[2 + 2] Photodimerization of Naphthylvinylpyridines through Cation-π Interactions in Acidic Solution

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Abstract: Irradiation of (E)-4-(2-(2-naphthyl)vinyl)pyridine (1a) and (E)-4-(2-(1-naphthyl)vinyl)pyridine (1b) with a 250 W high-pressure mercury lamp in acidic solution afforded synHT dimers in high stereoselectivities. Similar results were obtained by visible light irradiation. On the other hand, when the reactions were carried out under neutral conditions, the stereoselectivities were very low, and the yields were decreased by visible light irradiation. Comparison of the UV-vis spectra between the acidic and the neutral conditions elucidated that the red shift was observed in acidic solutions. These results show that HCl plays essential roles not only in the preorientation of substrates through cation-π interactions, but also in the changes in the absorption properties of substrates that enable visible light reactions.

Keywords: cation-π interaction; [2 + 2] photodimerization; cyclobutane derivative; naphthylvinylpyridine; stereoselective reaction

1. Introduction

Controlling the association mode of substrate alkenes during [2 + 2] photodimerization is a key subject in organic photochemistry [1–4], as it is essential for the regio- and stereoselective formation of cyclobutane dimers. Various approaches for the alignment of molecules have been developed using a variety of organized media [5], organic crystals [6–10], metal–organic frameworks [11,12], metal complexes [13,14], and supramolecular systems [15,16]. Previously, we reported that a cation-π interaction [17] between a pyridinium salt and a benzene ring plays an essential role on the product distribution in the [2 + 2] photodimerization of styrylpyridines [18–20]. This preorientation process is responsible for various stereoselective photodimerization reactions not only in solution, but also in crystals [21,22].

It has been reported that the size of the π-system is significantly correlated with the strength of the cation-π interactions; for example, the interaction energy of a sodium cation with naphthalene is 2–3.5 kcal/mol larger than that with benzene [23,24]. This prompted us to investigate the [2 + 2] photodimerization of naphthylvinylpyridines having more extended π-systems than those of styrylpyridines. In this paper, we report that the photodimerization of naphthylvinylpyridines 1a and 1b (Figure 1) in acidic solution provides synHT dimers with very high regio- and stereoselectivities through cation-π interaction, even under irradiation with visible light.
2. Results and Discussion

(E)-4-(2-(2-Naphthyl)vinyl)pyridine (1a) [25] and (E)-4-(2-(1-naphthyl)vinyl)pyridine (1b) [25] were employed as substrates for the photochemical reactions, the π-conjugate systems of which differed from each other (Figure 1). Irradiation of 1a in a 1.0 M THF solution with a 450 W high-pressure mercury lamp for 8 h under neutral conditions afforded all four possible dimers 2a–5a. SynHT dimer 3a was the major product, but the selectivity was quite low—as shown in Table 1 (entry 1). The conversion and the product ratios were determined based on 1H-NMR spectra. Though the reaction was carried out in a 0.067 M MeOH solution due to the much lower solubility of 1a than that in THF, a similar result was observed (entry 2). Photolysis in the presence of 1 equiv. of conc. hydrochloric acid resulted in remarkable changes in the product distribution (entry 3); the synHT adduct 2a increased to become the major product along with a small amount of 3a and 4a. As the amount of HCl loading increased to 3 equiv., the yield of the synHT dimer 2a increased to 93% (entry 4).

| Entry | Compd. | HCl (eq.) | Solvent b | Conv. (%) c | Products (%) |
|-------|--------|-----------|-----------|-------------|--------------|
| 1     | 1a     | 0         | THF       | 99          | 21 46 14 17 0 |
| 2     | 1a     | 0         | MeOH      | 82          | 22 50 12 4 11 |
| 3     | 1a     | 1         | MeOH      | 98          | 90 6 4 0 0 |
| 4     | 1a     | 3         | MeOH      | 99          | 93 2 3 2 0 |
| 5     | 1b     | 0         | MeOH      | 91          | 45 35 6 0 14 |
| 6     | 1b     | 1         | MeOH      | 91          | 75 0 0 0 25 |
| 7     | 1b     | 1         | MeOH/H2O  | 93          | 94 0 0 0 6 |
| 8     | 1b     | 3         | MeOH/H2O  | 93          | 94 0 0 0 6 |

* External irradiation was carried out through Pyrex filter in cooling water. A 1.0 M solution was employed unless otherwise noted. c Determined by 1H-NMR. d Naphtha [2,1-h] isouquinoline was obtained in 2% yield. e A 0.067 M solution was used. f A 0.67 M solution was used.

Figure 2a,b show the 1H-NMR spectra of 1a after irradiation in the absence and presence of 3 equiv. of HCl, respectively. A comparison clearly demonstrates the significant effect of the acid on the product distribution. Figure 2a shows multi-peaks around δ 3.7 to 4.8 for the methine protons of the four cyclobutane dimers. On the other hand, in the presence of 3 equiv. of HCl, the four methine protons appear at δ 4.59 and 4.62, indicating exclusive formation of 2a (Figure 2b).

Irradiation of 1b in the absence of the acid gave a mixture of 2b–4b and (Z)-isomer (entry 5). In the presence of 1 equiv. of HCl, the solubility of 1b decreased; therefore, the reaction was carried out in a 0.67 M MeOH solution. The acid demonstrated a significant effect similar to that in the case of 1a; synHT dimer 2b was obtained in 75% yield with no other dimers along with 25% of (Z)-isomer (entry 6). A survey of the solvents found that a 9:1 mixture of MeOH and H2O had a good solubility for 1b·HCl. Using this solvent system, irradiation of a 1.0 M solution of 1b in the presence of acid...
significantly improved the selectivity to 94%, suggesting the importance of concentration in obtaining good selectivities in these reactions (entries 7 and 8).

![Figure 2. 1H-NMR spectra in CDCl3 for (a) 1a after irradiation for 24 h; and (b) 1a after irradiation in the presence of 3 eq. of HCl and successive neutralization.](image)

Another remarkable feature observed under the acidic conditions was that visible light could also induce photodimerization. When the irradiation of 1a was carried out with a 250 W high-pressure mercury lamp through a UV-cut filter for 3 h, only (Z)-isomer was produced in 7% yield (Table 2, entry 1). On the contrary, in the presence of HCl, the reaction proceeded to provide syn-HT dimer 2a in a similar selectivity to that obtained by UV-light irradiation (entry 2). Irradiation of 1b in the absence of the acid gave dimers 2b and 3b in low yields, whereas in the presence of the acid, 2b was produced in a significantly high yield (entries 3 and 4).

| Entry | Compd. | HCl (eq.) | Solvent   | Conv. (%) | Products (%) bc |
|-------|--------|-----------|-----------|-----------|----------------|
| 1     | 1a     | 0         | THF       | 7         | 0 0 0 0 100    |
| 2     | 1a     | 1         | MeOH      | 93        | 3 2 2 0        |
| 3     | 1b     | 0         | MeOH      | 48        | 46 39 0 0 15   |
| 4     | 1b     | 1         | MeOH/H2O  | 90        | 88 0 0 0 10     |

* Spot irradiation was carried out through quartz fibers with a UV-cut filter. b A 1.0 M solution was employed unless otherwise noted. c Determined by 1H-NMR.

The remarkable differences in the photoreactivities whether in the presence or absence of HCl can be explained by differences in their absorption properties. UV-vis spectra for 1a, 1b, 1a-HCl, and 1b-HCl are shown in Figure 3. The longest absorption bands of 1a and 1b in MeOH appeared at 319.0 and 331.0 nm, respectively. On the other hand, in the presence of HCl these bands were shifted to longer wavelengths and observed at 331.0 and ca. 360 nm, respectively, the shoulders of which exceeded 400 nm. These changes in the absorption properties induced by the acid are thought to be responsible for the visible light photodimerization in acidic media.
Figure 3. UV-vis spectra in EtOH for (a) 1a (2.09 × 10⁻⁵ mol/L); (b) 1a·HCl (1.80 × 10⁻⁵ mol/L); (c) 1b (2.34 × 10⁻⁵ mol/L); and (d) 1b·HCl (1.82 × 10⁻⁵ mol/L).

The structures of the product dimers were determined from X-ray crystallographic analyses and the ¹H-NMR and MS spectra. The X-ray analyses were carried out for 2a, 2b·2HCl, 3b, and 4a, as single crystals suitable for X-ray analyses were obtained. Figure 4 clearly shows that 2a and 2b are synHT dimers, and 3b and 4a are synHH and antiHT dimers, respectively. Based on MS and ¹H-NMR analyses, 3a and 5a were assigned as synHH and antiHH dimers, respectively. In their MS spectra, the fragment peaks of m/z 231 and 280 were observed. The peak of m/z 231 corresponds to a naphthylethylpyridine moiety, and the peak of m/z 280 corresponds to a binaphthylethane moiety, indicating their head-to-head structures (Figures S8, S9, S12, and S13). The methine protons at δ 4.67 and 4.69 for 3a and δ 3.88 and 3.97 for 5a are very close to those of related synHH and antiHH dimers, respectively [18]. The assignment of 4b was also performed by MS spectra; the observations of a base peak of m/z 231 with no peak of m/z 280 are characteristic of the head-to-tail structures (Figures S10 and S11). In addition, since 2b was assigned as a synHT dimer by X-ray analysis, 4b should be an antiHT dimer.

Figure 4. X-ray structures of 2a, 2b·2HCl, 3b, and 4a.
To obtain mechanistic insights into the dimerization process, the dependence of product distribution on the irradiation time was investigated. Figure 5 shows plots of the yields of synHT dimer 2a vs. irradiation time. The yield of 2a increased with increased irradiation time, with the curve following second-order kinetics. This suggests that the dimerization process does not involve any other processes, such as a reverse reaction or isomerization reaction. The second-order kinetics was confirmed by plots of t vs. 1/[1a], in which a linear correlation was observed (Figure S14).

![Figure 5. Plots of the yield of 2a vs. irradiation time.](image)

The preference for the formation of the synHT dimer in the presence of HCl agrees with that in the photodimerization of styrylpyridine [18]. This synHT preference indicates that the intermediate naphthylvinylpyridinium salts form preorganized head-to-tail molecular dimers through intermolecular cation-π interactions, as shown in Scheme 1. The fact that the selectivities observed in the photodimerization of 1a and 1b are much higher than that in the case of styrylpyridine (71% selectivity) [18] suggests a significant effect of the naphthyl group on the intermolecular cation-π interactions, regardless of the differences in the π-conjugate systems.

![Scheme 1. Formation of a synHT dimer 2a through cation-π interactions.](image)

It has been reported that the larger aromatic π-conjugate systems are more effective for cation-π interactions. For example, the threshold collision-induced dissociation technique clarified that extended π-network leads to an increase in the strength of the cation-π interaction due to increased polarizability of the ligand [23]. The B3LYP calculations for the binding energy of Na⁺···naphthalene predicted that the energy is larger than that of Na⁺···benzene [24]. These experimental and theoretical studies agree with the higher selectivities observed in the photodimerization of 1a and 1b than that of styrylpyridine.

3. Materials and Methods

3.1. General Methods

Melting points were determined with a Yanaco model MP microscope (Yanaco, Tokyo, Japan). Column chromatography was carried out using silica gel 60 N (Kanto Chemical, Tokyo, Japan). Thin
layer chromatography (TLC) was carried out on a Merck silica gel 60 PF254 (Merck, Tokyo, Japan). IR spectra were obtained on FT/IR-410 spectrometer (JASCO, Tokyo, Japan) as neat films between NaCl plates, or KBr pellets. NMR spectra were recorded on JEOL EX-400 spectrometer (JEOL, Tokyo, Japan). 1H-NMR spectra were obtained at 400 MHz as dilute solution in CDCl3, and the chemical shifts were reported relative to internal TMS. Low-resolution mass spectra were recorded at ionizing voltage of 70 eV by electron impact. High-resolution mass spectra were recorded on Exactive Orbitrap LC-MS (Thermo-Fischer, Yokohama, Japan). UV/vis spectra were recorded on JASCO V-650DS spectrometer (JASCO, Tokyo, Japan) in MeOH. UV irradiation was performed using a 450 W high-pressure mercury lamp (USHIO UM453, Tokyo, Japan). Visible-light irradiation was performed using a 250 W high-pressure mercury lamp (ASAHI SPECTRA REX-250, Tokyo, Japan) through quartz fibers with a UV-cut filter.

3.2. Representative Procedure for Irradiation of Naphthylvinylpyridines under Acidic Conditions

A solution of naphthylvinylpyridine (0.1 mmol) in 100 μL of MeOH containing conc. HCl was irradiated for 8 h through a Pyrex filter with a 450 W high-pressure mercury lamp. The solution was neutralized with sat. NaHCO3, and the solvent was evaporated to give an oil. This oil was extracted with CH2Cl2 three times, and the combined organic layer was dried over anhydrous MgSO4. Evaporation of the solvent gave a crude product, which was subjected to column chromatography on silica gel with a 7:2:1 mixture of ethyl acetate, hexane, and methanol as an eluent. The product ratio was determined by the 1H-NMR spectrum of the crude product. Visible-light irradiation of the above-mentioned solution was carried out with a 250 W high-pressure mercury lamp for 3 h through a UV-cut filter. The work-up followed the same procedure as that described above.

Compound 2a: Pale-yellow crystals; m.p. 196–197 °C; 1H-NMR (400 MHz, CDCl3) δ 8.32 (d, J = 5.6 Hz, 4H), 7.72–7.75 (m, 4H), 7.63–7.65 (m, 4H), 7.42–7.45 (m, 4H), 7.17 (dd, J = 8.6, 2.0 Hz, 2H), 7.06 (d, J = 6.0 Hz, 4H), 4.72–4.77 (m, 2H), 4.60–4.64 (m, 2H); IR (KBr) 3018, 1597, 1552, 1509, 1414, 994, 861, 813, 763 cm−1; MS m/z 462 (M+, 0.6%), 232 (20), 231 (100), 230 (64), 203 (8), 202 (13). HRMS calcd. for C34H27N2 463.21742 (M + H)+, found 463.21501.

Compound 3a: Pale-yellow crystals; m.p. 113–114 °C; 1H-NMR (400 MHz, CDCl3) δ 8.43 (d, J = 4.4 Hz, 4H), 7.65–7.69 (m, 6H), 7.53 (d, J = 8.0 Hz, 2H), 7.34–7.42 (m, 4H), 7.15 (dd, J = 8.6, 2.0 Hz, 2H), 7.09 (d, J = 6.0 Hz, 4H), 4.66–4.70 (m, 4H); IR (KBr) 3053, 2972, 1599, 1508, 1422, 1115, 995, 820, 746 cm−1; MS m/z 462 (M+, 0.6%), 280 (26), 279 (18), 232 (39), 231 (100), 230 (96), 202 (13). HRMS calcd. for C34H27N2 463.21742 (M + H)+, found 463.21715.

Compound 4a: Pale-yellow crystals; m.p. 225–226 °C; 1H–NMR (400 MHz, CDCl3) δ 8.53 (d, J = 4.8 Hz, 4H), 7.80–7.89 (m, 8H), 7.46–7.52 (m, 6H), 7.21 (d, J = 6.0 Hz, 4H), 3.96–4.01 (m, 2H), 3.84–3.89 (m, 2H); IR (KBr) 3053, 2927, 1597, 1415, 1068, 817, 751 cm−1; MS m/z 462 (M+, 1.2%), 232 (26), 231 (100), 230 (89), 202 (18). HRMS calcd. for C34H27N2 463.21742 (M + H)+, found 463.21560.

Compound 5a: A colorless oil; 1H-NMR (400 MHz, CDCl3) δ 8.57 (d, J = 6.0 Hz, 4H), 7.78–7.83 (m, 6H), 7.75 (s, 2H), 7.45–7.48 (m, 4H), 7.40 (dd, J = 8.6, 2.0 Hz, 2H), 3.96–3.98 (m, 2H), 3.86–3.89 (m, 2H); IR (KBr) 3053, 2927, 1597, 1415, 1068, 817, 751 cm−1; MS m/z 462 (M+, 3.7%), 370 (13), 281 (11), 280 (44), 279 (27), 278 (15), 232 (37), 231 (100), 230 (89), 229 (13), 202 (15). HRMS calcd. for C34H27N2 463.21742 (M + H)+, found 463.21693.

Compound 2b: Pale-yellow crystals; 263–265 °C; 1H-NMR (400 MHz, CDCl3) δ 8.20 (d, J = 6.0 Hz, 4H), 7.97 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.43–7.50 (m, 6H), 7.36–7.40 (m, 2H), 7.02 (dd, J = 4.4, 1.2 Hz, 4H), 5.26 (dd, J = 9.6, 7.6 Hz, 2H), 4.86 (dd, J = 9.6, 7.6 Hz, 2H); IR (KBr) 3035, 2927, 1597, 1415, 1068, 817, 773, 681 cm−1; MS m/z 462 (M+, 0.2%), 232 (30), 231 (100), 230 (81), 203 (7), 202 (12), 153 (21), 152 (13). HRMS calcd. for C34H27N2 463.21742 (M + H)+, found 463.21440.

Compound 3b: White crystals; 206–208 °C; 1H-NMR (400 MHz, CDCl3) δ 8.45 (d, J = 6.0 Hz, 4H), 7.89 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.28–7.38 (m, 6H), 7.19–7.23 (m, 2H),
7.12 (d, J = 6.0 Hz, 4H), 5.40–5.42 (m, 2H), 4.61–4.63 (m, 2H); IR (KBr) 3050, 1941, 1601, 1548, 1509, 1408, 999, 784 cm⁻¹; MS m/z 462 (M⁺, 1.1%), 280 (10), 279 (7), 232 (27), 231 (100), 230 (62), 202 (10), 153 (15), 152 (11). HRMS calcd. for C₃₄H₂₇N₂ 463.21742 (M + H)+, found 463.21515.

Compound 4b: A pale-yellow oil: ¹H-NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 5.6 Hz, 4H), 7.86 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 6.4 Hz, 4H), 7.65 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.22–7.25 (m, 2H), 7.21 (d, J = 6.4 Hz, 4H), 4.60–4.65 (m, 2H), 4.07–4.12 (m, 2H); IR (KBr) 3049, 1598, 1559, 1507, 1413, 993, 800, 781 cm⁻¹; MS m/z 462 (M⁺, 1.9%), 232 (47), 231 (100), 230 (89), 202 (12). HRMS calcd. for C₃₄H₂₇N₂ 463.21742 (M + H)+, found 463.21515.

3.3. X-ray Crystallography

Single crystals of dimers were mounted on a CryoLoop (Hampton Research, Aliso Viejo, CA, USA). All measurements were made on a Rigaku RAXIS RAPID II imaging plate area detector (Rigaku, Tokyo, Japan) with graphite monochromated Cu-Kα radiation at −150 °C. The structures were solved by the direct method and refined by full-matrix least squares on F² using SHELXL 97 [26]. Crystal Data for 2a (M = 462.59 g/mol): monoclinic, space group P2₁, a = 10.5616(6) Å, b = 9.5453(6) Å, c = 13.5147(7) Å, β = 110.173(2)°, V = 1278.89(12) Å³, Z = 4, Dcalc = 1.201 g/cm³, 14,679 reflections measured, 4523 unique (Rint = 0.0404). The final R1 was 0.0761 (l > 2σ(l)) and wR2 was 0.2912 (all data). CCDC 747473 contains the supplementary crystallographic data for this paper. Crystal Data for 2b·2HCl·2H₂O (M = 571.54 g/mol): monoclinic, space group Cc, a = 13.6293(5) Å, b = 17.9154(7) Å, c = 12.9243(5) Å, β = 110.971(2)°, V = 2946.8(2) Å³, Z = 4, Dcalc = 1.288 g/cm³, 16,003 reflections measured, 4988 unique (Rint = 0.0583). The final R1 was 0.0552 (l > 2σ(l)) and wR2 was 0.1779 (all data). CCDC 747474 contains the supplementary crystallographic data for this paper. Crystal Data for 3b (M = 462.59 g/mol): monoclinic, space group P2₁/c, a = 13.4512(6) Å, b = 13.1979(5) Å, c = 14.7875(7) Å, β = 110.782(2)°, V = 2454.38(19) Å³, Z = 4, Dcalc = 1.252 g/cm³, 26,569 reflections measured, 4443 unique (Rint = 0.0451). The final R1 was 0.0570 (l > 2σ(l)) and wR2 was 0.2043 (all data). CCDC 747475 contains the supplementary crystallographic data for this paper. Crystal Data for 4a (M = 462.59 g/mol): orthorhombic, space group Pbcₐ, a = 22.5434(4) Å, b = 8.91677(10) Å, c = 49.7495(10) Å, V = 10,000.4(3) Å³, Z = 12, Dcalc = 0.922 g/cm³, 104,123 reflections measured, 9132 unique (Rint = 0.0690). The final R1 was 0.0648 (l > 2σ(l)) and wR2 was 0.2166 (all data). CCDC 747476 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

4. Conclusions

[2 + 2] Photodimerization of naphthylvinylpyridines in the presence of HCl in MeOH gave synHT dimers with excellent regio- and stereoselectivities. This synHT preference strongly suggests the formation of preorganized head-to-tail molecular dimers from the intermediate naphthylvinylpyridinium salts through intermolecular cation–π interactions. The much higher selectivities compared to that of styrylpyridine reveal the effectiveness of the extended π-systems on the selectivity of the photodimerization. Another remarkable feature observed under the acidic conditions was that the visible light was also capable of inducing [2 + 2] photocycloaddition. These results show that HCl plays essential roles in both the cation–π complex formation and the changes in the absorption properties of substrates that enable visible light reactions. As longer conjugate systems generally form a stronger cation–π complex with a cation, such systems are useful not only in [2 + 2] photocycloaddition, but also in various cation–π-controlled organic reactions.

Supplementary Materials: Supplementary materials are available online. Figures S1–S7: ¹H-NMR spectra for 2a–5a and 2b–4b, Figures S8–S13: MS spectra for 3a, 4b and 5a, Figure S14: Plots of 1/[1a] vs t.

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**Sample Availability:** Not available.