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# Estimation of Through-space Interaction between Two Aromatic Rings in Metacyclophanes

Akihiko Tsuge\* and Tetsuji Moriguchi\*

[2.n]Metacyclophanes of which various kinds of functional groups were introduced into the aromatic rings have been synthesized in order to evaluate the specific through-space interaction in cyclophane systems. The cationic character in the metacyclophanediazonium salts was found to be strongly affected by the electronic effect of the substituent on the opposite aromatic ring *via* the through-space interaction between two aromatic rings. Spectral properties of disubstituted metacyclophanes and stilbenophanes showed that a [2.n]metacyclophane can be regarded as a nonplanar molecule with one conjugated system due to a strong through-space interaction. Such an interaction of the [2.3]system has been proved to decrease in comparison with that of the [2.2]system.

## Introduction

Physical and chemical properties of small-sized cyclophanes have been stimulating subjects for many years,<sup>1)</sup> among other things considerable attention has been focused on a through-space interaction between aromatic rings because such a transannular interaction plays a decisive role in their unique characteristics. This transannular electronic effect in cyclophanes is particularly intriguing in terms of intramolecular charge-transfer systems since cyclophane compounds provide the forced proximity and particular orientation of  $\pi$ -systems.

On the other hand we have been interested in a through-space interaction<sup>2-4)</sup> between two aromatic rings in [2.2]metacyclophanes because this interaction is obviously responsible for their unusual reactivities.

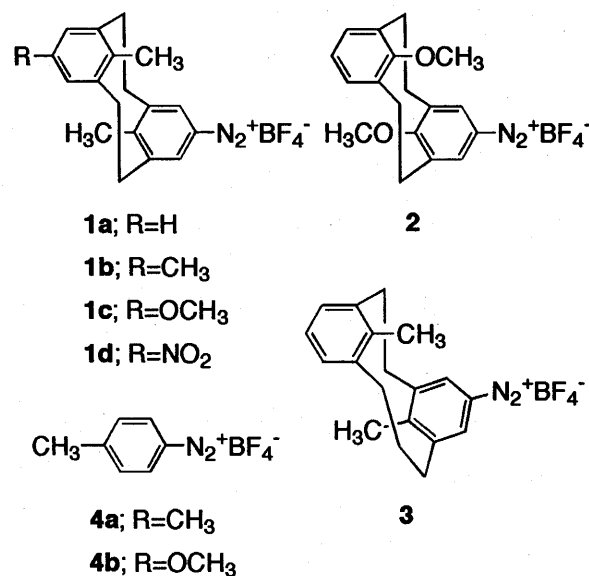
[2.n]Metacyclophanes which consist of two aromatic rings connected with the two bridges of different length have also been investigated.<sup>5-7)</sup> It was found out that [2.n]metacyclophanes usually exhibit different reactivities from those of [2.2]metacyclophanes, which is most probably attributed to the specific through-space interaction in [2.n]metacyclophanes, however, only little is known about this interaction.

These facts have prompted us to do systematic studies of transannular effects in [2.n]metacyclophanes, thus, we here report on the synthesis of various kinds of [2.n]metacyclophane derivatives and quantitative estimation of their through-space interaction.

## Results and Discussion

### [2.n]Metacyclophanediazonium Salts

It is predictable that an ionic portion incorporated into cyclophanes should undergo the changes of their electronic state, thus [2.2]metacyclophanediazonium salts (1a-d) which carry a functional group at their outer aromatic position and [2.3]metacyclophanediazonium salts (2) were synthesized.<sup>8)</sup>



Stretching vibration of N-N triple bond of these salts seems to be strongly affected by the outer substituents

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Dedicated to Professor Masashi Tashiro on the occasion of his retirement

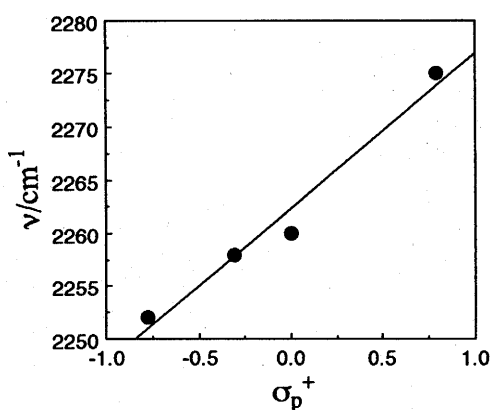
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This paper is submitted through Professor Shuntaro Mataka

(Table 1). When the stretching vibration is plotted against the Hammett constant of the substituent, a linear relationship is obtained (Figure 1), indicating that the electronic effect of the substituent on the opposite aromatic ring could be transmitted to the other ring *via* a through-space interaction.

**Table 1** IR data for the diazonium salts

Diazonium salt	$\nu(\text{N}_2)/\text{cm}^{-1}$
1a	2260
1b	2258
1c	2252
1d	2275
3	2262
4a	2275



**Figure 1** Correlation between stretching vibration of  $\text{N}_2$  group and the  $\sigma_p^+$  constant

It has been shown that cationic character of the arenediazonium ion can be estimated by its stability constant for the complexation with crown ether.<sup>9-14</sup> This constant is supposed to reflect the electronic nature of the aromatic ring to which the diazonio group is attached. If this estimation is applied to the cyclophane system in which the nature of the aromatic ring could give significant influences on a through-space interaction, fruitful information concerning this interaction would be obtained.

The stability constants were determined in 1,2-dichloroethane according to the reported method.<sup>14</sup> In Table 2 Ks values are summarized together with the spectral properties of the diazonium salts and their complexes.<sup>15,16</sup> The data of the referential *p*-substituted benzenediazonium tetrafluoroborates are also shown in Table 2. In any cases blue shifts of  $\lambda_{\text{max}}$  can be observed on complexation with 18-crown-6, probably due to the decrease of the ability of the diazonio moiety to withdraw electrons from the ring resulting in decreasing mesomeric effect in such *p*-disubstituted benzenes.

It is well known<sup>12,13</sup> that the cations with the more effective positive charge on the nitrogen atoms of the diazonium ion can form the stronger complexes and *vice versa*. The stability constants for 1a and 2 are about 10 times as small as those for 4a and 4b, respectively, which is chiefly derived from the decrease of electron density on cyclophanediazonium cations. In more detail one aromatic ring of the cyclophane positively increases  $\pi$ -electron density of the aromatic ring of the other side, consequently reducing cationic character of the diazonium ion.

Such an effect is significantly influenced by the substituent on the opposite aromatic ring. The electron-releasing group such as methyl and methoxyl groups in 1b and 1c decreases the stability constant. These results imply that the electron-releasing substituent could affect a cationic character of the diazonium salts by a through-space interaction. This concept is also supported by an increase in the stability constant for 1d in which the aromatic ring has the electron-withdrawing nitro group.

**Table 2** Stability constants (Ks) for the complexes

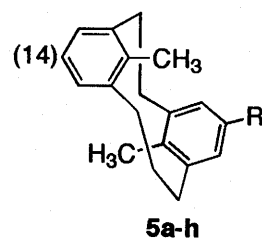
Diazonium salt	$\lambda^{\text{Fmax a)}$	$\lambda^{\text{Cmax b)}$	log Ks
1a	391	347	4.12
1b	409	360	3.73
1c	447	403	3.50
1d	356	328	4.58
2	355	327	3.73
3	376	325	4.89
4a	282	264	5.10
4b	321	298	4.67

a)  $\lambda_{\text{max}}$  of the free diazonium salt

b)  $\lambda_{\text{max}}$  of the complex

For 3 a larger stability constant was observed as compared with 1a. These observations suggest that a through-space interaction between two aromatic rings decreases in the [2.3] system, which stems from the difference in the distance of two aromatic rings between the [2.2] and [2.3] systems.

*Substituted [2.n]Metacyclophanes*



a: R=H    b: R=NO<sub>2</sub>    c: R=NH<sub>2</sub>    d: R=F  
e: R=OCH<sub>3</sub>    f: R=CHO    g: R=CH<sub>3</sub>

In order to evaluate a through-space interaction in metacyclophanes by their NMR and UV spectra various substituted [2.3]metacyclophanes<sup>17)</sup> have been prepared. Chemical shifts of aromatic proton (14 position) in **5a-g** are summarized in Table 3.

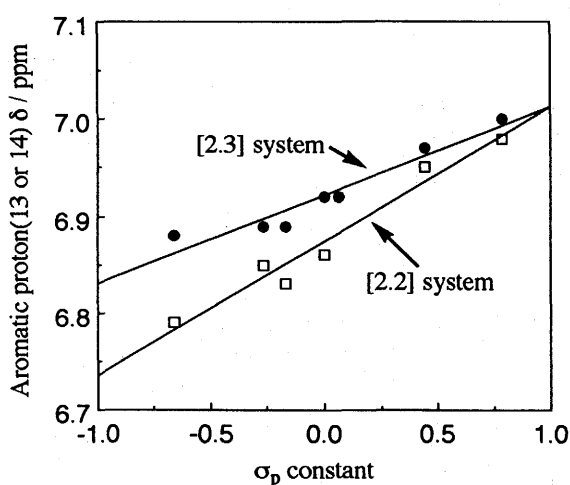
**Table 3** Spectral data of [2.3]metacyclophanes

Cyclophane	Chemical shift ( $\delta$ /ppm) <sup>a)</sup>	$\lambda_{\max}$ /nm <sup>b)</sup>
	Aromatic Ha(14)	
<b>5a</b>	6.92	275
<b>5b</b>	7.00	330
<b>5c</b>	6.88	303
<b>5d</b>	6.92	280
<b>5e</b>	6.89	289
<b>5f</b>	6.97	294
<b>5g</b>	6.89	280

a) In  $\text{CDCl}_3$ , 27 °C    b) In  $\text{CHCl}_3$

The NMR behavior of the aromatic protons is closely related to the ring current, which is remarkably subject to the effect of the opposite ring in the cyclophane systems.

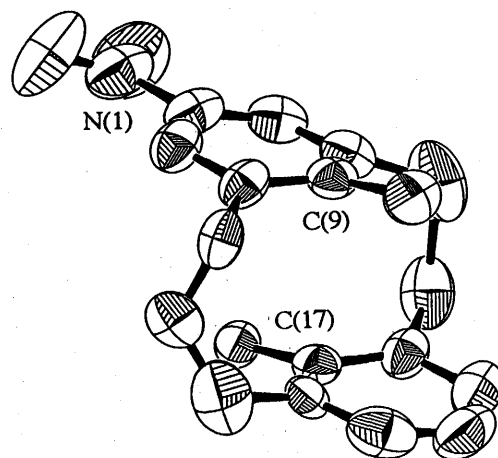
The Hammett substituent constants are widely used to express the electronic effects of substituents.<sup>18)</sup> Thus, when the chemical shifts for the proton at 14 position are plotted against  $\sigma_p$  of the substituents at 6 position, a straight line is obtained as shown in Figure 2. The corresponding correlation for the [2.2]metacyclophanes was also inserted in Figure 2. Such linear relationships imply that electronic effect of the substituent on the aromatic ring could be probably transmitted to the other ring *via* a through-space interaction.



**Figure 2** Correlation between chemical shift of aromatic proton and the  $\sigma_p$  constant of the substituent in the [2.3] and [2.2] system

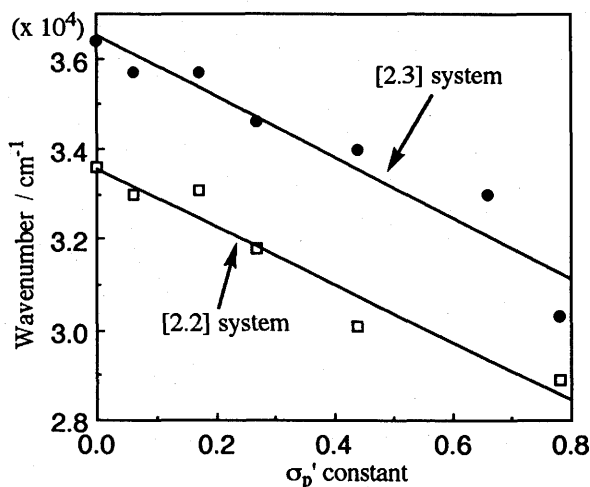
Furthermore, the difference in these slopes is

interesting, since it obviously reflects the different transannular interaction between two metacyclophane systems; more precisely the electronic nature is transmitted less effectively to the benzene ring on the other side in the [2.3] system than the [2.2]<sup>19)</sup> system. This difference in these two systems must reflect in part the different geometries of the [2.3] and the [2.2]metacyclophane skeletons.



**Figure 3** Perspective view of **5b**

Figure 3 shows the X-ray analysis of **5b** in which the C9-C17 distance (2.96 Å) is somewhat greater than the corresponding C8-C16 distance (2.82 Å) in the corresponding [2.2]metacyclophane.<sup>20)</sup> Accordingly a through-space interaction is reduced in the [2.3] system resulting in the decrease in the slope for [2.3]metacyclophanes. It can be presumed that the [2.n] system would undergo more enhanced through-space interaction as two benzene rings approximate more closely each other.



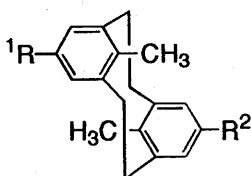
**Figure 4** Correlation between wavenumber and the  $\sigma_p'$  constant of the substituent in the [2.3] and [2.2] system

It is also expected that electronic spectra of metacyclophanes can provide information on the nature of

transannular electronic interaction in their  $\pi$ -electron system. The  $\lambda_{\max}$  values for the substituted [2.3]metacyclophanes can be characterized by bathochromic shifts in comparison with that of **5a** as summarized in Table 3.

The plot of the  $\lambda_{\max}$  values is shown in Figure 4 where the difference in the  $\sigma_p$  values of the substituent and hydrogen that is considered as the functional group at 14 position is adapted as the defined substituent constant in this cyclophane system. The data for the corresponding [2.2] system were also shown. The  $\lambda_{\max}$  values for the [2.3] system exhibit hypsochromic shifts as compared to those for the [2.2] system with a linear relationship against their defined  $\sigma_p$  values ( $\sigma_p'$ ).

In general the extent of conjugation in the system results in a bathochromic shift, it can therefore be speculated that there exists less extended conjugation in the [2.3] system than the [2.2] system. The linear relationships suggest that there exists a conjugated system in which a through-space interaction participates. The mode of the conjugation in the [2.n] systems can be correlated to a through-space interaction, in other words, distance or orientation of their two aromatic rings.



- 6a**;  $R^1=I$ ,  $R^2=NO_2$   
**6b**;  $R^1=OCH_3$ ,  $R^2=NO_2$   
**6c**;  $R^1=F$ ,  $R^2=CHO$   
**6d**;  $R^1=CH_3$ ,  $R^2=CHO$   
**6e**;  $R^1=NH_2$ ,  $R^2=NO_2$

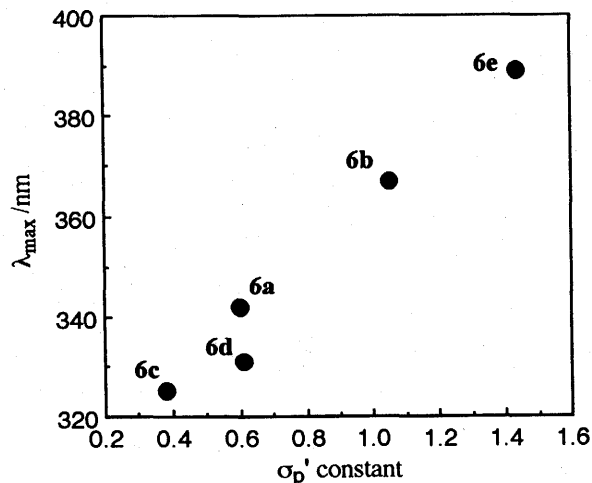
**Table 4** Absorption maxima<sup>a)</sup> for **6a-e**

Compound	$\lambda_{\max}$ /nm	$\log \epsilon$
<b>6a</b>	342	4.06
<b>6b</b>	367	4.94
<b>6c</b>	325	3.55
<b>6d</b>	331	3.58
<b>6e</b>	389	3.59

a) In  $CHCl_3$  at 25 °C

In order to gain a deeper insight into a through-space interaction we have prepared [2.2]metacyclophanes with a different kind of functional group on each ring.<sup>19,21)</sup> The absorption maxima of these disubstituted [2.2]metacyclophanes (**6a-e**) are summarized in Table 4. Here, the difference in the  $\sigma_p$  values of the functional groups is

defined as the substituent constant for disubstituted [2.2]metacyclophanes, which is shown in Figure 5.



**Figure 5** Correlation between  $\lambda_{\max}$  and  $\sigma_p'$  constant of the substituent in the [2.2] system

Interestingly  $\lambda_{\max}$  values for **6a-e** show a linear relationship against their defined  $\sigma_p$  values ( $\sigma_p'$ ). For example **6e** exhibits a great bathochromic shift which extends into the visible region. When the two substituents are of the same type such as in **6a** and **6c**, their spectra are similar to those of the corresponding monosubstituted [2.2]metacyclophanes because each of substituents decreases the conjugation of the other one.

In **6d** both substituents are not so strong in electron-donating and electron-accepting properties resulting in a smaller bathochromic shift as compared with **6e**. **6e** is expected to possess some interesting properties because it has two aromatic rings having a strong electron-withdrawing group and a strong electron-releasing group in close proximity. Such a deviation in  $\pi$ -electron state must influence the NMR spectra of these compounds. In fact the signals for two kinds of methyl protons of **6e** appear at  $\delta$  0.49 and  $\delta$  0.90, respectively. Such a significant difference in the chemical shifts results from extensive deviation of  $\pi$ -electron density between two aromatic rings due to a cooperative effect of the electron-donor and the electron-acceptor substituents.

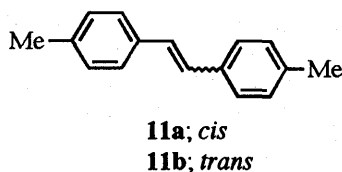
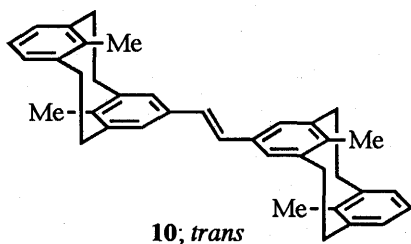
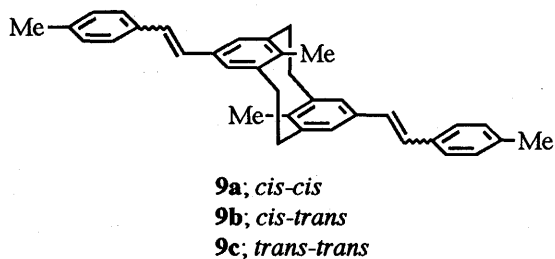
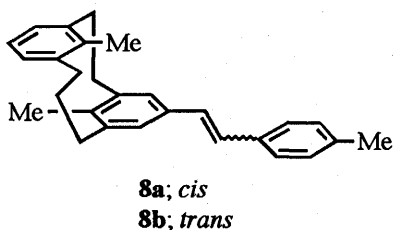
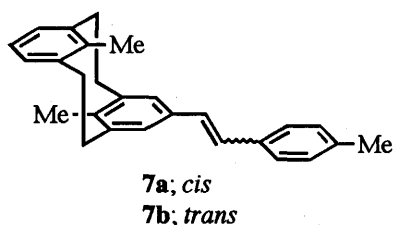
From these results it can be concluded that the [2.2]metacyclophane is a nonplanar molecule with one conjugated system due to a strong through-space interaction between two aromatic rings.

[2.n]Metacyclophanes consisting of a stilbene unit<sup>22,23)</sup>

Stilbenes are an important class of compounds with a wide range of applications in basic and applied research on  $\pi$ -conjugated materials.<sup>24)</sup> Small-sized cyclophanes can be regarded as fascinating molecules for developing new materials based on  $\pi$ -electron systems since their aromatic rings are situated in the forced proximity and particular orientation. In particular [2.2]metacyclophanes and related compounds possibly could play an

important role in the design and construction of a  $\pi$ -conjugated systems that are closely related to their through-space interaction.<sup>25-27)</sup>

To our best knowledge, however, the stilbene unit has only been incorporated into the macrocyclic system<sup>28,29)</sup> in which no obvious inter- or intramolecular  $\pi$ -electron interaction is observed. Therefore, we decided to synthesize and investigate the small-sized [2.n]metacyclophanes consisting of a stilbene unit (=stilbenophanes).



An apparent way to investigate the extent of the conjugation in the cyclophane system is to know the influence of the conjugated system on the wavelength in the UV spectra, thus,  $\lambda_{\max}$  values for stilbenophanes 7-10 are listed together with stilbenes 11a,b in Table 5.

All stilbenophanes exhibit a bathochromic shift as compared with the referential compounds 11, which can probably be ascribed to the effect of the cyclophane skeleton working as an electron-releasing group *via* a through-space interaction upon the stilbene chromophore.

Table 5  $\lambda_{\max}$  of stilbenophanes<sup>a)</sup>

Compound	$\lambda_{\max}$ /nm
7a( <i>cis</i> )	317
7b( <i>trans</i> )	332
8a( <i>cis</i> )	307
8b( <i>trans</i> )	327
9a( <i>cis-cis</i> )	322
9b( <i>cis-trans</i> )	338
9c( <i>trans-trans</i> )	344
10( <i>trans</i> )	348
11a( <i>cis</i> )	286
11b( <i>trans</i> )	300

a) In cyclohexane at 27 °C

Change of configuration from *trans* to *cis* produces a hypsochromic shift in cyclophane systems as well as the stilbene 11 because the *cis* isomers are supposed to be less elongated form. Although the *trans* stilbene 11b shows an absorption peak at 300 nm, it is shifted to 327 nm and 348 nm in stilbenophane 8b and 10, respectively.

Apparently such a bathochromic shift is ascribed to the extent of conjugation which can be enhanced by the through-space interaction in the cyclophane skeleton. This is consistent with the further bathochromic shift observed for the bis(cyclophane) compound 10. The  $\lambda_{\max}$  values of [2.3]stilbenophanes 8a and 8b are hypsochromically shifted from those of the corresponding [2.2]stilbenophanes 7a and 7b.

In stilbenophane 9 a bathochromic shift is enhanced in order of *cis-cis*, *cis-trans*, and *trans-trans* isomers, which strongly indicates that conjugation of two stilbene chromophores occurs through transannular interaction in [2.2]metacyclophane skeleton.

The present study reveals that novel  $\pi$ -conjugated systems based on a stilbene unit could be created by the [2.n]metacyclophanes employing their strong through-space interaction.

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