Reaction of 5,8-Diphenyl-5,8-dihydroanthra[1,9-bc:4,10-b'c']diquinoline or its Endoperoxide with Trifluoroacetic Acid

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5,8-Diphenyl-5,8-dihydroanthra[1,9-bc:4,10-b'c']diquinoline (ADQ, 3) and its endoperoxide (ADQepo, 4) were photochromic compounds with high heat stability. By heating above 100 °C, colorless ADQepo (4) was slowly converted to green ADQ (3) in toluene. Reaction of ADQepo with some protic acid gave ADQ (3) at room temperature. The mechanism of this reaction was proposed based on the measurement of electronic spectrum.

Keywords: Photochromism, Endoperoxide, Protic acid, Thermochromism, Indicator

1. Introduction

Benzo[1,2,3-kl:4,5,6-k'l']dixanthene (BDX, 1) and its endoperoxide (BDXepo, 2) are known as photochromic compounds with high heat stability.[1-3] Interest in photochromic behavior of BDX (1) was first studied by Schmidt and coworkers.[1,2] Photooxigenation of the red solution of BDX (1) in toluene by irradiation of visible light produces the colorless BDXepo (2). The colorless BDXepo (2) in toluene has been known to give BDX (1) slowly with the liberation of molecular oxygen by heating above 100 °C. Recently, it turns out that solution of BDXepo (2) colors rapidly by addition of acid at room temperature.[4] The mechanism of this reaction is still obscure.

According to molecular orbital calculations [5], a nitrogen analogue of BDXepo (2) has with higher proton affinity, and liberates oxygen quickly than the oxygen analogue (2). In order to make clear this mechanism, nitrogen analogues were synthesized, and the changes of electronic spectrum of these compounds in the presence of protic acid were investigated. For these nitrogen analogues 5,8-diphenyl-5,8-dihydroanthra[1,9-bc:4,10-b'c']diquinoline (ADQ, 3) and its endoperoxide (ADQepo, 4) were selected.[6]

Trifluoro acetic acid (TFA) was added to 3 or 4 in toluene and change of an electronic spectrum was measured.

2. Results and Discussion

2.1. Synthesis [7-9]

The synthesis of ADQepo (4) was carried out according to the synthetic route in Scheme 2. ADQ (3) was synthesized by the condensation reaction of 1,4-diaminoanthraquinone (5) with iodobenzene followed by a ring closure reaction of 1,4-bis(diphenylamino)anthraquinone (6). ADQepo (4) was obtained by photoooxygenation of 3 in toluene.
2.2. An assumption of reaction mechanism

A reaction mechanism shown in Scheme 3 was assumed. Path A and B were assumed as candidates for the deoxygenation.

Scheme 2  Synthetic Route of ADQepo (4)

Scheme 3  Assumption of Reaction Mechanism

2.3. Absorption spectrum change of ADQ (3) with TFA

Ten equivalents of TFA was added to the toluene solution of 3 (1.0×10^4 M). A change of the electronic spectrum from 0 to 7 min after addition with the passage of time is shown in Figure 1a. Absorption shoulder of ADQ (3) at 730 nm was decreased with time, and the new absorption maximum at 637 nm appeared. The absorbance of the band at 637 nm was gradually increased after the addition of TFA, and band at 730 nm of ADQ (3) was decreased and disappeared after 7 min. Pseudo-isosbestic points were observed at 410, 440, 467, and 670 nm.

The spectral changes from after 7 min to 2880 min (48 h) was shown in Figure 1b. The peak at 637 nm gradually decreased and the new absorption at 467 nm increased. In the meanwhile,
a pseudo-isosbestic point was observed at 510 nm and after 48 h (2880 min) the reaction reached to an equilibrium state.

When 100 equivalents of TFA were added to the toluene solution of 3, the same tendency in the case of the amount of ten equivalents was observed. Absorption of 3 disappears in 3 min, and the equilibrium state was reached in 20 min.

From these results, the absorption at 637 nm in Figure 1a should be assigned to the species of first protonation, and at 467 nm to that of second protonation.

It is reasonable, that the initial stage would be protonation at one nitrogen atom to give 7, and the second stage would be protonation at the other nitrogen to give 8. Among these, the difference of reaction velocity is considered to be very large between the first and the second protonation.

First protonation at one nitrogen atom, decreases the electron donating ability of the second nitrogen atom resulting in a lower basicity of the species 7 than that of 3.

2.4. Absorption spectrum change of ADQepo (4) with TFA

Two equivalents of TFA were added to the toluene solution of 4. A change of the electronic spectrum from 0 to 640 min after addition with the passage of time is shown in Figure 2. After 3 min from the addition of TFA, the absorption maximum of ADQepo (4) at 392 nm completely diminished and new absorption bands at 467 and 637 nm (7) appeared. The absorption at 467 nm of 8 has tendency to decrease and absorption at 637nm of 7 to increase with time. It is suggested that 8 is generated rapidly and the following reaction proceeds to give 7.

Furthermore, it was tried to detect the reaction of 4 to generate 8. Two equivalents of TFA was added to the toluene solution of 4 (5.0×10^4 M), and the electronic spectrum change was measured by time resolved multichannel spectrophotometer (Figure 3). Decrease in absorption of 4 at 392 nm and the increase in absorption of 8 at 467 nm were caught. Other absorption bands based on intermediates (9 or 10) have not been observed. Since the absorption at 467 nm was increasing within 0.19 s, it was suggested that the reactions to give 9 or 10 proceeded very quickly.

One equivalent of TFA was added to the toluene solution of 4. A change of the electronic spectrum from 0 to 20 min after addition with the passage of time was shown in Figure 4a. The absorption at 467 nm (8) and 637 nm (7) appeared already after 3 min from the addition of TFA. The absorption at 467 nm (8) and 637 nm (7) was increased with time. The spectral change after 30 to 320 min was shown in Figure 4b. It has observed that absorption maximum of 637 nm decreased gradually and the absorption shoulder at 730 nm (3) was increasing.

The increase at 730 nm was not observed when two equivalents of TFA were added. When there is a little quantity of acid, compound 3 is produced because of the equilibrium. From the results too, it was suggested that the first protonation tends to progress faster than the second.
2.5. Mechanism of the reaction of ADQepo (4) with TFA

From the results of the above experiments, it was concluded that the reaction proceeds via not path B but path A in Scheme 3 at the reaction of ADQepo (4) and TFA.

In order for the reaction from 8 via 7 to 3 to progress, the compounds with higher basicity than 8, 7 or 3 needs to exist. Probably they are 4 or 9. It is suggested that proton is exchanged between the reaction from 8 to 7, and from 7 to 3, and the reaction from 4 to 9, and from 9 to 10.

3. Conclusion

The reaction of ADQepo (4) to generate a colored form ADQ (3) is catalyzed by TFA by the mechanism through two-step protonations. These reactions are expected for the photochromic compounds 3 and 4 to apply as novel functional dyes.

4. Experimental

4.1. Method

Solvents and reagents were purified using literature method.[10,11] Melting points were determined with a Mitamura Riken Mel-Temp and were uncorrected. UV-Vis Spectra were recorded on a Shimadzu UV-2500, UV-2100 spectrophotometer and Otsuka Electronics IMUC-7000 time resolved multichannel spectrophotometer. 1H NMR spectra were recorded on Bruker AC-400, AC-200 spectrometer, using tetramethylsilane as an internal standard at room temperature. IR spectra were obtained on Perkin-Elmer 1600 FT-IR. Thin-layer chromatography (TLC) was performed on plastic sheets (1.0 x 4.0 cm) coated with Merck silica gel 60 F254 and Merck aluminum oxide 60 F254 neutral (type E). Column chromatography was performed using a Merck aluminum oxide 60, activity stage 1, active basic (70-230 mesh).

4.2. Synthesis

1,4-bis(diphenylamino)anthraquinone (6) [6]

A 100 ml three-necked round-bottomed flask equipped with a reflux condenser and a thermometer was charged with 1.0 g (4.20 mmol) of 1,4-diaminoanthraquinone (5), 6.84 g (33.5 mmol) of iodobenzene, 1.16 g (8.40 mmol) of potassium carbonate and 40 ml of bromobenzene. The reaction mixture was stirred for 180 h at 145-150 °C. The reaction mixture was steam distilled and filtered off. The residue was refluxed with 200 ml of toluene and filtered while the solution is hot. The solvent was removed under reduced pressure using a rotary evaporator. Recrystallization from toluene afforded pure 8 (1.26 g, 55 % yield). Black plates, mp 225-226 °C; 1H NMR (200 MHz, CDCl3) δ (ppm): 6.93-7.02 (t, 4H), 7.06-7.11 (dd, 8H), 7.42 (s, 2H), 7.48-7.53 (dd, 2H), 7.62-7.72 (dd, 2H); EI MS m/z: 542 (C38H26N2O2, 542.6).

(0.51 mmol) of hydroquinone, 0.61 g (1.04 mmol) of sodium chloride and 2.95 g (22.1 mmol) of anhydrous aluminum chloride. The reaction mixture was heated at 180 °C over a silicone oil bath, and the temperature was diligently maintained within a range of 175-185 °C for 2 h with stirring. The reaction mixture was charged with 50 ml of 1 M HClaq, cooled to room temperature, and filtered. The filtrate was added in 50 ml of 4 M NaOHaq. Precipitated green solid was collected by suction filtration and the residue was washed with 200 ml of hot water containing 1.0 g of NaOH and 2.0 g of Na2S2O4. After washing with water, the solid was extracted with toluene and purified by hot column chromatography on aluminum oxide active basic using toluene as an eluent. After the solvent was concentrated under reduced pressure using a rotary evaporator, recrystallization from toluene afforded pure 3 (126 mg, 27 % yield). Fine green plates, mp 349-351 °C; IR (KBr): disappearance of C=O stretching; EI MS m/z: 508 (C38H24N2, 508.6); UV-Vis, nm (logε) in toluene: 671 (3.95) 730 (sh).

5,8-Diphenyl-5,8-dihydroanthra[1,9-bc:4,10-b’c’] diquinoline endoperoxide (4)

Fifty milligrams (0.098 mmol) of 5,8-diphenyl-5,8-dihydroanthra[1,9-bc:4,10-b’c’] diquinoline (3) was dissolved in 200 ml of toluene. The solution was irradiated for 40 min on an ice bath with a 300 W tungsten lamp while air bubbling. After the solvent was concentrated under reduced pressure using a rotary evaporator, 5 ml of hexane was added. The precipitate was collected by suction filtration, to give 4 (30.4 mg, 61 % yield). Almost colorless powder, 1H NMR, 1H-1H COSY (400 MHz, CDCl3) δ/ppm: 6.06 (s, 2H), 6.53-6.56 (dd, 2H), 7.11-7.15 (t, 2 H), 7.25-7.31 (m, 8H), 7.34-7.36 (dd, 2H), 7.46-7.50 (t, 2H), 7.56-7.59 (t, 4H), 7.96-7.98 (dd, 2H); UV-Vis, nm (logε) in toluene: 392 (3.82), disappearance of 671 nm, 730 nm (sh) of 3.

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References