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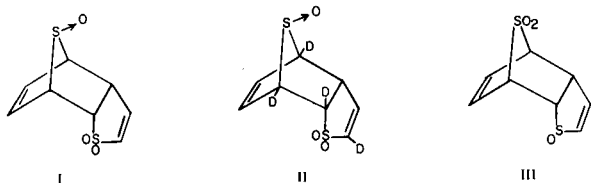
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Thiophene sesquioxide is shown to be *syn, endo-3a,4,7,7a-tetrahydro-4,7-epithiobenzo[b] thiophene 1,1,8-trioxide* (I) by  $^1\text{H}$  and  $^{13}\text{C}$  nmr evidence. Assignment of the  $^{13}\text{C}$  spectrum was facilitated by a cross-ring long-range  $^{13}\text{C}-^1\text{H}$  coupling. The mass spectrum of I is dominated by an unusual break-down to give benzene radical cation.

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In 1952 Davies and coworkers reported that peracid oxidation of thiophene gives a product,  $\text{C}_8\text{H}_8\text{O}_3\text{S}_2$ , which they assigned as a Diels-Alder adduct of thiophene sulfoxide and thiophene sulfone (2,3). Similar "sesquioxides" have also been obtained from some substituted thiophenes (4). We became interested in the possibility of using thiophene sesquioxide as a synthetic precursor to certain other heterocycles and decided to investigate its structure in more detail. We now report a complete spectroscopic characterization of this compound which firmly establishes its structure as *syn, endo-3a,4,7,7a-tetrahydro-4,7-epithiobenzo[b] thiophene 1,1,8-trioxide* (I).



Thiophene sesquioxide was prepared by the procedure of Davies and James (3). The product gave a positive test for sulfoxide (5), and the infrared spectrum confirmed the presence of sulfoxide ( $1070\text{ cm}^{-1}$ ) and sulfone ( $1148$  and  $1300\text{ cm}^{-1}$ ) groups. In order to facilitate nmr and mass spectral analysis, thiophene-2,5- $\text{d}_2$  was converted to the presumed tetra-deuterated product (II).

The  $^1\text{H}$  nmr spectrum of thiophene sesquioxide was closely coupled even at 100 MHz. Four multiplets were observed, each integrating for two protons, but the splittings could not be interpreted on a first-order basis. Attempts to simplify the spectrum using the lanthanide shift reagent  $\text{Eu}(\text{fod})_3$  were only partially successful. Although lanthanide-induced shifts have been observed with both sulfoxides (6) and sulfones (7), we assumed that the europium would complex preferentially, if not exclusively, with the more nucleophilic sulfoxide functionality (8). When  $\text{Eu}(\text{fod})_3$  was added to a solution of thiophene sesquioxide (in acetonitrile- $\text{d}_3$ ) two of the alkyl protons were strongly shifted downfield; the two other alkyl protons were less shifted, as were the four alkenyl protons. Although the splitting patterns remained too complex to interpret, these qualitative results clearly

ruled out alternative structures such as III, and strongly suggested the structure I. The spectrum of the tetra-deuterated compound II was much less complex. Protons 3 and 3a appeared as doublets; protons 5 and 6 as a closely coupled AB quartet. A lanthanide shift reagent study of II was performed using  $\text{Eu}(\text{fod})_3$ ; the relative induced shifts were: H-3, 0.23; H-3a, 1.00; H-5, 0.26; H-6, 0.26. These results are in qualitative agreement with those predicted for II using the axially symmetric McConnell-Robertson equation (9) with a Eu-O distance of  $3\text{ \AA}$ : H-3, 0.26; H-3a, 1.00; H-5, 0.44; H-6, 0.44. The "distance only" model (10) gives a better fit: H-3, 0.28; H-3a, 1.00; H-5, 0.24; H-6, 0.24. None of the alternative structures for thiophene sesquioxide is compatible with the LIS data; the *syn, endo* structure I must be correct.

In order to obtain complete  $^1\text{H}$  nmr parameters for I the spectrum was obtained at 300 MHz. At this field strength the spectrum was first-order, though still partially obscured by overlaps. By means of spin-decoupling experiments and comparison with the spectrum of II, all signals were unambiguously assigned. The results are summarized in Table I. The 4.0-Hz couplings for H-3a to H-4 and H-7 to H-7a are compatible with the *endo* stereochemistry of I. The most surprising feature is the

Table I

$^1\text{H}$  Nmr Parameters for Compound I (a)

Proton	Shift (b)	Coupling Constants, Hz	
H-2	6.80	$J_{2,3} = 6.0$	$J_{2,3a} = 2.0$
H-3	6.70	$J_{3,3a} = 2.7$	
H-3a	4.41	$J_{3a,4} = 4.0$	$J_{3a,7a} = 8.0$
H-4	4.16	$J_{4,5} = 4.6$	$J_{4,6} = 1.3$
H-5	6.09	$J_{5,6} = 6.8$	$J_{5,7} = 1.3$
H-6	6.18	$J_{6,7} = 4.5$	
H-7	4.36	$J_{7,7a} = 4.0$	
H-7a	4.16		

(a) Saturated solution in  $\text{DMSO}-\text{d}_6$  at  $45^\circ$ .

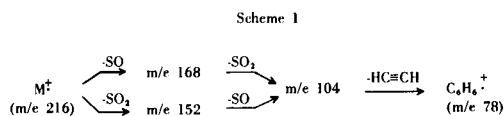
(b) Chemical shift in ppm from hexamethyldisilazane.

appearance of the signal for H-3a so far downfield ( $\delta$  4.41 ppm). It is tempting to ascribe this to the local magnetic anisotropy of the *syn* sulfoxide group, since H-7a is also rather far downfield from its expected position. A recent report (11) gives parameters for the spectrum of 2-methylthiophene sesquioxide which are similar to ours.

The 20 MHz  $^{13}\text{C}$  nmr spectra of compounds I and II were obtained, both with and without proton noise decoupling; the resulting data appear in Table II. The assignment of the resonances presented some difficulty. Selective or off-resonance proton decoupling was not feasible due to the closely coupled nature of the proton spectrum at 80 MHz. For the same reason, the  $^{13}\text{C}$  nmr spectrum of I without proton decoupling could not be analyzed beyond the one-bond couplings. Chemical shift considerations provided unambiguous assignments for C-2, C-3, and C-3a; these were confirmed by the spectrum of compound II. (The peaks for the deuterated carbons were too weak to be observed.) The proton-coupled spectrum of compound II made it possible to assign C-5 and C-6. In the alkenyl region of the spectrum (Figure 1), there appears, in addition to the doublet of doublets for C-3, a doublet and a doublet of doublets, both appreciably broadened. Using the ABX treatment, C-5 and C-6 are predicted to appear as doublets of doublets, with the smaller separation close in magnitude to the two-bond coupling. It seems highly unlikely that J (C-5 to H-6) would differ much in magnitude from J (C-6 to H-5). Two-bond couplings for alkenes show a wide variation (12,13) but small absolute values ( $< 2$  Hz) seem common. If we assume these couplings are small - and unresolved - in this case, the extra coupling may be ascribed to a three-bond, transoid coupling of C-5 to H-3a. The value of 7.0 Hz for this coupling appears to be of the expected magnitude (13). The broadened doublet must then be due to C-6. We are currently investigating the possibility that

such long-range  $^{13}\text{C}$ - $^1\text{H}$  couplings may be of help in interpreting spectra of other rigid compounds. The remaining assignments in the spectrum of I - for C-4, C-7, and C-7a - are based on chemical shift and one-bond coupling considerations and must be considered tentative.

The mass spectrum of thiophene sesquioxide shows some unusual features. The rearrangement-fragmentation paths common with other unsaturated sulfones and sulfoxides (14) seem less important in the spectrum of I. The dominant process (Scheme 1) appears to be loss of SO and  $\text{SO}_2$ , followed by expulsion of acetylene, to give the highly stable  $\text{C}_6\text{H}_6^{+\cdot}$  ion ( $m/e$  78); this is the base peak. Further breakdown then occurs to give the expected peaks at  $m/e$  51 and 39. Other major peaks appear at  $m/e$  150, 120, and 103. A fairly strong peak at  $m/e$  91 may be ascribed to  $\text{C}_7\text{H}_7^+$ . The mass spectrum of the tetradeuteriated analogue II showed the parent ion, as expected, at  $m/e$  220. The spectrum, as is common with deuteriated compounds, is increased in complexity. However, it appears to support the interpretation given for the spectrum of I; in particular, the base peak appears at  $m/e$  81, as expected for  $\text{C}_6\text{H}_3\text{D}_3^{+\cdot}$ . The smaller peaks at  $m/e$  152 and 168 also appear to be appropriately shifted by four mass units to 156 and 172.



There are two plausible mechanisms for the formation of I: (a) dimerization of thiophene sulfoxide, followed by oxidation of S-1; (b) reaction of thiophene sulfoxide with thiophene sulfone. Either mechanism would be expected to produce some of the alternate product III, which is not observed. However, III should readily lose sulfur dioxide to give a diene which would then further

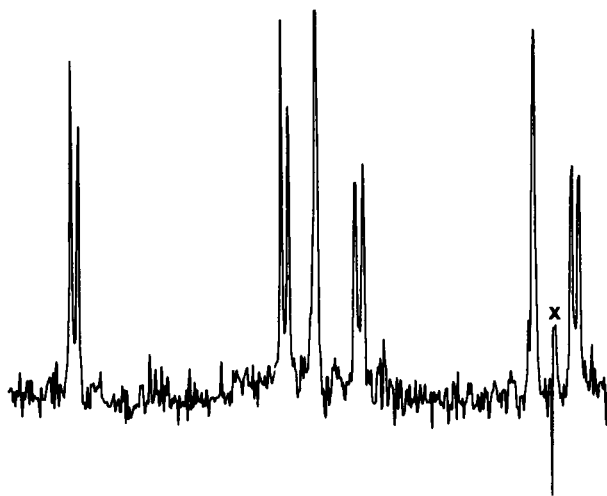
Table II

 $^{13}\text{C}$  Nmr Parameters for Compounds I and II (a)

Carbon	Shift, ppm (b)	$J_{\text{CH}}$ Hz (c)
C-2	134.96	191.3
C-2	138.17 (138.62)	174.3 (to H-3a:6.3)
C-3a	47.89 (47.61)	150.0 (to H-3:4.2)
C-4	62.45	163.8
C-5	126.82 (126.72)	179.5 (to H-3a:7.0)
C-6	128.62 (128.50)	181.5
C-7	63.76	161.3
C-7a	60.96	152.0

(a) Saturated solution in  $\text{DMSO-d}_6$ .(b) Chemical shifts in ppm downfield from TMS, using  $\text{DMSO-d}_6$  (= 39.60 ppm) as a secondary reference. Numbers in parentheses are chemical shifts for Compound II.

(c) One-bond carbon-hydrogen coupling constants. Long-range couplings, in parentheses, are from the spectrum of Compound II.

Figure 1. Alkenyl Region of the  $^{13}\text{C}$  Nmr Spectrum of Compound II; no proton decoupling. The width of the area shown is 500 Hz.

decompose under the reaction conditions. Whichever mechanism is correct, a Diels-Alder reaction in which thiophene sulfoxide acts as the diene must be involved. The *syn* stereochemistry of the sulfoxide at S-8 may be attributed to stabilization of the transition state by back-donation from the filled oxygen orbitals into the LUMO of the dienophile.

#### Acknowledgement.

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#### EXPERIMENTAL

Infrared spectra were obtained by means of a Perkin-Elmer IR-257. The 300 MHz  $^1\text{H}$  nmr spectra were obtained by means of a Varian HR-300 Spectrometer; 20 MHz  $^{13}\text{C}$  nmr and 80 MHz  $^1\text{H}$  nmr spectra were obtained by means of a Varian CFT-20 Spectrometer. Mass spectra were obtained at 70 e.v. by means of a Dupont 21-490B. Peaks of less than 20% relative abundance are not reported unless mentioned in the text. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. *Syn, endo-3a,4,7,7a-tetrahydro-4,7-epithiobenzo[b]thiophene 1,1,8-Trioxide (I)*.

Essentially the procedure of Davies and James (3) was used: A solution of 22 g. of thiophene and 60 ml. of 30% hydrogen peroxide in 200 ml. of glacial acetic acid was stirred at room temperature for seven days. The product could be isolated by precipitation with ether; or, more conveniently, by evaporation of the solvent under reduced pressure (15) followed by trituration of the residue with ethanol. In either case, yields from repeated runs were consistently 4.1 to 4.4 g. (about 15%) of pale tan powder. As previously observed (3), the melting point of this compound is actually a decomposition temperature which varies widely with the rate of heating; it cannot be used as a measure of purity. Repeated recrystallization from ethanol gave a white powder. *Anal.* Calcd. for  $\text{C}_8\text{H}_8\text{O}_3\text{S}_2$ : C, 44.4; H, 3.7; S, 29.7. Found: C, 44.6; H, 3.7; S, 29.6.

The solubility of thiophene sesquioxide is low even in polar solvents. For LIS studies,  $^1\text{H}$  nmr spectra were obtained in acetonitrile- $\text{d}_3$  at 80 MHz using the Pulse Fourier Transform (PFT) method. For 300 MHz  $^1\text{H}$  nmr spectra, a solution in  $\text{DMSO-d}_6$  was used. The reported parameters were obtained at 45°; the spectrum is better-resolved at this temperature, probably due to reduced viscosity. However, the spin-decoupling studies were performed at 25°. The 20 MHz  $^{13}\text{C}$  nmr spectrum of compound I (as a saturated solution in  $\text{DMSO-d}_6$ ) was obtained by the PFT method both with and without broad-band proton decoupling. Chemical shifts were determined using  $\text{DMSO-d}_6$  (= 39.6 ppm) as a secondary standard; one-bond coupling constants were estimated by measuring from center to center of the multiplets; ir (potassium bromide pellet) 1300 and 1148  $\text{cm}^{-1}$  (sulfone), 1070  $\text{cm}^{-1}$  (sulfoxide); ms: m/e (relative abundance) 216 (3), 168 (1), 152 (3), 150 (18), 120 (17), 104 (44), 103 (65), 91 (20), 78 (100), 77 (25), 51 (26), 39 (13), 28 (25).

*Syn, endo-3a,4,7,7a-tetrahydro-4,7-epithiobenzo[b]thiophene 1,1,8-Trioxide-2,4,7,7a-d<sub>4</sub>*.

A mixture of 16.8 g. of thiophene, 60 g. of deuterium oxide, and 100 g. of sulfuric acid- $\text{d}_2$  was stirred at 0-5° until  $^1\text{H}$  nmr analysis showed that deuterium incorporation was complete (4 hours). The organic layer was separated and washed with water, saturated sodium bicarbonate, and saturated sodium chloride, and dried over potassium carbonate. The yield of thiophene-2,5- $\text{d}_2$  was 7.62 g. (44%). This was reacted, using the above procedure, with 20 ml. of 30% hydrogen peroxide in 70 ml. of glacial acetic acid. The yield of pale tan product was 1.39 g. (14%). This material proved satisfactory for nmr studies without further purification. A LIS study was performed, using acetonitrile- $\text{d}_3$  as the solvent, TMS as the standard, and  $\text{Eu(fod)}_3$  (Aldrich "Resolve-Al EuFOD") as the shift reagent. The following chemical shifts were obtained ( $\delta$ , ppm; number of increments of  $\text{Eu(fod)}_3$  in parentheses).

H-3: (0) 6.61; (1) 7.02; (2) 7.37; (3) 7.54.  
H-3a: (0) 4.42; (1) 6.15; (2) 7.70; (3) 8.43.  
H-5: (0) 6.06; (1) 6.52; (2) 6.92; (3) 7.13.  
H-6: (0) 6.21; (1) 6.67; (2) 7.07; (3) 7.26.

The 20 MHz  $^{13}\text{C}$  nmr spectrum of Compound II was determined in the same manner as for Compound I; ms: m/e (relative abundance) 220 (4), 171 (7), 153 (11), 152 (15), 124 (29), 108 (62), 107 (74), 106 (60), 82 (20), 81 (100), 80 (38).

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