

Original paper

Photo-inhibition Effect from Strong Electron Withdrawing Nitro Group in N-[(E)-(4-Bromophenyl)Methylidene]-4-Nitroaniline

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Article Info:

Article history:

Received: 14 October 2015

Revised: 1 December 2015

Accepted: 14 December 2015

Available online: 15 March 2016

Keywords:

Organic synthesis, Imine, UV-Vis
Photo-reactivity, Photo-inhibition

Abstract

Light induced effect of N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline was investigated using UV-Vis spectrophotometer. This study revealed that the presence of strong electron withdrawing nitro group inhibited the photo-reactivity of the compound. Mainly, molecular structure and functional groups have tremendous influence on chromophoric compounds. The photoisomerization effect was not found in this compound, due to the photo-inhibition of nitro group present in the molecular system.

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1. Introduction

The light sensitive compounds which show the reversible photoisomerization properties are interested in the field of optics. The heart of the phenomenon in such systems is the reversible photoinduced shape transformation of the molecules containing the photochromic functional groups [1-3]. Thermodynamically more stable trans form isomerizes to cis form [4], when the suitable amount of energy is supplied to the molecular

system as shown in Figure 1. The process of cis-trans (reverse) process can be achieved by illuminating the light of 450 nm [5]. However, the reverse cis-trans isomerization is spontaneous [4, 6-9] and it do not need any external agency to perform.

The process of photoisomerization of olefinic compounds (C=C) with four ligands can be expressed in terms of twisted motion [10, 11]. But,

the photoisomerization of Schiff's base compounds (C=N) with three ligands is explained by either linear independent motion or linear combination: in-plane inversion and twisting at the N atom of C=N [12-15]. The photoisomerization pathway with peculiar electronic state is difficult to be analyzed experimentally. Unsubstituted imine has inversion path for isomerization but twisting pathway is determined by preliminary calculation [16, 17-19]. These calculations did not give proper evidence about two dimensional nature of nuclear coordinate [14, 15, 20]. There are some energy levels relevant to photochemical excitation; S₀, S₁ and T₁ for the ground state that excited singlet and triplet states respectively [16, 18, 20].

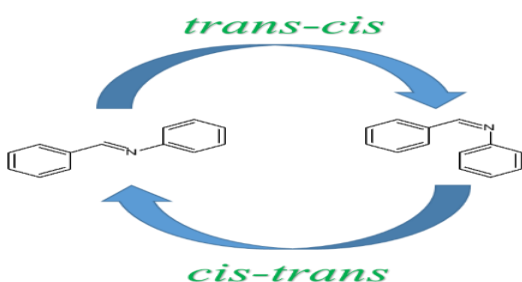


Figure 1: The diagram explaining the photoinduced phenomena. Energetically more stable *trans* will convert in to *cis* and vice versa [4].

The minima of the states S₁ and T₁ are not located geometrically [14]. The observed decay of photoisomerization [13, 17, 20] is fast in solid and solution states and the fast relaxation leads to gaining the original energy state S₀. The inversion [18, 20] and twisting [17, 18, 20, 21] relevant to two dimensional pathways at the energy levels S₀, S₁ and T₁ were determined by ab initio calculations for the unsubstituted imines. It has been found that there was a very narrow gap between S₀ and S₁ electronic states [17]. Hence, the fast switching process was found in the Schiff's base system during photoisomerization

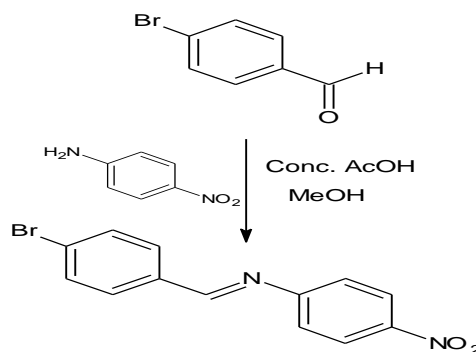
phenomenon [17, 22]. Also, the threshold energy [17, 22] required for the excitation from S₀ to S₁ state is low.

In this work, imine derivative was synthesized and photo-physical properties have been studied.

2. Materials and Methods

Materials used: 4-Bromo benzaldehyde (Aldrich), 4-nitro aniline (Aldrich), acetic acid (Fluka), methanol (Fluka), ethyl acetate (Fluka), sodium sulphate (Fluka), n-hexane (Fluka), ethanol (Fluka) and silica gel-60 (Merk).

Synthetic Procedure: Synthesis of N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline consists of nucleophilic substitution of aromatic aldehydes by para nitro aniline in presence of concentrated acetic acid catalyst. The synthetic scheme is given in Scheme 1 and the ¹H-NMR spectra is given in Figure 2.



Scheme 1: Scheme for the synthesis of N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline

A pale yellow coloured solid; yield: 88 %; melting point is 115.4-115.8o C; IR (KBr Pellet) γ_{\max} in cm^{-1} : 1624, 1580, 1508, 1437, 1289, 1169, 1106 (C=C aromatic), 820 (C-H); ¹H NMR (400 MHz, DMSO): δ 8.38 (s, 1H, CH=N), 8.28 (d, J = 10 Hz, 2H, Ar), 7.79 (d, J = 5 Hz, 2H, Ar), 7.66 (d, J = 10 Hz, 2H, Ar), 7.25 (d, J = 10 Hz, 2H, Ar).

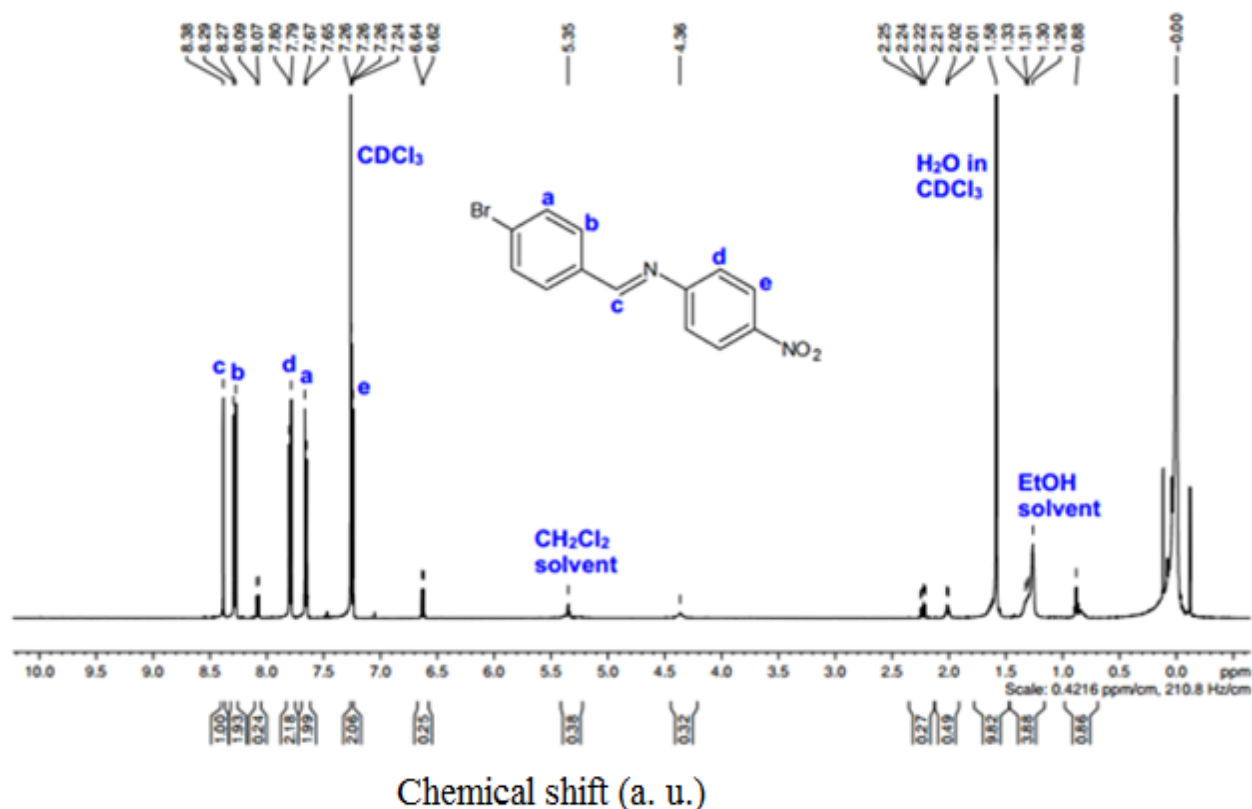


Figure 2: ¹H-NMR spectrum of N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline

3. Results and Discussion

For photoswitching studies, N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline was dissolved in chloroform at suitable concentrations. The absorption spectra were recorded using UV-Visible spectrophotometer obtained from Ocean Optics (HR2000+). Photoswitching behaviour of the imine was investigated by illuminating with OMNICURE S2000 UV source equipped with 365 nm filter with 5 mW cm⁻² intensity. The photoswitching property were performed using UV-visible spectroscopy with the presence and absence of UV light illumination.

Imine is also known as Schiff's base and azomethane. The photoisomerization and promising photo-reactivity of imines reported earlier [12-15, 17, 18, 20-22]. But, most of the imine derivatives are not photo-reactive in nature

due to their functional group effects and geometrical properties [16]. However, N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline has bromo and nitro functional groups at the 4 and 41 positions of imine (Scheme 1). Generally, nitro group is a strong electron withdrawing group. So, the π electrons of C=N bridge involve in the resonance stabilization (Figure 3). Hence, there is no photoisomerization takes place in this case. N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline showed the absorption spectrum with peak wavelength of 345 nm and threshold energy $E_{th} = 5.7618 \times 10^{-19}$ J (Figure 4). Surprisingly, N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline did not show photo-reactivity with the illumination of UV light. It means that photoisomerization is zero in case of this imine compound.

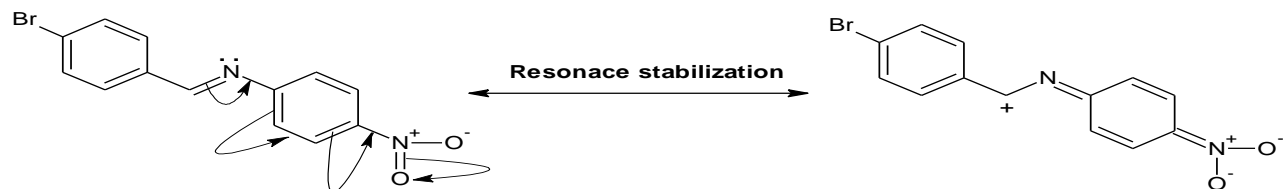


Figure 3: Resonance stabilization of imine with nitro group

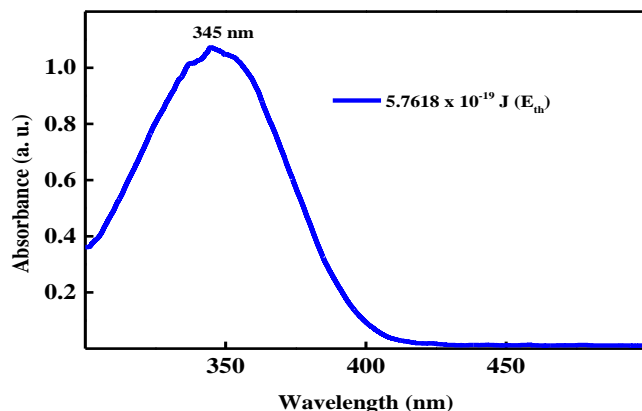


Figure 4: Absorption spectrum of imine derivative

4. Conclusions

The synthesis and photo-reactivity of N-[(E)-(4-bromophenyl)methylidene]-4-nitroaniline is reported. The absorption maxima of this compound was appeared at 345 nm region with the threshold energy 5.76×10^{-19} J. The photoswitching properties are not found in this case, due to the resonance effect initiated from strong electron withdrawing nitro group present at the terminal. In other words, photo-inhibition effect was found because of the significant effect of nitro group on the molecular system. Hence, it is confirmed that all the imine compounds are not photo-reactive in nature and the photoswitching effect of imine derivatives is weak.

Acknowledgement

This work was supported by DSS (Doctoral Scholarship Scheme 2013-2016) [Candidate: Yuvaraj A. R.] from the education ministry of Malaysia.

References

- [1] G. Hegde, P. Z. Fernandes, A. R. Yuvaraj, G. S. Mei, L. Rahman, M. M. Yusoff, Light sensitive molecule for photonic devices, *Macromol Symposium*, **353**(1) (2015) 115-20.
- [2] G. Hegde, A. R. Yuvaraj, W. Sinn-Yam, M. M. Yusoff, Fast photoswitching azo dyes, *Macromol Symposium*, **353**(1) (2015) 240-245.
- [3] S. N. Sidharth, A. R. Yuvaraj, T. J. Hui, B. K. Sarojini, M. M. Yusoff, G. Hegde, Light induced properties of chalcones correlated with molecular structure and photophysical properties for permanent optical storage device, *Advanced Material Research*, **1033-1036** (2014) 1149-1153.
- [4] A. R. Yuvaraj, W. S. Yam, T. N. Chan, Y. P. Goh, G. Hegde, New para-substituted non-symmetric isoflavones for their fast photo-switching ability: Synthesis and their liquid crystal characterization, *Spectrochimica Acta Part A: Molecular Biomolecular Spectroscopy*, **135** (2015) 1115-1122.
- [5] A. R. Yuvaraj, G. S. Mei, A. D. Kulkarni, M. M. Yusoff, G. Hegde, Aliphatic/aromatic spacers based azo dye dimers: synthesis and application for optical storage devices, *RSC Advances*, **4**(92) (2014) 50811-50818.
- [6] R. Dong, B. Zhu, Y. Zhou, D. Yan, X. Zhu, Reversible photoisomerization of azobenzene-containing polymeric systems driven by visible light, *Polymer Chemistry*, **4**(4) (2013) 912-915.
- [7] H. M. D. Bandara, S. C. Burdette, Photoisomerization in different classes of azobenzene, *Chemical Society Review*, **41**(5) (2012) 1809-1825.

- [8] R. Fernández, I. Mondragon, R. C. Sanfelice, F. J. Pavinatto, O. N. Oliveira, P. Oyanguren, Optical storage in azobenzene-containing epoxy polymers processed as Langmuir Blodgett films, *Material Science Engineering C*, **33**(3) (2013) 1403-1408.
- [9] S. Balamurugan, G. Y. Yeap, W. A. K. Mahmood, P. L. Tan, K. Y. Cheong, Thermal and photo reversible gel-sol transition of azobenzene based liquid crystalline organogel, *Journal of Photochemical Photobiology A Chemistry*, **278** (2014) 19-24.
- [10] D. E. Nicodem, M. G. de, J. A. Matos, Photoisomerization of chalcone: wavelength dependence, *Journal of Photochemistry*, **15**(3) (1981) 193-202.
- [11] M. A. Tehfe, F. Dumur, P. Xiao, M. Delgove, B. Graff, J. P. Fouassier, Chalcone derivatives as highly versatile photoinitiators for radical, cationic, thiol-ene and IPN polymerization reactions upon exposure to visible light, *Polymer Chemistry*, **5**(2) (2014) 382-390.
- [12] J. M. Howell, Resonance theory. IX. Charge distributions and isomer stability of the fluoro derivatives of methylenimine, *Journal of American Chemical Society*, **98**(4) (1976) 886-887.
- [13] N. D. Durga, The Chemistry of tetracyanoethylene, *Chemical Review*, **67**(6) (1967) 611-622.
- [14] A. Kropf, R. Hubbard, The Mechanism of bleaching rhodopsin, *Annals of the New York Academy of Sciences*, **74**(2) (1958) 266-280.
- [15] R. Macaulay, L. A. Burnelle, C. Sandorfy, Theoretical investigation of the carbon nitrogen double bond, *Theoretica Chimica Acta*, **29**(1) (1973) 1-7.
- [16] J. G. Radziszewski, J. W. Downing, C. Wentrup, P. Kaszynski, M. Jawdosiuk, P. Kovacic, Geometrical isomers of a bridgehead imine: E and Z-2-azabicyclo oct-1-ene, and 2-azabicyclo oct-1-ene, *Journal of American Chemical Society*, **107**(9) (1985) 2799-2801.
- [17] J. G. Radziszewski, J. W. Downing, M. Jawdosiuk, P. Kovacic, 4-Azahomoadamant-3-ene: Spectroscopic characterization and photoresolution of a highly reactive strained bridgehead imine. *Journal of American Chemical Society*, **107**(3) (1985) 594-603.
- [18] K. V. Bonacic, M. Persico, CI study of geometrical relaxation in the ground and excited singlet and triplet states of unprotonated Schiff bases: allylideneimine and formalimine, *Journal of American Chemical Society*, **105**(11) (1983) 3388-3395.
- [19] T. Yoshizawa, G. Wald, Pre-lumirhodopsin and the bleaching of visual pigments, *Nature*, **197**(4874) (1963) 1279-1286.
- [20] A. Padwa, Photochemistry of the carbon-nitrogen double bond, *Chemical Review*, **77**(1) (1977) 37-68.
- [21] K. V. Bonačić, J. Michl, Photochemical syn-anti isomerization of a Schiff base: A two-dimensional description of a conical intersection in formalimine, *Theoretica Chimica Acta*, **68**(1) (1985) 45-55.
- [22] R. S. Becker, K. Freedman, A comprehensive investigation of the mechanism and photophysics of isomerization of a protonated and unprotonated Schiff base of 11-cis-retinal, *Journal of American Chemical Society*, **107**(6) (1985) 1477-1485.

Cite this article as: Yuvaraj A. R., Md Lutfor Rahman, M. M. Yusoff, M. B. Suliman, Photo-inhibition Effect from Strong Electron Withdrawing Nitro Group in N-[(E)-(4-Bromophenyl)Methylidene]-4-Nitroaniline, *Chemistry of Advanced Materials*, **1**(1) (2016) 1-5.