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3,4-Didehydrothiophene: Generation, Trapping Reactions, and *Ab Initio* Study[1]

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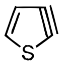
Despite the considerable efforts devoted in the last decade to the synthesis of strained cyclic cumulenes,[3] in the literature only the isolable 1,2,3-cyclononatriene[4] and the fugitive 1,2,3-cycloheptatriene[5] and 1,2,3-cyclohexatriene[6] have been registered. 1,2,3-Cyclooctatriene and 1,2,3-cyclopentatriene still remain unknown, but their structural features and energetics have been studied by computation.[4a] On the other hand, five-membered hetarynes have also aroused widespread synthetic endeavor[7] and theoretical curiosity[8] because of their inherent strain. Although both 2,3-didehydrothiophene (**1**)[9] and 3,4-didehydrothiophene (**2**)[10] had been suggested as reactive intermediates by Wittig in the early 1960s, the validity of such claims was later questioned.[7bc,11] Subsequently, hetaryne **1** was generated from thiophene-2,3-dicarboxylic anhydride and accordingly trapped.[12] Evidence for the existence of **2** has surprisingly never been obtained despite many experimental attempts.[12c,13] Inspired by the recent generation of benzyne from (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate,[14] we report herein unequivocal verification of **2** as an intermediate. It is believed that the five-membered **2** is the smallest cyclic cumulene ever characterized.



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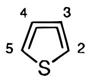

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The precursor of **2**, namely, phenyl[4-(trimethylsilyl)thien-3-yl]iodonium triflate (**4**), was prepared from 3,4-bis(trimethylsilyl)thiophene (**3**)[1] according to the literature procedure.[14] Thus, treatment of **3** with iodobenzene diacetate in the presence of trifluoromethanesulfonic acid gave **4** in 53% yield.[15] Addition of a CH_2Cl_2 solution of **4** to a CH_2Cl_2 solution of KF in the presence of 18-crown-6 as anticipated generated cumulene **2**, whose presence was convincingly endorsed by its trapping reactions with several dienes as shown in Scheme 1. Such a trapping exercise was first explored by generating **2** at room temperature in the presence of anthracene. In this manner a chromatographically inseparable mixture of the known 9,10-adduct **5a**[16] and the 1,4-adduct **5b** was obtained in a total yield of only 10%. The structures and ratio (2.7:1) of **5a** and **5b** were confirmed by ^1H- and ^{13}C-NMR spectral analyses.[15] Careful partial recrystallization of a mixture of **5a** and **5b** from MeOH nonetheless afforded a pure sample of **5a**, mp 267−268 °C (lit.[16] mp 268 °C).[15] Lower reaction temperatures did not seem to cause any significant effect on the yield and ratio of the products. Compelling proof for the remarkable reactivity of **2** was procured by its reaction with benzene, which yielded the adduct **6** in a meager 7% yield.[15] Moreover, the reaction of **2** with 2,3-dimethyl-1,3-butadiene unexpectedly gave in 27% total yield a chromatographically separable mixture (silica gel, *n*-pentane) of a [2 + 2] adduct **7a**, as well as an ene reaction product **7b**, in the ratio of 1:1.[15] The isolation of **7b** is consistent with the observation that ene reaction generally competes with cycloaddition in a trapping process comprising a distorted π-system and an alkene having allylic hydrogen atoms.[17] In other Diels−Alder reactions, furan, 2-methylfuran, and 2,5-dimethylfuran were all found to react readily with **2** to furnish adducts **8a**,[18] **8b**, and **8c**, in 31%, 17%, and 13% yields, respectively.[15] It appeared that **2** did not dimerize to provide 2,5-dithiabisnorbiphenylene,[13,19] even for the condition in which no trapping reagent was involved.

Cumulene **2** was also studied with the complete-active-space SCF (CASSCF) method.[20] This method was chosen instead of the more conventional single-configuration models because it was found that single-configuration descriptions such as RHF would not be adequate for benzyne and related compounds.[8b] The basis sets adopted in these calculations were 3-21G(d), 6-31G(d), and 6-311G(d,p). The standard *ab initio* molecular orbital calculations, including geometry optimization and frequency computations, were carried out using the Gaussian 94 programs.[21]

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(1) 3,4-Disubstituted Thiophenes. 2. Part 1: Ye, X.-S.; Wong, H. N. C. *J. Chem. Soc., Chem. Commun.*, in press.

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(18) Typical experimental procedures for the preparation of **8a** from **3**: To a stirred suspension of $PhI(OAc)_2$ (3.3 g, 10.2 mmol) in dry CH_2Cl_2 (50 mL) was added trifluoromethanesulfonic acid (1.8 mL, 20.3 mmol) slowly at 0 °C with a syringe. The mixture was stirred for 1 h at room temperature during which time the mixture became a clear yellowish solution. The solution was then cooled to 0 °C and 3,4-bis(trimethylsilyl)-thiophene (**3**) (2.5 g, 11.0 mmol) in CH_2Cl_2 (25 mL) was added dropwise with a syringe. After addition, the reaction mixture was stirred at room temperature for 20 min. After evaporation of the solvent, Et_2O was added to crystallize the residue. The solid formed was filtered, washed with Et_2O, and dried *in vacuo* to yield **4** (2.7 g, 53%): mp 169−172 °C; ^1H NMR (250.13 MHz, $CDCl_3$) δ 0.28 (s, 9H, Me_3Si), 7.43 (t, $J = 6.5$, 6.5 Hz, 2H, ArH), 7.52 (dd, $J = 6.7$, 1.1 Hz, 1H, ArH), 7.55 (d, $J = 2.9$ Hz, 1H, H-5), 7.80 (d, $J = 6.4$ Hz, 2H, ArH), 8.51 (d, $J = 2.9$ Hz, 1H, H-2); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ −0.41, 100.82, 115.19, 131.99, 132.27, 132.98, 137.09, 140.86, 144.14. Anal. Calcd for $C_{14}H_{16}O_3S_2SiF_3I$: C, 33.08; H, 3.17. Found: C, 33.03; H, 2.90. To a mixture of **4** (254 mg, 0.5 mmol), 18-crown-6 (79 mg, 0.3 mmol), and furan (1 mL) in dry CH_2Cl_2 (5 mL) under N_2 was added KF (87 mg, 1.5 mmol). The reaction mixture was stirred for 30 min at room temperature. The resulting precipitate was removed by filtration. The filtrate was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column (hexanes−EtOAc, 6:1) to give **8a** (23 mg, 31%) as colorless crystals: mp 70−72 °C; ^1H NMR (250.13 MHz, $CDCl_3$) δ 5.55 (d, $J = 0.9$ Hz, 2H), 6.73 (s, 2H), 6.92 (t, $J = 0.9$, 0.9 Hz, 2H); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 79.77, 112.08, 141.34, 151.38; MS *m/e* 150 (M^+, 32). Anal. Calcd for C_8H_6OS: C, 63.98; H, 4.03. Found: C, 64.15; H, 4.14.

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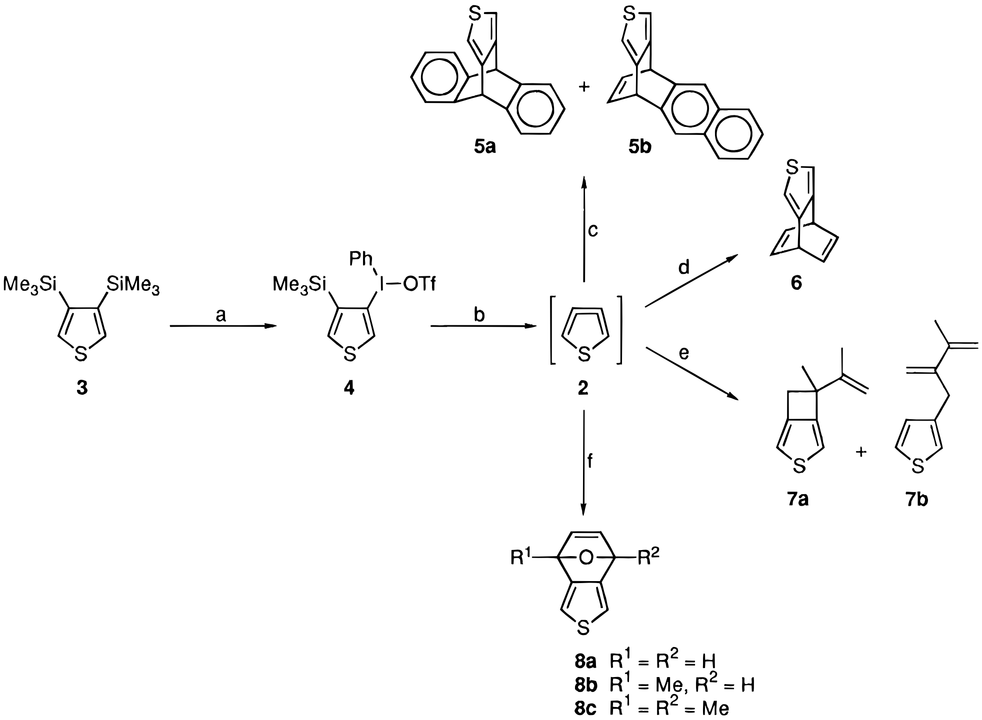
Scheme 1[a]



[a] (a) PhI(OAc)$_2$, TfOH, CH$_2$Cl$_2$. (b) KF, 18-crown-6, CH$_2$Cl$_2$, room temperature. (c) Anthracene. (d) C$_6$H$_6$. (e) CH$_2$=CMeCMe=CH$_2$. (f) Furan, 2-methylfuran, or 2,5-dimethylfuran.

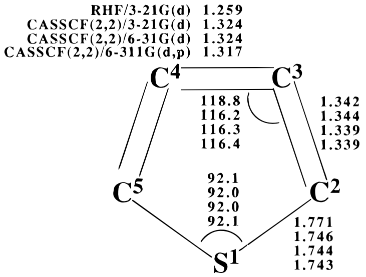


Figure 1.

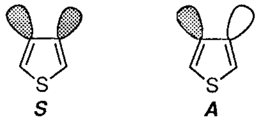


Figure 2.

Optimized CASSCF structures for **2**, along with that calculated at the RHF/3-21G(d) level,[8b] are summarized in Figure 1. It is seen that the CASSCF results are in close agreement with each other, while the RHF/3-21G(d) method yields an exceedingly short C^3−C^4 bond.

In our CASSCF calculations, we considered two configurations corresponding to double occupation of one or the other of the molecular orbitals which are predominantly the symmetric (S) and antisymmetric (A) combinations of the in-plane sp^2-type orbitals at C^3 and C^4 (Figure 2). In other words, they are CASSCF(2,2) calculations. If **2** were a pure biradical, CASSCF(2,2) treatments would lead to a substantial lengthening of the C^3−C^4 bond (compared to the RHF results) and almost equal populations for the S^2 and A^2 configurations. In fact, with the 3-21G(d) basis set, the CASSCF(2,2) optimized structure shows an elongation of C^3−C^4 of 0.065 Å relative to the RHF value. As a comparison, it is noted that the corresponding elongation for benzyne is 0.036 Å.[8b] At the CASSCF(2,2)/6-311G(d,p) level, the occupancies of the S and A orbitals are 1.64 and 0.36, respectively; there is very little variation in these occupancies when the basis set is changed to either 3-21G(d) or 6-31G(d). These occupancies indicate that the in-plane π bond of **2** has a fairly large degree of biradical character, as expected for such a highly bent bond.

The vibrational frequencies of **2** have also been calculated. At the CASSCF(2,2)/6-311G(d,p) level, they are (in cm^{-1}) 3405 (A$_1$), 3400 (B$_2$), 1635 (B$_2$), 1616 (A$_1$), 1421 (A$_1$), 1279 (B$_2$), 1199 (A$_1$), 884 (B$_1$), 866 (B$_2$), 832 (A$_1$), 815 (A$_2$), 739 (B$_2$), 660 (A$_1$), 620 (A$_2$), and 466 (B$_1$). The two highest-energy frequencies correspond to C−H stretching, the next five are mostly bond stretching around the ring, while the remaining eight are the bending modes. Considering that the scaling factor for HF/6-31G(d) frequencies is 0.8929,[22] the CASSCF(2,2)/6-311G(d,p) frequencies should be at most 10% too high. Finally, it is noted that, at all four levels of calculations reported here, all of the vibrational frequencies of **2** are real, indicating the structure to be an energy minimum.

In conclusion, evidence for 3,4-didehydrothiophene (**2**) as an intermediate has been obtained by the formation of its [2 + 2]- and [4 + 2]-cycloaddition adducts with dienes.

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Supporting Information Available: Listing of physical data, ^{1}H- and ^{13}C-NMR spectra, and the microanalysis and/or high-resolution mass spectrometric results for compounds prepared (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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