Transannular Interactions and Reactions of the Dithia[3.3]metacyclophanediazonium Salt

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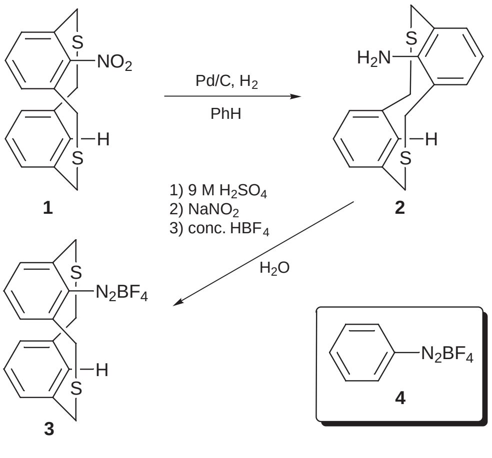
The transannular interaction between two aromatic rings of the dithia[3.3]metacyclophanediazonium salt is evaluated by several spectral measurements and the dediazoniation of the salt preferentially affords the biphenyl compound.

Conformations and the transannular interaction in small-sized cyclophane compounds have attracted great interest among organic and physical chemists.[1] Recently, we have investigated the transannular interaction of [2.2]metacyclophanes (MCPs)[2] whose conformation was the *anti* form. Vögtle *et al.*[3] reported the conformational behavior, that is, *syn*- and *anti*-isomers, of dithia[3.3]MCPs and related compounds. It might be expected that the transannular interaction between two aromatic rings of *syn*- and *anti*-conformers is quite different. However, information on chemical properties based on the transannular interaction of the dithia[3.3]MCPs is very limited. Thus, in this paper, we report the preparation, characterization and reactivities of *syn*-dithia[3.3]MCPs having a diazonium group on its internal position.

Syn-nitrodithia[3.3]MCP **1** was prepared as previously described method[4] using high dilution conditions. The compound **1** was readily reduced with hydrogen gas in the presence of 10% Pd/C as a catalyst to give aminodithia[3.3]MCP **2** in quantitative yield. The conformation of compound **2** is *anti* because of repulsion between the π-electrons in the two aromatic rings and hydrogen-bonding between amino protons and bridging sulfur atoms.[5] 2,11-Dithia[3.3]MCP-9-diazonium tetrafluoroborate **3** was prepared in aqueous media in 90% yield (Scheme 1). The structure of the salt **3** was confirmed by ^{1}H NMR, IR and elemental analysis.



Scheme 1

An IR absorption for the N_2 triple bond of the salt **3** was observed at 2226 cm^{-1} which is 72 cm^{-1} lower than that of benzenediazonium tetrafluoroborate **4**.[6] This is probably due to stabilization of the resonance structures by the opposite aromatic ring working as an electron releasing group implying that the triple bond character of the diazonium group of the MCP salt **3** is weaker than that of the salt **4** (Fig. 1).

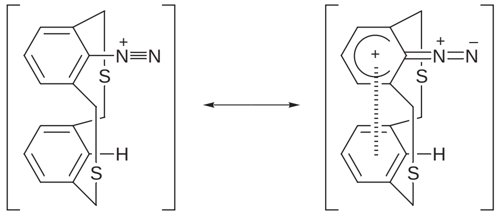
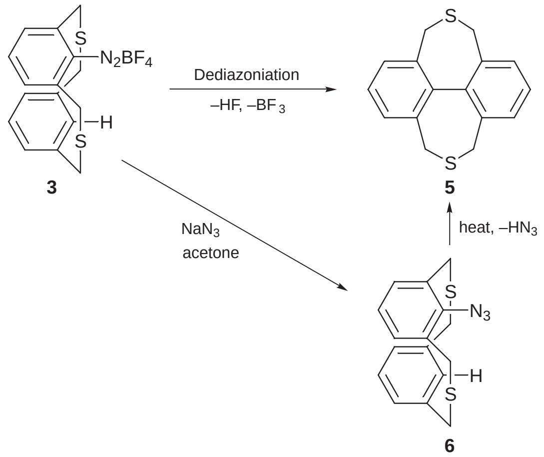


Fig. 1 Transannular stabilization of the dithia[3.3]MCP diazonium cation

In absorption spectra the λ_{max} of the MCP salt **3** appears at 397 nm in methanol at room temperature. On the other hand, the benzenediazonium tetrafluoroborate **4** shows λ_{max} at 259 nm under the same conditions.[7] Energy gaps between the HOMO and LUMO of the MCP π-system can be estimated by differences in the λ_{max} values. This difference ($\Delta\lambda_{max} = 138$ nm) means that the energy gap between the HOMO and LUMO of the MCP π-system is affected not only by the substituent effect of the diazonium cation but also the enhanced π-system of the whole MCP molecule. It is strong evidence in support of the existence of a transannular interaction between the arene diazonium moiety and the opposite aromatic ring in MCP.

MCP diazonium salt **3** was dediazotized under various conditions (Scheme 2). Interestingly, when solvolysis was performed in methanol or acetic acid only one product was isolated in yields of 71 and 80%, respectively. The product was characterized as the biphenyl compound **5** by MS, ^{1}H NMR, and EA.



Scheme 2

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Pyrolysis of **3** in the solid state (Schiemann reaction) gave the compound **5** in 66% yield. Furthermore, in the Gomberg–Bachmann reaction of the salt **3** in benzene with potassium acetate, the compound **5** was also obtained (50%).

In general, the radical or cationic species can be considered as a reactive intermediate in these reactions.[8] A diazonium group of an arenediazonium salt is eliminated to generate either the arene cation in solvolysis[6] and Schiemann[9] reactions or the arene σ radical by one electron-transfer from the AcO anion in the Gomberg–Bachmann reaction.[10] The diazonium group in the MCP molecule generates the cationic and the σ radical species by heterolytic and homolytic elimination, respectively. Then, transannular reaction proceeds preferentially because the distance between the cation or σ radical moiety and the opposite aromatic ring is very small.

On the other hand, on reaction of **3** with sodium azide, MCP azide **6** was obtained in excellent yield (95%). Transannular reaction does not occur in this reaction since the nucleophilicity of the azide anion seems much stronger than that of the opposite aromatic ring. When MCP azide **6** was decomposed at 180 °C for 5 hours, the compound **5** was also obtained (74%).

Interestingly, on decomposition of the MCP diazonium salt **3** and MCP azide **6**, hydrogen fluoride and trifluoroborane or hydrogen azide seem to be generated, respectively. In the Schiemann reaction hydrogen fluoride gas was detected by Kitagawa's hydrogen fluoride gas detector tube which is commercially available.

This study reveals that the strong transannular interaction exists between the aromatic ring and the aryl diazonium cation in the dithia[3.3]MCP structure. It should be noted that the transannular reaction occurred in all cases studied except for the reaction with sodium azide because the distance between π-cation or σ-radical moiety and the opposite aromatic ring is very small.

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

References: 10

Figures: 1

Schemes: 3

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