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RESEARCH ARTICLE

Structure of 2-nitro-2’-hydroxy-5’-methylazobenzene: Theoretical and spectroscopic study

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Abstract

Objectives. *2-Hydroxy-nitroazobenzenes comprise reagents for the synthesis of heteroaromatic compounds, in the molecules of which the benzene and azole cycles are annulated. These reagents are widely used in the production of chemical products for various industries. In particular, 2-2’-hydroxy-5’-methylphenylbenzotriazole is used as an effective photo stabilizer for polystyrene and polyethylene. A promising method for its preparation is the liquid-phase catalytic hydrogenation of 2-nitro-2'-hydroxy-5'-methylazobenzene (2NAB). The aim of the present study was to establish the structure of 2NAB in solutions of different composition.*

Methods. *Theoretical calculations were carried out within the framework of the density functional theory at a temperature of 298.15 K for the gas phase at B3LYP/6-311++G(d, p) and M06-2X/6-311++G(d, p) levels; for hexane, 2-propanol, toluene at B3LYP/6-311++G(d, p) level using the conductor-like polarizable continuum model. An experimental study to determine the probable isomeric structure of 2NAB in various solvents, including sodium hydroxide (NaOH) and acetic acid (CH_3COOH) additives, was carried out using infrared (IR) and ultraviolet (UV) spectroscopy.*

Results. *The most probable structure of 2NAB isomers for the gas phase and a number of solvents was determined. Experimental and theoretical IR and UV spectra were obtained. The thermodynamic characteristics of the reaction of intramolecular proton transfer from –OH to –N=N– group in the gas phase were calculated.*

Conclusions. *A comparison of the experimental and calculated results supports the conclusion that the cis-isomer should be considered most probable for the gas phase. For the studied solutions, a trans-isomer of 2NAB with hydrogen bonds formed between the hydroxyl group hydrogen and the β-nitrogen atom of the azo group of dye molecule should be considered as the most likely structure. In the studied individual and binary solvents, prototropic equilibrium is shifted towards the azo form of the dye, while intramolecular proton transfer is possible only in aqueous diethylamine and dimethylformamide solutions with additions of NaOH.*

Keywords: *2-nitro-2'-hydroxy-5'-methylazobenzene, intramolecular proton transfer, hydrogen bond, IR spectroscopy, UV spectroscopy, quantum chemical calculations*

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НАУЧНАЯ СТАТЬЯ

Структура молекулы 2-нитро-2’-гидрокси-5’-метилазобензола: Теоретическое и спектральное исследование

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Аннотация

Цели. *2-Гидроксинитроазобензолы – реагенты синтеза гетероароматических соединений, в молекулах которых аннелированы бензольный и азольный циклы, широко использующиеся при производстве химических продуктов для различных областей промышленности. В частности, 2-2’-гидрокси-5’-метилфенилбензотриазол используется в качестве эффективного фотостабилизатора полистирола и полиэтилена. Перспективным методом его получения является жидкофазная каталитическая гидрогенизация 2-нитро-2’-гидрокси-5’-метилазобензола (2НАБ). Целью нашей работы стало установление структуры 2НАБ в растворах различного состава.*

Методы. *Теоретические расчеты проводились в рамках теории функционала плотности при температуре 298.15 K для газовой фазы на уровнях B3LYP/6-311++G(d, p) и M06-2X/6-311++G(d, p), для гексана, 2-пропанола, толуола на уровне B3LYP/6-311++G(d, p) с использованием континуальной модели сольватации. Экспериментальное изучение предполагаемого изомерного строения 2НАБ в различных растворителях, в том числе с добавками гидроксида натрия (NaOH) и уксусной кислоты (CH_3COOH), проведено с помощью инфракрасной (ИК) и ультрафиолетовой (УФ) спектроскопии.*

Результаты. *Определена наиболее вероятная структура изомеров 2НАБ для газовой фазы и ряда растворителей. Получены экспериментальные и теоретические ИК-, УФ-спектры исследуемых веществ. Рассчитаны термодинамические характеристики реакции внутримолекулярного переноса протона от –ОН к –N=N– группе в газовой фазе.*

Выводы. *Сравнение экспериментальных и расчетных результатов позволило сделать заключение, что наиболее вероятным для газовой фазы следует считать цис-изомер, а для изученных растворов транс-изомер 2НАБ с водородными связями, образующимися между водородом гидроксигруппы и β-атомом азота азогруппы. В изученных индивидуальных и бинарных растворителях прототропное равновесие смещено в сторону азоформы красителя, а внутримолекулярный перенос протона возможен только в водных растворах диэтиламина и диметилформамила с добавками NaOH.*

Ключевые слова: *2-нитро-2'-гидрокси-5'-метилазобензол, внутримолекулярный перенос протона, водородная связь, ИК-спектроскопия, УФ-спектроскопия, квантово-химические расчеты*

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INTRODUCTION

Nowadays, substituted nitrobenzenes are among the most widely-used multi-purpose compounds. Among this class of substances, 2-hydroxynitroazobenzenes occupy a special position, since forming the initial products for the synthesis of heteroaromatic compounds, in whose molecules the benzene and azole rings are annulated. Substituted 2*H*-benzotriazoles are used as effective absorbers of ultraviolet (UV) light, light stabilizers of polymers, and analytical reagents for a number of cations. As such, they are used as additives to increase the light resistance of dyes, pigments, and enamels, for obtaining complex compounds with metals, and in other areas [1–8].

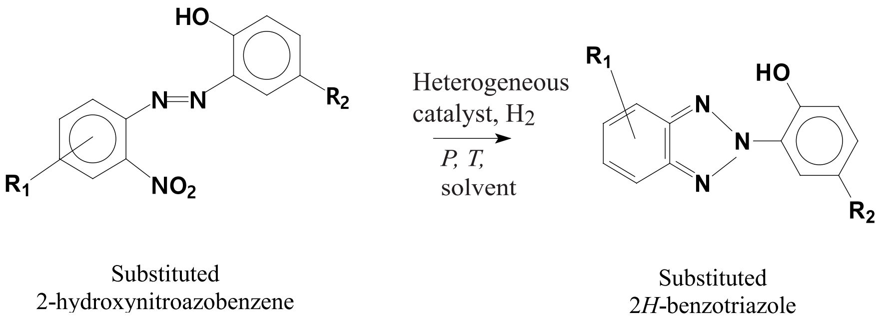
The main method for the preparation of substituted benzotriazoles remains the chemical reduction of the corresponding 2-hydroxynitroazobenzenes with zinc or hydrazine hydrate in an alkaline water–alcohol medium, or with dithionite in aqueous alkaline solutions [9, 10].

For the preparation of 2*H*-benzotriazoles, a promising method is liquid-phase hydrogenation of the corresponding 2-hydroxynitroazobenzenes. The latter contain nitro and azo groups that actively interact with hydrogen under hydrogenation conditions to form a triazole cycle (Scheme 1).

The selectivity of reductive cyclization under hydrogenation conditions is largely determined by the structure of the starting compound [11, 12]. In this regard, there is a need to have the most complete possible information about the electronic and spatial structure of 2-hydroxynitroazobenzenes, which subsequently determine the whole variety of chemical transformations.

In the present work, 2-nitro-2'-hydroxy-5'-methylazobenzene (2NAB) was chosen as the object of study. Comprising the starting compound for the synthesis of an effective photostabilizer of polystyrene and polyethylene, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (BT, Tinuvin®), it does not have any identified carcinogenic properties. Therefore, BT-stabilized films, in addition to other applications, can be used for food packaging.

It is known that azo dyes can exist in various tautomeric forms. For the 2NAB molecule, due



Scheme 1. Method for the preparation of substituted *2H*-besotriazoles.

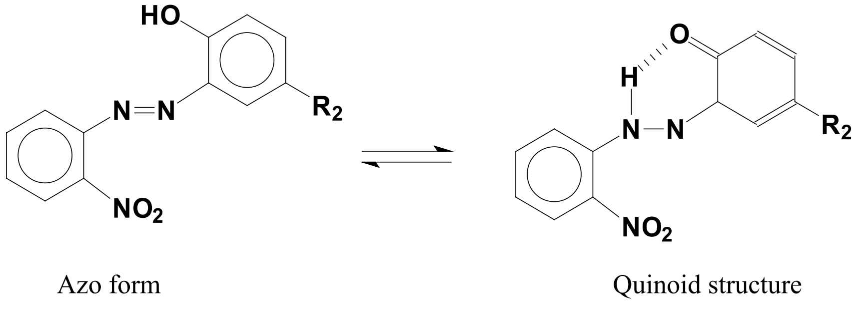
to the presence of a proton-donor hydroxyl group and its close spatial arrangement to the azo group, the possibility of intramolecular proton transfer (that is, prototropic equilibrium) can be assumed (Scheme 2).

Therefore, when considering the structure of 2NAB, it is necessary to take into account the possibility of the formation and presence of quinoid structures in the reaction mixture, as well as to calculate the thermodynamic characteristics of a possible process of intramolecular proton transfer.

MATERIALS AND METHODS

The calculations based on density functional theory for a gas phase at a temperature of 298.15 K were carried out using the Gaussian03 software package (*Gaussian Inc.*, USA) [13]. The Becke–Lee–Yang–Parr (B3LYP) density functional was primarily used. The 6-311++G(d, p)[1] basis set, having proven itself well in calculations of complex organic compounds, was selected. A number of calculations were carried out using the M06-2X[2] functional (high-nonlocality functional with double the amount of nonlocal exchange (2X)) and the conductor-like polarizable continuum model (cpcm). The ChemCraft[3] software (Russia) was used to visualize the calculation results and prepare initial approximations for subsequent geometry optimization.

In order to search for probable conformers for the 2NAB molecule, we scanned the C–C–N=N rotation angle of the nitrobenzene ring with respect to the –C–N= bond in the 2NAB molecule with a step of 10° at the B3LYP/6-311++G(d, p) level. Examples of scan results are shown in Fig. 1. Next, the rotation angles of the functional groups relative to the benzene rings were scanned at steps of 10° for the established configurations of conformers with different mutual positions of the $–NO_2$ and –OH groups (*cis*- and *trans*-). No new conformers were found.



Scheme 2. Eautomerism for the 2-nitro-2’-hydroxy-5’-methylazobenzene molecule.

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[1] 6-311++G(d, p) is a triple valence-split basis with diffuse functions on heavy atoms and hydrogen atoms and with the addition of d-type polarization functions for each atom from Li to Ca and p-type polarization functions for each light atom (H, He).

[2] The M06-2X functional, a hybrid meta-functional including 54% of the Hartree–Fock exchange, is one of the most accurate empirical functionals for working on mismatched electron density.

[3] Zhurko G.A. Chemcraft – graphical program for visualization of quantum chemistry computations. Ivanovo, Russia, 2005. Version 1.8, build 654. https://www.chemcraftprog.com. Accessed August 08, 2023.

Further, the structures corresponding to configurations with the lowest energies were completely optimized, the bond vibration frequencies were calculated, and infrared (IR) and UV spectra were modeled. In order to calculate the energy of an intramolecular hydrogen bond (IMHB), the structures of isomers that do not form hydrogen bonds due to the rotation of the –OH group by 180° relative to the –N=N– bond were optimized. The geometry of quinoid forms was determined for all obtained 2NAB conformers to evaluate the energy barriers and thermodynamic characteristics of proton transfer from the –OH group to the α or β nitrogen atoms of the azo group. The structure of transition states was established using quadratic synchronous transit (QST2 and QST3) methods and confirmed using the internal reaction coordinate procedure. The found structures of transition states were verified by establishing the first imaginary vibrational frequency corresponding to the transition of the hydrogen atom from the hydroxy group to the azo group.

The experimental IR spectrum of 2NAB molecules was obtained on potassium bromide (KBr) tablets using an Avatar 360 ESP spectrophotometer (*Nicolet Instrument Corporation*, USA). The spectrum was recorded using the built-in program and automatic recording of peaks in a frequency range of 400–4000 cm^{-1}. The preparation of the control sample and analysis sequence followed the standard procedure.

UV spectral studies were carried out with the use of a Leki SS2110 UV spectrophotometer (*Mediora OÜ*, Finland) in the wavelength range of 220–450 nm. Hexane, which does not exhibit specific solvation, was used in the preparation of a 2NAB solution, along with solvents used in liquid-phase hydrogenation reactions. The measurements were carried out with respect to the pure solvent at an absorbing layer thickness of 1 cm using quartz cuvettes. The wavelengths corresponding to the absorption maxima were obtained mathematically processing the obtained spectral curves using the accompanying software. The preparation of control solutions and the sequence of analysis followed the standard procedure.

RESULTS AND DISCUSSION

Geometry and thermodynamic calculations

Scanning of the rotation angles of the functional groups relative to the benzene rings in the 2NAB molecules showed that the 2NAB molecule can be in a state of *cis-trans* isomerism with a high probability of having an IMHB between the α or β nitrogen atom of the azo group and the hydrogen atom of the hydroxy group, which are in the *ortho* position relative to each other.

The results of quantum chemical calculations for possible spatial structures of 2NAB isomers with and without hydrogen bonds for transition states corresponding to the transfer of a proton from the hydroxy group to the α or β nitrogen atom of the azo group are given together with the quinoid structures in Tables 1–3 and in Figs. 1 and 2.

The calculations show a significant difference in ground state energies for different isomers: up to a value of 15.33 kJ/mol in calculations using B3LYP and 12.3 kJ/mol in calculations using M06-2X.

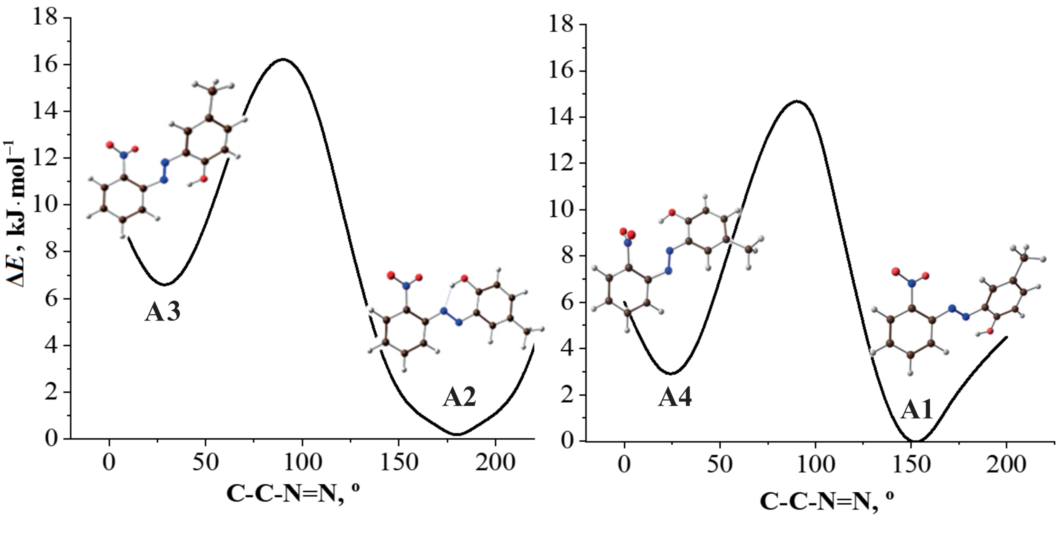


Fig. 1. Potential energy surface profiles obtained by scanning the rotation angle –C–C–N=N– of the nitrobenzene ring about the –C–N= bond in the 2-nitro-2'-hydroxy-5'-methylazobenzene (2NAB) molecule with a step of 10° at B3LYP/6-311++G(d, p) level. Relative energies of conformers are given in Table 1.

Table 1. Calculated relative energies Δ*E* of possible structures of 2NAB, barriers E_a, enthalpies ΔH^{o}_{298}, Gibbs free energies ΔG^{o}_{298} (kJ/mol) of intramolecular proton transfer from –OH to –N=N– group, and imaginary frequencies ν_i (cm^{-1}) for transition states (TS).

Isomer/state[a]		**IMHB**[a]	**B3LYP/6-311++G (d, p)**					**M06-2X/6-311++G (d, p)**				
			ΔE[b]	E_a	ΔH^{o}_{298}	ΔG^{o}_{298}	ν_i	ΔE[c]	E_a	ΔH^{o}_{298}	ΔG^{o}_{298}	ν_i
Trans	**A1**	α	16.2	71.7	42.2	44.05	1596	12.3	93.4	69.6	71.0	1443
	A`1	–	39.3					32.7				
	TS1	α	87.9					105.7				
	B1	α	58.8					82.3				
Cis	**A2**	β	3.5	15.8	−3.94	−2.54	1515	0.00	25.4	9.95	10.0	1421
	A`2	–	51.1					46.6				
	TS2	β	19.3					25.4				
	B2	β	0.00					10.2				
Trans	**A3**	β	10.5	15.2	6.60	7.49	1454	8.6	4.6	19.3	20.2	1335
	A`3	–	54.9					48.0				
	TS3	β	25.8					13.3				
	B3	β	17.2					28.0				
Cis	**A4**	α	18.8	79.3	48.2	50.6	1600	11.0	101	76.3	74.8	1478
	A`4	–	47.5					40.9				
	TS4	α	98.1					111.8				
	B4	α	67.6					87.2				

Note: [a]IMHB – intramolecular hydrogen bond; **A** – azo form with IMHB; **A`** – azo form without IMHB; **TS** – transition state for the reaction of intramolecular proton transfer; **B** – quinoid structures formed in the reaction of intramolecular proton transfer; numbers **1**, **2**, **3**, **4** correspond to the isomers with different position of –OH and –NO_2 groups regarding to –N=N– bond or without H-bond with different N atoms (α or β) in the azo group.

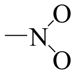
[b]Δ*E* – energies of the structures relative to that of **B2**.

[c]Δ*E* – energies of the structures relative to that of **A2**.

Table 2. Characteristics of the hydrogen bond for different conformers of 2NAB for the gas phase

Isomer/state	**IMHB (atom –N=N–)**	E_{IMHB}, **kJ/mol**			**Bond length, Å**		
		B3LYP	**M06-2X**	**[14]**	**B3LYP**	**M06-2X**	**[14]**
Trans	α	23.2	20.4	16.74–62.76	2.14	2.16	1.50–2.20
Cis	β	47.6	46.6		1.81	1.87	
Trans	β	44.4	39.3		1.77	1.82	
Cis	α	28.7	29.9		2.21	2.22	

Table 3. Frequencies in the IR spectrum of 2NAB

Group	**ν, cm⁻¹**				
	B3LYP/6-311++G (d, p)				**Experiment**
	A2	**A`2**	**A3**	**A`3**	
–OH	3361	3758	3322	3756	3410
 *	1580	1586	1594	1591	1618
–N=N–	1540	1555	1543	1554	1525
>CH–NO_2	1374	1385	1394	1394	1348
>CH–OH	1158	1143	1158	1148	1147

* The stretching vibrations of the N–O bond in the NO_2 group are given.

This indicates a high probability of the existence of the **A2** *cis* isomer in the gas phase, as well as a low probability of the presence of the **A3** structure. However, in solvents used in the processes of liquid-phase catalytic hydrogenation of nitro compounds, it is possible to expect a redistribution proportion of **A2** and **A3** conformations in the reaction mixture due to the presence of solvation interactions and a certain structuring of the medium.

It can be concluded from the data in Table 1 that the presence of IMHB with the β nitrogen atom of the azo group, in comparison with that of the α atom, lowers the energy of the ground state to a greater extent both for the *cis* and *trans* isomers. In both cases, the formation of an IMHB contributes to the stabilization of the molecule and the growth of its coplanarity. Calculation of the ΔG^{o}_{298} reaction for the formation of a quinoid structure using the B3LYP and M06-2X functionals showed somewhat different results. The calculation with the B3LYP functional indicates the possibility of quinone formation in the gas phase only in the case of the **A2** isomer; this is because the process of proton transfer with the formation of **B2** is characterized by a low energy barrier. The calculation with the M06-2X functional showed that quinones are not formed regardless of the conformer structure.

A comparison of the IMHB energies for the *cis* and *trans* isomers with the β and α nitrogen atoms of the azo group, calculated from the difference in the energies of the ground state of the corresponding isomers with and without hydrogen bonds (Table 2), shows that they differ by more than 1.5 times. According to the classification [14], the resulting hydrogen bond should be classified as moderately strong with a significant contribution from the electrostatic component. It can be assumed that the IMHB between the hydroxy group proton and the β nitrogen atom of the azo group will also be preserved in the presence of a solvent [11].

Spectra

To select the structure of the 2NAB isomer, whose presence is most likely for the liquid phase, the experimental IR or UV spectra can be used in protic and aprotic solvents (Tables 3, 5, and Fig. 3). Table 3 shows the vibrational frequencies for 2NAB corresponding to the structures of **A2** and **A3** isomers with and without hydrogen bonds.

In our opinion, the comparison of the experimental and theoretical values of vibration frequencies given in Table 3 does not suggest that the **A2** isomer is preferable. It should be emphasized that, in the experimental IR spectrum of 2NAB, there are no characteristic frequencies in the regions of 1570 and 1690 cm⁻¹ that correspond to the >C=O, >C=N, and >N–NH– bond vibration frequencies characteristic of the quinoid structure. Consequently, the prototropic equilibrium is shifted towards the 2NAB azo form [11].

Figure 3 shows the UV absorption spectra of 2NAB in hexane (Fig. 3c) in comparison with the calculated spectra of various 2NAB isomers in the gas phase (Figs. 3a and 3b). In the case of the **A3** isomer, the positions of the peaks can be seen to correspond exactly. Calculations within the framework of the M06-2X functional do not reproduce the general form of the experimental spectrum, that is, the position and intensity of electron transitions.

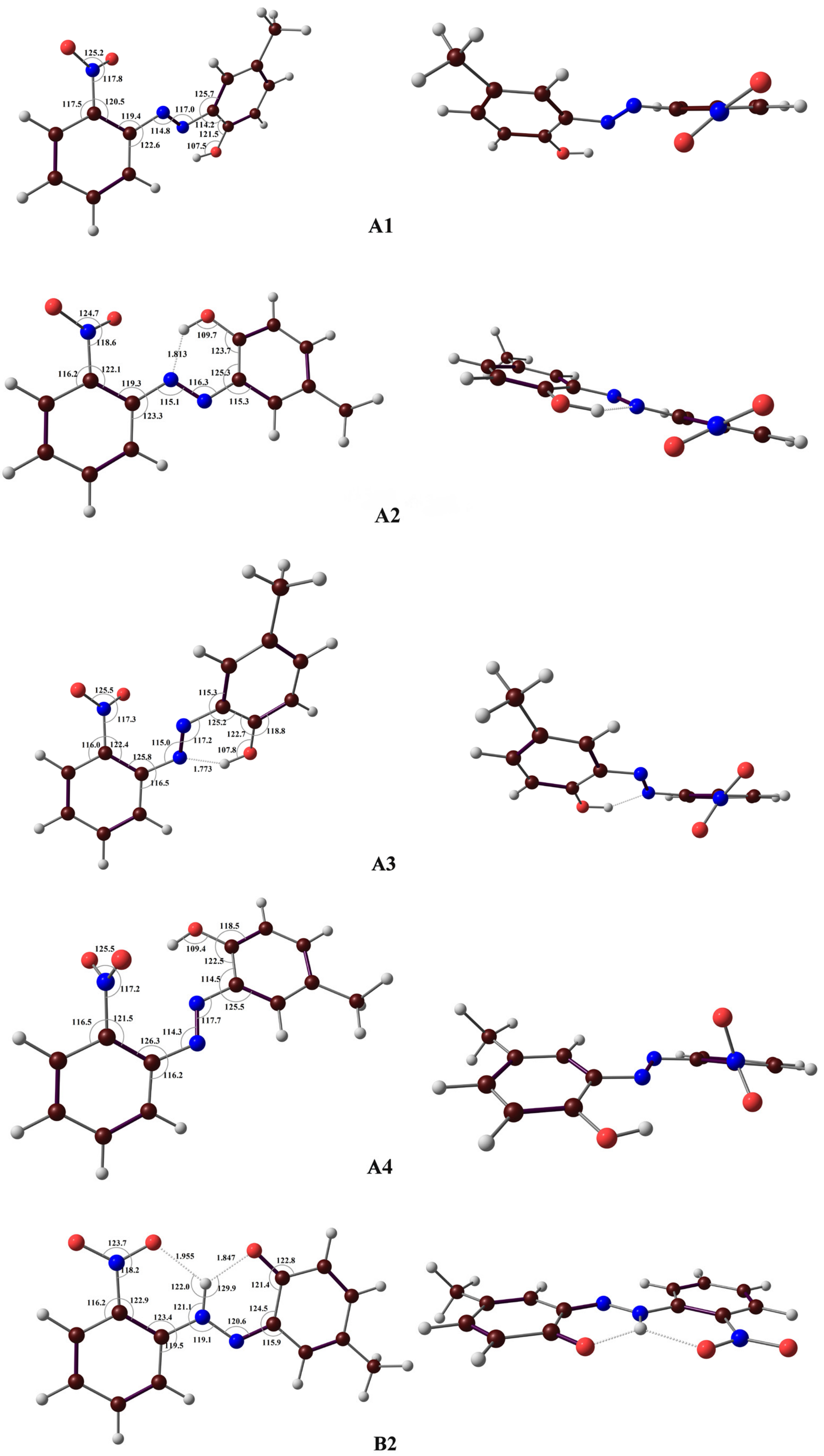
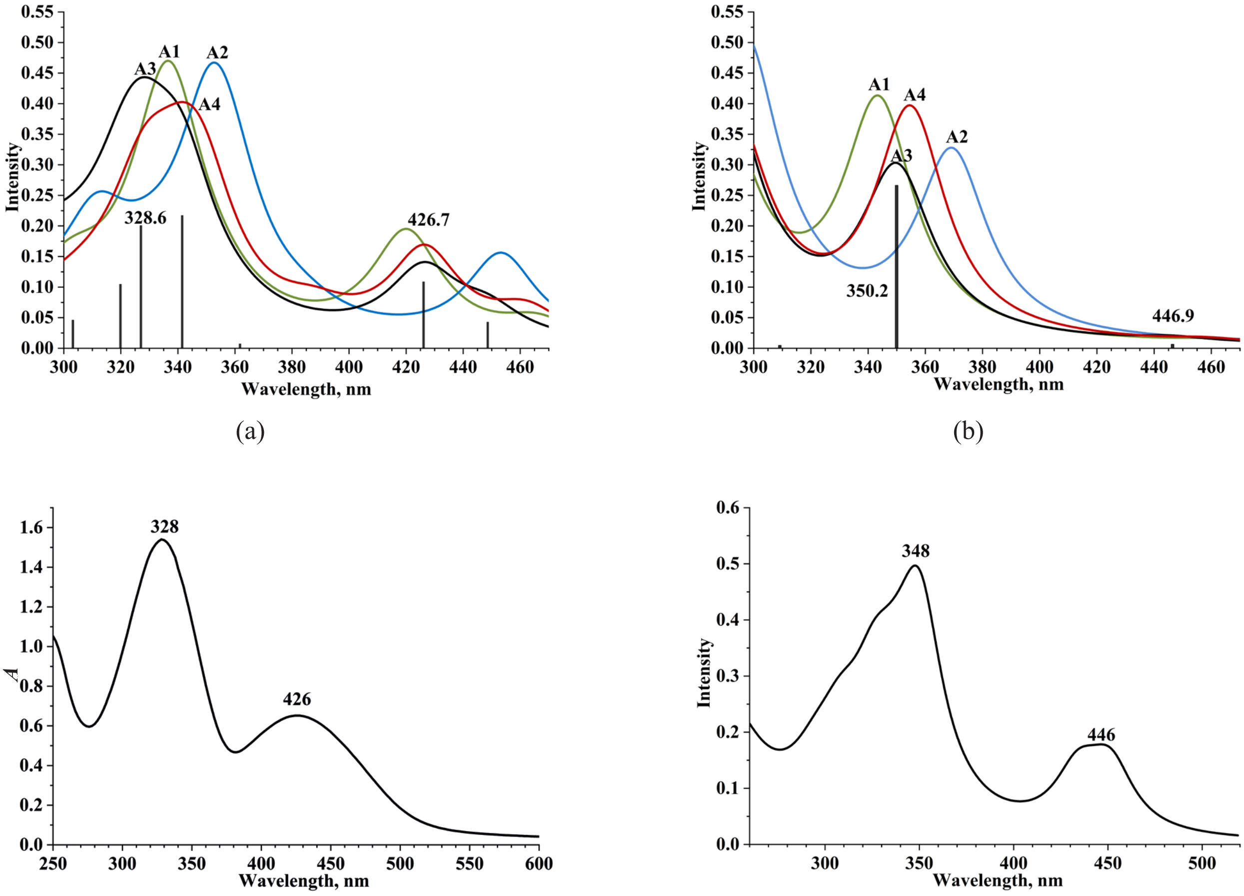


Fig. 2. Optimized structures of 2NAB conformers (B3LYP/6-311++G(d, p)) for the gas.



(a) (b)

(c) (d)

Fig. 3. UV absorption spectra of 2NAB: (a) B3LYP/6-311++G(d, p) calculations in the gas phase for the **A1**–**A3** isomers, the intensity and position of electron transitions are shown for isomer **A3**; (b) M06-2X/6-311++G(d, p) calculations for the **A1**–**A3** isomers in the gas phase; the intensity and position of electron transitions are shown for isomer **A3**; (c) experimental spectrum of 2NAB in hexane, where *A* is the optical density; (d) B3LYP/6-311++G(d, p) theoretical calculations for **A3** isomer in hexane in the CPCM model. For each theoretical spectrum (a, b, d), an approximation by a Lorentzian with a 30-nm halfwidth of the peak was performed.

To identify the 2NAB structure in solution, we carried out a complete reoptimization of **A2** and **A3** isomers geometry in the corresponding solvents within the CPCM framework and calculated the UV spectra. The results are presented in Table 4 and in Fig. 3d. It follows from the presented data that, just as in the gas phase, the closest wavelengths of the absorption maxima correspond to the **A3** isomer. For both isomers, a significant shift of the absorption maxima to the longwave region of the spectrum is observed.

The authors of a number of papers [11, 15] have noted that the transition of a proton from the hydroxy group to the azo group and the formation of the quinoid structure should make the UV absorption spectrum of 2NAB single-banded. In our experimental UV absorption spectra of 2NAB in hexane, toluene, 2-propanol, in its aqueous solutions, including those in the presence of base and acid additives, this is not observed (Tables 4 and 5). The position of the absorption maxima does not change even if sodium hydroxide in an aqueous solution of 2-propanol is present in an amount corresponding to the complete ionization of the molecule, i.e., at a ratio of 2NAB : NaOH = 1 : 1.42 or 2NAB : NaOH = 1 : 1.14. The authors of [11, 15] also state that hydroxy-substituted aromatic hydrocarbons can act as donors of a free electron pair with respect to alcohols in the formation of an IMHB as a result of specific solvation, and as acceptors with respect to dimethylformamide (DMF). However, the peak of the absorption maximum in the longwave region in both DMF and diethylamine (DEA), which are characterized by a high acceptor

Table 4. Wavelengths of absorption maxima λ_1 and λ_2 in the UV spectra of 2NAB in solution and molar extinction coefficients ε_1 and ε_2 in solvents

Sovent	$\lg\varepsilon_1^d$, L/(mol·cm)	λ_1, nm			$\lg\varepsilon_2^d$, L/(mol·cm)	λ_2, nm		
		Exp^d	B3LYP/6-311++G(d)				B3LYP/6-311++G(d)	
			A2	A3			A2	A3
n-Hexane	2.59	326	353	342	2.22	426	458	444
Toluene	3.85	326	357	349	3.67	424	461	448
2-Propanol	3.62	328	361	354	3.25	416	467	450

^{d}Experimental values.

capacity with respect to the proton, is also absent. This can be regarded as the fact that, in these solvents, IMHB in the 2NAB molecule is retained; moreover, there is no proton transfer from the hydroxy to the azo group.

The specific solvation of hydroxy-substituted aromatic hydrocarbons at the hydroxy group may characteristically not occur if strong IMHBs are formed, whose energy is higher than 20 kJ/mol [9, 11, 14–17]. The fact that the nitro group is not specifically solvated helps to reduce the universal component of solvation. The change in the thermochemical characteristics of solvation in organic solvents is associated mainly with the aromatic system and the delocalization of π-electrons.

Our experimental data (Table 5) indicate that, by only replacing individual solvents and water–2-propanol solvents by aqueous solutions or solutions in DMF and DEA with NaOH additives, a strong bathochromic shift occurs in the UV spectrum: the band at λ_2 = 414 nm disappears, and a new band appears in the region of 500 nm. According to [11, 15], the presence of an absorption band in the region of 480–550 nm indicates a shift in equilibrium from the azo form of the dye to its quinoid structure.

The authors of [11, 15, 18, 19] also note that substituted nitroazobenzenes are predominantly in the state of *trans* isomerism, especially when going to solvents with a high dielectric constant [18, 19]. The azo form in the UV absorption spectra is characterized by the appearance of a maximum at a wavelength of 320–350 nm, which is associated with π–π* transitions. The presence of an absorption maximum in the region of 420–440 nm indicates an increase in the common conjugation chain along with a higher electron density on the azo group due to its transfer from the phenyl ring [11, 15]. This absorption maximum is due to *n*–π* transitions, in which wavelength regions we noted the appearance of the corresponding maxima.

As noted in [11, 15], the weakening of the IMHB under the influence of a solvent will contribute to a convergence of the energy levels of nitrogen atoms of the azo group. This can also cause an increase in the contribution of orbital control [20] at the stage of associative addition of hydrogen to the azo group under hydrogenation conditions. This increases the contribution of the direction of 2NAB hydrogenation reaction through the formation of 2-nitro-2'-hydroxy-5'-methylhydrazobenzene (2NHB), as well as contributing to a decrease in the yield of products containing a triazole ring. Kinetic studies have proven that the concentration of NHB increases when the reaction is carried out in solvents with pronounced electron-donor properties [19]. At the same time, the ionization of the hydroxy group leads to the destruction of IMHB in the 2NAB molecule, thus increasing its coplanarity. This determines the possibility of simultaneous hydrogenation of both nitro and azo groups. It was experimentally confirmed [21, 22] that the transformation of 2NAB under hydrogenation conditions proceeds according to a parallel-sequential scheme. One of the parallel directions leads to the formation of products containing the triazole ring, while the second direction leads to the formation of the nitro-hydrazo derivative. The latter undergoes intramolecular rearrangement in the presence of sodium hydroxide to form a triazole ring.

When considering the possibility of cyclization of intermediate products formed upon 2NAB hydrogenation, the coplanarity of the considered 2NAB isomers should also be taken into account. From this point of view, cyclization of **A3** and

Table 5. Wavelengths of absorption maxima λ_1 and λ_2 in the UV spectra of 2NAB and molar extinction coefficients ε_1 and ε_2 for individual, binary, and mixed solvents

Sovent		λ_1, nm	$\lg\varepsilon_1$, L/(mol·cm)	λ_2, nm	$\lg\varepsilon_2$, L/(mol·cm)
Dimethylformamide (DMF)		333	3.94	413	3.86
Diethylamine (DEA)		333	3.83	413	3.81
Water–2-propanol	x_2	λ_1	$\lg\varepsilon_1$	λ_2	$\lg\varepsilon_2$
	0.26	328	1.30	410	0.93
	0.48	328	4.40	412	4.05
	0.68	328	3.62	414	3.25
	0.78	328	4.32	414	3.99
Water–2-propanol–NaOH $x_2 = 0.68$	2NAB : NaOH	λ_1	$\lg\varepsilon_1$	λ_2	$\lg\varepsilon_2$
	1 : 0.04	328	3.75	416	3.39
	1 : 0.29	328	3.85	414	3.49
	1 : 0.86	328	3.92	414	3.58
	1 : 1.42	328	3.75	414	3.39
	2NAB : CH_3COOH	λ_1	$\lg\varepsilon_1$	λ_2	$\lg\varepsilon_2$
	1 : 1.14	330	2.66	414	2.27
Water–NaOH	C_{NaOH}, mol/L	λ_1	$\lg\varepsilon_1$	λ_2	$\lg\varepsilon_2$
	0.01	330	2.22	496	2.23
	0.10	330	2.11	496	3.31
	1.00	330	3.30	496	3.30
DMF–NaOH	0.01	340	3.98	506	4.06
DEA–NaOH	0.01	345	3.83	516	3.99

A4 isomers can be considered as the most probable structure. Based on the results presented above, preference should be given to structure **A3** due to its higher coplanarity and the absence of a steric hindrance upon the formation of the triazole ring. The calculation of the potential barrier for the nitro group rotation around the C–N bond showed that it does not exceed 13.2 kJ/mol. This will tend to promote the formation of a cycle upon the redistribution of bonds in the associative 2NAB–hydrogen complexes formed under the conditions of 2-hydroxynitroazobenzene hydrogenation. It is also likely that the cyclization will proceed according to a synchronous mechanism of the "*head to head*" type due to the 2NAB molecule being characterized by the separation of charges that can move due to a high degree of conjugation [12, 20].

CONCLUSIONS

The experimental results and theoretical calculations of the 2NAB structures, which are in good agreement with each other, do not contradict our assumptions about possible tautomeric states of 2NAB molecules in solutions. On the basis of the totality of the obtained data, we can conclude that a *trans* isomer structure with a hydrogen bond formed between the hydrogen of the hydroxy group and the β-nitrogen atom azo groups of the dye is most probable for solutions in water, DMF, hexane, and toluene, as well as in water–2-propanol solvents with additions of NaOH and CH_3COOH. Intramolecular proton transfer is possible only in aqueous, DEA, and DMF solutions having additions of NaOH. The formation of quinoid structures is not characteristic of the other studied solvents or the gas phase.

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Authors' contributions

A.A. Fedorova – conducting calculations, analyzing and systematizing the material, reviewing publications on the topic of the article, writing the text of the article;

O.V. Lefedova – carrying out the synthesis and analysis of compounds, IR spectroscopy, writing the text of the article;

S.A. Shlykov – analysis of the results, writing the text of the article, technical and scientific editing.

The authors declare no conflicts of interest.

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