Evaluation of Transannular Interaction in [2.3]Metacyclophanes

Akihiko Tsuge,* Mikio Yasutake, Tetsuji Moriguchi, Kazunori Sakata, Takehiko Yamato,[†] Shuntaro Mataka,[††] and Masashi Tashiro[††]
Department of Chemistry, Kyushu Institute of Technology, Tobata-ku, Kitakyushu 804
[†]*Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga, Saga 840*
[††]*Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816*

(Received January 6, 1997; CL-970011)

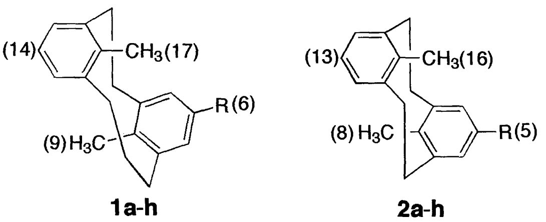
[2.3]Metacyclophanes(=MCPs) which carry various functional groups at their outer aromatic position have been synthesized. The transannular interaction between two aromatic rings of [2.3]MCPs estimated by their NMR and UV spectra has been proved to decrease in comparison with that of the [2.2]MCP system.

Physical and chemical properties of [2.2]MCPs have been stimulating subjects for many years,[1] among other things considerable attention has been focused on their transannular interaction between two aromatic rings because such a through-space interaction plays a significant role in their unique characteristics.

[2.n]MCPs which consist of two aromatic rings connected with the two bridges of different length have also been investigated.[2-4] It was found out that [2.n]MCPs usually exhibit different reactivities from those of [2.2]MCPs,[5] which is most probably attributed to the particular transannular interaction in [2.n]MCPs, however, only little is known about such interaction in those compounds. The transannular interaction in [2.2]MCP system was already characterized by UV spectral properties of the chromophore introduced in their skeleton and NMR spectra of the substituted [2.2]MCPs.[6,7] This has prompted systematic studies of transannular effects in [2.n]MCPs.

This paper describes the synthesis of substituted [2.3]MCPs and an estimation of the transannular interactions in these compounds based on their NMR and UV spectra.

The basic [2.3]MCP skeleton (**1a**)[3] and nitro [2.3]MCP (**1b**)[5] were synthesized according to the previous method. Reduction of **1b** with Pd/C under H_2 afforded amino [2.3]MCP (**1c**). **1c** was treated with isopentyl nitrite in EtOH, followed by the addition of 42% tetrafluoroboric acid to yield [2.3]MCP diazonium salt (**1d**). The salt **1d** was pyrolyzed under the reduced pressure to afford fluoro [2.3]MCP (**1e**). Methoxy [2.3]MCP (**1f**) was obtained by the reaction of **1d** in MeOH. Reduction of formyl [2.3]MCP (**1g**)[4] with Pd/C under H_2 gave the corresponding methyl [2.3]MCP (**1h**).



1a-h **2a-h**

a: R=H b: $R=NO_2$ c: $R=NH_2$ d: $R=N_2{}^+BF_4{}^-$
e: R=F f: $R=OCH_3$ g: R=CHO h: $R=CH_3$

$$\mathbf{1b} \xrightarrow{\text{i}} \mathbf{1c} \qquad \mathbf{1d} \xrightarrow{\text{iii}} \mathbf{1e}$$
$$\mathbf{1c} \xrightarrow{\text{ii}} \mathbf{1d} \qquad \mathbf{1d} \xrightarrow{\text{iv}} \mathbf{1f}$$
$$\mathbf{1g} \xrightarrow{\text{v}} \mathbf{1h}$$

Reagents and conditions: i, Pd/C, H_2, benzene, 93%, ii, HCl, $C_5H_{11}ONO$, 42% HBF_4, EtOH, 85%, iii, 100 °C, 90%, iv, MeOH, 88%, v, Pd/C, H_2, benzene, 53%.

Scheme 1.

Table 1. Spectral data of [2.3]MCPs and [2.2]MCP

Cyclophane	Chemical shift (δ/ppm)[a]	λmax (nm)[b]
	Aromatic Ha(14)	
1a	6.92	275
1b	7.00	330
1c	6.88	303
1e	6.92	280
1f	6.89	289
1g	6.97	294
1h	6.89	280

[a]In $CDCl_3$, 27 °C. [b]In $CHCl_3$.

Chemical shits of aromatic proton (14 position) in **1a-h** are summarized in Table 1.

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 MCP systems.

The Hammett substituent constants are widely used to express the electronic effects of substituents. Thus, when the chemical shifts for the proton at 14 position are plotted against σ_p of the substituent at 6 position, a straight line is obtained as shown in Figure 1. The corresponding correlation for the [2.2]MCPs was also inserted in Figure 1. Such linear relationships imply that electronic effect of the substituent on the aromatic ring could be probably transmitted to the other ring *via* transannular interaction.

Furthermore, the difference in these slopes is interesting since it obviously reflects the different transannular interaction between two MCP systems; more precisely the electronic nature is transmitted less effectively to the benzene ring on the other side in the [2.3]MCP system than the [2.2]MCP[7] system. This difference in these two systems must reflect in part the different geometries of the [2.3] and the [2.2]MCP skeletons.

Figure 2 shows the X-ray analysis of **1b**[8] in which the C9-C17 distance (2.96 Å) is somewhat grater than the corresponding C8-C16 distance (2.82 Å) in **2a**.[9] Accordingly transannular interaction is reduced in the [2.3]MCP system resulting in the decrease in the slope for [2.3]MCPs. It can be presumed that [2.n]MCP system would undergo more enhanced transannular interaction as two benzene rings approximate more closely each other.

It is also expected that electronic spectra of MCPs can provide information on the nature of transannular electronic interaction in

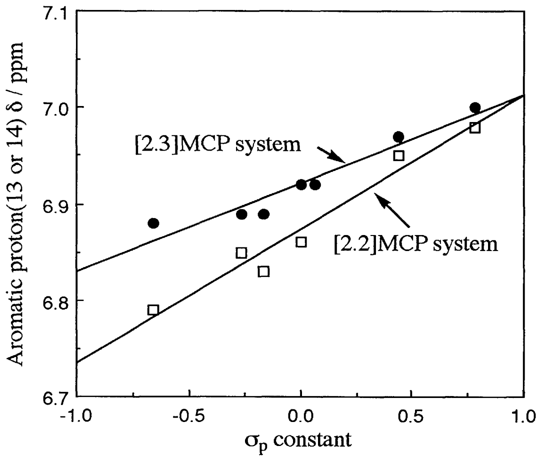


Figure 1. Correlation between chemical shift of aromatic proton cand the σ_p constant of the substituent in the [2.3] and [2.2]MCPs system.

their π-electron system. The UV spectrum of [2.3]MCP(**1a**) is designated the "cyclophane spectrum".[10] The λ_{max} values for the substituted [2.3]MCPs can be characterized by bathochromic shifts in comparison with that of **1a** as summarized in Table 1.

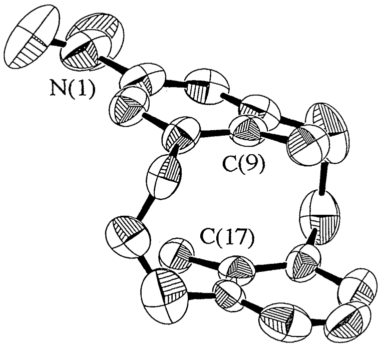


Figure 2. Perspective view of **1b**.

The plot of the λ_{max} values is shown in Figure 3, where the difference in the σ_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 MCP system. The data for the corresponding [2.2]MCP system were also added. The λ_{max} values for the [2.3]MCPs exhibit hyspochromic shifts as compared to those for the [2.2]MCPs with a linear relationship against their defined σ_p values(σ_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 [2.3]MCP system than [2.2]MCP system. The linear relationships suggest the conjugated system involving the transannular interaction. The mode of the conjugation in [2.n]MCP systems can be correlated to the transannular interaction, in other words, distance or orientation of their two aromatic rings. Consequently the results obtained here are apparently in accord with the geometry of [2.3]MCPs.

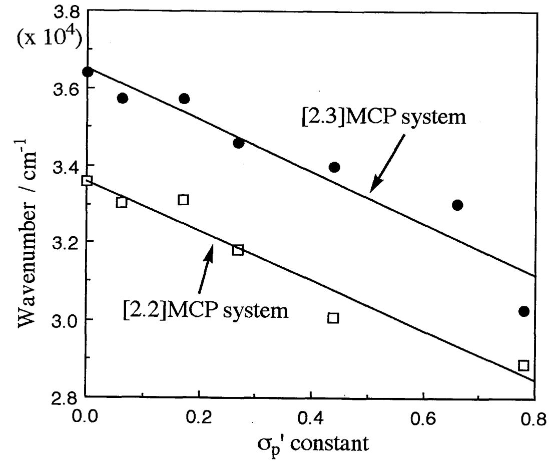


Figure 3. Correlation between wavenumber and the σ_p constant of the substituent in the [2.3] and [2.2]MCP system.

In the [2.3]MCP system there exits a reduced transannular interaction as compared with that in the [2.2]MCP system, nevertheless, by which the electronic effect is transmittable between two aromatic rings and one conjugated system is produced in the nonplaner molecule.

References and Notes

1 For example, see: D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *J.Am.Chem.Soc.*, **82**, 6302 (1960); N. L. Allinger, M. A. DaRooge, and R. B. Hermann, *J.Am.Chem. Soc.*, **83**, 1974 (1961); F. Vögtle and P. Neumann, *Angew. Chem., Int.Ed.Engl.*, **11**, 73 (1972).

2 For example, see: R. W. Griffin, Jr. and R. A. Coburn, *J. Am.Chem.Soc.*, **89**, 4638 (1967); D. Krois and H. Lehner, *J.Chem. Soc., Perkin Trans 1*, **1982**, 477.

3 T. Yamato, H. Sakamoto, K. Kobayashi, and M. Tashiro, *J. Chem.Res.*, **1986**, (*S*) 352; (*M*) 2886.

4 T. Yamato, J. Matsumoto, S. Kabu, Y. Takezaki, and M. Tashiro, *J.Chem.Res.*(*S*), **1993**, 44.

5 T. Yamato, J. Matsumoto, K. Tokuhisa, K. Takezaki, and M. Tashiro, *Chem.Express*, **6**, 663 (1991).

6 A. Tsuge, T. Moriguchi, S. Mataka, and M. Tashiro, *J.Chem.Soc.,Perkin Trans 1*, **1993**, 2211; A. Tsuge, T. Moriguchi, S. Mataka, and M. Tashiro, *Bull.Chem.Soc. Jpn.*, **67**, 277 (1994).

7 A. Tsuge, T. Moriguchi, S. Mataka, and M. Tashiro, *J. Org. Chem.*, **60**, 4930 (1995).

8 Crystal Data for **1b**: $C_{19}H_{21}NO_2$, M=295.38, monoclinic, space group $P2_1/a$(No.14), a=11.869(2), b=9.003(2), c=14.320(2) Å, β=93.753(10)°, V=1527.0(4) Å^3, Z=4, D_{calc}=1.285 g/cm^3, μ(CuKα)=6.57 cm^{-1}, Rigaku AFC7R diffractometer, 1523 reflections with I>3.00σ(I), R=0.078, R_w=0.056.

9 A. W. Hanson, *Acta Cryst.*, **15**, 956 (1962).

10 L. L. Ingrahan, *J.Chem.Phys.*, **27**, 1228 (1957).