Photochemical Properties of 4, 4'-[1, *n*-alkanediylbis[(E)-2-(4-oxyphenyl) ethenyl]]bispyridine*

Zhang Wen-Qin Wang Qin-Geng Zheng Yan Xu Li-Yong

Ren Rong-Liang¹ Liu Jin-Lan¹

(Department of Chemistry; ¹ Department of Physics, Tianjin University, Tianjin 300072)

Abstract 4, 4'-[1, *n*-alkanediylbis[(E)-2-(4-oxyphenyl) ethenyl]]bispyridine [*n* = 2 (**Ia**), 3 (**Ib**), 4 (**Ic**), 6 (**Id**)] were synthesized by the nucleophilic substitution of (E)-4-[2-(4-hydroxyphenyl) ethenyl] pyridine with 1, *n*-dibromoalkane. The structures of **Ia** ~ **Id** were identified by elemental analysis, IR, UV and ¹H NMR. The dilute solution of **Ia** ~ **Id** was irradiated alternatively by medium pressure mercury lamp and low pressure mercury lamp. The intramolecular photocycloaddition was observed and this reaction speeds up with the extension of the alkanediyl chain. It was also found that the photocycloaddition was increased in the presence of zinc cation because of its chelation with the nitrogen atom of the pyridine group. The fluorescence of these compounds is weak and the intermolecular excimer fluorescence is detected at higher concentration.

Keywords: Bispyridine, Intramolecular photocycloaddition, Excimer, Fluorescence (FL)

Recently, chemists are interested in researches on molecular switches^[1]. Among them, photochemical molecular switch is supposed to be the fastest one which might be applied to make the molecule-based computers in the future^[2]. The photocycloaddition of heteroarylethenes has been studied systematically by our group. Irradiated under UV light, heteroarylethenes undergo reversible photocycloaddition^[3-6] through the excited singlet state. This reversible photoreaction causes large shift in the absorption spectra or in the emission spectra, which makes these compounds suitable for ideal molecular switches. However, the photocycloaddition is a bimolecular process, and the forward reaction is pretty slow and strongly depends on the concentration^[7-8] of the alkene. In this paper, two parts of alkenes were linked with a flexible alkanediyl chain and the intermolecular process is changed into an intramolecular one. The photochemical switching prop-

erties of the latter were investigated by UV and FL.

1 Experiment

1.1 Apparatus

Melting points were taken on a Yanagimoto MP-500 apparatus (uncorrected). Elemental analyses were determined on a Yanaco CHNCORDER MF-3 apparatus. The IR spectra were recorded on a BIO-RAD FTS 3000 infrared spectrometer. The UV and FL spectra were performed on a HP 8453 UV-visible and on a 970CRT FL (sensitivity: 4) spectrophotometer, respectively. The ¹H NMR was taken from a Varian Gemini 200 instrument using TMS as internal standard.

1.2 Preparation of 4, 4'-[1, *n*-alkanediylbis[(E)-[2-(4-oxyphenyl) ethenyl]]bispyridine

20 mmol of trans-4-[2-(4-hydroxyphenyl) ethe-

ethenyl]pyridine^[9], 40 mmol of anhydrous potassium carbonate, 40 mL of DMF were put in a round bottom flask. Then 10 mmol of 1, *n*-dibromoalkane was added dropwise at room temperature under magnetic stirring. After that the reaction mixture was stirred for another 24 h. The precipitate was collected by filtration and was recrystallized from DMF.

1a yield 10% , mp 247 ~ 249 °C ; IR (KBr): 1640(w), 1588(s), 1506(s), 1452(s), 1232(s), 968(s), 830(s) cm^{-1} ; UV (1, 4-dioxane): $\lambda_{\text{max}} = 326 \text{ nm}$ ($\lg \varepsilon = 4.76$); $^1\text{H NMR}$ (DMSO- d_6): δ 8.50 (d, 4H, $\text{C}_5\text{H}_4\text{NCH}=\text{CH}-$, $J=5.6 \text{ Hz}$), 7.6 ~ 7.0 (m, 16H, ArH), 4.37 (s, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$). Anal. Calcd. for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_2$: C, 80.00; H, 5.71; N, 6.67. Found: C, 80.10; H, 6.06; N, 6.89.

1b yield 26% , mp 189 ~ 191 °C ; IR (KBr): 1640(w), 1590(s), 1514(s), 1468(s), 1246(s), 968(s), 828(s) cm^{-1} ; UV (1, 4-dioxane): $\lambda_{\text{max}} = 324 \text{ nm}$ ($\lg \varepsilon = 4.73$); $^1\text{H NMR}$ (CDCl_3): δ 8.52 (d, 4H, $\text{C}_5\text{H}_4\text{NCH}=\text{CH}-$, $J=5.6 \text{ Hz}$), 7.4 ~ 6.9 (m, 16H, ArH), 4.19 (t, 4H, $-\text{OCH}_2-$, $J=6.4 \text{ Hz}$), 2.28 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2-$). Anal. Calcd. for $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}_2$: C, 80.18; H, 5.99; N, 6.45. Found: C, 79.80; H, 6.03; N, 6.26.

1c yield 80% , mp 246 ~ 248 °C ; IR (KBr): 1632(w), 1581(s), 1506(s), 1470(m), 1239(s), 969(s), 828(s) cm^{-1} ; UV (1, 4-dioxane): $\lambda_{\text{max}} = 326 \text{ nm}$

($\lg \varepsilon = 4.71$); $^1\text{H NMR}$ (DMSO- d_6): δ 8.54 (d, 4H, $\text{C}_5\text{H}_4\text{NCH}=\text{CH}-$, $J=5.6 \text{ Hz}$), 7.6 ~ 7.0 (m, 16H, ArH), 4.12 (t, 4H, $-\text{OCH}_2-$, $J=6.4 \text{ Hz}$), 1.92 (m, 4H, $-\text{OCH}_2\text{CH}_2-$). Anal. Calcd. for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2$: C, 80.30; H, 6.25; N, 6.25. Found: C, 79.96; H, 6.40; N, 6.38.

1d yield 67% , mp 207 ~ 208 °C ; IR (KBr): 1630(w), 1584(s), 1503(s), 1479(s), 1239(s), 972(s), 831(s) cm^{-1} ; UV (1, 4-dioxane): $\lambda_{\text{max}} = 326 \text{ nm}$ ($\lg \varepsilon = 4.68$). $^1\text{H NMR}$ (DMSO- d_6): δ 8.50 (d, 4H, $\text{C}_5\text{H}_4\text{NCH}=\text{CH}-$, $J=5.6 \text{ Hz}$), 7.6 ~ 7.0 (m, 16H, ArH), 4.01 (t, 4H, $-\text{OCH}_2-$, $J=6.4 \text{ Hz}$), 1.75 (s, br, 4H, $-\text{OCH}_2\text{CH}_2-$), 1.49 (s, br, 4H, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$). Anal. Calcd. for $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_2$: C, 80.40; H, 6.72; N, 5.88. Found: C, 80.40; H, 6.83; N, 5.93.

1.3 Photolysis

Solutions containing $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of **1a** ~ **1d** in different media were put in quartz colorimetric cells and irradiated with a 125 W medium pressure mercury lamp (MPML) or a 20 W low pressure mercury lamp (LPML) for certain time. The photochemical changes were traced by UV (Fig. 1 and 2). In order to compare the changes, (E)-4-[2-(4-methoxyphenyl)ethenyl]pyridine (**1o**) was chosen as a reference.

2 Results and Discussion

The yields of **1a** and **1b** are rather low. It is easy to understand that 1, 2-dibromoethane adopts anti-conformation, and the back side attack of the nucleophile is restricted by the other bromine atom. As for **1b**, the energy of the intermediate is calculated by molecular orbital package (MOPAC) program. The heat of formation of the gauche conformation is 105.62 $\text{kJ} \cdot \text{mol}^{-1}$, while that of the anti-conformation is 105.96 $\text{kJ} \cdot \text{mol}^{-1}$, indicating that the gauche conformation is the probable conformation. So the back side attack of the second nucleophile is restricted by the first one, which results in low reaction yields. When phenoxide is chosen as the nucleophile, 1, 4-dibromobutane also has higher yield (98%) than that of 1, 3-dibromopropane (47%)^[10]. This kind of nucle-

ophilic substitution restriction does not exist in 1, 4- or 1, 6-dibromoalkane.

The stretch vibration of pyridine skeleton in the IR spectra of **Ia** ~ **Id** was found at the range of 1581 ~ 1590 cm^{-1} . The C – O stretch vibration between phenyl and alkyl was recorded at about 1240 cm^{-1} . The out-of-plane bending vibration of =C – H bond was observed at 968 ~ 972 cm^{-1} , which indicates that the phenylethenylpyridine group in **Ia** ~ **Id** has trans configuration. The UV and FL spectra of **Ia** ~ **Id** with a maximum absorption at 326 nm and a maximum emission at 408 nm are alike to each other because of the similarity of chromophore structures.

$1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of **Io** in $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl-H₂O solution or in $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ZnSO₄-EtOH solution was irradiated under MPML for 1 min (Fig. 2). The maximum peak of **Io** decreased rapidly at first, then the change stopped although with extending the irradiation time, indicating that the only photochemical reaction of **Io** is trans-cis isomerization and the equilibrium is established very quickly^[5,7]. The recorded spectrum is the absorption of the mixture of trans and cis isomers. It was supposed that in the dilute solution, the intermolecular photocycloaddition is difficult to occur because of the low collision probability and the short life time of the excited singlet state. When $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of **Ia** ~ **Id** in $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl-H₂O was irradiated under the same condition, the absorption also decreases rapidly at the beginning, which means these bifunctional compounds

undergo similar trans-cis isomerization. However, when the irradiation time was extended, the absorption spectra of **Ia** ~ **Id** decline smoothly with the order of **Ia** > **Ib** > **Ic** > **Id**^[11]. The enthalpy change of **Ia** ~ **Id** before and after intramolecular photocycloaddition was calculated by using MOPAC program. It was found that the intramolecular photocycloaddition of **Ia** and **Ib** are heat absorption reactions while that of **Id** is heat releasing. The enthalpy changes from **Ia** to **Id** are 39.7, 34.3, 2.9 and -5.9 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. The calculated results coincide with the experimental one. Furthermore, it was also found that the order of magnitude of the photocycloaddition reaction rate in different media is: $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl (water) > $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl (ethanol) > ethanol. These results proved that acidic water is the best medium^[7] for the photocycloaddition. The investigation also revealed that when **Ia** ~ **Id** were irradiated under MPML in $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ZnSO₄-ethanol solution, the absorption spectrum decreased rapidly and **Ia** ~ **Id** almost showed similar rate. However, even in the presence of Zn²⁺, **Io** only underwent trans-cis isomerization. This result suggests that there exists large ring chelation between zinc cation and the pyridine nitrogen atom, which makes the double bond of **Ia** ~ **Id** approach to each other and easy to proceed intramolecular photocycloaddition.

When the photocycloaddition products were irradiated under LPML for 30 s, the decreased peak arises again (Fig. 1(#)) and 2(#)), which shows that these

Fig. 1 UV spectra of $10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of **Ib** and **Id** in $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl

0) 0; 1) 1; 2) 5; 3) 20; 4) 60 min; irradiated under MPML; #) 30 s under LPML

Fig. 2 UV spectra of $10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of **Io** and **Ia** in $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ZnSO_4 -ethanol solution

0) 0; 1) 1; 2) 5; 3) 20; 4) 60 min; irradiated under MPML, #) 30 s under LPML

compounds exhibit photochemical switching characters. This change indicates that under the irradiation of LPML, the original bifunctional compound is reproduced by photolysis, and the backward reaction is faster than the forward one.

The fluorescence spectra of **Io**, **Ib** or **Id** in ethanol were measured. At lower concentration, the monomer emission spectrum ($\lambda_{\text{max}} = 408 \text{ nm}$) is weak, indicating that the excited energy is converted into chemical energy *via* trans-cis isomerization^[5,7]. At

higher concentration, a new emission peak ($\lambda_{\text{max}} = 486 \text{ nm}$) appears. Since all of these compounds show similar emission spectra, this new peak is attributed to the intermolecular excimer fluorescence. The formation of the intermolecular excimer restricts the trans-cis isomerization, so the excimer fluorescence is stronger than that of the monomer. Isoemissive points in **Io** and **Ib** were observed in Fig. 3, suggesting that there exist only monomer and intermolecular excimer fluorescences. In the case of **Id**, the extension of the carbon

Fig. 3 FL spectra of **Io** ($2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$), **Ib** and **Id** ($a \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$)

a: 1) 0.1, 2) 0.4, 3) 1.0, 4) 4.0, 5) 10.0, 6) 15.0, 7) 25.0, $[\text{ZnSO}_4] = 1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$

chain makes the two chromophore interact with each other easily, and the intramolecular excimer fluorescence appears, which is less effected by the concentration quenching. So the recorded spectra of **Id** comprise the fluorescence of the monomer as well as that of intermolecular and intramolecular excimers, which make the lose of the iosemmissive point. When the concentration excesses $4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, the excimer fluorescence trail off following the order **Io** > **Ib** > **Id**. This should be due to the concentration quenching of multiple molecular aggregation. With the extension of the alkanediyl chain, the multiple molecular aggregation is restrained. For example, the excimer fluorescence of **Ib** disappears at $2.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, while that of **Id** does not (Fig. 3, **Id**, curve 7). The intramolecular excimer fluorescence of **Ib** ~ **Ic** with or without the presence of Zn^{2+} can not be detected at any concentration, suggesting that in the presence of zinc, the intramolecular excimer complex underwent photocycloaddition easily and did not illuminate.

References

- 1 Michael D W. *J. Chem. Edu.*, **2001**, **78**(3): 321
- 2 Gosztola D, Niemczyk M P, Wasielewski M. *J. Am. Chem. Soc.*, **1998**, **120**: 5118
- 3 Zhang W Q, Wang M Z, Wang H G. *Science in China(Series B)*, **1996**, **39**(1): 105
- 4 Zhang WQ, Zhang MJ, Wang JX, Yang XR, Wang SL, Jiang Q, An Y. *Acta Chimica Sinica*, **1998**, **56**(6): 612 [张文勤, 张明杰, 王家喜, 杨学茹, 王淑丽, 江 琴, 安 颖. 化学学报 (*Huaxue Xuebao*), **1998**, **56**(6): 612]
- 5 Zhang W Q, Zhuang J P, Li C B, Sun H, Yuan X N. *Chinese J. Chem.*, **2001**, **19**(7): 695
- 6 Zhang WQ, Zhang ZM, Zheng Y, Wang SL, Zhao SN. *Acta Phys.-Chim. Sin.*, **2000**, **16**(3): 207 [张文勤, 张志明, 郑 艳, 王淑丽, 赵抒娜. 物理化学学报 (*Wuli Huaxue Xuebao*), **2000**, **16**(3): 207]
- 7 Zhang WQ, Zhang XH, Zheng Y, Shen G, Zhuang JP. *Photographic Sci. Photochem.*, **2000**, **18**(2): 144 [张文勤, 张西慧, 郑 艳, 沈 刚, 庄俊鹏. 感光科学与光化学 (*Ganguangkexue yu Guanghuaxue*), **2000**, **18**(2): 144]
- 8 Zhang W Q, Shen G, Zhuang J P, Zheng P W, Sun H. *J. Photochem. Photobiol. A, Chem.*, in press
- 9 Lees W A, Burawoy A. *Tetrahedron*, **1963**, **19**: 419
- 10 Wang Shuli. Master dissertation. Tianjin University, 1998
- 11 Zhang WQ, Wang SL, Zhao HT, Zhuang JP, Sun H, Zhao SN, Zheng Y, Li CB. *Chem. J. Chinese Universities*, **2000**, **21**(8): 1211 [张文勤, 王淑丽, 赵海涛, 庄俊鹏, 孙 浩, 赵抒娜, 郑 艳, 李春葆. 高等学校化学学报 (*Gaodeng Xuexiao Huaxue Xuebao*), **2000**, **21**(8): 1211]

4, 4'-[1, *n*- 亚烷基双[(E)-2-(4- 氧苯基)乙烯基]]双吡啉的光化学性质*

张文勤 王勤耕 郑 艳 徐立勇 任荣良¹ 刘金兰¹

(天津大学化学系; ¹天津大学物理系, 天津 300072)

摘要 通过 E-[4-[2-(4- 羟基苯基)乙烯基]吡啉与 1, *n*- 二溴烷烃亲核取代反应合成了 4, 4'-[1, *n*- 亚烷基双[(E)-2-(4- 氧苯基)乙烯基]]双吡啉 [*n* = 2(**Ia**), 3(**Ib**), 4(**Ic**), 6(**Id**)]。用元素分析、红外、紫外和质子核磁共振谱鉴定了 **Ia** ~ **Id** 的结构。将 **Ia** ~ **Id** 的稀溶液用中压汞灯和低压汞灯交替照射, 发现其分子内光环加成反应的存在, 并且随着亚烷基碳链的延长, 反应速度加快。研究还发现锌离子可以与吡啉环上氮原子发生螯合作用使分子内光环加成反应加快。本文化合物荧光很弱, 在较高浓度下有较强分子间激基缔合物荧光。

关键词: 双吡啉, 分子内光环加成, 激基缔合物, 荧光

中图分类号: O641, O644