σ-Delocalized Hexakis(methylthio)benzene Dication: A Possible Intermediate of Pummerer-type Rearrangement of Monooxide of Hexakis(methylthio)benzene

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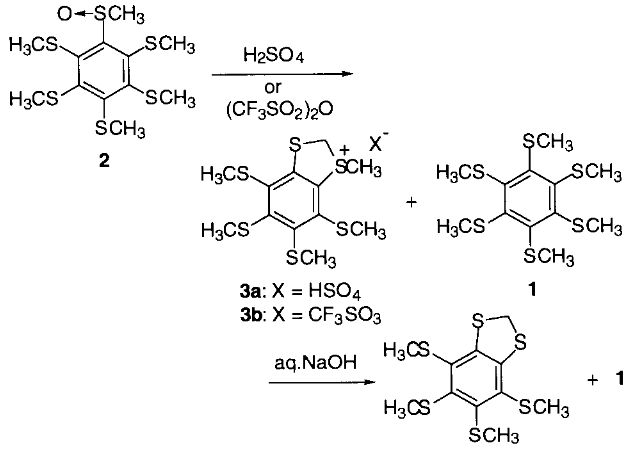
The Pummerer-type rearrangement of monooxide of hexakis(methylthio)benzene with H_2SO_4 or $(CF_3SO_2)_2O$ gives the cyclic methylsulfonium salt. A σ-delocalized hexathia dication is proposed as an intermediate.

The study of dicationic benzene and hexa-heteroatom-substituted benzenes has attracted considerable attention in regards to their electronic structures such as π-delocalized dications.[1] Among them, dicationic hexaiodobenzene is quite unique and considered to form the singlet dication which is σ-delocalized over the six iodine atoms.[2] As part of the studies on σ-bonded multi-thia dications among bifunctional sulfur atoms,[3] we are interested in hexakis(methylthio)benzene (**1**).[4] Herein we report the Pummerer-type rearrangement of monooxide of hexakis(methylthio)benzene (**2**) with H_2SO_4 or $(CF_3SO_2)_2O$. We propose the σ-delocalized hexakis(methylthio)benzene dication (**5a**) as an intermediate, which is the first cyclic 6-center 10-σ-electron (6c-10e) system with group 16 elements.[2]

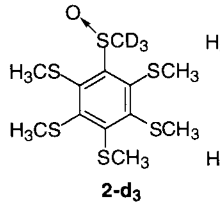
Treatment of **2** with conc. H_2SO_4 at room temperature gave the cyclic methylsulfonium salt **3a** and **1**. This reaction mixture was hydrolyzed by aqueous NaOH to afford the 1,3-dithiolane derivative **4** (29%) and **1** (28%) as shown in Scheme 1.[5] The ^1H NMR spectrum of the reaction mixture of **2** in D_2SO_4 exhibits five singlet peaks at δ 2.31 (3H), 2.44 (3H), 2.51 (3H), 2.72 (3H), and 2.94 (3H) and an ABq peak at δ 4.29 and 4.74 (J = 13.7 Hz, 2H) due to **3a** and a singlet peak of **1** at δ 2.59. No H-D exchange with the solvent D_2SO_4 took place during the course of the reaction. The FAB-MS spectrum also supports the structure **3a**, which shows the parent peak at *m/z* (%) 353 (100) $[M-HSO_4]^+$ in the H_2SO_4 matrix. The reaction of **2** with 1 equiv of $(CF_3SO_2)_2O$ in dry CH_3CN followed by the same quenching also afforded **4** (36%) via **3b** and **1** (36%).

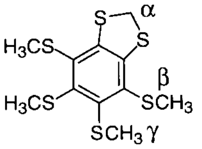


Scheme 1.

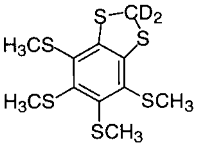
It is well known that the reaction of a compound, having both sulfinyl and sulfenyl groups *in close proximity*, with H_2SO_4 or $(CF_3SO_2)_2O$ provides a σ-bonded dithia dication via a transannular effect between sulfur atoms.[3] We have already found that 2-(methylsulfinyl)-2'-(methylthio)biphenyl in the presence of $(CF_3SO_2)_2O$ affords the corresponding cyclic methylsulfonium salt.[6] This reaction proceeds via the formation of a dithia dication followed by its deprotonation and subsequent nucleophilic addition by the neighboring sulfide sulfur atom on the carbon atom of the resulting methylidene sulfonium group. The formation of **3a** and **3b** presented here could also proceed via a similar reaction pathway, i.e., dithia dication of **1**.

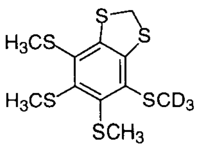
A dication of **1** has not been detected by any spectroscopic methods as yet. To understand the characteristics of this dicationic species, the reaction of the deuterium-labeled monosulfoxide **2-d$_3$**[7] with $(CF_3SO_2)_2O$ was conducted. Surprisingly, the D-labeled-methyl group was evenly distributed in the products.[8] The distribution pattern of a mixture of products **4-d$_n$** (n = 0, 2, or 3) was assessed by the ^1H NMR and EI-MS spectroscopies. In the ^1H NMR, the integration ratio of α, β, and γ protons for **4-d$_n$** was found to be 1:2.76:2.76.[8] If this reaction proceeds via any type of delocalized dication, the ratio of product distribution should be (**4**+**4-d$_2$**):**4-d$_3$**:**4'-d$_3$** = 1:1:1. So as to fit the NMR integration data and the assumption above, the ratio of **4** and **4-d$_2$** was calculated. The ratio of **4**:**4-d$_2$**:**4-d$_3$**:**4'-d$_3$** was, thus, determined to be 0.71:0.29:1:1. The k_H/k_D for the proton abstraction in the present reaction is 2.4. In the mass spectrum of the product mixture, the observed isotopic distribution pattern in the range *m/z* 338-344 of parent peaks for **4-d$_n$** was more or less similar to the calculated one: *m/z* [%, observed (calcd)]: 338 [39.8 (34.1)], 339 [7.4 (5.9)], 340 [40.7 (23.5)], 341 [100 (100)], 342 [7.8 (21.7)], 343 [30.3 (27.7)], 344 [4.6 (4.9)].[8,9] These results clearly support that the dication generated in the present reactions is either delocalized or exists as a rapid equilibrium between localized ions.

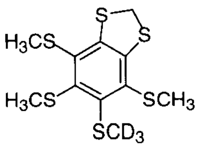

2-d$_3$



4


4-d$_2$

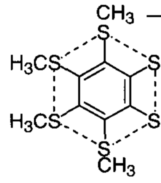

4-d$_3$


4'-d$_3$

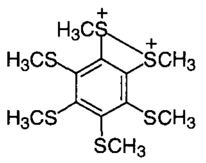
The molecular and electronic structure of the dicationic species was evaluated by ab initio and density functional theory (DFT) calculations. The calculations were carried out by utilizing

Spartan[10] and Gaussian 94.[11] The dicationic species calculated here include σ-delocalized hexathia dication (6c-10e) **5a**, σ-localized dithia dication (2c-2e) **5b**, trithia dication (3c-4e) **5c**, quinoid π-delocalized dication **5d**, and anti-quinoid π-delocalized dication **5e**, all of which are postulated as singlet dications. The species **5a**, **5b**, and **5c** would arise from a through-space interaction between sulfur atoms, whereas **5d** and **5e** would be formed via a through-bond interaction.

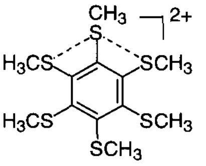
At the RHF/3-21G(*) level, **5b**, **5d**, and **5e** were calculated to be an energy minimum; **5a** and **5c** were obtained by imposing appropriate symmetries. In order to examine the effect of electron correlation on each dicationic species, B3LYP/6-31G* DFT calculations were carried out at the RHF/3-21G(*) geometries. As may be seen from Table 1, the dication **5a** is dramatically stabilized as compared to **5b** and **5c** and becomes the most stable at the B3LYP/6-31G*//RHF/3-21G(*) level.



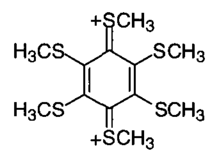
5a



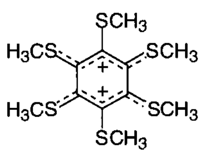
5b



5c



5d



5e

Table 1. Calculated total energies (hartrees) and relative energies (kcal mol^{-1}, in parentheses) of **5a**–**5e**

Species	Symmetry	B3LYP/6-31G*// RHF/3-21G(*)	B3LYP/6-31G*
5a	D_{3d}	−2856.58654 (0)	−2856.59321 (0)
5b	C_2	−2856.54476 (26.2)	—
5c	C_s	−2856.55814 (17.8)	—
5d	C_2	−2856.56655 (12.5)	−2856.58353 (6.1)[a]
5e	C_2	−2856.57218 (9.0)	−2856.57811 (9.5)

[a] The structure cannot be designated as quinoid, since the calculated bond lengths have an intermediate character between quinoid and anti-quinoid forms.

The geometries of **5a**, **5d**, and **5e** were then reoptimized at the B3LYP/6-31G* level. All of the optimized geometries were confirmed to be a minimum by vibrational frequency calculations. The relative energies shown in Table 1 indicate that **5a** is the most stable at the B3LYP/6-31G* level, the structure of which is shown in Figure 1. Between adjacent sulfur atoms the S···S distances of **1** and **5a** at the B3LYP/6-31G* level are 3.242 and 3.186 Å, respectively, well within twice the van der Waals radius of sulfur (3.60 Å). These S···S distances are sufficiently short to provide σ-overlap of the sulfur p-orbitals in the plane of the benzene ring.

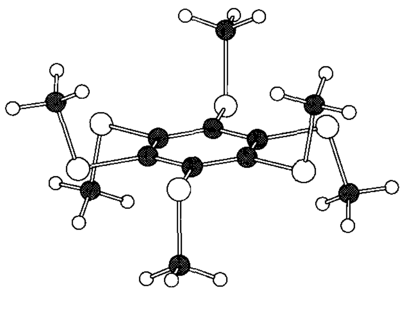


Figure 1. Three-dimensional view of the B3LYP/6-31G* optimized structure of **5a** (D_{3d} symmetry). Selected bond lengths [Å] and angles [deg]: C-C 1.399, C_{Ar}-S 1.787, S-C_{Me} 1.839, S···S 3.186; C-C-C 120.0, C-C-S 120.0, C-S-C 103.5.

In summary, we propose that the σ-delocalized hexathia dication **5a** is the most stable form of the dication of **1** and the intermediate for the present Pummerer-type rearrangement of **2** into **3**. The delocalization of the two positive charges equally over all the six sulfur atoms in **5a** is much more favorable than a rapid equilibration in **5b**-**5e**. The species **5a** may be regarded as a cyclic 6-center 10-σ-electron system which gives rise to Hückel aromaticity.[2] This may be one of factors which prefers **5a** to the other dications.

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References and Notes

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5 **3a**: ^{13}C NMR (D_2SO_4): δ = 21.1, 23.4, 24.6, 25.9, 27.1, 42.4, 139.5, 139.9, 143.4, 146.5, 150.1, 159.4.
4: ^{1}H NMR ($CDCl_3$): δ 2.51 (s, 6H), 2.52 (s, 6H), 4.32 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 19.5, 21.9, 31.3, 134.8, 145.1, 147.7; EI-MS: *m/z* (%): 338 (100) [M]$^+$.
6 H. Shima, R. Kobayashi, T. Nabeshima, and N. Furukawa, *Tetrahedron Lett.*, **37**, 667 (1996).
7 The deuterium content of methylsulfinyl group in **2-d$_3$** was more than 99%, judged by ^{1}H NMR and mass spectroscopies.
8 The reaction of **2-d$_3$** with H_2SO_4 gave almost the same results as that using $(CF_3SO_2)_2O$.
9 The calculated isotope pattern of **4**: *m/z* (%): 338 (100), 339 (17.3), 340 (28), 341 (4.5), 342 (3.4).
10 Spartan, Version 4.1: Wavefunction Inc., Irvine, CA, USA.
11 Gaussian 94, Revision D.2: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian Inc., Pittsburgh, PA, USA (1995).