Studies of Charge Resonance Bands Formed in \(\alpha\)- and \(\gamma\)-Styrylpyridinium Tetraphenylborate Derivatives

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The charge resonance (CR) interactions in \(\alpha\)-substituted-(4-nitrostyryl)pyridinium derivatives have been investigated. The CR bands of dimer radical cation in \(\alpha\)-substituted bichromophoric compounds were observed with a peak around 1010 nm upon irradiation at 405 nm in acetonitrile (ACN) at room temperature. These bands were weak because of their restricted geometrical conformation as compared with \(\gamma\)-substituted one. The CR band of dimer radical cation in \(\alpha\)-substituted monochromophoric compound was observed at 993 nm in 1,2-dimethoxyethane. No CR band for this compound in ACN as a polar solvent strongly suggested that radical is difficult to be generated because of increased distance between the tetraphenylborate anion as a donor to the styrylpyridinium chromophore as an acceptor.

Keywords: charge resonance band, dimer radical cation, \(\alpha\)- and \(\gamma\)-substituted-(4-nitrostyryl)pyridinium derivatives

1. Introduction

We have been studying the charge resonance (CR) band of organic materials by electronic interaction of chromophores for developing materials showing fast absorption changes in the near infrared (NIR) region. The CR band of dimer radical cation is due to the splitting of the energy levels of both the ground and the excited states by the electronic interaction between two chromophores. [1-2] The CR band had been observed for intermolecular and intramolecular dimer radical cations formed by steady photolysis at very low temperature and by nanosecond laser flash photolysis at room temperature in solution. [3-14]

By using 1-alkyl-4-(4-nitrostyryl)pyridinium (NS\(^t\)) tetraphenylborate (TPB\(^t\)), we reported, for the first time, the existence of a CR band as a broad band around 950 nm in the NIR region at room temperature in organic solution upon steady photoexcitation. [15] Higher stability of radical in the styrylpyridinium system was controlled by the long and planer structure with extensive charge delocalization due to the nitro group at the para-position of the styryl group and by the prohibition of the reverse electron transfer reaction to oxidized TPB$^+$ due to its decomposition after one-electron oxidation. We have also reported that intramolecular dimer radical cations in bichromophoric compounds showed different CR bands in the NIR region by their geometrical configuration. [16-18] 1,3-Bis(4-(4-nitrostyryl)pyridinium)propane tetraphenylborates [16-17] and meso-2,4-bis(4-(4-nitrostyryl)pyridinium)pentane tetraphenylborates [18], in which chromophores were connected by the tri-methylene chain bridge, showed very stable two CR bands with peaks at about 950 nm and 1700 nm in acetonitrite at room temperature. These bands were attributed to sandwich-type dimer radical cations at about 950 nm and partially overlapped ones at about 1700 nm.

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It was suggested that the behavior of CR bands was remarkably affected by the geometrical structure, the length of the bridge between chromophores and the structure of electron-withdrawing group at para-position of the styryl group.

In the present paper we have studied the CR bands for α-substituted-(4-nitrostyryl)pyridinium derivatives in organic solution upon photoexcitation at room temperature in comparison with γ-substituted one.

2. Materials and Experimental

2.1. Materials
2-(4-Nitrostyryl)pyridine (2SP) and 4-(4-nitrostyryl)pyridine (4SP) were synthesized from aldol condensation of 4-nitrobenzaldehyde and α- and γ-picolone according to the previous report. [19] 1-(2-(4-Nitrostyryl)pyridinium)-3-(4-(4-nitrostyryl)pyridinium)propane (2S4SPr) dibromides salt was prepared, via two step quartemization from 2SP and dibromopropane followed by the reaction with 4SP. 1,3-Bis(2-(4-nitrostyryl)pyridinium)-propane(2S2SPr) dibromides salt was obtained by aldol condensation of bis(2-methylpyridinium)-propane dibromides prepared from 2-methylpyridine and dibromopropane. The direct quartemization of 2SP with 1,3-dibromopropane was not successful probably because of steric hindrance. N-hexadecyl-2-(4-nitrostyryl)pyridinium (2SHD) bromide salt was prepared from quartemization of 2SP with 1-hexadecylbromide. Counter ions of all styrylpyridinium salts were exchanged with tetraphenylborates (TPB) in

![Figure 1: Synthetic routes for α-substituted-styrylpyridinium derivatives and their abbreviations.](image-url)
methanol. Fig. 1 shows the synthetic routes for α-substituted-(4-nitrostyryl)pyridinium derivatives. 1-(2-(4-Nitrostyryl)pyridinium)-3-(4-(4-nitrostyryl)pyridinium)propane ditetraphenylborates salt (2S4SPr) 2-(4-Nitrostyryl)pyridine (1.67 g, 7.38 mmol) and 1,3-dibromopropane (2.24 g, 11.1 mmol) were refluxed in acetonitrile (ACN) (30 ml) for 10 h. After cooling to room temperature, the precipitate was filtered off and dried in vacuum to yield 0.226 g of 1-bromo-3-(2-(4-nitrostyryl)pyridinium)propane bromide as a yellow solid. A little excess of 4-(4-nitrostyryl)pyridine (0.140 g, 0.617 mmol) was added to ACN (20 ml) solution of 1-bromo-3-(2-(4-nitrostyryl)pyridinium)propane bromide (0.220 g, 0.514 mmol) and was refluxed for 18 h. After cooling to room temperature, the precipitate was filtered off and dried in vacuum to yield 0.134 g of l-(2-(4-nitrostyryl)pyridinium)-3-(4-(4-nitrostyryl)pyridinium)propane dibromides salt as a yellow solid. A solution of tetraphenylborate (0.073 g, 0.214 mmol) in methanol (2 ml) was slowly added to a methanol solution (50 ml) of bromides salt (0.700 g, 0.107 mmol) synthesized above. Ion exchange from bromide to tetraphenylborate occurred fast and the resulting yellow precipitate was filtered off and washed with excess methanol. Drying in vacuum afforded 2S4SPr (0.079 g) as a yellow solid. 1H NMR (CD3COCD3, δ ppm) : 2.916 (2H, m, -CH2-), 4.902 (2H, t, -CH2-4SP), 5.213 (2H, t, -CH2-2SP), 6.799 (8H, t, TPB-H y), 6.952 (16H, t, TPB-H ), 7.375 (16H, s-broad, TPB-H a), 7.985 - 8.841 (2SP and 4SP aromatic)

1,3-Bis(2-(4-nitrostyryl)pyridinium)propane ditetraphenylborates salts (2S2SPr) α-Picoline (11.3 g, 0.121 mol) and 1,3-dibromopropane (12.2 g, 0.061 mol) in ACN (20 ml) were refluxed for 6 h. The precipitate was filtered off and washed with excess CHCl3. Drying in vacuum afforded 10.9 g of bis(2-methylpyridinium)propane dibromides salt as a gray solid. The gray solid (5.822 g, 15.0 mmol) and 4-nitrobenzaldehyde (4.99 g, 33.0 mmol) in acetic anhydride (13 ml) and methanol (13 ml) were refluxed for 3 days. After cooling to room temperature, the yellow precipitate was filtered off and washed with excess CHCl3. Recrystallization from methanol gave 2.028 g of 2S2SPr dibromides salt. It was exchanged to tetraphenylborate salt. 1H NMR (CD3COCD3, δ ppm) : 2.939 (2H, m, -CH2-), 5.263 (4H, t, -CH2-2SP), 6.759 (8H, t, TPB-H y), 6.910 (16H, t, TPB-H ), 7.375 (16H, s-broad, TPB-H a), 7.985 - 8.841 (2SP and 4SP aromatic)

2.2. Measurements

Absorption spectra were recorded at room temperature on a Hitachi U-3500 spectrophotometer before and after irradiation in vacuo by a 150 W Hg - Xe lamp through a band pass filter (λex = 405 nm). The use of a band pass filter was effective to prohibit the excitation of radicals and dimer radical cations, which might transform to another forms at the excited state. All absorption spectra reported were the difference between those after and before irradiation.

3. Results and Discussion

Figure 2 shows the spectral changes of 2SHD as a monochromorphic compound irradiated for 4 min in organic solvents, 1,2-dimethoxyethane (DME) as a less polar solvent and ACN as a polar solvent, at 405 nm. The main absorption peaks of 2SHD of 0.1 mM were observed at 339 nm in DME and at 335 nm in ACN before irradiation, respectively. Upon irradiation in DME new absorption bands were observed both in the visible (VIS) region and NIR region, as shown in Fig. 2a. The bands in the VIS region at 436 nm and 593 nm were assigned to the short and long axis transition of nitrostyrylpyridinyl radical or local excitation (LE) of its dimer radical cation. [15, 18, 20-22] Another band in the NIR region with a peak at 993 nm was assigned to the CR band of dimer radical cation, which is formed by the electronic intermolecular interaction between a photogenerated nitrostyrylpyridinyl radical (NS') and nitrostyrlypyridinium cation (SP'). It should be noted that very weak absorption spectra were

![Fig. 2. Difference absorption spectra in 350 - 1400 nm region of 2SHD irradiated for 4 min (a) in DME (0.5mM), (b) in ACN (0.5 mM) and (c) in ACN (1.0 mM) through a band pass filter (405 nm). The inset shows the enlarged spectra in 750 - 1400 nm region.](image-url)
observed in ACN as shown in Fig. 2b and 2c. These results indicated that the increased distance between the donor (TPW) and the acceptor (SP\textsuperscript{+}) in polar solvents dramatically decreased the photogenerated radicals. Another factors to affect the extent of dimer radical cation formation in less polar solvents for monochromophoric compounds have been reported. \[17, 20\] The hydrophobic interaction of longer hexadecyl groups were very effective to promote the association of styrylpyridinyl radicals with styrylpyridinium cation. \[17\]

Figure 3 shows the difference absorption spectra of 2S2SPr and 2S4SPr as bichromophoric compounds upon photoexcitation for 4 min in ACN at room temperature at 405 nm. New absorption bands were observed both in the VIS and NIR regions as shown in Fig. 3. For 0.25 mM 2S2SPr, no noticeable absorption could be found in the NIR region, although radical formation was shown by absorption in the VIS region as shown in Fig. 3a. The NIR absorption was observed at 1011 nm when the concentration was increased to 0.5 mM as in Fig. 3b. The absorption bands of 2S2SPr at 439 nm and 567 nm were assigned to the short and long axis transition of nitrostyrlypyridinyl radical (SP\textsuperscript{+}) or local excitation (LE) of its dimer radical cation in the same manner as for monochromophoric compound. The absorption spectra for with 1,3-bis(4-(4-nitrostyryl)pyridinium)-propane ditetraphenylborates salts (4S4SPr) irradiated in ACN showed a stronger CR band at 950 nm and another broader CR band at 1740 nm as shown in Fig. 4. \[16\] Absorption bands of 2S4SPr were also observed at 419 nm and 580 nm in the VIS region and 1007 nm in the NIR region as shown in Fig. 4c. All absorption bands in similar shape and peak wavelength were stronger at the same concentration, as compared with those of 2S2SPr which means that the character of 4SP may affect the formation and stability of radical. These results indicated that the relative contents of dimer radical cations considerably depended on geometrical structure or stability of dimer radical cation formed by photoexcitation.

The appearance of CR band in the NIR region is due to interaction between the styrylpyridinium cation and its radical formed by photoinduced electron transfer from TPB anion to SP cation as shown in the Fig 5. The CR transition between the sub-levels derived from splitting of HOMO and LUMO energy levels is approximately equal to twice of the stabilization energy of dimer radical.

![Fig. 3. Difference absorption spectra in 350 - 1400 nm region of (a) 2S2SPr (0.25 mM), (b) 2S2SPr (0.5 mM) and (c) 2S4SPr (0.25 mM) irradiated for 4 min in ACN through a band pass filter (405 nm). The inset shows the enlarged spectra in 750 - 1400 nm region.](image1)

![Fig. 4. Difference absorption spectra in 350 - 2000 nm region of 4S4SPr (0.25 mM) irradiated for 4 min in ACN through a band pass filter (405 nm). The inset shows the enlarged spectra in 800 - 2000 nm region.](image2)

![Fig. 5. Schematic representation of the energy diagram of monomer radical and dimer radical cation.](image3)
cation, which gives a specific absorption in the NIR region. The oxidized TPB anion is known to decompose rapidly, which also contributed to the stability of dimer radical cation because of prohibition of reverse electron transfer reaction.

Hirayama has reported that two chromophores bridged with propane can take a favorable conformation for intramolecular interaction between two chromophores. [23] But the bands of α-styrylpyridinium derivatives in bichromophoric compounds showed weaker absorption in the NIR region as shown in Fig. 3 as compared with those of 4S4SPr in Fig. 4. Intramolecular interaction in bichromophoric compound increased when the character of 4SP increased in the order of 2S2SPr → 2S4SPr → 4S4SPr. These results indicate that the character of 4SP is more effective to form both radicals and dimer radical cations. The comparison between monochromophoric and bichromophoric compounds at the same chromophore concentration can also give information on interaction characteristics of dimer radical cations. The bichromophoric compound can interact as both intramolecular and intermolecular dimer radical cations, whereas monochromophoric compound can make only intermolecular interaction. As shown in Fig. 2c, no CR band of 2SHD in ACN even at 1.0 mM concentration means that a-substituted styrylpyridinium derivative is difficult to take intermolecular dimer radical cation in the polar solvent such as ACN. These results indicate that the observed CR bands around 1010 nm for 2S2SPr in 0.5 mM in ACN as shown in Fig. 3b was concluded to be originated from the intramolecular interaction of dimer radical cation. Much smaller absorption than 4S4SPr is most probably due to the restricted conformation of two chromophores difficult to arrange in a sandwich type for intramolecular interaction as those in γ-substituted styrylpyridinium derivatives. These results confirm the importance of the shape of chromophores together with other factors such as bridge type, solvent, stability of radical and bridge length and so on.

4. Conclusion

The CR bands of dimer radical cation formed by photoexcitation in solution at room temperature were studied for α-substituted-(4-nitrostyryl)-pyridinium derivatives. The absorption spectral changes of 2SHD showed a small CR band at 993 nm in DME. But no CR band was observed in the NIR region in ACN. These results mean that the solvent effect on the absorption played an important role in formation of radicals and dimer radical cations. The absorption spectral changes of 2S2SPr and 2S4SPr as bichromophoric compounds showed a peak around 1010 nm as the CR band which is predominantly originated from intramolecular interaction from comparison with 2SHD at the same chromophore concentration. Smaller CR band of 2S2SPr was caused by its restricted conformation for intramolecular interaction. In bichromophoric compounds the CR bands were increased in the order : 2S2SPr → 2S4SPr → 4S4SPr. This suggests that the character of 4SP is more effective to promote the formation of radical as compared with 2SP.

References

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