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# Valence Isomerization between Water-soluble Norbornadiene and Quadricyclane Derivative

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**Synopsis.** Photoisomerization of 3-(arylcarbamoyl)-norbornadiene-2-carboxylic acid **1** to the corresponding quadricyclane derivative **2** in an aqueous alkaline solution was clean and dependent upon the *p*-substituent of the aryl group. The exothermically reversal reaction of **2** to **1** was also clean but independent upon the substituent.

Valence isomerization between norbornadiene and quadricyclane has attracted much attention from solar energy storage.[1] This system has inherently an inevitable problem: norbornadiene cannot absorb sunlight. To overcome the great disadvantage, we have proposed introduction of substituents to norbornadiene.[2] Moreover, we first used water, safe and inexpensive, as the reacting media.[3] Usually, organic solvent had been used in similar systems. In this paper, we describe the effect of the substituents of aryl group in valence isomerization between 3-(arylcarbamoyl)norbornadiene-2-carboxylic acid **1** and 3-(arylcarbamoyl)quadricyclane-2-carboxylic acid **2** in water.

## Results and Discussion

Norbornadiene-2,3-dicarboxylic anhydride and *p*-substituted aniline gave norbornadiene derivative **1** in a high yield.[2] The norbornadiene derivative **1** was highly soluble in an aqueous alkaline solution because of the carboxyl group. In an aqueous alkaline solution **1** has absorption band in longer wavelength than 400 nm and absorbs sunlight (Fig. 1). When an aqueous sodium carbonate solution of norbornadiene derivatives **1a—d** was irradiated by light of 366 or 334 nm, the corresponding quadricyclane derivatives **2a—d** were quantitatively formed even in the presence of air (Table 1). The photoisomerization by light of longer wavelength than 300 nm including sunlight was so clean that isosbestic points were observed in UV spectral changes. On irradiating light of 313 nm **1a**, **b** photoisomerized to **2a**, **b** quantitatively, but **1c**, **d** didn't (Table 1). This reaction is photochromic,[4] so **2** isomerizes again to **1** by light which is able to be absorbed by **2**. Under the conditions, **2c**, **d** isomerized to **1c**, **d** to attain a photostationary state. These facts may be rationalized by taking into consideration that introduction of a substituent into phenyl group to make **1** absorb light of the longer wavelength affects **2** concomitantly to absorb light of longer wavelength. Similarly, the quantum yield of the photoisomerization decreased with increasing the absorption edge of **1**. Therefore, bathochromic shift of absorption band of **1** induces decrease of both the chemical and the quantum yield of the photoisomerization. Wavelength dependency of the quantum yield is given in Table 1.

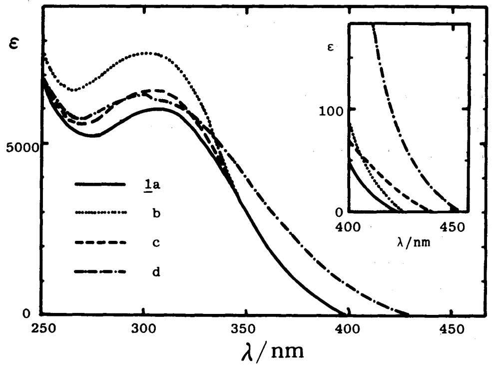
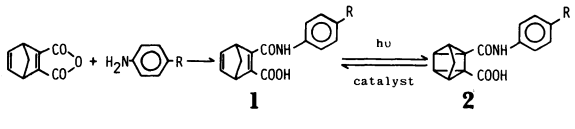


Fig. 1. Ultraviolet and visible spectra of 1 in 0.1 M Na2CO aq (1 M = 1 mol dm$^{-3}$).

The isomerized **2** was so stable in a boiling aqueous sodium carbonate solution that none of **1** and other products could be produced under the conditions. However, addition of a catalytic amount of cobalt 5,10,15,20-tetrakis(*p*-carboxyphenyl)porphyrin (Co-TPPC) in the solution at room temperature induced a sudden isomerization of **2** to **1** quantitatively under release of heat. The exothermically catalytic reaction was of pseudo-first order. The rate constant was about 7 M$^{-1}$ s$^{-1}$ and independent upon varieties of *p*-sub-

Table 1. Photo- and catalytic isomerization of **1** and **2** in $Na_2CO_3$ aq



| | R | Yield/% | Photoisomerization of 1 to 2[a)] Chemical Yield/% 313 | 334 | 366 nm | Quantum Yield 313 | 334 | 366 nm | Catalytic Isomerization of 2 to 1 k[b)] M$^{-1}$s$^{-1}$ | −ΔH[c)] kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| a | H | 93 | 100 | 100 | 100 | 0.10 | 0.04 | 0.04 | 7—8 | 55—63 |
| b | Cl | 68 | 100 | 100 | 100 | 0.07 | 0.03 | 0.03 | 6—8 | 56—64 |
| c | $CH_3$ | 82 | 95 | 100 | 100 | 0.06 | 0.01 | 0.01 | 6—7 | 55—65 |
| d | $OCH_3$ | 85 | 77 | 100 | 100 | 0.03 | 0.01 | 0.003 | 7—8 | 55—63 |

a) These values were determined by UV spectral analysis. b) These values were measured at 25 °C by $^1$H NMR technique. c) These values were measured by using a corrected copper-constantan thermocouple.

stituents of **2**. The heat of molar storage was about 60 kJ mol$^{-1}$ and also independent upon the structure of **2a—d**. These facts may be explained as followings; a substituent introduced into phenyl group is so far from the reaction center, double bonds of **1** and so banana bonds of **2**.

From the viewpoint of the conversion efficiency in solar energy,[5] introduction of a substituent is effective little, but in view of utilizing light of longer wavelength of sun, the introduction is of some improvement. This water-soluble solar energy storage system may be promising for actual use by the following two points: i) this system can utilize the light of 450 nm; ii) this system is so clean in both photo- and catalytic reaction.

## Experimental

*Apparatus.* All melting points were measured with a Yanagimoto micro melting point appratus and uncorrected. Ultraviolet and visible spectra were measured with a Shimadzu UV-200 spectrometer. Infrared spectra were measured with a JASCO IRA-1 spectrometer. $^1$H NMR spectra were recorded on a JEOL JMN-PS-100 spectrometer. Mass spectra were recorded with a JEOL JMS-DX-300 spectrometer. Elemental analyses were performed at the Microanalysis Center of Kyoto University.

*Materials.* Compound **1** was prepared from norbornadiene-2,3-dicarboxylic anhydride and *p*-substituted aniline, and the isomerized **2** was prepared by photoreaction of **1** in a similar manner reported previously.[2] Co-TPPC was synthesized according to the literature,[7] and purified by recrystallization from methanol and chloroform.

*Physical Properties.* ***1a***:[2] UV (0.1M $Na_2CO_3$ aq (1 M=1 mol dm$^{-3}$)), 228 ($\varepsilon$ 13900) and 302 nm (6570). ***1b***: yellow crystals; mp 187—189 °C (from acetonitrile); UV (0.1 M $Na_2CO_3$ aq) 235 ($\varepsilon$ 14600) and 307 nm (7660); IR (KBr) 2400—3640 (br, COOH and NH) and 1685 cm$^{-1}$ (C=O); $^1$H NMR ($CDCl_3$) $\delta$=2.06—2.36 (2H, m), 4.1—4.3 (2H, m), 6.85—7.05 (2H, m), 7.29 (2H, a half of ABq, $J$=9 Hz), 7.57 (2H, a half of ABq, $J$=9 Hz), and 9.3—9.5 (1H, br); Found: C, 62.15; H, 4.10; N, 5.05; Cl, 12.37%; M$^+$, 289 and 291. Calcd for $C_{15}H_{12}NO_3Cl$: C, 62.19; H, 4.17; N, 4.83; Cl, 12.24%; M, 289 and 291. ***1c***: yellow needles; mp 197—198 °C (from acetonitrile); UV (0.1 M $Na_2CO_3$ aq) 231 ($\varepsilon$ 14400) and 308 nm (6070); IR (KBr) 2860—3440 (br, COOH), 3290 (NH), and 1690 cm$^{-1}$ (C=O); $^1$H NMR ($CDCl_3$) $\delta$=2.13—2.40 (2H, m), 2.36 (3H, s), 4.08—4.36 (2H, m), 6.92—7.1 (m, 2H), 7.24 (2H, a half of ABq, $J$=8 Hz), 7.54 (2H, a half of ABq, $J$=8 Hz), and 8.6—8.8 (1H, br); Found: C, 71,44; H, 5.55; N, 5.16%; M$^+$, 269. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20%; M, 269. ***1d***:[2] UV (0.1 $Na_2CO_3$ aq) 231 ($\varepsilon$ 14800) and 300 nm (6420). ***2a***:[2] UV (0.1 M $Na_2CO_3$ aq) 258 nm ($\varepsilon$ 15900); Found: $m/z$ 255.0901. Calcd for $C_{15}H_{13}NO_3$: M, 255.0895. ***2b***: white crystals; mp 168—172 °C (from acetonitrile); UV (0.1 M $Na_2CO_3$ aq) 262 nm ($\varepsilon$ 16400); IR (KBr) 2400—3680 (br, COOH and NH), 1690, and 1640 cm$^{-1}$ (C=O); $^1$H NMR ($CDCl_3$) $\delta$= 2.14—2.94 (6H, m), 7.22 (2H, a half of ABq, $J$=8 Hz), and 7.48 (2H, a half of ABq, $J$=8 Hz); Found: $m/z$ 289.0509 and 291.0474. Calcd for $C_{15}H_{12}NO_3{}^{35}Cl$ and $C_{15}H_{12}NO_3{}^{37}Cl$: M, 289.0506 and 291.0476. ***2c***: white crystals; mp 152—155 °C (from acetonitrile); UV (0.1 M $Na_2CO_3$ aq) 261 nm ($\varepsilon$ 19200); IR (KBr) 2940—3640 (br,COOH), 3300 (NH), and 1690 cm$^{-1}$ (C=O); $^1$H NMR ($CDCl_3$) $\delta$=2.1—2.9 (6H, m) 2.3 (3H, s), 7.05 (2H, a half of ABq, $J$=8 Hz), and 7.39 (2H, a half of ABq, $J$=8 Hz); Found: $m/z$ 269.1041. Calcd for $C_{16}H_{15}NO_3$: M, 269.1052. ***2d***:[2] UV (0.1 M $Na_2CO_3$ aq) 262 nm ($\varepsilon$ 14500). Found: $m/z$ 285.1004. Calcd for $C_{16}H_{15}NO_4$: M, 285.1001.

*Measurements.* *Quantum Yield*: An apparatus and actinometer as described previously were used.[2] A $Na_2CO_3$–$H_2O$ solution of **1** was irradiated at an each wavelength and absorbance of **1** at the wavelength was measured at an appropriate time interval. According to the method described by Kaupp and Prinzbach,[6] the quantum yield was determined.

*Rate Constant*: After a $Na_2CO_3$–$D_2O$ solution of Co-TPPC was added to a $Na_2CO_3$–$D_2O$ solution of **2** in a NMR sample tube, signals of **1** and **2** were integrated at an appropriate time interval. According to the method described previously,[2] the second order rate constant in the pseudo-first order reaction was determined.

*Isomerization Heat*: A $Na_2CO_3$–$H_2O$ solution of Co-TPPC was added to a $Na_2CO_3$–$H_2O$ solution of **2** in a test tube. Heat release in the solution was measured by using a corrected copper-constantan thermocouple. After correction of the heat of mixing and the radiative heat, the isomerization heat was determined.

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