Generation of 1,3-Dithia-, 1-Selena-3-thia-, and 1,3-Diselena-2-tellurole by Neutralization-Reionization Mass Spectrometry[☆]

Detlef Schröder[a], Helmut Schwarz*[a], Björn Löbrecht[a], Wolfram Koch[a], and Satoshi Ogawa[b]

Institut für Organische Chemie der Technischen Universität Berlin[a],
D-10623 Berlin, Germany

Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University[b],
Morioka 020-8551, Japan

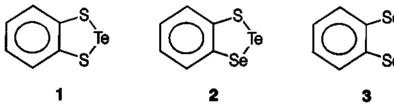
Received February 16, 1998

Keywords: Telluroles / Neutralization−reionization mass spectrometry / DFT calculations

2,2-Dichloro-1,3-dichalcogena-2-telluroles of sulfur and selenium, $C_6H_4[XTe(Cl)_2Y]$ with X, Y = S, Se, serve as precursors to generate the cation radicals of 1,3-dichalcogena-2-telluroles $C_6H_4[XTeY]^{+\bullet}$ as well as the corresponding neutral counterparts by means of neutralization-reionization mass spectrometry. These neutral 2-telluroles are intrinsically stable for at least 1 μs in the gas phase. The most abundant fragmentation channel at the neutral and cationic stages is due to loss of atomic tellurium to afford the corresponding benzo-1,2-dichalcogena-cyclobutenes. For the latter, partial isomerization to the related dichalcogena-*ortho*-quinones is indicated by the mass-spectrometric fragmentation pattern.

Fused aromatic ring systems comprise a huge body of heterocyclic chemistry including several natural products, e.g. indole derivatives. Heterocycles containing chalcogens are of particular relevance in redox processes, but knowledge about heteroindenes with several chalcogenes directly attached to each other is limited[1]. In particular, benzo-dichalcogena-2-telluroles, viz. 1,3-dichalcogena-2-tellurain-denes, have not been isolated so far.

Scheme 1

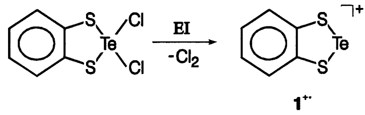


In this contribution, we describe the generation of the ionized and neutral 1,3-dichalcogena-2-telluroles **1**−**3** (Scheme 1) by means of neutralization-reionization mass spectrometry (NR)[2].

Results and Discussion

The cation radicals of the 1,3-dichalcogena-2-telluroles **1**−**3** are readily formed upon electron ionization (EI) of the corresponding 2,2-dichlorides, as shown in Scheme 2 for the dithia compound. The ease of one-electron oxidation of 1,2,3-trichalcogenoles has been demonstrated previously,[1] but the mass spectra do not reveal whether two chlorine atoms or molecular chlorine is lost from the precursors upon ionization. Thermal dechlorination appears unlikely, however, because $Cl_2^{+\bullet}$ is hardly observed in the EI mass spectra. None of the precursors yields a significant signal for the respective molecular ion of the corresponding dichloride, while weak isotope patterns for the monochloro derivatives were observed.

Scheme 2



The metastable ion (MI) and collisional activation (CA) mass spectra of the cation radicals $\mathbf{1}^{+\bullet}$−$\mathbf{3}^{+\bullet}$ (Table 1) are dominated by loss of atomic tellurium (Δm = 130) yielding the corresponding $C_6H_4XY^{+\bullet}$ cations (X, Y = S, Se), while loss of neutral C_6H_4XY concomitant with $Te^{+\bullet}$ is hardly observed. Location of the positive charge on the organic fragment can be accounted for by the fact that already the dithiete $C_6H_4S_2$ has an ionization energy (IE) of ca. 8.2 eV[3] which is significantly lower than that of atomic Te (IE = 9.0 eV)[4]; thiaselenete C_6H_4SSe and diselenete $C_6H_4Se_2$ are expected to have IEs even lower than 8.2 eV. Additional fragmentation channels of the cation radicals are due to bond cleavages involving the other chalcogene atoms, while degradation of the hydrocarbon backbone is negligible. Interestingly, also losses of the chalcogene dimers S_2, SeS, Se_2, TeS, and TeSe, respectively, are observed to some extent. The three former of these fragments indicate the possible occurrence of some rearrangements prior to fragmentation because the connectivities of these diatomic entities are not contained in the precursor molecules (see below).

In neutralization-reionization (NR) mass spectrometry, fast-moving ions are subjected to a double-collision event in which first the ion is neutralized, then any remaining ions are deflected, and subsequently the neutrals are reionized

Table 1. Mass differences (Δ*m* in amu) in metastable ion (MI) and collisional activation (CA) mass spectra of $\mathbf{1}^{+\bullet}$–$\mathbf{3}^{+\bullet}$ (data are given as percentages of the base peak)[a]

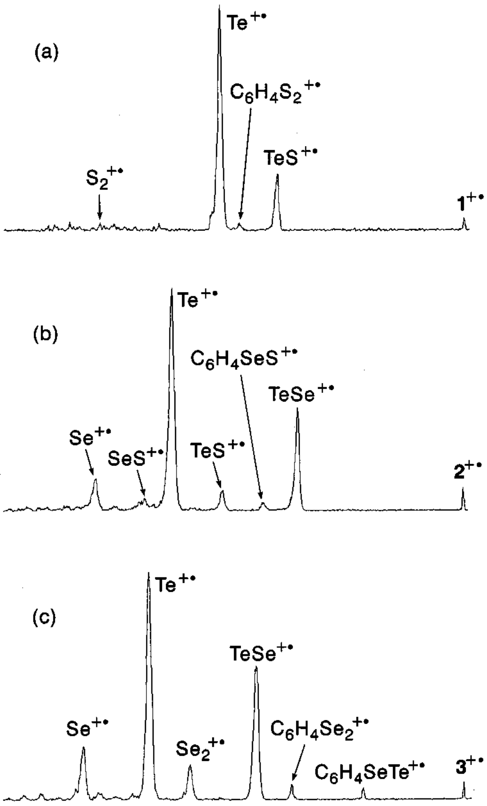
Δ*m* (amu)[b] neutral lost[c]		−32 S	−64 S_2	−80 Se	−108 C_6H_4S	−112 SeS	−130 Te	−156 C_6H_4Se	−160 Se_2	−162 TeS	−194 TeS_2
$\mathbf{1}^{+\bullet}$	MI		3				100				
	CA	3	10		5		100		8	2	1
$\mathbf{2}^{+\bullet}$	MI			4			100			1	
	CA	2		12	15	8	100	3		4	
$\mathbf{3}^{+\bullet}$	MI			10			100		3		
	CA			15			100	8	3		

[a] For the sake of clarity in the MI spectra intensities of less than 1% are omitted, and for the CA spectra only the leading fragments are given. – [b] All data refer to the most abundant isotopes ^{32}S, ^{80}Se, and ^{130}Te, respectively. – [c] Some of the neutrals may also arise from multiple fragmentations, e.g. Δ*m* = 206 may either correspond to loss of intact C_6H_4Te or to consecutive losses of Te and C_6H_4.

to allow for conventional mass-spectrometric detection[2]. Often, xenon is used as a collision gas for the neutralization of cations having kinetic energies in the keV range. For $\mathbf{1}^{+\bullet}$–$\mathbf{3}^{+\bullet}$, however, no recovery signals due to the reionized neutrals **1**–**3** are detectable when xenon is used for neutralization of the cation radicals, while recovery signals are observed when other collision gases are used. Target gas effects in NR mass spectrometry have been analyzed by Holmes[5] and have been associated with the thermochemistry of the neutralization step. In analogy to other heteroindenes, we can certainly estimate that the ionization energies of **1**–**3** are below 8 eV. Thus, due to the high ionization energy (IE) of xenon (12.1 eV), electron transfer from xenon to the cation radicals $\mathbf{1}^{+\bullet}$–$\mathbf{3}^{+\bullet}$ is highly endothermic and requires a large amount of energy transfer in the collision. As a consequence, the Franck–Condon factors for neutralization are unfavorable and fragments prevail the NR mass spectra instead. Therefore, we have examined some other collision gases for which electron transfer to the cation radicals $\mathbf{1}^{+\bullet}$–$\mathbf{3}^{+\bullet}$ is less endothermic, and the best results were obtained using cyclopropane (IE = 9.9 eV) and trimethylamine (IE = 7.8 eV), respectively.

The NR spectrum of $\mathbf{1}^{+\bullet}$ is dominated by signals due to $Te^{+\bullet}$ and $TeS^{+\bullet}$ (Figure 1a), but an unambiguous signal due to the reionized neutral parent is also detected. Similarly, recovery signals for the reionized neutral counterparts are present in the NR spectra of $\mathbf{2}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ along with $Te^{+\bullet}$, $TeS^{+\bullet}$, and $TeSe^{+\bullet}$ fragments (Figures 1b and 1c). The mere observation of the recovery signals implies that in the gas phase the neutral 1,3-dichalcogena-2-telluroles **1**–**3** correspond to stable species which can survive the flight time between the neutralization and the reionization events (about 1 μs). Although this time interval appears to be short, these telluroles can be considered as being long-lived as far as unimolecular processes are concerned, because the microsecond range is likely to allow for energy distribution over all internal modes. In addition to the recovery signals, several fragment ions are observed which are in accord with the structures **1**–**3** as deduced from the connectivities of the corresponding 2,2-dichlorides used as precursors. Note that the weak, but yet significant loss of atomic Se in Figure 1c points toward the formation of the hitherto unknown benzoselenatellurete, C_6H_4SeTe, from **3**.

Figure 1. NR mass-spectra (trimethylamine/O_2, both 80% *T*) of *B*(1)-mass-selected $C_6H_4\{XTeY\}^{+\bullet}$ cation radicals generated by electron ionization of (a) $C_6H_4\{STe(Cl)_2S\}$, (b) $C_6H_4\{STe(Cl)_2Se\}$, and (c) $C_6H_4\{SeTe(Cl)_2Se\}$



One particular series of fragments in the NR spectra should, however, be discussed in some more detail. Thus, the CA and NR spectra of $\mathbf{1}^{+\bullet}$–$\mathbf{3}^{+\bullet}$ show weak, but yet distinct signals due to the $S_2^{+\bullet}$, $SeS^{+\bullet}$, and $Se_2^{+\bullet}$, respectively, which are *not* in keeping with the proposed connectivities, because these do not contain S–S, Se–S, and Se–Se bonds, respectively. The most pronounced signal in this respect is the $Se_2^{+\bullet}$ fragment in the NR spectrum of $\mathbf{3}_3^{+\bullet}$ (Figure 1c).

Conceptually, there exist at least two possible scenarios – occurring either at the cationic or the neutral stage – which can account for this result. Route ⓐ involves rearrangement of the 2-telluroles (X, Y = S, Se) to the corresponding 1-telluroles **4** and subsequent formation of XY. In contrast, route ⓑ involves a stepwise fragmentation in which first atomic tellurium is lost to yield the dichalcogeno-*ortho*-quinones **5** which may rearrange via X−Y bond formation to bicyclic **6** from which XY can subsequently be formed. In order to get a handle for the distinction of these routes, we have examined the $C_6H_4XY^{+\bullet}$ cation radicals (X, Y = S, Se) which are also formed upon electron ionization of the dichloro telluroles used as precursors for $\mathbf{1}^{+\bullet}$−$\mathbf{3}^{+\bullet}$.

Scheme 3

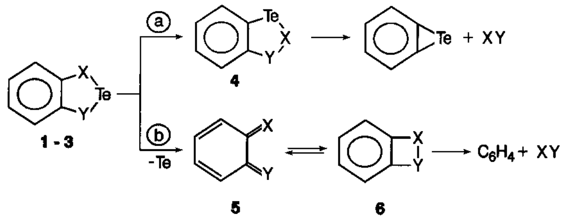
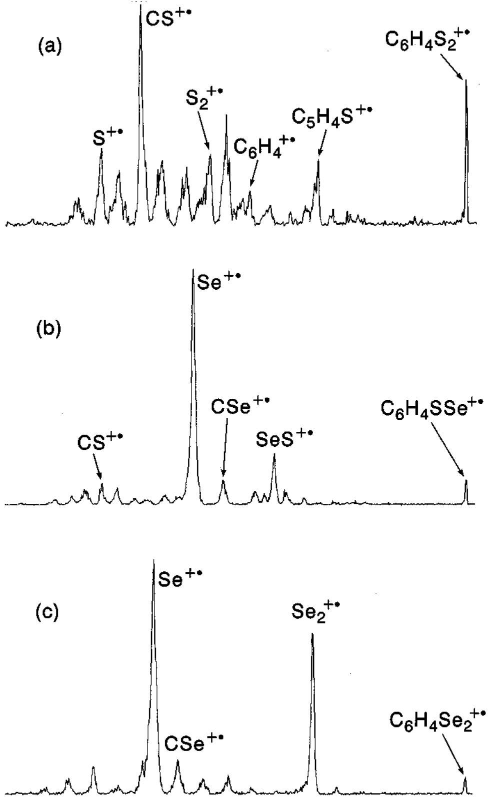


Figure 2. NR mass-spectra (cyclopropane/O_2, both 80% *T*) of *B*(1)-mass-selected $C_6H_4XY^{+\bullet}$ cation radicals generated by electron ionization of (a) $C_6H_4\{STe(Cl)_2S\}$, (b) $C_6H_4\{STe(Cl)_2Se\}$, and (c) $C_6H_4\{SeTe(Cl)_2Se\}$



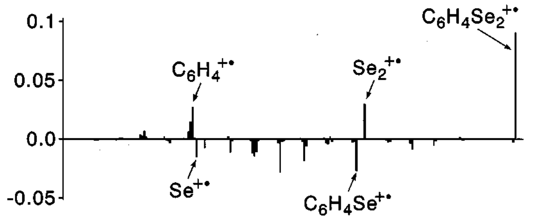
Besides sizable recovery signals, the NR spectra of these $C_6H_4XY^{+\bullet}$ ions show numerous fragments. In fact, the particularly rich fragmentation pattern in the NR spectrum of $C_6H_4S_2^{+\bullet}$ (Figure 2a) can account for the seemingly noisy low-mass region in the NR spectrum of $\mathbf{1}^{+\bullet}$ (Figure 1a) in that this is due to the many fragments formed upon reionization of neutral $C_6H_4S_2^{+\bullet}$. Notwithstanding, all three ions give rise to the corresponding signals due to formation of XY according to route ⓑ in Scheme 3.

Neutral benzodithiete $C_6H_4S_2$ has previously been examined by matrix isolation methods as well as photoelectron spectroscopy[3][6]. These studies have provided strong evidence for the existence of benzodithiete (**6**; X, Y = S), whereas contribution of the dithioquinone structure **5** (X, Y = S) was excluded[7]. Similarly, several substituted 1,2-dichalcogenacyclobutenes of sulfur and/or selenium have been characterized by various means[8][9]. Nevertheless, trapping reactions of dithiete with appropriate dienophiles led to cycloaddition products consistent with the formation of transient **5** (X, Y = S)[3].

Qualitatively, the NR spectra lead to a similar conclusion in that formation of the dichalcogenes XY is consistent with **6**, while the signals due to CS and/or CSe losses point towards **5**. Thus, for $C_6H_4S_2^{+\bullet}$ (Figure 2a), the loss of neutral CS and the complementary signal due to reionized CS can be considered to be indicative for the quinone structure **5** (X, Y = S), while the $S_2^{+\bullet}$ fragment is in keeping with structure **6**. The ratios of the corresponding (CX + CY) versus XY fragments decrease from ca. 3:1 for X, Y = S (Figure 2a), to about 1:1 for X = S, Y = Se (Figure 2b) and ca. 1:8 for X, Y = Se (Figure 2c). This trend can be interpreted in the sense that the bicyclic structure **6** is favored over **5** the more Se is incorporated. Moreover, the increasing abundance of the XY fragments going from X, Y = S to X, Y = Se provides a rationale for the $XY^{+\bullet}$ signals in the NR spectra of $\mathbf{1}^{+\bullet}$−$\mathbf{3}^{+\bullet}$ by involving route in Scheme 3. In fact, the low-mass parts of the NR spectra shown in Figure 1 can by and large be represented by a superposition of the NR spectra of the C_6H_4XY fragments with that of atomic Te.

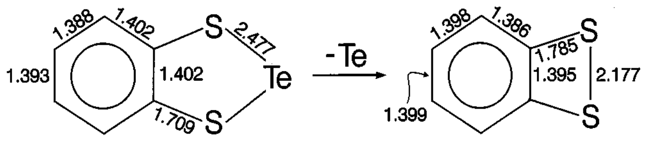
In order to distinguish at which stage of the experiment formation of XY from C_6H_4XY takes place, we subjected $C_6H_4Se_2$ to some additional experiments because the corresponding fragment $Se_2^{+\bullet}$ is most pronounced in Figure 1c. In the MI spectrum of $C_6H_4Se_2^{+\bullet}$, loss of atomic Se leading to $C_6H_4Se^{+\bullet}$ is observed almost exclusively (100%). Formation of $Se_2^{+\bullet}$, as the only other fragment, is very minor (3%) and may be due to collisional activation with residual gas in the high-vacuum device. In fact, the 100:3 ratio of $C_6H_4Se^{+\bullet}$ and $Se_2^{+\bullet}$ becomes 100:30 upon collisional activation; in addition, a series of other fragments is formed among which $C_6H_4^{+\bullet}$ is most intense (8%). Accordingly, the fragmentation of the cation via route ⓑ in Scheme 3 can in part account for the $Se_2^{+\bullet}$ signal in the NR spectrum of $\mathbf{3}^{+\bullet}$, but nevertheless, the cation route cannot be a major route because otherwise also $C_6H_4Se^{+\bullet}$ must be much more intense. Accordingly, isomerization via route ⓐ of Scheme 3 can only be neglected, if Se_2 can be formed at the neutral stage. Conventional mass spectrometry cannot provide distinct information about the neutral's reactivity, but some variants of the NR method can be applied[10d]. One of the most sensitive and also straightforward approaches in this respect represents the NIDD method[10] which is based on the comparison of two different ways to accomplish two-electron transfer either from an anion to a cation or vice versa. To this end, charge reversal (CR)[11] and NR mass spectra are compared with each other. In brief, the resulting NIDD spectra reflect the reactivity of the neutral species, and the scheme is defined as such that reactions occurring at the neutral stage appear as positive peaks, while processes taking place in the ionic stage give rise to negative signals.

Figure 3. NIDD mass spectrum of *B*(1)-mass-selected $C_6H_4Se_2^{-\bullet}$ anion radicals generated by electron ionization of $C_6H_4\{SeTe(Cl)_2Se\}$ in the negative mode; note that reionization leads to cations; the NIDD spectrum was obtained by subtracting the normalized ion intensities in the CR mass spectrum (O_2, 80% *T*) of $C_6H_4Se_2^{-\bullet}$ from those in the corresponding NR mass spectrum (O_2/O_2, each 80% *T*); for further details of the NIDD method, see ref.[10]



The NIDD spectrum of the $C_6H_4Se_2^{-\bullet}$ anion radical (Figure 3) shows three prominent signals at the positive scale, i.e. an intense recovery signal due to neutral counterpart reionized to the cation radical and signals due to reionized Se_2 and C_6H_4. As the latter two fragments are complementary to each other and appear on the positive scale, this observation identifies the occurrence of the reaction $C_6H_4Se_2 \rightarrow C_6H_4 + Se_2$ at the neutral stage. Accordingly, route ⓑ in Scheme 3 can account for the observation of $Se_2^{+\bullet}$ in the NR spectrum of $\mathbf{3}^{+\bullet}$, and although we cannot definitively rule out the isomerization to **4**, there is no need to invoke it. Further, we may assume that the anion radical $C_6H_4Se_2^{-\bullet}$ has an open structure similar to **5** (X, Y = Se), such that the formation of the Se_2 fragment indicates rearrangement to the bicyclic benzodiselenete at the neutral stage.

Figure 4. Calculated structures of C_{2v}-symmetrical **1** and **6** (X, Y = S) using the B3LYP method (bond lengths in Å); for the sake of clarity, the hydrogen atoms are left out (all C−H bond lengths are close to 1.085 Å)



In order to assess the stability of the neutral 2-telluroles, we briefly examined the thermochemistry of the reaction **1** → Te + **6** (X, Y = S) by ab initio methods using the B3LYP method (Figure 4). The calculated structures are consistent with the description of **1** as 1,3-dithia-2-tellurole and formation of benzodithiete upon loss of tellurium. Both species exhibit singlet ground states and the similarity of the C−C bond lengths in the carbon skeleton suggest that these systems maintain aromaticity without any tendency for bond localization. At the B3LYP level of theory we could not locate **5** (X, Y = S) on the singlet surface, but a low-lying triplet state of **5** (X, Y = S) was found which is only about 15 kcal/mol less stable than singlet **6** (X, Y = S). Interestingly, the endothermicity associated with loss of tellurium from neutral **1** is predicted to be as small as 43 kcal/mol. This rather low value is consistent with loss of atomic Te as a low-lying fragmentation channel at the neutral stage and thus can account for the intense signals due to atomic Te present in the NR spectra. As we may expect that the reactions **1** → Te + **6** are even less endothermic when selenium is involved, the computational results add further confidence to the assignment of route ⓑ as the origin for the formation of $S_2^{+\bullet}$, $SeS^{+\bullet}$, and $Se_2^{+\bullet}$ under the experimental conditions.

Conclusions

Neutral 1,3-dithia-, 1-selena-3-thia-, and 1,3-diselena-2-telluroles can be generated by one-electron reduction of the corresponding cation radicals by means of neutralization-reionization mass spectrometry. In this respect, it is, however, of prime importance to choose appropriate neutralization agents, because otherwise long-lived neutrals cannot be assessed and dissociation by loss of atomic tellurium prevails. Thus, this study indicates that target-gas effects are particularly important in the neutralization of heavy, polyatomic ions. Finally, the present experimental results provide evidence for the formation of 3,4-benzo-1,2-dichalcogenacyclobutenes of sulfur, selenium, and tellurium.

Financial support by the *Deutsche Forschungsgemeinschaft*, the *Volkswagen-Stiftung*, the *Fonds der Chemischen Industrie*, and the *Gesellschaft von Freunden der Technischen Universität Berlin* is gratefully acknowledged. S. O. acknowledges a travel support by the *Iwate Network System*. We thank *R. Steudel* for initiating the contact between the German and Japanese research groups.

Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of *BEBE* configuration (*B* stands for magnetic and *E* for electric sectors), which has been described elsewhere[12]. The cation radicals of the 1,3-dichalcogena-2-telluroles were generated by electron ionization (EI, 70 eV) of the corresponding 2,2-dichlorides. After acceleration to a kinetic energy of 8 keV, the ions of interest were mass-selected using the magnetic and electric sectors as indicated further below. Metastable ion (MI) and collisional activation (CA) spectra of *B*(1)/*E*(1)-mass-selected ions were obtained by monitoring the fragments formed in the field-free region preceding *B*(2) by scanning *B*(2); for CA, helium (80% transmission, *T*) was used as a collision gas. NR experiments were performed by colliding *B*(1)-mass-selected cations with either xenon, cyclopropane, or trimethylamine (80% *T*), deflecting the remaining ions by applying a potential of 1 kV, reionizing the fast neutrals by collision with oxygen (80% *T*), and scanning *E*(1) to monitor the cations formed. The NR spectra recorded for *B*(1)/*E*(1)-mass-selected ions show similar fragmentation pattern, but somewhat poor signal-to-noise ratios. All spectra were accumulated and on-line processed with the AMD/Intectra data system; 5−40 scans were averaged to improve the signal-to-noise ratio. The natural abundances (I_{nat}) of the chalcogenides' isotopes pose quite some restrictions for the mass selection of isotopically pure ion[13]. Accordingly, from the clusters of isotope patterns those ions were chosen which contain the most abundant isotopes, i.e. ^{32}S (I_{nat} = 95%), ^{80}Se (I_{nat} = 50%), and ^{130}Te (I_{nat} = 34%), respectively. Nevertheless, the correspondingly mass-selected ions are not isotopically pure, e.g. the combination $^{80}Se^{130}Te$ is always accompanied by about 20% of $^{82}Se^{128}Te$. The intensities tabulated further below were corrected according to the natural isotope distributions. Charge reversal (CR)[11] and NR experiments were also performed with $C_6H_4Se_2^{-•}$ anion radicals using oxygen as collision gas in all cases. The CR and NR spectra can be used to assess the unimolecular reactivity of the neutral species by converting them to neutral and ion decomposition difference (NIDD) spectra; for details of the NIDD approach, see ref.[10].

The 2,2-dichloro-1,3-dichalcogena-2-telluroles were prepared in analogy to a previously described method for substituted derivatives[14], and the synthesis of the compounds as well as their spectroscopic characterization will be published elsewhere.

Some quantum-chemical calculations employing the B3LYP density functional were performed using Gaussian94[15]. For tellurium, a relativistic effective core potential with a valence basis set of DZP quality was used[16], while all other atoms were described by the standard 6-311G* basis sets included in Gaussian94.

☆ Dedicated to Professor *Achim Müller*, Bielefeld, on the occasion of his 60th birthday.

[1] [1a] S. Ogawa, T. Kikuchi, S. Niizuma, R. Sato, *J. Chem. Soc., Chem. Commun.* **1994**, 1593. – [1b] S. Ogawa, T. Kikuchi, A. Sasaki, S. Chida, R. Sato, *Tetrahedron Lett.* **1994**, *35*, 5469. – [1c] S. Ogawa, S. Nobuta, R. Nakayama, Y. Kawai, S. Niizuma, R. Sato, *Chem. Lett.* **1996**, 757. – [1d] S. Ogawa, T. Ohmiya, T. Kikuchi, Y. Kawai, S. Niizuma, R. Sato, *Heterocycles* **1996**, *43*, 1843. – [1e] See also: T. M. Barclay, A. W. Cordes, J. D. Goddard, R. C. Mawhinney, R. T. Oakley, K. E. Preuss, R. W. Reed, *J. Am. Chem. Soc.* **1997**, *119*, 12136.

[2] Review: N. Goldberg, H. Schwarz, *Acc. Chem. Res.* **1994**, *27*, 347.

[3] P. de Mayo, A. C. Weedon, G. S. K. Wong, *J. Org. Chem.* **1979**, *44*, 1977.

[4] If not mentioned otherwise, all auxiliary thermochemical data were taken from: S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *Gas Phase Ion and Neutral Thermochemistry, J. Phys. Chem. Ref. Data, Suppl. 1*, **1988, 17**.

[5] J. L. Holmes, *Mass Spectrom. Rev.* **1989**, *8*, 513.

[6] For surveys, see: [6a] J. Voss, in *Methoden der Organischen Chemie (Houben-Weyl)*, vol. E11 (Ed.: D. Klamann), Thieme, Stuttgart **1984**, p. 224. – [6b] H. Meier, N. Hanold, in *Methoden der Organischen Chemie (Houben-Weyl)*, vol. E11 (Ed.: D. Klamann), Thieme, Stuttgart **1984**, p. 1581.

[7] For a similar situation in C_6S_6, see: [7a] D. Sülzle, N. Beye, E. Fanghänel, H. Schwarz, *Chem. Ber.* **1989**, *122*, 2411. – [7b] G. Frenking, *Angew. Chem.* **1990**, *102*, 1516; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1410.

[8] Thiaselenetes: [8a] F. Diehl, A. Schweig, *Angew. Chem.* **1987**, *99*, 348; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 343. – [8b] N. Tokitoh, H. Ishizuka, A. Yabe, W. Ando, *Tetrahedron Lett.* **1989**, *30*, 2955.

[9] Diselenetes: [9a] See ref.[8b]. – [9b] K. B. Borisenko, M. Broschag, I. Hargittai, T. M. Klapötke, D. Schröder, H. Schwarz, I. C. Tornieporth-Oetting, P. S. White, *J. Chem. Soc., Dalton Trans.* **1994**, 2705.

[10] [10a] D. Schröder, N. Goldberg, W. Zummack, H. Schwarz, J. C. Poutsma, R. R. Squires, *Int. J. Mass Spectrom. Ion Processes* **1997**, *165*/*166*, 71. – [10b] J. N. Harvey, D. Schröder, H. Schwarz, *Bull. Soc. Chim. Belg.* **1997**, *106*, 447. – [10c] C. A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1998**, *172*, 181. – [10d] C. A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *J. Chem. Soc. Rev.* **1998**, *27*, 91.

[11] M. M. Bursey, *Mass Spectrom. Rev.* **1990**, *9*, 555.

[12] [12a] R. Srinivas, D. Sülzle, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 368. – [12b] R. Srinivas, D. Sülzle, W. Koch, C. H. DePuy, H. Schwarz, *J. Am. Chem. Soc.* **1991**, *113*, 5970. – [12c] C. A. Schalley, D. Schröder, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 173.

[13] The isotope patterns were calculated using the Sheffield ChemPuter which is available via the Internet: http://www.shef.ac.uk/chem/chemputer/isotopes.html (© M. Winter, **1997**).

[14] S. Ogawa, M. Yamashita, R. Sato, *Tetrahedron Lett.* **1995**, *36*, 587.

[15] Revision B.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94*, Gaussian, Inc., Pittsburgh, PA, **1995**.

[16] A. Bergner, M. Dolg, W. Küchle, H. Stoll, *Mol. Phys.* **1993**, *80*, 1431.

[98031]