

Synthesis and Property of [6]-1,4-Cyclophaneanthraquinone: A Novel Anthraquinone Derivative Undergoing Photovalence Isomerization

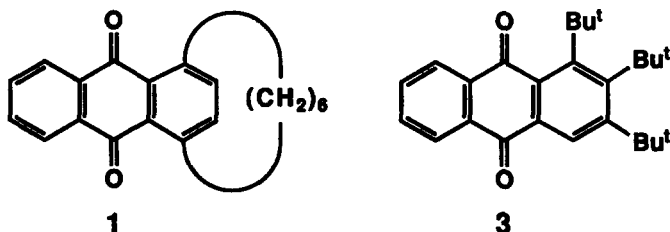
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Key Words: Cyclophaneanthraquinone; Photovalence isomerization; Dewar-anthraquinone; Photochromism

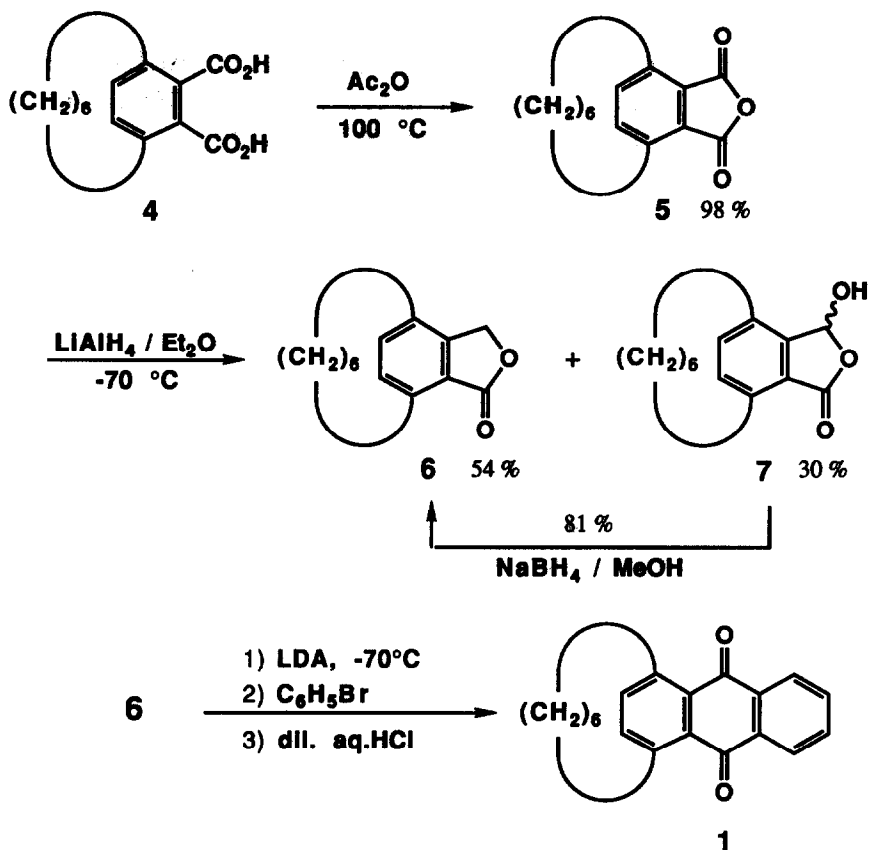
Abstract: [6]-1,4-Cyclophaneanthraquinone (1) has been synthesized. Both the lowest singlet and triplet excited states of 1 possess $\pi\pi^*$ nature. Correspondingly, upon irradiation, 1 undergoes valence isomerization to afford Dewar-anthraquinone (2) quantitatively, and neither intramolecular nor intermolecular hydrogen abstractions were observed.

Previously, we have reported that both the T_1 and the S_1 states of 1,2,3-tri-*t*-butylantraquinone (3) are $\pi\pi^*$ in nature, and correspondingly it shows unique photochemical reactivities.^{1,2} We have attributed the reason why the lowest excited state is $\pi\pi^*$ in nature, instead of $n\pi^*$, to the molecular deformation caused by the substitutional modification. Our present interest is whether this is also the case even for different types of molecular deformations. We have intended to design an anthraquinone molecule possessing a simple boat-form deformation, whereas 3 would have a complicated zigzag form deformation extending even to the carbonyl group at C₁₀ position. Methods for introducing boat-form deformation into aromatic molecules have been established by Tobe, Tochtermann and Bickelhaupt in the so-called cyclophane chemistry.^{3,4} Thus, we have synthesized [6]-1,4-cyclophaneanthraquinone (1) and examined its photophysical properties.



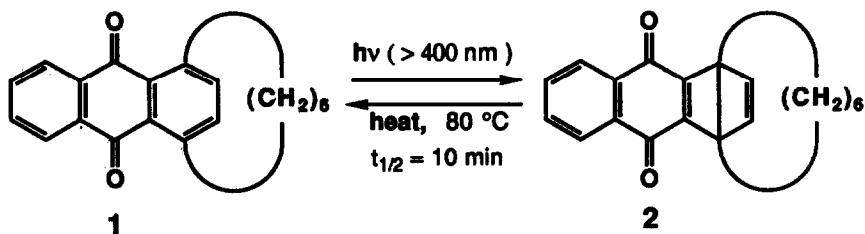
[6]-1,4-Cyclophaneanthraquinone (1) was synthesized according to Scheme 1 starting from [6]paracyclophane dicarboxylic acid (4) prepared by the method reported by Tochtermann.⁴ The reduction of acid anhydride (5) by lithium aluminumhydride afforded phthalide (6) and hydroxyphthalide (7) in the yields indicated. The hydroxyphthalide (7) could be converted to 6 by the reduction with sodium borohydride. The reaction of 6 with bromobenzene in the presence of lithium diisopropylamide afforded 1 by using the method developed by Sammes and Dodsworth.⁵ 1; mp. 201-202 °C, ¹H-NMR (CDCl₃, 30 °C): δ ppm 8.22-8.24 (m, 2H), 7.74-7.76 (m, 2H), 7.54 (bs, 2H), 3.4-4.3 (very broad signal, 2H), 2.4-3.0 (very broad signal, 2H), -0.5-2.0 (very broad signal, 8H); UV (CH₂Cl₂): λ_{\max} nm (ϵ_{\max}) 249 (33000), 437 (3600); Exact mass: Calcd. 290.13074. Found, 290.13219. The yield for the last step was around 10%, but it was very sensitive to reaction conditions, and in some cases only a trace amount of 1 was obtained. Spectroscopic data

for the intermediate products are reported in footnote.⁶



Scheme 1.

As seen in Figure 1, the electronic spectrum of **1** is characteristic revealing the longest wavelength absorption band with an extinction coefficient of $3600\text{ cm}^{-1}\text{M}^{-1}$, whereas the extinction coefficient for the longest absorption band for the parent molecule is below $100\text{ cm}^{-1}\text{M}^{-1}$ due to the weak intensity of the $n\pi^*$ transition. Judging from the large extinction coefficient for the longest absorption band of **1**, the lowest excited singlet state of **1** should strongly bear $\pi\pi^*$ nature. We have a theoretical evidence for this.⁷ Correspondingly, **1** reveals a unique photochemical reactivity to undergo valence isomerization to hexano-Dewar-anthraquinone (**2**). This kind of photovalence isomerization of aromatic compounds generally involves singlet excited state and not triplet state.⁸ Therefore, the reaction of **1** to **2** should not be efficient if the lowest singlet excited state responsible for the reaction is $n\pi^*$ in nature, because in such case the initial excited state is localized on the carbonyl moiety whereas the key bond rearrangement process is located on the phenyl ring.⁹ Thus, the change of the electronic configuration of S_1 from $n\pi^*$ to $\pi\pi^*$, which is caused by the boat-form deformation, facilitates the valence isomerization of **1** to **2**, though this deformation in **1** would also give a potential driving force for the reaction.



Irradiation was performed with a high pressure Hg-lamp through a Toshiba L-42 glass filter ($> 400 \text{ nm}$) with a degassed solution of **1** in CDCl_3 . In the $^1\text{H-NMR}$ following the photoreaction, the signals due to **1** decreased and new signals due to **2**: δ ppm 7.76-7.94 (m, 2H), 7.26-7.46 (m, 2H), 6.53 (bs, 1H) and 6.46 (bs, 1H), appeared in addition to a complicated change in aliphatic proton region. As shown in Figure 2, the electronic spectra following the photoreaction of **1** in methylcyclohexane revealed isosbestic points at 307 nm and 363 nm indicating that the reaction is chemically quantitative. Although **1** possesses benzylic hydrogens adjacent to carbonyl oxygens, no intramolecular hydrogen abstraction by the carbonyl oxygen was observed. When a solution of **1** in isopropyl alcohol was irradiated, no indication for photoreduction of **1** was observed. Phosphorescence of **1** was too weak to detect, and hence direct information for the nature of T_1 could not be obtained. However, the reaction behavior of **1** indicates that the lowest excited triplet state of **1** is also $\pi\pi^*$ in nature.

The hexano-Dewar-anthraquinone, **2**, reverts to **1** thermally with a half-life time of 10 min at 80°C . The reaction was quantitative under anaerobic condition, and the electronic spectra following the thermolysis of **2** in degassed methylcyclohexane showed the same feature to Fig. 2 with a reverse direction of the spectral change.

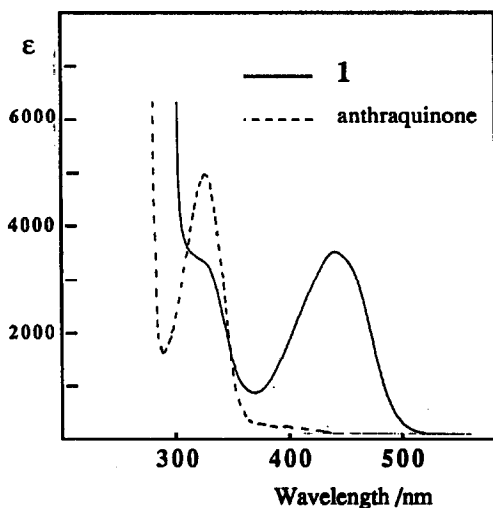


Figure 1 Electronic spectra of **1** and anthraquinone in methylene chloride.

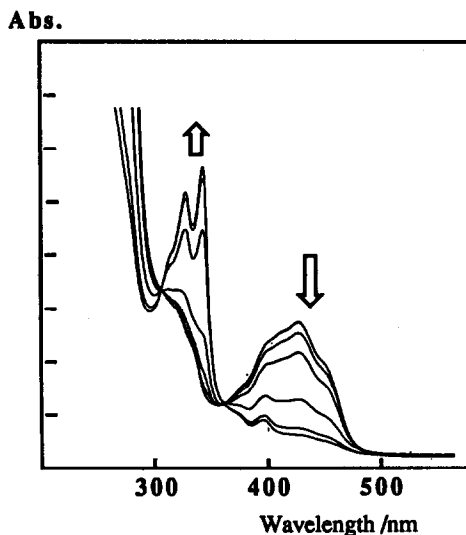


Figure 2 Electronic spectra following the photoreaction of **1** to **2** in methylcyclohexane.

The cycloreversion of **2** to **1** proceeds either thermally or photochemically, and both the processes are chemically quantitative. Thus, the present pair of valence isomers may possess a fundamental potentiality as a light energy storage system as well as a photoresponsive material. Further studies including theoretical treatment of the excited states are in progress.

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References and Notes

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6. **6** : $^1\text{H-NMR}$ (CDCl_3) ; δ ppm 7.36 (m, 2H), 5.27 (bs, 2H), 2.5-3.0 (very broad signal, 2H), 1.9-2.5 (very broad signal, 2H), -1.5-1.9 (very broad signal, 8H) : IR (KBr) ; cm^{-1} 1770.
7 : $^1\text{H-NMR}$ (CDCl_3) ; δ ppm 7.46 (bs., 2H), 6.64 (bs, 1H), 2.5-3.0 (very broad signal, 2H), 1.9-2.5 (very broad signal, 2H), -1.5-1.9 (very broad signal, 8H) : IR (KBr) ; cm^{-1} 3330, 1720.
7. A semi-empirical calculation shows that when one of the phenyl rings of anthraquinone is bent in chair form, the $\pi\pi^*$ state is very much stabilized and comes below the $n\pi^*$ state as the bent angle is large.
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