

Anodic oxidation of *m*-terphenyl thio-, seleno- and telluroethers: Lowered oxidation potentials due to chalcogen $\cdots\pi$ interaction*

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Abstract: The electrochemistry of *m*-terphenylthio-, seleno-, and telluroethers was studied using cyclic voltammetry in acetonitrile. All of the compounds studied showed irreversible oxidations. The first oxidation potentials for the thio- and selenoethers are less positive than expected. This facilitation in oxidation is ascribed to through-space S $\cdots\pi$ and Se $\cdots\pi$ interaction, respectively, on removal of an electron. No evidence for a comparable effect was found for the phenyltelluro-ethers studied.

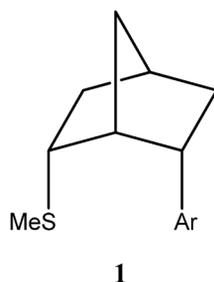
Keywords: electrochemistry; facilitated oxidation; photoelectron spectroscopy; sulfur; Se $\cdots\pi$ interaction; substituted *m*-terphenyls.

INTRODUCTION

Electron-rich neighboring groups are known to lower the oxidation potentials of thioethers owing to donation of an unshared pair of electrons [1]. It has been postulated that neighboring electron-rich arenes may also facilitate oxidation of thioethers. For example, it has been suggested [2] that the aromatic ring of a phenylalanine positioned over Met-35 in amyloid- β -peptides lowers the oxidation potential of the thioether moiety, rendering it a better reducing agent [2]. It has even been proposed that electron transfer in proteins may occur via alternating S $\cdots\pi$ interactions [3]. However, there is little chemical evidence in support of this hypothesis. Stabilization of thioether radical cations by arenes has been reported based on electron paramagnetic resonance (EPR) and time-resolved fluorescence detected magnetic resonance spectroscopy [4]. Recently, we reported [5] evidence for S $\cdots\pi$ interaction in conformationally constrained norbornyl compounds **1** with juxtaposed thioether and aromatic moieties, which results in lowered oxidation potentials. In these compounds, there is through-space interaction resulting from mixing of the lone-pair sulfur *p*-orbital and arene π -MO. This results in a lowered ionization energy for these compounds as measured by photoelectron (PE) spectroscopy. In addition, the oxidation potentials of these compounds are lowered due to S $\cdots\pi$ interaction. Owing to the difference in time scale, significant changes in molecular geometry resulting in bond formation between the thioether and arene moieties

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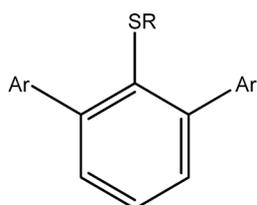


are possible in electrochemical measurements and are reflected in E° , but such molecular changes do not occur in the shorter time scale of the PE spectroscopic experiment (in which vertical-nonadiabatic-ionization occurs).

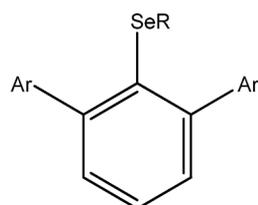
This paper reports the extension of these results to conformationally constrained *m*-terphenyl-thioethers, in which through-space S $\cdots\pi$ interaction results in lowered oxidation potentials. Furthermore, in these systems the thioethers may interact with one or both flanking arenes. In addition, this molecular framework was used to investigate the feasibility of Se $\cdots\pi$ and Te $\cdots\pi$ interactions on electron removal.

RESULTS AND DISCUSSION

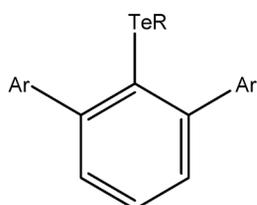
The synthesis and structural characterization of the compounds studied here, **2–4**, have been reported elsewhere [6]. Related systems as well as **2b** as shown by its X-ray crystal structure [6] are known to adopt the conformation shown in **5** in which resonance interaction between the π -systems, the *p*-lone-pair on chalcogen, and the phenyl ring to which it is attached are geometrically unfavorable; whereas through-space interaction of the *m*-aryl groups and the *p* lone-pair on chalcogen is favorable. Many



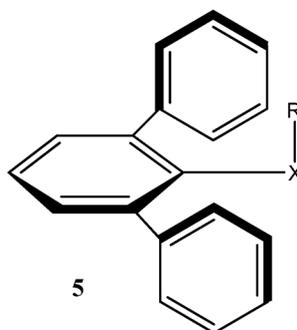
- 2a**, R = Me, Ar = Ph
b, R = Me, Ar = *o*-MeOC₆H₄
c, R = Me, Ar = *p*-MeOC₆H₄
d, R = Me, Ar = 2,5-(MeO)₂C₆H₃
e, R = Me, Ar = 2-Npht
f, R = Ph, Ar = *o*-MeOC₆H₄



- 3a**, R = Me, Ar = *o*-MeOC₆H₄
b, R = Me, Ar = *p*-MeOC₆H₄
c, R = Me, Ar = 1-Npht
d, R = Ph, Ar = *o*-MeOC₆H₄
e, R = Ph, Ar = *p*-MeOC₆H₄



- 4a**, R = Ph, Ar = *o*-MeOC₆H₄
b, R = Ph, Ar = 1-Npht



metalated *m*-terphenyl systems have been reported [7]. The aryl substituents flanking the metal sterically encumber it, but π -interaction with the neighboring arenes has also been reported, e.g., for lithium *m*-terphenyls [8]. Most relevant to our work is the reported [9] interaction of silyl cations with neighboring arenes in silyl *m*-terphenyl systems.

The oxidation of the *m*-chalcogenoethers was studied in acetonitrile using the technique of cyclic voltammetry. More than one oxidation peak was observed, but all of them were irreversible. The peak potentials of the first redox wave for each compound corresponding to the oxidation of the heteroatom centers: S, Se, and Te are listed in Table 1 along with the reference *m*-terphenyl derivatives **6**, which were measured under the same conditions. Figure 1 shows a typical example of the first redox wave obtained in acetonitrile containing 1 mM of compound **3b**. In comparing methylthioethers **2a–e** with the corresponding *m*-terphenyl derivative **6**, the oxidation potential for **2** is significantly less positive. Consequently, it is surmised that an electron is removed from the sulfur lone-pair *p*-orbital in **2** or a HOMO that is a combination of sulfur *p*-lone-pair and π -MO. Furthermore, the seleno- and tellurocompounds are even easier to oxidize than the corresponding thioethers as expected. To compare the oxidation potentials reported in Table 1 it must be noted that for the total irreversible oxidations E° , the formal potential, and k° , the heterogeneous electron-transfer rate constant, largely determine the peak potential E_p at constant scan rate [10]. However, for a related series of sulfides, ionization energy differences follow peak potential differences [11,12], suggesting that changes in E_p are determined largely by changes in E° with k° and solvation energy changes being relatively constant. This enables us to interpret the effect of 2,6-diaryl substituents on the oxidation potentials of chalcogenoethers. For example, compare the first oxidation potentials of **2a–e** with that of thioanisole, which is reported to be 1.12 V [13] in acetonitrile vs. the same reference electrode as that used for the data in Table 1. The pre-

Table 1 Peak potentials^a of the first redox wave for oxidation of *m*-terphenyl thio-, seleno-, and telluroethers and reference compounds.

Compound	E_{p1} , V
6a	1.49
2a	1.12
6b	1.22
2b	1.08
2f	1.04
3a	0.96
3d	0.92
4a	0.57
2c	1.02
3b	0.86
3e	0.90
6d	0.98
2d	0.80
6e	1.27
3c	0.86
4b	0.59
6f	1.22
2e	0.95

^aPt electrode in 0.1 M NaClO₄ in CH₃CN, 0.1 V s⁻¹ scan rate, vs. Ag/0.1 M AgNO₃ in CH₃CN reference electrode.

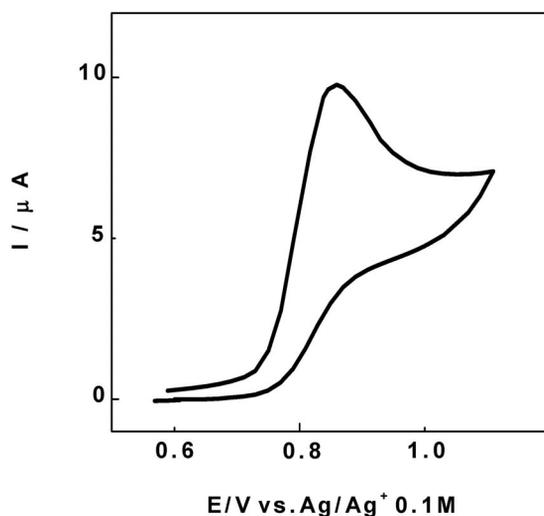
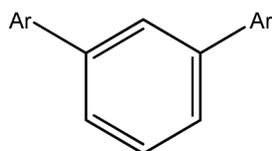
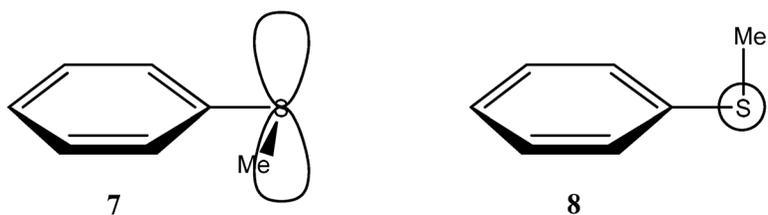


Fig. 1 Typical example of CV curve in 0.1 M NaClO₄ in acetonitrile containing 1 mM of **3b**. Scan rate 0.1 V/s, reference electrode Ag/0.1 M AgNO₃ in acetonitrile.



6a, Ar = Ph, **b**, Ar = *o*-MeOC₆H₄
c, Ar = *p*-MeOC₆H₄, **d**, Ar = 2,5-(MeO)₂C₆H₃
e, Ar = 1-Nphth, **f**, R = 2-Nphth

dominant conformation of thioanisole [14] is the planar conformation shown in **7**. In this geometry, the *p*-orbital lone-pair electrons on sulfur overlap with the benzene π -system. On removal of an electron from the highest occupied molecular orbital (HOMO) of **7**, the radical cation can be delocalized over the sulfur and π -system [15]. However, substituents in the 2,6-positions disfavor this conformation for steric reasons, and the thioanisole moiety adopts the perpendicular conformation **8**. In this conformation, the *p*-orbital on sulfur is orthogonal to the π -system. Removal of an electron from the HOMO of **8** does not result in a delocalized radical cation but rather one localized on sulfur. Consequently, it is easier to remove an electron from **7** than from **8**. For thioanisole the lowest ionization energy for the predominant conformer **7** is 8.02, and that for conformer **8**, 8.55 eV [16]. Similarly, the lowest ionization energy of 2,4,6-trimethylthioanisole is higher than that for thioanisole (conformer **7**), despite the electron-releasing effect of the methyl groups [16b,17]. Therefore, one anticipates the oxidation potentials of **2a–e** to be raised relative to that of thioanisole because conformation **8** is preferred in **2a–e**, but



conformation **7** is preferred in thioanisole. In addition, aryl substituents can interact by resonance effects. Thus, ordinarily the 2,6-diaryl substituents in **2a–e** might be expected to stabilize cationic systems, i.e., the corresponding radical cations by resonance, but this is precluded, or at least mitigated, by their geometries in which the 2,6-aryl rings are more or less perpendicular to the phenyl ring to which they are attached [6]. Consequently, one anticipates that the oxidation potentials of **2a–e** would be more positive than that of thioanisole. However, except for **2a**, which is the same, they are all less positive (by 40, 100, 320, and 170 mV for **2b–e**, respectively). While resonance may play a role in this effect, we propose that through-space interaction between the sulfur *p*-orbital lone-pair and the 2,6-aromatic π -systems on oxidation also helps account for this result. To support the suggestion of through-space interaction of the neighboring π -systems and MeS- moiety in **2**, the PE spectra of **2b** and **2d** were measured. Unfortunately, overlap of the π - and lone-pair ionizations resulted in a broad peak which could not be meaningfully interpreted. However, the PE spectrum of **2a**, see Fig. 2, showed well-resolved ionizations in the low energy region. The peak of lowest ionization energy appeared at 7.86 eV and is ascribed to sulfur lone-pair and π -mixing in analogy to that previously reported for **1**, Ar=Ph [5]. This assignment is further supported by comparison of the He(I) and He(II) PE spectra shown in Fig. 2. The ionization at 7.86 eV decreases relative to the other ionizations on going from He(I) to He(II) mono-

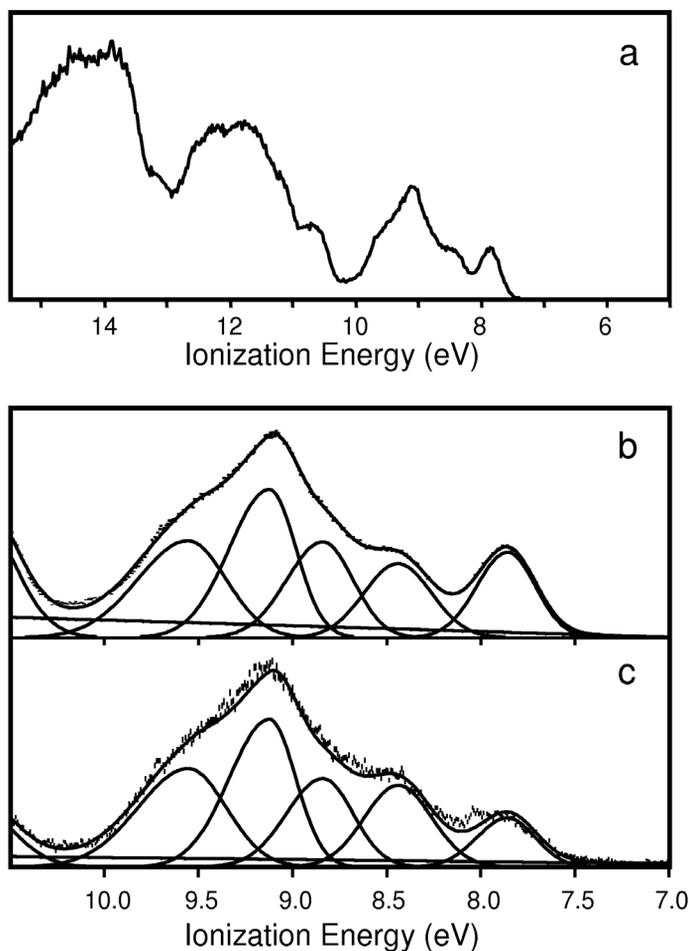


Fig. 2 He(I) gas-phase PE spectrum of **2a** (a), close-up of the low-energy region of the He(I) gas-phase PE spectrum of **2a** (b), close-up of the low-energy region of the He(II) gas-phase PE spectrum of **2a** (c).

chromatic radiation. It is known [18] that the probability of ionization from a sulfur p -type orbital decreases 60–70 % relative to ionizations from a carbon π -molecular orbital on changing the ionizing source from He(I) to He(II). Consequently, the ionization at 7.86 eV has mixed sulfur p -lone pair and carbon π character. Similarly, the lowest oxidation potential of **2f** (1.04 V) is 200 mV less positive than that of diphenylsulfide (1.24 V) [13]. However, analysis of this system is significantly different from that for **2a–e**. That is, the geometry of **2f** is analogous to that of **2a–e** in that the steric effect of the 2,6-di-*o*-MeOC₆H₄ substituents should result in deconjugation of the sulfur-substituted aryl ring but the S-Ph moiety should adopt a planar geometry. This overall twist geometry is similar to that of diphenylsulfide [19] in which the p -orbital on sulfur overlaps with one π -system but not the other [20]. Consequently, **2f** should have approximately the same oxidation potential as diphenyl sulfide since a phenyl ring is conjugated with the sulfur in both cases. Since **2f** has a lower first oxidation potential than diphenyl sulfide, S $\cdots\pi$ through-space interaction occurs in this case as well.

The methylseleno compounds follow the same trends as outlined for the sulfur compounds. That is, methylseleno compounds **3a–c**, in which the 2,6-diaryl groups favor the nonconjugated perpendicular conformer, should show more positive first oxidation peaks than selenoanisole ($E_{1/2} = 0.965$ V vs. Ag/0.1 M AgNO₃ in CH₃CN) [21], but either have the same oxidation (**3a**) or are less positive (**3b** and **3c** by 105 mV). The geometric effect ascribed to the 2,6-diaryl moieties was also reported for 2,6-dimethyl groups resulting in a higher oxidation potential for 2,6-dimethyl methyl phenylselenide than methyl phenylselenide despite the electron-donating effects of the methyl groups [21]. Similarly, PE spectroscopic studies on methyl phenylselenide and its derivatives show that the lowest ionization energy for the planar conformer is at lower energy than that for its perpendicular conformer [22]. For the phenylseleno compounds, the 2,6-disubstituted compounds **3d** and **3e** oxidize slightly more easily than diphenylselenide (0.94 [23], 0.97 [24] V) by 20 or 50 and 40 or 70 mV, respectively [25]. As pointed out for the phenylthio compound **2f**, one expects the oxidation potentials for **3d**, **3e**, and diphenyl selenide to be the same since the phenyl π -system is conjugated with the selenium in all three cases [19,20]. Since **3d** and **3e** oxidize only slightly more easily than diphenyl selenide, Se $\cdots\pi$ through-space interaction is modest in **3d** and **3e**.

Finally, the phenyl tellurium compounds **4a** and **4b** oxidize at close to the potential of diphenyl telluride (0.95 V vs. Ag/AgCl [20] which corresponds approximately to 0.6 vs. Ag/0.1 M AgNO₃ in CH₃CN) [26]. Thus, there does not appear to be any Te $\cdots\pi$ through-space interaction in these compounds. It is interesting to compare the effect of 2,6-diaryl substituents on the oxidation potentials of diphenyl chalcogenides. In comparing the oxidation potentials for analogously substituted 2,6-di(*o*-methoxyphenyl) diphenyl chalcogenides with its parent diphenyl chalcogenide (**2f** vs. Ph₂S: 200 mV; **3d** vs. Ph₂Se: 20, 50 mV; **4a** vs. Ph₂Te: ca. 0 mV decrease for *m*-terphenyl chalcogenoether) the chalcogen $\cdots\pi$ interaction decreases from S to Se to Te. This may be due to the reduced need for through-space stabilization owing to greater cation stability on going from S to Se to Te.

In sum, our experimental results support the notion that oxidation potentials are lowered as a result of through-space S $\cdots\pi$ and Se $\cdots\pi$ but not Te $\cdots\pi$ interaction in *m*-terphenyl sulfides, selenides, and tellurides. Studies on the structure and bonding in the radical cations obtained from these systems are underway.

EXPERIMENTAL

Cyclic voltammetry

All electrochemical experiments were performed using a GAMRY potentiostat model CMS 100 connected to a computer for data acquisition. Commercial (Acros) dry analytical grade acetonitrile was repeatedly distilled before use. Analytical grade NaClO₄ (Fisher Chemicals) was vacuum-dried before use. A three-compartment electrochemical cell was used. The side arms were fitted with the reference electrode (0.1 M AgNO₃ in acetonitrile-silver wire, which was calibrated with a 1 mM

ferrocene/ferricinium couple before each series of experiments) and a Pt counterelectrode with a surface area of approximately 1 cm². A 2-mm-diameter Pt disk electrode was used as the working electrode and was polished with alumina powder (1 and 0.3 μm), washed repeatedly with ultrapure water and acetone, then oven-dried before use.

Photoelectron spectroscopy

PE spectra were recorded using an instrument that features a 36-cm hemispherical analyzer [27] and custom designed photon source, sample cells, and detection and control electronics [28]. The excitation source is a quartz capillary discharge lamp with the ability, depending on operating conditions, to produce He(I) (21.218 eV) or He(II) (40.814 eV) photons. The ionization energy scale was calibrated using the ²P_{3/2} ionization of Ar (15.759 eV) and the ²E_{1/2} ionization of methyl iodide (9.538 eV). The argon ²P_{3/2} ionization also was used as an internal calibration lock of the absolute ionization energy to control spectrometer drift throughout data collection. During He(I) and He(II) data collection, the instrument resolution, measured using the half full-width-at-half-maximum of argon ²P_{3/2} ionization, was 0.020–0.030 eV. All of the spectra were corrected for the presence of ionizations caused by other emission lines from the discharge source [29]. The He(I) spectra were corrected for the He(Iβ) line (1.866 eV higher in energy and 3 % the intensity of the He(Iα) line), and the He(II) spectra were corrected for the He(IIβ) line [7.568 eV higher in energy and 12 % the intensity of the He(IIα) line]. All data also were intensity corrected with an experimentally determined instrument analyzer sensitivity function that assumes a linear dependence of analyzer transmission (intensity) to the kinetic energy of the electrons within the energy range of these experiments. The samples went into the gas phase cleanly with no visible changes in the spectra during data collection.

In the figures of the data, the vertical length of each data mark represents the experimental variance of that point [30]. The valence ionization bands are represented analytically with the best fit of asymmetric Gaussian peaks, as described in more detail elsewhere [30]. The Gaussians are defined with the position, amplitude, half-width for the high binding energy side of the peak, and the half-width for the low binding energy side of the peak. The peak positions and half-widths are reproducible to about ±eV (≈3σ level). The parameters describing an individual Gaussian are less certain when two or more peaks are close in energy and are overlapping. When a region of broad ionization intensity spans numerous overlapping ionization bands, the individual parameters of the Gaussian peaks used to model the total ionization intensity are not characteristic of individual ionization states. Confidence limits for the relative integrated peak areas are about 5 %, with the primary source of uncertainty being the determination of the baseline under the peaks. The baseline is caused by electron scattering and taken to be linear over the small energy range of these spectra. The total area under a series of overlapping peaks is known with the same confidence, but the individual peak areas are less certain.

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