Flexible Molecular Tweezer Based on a Dioxa[2.2]orthocyclophane Linked with Weak Electron Acceptor

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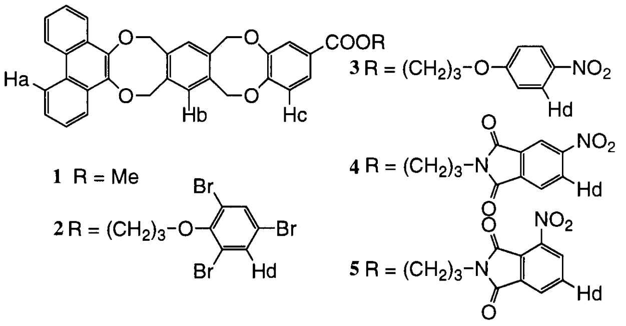
(Received February 16, 2000; CL-000159)

A flexible receptor having three aromatic chromophores can bind a weak electron acceptor which is linked covalently to the receptor with an appropriate alkyl chain. The receptor has tweezer type conformation when the acceptor was entrapped within its cavity. Sandwich type donor-acceptor-acceptor arrangement was realized in solution.

Molecular tweezers,[1] containing two aromatic chromophores connected by spacer are suitable receptors for planar guests since they can hold the guest with the two aromatic arms through π-stacking interactions.[2] The two aromatic arms of the host can bind the electron acceptor guests through charge transfer interaction forming sandwich type layered complexes.[3] Although rigid tweezers,[4] having a preorganized face-to-face arrangement of the two aromatic chromophores are favorable for strong binding, a flexible tweezer[5] has the adaptability for the variation of guests. In a previous paper,[6] we reported that the flexible tweezer (**1**) based on a dioxa[2.2]orthocyclophane[7] can bind strong π-electron deficient guests to form a layered donor-acceptor-acceptor arrangement in the crystalline state. In a case of a relatively weak electron accepting guest, however, no intermolecular complex formation with host **1** was observed in solution. A large entropic cost[8,9] prevented the formation of the intermolecular complex in organic solvents. In order to overcome the unfavorable entropic cost, we linked the guest to the host with an appropriate methylene chain. In this paper, we report on the intramolecular complex formation and molecular structures of these tethered host-guest compounds.

As the weak electron acceptor, 2,4,6-tribromoanisole, 4-nitroanisole, *N*-methyl-3-nitrophthalimide, and *N*-methyl-4-nitrophthalimide were selected.[10] These weak electron acceptors were connected with ester linkage to host **1**.



The NMR chemical shift difference for the aromatic protons in these tethered compounds with respect to the references should give an information of the extent of the intramolecular interaction between the tweezer and guest chromophores in solution. In these tethered compounds, there are roughly two conformers, open and closed forms (Figure 1). As can be easily seen, the entropy of the open form is far larger than closed one.[11] The entropy changes are primarily a consequence of losses of internal rotation of the tether moiety in the closed form. Because of the large entropy difference, the ratio of close/open should be temperature dependent; the lower the temperature the larger the ratio of the smaller entropy form.[12] Hence, the NMR measurements at lower temperature were carried out.

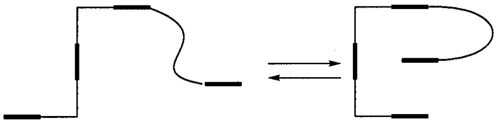


Figure 1. Open and closed forms of tethered compounds.

Table 1 shows the comparison of the chemical shift of the aromatic protons in the tethered host-guest compounds. As is clearly seen, the chemical shift on the phenanthrene moiety of **2** did not change from its reference compound even at the low temperature. The same is true for both the durene and benzoate moieties. Very small chemical shift changes were observed for the aromatic protons of the guest moiety. The chemical shift change might be due to the change of the relative population within the open form, since there should be a significant amount of conformers in the open form and their population should be temperature dependent. Intramolecular π-π stacking between the aromatic rings of the host and guest is not probable because of the observed downfield shift. The conformational behavior of **3** is quite similar to that of **2** because very small downfield shift of the guest in **3** along with almost no change of chemical shift in the host moiety were observed.

Table 1. Selected chemical shift of **2**,**3**,**4** and their reference compounds

Compounds		Ha	Hb	Hc	Hd	Hd	Hd
Reference	25℃	8.58	7.17	6.89	7.58	8.08	8.58
2	25℃	8.58	7.15	6.90	7.64		
	-60℃	8.58	7.19	6.91	7.68		
3	25℃	8.57	7.15	6.90		8.16	
	-60℃	8.59	7.20	6.90		8.21	
4	25℃	8.44	7.22	6.56			7.89
	-60℃	8.19	7.38	6.00			6.46

On the other hand, the pattern of the chemical shift movement of **4** is quite different to those of **2** and **3**. The chemical shift of the proton in the phenantherene ring shifted upfield by 0.14 ppm from that of the reference compound at room temperature. The upfield shift is more pronounced at –60 ˚C. Similar upfield shift was observed in the aromatic proton of benzoate moiety. Figure 2 shows the temperature dependent chemical shift movement for **4**. The upfield shift of the two terminal chromophores within the host moiety is clearly seen. The gradients of these two lines are rather similar. The upfield shift of the proton in the guest is more pronounced and the gradient of the plot is larger than these two lines. The large upfield shift of the guest strongly suggests the sandwich type layered stacking of the three aromatic moieties, phenanthrene-guest-benzoate, as was found in the crystalline complex of **1**•TCNQ.[6a]

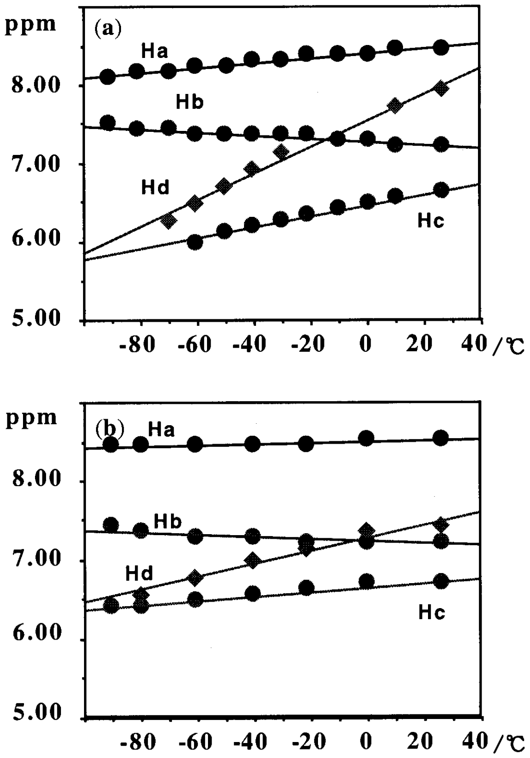


Figure 2. Temperature dependent chemical shift of **4**(a) and **5**(b).

In such a sandwich arrangement the central ring should have large influence due to the ring current effect of the aromatic rings above and below and should have large upfield shift than that of either one of the two outside rings. The chemical shift of the proton in the durene ring within the host moiety, however, moved downward when lower the temperature. This characteristic downfield shift further supports the sandwich arrangement. In this arrangement, the durene proton is placed in the deshielding region of the guest aromatic ring. Thus, the chemical shift movement of all the protons can be clearly explained by the formation of the intramolecualr complex of the host and guest with sandwich arrangement of the three aromatic rings. In other words, the guest moiety was bound within the tweezer shaped host in the closed form.

Very similar movement of the chemical shift of the aromatic protons was observed in **5** though to the lesser extent than **4** (Figure 2). Again the formation of the intramolecular charge transfer complex, in which the guest resides within the tweezer shaped host, was realized in **5**. Smaller shift differences in **5** with respect to those in **4** reflected the weaker electron accepting ability of 3-nitro than 4-nitro derivative.[10] Weaker charge transfer interaction between the host and guest resulted in smaller close/open ratio in **5** even at the lower temperature.

In conclusion, even a weak electron acceptor can form the intramolecular sandwich type layered complex with host having the tweezer conformation in solution.

References and Notes

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