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Conformational Properties of the *N*-Tosylsulfilimines of Dibenzothiophene, Phenoxathiin, and Thianthrene[1]

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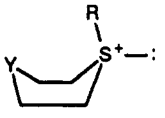
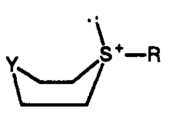
The X-ray and MNDO-derived structures and aromatic solvent induced shifts (ASIS) of the *N*-(*p*-toluenesulfonyl)sulfilimines of dibenzothiophene (**1e**), phenoxathiin (**2e**), and thianthrene (**3e**) are reported. In **1e**, the dibenzothiophene ring system remains essentially planar, with the phenyl rings inclined only 3.7°. The sulfilimine substituent is pseudoaxial (*pa'*). In **2e**, the phenoxathiin ring system is gently folded in a "boat" conformation with the phenyl rings inclined 16.9°; the Cremer and Pople puckering factors are $Q = 0.267$ (3) Å, $\varphi = 179.6$ (6)°, and $\theta = 104.5$ (6)°. The substituent is *pa'*. In **3e**, the thianthrene ring system is sharply folded in a "boat" conformation with the phenyl rings inclined 52.7° ($Q = 0.842$ (6) Å, $\varphi = 179.9$ (4)°, and $\theta = 92.9$ (4)°). The substituent is pseudoequatorial (*pe'*). In each structure, the substituent is asymmetrically oriented with respect to the vertical plane bisecting the central ring. ASIS analysis of the peri hydrogens of **1e**–**3e** establishes that the solid state substituent orientations of all three derivatives are maintained in solution (**1e**, $\delta_{\mathrm{CDCl_3}} - \delta_{\mathrm{C_6D_6}} = +0.46$ ppm; **2e**, +0.18 ppm; **3e**, −0.13 ppm). MNDO calculated ΔH_f of the respective *pa'* vs *pe'* conformers suggest that the stereochemistry observed in the crystal structures may be thermodynamically favored ($\Delta\Delta H_f$: **1e**, (spontaneous convergence to *pa'*); **2e**, 0.66 kcal mol^{-1} favoring *pa'*; **3e**, 0.76 kcal mol^{-1} favoring *pe'*).

Introduction

Dibenzothiophene (**1a**) and tricyclic 6,6,6 diaryl sulfides with sulfur at the meso position (e.g., phenoxathiin (**2a**), thianthrene (**3a**), phenothiazine (**4a**), thioxanthene (**5a**), and thioxanthenone (**6a**)) form conformationally restricted S-monosubstituted derivatives with the substituent in either a pseudoaxial (*pa'*) or pseudoequatorial (*pe'*) orientation. Structural analyses suggest that the orientation of the substituent is dependent on (1) in **2**–**6**, the presence and nature of additional substituents on the opposite meso atom Y; (2) the presence of additional substituents on the phenyl rings, especially at the peri positions; and (3) in solution, specific interactions with the solvent. While there do not appear to be any general correlations in substituent orientation between systems, internal comparisons of the known S-monosubstituted derivatives of each parent sulfide indicate similar conformations. Thus, S-monosubstituted derivatives of **1a** are *pa'*, of **2a** *pa'*, of **3a** *pe'*, of **4a** *pa'*, of **5a** *pe'*, and **6a** *pe'* (see Chart I).



pa'



pe'

Table I. Selected Bond Distances[a,b]

bond	1e	2e	3e
S1–N	1.632	1.632	1.631
C2–S1	1.788	1.751	1.791
N–S2	1.623	1.618	1.615
C5–S1	1.773	1.757	1.773
C2–C3	1.391	1.390	1.393
C4–C5	1.400	1.380	1.405
C3–C4	1.468		
C3–O3		1.364	
C4–O3		1.362	
C3–S3			1.755
C4–S3			1.778
S2–O1	1.428	1.439	1.442
S2–O2	1.442	1.438	1.438
S2–C14	1.769	1.769	1.786

[a] In angstroms. [b] Estimated standard deviations: **1e**, 0.002–0.003 Å; **2e**, 0.002–0.004 Å; **3e**, 0.005–0.010 Å.

Table II. Selected Bond Angles[a,b]

angle	1e	2e	3e
O3–C3–C2		124.4	
O3–C4–C5		124.2	
S3–C3–C2			121.7
S3–C4–C5			120.7
C3–C2–S1	112.2	122.4	117.2
C4–C5–S1	112.8	122.9	117.7
C2–S1–C5	90.4	99.1	100.2
C3–O3–C4		121.7	
C3–S3–C4			100.6
C2–S1–N	107.5	103.4	106.9
C5–S1–N	100.5	105.8	101.6
S1–N–S2	114.4	112.0	112.9
N–S2–O1	105.0	104.9	103.9
N–S2–O2	112.5	112.1	111.5
N–S2–C14	104.7	105.8	108.9
O1–S2–C14	108.6	108.8	107.9
O2–S2–C14	106.6	107.0	106.3

[a] In degrees. [b] Estimated standard deviations: **1e**, 0.1–0.3°; **2e**, 0.2–0.5°; **3e**, 0.5–1.1°.

Recently, the crystal structure of the *N*-*p*-toluenesulfonyl (tosyl) sulfilimine of 2,4,9-trimethylthioxanthene was reported;[4,5] this study extended the structural analyses of tosyl sulfilimines derived from dialkyl,[6] alkyl aryl,[7] and diaryl[8] sulfides to the tricyclic 6,6,6 diaryl sulfides. Herein, we report the solid and solution state conformations of the

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[1] Presented in part at the 18th Middle Atlantic Regional Meeting of the American Chemical Society, Newark, NJ, May 22, 1984; also presented in part at the 9th European Crystallographic Meeting, Turin, Italy, September 2–6, 1985.

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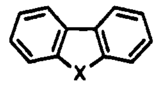
Chart I



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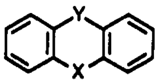

2, Y = O
3, Y = S
4, Y = NH
5, Y = CH_2
6, Y = C=O

a, X = S; b, X = S=O; c, X = S^+MeX^-; d, X = $S^+C^-(COOR)_2$;
e, X = S N^--tosyl

compd	substit orientn	ref
1a		9
1b	*pa'*	10
1c	*pa'*	8
1e	*pa'*	this work
2a		11
2b	*pa'*	12
2e	*pa'*	this work
3a		13
3b	*pe'*	14
3d	*pe'*	12
3e	*pe'*	this work
4a		15
4b	*pa'*	16
5a		17
5b	*pe'*	18
5d	*pe'*	19
6a		20
6b	*pe'*	21
6d	*pe'*	22

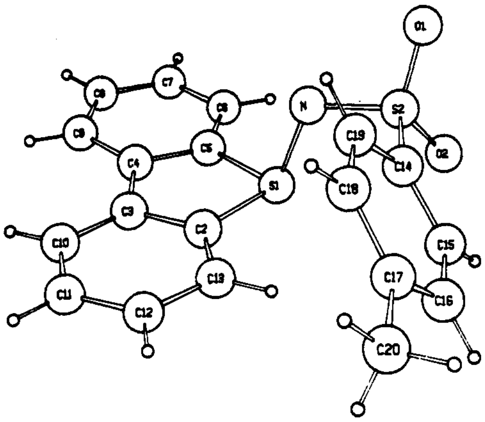

Figure 1. Solid-state geometry of 1e.

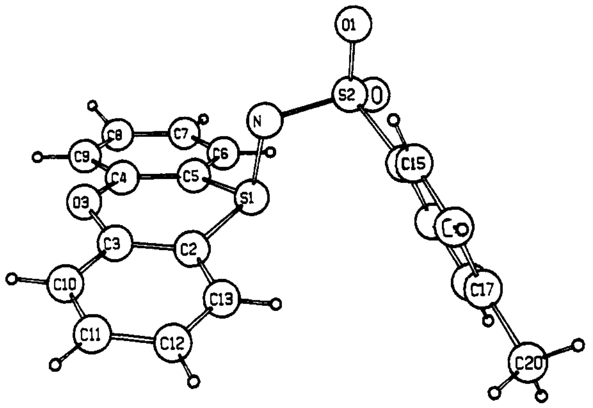

Figure 2. Solid-state geometry of 2e.

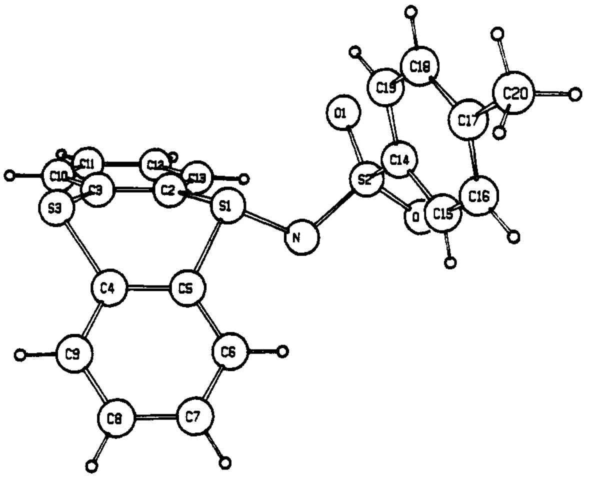

Figure 3. Solid-state geometry of 3e.

Table III. Selected Torsion Angles[a,b]

angle	1e	2e	3e
C10-C3-O3-C4		164.7	
C10-C3-S3-C4			135.5
C3-O3-C4-C9		-164.6	
C3-S3-C4-C9			-137.7
C13-C2-S1-C5	179.9	-162.4	-131.6
C2-S1-C5-C6	178.2	164.5	132.5
O3-C3-C2-S1		-5.1	
S3-C3-C2-S1			-2.6
O3-C4-C5-S1		5.5	
S3-C4-C5-S1			4.1
C3-C2-S1-C5	-1.0	19.4	50.5
C4-C5-S1-C2	2.2	-19.7	-51.0
C3-C2-S1-N	100.1	-89.4	156.1
C4-C5-S1-N	-105.6	87.1	-160.7
C2-S1-N-S2	112.0	-137.9	106.9
C5-S1-N-S2	-154.3	116.4	-145.6
S1-N-S2-C14	-77.4	64.1	66.5
S1-N-S2-O1	168.3	179.1	-178.7
S1-N-S2-O2	38.0	-52.2	-50.5
N-S2-C14-C15	117.7	80.7	73.2

[a] In degrees. [b] Estimated standard deviations: 1e, 0.2–0.6°; 2e, 0.4–1.0°; 3e, 1.0–2.2°.

tosylsulfilimines of dibenzothiophene (1e),[23] phenoxathiin (2e), and thianthrene (3e),[5,24] as determined by single-crystal X-ray diffraction and aromatic solvent induced shift (ASIS) methods, respectively. In addition, we report briefly on the results of a theoretical (MNDO) study of

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(24) The tosylsulfilimine of phenothiazine (4e) is unstable.

Table IV. Crystal, Data Collection, and Refinement Parameters

parameter	1e	2e	3e
formula	$C_{19}H_{15}NO_2S_2$	$C_{19}H_{15}NO_3S_2$	$C_{19}H_{15}NO_2S_3$
mw (Daltons)	353.47	369.46	385.53
a, Å	8.009 (1)	10.311 (1)	8.449 (1)
b, Å	7.189 (1)	13.470 (1)	11.278 (1)
c, Å	14.251 (1)	12.858 (1)	18.626 (2)
α, deg	90	90	90
β, deg	94.31 (5)	105.78 (2)	90
γ, deg	90	90	90
V, Å	818.2	1718.6	1774.8
space group	$P2_1$	$P2_1/c$	$P2_12_12_1$
Z	2	4	4
radiatn, Å	0.71073	1.5418	1.5418
temp, °C	22	22	22
μ, cm^{-1}	3.3	29.11	38.63
D_c, g/cm^3	1.435	1.428	1.443
crystl dimensns	0.2 × 0.35 × 0.4	0.15 × 0.3 × 0.35	0.15 × 0.2 × 0.25
transmssn coeff	0.77–1.12	0.79–1.30	0.87–1.37
$\lambda^{-1} \sin\theta$ limits, A^{-1}	0.037–0.704	0.017–0.626	0.017–0.626
no. data	3825	3575	2108
no. data with $I > x\sigma_I$	2982 ($x = 5$)	3031 ($x = 3.0$)	1774 ($x = 1.8$)
no. paramtrs refined	217	227	227
R	0.035	0.043	0.061
R_w	0.043	0.059	0.067
$P(1/\omega = \sigma^2(F_o) + 0.25\,(pF_o)^2)$	0.01	0.01	0.01

1e–3e, which was undertaken in an attempt to shed additional light on the conformational preferences of these derivatives.

Results and Discussion

Molecular conformations of **1e–3e** obtained from X-ray are illustrated in Figures 1–3, respectively. Selected bond lengths and bond and torsion angles are presented in Tables I–III. Crystal, data collection, and refinement parameters are detailed in Table IV.

Molecular Stereochemistry in the Solid State. The molecular conformations of **1e–3e** vary from planar to strongly folded. In **1e**, the dibenzothiophene ring system is essentially coplanar, with the phenyl rings inclined only 3.7°. The corresponding angles in **1a**, **1b**, and **1c** are similarly small at 1.6, 4.4, and 1.1°, respectively. Comparable bond lengths and angles among **1a–e** are also very similar (see supplementary material, Table S-I). The sulfilimine substituent in **1e** is *pa'* and the S^{IV}–N bond is projected approximately perpendicular to the dibenzothiophene moiety (torsion angle C–C–S^{IV}–N ±102°).

In **2e**, the phenoxathiin ring system is gently folded in a "boat" conformation with the phenyl rings inclined 16.9°; the Cremer and Pople puckering factors[25] are $Q = 0.267$ (3) Å, $\varphi = 179.6$ (6)°, and $\theta = 104.5$ (6)°. Interestingly, **2e** is significantly less folded than **2a** (42°) or **2b** (28°); comparable bond lengths and angles among **2a–e**, however, remain similar (Table S-II). Similarly to **1e**, the substituent in **2e** is *pa'* with the S^{IV}–N bond nearly perpendicular (torsion angle C–C–S^{IV}–N ±88°).

In **3e**, the thianthrene ring system is sharply folded in a pronounced "boat" conformation with the phenyl rings inclined 52.7° ($Q = 0.842$ (6) Å, $\varphi = 179.9$ (4)°, and $\theta = 92.9$ (4)°). The extent of folding is quite similar to that of **3a** (52°) and **3d** (44.3°); bond lengths and angles are again similar (Table S-III). In contrast to **1e** or **2e**, however, the substituent in **3e** is *pe'* and consequently the S^{IV}–N bond is projected approximately along the line bisecting the central ring (torsion angle C–C–S^{IV}–N ±158°).

In all three crystal structures **1e–3e**, the tosyl substituent is asymmetrically oriented with respect to the vertical plane bisecting the central ring. The conformations of the tosyl groups about their respective S^{IV}–N bonds (64–77°, Figure 4) fall within the range observed for numerous similar N-substituted arenesulfonamides.[26] This consistency suggests that crystal packing and/or intermolecular interactions are only minimally important to the tosyl group orientation. Examination of nonbonded contacts indicates that there are no short *inter*molecular contacts involving S or O atoms; however, there are several short *intra*molecular contacts between sulfonyl oxygens and peri hydrogens.

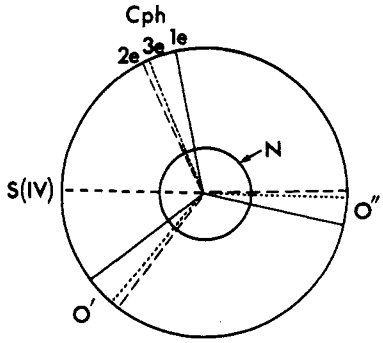

Figure 4. Newman projection of S^{VI} [O′O″NC] tetrahedra perpendicular to the S^{IV}–N bond. Torsion angles (same enantiomers):

bond	1e	2e	3e
S^{IV}–N–S^{VI}–C	77.4	64.1	66.5
S^{IV}–N–S^{VI}–O′	−168.3	179.1	−178.7
S^{IV}–N–S^{VI}–O″	−37.9	−52.1	−50.5

Molecular Conformations in Solution. The aromatic solvent induced shift (ASIS[27]) ^{1}H NMR technique has been extensively utilized for the determination of the conformations of a number of derivatives of **2a**,[12] **3a**,[14] and others[18,19,28] in solution. Specifically, C_6D_6 induces an upfield shift of the proximal peri protons vs $CDCl_3$ when solvating substrates with *pa'* substituents and a downfield shift when solvating substrates with *pe'* substituents. In nonseverely interacting solvents, the solution conformation generally matches the solid state.[31]

ASIS analysis confirms that the substituent orientations of **1e–3e** are maintained in solution (**1e**, $\delta_{CDCl_3} - \delta_{C_6D_6} = +0.46$ ppm; **2e**, +0.18 ppm; **3e**, −0.13 ppm) (Table S-VI). ASIS analysis has (apparently) not been previously applied to derivatives of **1a**; however, the upfield shift is consistent with a *pa'* substituent[27] and the sulfoxide (**1b**, also *pa'* in the solid state[10]) gives a comparable upfield shift ($\delta_{CDCl_3} - \delta_{C_6D_6} = +0.39$ ppm). The induced shifts of **2e** and **3e** are smaller than their corresponding sulfoxides (**2b**, +0.26 ppm;[12] **3b**, −0.3 ppm[14]).

MNDO-Derived Structures. MNDO-derived structures deviate significantly from the X-ray structures, e.g., in **2e** and **3e**, the extent of folding is underestimated by

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[29] This assumes that the conformations found in the crystal structures are in fact the lowest energy conformers; it is possible that such is not the case. Additional work in this series, however, indicates that the *pe'* conformers of **5e** and **6e** are both calculated to be slightly thermodynamically more stable than their respective *pa'* conformers (in agreement with their expected *pe'* conformations). These findings suggest that the results are not merely fortuitous, but rather that MNDO is—albeit poorly—giving an assessment of the most stable conformer.

[30] A definitive statement requires ASIS analysis of a *pe'* derivative of **1a**; to our knowledge, none have been reported.

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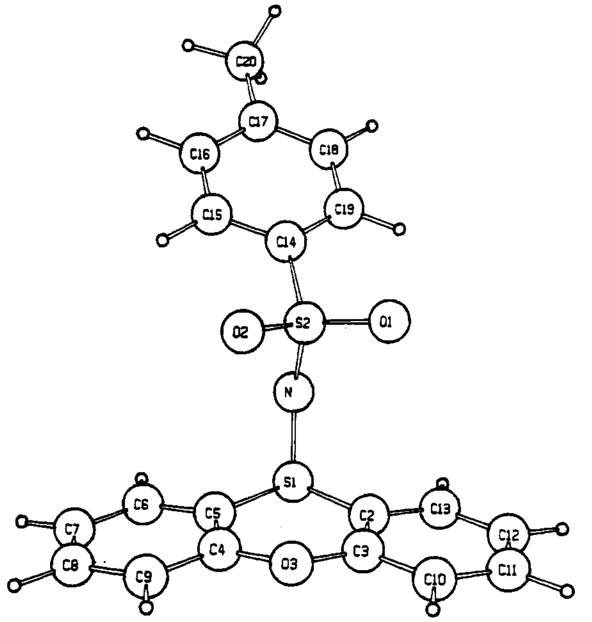


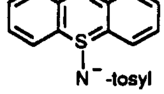
Figure 5. MNDO-derived geometry of **2e** (note: **1e** and **2e** display similar symmetry).

a factor of at least 2. In addition, the substituents are symmetrically oriented along the vertical plane bisecting the central ring, i.e., the most favorable orientation in the gas phase (Figure 5). The estimates of the carbon skeleton framework are reasonable; however, estimates of the various bond lengths and bond angles involving heteroatoms—particularly in the sulfonylsulfilimine moieties—are much less accurate, differing by as much as 0.1 Å and 8.5° from the solid state structures (Tables S-VIII, -IX, and -X).

MNDO-calculated ΔH_f—providing a theoretical estimate of the relative thermodynamic stabilities of the *pa'* vs *pe'* conformers—suggest that the conformations observed in the crystal structures are thermodynamically favored ($\Delta\Delta H_f$: **1e**, (spontaneous convergence to *pa'*); **2e**, 0.66 kcal mol^{-1} favoring *pa'*; **3e**, 0.76 kcal mol^{-1} favoring *pe'*)[29] (Table S-V).

Involvement of Sulfur(IV) in π-Conjugation and Heteroaromaticity. I. S Aromaticity in S-Substituted Dibenzothiophenes. The *pa'* substituent orientations in **1b–e** precludes π-conjugation with the remaining S^{IV} lone pair. Within the limits of precision of this study, the S^{IV}–C bond lengths and C–S^{IV}–C angles are insensitive to the nature and size of the substituent (Tables S-I and -II) and there is no significant bond alternation in the phenyl rings; these findings certainly arise in part from the severe conformational constraints imposed by the interannular bridge.

II. Heteroaromaticity in 2e and 3e. As partial ylides, the fully aromatic dipolar resonance forms **2e'** and **3e'** may contribute to the resonance stabilization of **2e** and **3e**. However, while the MNDO-derived structures—with shortened S^{IV}–C and S^{II}–C or O–C bond lengths and significantly reduced folding (Tables S-VIII, -IX, and -X)—imply strong contributions from these forms, they are clearly *not* significant in the solid-state structures.



2e', X = O
3e', X = S

III. O Aromaticity in S-Substituted Phenoxathiins. As in **1b–e**, the *pa'* substituent orientation precludes π-conjugation with the remaining S^{IV} lone pair. However, the oxygen bridge results in much greater conformational flexibility. The shortened C–O separations (1.364 Å) and increased C–O–C bond angles (121.8°) are suggestive of sp^2 hybridization, and the angle of inclination between the phenyl rings (16.9°) is much less than in either **2a** (42°) or **2b** (28°). These results suggest that the bridging oxygen atom (but *not* S^{IV}) is at least partially involved in π-conjugation.

IV. S Aromaticity in S-Substituted Thianthrenes. Although the *pe'* substituent orientation would allow conjugation by the remaining S^{IV} lone pair, the sharply folded conformations observed in **3b–e**—each comparable to **3a**—precludes significant π-conjugation through either sulfur atom.

Conclusions

(A) S monosubstitution with a tosylsulfilimine moiety results in derivatives with conformations similar to other S-monosubstituted derivatives, e.g., sulfoxides or methylides. Although the existing data set is limited, the consistency in the results to date—ranging from small to large substituents—suggests a more general rule, i.e., that all S-monosubstituted derivatives of an individual tricyclic 6,6,6 diaryl sulfide will have similar conformations.

(B) The solid-state substituent orientations of the sulfilimines are matched in solution, as shown by the ASIS technique. As there do not appear to be any reported exceptions, these results also suggest a more general rule, i.e., that the solution conformations of all S-monosubstituted derivatives of **1–6** will match their solid-state conformations. The ASIS technique *may* be valid for substituted dibenzothiophenes.[30]

(C) MNDO calculations are deficient in estimating the structures of the sulfilimine derivatives; in general, the defects in the theoretical models appear to arise from imposition of overly aromatic character in the heterocyclic rings and poor parameterization of S^{IV} and S^{VI} species.[31] Comparisons of the ΔH_f of the *pa'* vs *pe'* conformers of S-monosubstituted derivatives of **2–6** *may* be valid in predicting molecular conformations.[32]

(D) In **2e** and **3e**, the presence of the lone pair donors at the opposite meso position does not provide significant resonance stabilization via the fully aromatic dipolar valence tautomers.

(E) The substituent orientation of **1–3** appears to be dictated by the degree of folding and the clear preference for the remaining lone pair on S^{IV} to avoid π-conjugation with the adjacent phenyl rings. If the heterocyclic ring system is approximately planar (**1**, **2**), the substituent orients *pa'*, thereby precluding π-conjugation; if the heterocyclic ring system is sharply folded (**3**), the remaining lone pair on S^{IV} cannot conjugate regardless of substituent orientation, and steric and intramolecular interactions are dominant.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AM-300 WB NMR spectrometer; Me_4Si was utilized as an internal calibration standard. X-ray single-crystal diffraction data were collected at 22 °C on an Enraf-Nonius CAD-4 four-circle computer-controlled diffractometer using graphite-monochromated Mo K_α radiation for **1e** and Cu K_α radiation for **2e** and **3e**. In each case, the lattice parameters and their standard deviations (Table IV) were determined by least squares from the

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(32) R. F. X. Klein, this lab, work in progress, see ref 29.

setting angles of 25 reflections. Data were corrected for Lorentz and polarization effects and for absorption by means of DIFABS[33] (based on spherical polar angles); the phase problems for all structures were solved directly, using MULTAN.[34] Hydrogen atoms were entered in calculated positions with isotropic temperature factors 1 Å^2 greater than that of the carbon atoms to which they are bound. Atomic scattering factors were taken from standard tables.[35] Enantiomorphs for **1e** and **3e** were not determined; however, the internal consistency of the pairs of chemically equivalent bond lengths and angles in each structure and the congruency of bond lengths and angles with other members of the family is sufficient evidence that neglect of enantiomorph determination has not led to systematic errors in metrical details that might compromise the conclusions reached in this study. In **3e**, the quality and extent of the data are such that anomalous scattering by S (under Cu K_α radiation) is barely significant. In **1e**, where the X-ray diffraction data set is more extensive than for **3e**, the anomalous scattering by S (under Mo K_α radiation), while (in principle) detectable, would lead to differences in bond lengths of no more than a few thousandths of an Å, a perturbation much less than that (0.05 Å, or $>5\sigma$) for which we have perceived structural differences to be significant.

Molecular Orbital Calculations. MNDO[36] calculations were performed with use of the MOPAC[37] program on a VAX 11/750 VMS computer. Initial bond lengths and angles were obtained from standard literature tables[38] and X-ray data. All geometric parameters were optimized with no specific assumptions; the keyword PRECISE was utilized—the maximum gradient at optimization was less than 5.0 for all conformers.

Molecular Diagrams. Three-dimensional representations of X-ray and MNDO structures were drawn with the PLUTO program (SDP, from Frenz and Associates and Enraf Nonius) interfaced to a Tektronix 4106 graphics terminal and a Tektronix 4662 plotter.

Chemistry. Sulfilimines **1e**–**3e** were prepared by the modified Chloramine-T method.[39] X-ray quality crystals were prepared by recrystallization from $CHCl_3$/c-C_6H_{12} 1:1. Melting points (°C) and ν(S=N) (cm^{-1}) are as follows: **1e**, 169, 901; **2e**, 171, 923; and **3e**, 167, 924. Additional experimental data are summarized in the supplementary material section.

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Supplementary Material Available: Comparative bond distances and angles vs similar derivatives, comparative bond distances and angles vs other nonsimilar tosylsulfilimines, atomic coordinates and anisotropic displacement parameters, hydrogen atom parameters, bond distances and angles, ASIS (^{1}H NMR) and ^{13}C NMR parameters, MNDO heats of formation, selected bond distances and angles, and optimized geometries (Cartesian coordinates) for **1e**, **2e**, and **3e** (22 pages). Ordering information is given on any current masthead page.

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Stilbenes from Sulfur-Mediated Dehydrodimerization of Substituted Toluenes

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When provision is made for removal of coproduct hydrogen sulfide, the reaction of sulfur with methyl *p*-toluate (MPT; **1**) at 280 °C leads to 70+% yields of the product dimethyl *trans*-4,4′-stilbenedicarboxylate (DMSC, **2**) if conversion of the MPT is restricted to ca. 10%. Diphenyl ether or excess MPT serves as the reaction solvent. Other products of the reaction include dimethyl 4,4′-bibenzyldicarboxylate (DBD, **3**), 1,2,3-tris(4-carbomethoxyphenyl)propane (**4**), 1,2,3-tris(4-carbomethoxyphenyl)propene (**5**; mixture of *E* and *Z* isomers), and 2,3,4,5-tetrakis(4-carbomethoxyphenyl)thiophene (**6**). The products are consistent with the reversible formation of 4-carbomethoxybenzyl radicals from sulfur and MPT where removal of the hydrogen sulfide drives the reaction forward.

Introduction

It has been known since early in this century that at least small quantities of stilbene can be isolated from the reaction products of toluene and sulfur[1] and that other aryl methanes are coupled by sulfur to the corresponding 1,2-diarylethylenes.[2] Processes for carrying out this reaction efficiently on toluene were described in a patent by Bhasin and Williamson.[3] Toland demonstrated that toluenes

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