Stabilization of nitrous acid



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Abstract

Nitrous acid (HNO ₂) was stabilized via supporting on Polyvinylpolypyrrolidone (PVPP) and the thermal stabilization and structure were estimated using thermogravimetric analysis measurement and spectroscopic methods, respectively. Some novel heterocyclic azo dyes were synthesized by selective diazotization of aromatic amines followed by coupling with some susceptible aromatic compounds. The stereochemistry structure of the synthesized dyes were optimized using B3LYP at 6-311 G(d, p) basis set and their electron excitation properties were evaluated using calculations of density functional theory. UV-Visible analysis was applied for Photophysical properties evaluation of the new dyes and compared with computed vertical excitation obtained from TD-DFT. Also, the azo-hydrazone tautomerism of the triazine azo dyes was investigated and the results show that for all of the synthesized dyes both azo and hydrazone tautomeric forms exist, while3a-5shows more notable hydrazone form than others.

Keywords: Polyvinylpolypyrrolidone, Nitrous acid, Azo dyes, azo-hydrazone tautomerism

1. Introduction

Nitrous acid as a weak inorganic acid has significant applications in organic reactions such as diazotization, nitrosonation and Sandmeyer Reaction, ^[1, 2] but its instability in temperatures upper 5 °C causes some restrictions to using it. In this work, we stabilized nitrous acid via supporting on polyvinylpolypyrrolidone (PVPP) and then utilized it in synthesis of some novel azo dyes. However, PVPP has been reported as an efficient support in https://assignbuster.com/stabilization-of-nitrous-acid/

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many cases such as trifluoroboride and nitric acid. ^[3, 4] PVPP-HNO ₂ has many advantages that make it environmentally acceptable in both industrial and laboratory viewpoints. It is applicable for a long time after preparation and the polymer easily remove by washing with water.

In particular, nitrous acid absorbed on polyvinylpolypyrrolidone takes part in azo coupling reaction and the polymer remains almost completely intact. However, the literature describing arylamines conversion to diazonium salts using polyvinylpolypyrrolidone supported nitrous acid (PVPP-HNO ₂) is not available. Herein, we wish to present a convenient procedure for diazotization reaction using this stable reagent.

Azo colorants from aromatic heterocyclic amines have sublimation fastness, excellent light and color strength. ^[5] They are one of the important groups of synthetic organic dyes. They are applied in various fields such as electronic photography, liquid crystal displays, paper printing, bleaching, polymers, laser technology, dyeing, color formers, data storage and solar energy conversion. ^[6] They also have been known as antibacterial, antifungal and anti-tumor compounds. ^[7, 8]

The compound 1, 3, 5-triazine has an alternative six-membered heterocyclic ring with an equal number of nitrogen and carbon atoms. ^[9] The triazines are analogues of benzene rings, which makes them as an aromatic compound like benzene. 1, 3, 5-Triazine, a common reagent which is used as herbicides and pharmaceuticals. ^[9]

The diazonium salts of triazines derivatives have been reported as a diazotization targets in the synthesis of a variety of heterocyclic azo dyes ^[10, 11] but no report found in direct diazotization of triazines with more than one aromatic amine group.

The existence of azo-hydrazone equilibrium in azo colorants having the hydroxyl group at ortho or para position to azo linkage was proved in 1983. ^[12] In hydrazone form, due to the hydrogen bonding, a coplanar sixmembered ring is formed with higher thermal stability than azo form ones. ^[13] After reductive cleavage, the azo chromophoric system gives carcinogenic amines, ^[14] while in the hydrazone tautomer will be cleaved the C-N bond instead of N= N bond. ^[15] The study of azo-hydrazone tautomerism gives the great information for degradation of azo chromophores with least toxicological effect on the environment.

Finally, we report preparation of polyvinylpolypyrrolidone supported nitrous acid (PVPP-HNO ₂) and synthesis of novel azo dyes by diazotization of 6phenyl-1, 3, 5-triazine-2, 4-diamine (1)and 1, 3, 5-triazine-2, 4, 6-triamine (2), followed by coupling with hydroxyl and amine substituted of aromatic compounds (Scheme 1).

The absorption spectra were obtained using a UV-Visible spectrophotometer and the structures of the triazine azo dyes were confirmed by spectral analysis. Also, DFT calculation was used for study of their azo-hydrazone tautomerism. The structures in azo and hydrazone forms were optimized in the TD-SCF method using B3LYP/6-311 G(d, p) basis sets.

3. Results and discussions

3. 1. Stabilization of HNO 2 over PVPP

PVPP-HNO 2 was prepared by a simple route. As regards the nitrous acid is extremely unstable in temperatures over than 5 °C, polyvinylpolypyrrolidone which previously has been applied as an efficient support, ^[3, 4] was used and the spectroscopic and experimental results showed that PVPP can stabilize nitrous acid by formation of PVPP-HNO 2. Thermal gravimetric analysis (TGA) investigation of the polymer and PVPP-HNO 2 was performed to study their thermal stability (Fig. 1). The thermal decomposition of PVPP starts at near 330 °C and a sharp burning of polymer chains in pure PVPP sample occurs between 360 °C with the weight loss of \sim 75% of the initial weight. TGA spectra of PVPP-HNO 2 demonstrate a mass degradation at 70 °C in PVPP-HNO₂, whereas there is no similar situation in TGA spectra of pure PVPP. In other words, TGA spectra of PVPP-HNO 2 show that stability of nitrous acid has been increased to 70 °C. Due to that, the probable hydrogen bonding causes the stability of nitrous acid via prevention of its decomposition to nitrogen oxides. Furthermore the results of acid-base titration show that the PVPP-HNO 2 is clearly more acidic than pure PVPP. While pH of the 0. 1% solution of PVPP in water is about 7.0, but the same of PVPP-HNO 2 is about 2. 92. In other word, [H $^+$] is 1. 2Ã-10 $^{-3}$ M and it shows that [HNO ₂] is about 0. 0032 M and it reveals there is about 0. 02 g of nitrous acid in 1 g of PVPP-HNO 2 which shows good accordance with TGA results.

PVPP-HNO 2 was prepared in different ratios of PVPP and HNO 2. The best result that showed the maximum capacity of acid in the polymer was 20% https://assignbuster.com/stabilization-of-nitrous-acid/

w/w. The ratios determined by acid-base titration was consistent with TGA degradation analysis.

Besides, the synthesis of PVPP-HNO $_2$ was confirmed by FT-IR spectrum. It shows carbonyl band at 1658 cm $^{-1}$, whereas the same band in pure PVPP has appeared at 1668 cm $^{-1}$. This can attribute to hydrogen bonding between nitrous acid and PVPP (Figure 2). This type of interaction has been reported between PVPP and polyphenols. ^[16]

The existence of the N-O band stretching at 1380 and 1572 cm $^{-1}$ in PVPP-HNO ₂ and absence of this band on PVPP, gives the indication that nitrous acid has been linked to PVPP polymer (Figure 3).

3. 2. Synthesis and characterization of azo dyes

A simple and facile synthetic route was presented for the preparation of triazine azo dyes. We found that these products can participate in azo coupling reaction to form various and already known azo dyes. Therefore, we treated diazonium salts with 1-naphtol, 2-naphtol and other amino and hydroxy aromatic compounds to obtain a variety of azo dyes in good yields.

The compound 4-amino-6-phenyl-1, 3, 5-triazine-2-diazonium was synthesized from mixture of 6-phenyl-1, 3, 5-triazine-2, 4-diamine (1)and PVPP-HNO ₂ in 1 mmol of diamine to 2. 0 g of PVPP-HNO ₂ ratio and further coupled with 1 mmol of 2-naphthol in DMSO to obtain 1-((4-amino-6-phenyl-1, 3, 5-triazin-2-yl)diazenyl)naphthalen-2-ol (3a-2)in good yield. Other derivatives have been synthesized by different coupling components (Scheme 2).

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The chemical structure of the new dyes was confirmed by ¹ H and ¹³ C NMR spectroscopy. 2-naphtholic dyes3a-2and3b-2contain the hydroxyl group at ortho-position to the azo bridge and have the susceptibility to make a sixmembered ring due to intramolecular hydrogen transfer. The result of this type of interaction is chemical shift deshielding of hydroxyl group proton than usual. ¹ H NMR spectra summarized in Table 1 indicates the dye3a-5 shows an extra singlet at \hat{l} 12. 11 ppm attributed to N-H proton which is in hydrazone form. The protons of NH $_2$ in the heterocyclic ring of series3ashow singlet peaks at \hat{I} 8. 16 to 8. 63 ppm while the same at series3bappear at l' 6. 77 to 6. 99 ppm. The ¹³ C NMR spectrum of heterocyclic ring carbons shows down field peaks at I' 180-190 ppm. Except compound3a-4which have three non-aromatic carbons, all of the other compounds just have aromatic carbons. ¹³ C NMR spectrum of 3a-4 shows two peaks at 1² 96. 2 and 151. 3 ppm that attributed to the carbons which have been linked to azo group and the hydroxyl group, respectively and a peak at Î 162. 0 ppm which assigned as ester carbon of coumarin ring. Infrared spectra of the synthesized chromophores show the band at 1500-1570 cm $^{-1}$ related to the N = N bond. A unique band at 2200 cm $^{-1}$ in 3a-5 reveals the existence of C= N group which can be another evidence for the existence of hydrazone form in this compound. Electron ionization mass spectroscopy (El-MS) was used to verify structure of the synthesized azo dyes. The base peak in all of the dyes is due to fragmentation of the molecules in the azo bridge. Series3aand3bshow a base peak at m/z 171 and 110, respectively which attributed to the ionized heterocyclic rings.

3. 3. Photo-physical properties and solvent effects

To find out the color properties with structural correlation of the synthesized azo dyes, UV-Visible spectra of the dyes were recorded in solvents such as n-hexane, ethanol, acetonitrile and dimethyl sulfoxide at concentration of ~10 ⁻⁴ M and at room temperature. The results are tabulated in Table 1. Although a moderate bathochromic shift in ethanol and acetonitrile was seen, but generally no significant bathochromic shift was observed. The UV-Vis absorption spectra of all of the dyes in all solvents show the main band at 290-330 nm which can be assigned to moderate energy transition of the aromatic ring. All of the3bseries and compounds3a-2, 3a-4and3a-5in all solvents, two bands are displayed arising from the $I\inat/I\in$ * transitions in the backbone. The second bands appear at 360-500 nm can be assigned to azo bridge or intermolecular azo-aromatic chromophore.

3. 4. Computational study:

Gaussian 03 program package was employed to study Time-Dependent Density Functional Theory (TD-DFT) and the profusion of the synthesized azo dyes in their azo and hydrazone tautomeric forms. ^[17] TD-DFT calculations were applied using B3LYP/6-311 G(d, p) basis set with the default convergence criteria and without any limitation on the geometry. The TD-DFT provide the most powerful and effective computational tool for examining the ground and excited state properties of the azo molecules compared with obtained UV-Vis data. Time-dependent DFT method was applied for determination of the UV-Vis spectra, electronic transitions, and vertical excitation energies. 3. 4. 1. UV-Vis spectral analysis

The UV-Vis spectra of azo dyes molecules were measured in dimethyl sulfoxide solution as shown in Figure 4. The calculated absorption maximum wavelength ($\hat{l} \gg m_{ax}$), electron transition energies and oscillator strength both in solvent phase (DMSO as solvent) along with recorded UV-Visible data are shown in tables 2 and 3.

The main characteristic of the spectra is determined by the general structure of the molecules. Each molecule has a double band Nâ• SN (azo group) which is directly conjugated with a homocyclic and heterocyclic aromatic ring. This group has a wide electronic delocalization. Therefore, it is possible to predict the presence of the main absorption band associated to a \mathbb{I} . delocalized system that involves the fragment Nâ• SN and other associated internal transitions that emerge from the aromatic and/or heterocyclic system. In this sense and in according with the structure of the compounds, we can determine that the first absorption band $\hat{I} \gg 1$ located in the range of 290-320 nm with low intensity that appears as shoulder is attributed to \ddot{I} ۉ†' \ddot{I} € * transition that involves the aromatic rings, while the second absorption band \hat{I} > 2 located in the range of 300-400 nm, attributed to a $\hat{I} \in \hat{a}^+$ \ddot{I} € * transition. This transition involves the azo bridge. The remaining absorption band located at lower energy corresponds to $\hat{I} \gg 3$ and is assigned as the type nâ†' Ï€ * transition. A similar behavior of the previous transition is observed. In tables 2 and 3, the experimental and calculated maximum absorption and the corresponding orbital contribution are shown. As observed, shorter wavelengths (l
[°] 1) and in some cases l
[°] 2 belong to lower

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occupied MOs such as HOMO-4, HOMO-6 and HOMO-8 and LUMO while longer wavelengths ($\hat{I} \gg 3$) involves frontier molecular orbitals (FMOs). The description of FMO will be discussed in the DFT section.

An example of the involved MOs for compound3a-2is presented in Figure 5. The entire former assignations were corroborated using TD-DFT calculations. The involved MOs for all of the synthesized compounds are presented in Figure S1-9.

3. 4. 2. DFT calculations

For prediction of the molecules electronic spectra, the TD-DFT calculation is used because of low computational cost and high accuracy.

The electronic structure of the molecule in ground state can be determined from the wave function of the electron moving within molecule because molecular orbital can be treated as electron channels. ^[18] The Gauss View program is applied to calculate group contribution of molecular orbitals, i. e. the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). In almost every calculated transitions, the FMO are involved, *vide supra*. The FMO of all compounds shows similar characteristics as observed in supplementary data (Fig. S1-9).

In all cases, HOMO is delocalized over the homo-aromatic ring and azo bridge. The HOMO-1 is composed in every case mainly by the azo bridge. In terms of unoccupied MOs, the LUMO is mainly centered over the homocyclic and heterocyclic aromatic rings and azo bridge. On the other hand LUMO+1 of naphtholic compounds3a-1, 3a-2, 3b-1and3b-2is located almost over the triazine ring while in other compounds, LUMO+1 attributed to non-triazine aromatic rings.

The ionization potential (IP), electron affinity and GAP energies do not follow any trend and the calculated values are similar and do not depend on the substituted coupled to triazine rings. ^[19] The estimated reactivity indexes such as chemical potential ($\hat{1}$ /₄), chemical hardness ($\hat{1}$ ·) and electrophilicity ($\ddot{1}$ ‰) are reported for make the approach of the potential reactivity of these synthesized dyes (Table 4).

Chemical hardness is a measure of the resistance of chemical species to change its electronic configuration. ^[19] It is an index of the stability and chemical reactivity of compounds. The highest value of \hat{I} is shown by compounds3a-5and3b-4in3aand3bseries, respectively, which have 2nitroaniline as coupling aromatic agent and are the most electron attracting substituent. On the other hand, the smallest value is shown by3a-2and3b-2which have 2-naphtol in the structure as a good electron-donor substituent. Chemical potential characterizes the tendency of escaping of electrons from the equilibrium system. ^[19, 20] This index shows an opposite behavior to that of \hat{I} , where the highest value belongs to3a-2and3b-2which have electron donor substituent and the smallest value is shown by3a-1and3b-4which the second compound acts as an electron acceptor substituent while the first can acts as an electron acceptor via induction. Electrophilicity index (I[®]) could give information comparing two in which one is nucleophile/electrophile via lower/higher ï‰. ^[20] For example comparing between3a-1and3a-2shows that3a-1has higher I‰ and it can attribute to more electron attraction of 4hydroxy substituent rather than 2-hydroxy in the naphtholic system. Another attractive comparison between3a-1and3b-1shows more electron attraction in triazine ring in3a-1. A phenyl group which replaced with the amine group has increased electrophilicity of3a-1than to3b-1. Although some contradictions are found in case3a-5that it can appropriate to azo-hydrazone tautomerism that it will be discussed in the tautomerism section.

3. 4. 3. Optimized geometries of azo-hydrazone tautomeric forms

The optimized ground state geometries of the dyes in azo-hydrazone tautomeric forms are shown in figures 6 and 7.

Figure 7. Ground state optimized structure of dyes3aseries in their azo and hydrazone tautomeric forms

Optimized ground state geometries of the compounds in azo forms are almost planar such as3a-1and3a-2which show a mild dihedral angular twist less than 5° at N15-N14-C11-N12 and at N7-N14-C9-C14. All hydrazone forms show a dihedral angle twist by near 30° which follows no trend.

Optimized bond lengths of the synthesized triazine azo dyes (3aand3b) have been calculated. The O-H bond lengths of azo forms for all of the naphtholic series (3a-1, 3a-2, 3b-1and3b-2) is 0. 960 Å. Similarly, the N-H bond lengths are 1. 015 Å for3a-1and3a-2and 1. 000 Å for3b-1and3b-2. This calculated information shows no significant trend to determine azo-hydrazone tautomerism but the obtained N-N bond can signify the single-double bond character of the bond. The N-N bond length in hydrazone form falls shorter to the model value of 1. 400 Å for single bond. ^[21] N-N bond length in3aand3bazo series are 1. 232 Å and this bond length in3aand3bhydrazone forms are 1. 400 Å except in3a-5which N-N bond length in hydrazone form is 1. 330 Å and this confirms our ¹ H NMR observation in the existence of3a-5in both azo-hydrazone forms in significant ratio, while in other compounds this rate of ratio is not impressive.

3. 4. 4. Calculated energies of azo-hydrazone tautomeric forms

The free energies (E/hartree) and relative energies (Î" E/ kJmol ⁻¹) of the synthesized dyes in both azo and hydrazone forms calculated using the B3LYP/6-311G (d, p) level to check theoretical stability difference between tautomeric forms and the values tabulated in Table 5. Contrary to this expectation that hydrazone forms have relative stability than azo tautomers, ^[15, 22] in our TDDFT calculations, only hydrazone form of3a-1shows more relative stability than the same of azo form by 26. 26 kJmol ⁻¹ . 2-naphtholic dyes3a-2and3b-2show a significant stability in azo forms than hydrazone forms by 1260. 48 and 498. 94 kJmol ⁻¹ , respectively. In the other compounds there is no difference between the stability of azo and hydrzone form and it shows that in comparison to experimental data, there is no notable accordance in TDDFT structures energy.

4. Conclusion

In summary, we have successfully developed an efficient protocol to stabilize nitrous acid by supporting on polyvinylpolypyrrolidone (PVPP). Synthesized PVPP-HNO ₂ confirmed by simple titration and FT-IR analysis. The TGA results show that the supported system has acceptable thermal stability. In the

following, we have synthesized nine heterocyclic triazine azo dyes and they were confirmed by FT-IR, ¹ H NMR, and mass spectral analysis. UV-Visible spectral analysis was compared with calculated data. TDDFT calculations were performed showing enough adaption with experimental observations. The optimized structure of azo and hydrazone form using B3LYP/6-311 G(d, p) basis set of calculation shows that azo is more stable form in all of the synthesized dyes except3a-5, which exist in both azo and hydrazone forms.

Acknowledgement. We are thankful to the Yasouj University for partial support of this work.

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