

A NEW DOUBLE BOND BRIDGED DIBENZODITHIOCIN: PREPARATION, CHARACTERIZATION, AND ITS TRANSANNULAR $p\pi \rightarrow S^+ - S^+ <$ INTERACTION

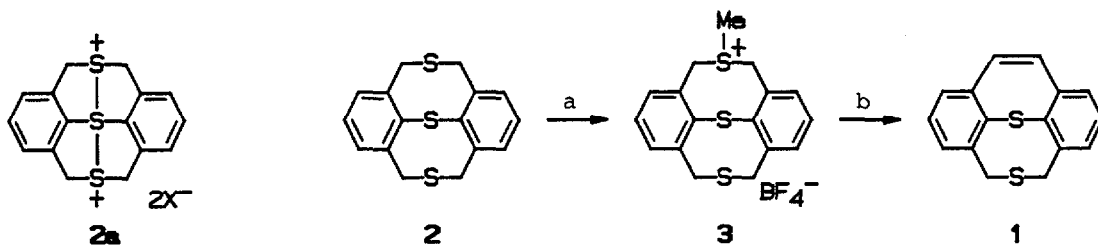
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Abstract: A new heterocyclic compound, 1,11-(etheno)-5H,7H-dibenzo[b,g][1,5]dithiocin (**1**) has been prepared by treatment of mono-sulfonium salt of 1,11-(methanothiomethano)-5H,7H-dibenzo[b,g][1,5]dithiocin with *t*-BuOK in a one step; the reactivities and the transannular $p\pi \rightarrow S^+ - S^+ <$ interaction in **1** are described.

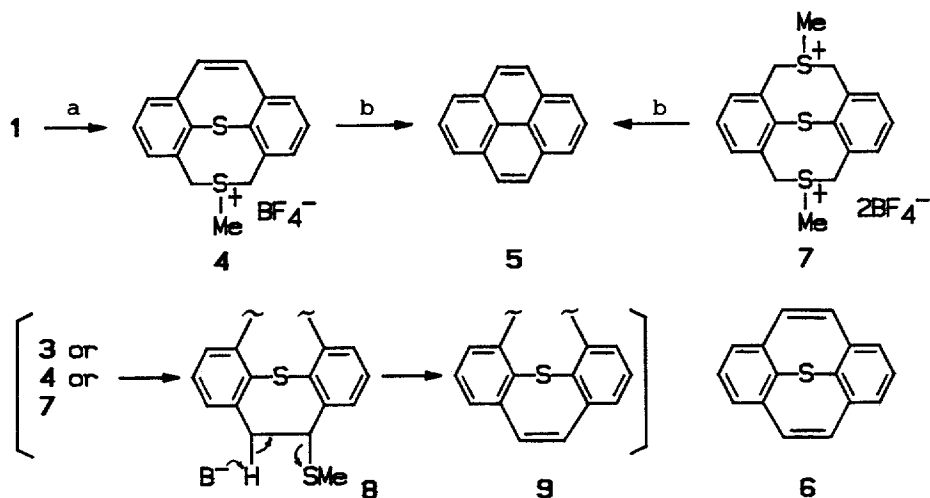
We recently reported the synthesis of a new sulfur-bridged dithia[3.3]-metacyclophane, 1,11-(methanothiomethano)-5H,7H-dibenzo[b,g][1,5]dithiocin (**2**) and the transannular bond formation between the three sulfur atoms, i.e., dicationic salt **2a**.¹ This characteristic behavior of **2** has promoted our interest in investigation of the structure and the reactivity of the analogous compound of **2**. Here, we wish to report the preparation, and the physical and chemical properties of another new heterocyclic compound, 1,11-(etheno)-5H,7H-dibenzo[b,g][1,5]dithiocin (**1**) together with some intriguing reactivities of sulfonium salts of **1** and **2**.

In general, the transformation of sulfide linkages in dithia[3.3]metacyclophane to carbon-carbon double bonds can be performed by a reaction sequence of a Stevens rearrangement followed by a Hofmann elimination.² Interestingly, we have found that the formation of a double bond from sulfonium salt **3**⁴ took place in a one-step, afforded the compound **1**⁵ upon treatment with *t*-BuOK (Scheme 1).



Scheme 1. a, $(MeO)_2CH^+BF_4^-$; b, *t*-BuOK

The mass spectrum of **1** exhibits, among other peaks, an intense molecular ion peak (M^+ , m/z 268) and a base peak at m/z 202 corresponding to pyrene (**5**). The 500-MHz ^1H NMR spectrum of **1** in CDCl_3 showing the benzyl protons as a distinct AB quartet at δ 3.66 and 5.58 ($J=15$ Hz), is assigned to the chair conformer by comparing to that of analogous compounds⁶. No other isomers were found in the spectrum at all. An X-ray crystallographic analysis⁷ of **1** indicates that the dithiocin ring has the chair form in the solid state.

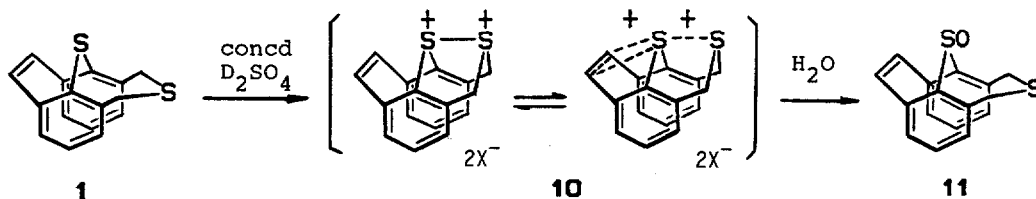


Scheme 2. a, $(\text{MeO})_2\text{HC}^+\text{BF}_4^-$; b, $t\text{-BuOK}$

The chemical behaviors of quadruply *ortho*-bridged diphenyl compounds containing heteroatoms are of considerable interest.¹ Compound **1** reacted with $(\text{MeO})_2\text{HC}^+\text{BF}_4^-$ to give mono-sulfonium salt **4**⁸ in 93% yield.³ Treatment of **4** with $t\text{-BuOK}$ even at -80°C resulted in pyrene **5** (90%) as a sole product by extrusion of the central aryl sulfur atom. The formation of compound **6** was not observed at all. Extrusion of the sulfur atom and generation of **5** was also observed by direct treatment of bis-sulfonium bisfluoroborate (**7**)⁹ with $t\text{-BuOK}$ (Scheme 2). This interesting one-step transformation of either **4** or **7** to **5**, seems to proceed through the initial formation of Stevens type rearranged product such as **8** which undergoes elimination to produce **9**.¹⁰ Conversion of compounds **4** and **7** to **5** should be performed by the C-S bond fission which suggests the release of its high strain energy of **6**. In contrast to **3** and **4**, the reaction of 6-methyl-sulfonium salt of **12** (*vide infra*) with KOH in MeOH afforded 6-methylthio-dibenzo[*b,e*]thiepin.¹¹

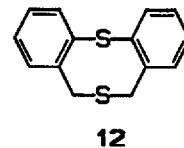
Sulfide **1** was treated with trifluoroacetic acid- d_1 ($\text{CF}_3\text{CO}_2\text{D}$), and recovered, however, **1** did not contain the deuterium. Interestingly, on

dissolution in concentrated sulfuric acid-d₂ (concd D₂SO₄) (98%) at room temperature, sulfide **1** resulted in a deep-red colored solution.¹² In the 500-MHz ¹H NMR, two methylene signals adjacent to the sulfenyl group for **1** in CDCl₃ (vide supra) disappeared and new AB quartet peaks appeared at downfield, δ 5.35 and 5.82 (J=16 Hz) in concd D₂SO₄, indicating the formation of dithia dication **10**¹³ (Scheme 3), while in the ¹³C NMR, the absorption of the methylene carbon atoms was shifted to downfield from δ 41.0 to 63.9. Furthermore, the transannular interaction between the double bond and dithia dication in the structure **10** is supported by the ¹³C NMR spectroscopic data indicating that the olefinic carbon signal at δ 125.7 in CDCl₃ shifts to δ 137.9 in concd D₂SO₄. These spectra did not change for at least two weeks at room temperature, suggesting that **1** is very stable in concd H₂SO₄ solution. Hydrolysis of the D₂SO₄ solution of **1** led to 1,11-(etheno)-5H,7H-dibenzo[b,g][1,5]dithiocin S-oxide (**11**)¹⁴ in 86% yield and none of sulfide **1** was obtained. No addition products to the double bond and the incorporation of deuterium were observed at all.



Scheme 3

The reaction of **1** with NO⁺PF₆⁻ (2 equiv) as one-electron-oxidizing agent gave the dication salt **10** which was reacted with H₂O to afford the sulfoxide **11** in 91% yield. The reaction of sulfide **1** in concd D₂SO₄ may proceed through the initial formation of the monocationic species such as the cation radical by an electron-transfer or the sulfidonium cation of **1**, which is subsequently converted into the dithia dication **10**. This finding is quite different from that of sulfide **12** which is unstable in concd H₂SO₄ and the ¹H and ¹³C NMR spectra of the D₂SO₄ solution of **12** showed complex signals. Actually the products obtained after the hydrolysis were composed of a complex mixture which was not characterized further.¹⁵ These results demonstrate that the dication **10** is remarkably stabilized by transannular participation of the double bond to the (>S⁺-S⁺<) dicationic center, namely pπ->S⁺-S⁺< interaction. Further studies on this transannular interaction are in progress.



References and Notes

- 1) H. Fujihara, J.-J. Chiu, and N. Furukawa, J. Am. Chem. Soc., 1988, **110**, 1280.
- 2) R. H. Mitchell and V. Boekelheide, J. Am. Chem. Soc., 1974, **96**, 1547.
- 3) R. F. Borch, J. Org. Chem., 1969, **34**, 627.
- 4) **3**: ^1H NMR (500 MHz, CD_3CN) δ 3.19 (s, 3H), 3.87, 5.03 (ABq, $J=14.5$ Hz, 4H), 4.52, 5.73 (ABq, $J=15$ Hz, 4H), 7.31 (d, 2H), 7.36 (t, 2H), 7.47 (d, 2H); ^{13}C NMR (CD_3CN) δ 27.9, 40.6, 50.5, 132.3, 132.5, 135.5, 136.9, 137.0, 150.0.
- 5) **1**: Mp 198–198.5 °C; IR (KBr, cm^{-1}) 1449, 1428, 1406, 812, 769, 752; ^1H NMR (500 MHz, CDCl_3) δ 3.66, 5.58 (ABq, $J=15$ Hz, 4H), 7.12 (t, 2H), 7.16 (d, 2H), 7.22 (d, 2H), 7.33 (s, 2H); ^{13}C NMR (CDCl_3) δ 41.0, 125.7, 127.6, 128.8, 130.9, 132.2, 141.0, 143.8; MS(m/z): 268 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{S}_2$: C, 71.60; H, 4.51; S, 23.89%. Found: C, 71.52; H, 4.52; S, 23.79%.
- 6) R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, J. Chem. Soc. Perkin Trans 1, 1976, 913.
- 7) An X-ray crystallographic work of **1** will be published in elsewhere.
- 8) **4**: ^1H NMR (500 MHz, CD_3CN) δ 3.17 (s, 3H), 4.53, 6.28 (ABq, $J=13$ Hz, 4H), 7.35 (t, 2H), 7.49 (s, 2H), 7.51 (d, 2H), 7.60 (d, 2H); ^{13}C NMR (CD_3CN) δ 27.5, 53.1, 129.6, 129.8, 133.0, 133.3, 134.2, 141.9. Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{BF}_4\text{S}_2$: C, 53.65; H, 4.22%. Found: C, 54.08; H, 4.16%.
- 9) **7**: ^1H NMR (500 MHz, CD_3CN) δ 3.20 (s, 6H), 4.57, 5.73 (ABq, $J=13.5$ Hz, 8H), 7.52 (t, 2H), 7.67 (d, 4H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 27.6, 48.0, 131.6, 134.2, 136.7, 141.6. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{B}_2\text{F}_8\text{S}_3$: C, 42.71; H, 3.98%. Found: C, 42.73; H, 4.01%.
- 10) T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, J. Chem. Soc., 1965, 1271.
- 11) K. Ohkata, K. Okada, K. Maruyama, and K. Akiba, Tetrahedron Lett., 1986, **27**, 3257.
- 12) Concentrated sulfuric acid also acts as an oxidizing agent: A. J. Bard, A. Ledwith, and H. J. Shine, Adv. Phys. Org. Chem., 1976, **12**, 155.
- 13) Dication **10**: ^1H NMR (500 MHz, D_2SO_4) δ 5.35, 5.82 (ABq, $J=16$ Hz, 4H), 7.26 (d, 2H), 7.29–7.37 (m, 6H); ^{13}C NMR (D_2SO_4) δ 63.9, 130.2, 133.0, 133.3, 133.6, 134.1, 137.9, 138.4.
- 14) (a) **11**: Mp 226–226.5 °C; IR (KBr, cm^{-1}) 1448, 1432, 1408, 1047, 1032, 816, 776, 739; ^1H NMR (500 MHz, CDCl_3) δ 4.46, 5.28 (ABq, $J=15$ Hz, 4H), 7.15 (t, 2H), 7.25 (d, 2H), 7.28 (d, 2H), 7.36 (s, 2H); ^{13}C NMR (CDCl_3) δ 58.2, 127.1, 127.2, 130.8, 132.0, 132.1, 132.7, 133.5, 140.5; MS(m/z): 284 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{OS}_2$: C, 67.57; H, 4.25; S, 22.55%. Found: C, 67.51; H, 4.19; S, 22.80%.
 (b) The oxygen atom of **11** is attached to the central aryl sulfur atom likely in the case of hydrolysis of **2a**¹. However, the configuration of the sulfoxide was not determined by the present nmr spectrum.
 (c) Dissolution of sulfoxide **11** with concd D_2SO_4 produced the dication **10** which was hydrolyzed to afford sulfoxide **11**.
- 15) Although the formation of dithia dication of **12** in the reaction of the corresponding sulfoxides with concd H_2SO_4 has been reported: K. Ohkata, K. Okada, and K. Akiba, Tetrahedron Lett., 1985, **26**, 4491; H. Fujihara, A. Kawada, and N. Furukawa, J. Org. Chem., 1987, **52**, 4254.

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