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Synthesis and Structure of 1,10-*o*-Benzeno[2.2]orthocyclophane-*o*-quinones. Evaluation of Attractive Energy between Donor and Acceptor

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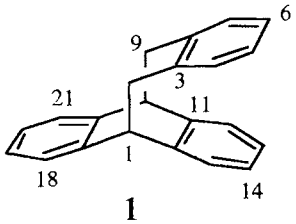
The title compounds were synthesized to evaluate the intramolecular charge transfer interaction between the donor (dimethoxybenzene) and the acceptor (*o*-benzoquinone) of defined arrangement.

The elucidation of the effect of through space interaction between π electron systems on their physical and chemical properties continues to be an area of great current interest. [1] Studies on charge transfer (CT) interactions between a donor and an acceptor π systems have been of special interest and many intramolecular donor-acceptor complexes have been reported so far.[2] The rigid skeletons such as [2.2]- and [3.3]-paracyclophanes were utilized for the fixation of relative disposition of the two CT components.[3] Mainly electronic spectra were discussed as the result of the fixations. The rigid skeleton for this purpose is at the same time a drawback for the evaluation of the energetics of the CT system itself.



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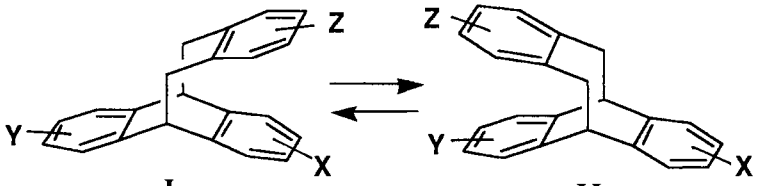
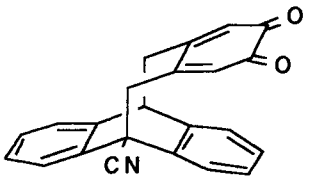


I **II**

We have shown that 1,10-*o*-benzeno[2.2]orhtocyclophane (**1**) can be a good candidate for evaluation of π-π interaction between the upper and the lower π decks,[4,5] which is free from the effect of severe distortion of the aromatic rings imposed on the other [2.2]cyclophanes.[6] Moreover the energetics of the π-π interaction between the upper and the lower decks can be evaluated by use of dynamic equilibrium (I ⇄ II) and relative population of the two conformers I and II, as long as the two lower π systems are different with each other.

Incorporation of *o*-benzoquinone into the [2.2]orthocyclophane would give an important information about CT interaction. We have then synthesized 1,10-*o*-benzeno[2.2]orhtocyclophane-*o*-quinones (**2**-**4**) and examined their physical properties including the energetics of the intramolecular CT interactions.



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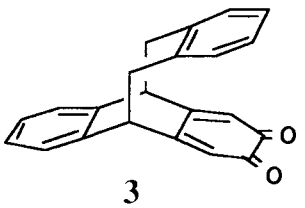

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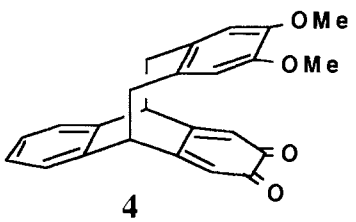

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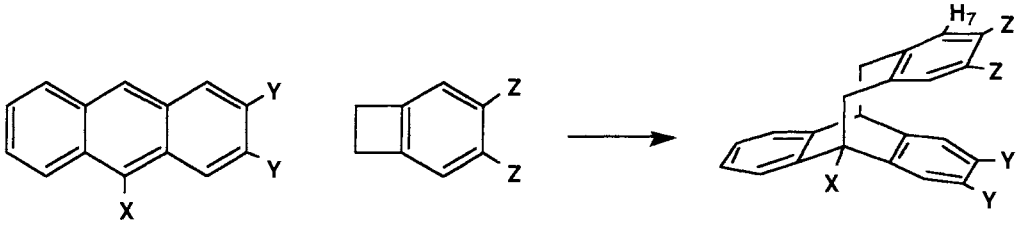
The basic skeleton can be easily constructed by use of thermal [4+4]cycloaddition of *o*-quinodimethanes with anthracenes.[6] When heated at 250 °C in a sealed tube, 4,5-dimethoxybenzocyclobutene (**8**) reacted with 9-cyanoanthracene (**5**) to give 1,10-*o*-benzeno[2.2]orthocyclophane (**9**) in 80% yield. Hydrolysis of **9** by BBr_3 and successive oxidation by DDQ gave the desired *o*-quinonophane (**2**) in quantitative yield. The other quinonophanes (**3** and **4**) were obtained in a similar manner, though the yields of the cycloadducts of **6** with **7** or **8** were low (20% for **10**, 19% for **11**).



5 X=CN, Y=H
6 X=H, Y=OAc

7 Z=H
8 Z=OMe

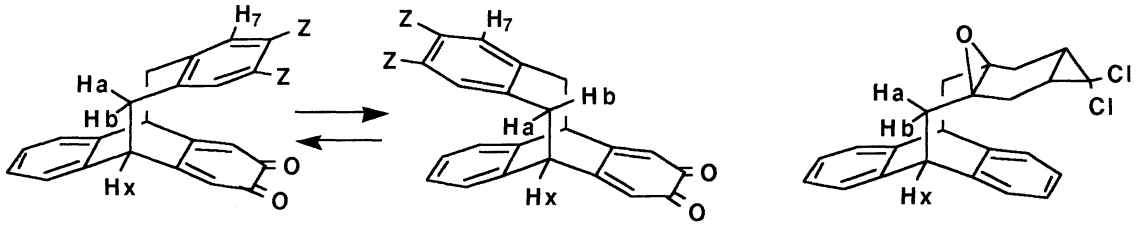
9 X=CN, Y=H, Z=OMe
10 X=H, Y=OAc, Z=H
11 X=H, Y=OAc, Z=OMe
12 X=CN, Y=Z=H

In the ^1H NMR spectra for **2** the signal due to methylene protons adjacent to the cyano group appears as a sharp singlet at room temperature suggesting a rapid equilibrium between the two equivalent folded structures by the flipping of the *o*-benzoquinone ring. Variable temperature NMR spectra for **2** were then examined in order to obtain the activation energy of this dynamic process. At -90 °C, the methylene signals appeared as a well split AB quartet. When the temperature was raised, each signal became broad at around -60 °C and coalesced at -44 °C. The free energy of activation for the flipping process was deduced to be 11 kcal/mol from the coalescence temperature method. The value is fairly large compared to that found in 1-cyano-1,10-*o*-benzeno[2.2]orthocyclophane (**12**; 7 kcal/mol).[5]

Mainly two reasons can be possible for explanation of the higher energy. One is some stabilization of ground state due to an attractive interaction of charge transfer from the donor (benzene ring) to the acceptor (*o*-benzoquinone). The other is destabilization of the transition state (TS) of the flipping process. The destabilization of the flipping transition state for **2** could be reasonably explained when we consider the difference of bond angles around juncture between the methylene bridge and upper π-system ($\angle C_2$-C_3-C_8 and $\angle C_3$-C_8-C_9) of **12** and **2**. Since the angles of **2** are smaller than those of **12** at its ground state, extent of the angle expansion at the TS is larger in **2** than **12**. Hence **2** is more destabilized at the TS than **12**. This explanation can be supported by our recent experiments[8] and MM2 calculations.[9]

In order to clarify whether the CT stabilization is truly operative or not, the conformational analysis of **3** which has *o*-benzoquinone moiety in the lower deck was performed. If the CT attractive interaction is effective, the syn structure (**3S**) should be predominant than the anti (**3A**). Through variable temperature ^1H NMR analysis, it has proven not to be the case. The coupling pattern of bridge protons appeared as A_2X (J_{AX}=6.5 Hz) throughout all the temperature measured (-60 °C—30 °C), showing no energy difference between the syn and the anti conformers. It is of great interest that there is no net stabilizing interaction between the benzene and the *o*-benzoquinone in fully stacked orientation though the latter is believed to be a good acceptor.[10]

On the other hand, it is found that there is a small stabilizing interaction between the *o*-benzoquinone and 1,2-dimethoxybenzene in **4**. The ^1H NMR signals of the bridge protons appear as an ABX pattern [δ 3.16 ppm (Ha), 3.30 ppm (Hb), 4.13 ppm (Hz); Jab=14.7, Jax=5.1, Jbx=8.8 Hz] at -80 °C, suggesting that the two



3S Z=H
4S Z=OMe

3A Z=H
4A Z=OMe

13

conformers (**4S** and **4A**) are energetically not equivalent. When we compare the coupling constants with those of the reference compound (**13**; Jax=2.1 and Jbx=11.3 Hz), whose structure is known to be fixed as shown, it is deduced that the relative ratio of the two conformers is 7:3 and the free energy difference between the two is 0.3 kcal/mol.

The evidence for the predominance of the syn structure can be obtained by comparison of the chemical shift of the aromatic protons of the upper deck of **4** (δH_7=6.45 ppm) with that of the reference compound (**9**; δH_7=6.31 ppm). Since the effect of magnetic anisotropy of *o*-benzoquinone is very small compared to that of benzene,[11] upfield shift for the protons of the upper deck is smaller in **4S** than in **4A** (≈6.31 ppm of **9**). Preference of **4S** is further supported by the chemical shift difference of the methylene protons. In **4S** the proton Ha should appear at the higher field than Hb because Ha is placed just above the benzene ring and hence has large influence of the ring current effect.

The electronic spectra of **2**, **3**,and **4** are shown in Fig. 1 together with that of the reference compound (4,5-dimethyl-*o*-benzoquinone). Although a clear valley around 330 nm can be observed in the reference compound, there is no clear valley in this region and a new broad absorption maximum at 325 nm can be seen in **2**. Similar broad bands at around 350—400 nm are observed also in **3** and **4**. From CNDO/S calculations it can be clarified in every case, that these new absorption bands are due to the charge transfer excitation from the donor to the acceptor. It is of great interest to find that in spite of no clear charge transfer attractive interaction between the benzene and *o*-benzoquinone in the compounds **2** and **3** in their ground state, the charge transfer excitation can be observed in the both compounds. These experiments clearly show that the 1,10-*o*-benzeno[2.2]orthocyclophane is an excellent system to evaluate attractive energy between a donor and an acceptor with the defined arrangement.

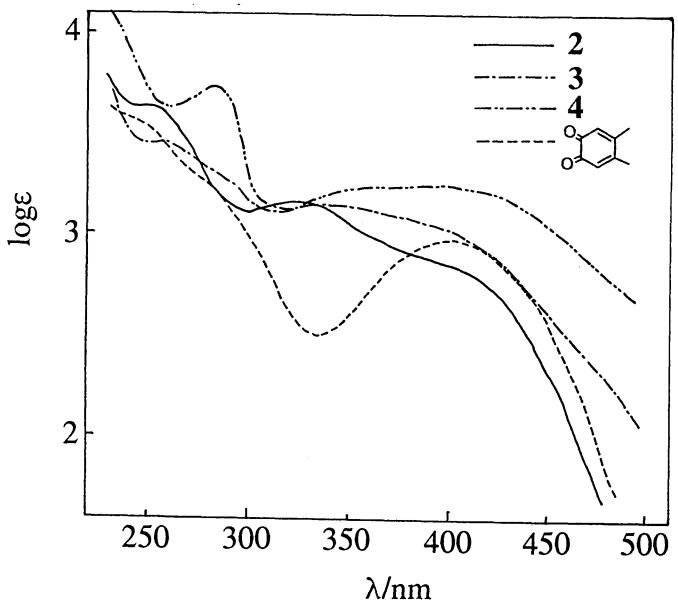


Fig. 1. The electronic spectra.

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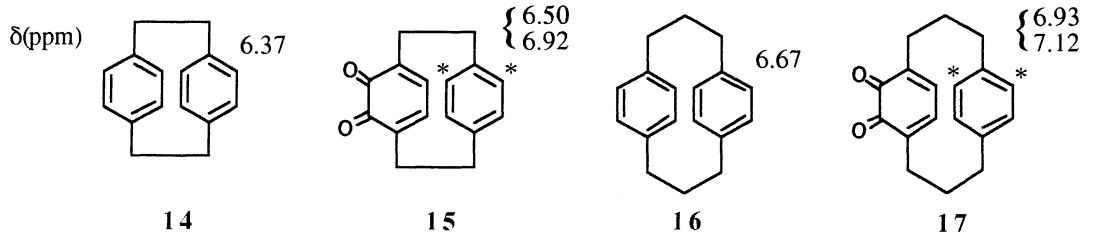
11) A comparison of the chemical shifts of the benzene protons for [2.2]- and [3.3]paracyclophanes (**14** and **16**) to those of cyclophanequinones[10] clearly suggests that the upfield shifts of benzene protons of **15** and **17** are smaller than those of **14** and **16**, respectively.



14 **15** **16** **17**

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