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Dibenzo macrocyclic acetylenic sulfide and a comparable silane†

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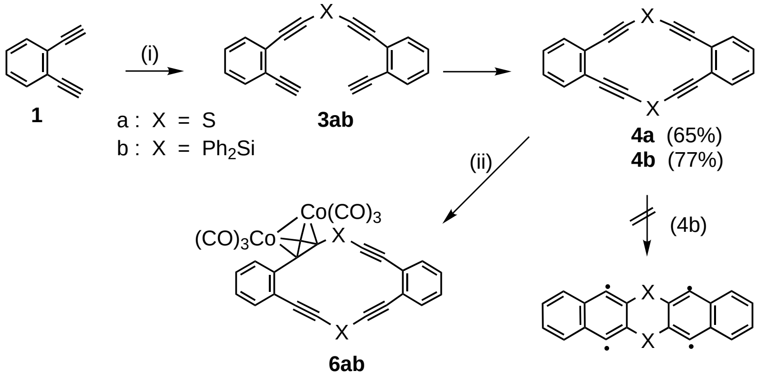
Abstract—The syntheses, X-ray structures and characterization of a dibenzo macrocyclic acetylenic sulfide **4a** and a comparable silane **4b** are described. © 2002 Elsevier Science Ltd. All rights reserved.

Conjugated or homoconjugated all-carbon and carbon-rich linear or cyclic molecules continue to be of intense interest.[1] Both experimental and theoretical studies suggest that these molecules may exhibit interesting electronic and optical properties. Studies of these novel systems are also highly relevant in materials research, particularly in the search of organic conducting and non-linear optical materials.[2] Recently, we reported the synthesis of oligoacetylenic sulfides through an iteration of the sulfurization and coupling reaction cycles. Linear oligomers having up to eight acetylene units with alternating sulfur atoms were prepared.[3] Subsequently, the corresponding oligoacetylenic sulfide platinum(II) complexes were also synthesized and characterized.[4] In this article, we report our results on the syntheses and characterization of the dibenzo derivatives of a cyclic acetylenic sulfide and silane.

Initially, a stepwise approach was used in the syntheses of the 14-membered macrocyclic systems (Scheme 1). 1,2-Diethynylbenzene (**1**) was prepared according to the literature procedure.[5] Mono-deprotonation of **1** with 1 equiv. of LIHMDS followed by either 0.5 equiv. of bis(benzenesulfonyl) sulfide **2**[6] (for sulfurization) or dichlorodiphenylsilane (for silylation) afforded intermediates **3a** and **3b**. A repeat of the deprotonation followed by sulfurization or silylation cycle afforded the targeted dibenzo acetylenic sulfide **4a** and silane **4b** in 65 and 77% yield, respectively, after column chromatography. One-step preparation of compounds **4a** and **4b** using 2 equiv. of base and 2 equiv. of the sulfurization or silylation agents also yielded the desired products. However, the yields were 50% of those of the previous method. The dibenzoacetylenic macrocyclic sulfide **4a** is a new compound while the macrocyclic



Scheme 1. *Reagents and conditions*: (i) a. LIHMDS, 0°C to rt; b. 0.5 equiv. of **2** ($PhSO_2SSO_2Ph$) or Ph_2SiCl_2; (ii) $Co_2(CO)_8$, benzene.

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† This paper is dedicated to Professor Barry Sharpless on the occasion of his 60th birthday.

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silane had been reported in the patent literature.[7] These dibenzo acetylenic macrocyclic compounds were fully characterized by spectroscopic methods.[8]

The ^{13}C NMR data showed the macrocyclic structures to be highly symmetrical with two acetylenic *sp* carbon signals and three aromatic sp^2 carbon signals for the macrocyclic ring systems. Their structures were further confirmed by X-ray analyses (Fig. 1). The X-ray structures showed that the macrocyclic molecules have C_{2v} symmetry. The sulfur analog **4a** was v-shape with a dihedral angles of 15.8°, while the silicon analog **4b** was almost planar.

The PM3 optimized geometry of **4a** was in good agreement with the X-ray structure. For **4b**, in contrast to the PM3 optimized geometry (Fig. 1), the diphenyl groups in the silane analog were approximately symmetrically arranged above and below the dibenzo plane in the solid state, which is presumably due to the packing effect.

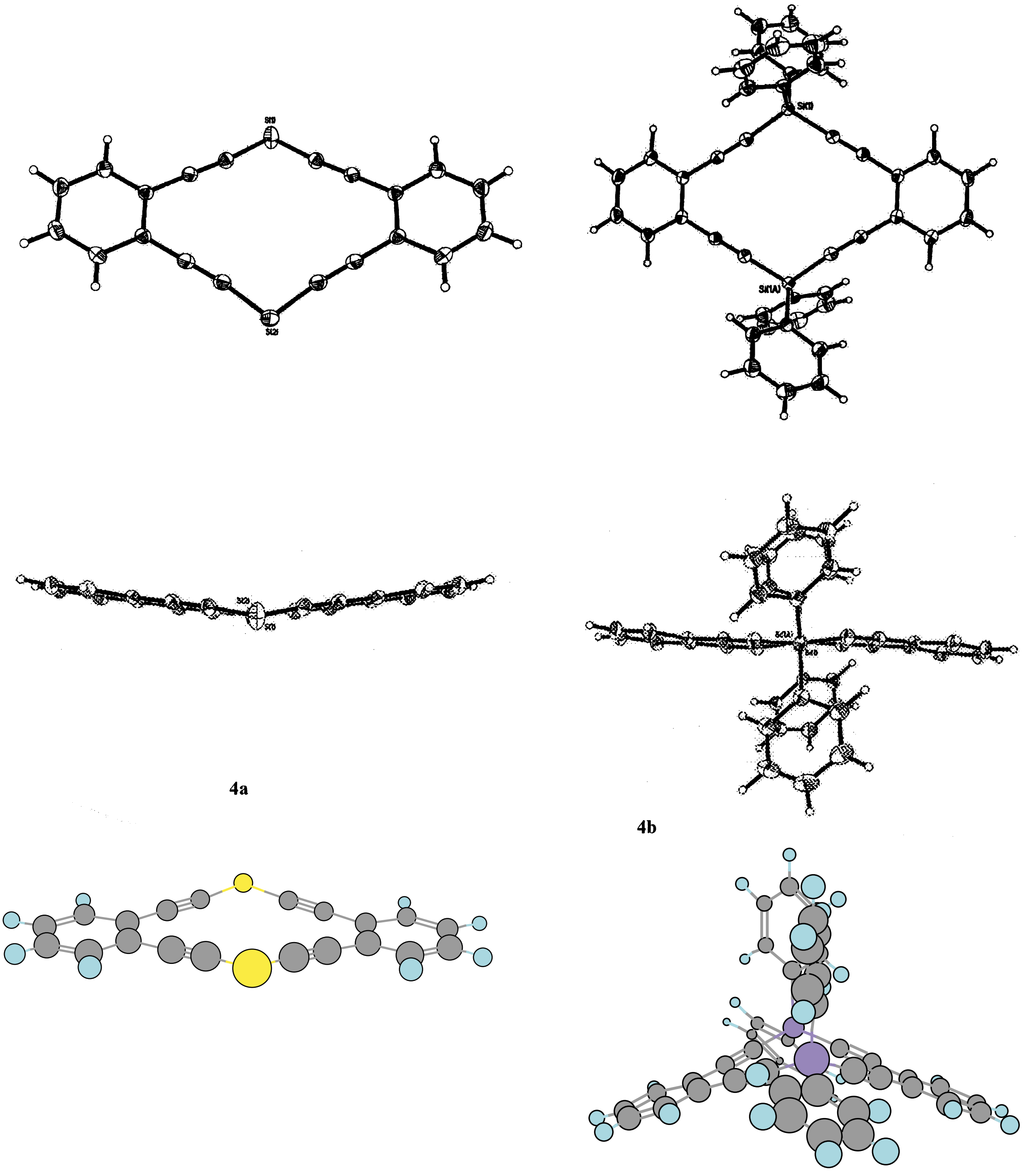

Figure 1. X-Ray structures of **4a** and **4b**, view from top (above) and side (middle).

The UV absorption of **4a** and **4b** suggested that the degree of conjugation between the acetylene units across the heteroatoms is weak (Table 1). This result was similar to that of the oligoacetylenic sulfides we previously reported. Although the two acetylene units in **4b** lay almost in the same plane in the solid state, according to the PM3 semi-empirical calculations, the sulfur analog **4a** exhibits a higher degree of conjugation between the acetylene units. Consistently, the absorption maximum of the sulfur analog **4a** appeared at a slightly longer wavelength as compared to that of **4b**. Furthermore, the sulfur analog was oxidized more easily in cyclic voltammetry experiments (Table 1).

The preparation of the cobalt complexes of **4a** and **4b** was also carried out. Reaction with $Co_2(CO)_8$ in benzene gave the mono-adducts (**6a**, **6b**) in 96 and 19% yield, respectively. The mono-cobalt complex **6b** could be obtained in good crystalline form after recrystallization from CH_2Cl_2/hexane. Its structure was confirmed by X-ray analysis (Fig. 2). Although excess reagent was used, only the mono-adduct could be detected. This is not surprising because adducts **6a** and **6b** are already highly strained.

The macrocyclic acetylenic silane **4b** decomposed before melting at 273°C. In contrast, the macrocyclic sulfide **4a** decomposed violently with a flash of orange light at 176°C, with the formation of black powder. Similar dramatic thermal behavior had been reported for the high-energy, high C/H ratio benzo-oligoalkynes.[9]

Both the dibenzocyclic acetylenic sulfide and silane can be viewed as bis-enediyne structures linked together with heteroatoms through the acetylene terminals. Enediyne structures including 1,2-diethynylbenzene are known to undergo Bergman cyclization to yield 1,4-didehydrobenzene structures.[10] The Bergman cyclization also constitutes the basis for the biological activity of certain potent antitumor antibiotics.[11] We envisage

Table 1. Results of calculations and physical measurements

	λ_{max}[a]/nm ($\varepsilon_{max}/10^4$ M^{-1} cm^{-1})	Calcd HOMO[b] (eV)	Calcd LUMO[b] (eV)	Calcd energy gap (eV)	CV-HOMO[c] (eV)	CV-LUMO[d] (eV)	Optical band gap[a] (eV)
4a	285 (3.8)	−8.105	−3.908	4.197	−4.965	−1.009	3.956
4b	275 (4.8)	−8.855	−3.032	5.823	−5.045	−0.930	4.115

[a] Measured in cyclohexane.

[b] Calculated by PM3 semi-empirical method in Mopac 6.

[c] Derived from the cyclic voltammetry measurements measured in Bu_4NFP_4/CH_2Cl_2 with scan rate 100 mV s^{-1} using SCE as a reference.

[d] Derived from the difference.

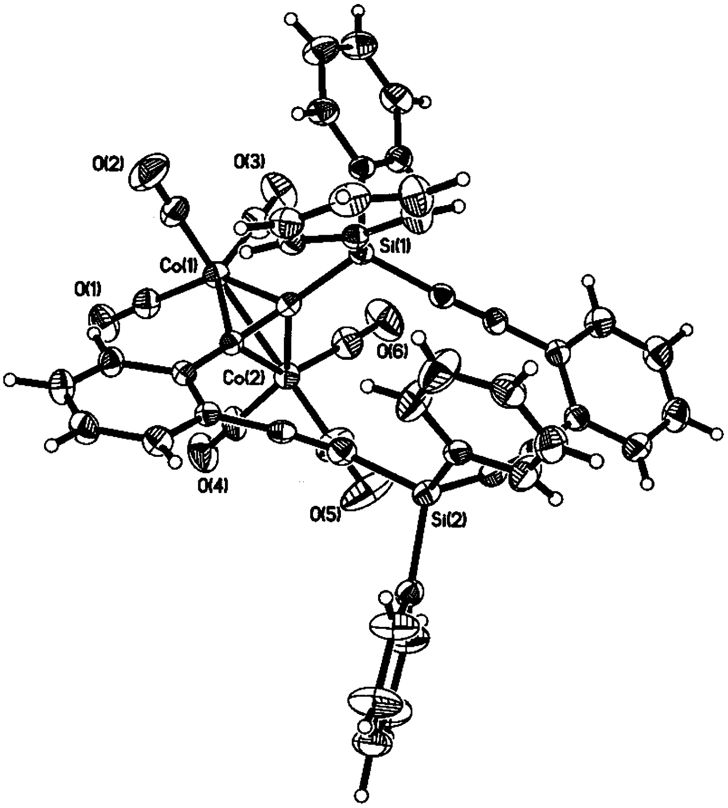

Figure 2. X-Ray structure of **6b**.

that **4a** and **4b** could undergo double Bergman cyclization to yield the bis-didehydrobenzene intermediate **5**. Because of the thermal instability of **4a**, only **4b** was subjected to the attempted cyclization. To our disappointment, the cyclization of **4b** did not take place even up to 170°C or under microwave irradiation with 1,4-cyclohexadiene as the hydrogen atom donor.[12] The strain imposed by the double enediyne units may be too high to forbid the cyclization. Similar observations were also reported recently on a bis-enediyne macrocarbocyclic system.[13] Attempted cyclization on precursor **3b** also failed.

In summary, dibenzo acetylenic sulfide and silane were synthesized, with their structures confirmed by X-ray analyses. Mono-cobalt complexes were also prepared but attempted double Bergman cyclization of **4a** failed. Further studies of these and related macrocyclic acetylenic systems such as formation of other metal complexes and the thermal decomposition are in progress.

Acknowledgements

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8. *Selected spectral data.* **4a** λ_{max} (cyclohexane)/nm, 285; ν_{max} (KBr)/cm^{-1}, 2332, 2362, δ (^{1}H) (CDCl$_3$, 270 MHz) 7.17–7.32 (m); δ (^{13}C) (CDCl$_3$, 67.8 Hz) 75.7, 93.7, 124, 128, 131; m/z (EI): calcd 312.0066 for $C_{20}H_8S_2$, found 312.0067. **4b** λ_{max} (cyclohexane)/nm, 275; ν_{max} (KBr)/cm^{-1}, 2099, 2166; δ (^{1}H) (CDCl$_3$, 400 MHz): 7.27–7.60 (m); 7.35–7.88 (m, SiPh$_2$); δ (^{13}C) (CDCl$_3$, 100.57 MHz): 92.3, 106.1, 125.6, 128.0, 128.6, 130.2, 132.2, 132.3, 135.0); m/z (EI): calcd 612.1722 for $C_{44}H_{28}Si_2$, found 612.1706.
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