



***E/Z*-Photoisomerization of *N,N'*-Bis (4-dimethylaminobenzylidene)1,2-diaminoethane and *N,N'*-Bis(4-dimethylaminobenzylidene) 1,3-diaminopropane in Chloroform**

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Abstract: The *E/Z*-Photoisomerization of Schiff bases *N,N'*-bis(4-dimethylamino benzylidene)1,2-diaminoethane (BDAE) and *N,N'*-bis(4-dimethylaminobenzylidene)1,3-diaminopropane (BDAP) were studied by UV-Vis absorption spectroscopy and theoretical chemistry calculations. Photochemical investigations in solution depict the time resolved spectral changes, recorded before and after irradiation. The shift indicates the transformation from *E* to *Z* configuration of the C=N bond in solution for BDAE and BDAP. Spectra profiles and kinetic constants were evaluated using multivariate curve resolution and non-linear least squares curve fitting by toolbox of MATLAB program using the corresponding absorption spectra-time data. The experimental results show that BDAP can perform the photochromism easier than BDAE, may be due to the molecular topology difference.

Keywords: Schiff base, Photochromism, Kinetic constant, Molecular topology

Introduction

The 21st century will be a phonic century, during which the information will be transferred and processed by a new kind of media light. So, a whole family of functional compounds or material has to develop to meet the need in the filed of high density information storage system, electro-or light-driven information display device, optical calculation and other non-

linear optical devices. Photochemical control of biomolecules both *in vitro* and *in vivo* is of increasing interest in molecular and cellular biology¹. For application to living systems, photochemical reactions are advantageous because the reactions can be controlled from outside without addition of chemicals for initiation of biomolecular's functions. Caged compounds which can be removed by photo irradiation have been attached to DNA, RNA and proteins for initiation of biological phenomena¹. The thermal²⁻⁴ and photo⁵⁻⁷ interconversions of the *syn* and *anti* isomers of imines are a subject of long-standing interest. The mechanism for the thermal interconversion of imine diastereomers is currently the subject of considerable debate⁸⁻¹⁰ and has been considered in terms of either a planar inversion mechanism or a rotation mechanism. The rotation or torsion mechanism involves a twisting about the C-N double bond. In order to bring about this change in geometry, there must be a reduction in the double bond character of the imine bond in the transition state relative to the ground state. Multivariate curve resolution-alternating least squares (MCR-ALS) has already been applied to very diverse second-order calibration problems, as for example, series of titrations, chromatographic runs, or kinetic data¹¹⁻¹³. Photochemical *cis*-*trans* isomerizations of C=C¹⁴ and N=N¹⁵ double bonds have been investigated thoroughly, yet limited information is available on photoisomerization of a C=N double bond¹⁶. There has been virtually no report on the isomerization of a compound containing the C=N double bond derived especially from a diaryl ketone. In this work *E/Z*-Photoisomerization of *N,N'*-bis(4-dimethylaminobenzylidene)1,2-diaminoethane and *N,N'*-bis(4-dimethylaminobenzylidene) 1,3-diaminopropane investigated.

Experimental

All the reagents were analytically pure and were purified before use. UV-Vis absorption spectra were recorded with a Shimadzu UV-3100 UV-VIS-NIR recording spectrophotometer. All the solutions were stored in the dark for more than 72 h before use to prevent photochromism caused by room light. A light source of a high-pressure Hg lamp with grating monochromator was used in the photochromism study (Figure 1). A Pentium IV personal computer with windows XP operating system was used. Singular value decomposition (SVD), multivariate curve resolution and non-linear least squares curve fitting were performed by the MATLAB version 7.0.

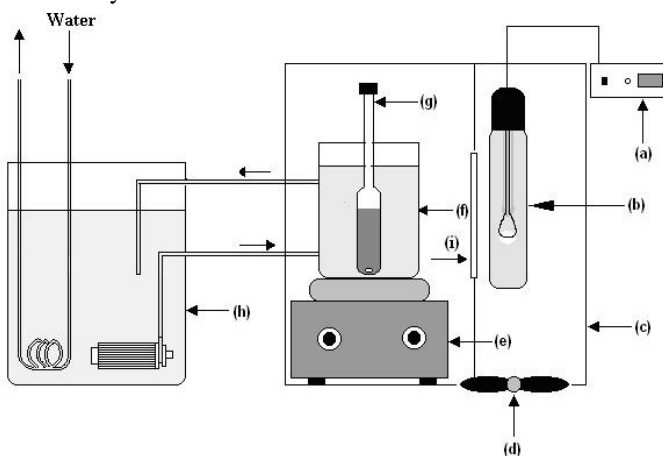


Figure 1. Photolytic setup; a) Power supply; b) high-pressure Hg lamp; c) Photoreactor with aluminium foil as reflector for a full irradiation of catalyst; d) Fan; e) Magnetic stirrer; f) 2 L Pyrex beaker; g) Photolytic cell; h) Water thermostat (Haake model F 122); i) monochromator.

Synthesis of N, N'-bis(4-dimethylaminobenzylidene)1,2-diaminoethane (BDAE)

N,N'-Bis(4-dimethylaminobenzylidene)1,2-diaminoethane (C₂₀H₂₆N₄), (BDAE), was prepared by reaction of ethylenediamine (en) (0.3 mmol, 18 mg) and 4-dimethylaminebenzaldehyde (0.6 mmol, 89 mg) which were dissolved in chloroform (10 mL). The mixture was stirred at room temperature for 4 h. The solid product was filtered off and recrystallized from ethanol, affording small colourless crystals. IR (KBr pellet, 400-4000 cm⁻¹) 1620 (C=N). ¹H NMR (CDCl₃) 3.90 (s, 4H, NCH₂CH₂N); 2.95 (m, 12H, -CH₃), 6.7-7.8 (m, 8H, ArH); 8.2 (s, 2H, 2CH=N).

Synthesis of N, N'-bis(4-dimethylaminobenzylidene)1,3-diaminopropane (BDAP)

N,N'-bis(4-dimethylaminobenzylidene)1,3-diaminopropane (BDAP) was prepared through a facile and convenient method. Propanediamine (0.3 mmol, 22 mg) and 4-dimethylamino-benzaldehyde (0.6 mmol, 89 mg) were dissolved in chloroform (10 mL). The mixture was stirred at room temperature for 4 h. Recrystallization from ethanol solution afforded small crystals. Anal. Calc. for C₂₁H₂₈N₄: C, 74.96; H, 8.39; N, 16.65%. Found: C, 74.70; H, 8.33; N, 16.48%. IR (KBr, cm⁻¹): $\nu = 1620$ (C=N). ¹H NMR (CDCl₃): $\delta = 2.11$ (m, 2H, -CH₂-), 3.16 (s, 12H, -CH₃), 3.71 (t, 4H, -CH₂-N=), 6.81-7.50 (m, 8H, ArH), 8.32 (d, 2H, -CH=N-). MS (EI, 70 eV): m/z (%) = 336 (14) [M]⁺, 189 (100) [M-C₉H₁₁N₂]⁺, 175 (60) [M-C₁₀H₁₃N₂]⁺.

Results and Discussion*Photoisomerization of N, N'-bis(4-dimethylaminobenzylidene)1,2-diaminoethane (BDAE)*

The electronic spectrum of the BDAE was recorded in chloroform at room temperature. The absorption spectra of the Schiff base are characterized by three absorption bands in the region 250-445 nm. In the spectra of the Schiff-base ligand, the aromatic bands at 250 nm is attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at 337 nm is assigned to the imino $\pi \rightarrow \pi^*$ transition. The longer wavelength band (395 nm) is assigned to intramolecular charge transfer while the shorter wavelength is due to $\pi \rightarrow \pi^*$ transitions within the C=N bands influenced by CT interaction¹⁷⁻¹⁹. Photochemical investigations using a high-pressure mercury lamp at 350 nm, were carried out on millimolar solution of *N, N'*-bis(4-dimethylaminobenzylidene)1,2-diaminoethane in chloroform. Figure 2 depicts the time resolved spectral changes, recorded before and after irradiation. The first absorption showed three major peaks at 250, 337 and 397 nm which are identified as characteristic $\pi \rightarrow \pi^*$ absorption bands of *E,E* isomer of BDAE. In the first series time interval of irradiation were one, two and three minute for total of 18 minutes in which the absorption peaks at 397 nm is increased and shifted to 379 and 412 nm. In second series five minute time intervals of irradiation for total of 60 minutes in which the absorption maximum at 337 nm decreased and 290, 379 and 412 nm is increased with an isosbestic point at 305 nm. The shift indicates the transformation from *EE* to *ZZ* configuration of the C=N bond.

Photoisomerization of N, N'-bis(4-dimethylaminobenzylidene)1,3-diaminopropane (BDAP)

Millimolar solution of compounds BDAP in chloroform was irradiated in high-pressure Hg lamp using Photolytic set-up. Figure 3 depicts the time resolved spectral changes, recorded before irradiation and every 1 min after irradiation for BDAP. The absorption maximum at 330 nm decreased, 268 nm increased and 400 nm increased with two isosbestic points at 280 and 343 nm. The shift indicates the transformation from *EE* to *ZZ* configuration of the C=N bond.

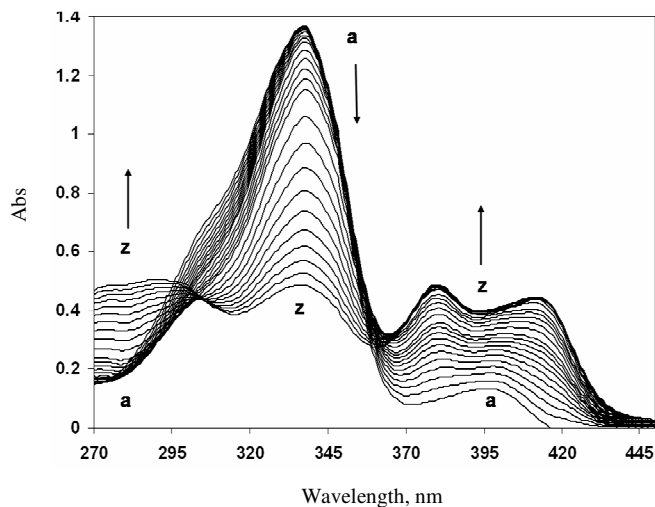


Figure 2. UV-Vis absorption spectral changes for 1.0 mM *N,N'*-bis(4-dimethyl aminobenzylidene)1,2-diaminoethane (BDAE) with UV irradiation in chloroform. From a to z, each irradiation time = 300 s; total, 4680 s.

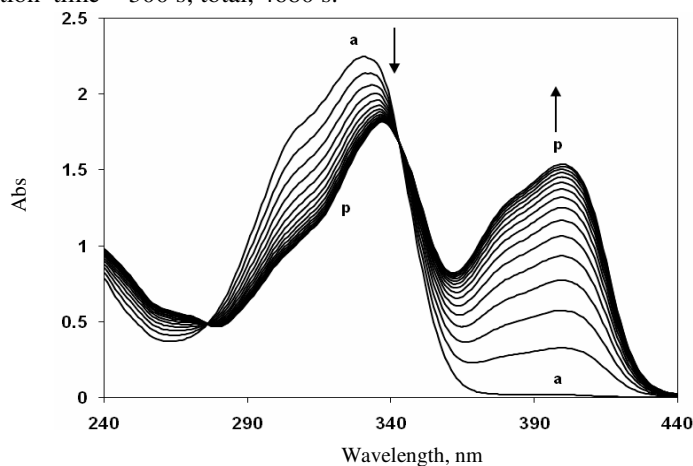
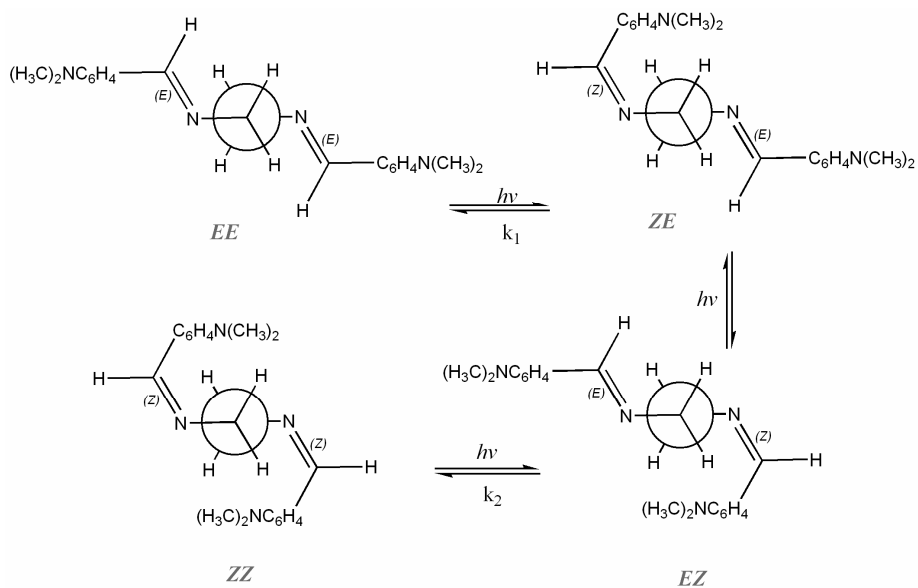
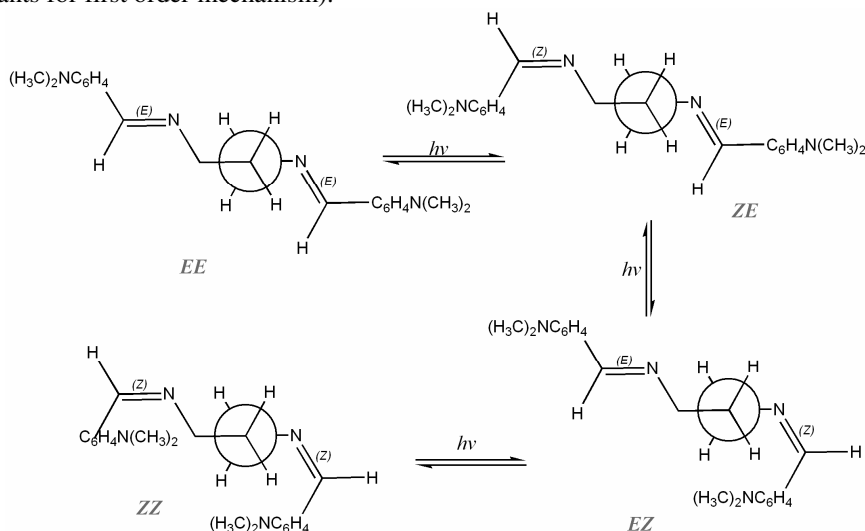


Figure 3. UV-Vis absorption spectral changes for 1.0 mM BDAP with UV irradiation in chloroform. From a to p, each irradiation time = 60 s; total, 900 s.

Kinetic constants and quantum yields

As any other resolution method, the aim of MCR-ALS is the optimal decomposition of a data matrix D into the product of two small matrices, C and S^T . This decomposition is the result of the validity of Beer-Lambert's law for absorption measurements. $D = CS^T + E$, D is the original measurement and contains as rows the absorption spectra measured as a function of the reaction time. The matrices C and S^T contain, as columns, the kinetic profiles of the compounds involved in the process and as rows, their related spectra, respectively. E is the error-related matrix. Decomposition of the D matrix is achieved by the iterative optimization under the suitable constraints for C and S^T . Spectra profiles were evaluated using MCR-ALS¹¹. The best MCR-ALS results were obtained by assuming three components for BDAE and

two components for BDAP defined by applying the constraints of non-negativity (for both concentrations and signals), unimodality of the concentrations and closure (the sum of the concentrations of the isomers). Under such conditions, a lack of fit of 1.58% and $2.3 \times 10^{-3} \%$ were obtained for BDAE and BDAP respectively. These factors could be attributed to the three and two isomer for BDAE and BDAP. If four groups in compound BDAE and BDAP are totally different, there are four isomers based on two double bond, e.g., (*E,E*), (*E,Z*), (*Z,E*) and (*Z,Z*) isomers, in which there are only three isomers, e.g., (*E,E*), (*EZ = ZE*) and (*Z,Z*). The photoisomerizations are presented in Scheme 1 and 2 (that k_1 and k_2 are kinetic constants for first order mechanism).



The ground state energy difference between *EE*, *EZ* and *ZZ* isomers could be determined exactly by direct measurements (optimized with the AM1 method). It can be concluded that the ground state energy increases in the order $EE < EZ < ZZ$. It was calculated that the *EE* isomer is the most stable, followed by the *EZ* and *ZZ* isomers. The energy differences are $U_{ZZ}^0 - U_{EZ}^0 = 4.2 \text{ kcal mol}^{-1}$ and $U_{EZ}^0 - U_{EE}^0 = 6.1 \text{ kcal mol}^{-1}$ (for BDAE) and $U_{ZZ}^0 - U_{EZ}^0 = 0.9 \text{ kcal mol}^{-1}$ and $U_{EZ}^0 - U_{EE}^0 = 9.6 \text{ kcal mol}^{-1}$ (for BDAP), respectively. Because the difference between the forecasted energies of isomers *EZ* and *ZZ* (for BDAP) is minimal, it can be said that isomer *EE* is quickly changed into isomer *ZZ*.

The calculated spectra profile is shown in Figure 4 (BDAE). Kinetic constants were evaluated using non-linear least squares curve fitting by toolbox of MATLAB program using the concentration profiles and definition of exponential function (fitted exponential curves shown in Figure 5 and 6 with (-)). Kinetics constant value (k_1 and k_2) of BDAE are $8.8995 \times 10^{-2} \text{ min}^{-1}$ and $2.7454 \times 10^{-2} \text{ min}^{-1}$ (RMSE = 2.79×10^{-5}) respectively. For BDAP the obtained kinetics constant values is $2.0 \times 10^{-1} \text{ min}^{-1}$ (RMSE = 9.6×10^{-4}) (RMSE is root mean squares of errors).

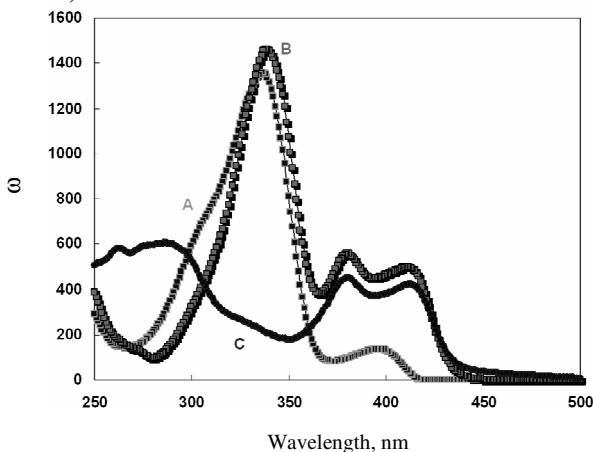


Figure 4. The pure absorption spectra of *EE* (A), *EZ* or *ZE* (B), *ZZ* (C) isomers of BDAE in chloroform

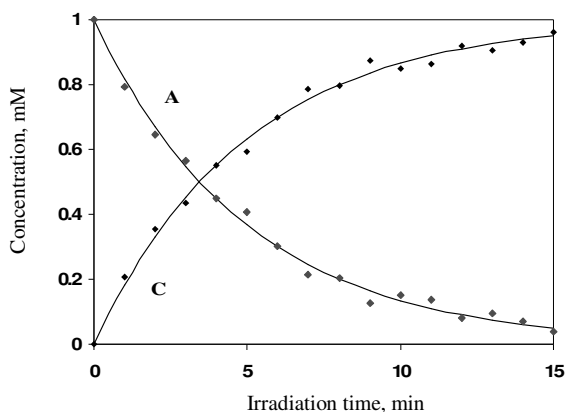


Figure 5. The concentration profiles of *EE* (A) and *ZZ* (C) isomers of BDAP (MCR-ALS (■) and fitted exponential function (—)).

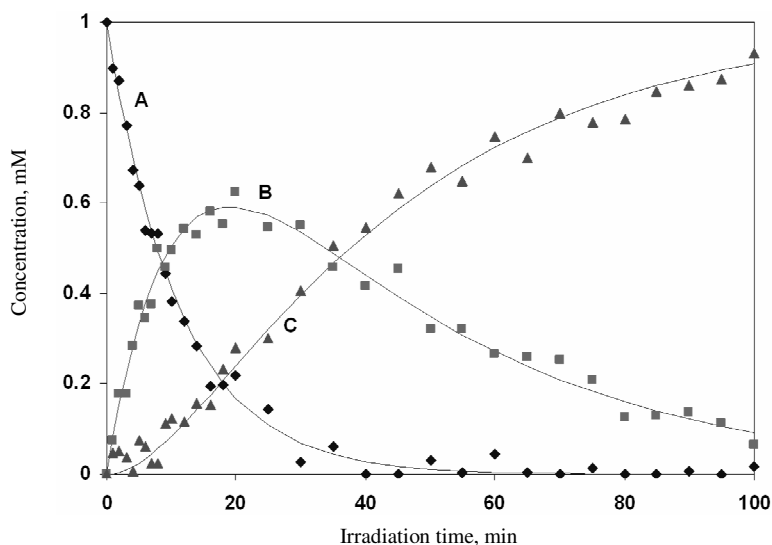


Figure 6. The concentration profiles of *EE* (A), *EZ* or *ZE* (B), *ZZ* (C) isomers of BDAE (MCR-ALS (■, ▲) and fitted exponential function (—)).

Quantum yield is a useful parameter to indicate the efficiency of a photochemical reaction which is defined as the number of probe molecules undergoing a specific chemical reaction divided by the number of photons absorbed. The quantum yield of photoisomerization can be calculated from the observed first-order rate constant, where a specific form of quantum yield, ϕ based on first-order kinetics was indicated in Eq. (1)²⁰:

$$\phi = k / 2.303I_{0,\lambda} \varepsilon_{\lambda} l \quad (1)$$

Where $I_{0,\lambda}$ is the incident light intensity at specific wavelength (Einstein $\text{l}^{-1} \text{s}^{-1}$). According to the data provided by the Southern New England Ultraviolet Company, intensity of 350 nm is 3.11×10^{-6} (24 W) $\text{E l}^{-1} \text{s}^{-1}$, ε_{λ} = molar absorptivity of compounds at 350 nm and l = cell path length (1 cm). For BDAE the obtained quantum yield values are 0.255 and 0.0594 for first and second stage respectively and 0.526 for BDAP.

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