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Evaluation of Transannular Interaction of [2.3]Metacyclophane-diazonium Tetrafluoroborate and its Dediazoniated Derivatives

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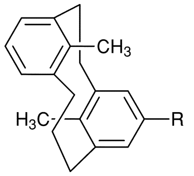
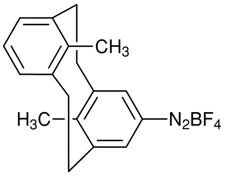
Transannular interactions of [2,3]metacyclophane-diazonium tetrafluoroborate and its dediazoniated derivatives have been evaluated by ^{1}H NMR, IR, UV and stability constant determination.

A transannular interaction between two aromatic rings in small-sized cyclophanes has attracted great interest among physical organic chemists.[1] However, extensive studies[2,3] on this subject for [2.*n*]metacyclophane (MCP) systems seem to be very limited. In this paper, we have prepared 8,16-dimethyl[2.3]MCP-diazonium tetrafluoroborate (**4**) and various kinds of 6-substituted[2.3]MCPs (**7**) by dediazoniation of **4**. To elucidate the difference in the transannular interaction between the [2.2]MCP and [2.3]MCP systems in detail, we determined the stability constant of the salt with 18-crown-6 and examined the spectral properties of 6-substituted[2.3]MCPs (**7**).



1 R = H
2 R = NO_2
3 R = NH_2
4 R = N_2BF_4
7a R = F
7b R = $OCOH_3$
7c R = $OCOCH_3$
7d R = CHO
7e R = CH_3



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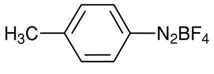

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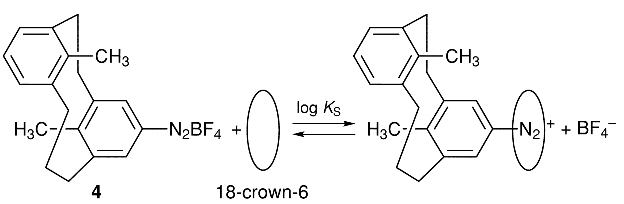
We measured the IR spectra of **4**–**6** to obtain clear evidence of the transannular interaction. Data are also listed in Table 1. The differences between wavenumbers of the N_2 triple bond of [2.*n*]MCP-diazonium tetrafluoroborate ($n = 3,2$) (**4**, **5**) and that of toluene-*p*-diazonium tetrafluoroborate (**6**) are 15–17 cm^{-1}. On the other hand, the wavenumbers of the N_2 triple bond of the [2.3]MCP salt (**4**) and the [2.2]MCP salt (**5**)[7] appear at 2258 and 2260 cm^{-1}, respectively; the difference between these two wavenumbers is very small. It is found that the N_2 triple bond character of the [2.3]MCP salt (**4**) is similar to that of the [2.2]MCP salt (**5**);[8] however, the N_2 triple bonds in [2.*n*]MCP salts are apparently lengthened compared with that of the salt **6**. This implies that transannular interactions of [2.*n*]MCP salts stabilize resonance structures of aryldiazonio skeletons.

Table 1 Selected physical data of the diazonium salts **4**, **5** and **6**

Diazonium salt	ν/cm^{-1a}	$\lambda_{diazonium}/nm^b$	$\lambda_{complex}/nm^b$	log K_s
5	2260	376	325	4.12[c]
4	2258	391	347	4.89[d]
6	2275	282	264	5.10[e]

[a]In KBr. [b]In $C_2H_4Cl_2$ at 20 °C. [c]Ref. 3. [d]These values were calculated by two different methods, see experimental. [e]Ref. 9.

Determination of the stability constants (log K_s) for the complex of diazonium salt (**4**) with 18-crown-6 was carried out in 1,2-dichloroethane at 20 °C by Benesi–Hildebrand methods (Scheme 2). This is a thermodynamic determination by using the electronic absorption spectra according to Hashida and Matsui.[9] They also measured the stability constant for the toluene-*p*-diazonium salt (**6**) under the same conditions (log $K_s = 5.10$). From this method log K_s of **4** is 4.89. On the other hand, we have reported that the log K_s of the salt **5** is 4.12.[3] The value for the [2.2]MCP salt (**5**) is *ca.* 0.77 smaller than that of the [2.3]MCP salt (**4**). Both stability constants for the [2.*n*]MCP salts are larger than that of **6**. This difference indicates the stabilization of the aryldiazonium cation by the electron-releasing effect of an opposite aromatic ring.



Scheme 2

Table 3 Selected ^{1}H NMR data[a] for 6-substituted[2.3]MCPs

Compound	Substituent	$\sigma_p{}^0$	$\delta_{14\text{-}ArH}$	$\delta_{9\text{-}Me}$	$\delta_{17\text{-}Me}$
3	NH_2	–0.38	6.88	0.62	0.94
7b	OCH_3	–0.16	6.89	0.66	0.85
7e	CH_3	–0.12	6.90	0.68	0.76
1	H	0.00	6.92	0.72	0.72
7a	F	0.17	6.92	0.67	0.85
7d	CHO	0.49	6.98	0.67	0.80
2	NO_2	0.82	7.00	0.75	0.81

[a]In $CDCl_3$ at room temp.

The maximum absorption wavelengths (λ_{max}) of these free diazonium salts ($\lambda_{diazonium}$) and their complexes with 18-crown-6 ether ($\lambda_{complex}$) are also summarized in

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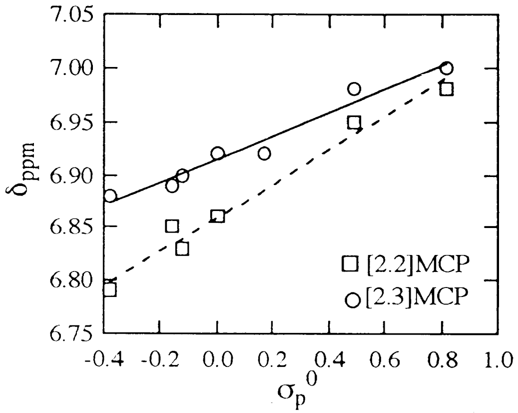

Fig. 1 Correlation between the chemical shift of the external aromatic proton and the σ_p^0 constant of the substituent in the [2.2] and [2.3]MCP systems

Table 1. The λ_{max} of free MCP diazonium salts (**4**, **5**) appear in a bathochromic region as compared with that of the toluene-*p*-diazonium salt (**6**). These results imply that the π conjugate systems in MCP systems are lengthened. The difference between λ_{max} of free [2.2]MCP diazonium salts (**5**) and that of its complexes is *ca.* 51 nm. On the other hand, in [2.3]MCP diazonium salt (**4**) the difference is *ca.* 44 nm. Furthermore, such a difference for the toluene-*p*-diazonium salt (**6**) is only *ca.* 18 nm. This suggests that the changes is the energy gaps between HOMO and LUMO in [2.*n*]MCP systems are larger than that in a non-MCP system.

The chemical shifts of the aromatic protons (14 position) are summarized in Table 3. The NMR behaviour 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 (σ_p^0) are widely used to express the electronic effects of *para* substituents. Thus, when the chemical shifts for the proton at the 14 position are plotted against σ_p^0 values of the substituent at the 6-position, a straight line is obtained as shown in Fig. 1; a least-squares treatment gives an equation, $\delta_{ppm} = 6.91 + 0.108\sigma_p^0$ with a correlation coefficient (r) of 0.981. The corresponding correlation ($\delta_{ppm} = 6.86 + 0.159\sigma_p^0$, $r = 0.987$) for the [2.2]MCPs (**8**)[2c] is also shown in Fig. 1. Such linear relationships imply that the electronic effect of the substituent on the aromatic ring could be transmitted to the other ring *via* transannular interaction. The reason for using σ_p^0 values for these MCP compounds is because substituents at the 5- or 6-position are located at pseudo *para* positions against the proton at the 13- or 14-position, respectively. Furthermore, the difference in these slopes seems to be interesting since it obviously reflects the different transannular interaction between two MCP systems; more precisely the electronic nature is transmitted less effectively to the aromatic ring on the other side in the [2.3]MCP system that the [2.2]MCP system. This difference in these two systems must reflect, in part, the different geometries of the [2,3] and the [2.2]MCP skeletons.

It is also expected that the electronic spectra of MCPs can provide information on the nature of transannular electronic interaction in their π-electron system. The UV spectrum of [2.3]MCP is designated the 'cyclophane spectrum'. The λ_{max} values for the 6-substituted[2.3]MCPs (**2**, **3** and **7**) can be characterized by bathochromic shifts in comparison with that of **1** as summarized in Table 4.

Table 4 Absorption spectral data[a] for 6-substituted[2.3]MCPs

Compound	Substituent	σ_p	λ_{max}/nm
3	NH_2	−0.66	303
7b	OCH_3	−0.27	289
7e	CH_3	−0.17	280
1	H	0.00	275
7a	F	0.06	280
7d	CHO	0.44	294
2	NO_2	0.78	330

[a] In $CHCl_3$ at room temp.

In general the extent of conjugation in the system results in a bathochromic shift of the UV spectra, it can therefore be speculated that there exists less extended conjugation in a [2.3]MCP system than a [2.2]MCP system. The linear relationships suggest a conjugated system that involves the transannular interaction. The mode of the conjugation in [2.*n*]MCP systems can be correlated to the transannular interaction which is closely related to distance or orientation of their two aromatic rings.

From these results, a conjugated system could be produced in such a nonplanar molecule as a [2,3]MCP compound.

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Techniques used: ^1H NMR, IR, UV–VIS, elemental analysis and mass spectrometry

References: 11

Figures: 3

Schemes: 4

Table 2: Dediazoniation of the [2.3]MCP diazonium salt **4**

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