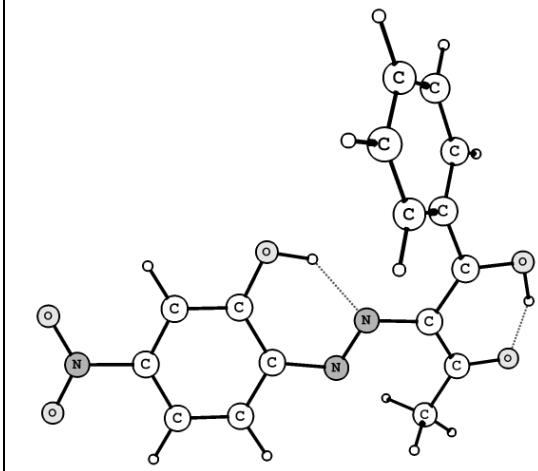
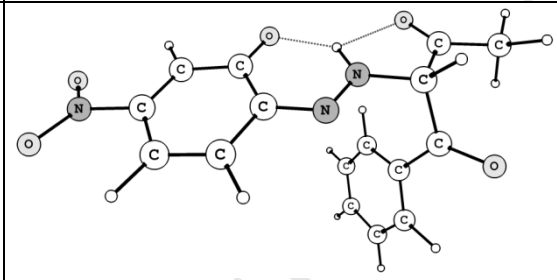
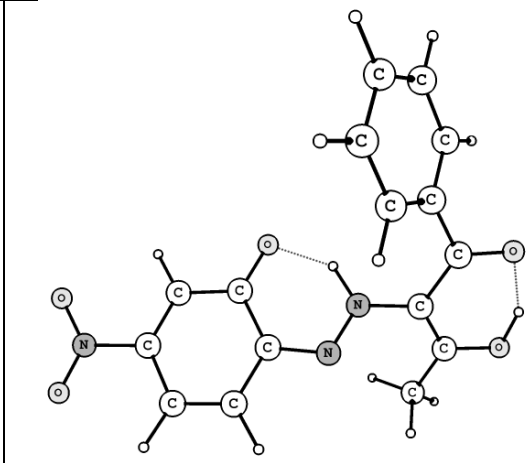


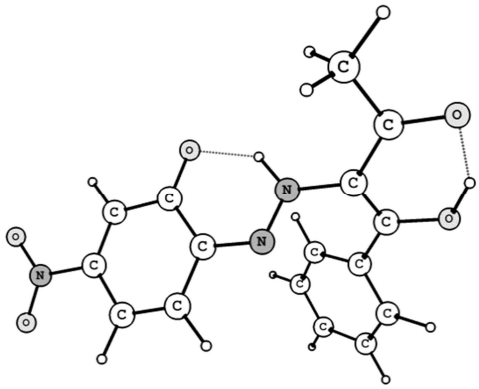
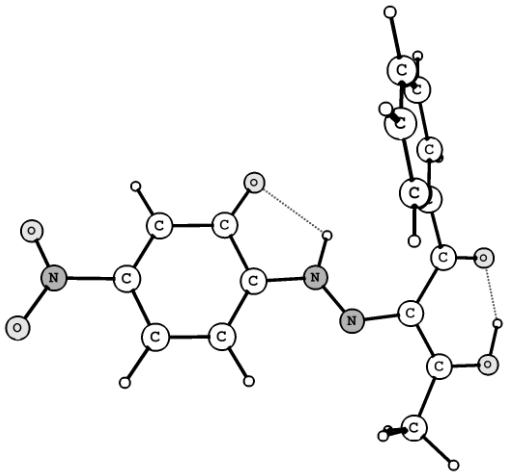
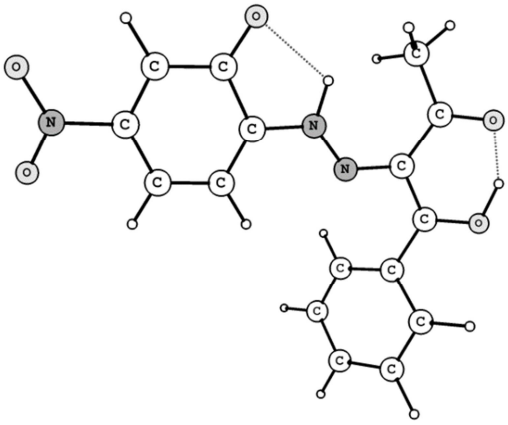
X

Scheme 5. Sketches of the possible tautomers of **1**. In **2** only tautomers **I**-**IV** are potentially possible.

Table 3. The most stable isomers of **I**-**X** of **1** in DMSO and their predicted absorption maxima (as position* and oscillator strength).

	Structure	ΔE [kcal/mol]	Dipole moment [D]	Long-wavelength absorption	
				λ_{max} [nm]	f
1(I)		0.00	6.0	357 355	0.056 0.735
1(II)		13.51	3.0	323 322	0.107 0.070

1(III)		6.32	6.0	367	0.704
1(IV)		7.42	5.4	442 354	0.012 0.590
1(V)		19.10	8.6	415 408	0.023 0.200
1(VI)		17.23	6.1	446	0.327

1(VII)		17.62	5.2	445	0.234
1(VIII)	No stable structure found				
1(IX)		23.29	13.3	531	0.444
1(X)		24.81	14.9	523	0.532

* taking into account that TD-M06-2X systematically underestimates the band positions (see the Experimental part) these values should not be considered as absolute values, but as indication of a spectral shift.

As seen from Table 3, the structures, related to transfer of the OH proton in **1** (**V**-**VII** and **IX**-**X**) are unstable, which is expected because such transfer reduces the aromatic character of the phenyl ring [26]. The tautomer **1(I)** is substantially more stable and the energy difference to the nearer as stability forms (**1(III)** and **1(IV)**) excludes their existence in measurable amounts in solution. The stability of **1(I)** could be also confirmed from the crystallographic data for structurally similar compounds, which show that in solid state the hydrazone tautomer only exists stabilized through H3CC=O…HN intramolecular hydrogen bonding [39]. All these three, most stable according to the calculations structures, have similar dipole moment and are stabilized by intramolecular hydrogen bonding which means that the change of the solvent in the solvent model could not change the relative stability. Even if there are specific interactions with the solvent, which the solvation model does not take into account, structures **1(I)**, **1(III)** and **1(IV)**, as given in Table 3, could be inert to proton acceptor solvents and with similar possibility to interact with proton-donor solvents. Therefore, assuming that the order of relative stability is the same in the used solvents and in DMSO one should look not for tautomers, but for isomers from the group of **1(I)**. According to the data shown in Scheme S1 (summarized in Figure S12) there are four isomers with relative energy, which suppose that they are presented in solution. As seen **1(Ib)** should be dominating (~75%) with substantial contribution of **1(Id)** (~20%), followed by minor amounts of **1(Ic)** and **1(Ia)**. A careful consideration allows grouping these structures based on their ability to interact with DMSO. On one side in **1(Ia)** and **1(Ib)** the OH proton is involved in a intramolecular hydrogen bonding, which makes it not accessible for interaction with the solvent. On the other side in the couple **1(Ic)**/**1(Id)** the proton can interact with DMSO, which could lead to further stabilization. The actual effect of taking the specific solute-solvent interactions into account by adding a DMSO

molecule in the DMSO solvent field is shown in Figure 3. As a result the **Id** conformer is strongly stabilized, followed by **Ic** (10-15%). The remaining two could not be presented in a DMSO solution. From the view point of UV-Vis spectroscopy the structures **Id** and **Ic** could hardly be distinguished – the conjugated system is the same and, correspondingly, their spectra should be very similar (see Table S1 with the predicted absorption in DMSO), which is the reason to see a single spectral envelop and no measurable changes after dissolution in non-polar solvents, as observed by NMR. The calculations for **2** confirm the conclusions. On one side tautomers **2(V**-**X)** are impossible, on the other – the structures, which rely to stabilization through phenolic OH intramolecular hydrogen bonding, are strongly destabilized. As a result – the isomer types **2(Id)** and **2(Ic)** are the most stable structures (the second higher in energy by 1.08 kcal/mole in DMSO).

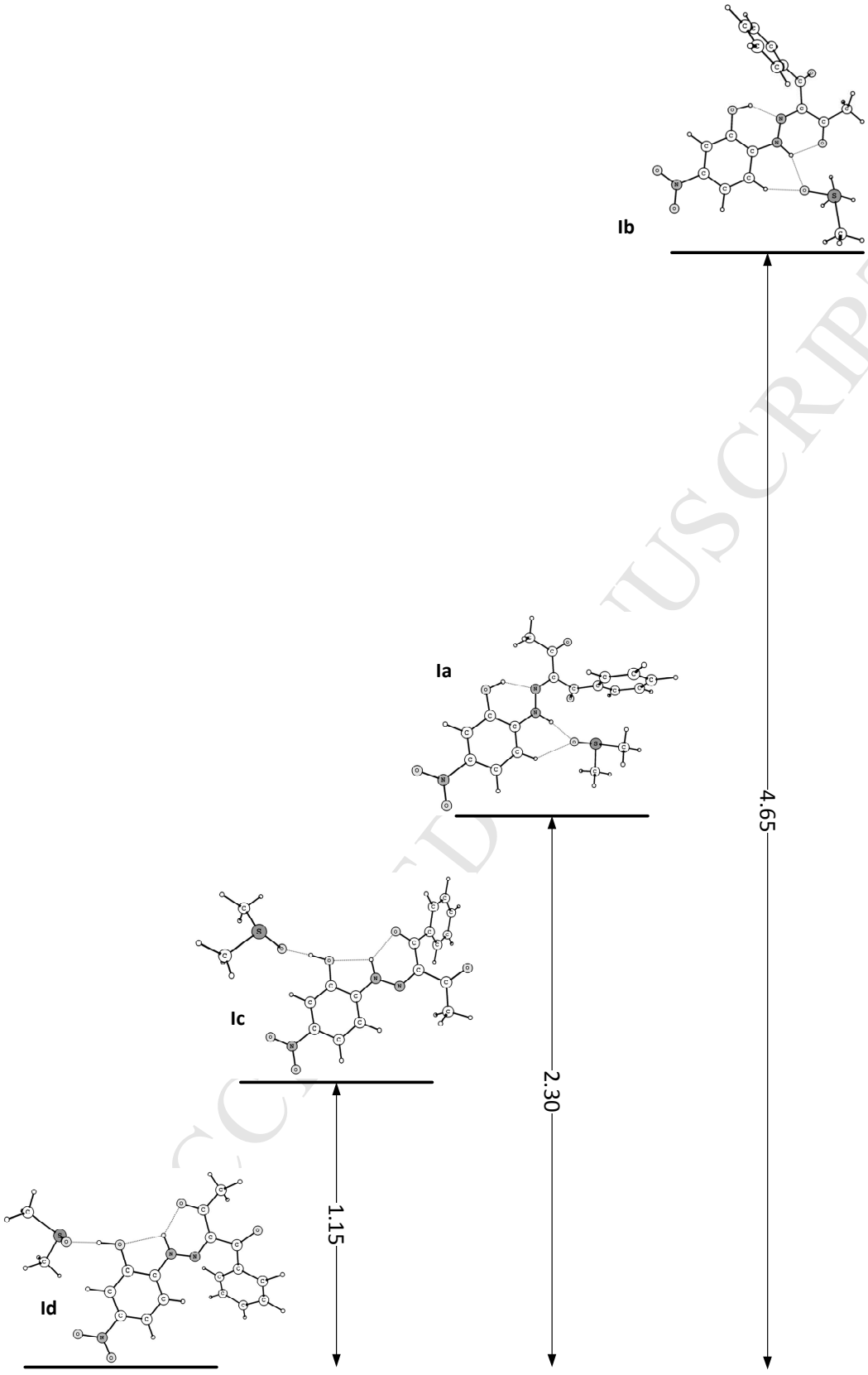


Figure 3. Relative energies (in kcal/mole units) of the most stable isomers of **I** in DMSO taking specific interactions into account. The positions of the double bonds can be seen in Scheme S1.

The interpretation of the NMR data supports the results from the calculations. The structures **IV** and the structurally similar isomer of **III** (**IIIa**-**IIIb**, see Scheme S2) are not possible as no high frequency resonance (~ 15 ppm) is observed or large isotope effects (see previously). The observation of a NH to C=N cross-peaks in the HMBC do not suggest existence of **III** and the structurally similar isomers of **IV** (**IVc**, Scheme S2). Tautomer **II** is not observed as CH resonance around 5 ppm is missing.

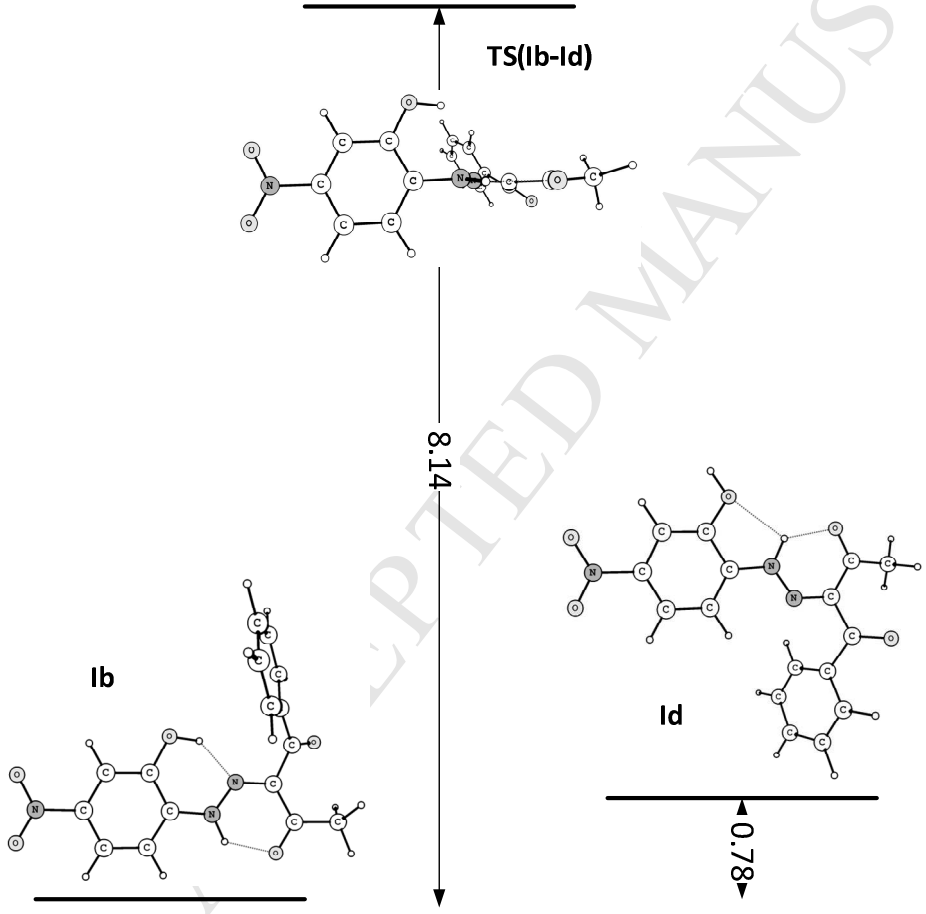


Figure 4. Schematic diagram for transition from **Ib** to **Id** and back in DMSO (the values are in kcal/mol). The positions of the double bonds can be seen in Scheme S1.

The structures of the major form of **1** in polar solvents are clearly very similar as judged from the NH and OH chemical shifts (Table 4). In the non-polar solvents, $CDCl_3$ and toluene-d_8 the OH chemical shift (Table 4) indicates either no hydrogen bonding in line with a structure in which the C=O groups points away from the aromatic ring marked `. This is supported by the H-6`chemical shift (see previously) (Table 4). For the minor form the situation is much the same (Table 4).

Table 4. NH, OH, methyl and H-6´ chemical shifts for **1** and **2**.

Compound	NH	OH	CH_3	H-6`	Solvent
1 (major form)	14.76	8.42	2.66	7.13	$CDCl_3$
1 (minor form)	12.42	7.00	2.59	~7.84	
1 (major form)	14.14	11.52	2.50	7.20	DMSO-d_6
1 (minor form)	11.70	11.34	2.56	7.75	
1 (major form)	14.31	11.94	2.58	7.38	DMF-d_7
1 (minor form)	11.94	11.94	2.57	~7.8	
1 (major form)	14.31	6.97		6.47	Toluene-d_8
1 (minor form)	12.30	n.o.	n.o.	n.o.	
1 (major form)	14.26	10.58	2.56	7.23	Acetonitrile-d_3
1 (minor form)	11.93	10.58	2.59	n.o.	
2 (major form)	14.40	-	2.63	7.40	$CDCl_3$
2 (minor form)	12.14	-	2.625	7.78	
2 (major form)	14.11	-	2.57	7.27	DMSO-d_6
2 (minor form)	11.58	-	2.57	7.86	
2 (major form)	14.40	-	2.55	7.30	Acetonitrile-d_3
2 (minor form)	11.75	-	2.58	n.o.	
2 (major form)	14.32	-	2.54	7.40	Tetrahydrofuran-d_8
2 (minor form)	11.85	-	2.56	7.85	

The following structures are possible, namely **Ia**-**Id** in **1** and **Ic**-**Id** in **2**. A major difference between the major and the minor species is the chemical shift of H-6´. A small difference is also seen for H-2". In the HMBC spectrum no cross peaks are seen from the OH resonance neither in the major or the minor form. The carbonyl resonances next to the methyl groups were

unambiguously assigned by deuterium isotope effects caused by partial deuteriation of the methyl groups, but also by a HMBC correlation from the CH_3 to CO in the major form.

The very low chemical shift of H-6´$_{ma}$ can only be due to ring current effects. These must come from the ´-ring (Scheme 3) and can only occur in structure **Id** (see Fig. 3). From the NOESY spectrum cross peaks from NH_{ma} are seen to H-6´, H-2"and H-3´ and/or H-5´. The OH_{ma} resonance shows a cross peak to H-3´ or H-5´ and as H-5´ is far away this is probably to H-3´ indicating that the OH_{ma} group is pointing towards H-3´ (see structure **Id**). It is obvious from the NOESY spectrum that both the NH_{ma} and the OH_{ma} hydrogens exchange with water. Furthermore, the water signal shows a weak cross peak to H-3´ suggesting that the water is hydrogen bonded to the DMSO molecule, which is hydrogen bonded to OH_{ma}.

As the major compound is assigned to **Id**, the minor compound could be found by exclusion. On one side, **Id** and **Ib** are rotamers and the barrier to rotation around the single C-N bond is low. As seen from Figure 4 the barrier of rotation in **1** is 8.14 kcal/mol without to account the specific interaction with the solvent. If it is accounted, the energy of **Ib** will rise (see Figure 3) and the transition state, where the OH proton can interact with DMSO molecule, would be stabilized, which will even more decrease the rotation barrier. For this reason **Id** and **Ib** would not show too different sets of signals. The question is therefore which of the form **Ia** or **Ic** corresponds to the minor form. The spatial closeness of the CH_3 protons and the NH proton would suggest that a cross peak could be observed in the NOESY spectrum. No cross peak is observed and therefore the most likely structure for the minor form is **Ic** in DMSO-d_6. The barrier of transition from **Id** to **Ic**, as shown in Figure 5, is sufficient to measure separate signals. Actually the interpretation for coexistence of **Id** as major component and **Ic** as minor one fully corresponds to the theoretical predictions summarized in Figure 3 and the

crystallographic data [39] in similar compounds. Of course a very straightway support of this conclusion comes from similarity of the NMR signals of the major and minor from of **1** and **2**. In **2** forms **Ia** and **Ib** do not exist, consequently **Ic** and **Id** are the only forms available. As a side results it could be claimed that theoretical calculations predict correctly the real situation in solution.

The combined assignment of existing forms in solution could answer the question of the effect of the additional OH group in the stator of the potential rotary switch **1**. Obviously, at least in DMSO, the OH group as presented in **1(Id)** and **1(Ic)** does not interact with the rotor and consequently cannot play a direct role in the rotation process. It could be expected to act as an electron acceptor substituent, influencing together with the nitro group the neighboring hydrazone nitrogen atom from the axle. However, the effect of the OH group by itself is not large taking into account that in the case of a compound without it [40] again the **Id**-like and **Ic**-like (as interaction of the MeC=O/PhC=O groups with NH from the axle) isomers are presented in solution in proportion 85%/15%, as shown by NMR, which is very similar to the predicted by the theoretical calculations above.

Here is the moment to comment the findings of Mahmudov *et al.* that the title compound exists in DMSO as a mixture of 22% Z-enol-azo-II and 78% hydrazo-III forms [24]. Comparing Scheme 2 (R'=Ph and R=CH_3) and Table 1, Z-enol-azo-II corresponds to **1(III)**, while hydrazo-III is **1(Id)**. The minor component cannot be **1(III)**, because it is unstable to exist in solution according to the theoretical calculations from Table 1 and the NMR results. Even if we assume that it is available, the barrier of proton transfer between **1(III)** and **1(Ib)** is less than 1 kcal/mol, which means that they cannot be separated on the NMR scale. As already discussed

above **1(Id)** and **1(Ib)** also cannot have separate signals. Obviously a misinterpretation of the NMR data in the original paper leads to incorrect conclusions.

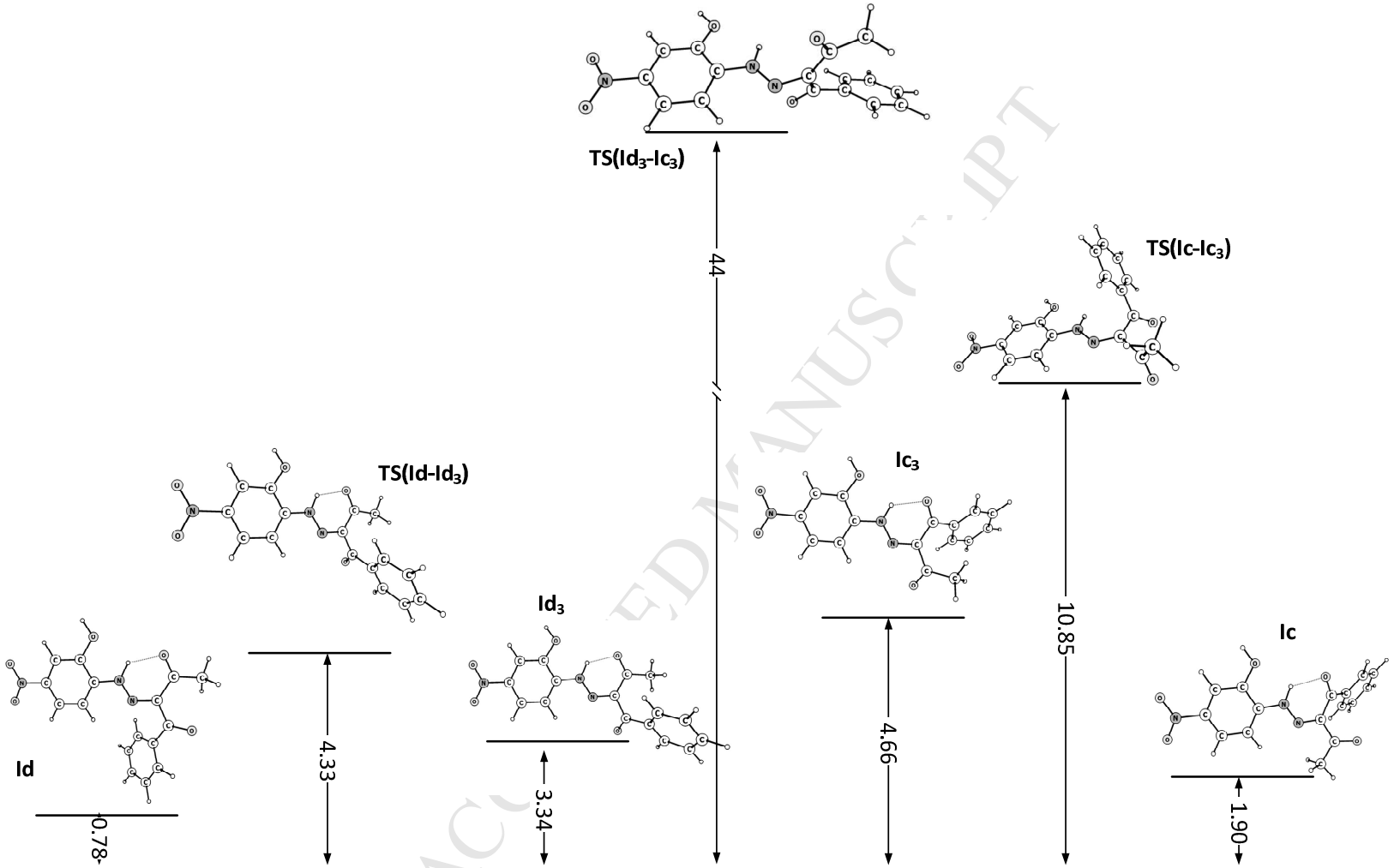


Figure 5. Schematic diagram for transition from **Id** to **Ic** and back in **1** in DMSO (the values are in kcal/mol). The positions of the double bonds can be seen in Scheme S1. The energetics in **2** is virtually the same.

Two additional factors influence the specific processes in **1** in solution, namely the concentration and the water content. The spontaneous deprotonation shown in Figures 1 and S1 is concentration dependent. The increase of the concentration leads to disappearing of the deprotonated form, which happens at relatively low concentrations. For instance, in DMSO at ~5. 10^{-4} mol/l only neutral form is observed (see Figure S2). This behaviour suggests that in the NMR concentration scale no deprotonated form exists. The increase of the temperature causes a slight rise of the band at 540 nm and correspondingly decreases the intensity of the neutral form band (Figure S13). Most probably **1(Id)** and **1(Ic)** aggregate in solution and with dilution the monomers are deprotonated by the solvent. The OH deprotonated forms exist in the same ratio (**1(Id$^-$)** is more stable with 1.2 kcal/mol comparing to **1(Ic$^-$)**), their spectra are very similar (Table S1) and again cannot be distinguished by UV-Vis spectroscopy. It could be expected that the OH proton, not involved in an intramolecular hydrogen bonding, is responsible for the aggregation behaviour. On Figure 6 the border cases of the possible dimers of **1(Id)** are shown. Although the sandwich dimer is shown to be almost 8 kcal/mol more stable by the calculations, this value should be considered with care, because no basis set superposition error correction is taken into account. The more important fact is that in both cases OH…O=CPh is the preferred interaction, which defends the OH group from deprotonation.

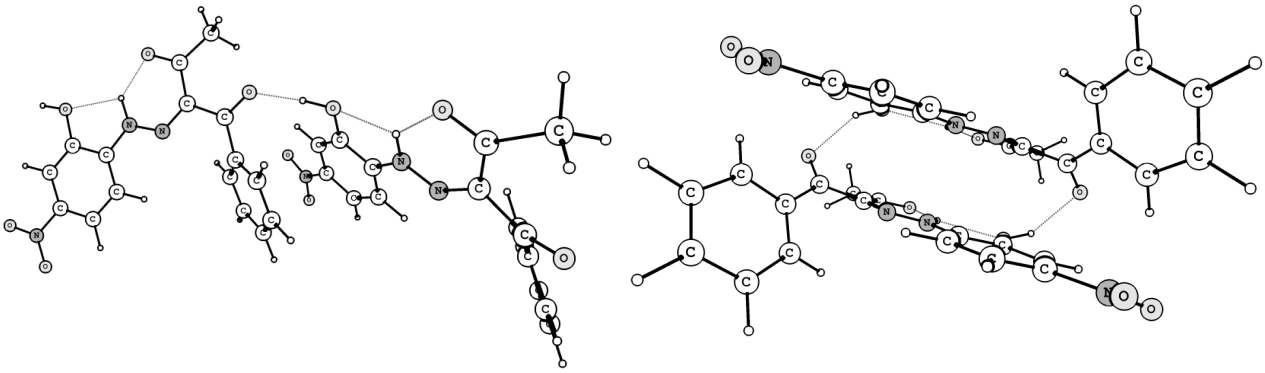


Figure 6. Theoretically predicted border cases of dimers of **1**: linear (left) and sandwich (right).

The water content is another important factor influencing the absorption spectra. The effect is well illustrated on Figure 7. It is clear that the addition of water leads to disappearance of the deprotonated specie(s). According to the calculations the DMSO molecule forms more stable complexes with the **1(Id)**/**1(Ic)** compared to the water molecule (stabilization energy 13 kcal/mol against 9 kcal/mol, the complexes are shown in Figure S14). According to the NMR data, discussed above, the water molecules do not interact with the dye directly, but through the DMSO molecule. This behaviour is logical taking into account Kamlet-Taft solvatochromic parameters of both solvents [41] (π^*=1.00, α=0, β=0.76 for DMSO; π^*=1.09, α=1.17, β=0.4 for water). DMSO is stronger proton acceptor solvent (β term), which could form more stable solute solvent complex and deprotonate the OH group easier (see Figure S15). In turn the water molecule being proton donor returns the deprotonated dye in its neutral state.

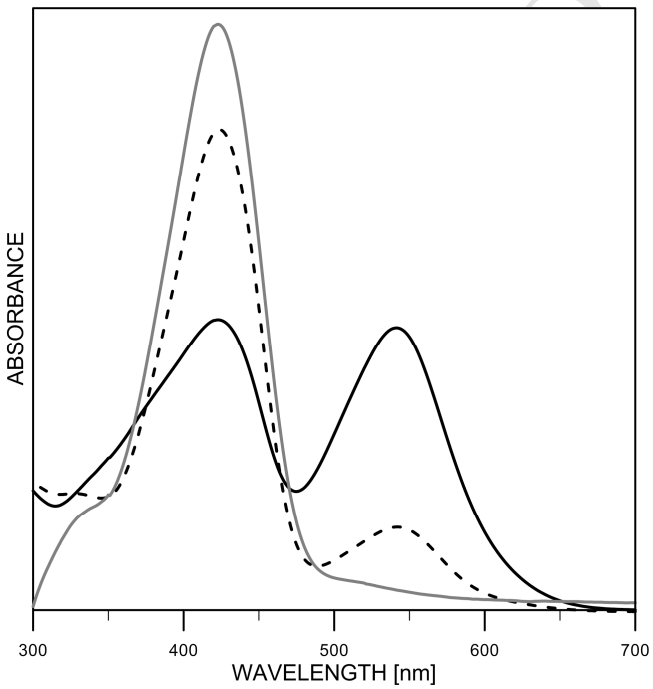


Figure 7. Absorption spectra of **1** in: dry DMSO (solid black line), DMSO as purchased (dashes), DMSO with further addition of water (20% water to the commercial DMSO, solid gray line).

Conclusions

2-(2-(2-Hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione can be potentially presented in several tautomeric forms. However, the spectral investigations in DMSO and other solvents and the quantum chemical calculations strongly indicate that the dye exists as a mixture of two isomers of a single tautomer. As a result of detailed assignment of the NMR signals it was shown that the previous interpretation made by Mahmudov *et al.* is not correct. The OH group, implemented in the phenyl ring, is not tautomeric for aromaticity reasons.

Having in mind that the title compound is a potential rotary switch it could be expected that the additional OH group could influence the process of rotation or could stabilize one of the conformers. Instead, it forms hydrogen bonds with the solvent leading to deprotonation in diluted solutions.

Experimental part

Synthesis:

Reagents and solvents were purchased from Sigma-Aldrich, Acros and Alfa-Aesar, and used without further purification. Fluka silica gel /TLC-cards 60778 with fluorescence indicator 254 nm were used for TLC chromatography. Merck silica gel 60 (0.040-0.063 mm) and basic alumina (Brockmann activity, 0.05-0.15 mm) were used for flash chromatography purification of the products. Melting points were determined on a Gallenkamp apparatus and are uncorrected. HRMS LC/MS was carried out on a Bruker MicrOTOF-QII-system with ESI-source

with nebulizer 1.2 bar, dry gas 8.0 l/min, dry temperature 200 ^{o}C, capillary 4500 V, end plate offset -500 V. The title 2-(2-(2-Hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione **1** and 2-(2(2-Methoxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,2,3-trione **2** were synthesized as follows.

*2-(2(2-Hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,2,3-trione **1***:

A solution of 2-amino-5-nitrophenol (3.85 g, 25 mmol), NaOH (1.0 g, 25 mmol) in distilled water (50 mL) was stirred at 0^{o}C for 15 min, sodium nitrite (1.73 g) was added and left stirring at 0^{o}C for 20 min. To this mixture was added slowly (1h) conc. HCl (5.0 mL) at 0-5^{o}C, and the mixture left stirring at 0-5 ^{o}C for 20 min. The diazonium solution was slowly added to a stirred mixture of sodium acetate (8.0 g) and 1-phenylbutane-1,3-dione (4.06 g, 25 mmol) in ethanol (100 mL) at 0^{o}C. After complete addition, the mixture left stirred for 2h at 0 ^{0}C and left stand in cold overnight. The light brown precipitate was filtered, washed with water. The moist residue was suspended in water (500 mL) and stirred at 40 ^{o}C for 1h, filtered and the residue dried in vacuum at room temperature. The residue was purified by flash column chromatography on silica gel with dichloromethane/ethyl acetate (20:1) to obtain **1** (4.8 g, 58%) as a yellow solid, m.p.201-203 ^{o}C. HRMS (ESI) *m/z* calcd. for $C_{16}H_{12}N_3O_5$ ($M\text{-}H^+$) 326.0772, found 326.0805.

2-(2(2-Methoxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,2,3-trione **2**:

A solution of 2-methoxy-4-nitroaniline (1.68 g, 0.01 mole) in concentrated HCl (6.0 mL) was stirred for 15 minutes at rt. And then diluted with distilled water (6.0 mL). The mixture was cooled to 0 ^{0}C. Sodium nitrite (0.70 g, 0.01 mole) was gradually added and the mixture left

stirred at 0 ^{0}C for 20 min. The diazonium solution was slowly added to a stirred mixture of sodium acetate (6.0 g) and 1-phenylbutane-1,3-dione (1.62 g, 0.01 mole) in ethanol (50 mL) at 0 ^{0}C. After complete addition, the mixture left stirred for 2h at 0 ^{0}C and 4h at rt. The massive yellow precipitate was filtered off and washed with water, and recrystallization from absolute ethanol to give **2** (2.93 g, 86%) as a light yellow needles, m.p. 175-176 ^{o}C. HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}N_3O_5$ ($M+H^+$) 342.1085, found 342.1093.

Deuteriation was achieved by dissolving the compound in CH_3OD with subsequent evaporation of the methanol.

Spectral measurements:

Spectral measurements were performed on Jasco V-570 UV-Vis-NIR spectrophotometer, equipped with a thermostatic cell holder (using Huber MPC-K6 thermostat with precision 1^{o}C), in spectral grade solvents at ambient temperature. The sample was protonated/deprotonated by addition of H_2SO_4/NaOH correspondingly.

The NMR spectra were recorded at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C at a Bruker 400 Avance III NMR spectrometer. TMS or the solvent signal was used as reference. NOE and HMBC spectra are recorded using standard pulse programs and conditions.

Quantum-chemical calculations:

Quantum-chemical calculations were performed by using the Gaussian 09 program suite [42] using M06-2X fitted hybrid meta-GGA functional [43,44] with TZVP basis set [45]. It is worth mentioning that this method has been recently demonstrated as very suitable for

describing tautomeric behavior in azonaphthols and related Schiff bases [46] as well as for prediction of the absorption spectra of organic dyes [47–49]. However, it is worth to note that TD-M06-2X systematically underestimates the band positions [47,48], which has to be taken into account when the values in Tables 3 and S1 are considered.

The tautomeric forms of **1**, their dimers and solvent complexes were optimized without restrictions in DMSO solvent medium under normal optimization conditions by using ultrafine grid in the computation of the two-electron integrals and their derivatives. The optimized structures were then characterized as true minima by vibrational frequency calculations. In all cases the solvent medium was described by using the PCM model, namely IEFPCM[50], as implemented in Gaussian 09. No basis set superposition error was taken into account in the PCM calculations.

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Highlights:

- The title compound exists as a single tautomer in various solvents.
- Two isomers are in equilibrium as shown by NMR, UV-Vis spectroscopy and theoretical calculations.
- Previous assignment of the tautomerism of the title compound, made by Mahmudov at al., is not correct.