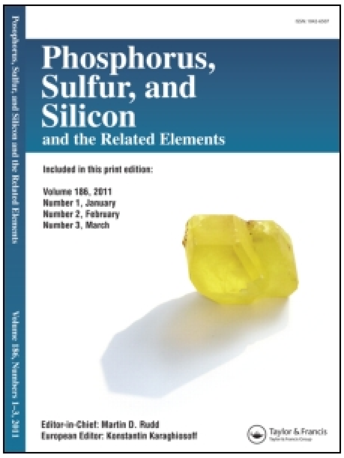


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STABILIZATION OF OXIDIZED SULFUR AND SELENIUM CENTERS IN ORGANIC CHALCOGENS BY THREE-ELECTRON SULFUR-SULFUR, SELENIUM-SELENIUM, AND SULFUR-SELENIUM BONDS. A THEORETICAL STUDY USING THE SEMIEMPIRICAL PARIMETRIC METHOD 3 (PM3)

Robert Müller[a]; JÜrgen Heinze[a]
[a] Albert-Ludwigs-Universität, Inst. Phys. Chem. I, Freiburg, Germany

To cite this Article Müller, Robert and Heinze, JÜrgen(1998) 'STABILIZATION OF OXIDIZED SULFUR AND SELENIUM CENTERS IN ORGANIC CHALCOGENS BY THREE-ELECTRON SULFUR-SULFUR, SELENIUM-SELENIUM, AND SULFUR-SELENIUM BONDS. A THEORETICAL STUDY USING THE SEMIEMPIRICAL PARIMETRIC METHOD 3 (PM3)', Phosphorus, Sulfur, and Silicon and the Related Elements, 141: 1, 111 — 134

To link to this Article: DOI: 10.1080/10426509808033726

URL: http://dx.doi.org/10.1080/10426509808033726

Phosphorus, Sulfur and Silicon, 1998, Vol. 141, pp. 111-134
Reprints available directly from the publisher
Photocopying permitted by license only

STABILIZATION OF OXIDIZED SULFUR AND SELENIUM CENTERS IN ORGANIC CHALCOGENS BY THREE-ELECTRON SULFUR-SULFUR, SELENIUM-SELENIUM, AND SULFUR-SELENIUM BONDS. A THEORETICAL STUDY USING THE SEMIEMPIRICAL PARIMETRIC METHOD 3 (PM3)

ROBERT MÜLLER* and JÜRGEN HEINZE

Albert-Ludwigs-Universität, Inst. Phys. Chem. I, Albertstr. 21, D-79104 Freiburg, Germany

(Received 01 January, 1998; In final form 17 June, 1998)

The chalcogen-chalcogen interactions in a series of three organosulfur and organoselenium compounds (1,ω-bis(methylthio)alkanes (**1**), 1,ω-bis(methylseleno)alkanes (**2**), and 1-(methylthio),ω -(methylseleno)alkanes (**3**)) at total charges of 0, +1 and +2, were theoretically investigated by the semiempirical Parimetric Method 3 (PM3). Special attention was paid to the radical cations of these compounds as they were shown by pulse radiolysis experiments to be stabilized by *intra*molecular two-center three-electron (2c-3e) bond between both chalcogens. PM3 calculations indicate that the dissociation energies of these 2c-3e S-S, Se-Se, and S-Se bonds were respectively 31–44, 66–83, and 46–64 kcal mole^{-1}. Follow-up reactions of the radical cations were examined for high and low ratios [neutral compound] / [radical cation], corresponding to experimental conditions of pulse-radiolysis, and electrochemical measurements, respectively.

Keywords: three-electron bonds; organosulfur compounds; organoselenium compounds; semiempirical computations; ab initio computations; PM3; electrochemistry; pulse-radiolysis

---

* Present address: Université de Liège, Sart Tilman B6, B-4000 Liège (Belgium); E-mail: jfr.muller@ulg.ac.be.

1. INTRODUCTION

Two-center, three-electron (2c-3e) bonds were first described in 1931 by Linus Pauling[1]. Two of the electrons form a σ bond while the third is promoted into an antibonding σ^* level (Fig. 1). Hückel theory with overlap integrals included predicts that such bonds are significantly stabilized only when the two initial levels are of (almost) equal energy, and the overlap between the orbitals is not too large (i.e. the overlap integral $S < 1/3$). Otherwise, the stabilization provided by the two bonding electrons is canceled by the third electron occupying the antibonding molecular orbital[2]. Clark's theoretical study predicted the existence of similar odd-electron bonds for several radical cations and pointed out that the strongest 2c-3e bond is expected between molecules with the same ionization energy[3].

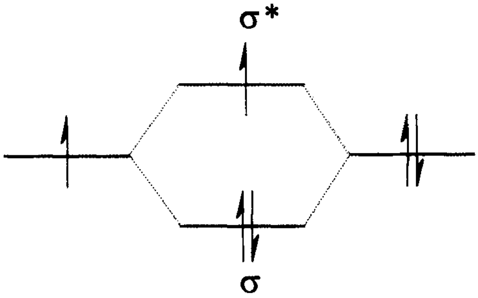
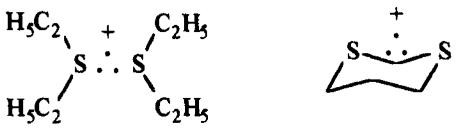


FIGURE 1 Formation of a 2c-3e bond between an oxidized and a neutral sulfur atom

During the past 20 years, 2c-3e sulfur-sulfur bonds have generated considerable interest in chemistry. These bonds are formed by interaction of the unpaired 3p electron from an oxidized sulfur atom with the electrons of a free 3p lone pair of another sulfur atom. This complexation of the initial sulfur radical cation by another sulfur atom can not only occur *inter*molecularly, but also *intra*molecularly if both sulfur atoms are separated by a flexible carbon chain, either open or cyclic (Fig 2).

The existence of such S-S bonds from thioethers has been proven by ESR experiments in the liquid[4–8] and solid[9] phase, by optical and kinetic pulse radiolysis investigations in the liquid phase[10–19], and by mass spectrometry in the gas phase[20–23]. Several examples of S-S bonds



I II

FIGURE 2 Stabilization of sulfur radical cations by 2c-3e bond: I: *inter*molecular bond (diethylsulfide); II: *intra*molecular bond (1,3-dithiacyclohexane)

where one of the sulfurs has been substituted by oxygen[24,25], nitrogen[25–28], phosphorus[17,29], and halogens (Cl, Br, I)[30–37] have been reported.

In the case of organoselenium compounds similar *inter*molecular 2c-3e Se-Se bonds were already unambiguously proved to exist in 1975 by the ESR spectrum of γ-irradiated single crystal of dimethyl selenide[38]. Furthermore, electrochemical investigations of organoselenium compounds bearing two selenium atoms evidenced unusual stabilization of the radical cation which was ascribed to *intra*molecular Se-Se bond formation[18,39,40]. Evidence of 2c-3e bonding was also obtained for organoselenium compounds where one of the two selenium atoms was exchanged by oxygen[39–41], nitrogen[41,43], and sulfur[41,44]. More recently our group proved the reversible dimerization of the 1,4-bis(methylseleno)benzene radical cation into a dimeric dication[45]. Geometric optimization of this structure by the PM3 semiempirical method showed that the dication is formed by two *inter*molecular 2c-3e Se-Se bonds (Fig. 3)!

Whereas voltammetric experiments of cyclic aromatic organoselenium compounds, allowing the formation of 2c-3e bonds, indicated the occurrence of a relative fast heterogeneous electron transfer during their electrochemical oxidation at platinum electrodes[40–44], open and cyclic bis-selenides have been reported to exhibit relatively slow electron transfer kinetics as shown by the high potential difference between the oxidation and reduction peak potentials[18,39]. Since the heterogeneous electron transfer rate constant is related to the extent of the geometric alterations in the transition state between the oxidized and the reduced forms of the depolarizer[46], it was expected that open and cyclic bis-selenides would undergo important structural changes upon their oxidation.

This lead us to realize the following theoretical study, in which a series of series of open chain 1,ω-bis(methylthio)alkanes (**1**), 1,ω-bis(methylse-

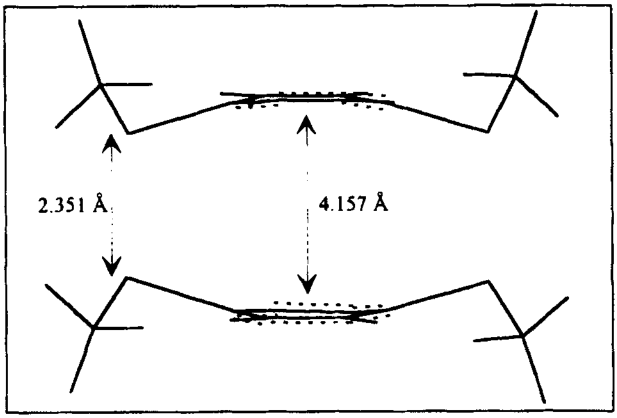


FIGURE 3 Structure of the dication with two 2c-3e Se-Se bonds obtained by the reversible dimerization oftwo 1,4-bis(methylseleno)benzene radical cations

leno)alkanes (**2**), and 1-(methylthio),ω-(methylseleno)alkanes (**3**) (Fig. 4) were investigated by semiempirical PM3 calculations in order to study the geometric changes occurring during 2c-3e S-S, Se-Se, and S-Se bond formation, as well as possible follow-up reactions of their radical cations. These compounds have been chosen because their radical cations were shown by pulse radiolysis experiments to lead to *intra*molecular 2c-3e bonds[18].

All structure optimizations were performed for compounds **1–3** in the "linear" and "cyclic" (anti) conformation (Fig. 5) with total positive charges from 0 to +2.

2. METHOD

All calculations have been made by using the HyperChem package from Hypercube Inc. (release 5.01 for Windows 95) on a personal computer with IBM P166+ processor and an internal memory of 96 Mb. After obtaining starting structures by MM+ molecular mechanics, structure optimizations were performed by the semiempirical PM3 method (including Se parameters)[47], using Unrestricted Hartree-Fock field (UHF) and the

Polak-Ribiere algorithm. Computations were stopped after reaching a RMS gradient of 0.001 kcal Å^{-1} mole^{-1}. Additional *ab initio* structure optimizations were realized at the UHF/6–31G* level[48] (RMS gradient ≤ 0.050 kcal Å^{-1} mole^{-1}) in order to validate the PM3 results.

CH_3-X-$(CH_2)_n$-Y-CH_3

1: X=Y=S
2: X=Y=Se
3: X=S, Y=Se

a) n=1
b) n=2
c) n=3
d) n=4
e) n=5

FIGURE 4 Studied compounds

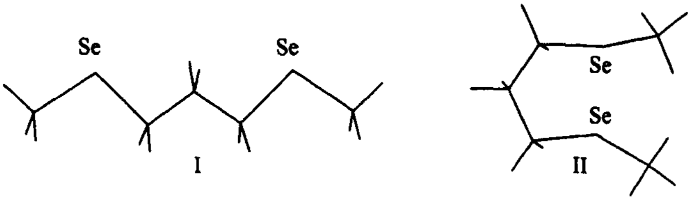


FIGURE 5 Radical cation of **2c** in its linear (I) and cyclic (II) conformation

3. RESULTS AND DISCUSSION

3.1. Preliminary calculations

Compared to the full *ab initio* treatment needing huge computation power, semiempirical self-consistent field molecular orbital methods like PM3 can nowadays be used with common personal computers. This decrease of computation complexity is achieved by approximating coulomb and exchange energies from empirical parameters rather than computing the millions of integrals that are generated during a full *ab initio* treatment of an organic compound. In order to verify the accuracy of the HyperChem PM3 computations, additional *ab initio* calculations were performed at the UHF/6–31G* level. Since similar computations, previously published by McKee, proved the existence of *intra*molecular 2c-3e sulfur-sulfur bonds in the radical cations of acyclic dithiols HS-$(CH_2)_n$-SH (with n = 1 to

4)[49], the organosulfur compounds **1** were chosen for this comparison between PM3 and UHF/6–31G* computations. Structure optimizations of compounds **2** and **3** could not be realized at the UHF/6–31G* level since elements heavier than Ar are not parameterized in the Hyperchem 6–31G* basis set.

Results of the structure optimizations of 1,ω -bis(methylthio)alkanes (**1**) radical cations (Table I; Fig. 6) indicate an excellent linear relationship between total energies computed at the PM3 and the UHF/6–31G* levels.

Although PM3 computations overestimate the 2c-3e bond dissociation energies (E_{cyclic}-E_{linear}) and are less exact than the full *ab initio* treatments, the obtained results give *qualitative* informations about 2c-3e bond formation between two sulfur atoms. Thus, PM3 computations give indications of general trends and should allow comparison within a series of compounds as **1a-e**. Since selenium is also parameterized in the PM3 model, it can be assumed that similar conclusions are also valid for Se-Se and S-Se 2c-3e bonds.

TABLE I Total energies of linear and cyclic radical cations of 1,ω -bis(methylthio)alkanes (**1**) at the PM3 and UHF/6–31G* level. (a) same value as for the linear conformation (see text)

CH_3S-$(CH_2)_n$-$SCH_3^{\cdot+}$ (1)		Total energy (kcal mole^{-1})	
		PM3	*UHF/6–31G**
n=1	linear	-19454.95	-572914.49
	cyclic	(a)	(a)
n=2	linear	-22885.24	-597409.86
	cyclic	-22916.29	-597414.44
n=3	linear	-26333.96	-621906.25
	cyclic	-26377.65	-621919.06
n=4	linear	-29783.24	-646402.31
	cyclic	-29827.19	-646414.71
n=5	linear	-33232.13	-670897.62
	cyclic	-33275.71	-670904.81

TABLE II Results of PM3 calculations for the molecules 1–3 in their linear and cyclic conformation at total charges from 0 to +2. (a) Compound **1**: X=Y = S, compound **2**: X=Y = Se, compound **3**: X = S and Y = Se; (b) distance in Å; (c) total energy in kcal mole^{-1}; (d) same values as for the linear conformation

Structure	*Charge*		*CH_3-S-$(CH_2)_n$-S-CH_3 (1)*				
			a) n = 1	*b) n=2*	*c) n=3*	*d) n = 4*	*e) n=5*
Linear	0	Charge X$^{(a)}$	0.040	-0.031	-0.021	-0.030	-0.027
		Charge Y$^{(a)}$	0.040	-0.031	-0.021	-0.030	-0.027
		Distance X-Y$^{(a,b)}$	2.915	4.381	5.445	6.822	7.954
		Total energy$^{(c)}$	-19635.4	–23083.6	-26531.7	–29980.7	-33429.1
	+1	Charge X$^{(a)}$	0.381	0.727	0.750	0.742	0.744
		Charge Y$^{(a)}$	0.381	0.031	0.013	-0.005	-0.011
		Distance X-Y$^{(a,b)}$	2.261	4.338	5.414	6.792	7.929
		Total energy$^{(c)}$	-19454.9	–22885.2	-26334.0	–29783.2	-33232.1
	+2	Charge X$^{(a)}$	0.883	0.796	0.775	0.769	0.753
		Charge Y$^{(a)}$	0.883	0.796	0.775	0.769	0.753
		Distance X-Y$^{(a,b)}$	2.988	4.410	5.496	6.839	7.989
		Total energy$^{(c)}$	-19144.0	–22611.0	-26075.5	–29534.0	-32991.8
Cyclic	0	Charge X$^{(a)}$	(d)	-0.029	0.059	0.049	0.056
		Charge Y$^{(a)}$	(d)	-0.029	0.054	0.049	0.038
		Distance X-Y$^{(a,b)}$	(d)	3.949	2.038	2.010	2.005
		Total energy$^{(c)}$	(d)	-23085.9	–26527.9	-29976.9	-33425.8
	+1	Charge X$^{(a)}$	(d)	0.313	0.283	0.257	0.259
		Charge Y$^{(a)}$	(d)	0.313	0.277	0.257	0.252
		Distance X-Y$^{(a,b)}$	(d)	2.176	2.072	2.074	2.052
		Total energy$^{(c)}$	(d)	-22916.3	–26377.7	-29827.2	–33275.7
	+2	Charge X$^{(a)}$	(d)	0.649	0.512	0.534	0.515
		Charge Y$^{(a)}$	(d)	0.649	0.512	0.534	0.513
		Distance X-Y$^{(a,b)}$	(d)	2.3045	1.861	2.237	2.207
		Total energy$^{(c)}$	(d)	-22604.9	–26060.9	-29525.9	–32976.2

TABLE II Continued

Structure	*Charge*		*CH_3-Se-$(CH_2)_n$-Se-CH_3 (2)*				
			a) n = 1	*b) n=2*	*c) n = 3*	*d) n = 4*	*e) n=5*
Linear	0	Charge X$^{(a)}$	0.016	-0.039	-0.029	-0.038	-0.036
		Charge Y$^{(a)}$	0.016	-0.039	-0.029	-0.038	-0.036
		Distance X-Y$^{(a,b)}$	2.478	4.429	5.241	6.783	7.752
		Total energy$^{(c)}$	−20079.4	-23519.0	−26966.8	-30415.7	−33864.2
	+1	Charge X$^{(a)}$	0.323	0.287	0.297	0.570	0.573
		Charge Y$^{(a)}$	0.323	0.287	0.297	-0.010	-0.021
		Distance X-Y$^{(a,b)}$	2.360	4.365	5.223	6.776	7.725
		Total energy$^{(c)}$	−19907.7	-23315.5	−26762.2	-30217.9	−33666.9
	+2	Charge X$^{(a)}$	0.643	0.633	0.617	0.604	0.593
		Charge Y$^{(a)}$	0.643	0.633	0.617	0.604	0.593
		Distance X-Y$^{(a,b)}$	2.640	4.540	5.379	6.861	7.843
		Total energy$^{(c)}$	−19580.8	-23047.9	−26509.0	-29968.3	−33424.8
Cyclic	0	Charge X$^{(a)}$	(d)	-0.137	−0.050	-0.047	−0.145
		Charge Y$^{(a)}$	(d)	-0.137	−0.051	-0.047	−0.145
		Distance X-Y$^{(a,b)}$	(d)	2.303	2.119	2.242	2.109
		Total energy$^{(c)}$	(d)	-23544.2	−27001.5	-30449.4	−33900.8
	+1	Charge X$^{(a)}$	(d)	0.200	0.162	0.139	0.147
		Charge Y$^{(a)}$	(d)	0.200	0.161	0.139	0.130
		Distance X-Y$^{(a,b)}$	(d)	2.316	2.256	2.256	2.267
		Total energy$^{(c)}$	(d)	-23381.1	−26845.2	-30296.8	−33748.5
	+2	Charge X$^{(a)}$	(d)	0.475	0.249	0.369	0.366
		Charge Y$^{(a)}$	(d)	0.475	0.249	0.369	0.353
		Distance X-Y$^{(a,b)}$	(d)	2.514	2.041	2.458	2.459
		Total energy$^{(c)}$	(d)	-23063.6	−26526.9	-29986.8	−33440.3

TABLE II Continued

Structure	*Charge*		*CH_3-S-$(CH_2)_n$-Se-CH_3 (3)*				
			a) n= 1	*b) n=2*	*c) n=3*	*d) n=4*	*e) n=5*
Linear	0	Charge $X^{(a)}$	0.070	-0.027	-0.022	-0.029	-0.027
		Charge $Y^{(a)}$	-0.021	-0.041	-0.028	-0.039	-0.036
		Distance X-$Y^{(a,b)}$	2.680	4.396	5.356	6.794	7.860
		Total energy$^{(c)}$	-19857.5	–23301.4	-26749.2	-30198.2	–33646.7
	+1	Charge $X^{(a)}$	0.384	0.717	0.747	0.741	0.734
		Charge $Y^{(a)}$	0.286	0.026	0.006	-0.014	-0.020
		DistanceX-$Y^{(a,b)}$	2.290	4.354	5.346	6.765	7.848
		Total energy$^{(c)}$	-19683.0	–23104.1	-26551.9	–30001.0	-33450.2
	+2	Charge $X^{(a)}$	0.855	0.787	0.771	0.770	0.761
		Charge $Y^{(a)}$	0.725	0.630	0.618	0.602	0.594
		Distance X-$Y^{(a,b)}$	2.880	4.463	5.452	6.842	7.920
		Total energy$^{(c)}$	-19361.8	–22830.1	-26292.5	–29751.1	-33207.8
Cyclic	0	Charge $X^{(a)}$	(d)	0.050	0.015	0.034	0.035
		Charge $Y^{(a)}$	(d)	-0.010	–0.004	-0.028	–0.027
		Distance X-$Y^{(a,b)}$	(d)	2.520	2.092	2.131	2.237
		Total energy$^{(c)}$	(d)	-23311.6	–26766.6	-30215.7	–33665.3
	+1	Charge $X^{(a)}$	(d)	0.280	0.247	0.228	0.221
		Charge $Y^{(a)}$	(d)	0.229	0.181	0.154	0.153
		Distance X-$Y^{(a,b)}$	(d)	2.219	2.139	2.142	2.142
		Total energy$^{(c)}$	(d)	-23150.3	–26614.5	-30064.3	–33514.4
	+2	Charge $X^{(a)}$	(d)	0.667	0.411	0.569	0.543
		Charge $Y^{(a)}$	(d)	0.485	0.323	0.369	0.355
		Distance X-$Y^{(a,b)}$	(d)	2.452	1.931	2.382	2.367
		Total energy$^{(c)}$	(d)	-22835.8	–26297.7	-29758.5	–33210.6

3.2. Evidence of 2c-3e bond formation in the radical cations of 1, 2 and 3

3.2.1. 1,ω-bis(methylthio)alkanes

Comparison of the linear and cyclic forms of **1** (Table II) at total charges 0, +1 and +2, showed that both neutral compounds had nearly the same total energy, indicating negligible interaction between the two sulfur atoms. Furthermore, the (Mulliken) charges on both sulfurs were identical within each compound. This is no more the case for the radical cations of the linear molecules (**1b-e**), exception being **1a** (see below): most of the positive charge is carried by one sulfur atom, the other stayed uncharged. For the cyclic compounds **1b-e** the positive charge is equally distributed on both sulfur atoms, indicating the formation of 2c-3e S-S bonds. Distance between the sulfur atoms is 2.05 to 2.18 Å, which is close to the one computed during this work for the $(H_2S)_2^{\cdot+}$ radical cation (2.05 Å), studied previously by Clark[50]. Since the sulfur atoms of the **1a** radical cation in its linear geometry are also equally charged, it must be assumed for proximity reasons that both S atoms interact and form a 2c-3e bond as shown for the other *cyclic* radical cations. Comparing the total energy of the linear and the cyclic radical cations **1b-e** allowed to estimate the bond dissociation energy to 31.1 – 44.0 kcal mole^{-1}.

Moreover, the dications of **1a-e** in their open and cyclic conformation showed an equally distributed positive charge on the two sulfur atoms. Corresponding cyclic structures are 6.1 to 15.6 kcal mole^{-1} less stable than their linear conformers. This may be related to coulombic repulsions between the sulfur atoms resulting from the relatively high positive charge (+0.51 to +0.65).

3.2.2. 1,ω-bis(methylseleno)alkanes

As shown in Table II, 1,ω -bis(methylseleno)alkanes (**2**) give rise to cyclic radical cations which are much better stabilized toward their linear structures, than their sulfur analogs. Corresponding dissociation energies and lengths of the 2c-3e Se-Se bonds are respectively 65.6 – 83.0 kcal mole^{-1} and 2.26 – 2.32 Å. Several differences exist however compared to their sulfur analogs: in the case of **2b-e** both cyclic neutral and dicationic compounds are respectively stabilized by 25.2 – 36.6 kcal mole^{-1} and 15.5 – 18.5 kcal mole^{-1} comparing to the corresponding linear conformers. This last results confirms experimental work showing *intra*molecular Se-Se

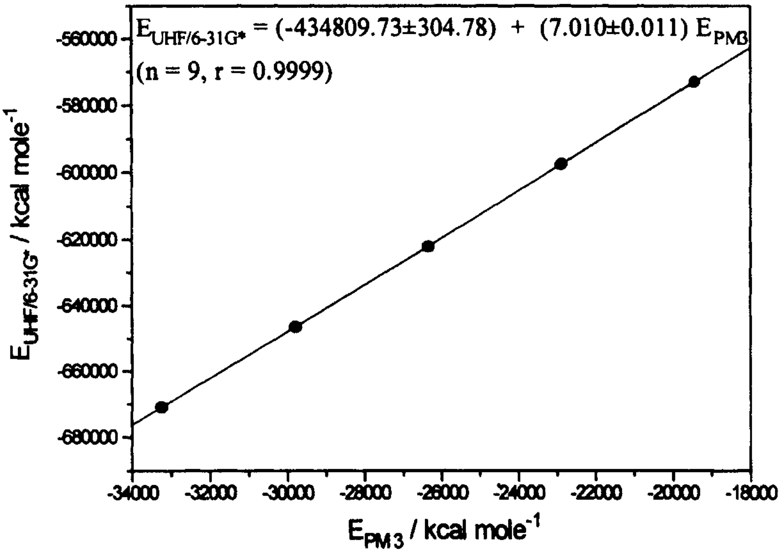


FIGURE 6 Linear correlation between the PM3 and the *ab initio* UHF/6–31G* total energy of the linear and cyclic radical cations of 1,ω-bis(methylthio)alkanes (**1**)

bonds in the dications of 1,5-diselenacyclooctane[39,51] and 5H,7H-dibenzo[b,g][1,5]diselenocin[52] (closed cyclic diselenides with similar structure to **2c**). Furthermore, the positive charge of the linear radical cations **2a-c** is equally distributed on both selenium atoms, whereas for the radical cations of **2d** and **2e** (as for the sulfur analogs **1b-d**) only one of both chalcogen atoms is oxidized. All these differences can be rationalized by considering that the selenium atom is more polarizable than the sulfur atom, the valence electrons being farther away from the nucleus and therefore more exposed to the influence of neighboring groups.

3.2.3. 1-(methylthio),ω-(methylseleno)alkanes

PM3 calculations of the mixed sulfur-selenium compounds **3a-e** in their linear and cyclic conformations showed that the sulfur atom carries the positive charge. This can already be seen for the neutral compounds **3b-e** and their dications, in both geometric configurations, and is very well evidenced for the linear radical cations **3b-c** where the entire positive charge is localized on the sulfur atom. It should be mentioned that this result is at the first glance in opposition to electrochemical studies of mixed sulfur – selenium compounds showing that the selenium atom is first oxidized[18,44]. This discrepancy can be rationalized by considering that the electron is first withdrawn from the selenium atom (due to its higher polarizability), and that the positive charge is afterwards delocalized onto the sulfur atom in order to form the most stable radical cation.

Cyclic radical cations of **3b-e** as well as the linear radical cation of **3a** are stabilized by 2c-3e *intra*molecular bonds between the oxidized sulfur atom and the neutral selenium atom. The bond length varies between 2.14 and 2.22 Å whereas the corresponding dissociation energy lies between 46.2 – 64.2 kcal $mole^{-1}$.

Moreover, the cyclic compounds **3b-e** in the neutral and dicationic state are already stabilized respectively by 10.2 – 18.6 and 2.8 to 7.4 kcal $mole^{-1}$ compared to their linear conformers.

Comparison of the 2c-3e bond dissociation energies for the (cyclic) radical cations of **1–3** indicated that the bond strength follows the increasing series: S-S < S-Se < Se-Se. Moreover, the dissociation energy of a S-Se bond can be approximated within 5% by the average between the corresponding S-S and Se-Se bond dissociation energies (Fig. 7).

This behavior can be rationalized according to Clark's study[3] which indicated that the dissociation energy D_{AB} of an asymmetrical *inter*molecular complex (formed from molecules A and B) is related to the dissociation energies of the symmetrical complexes (D_{AA} and D_{BB}), and the difference of ionization potentials (ΔIP) of both neutral molecules A and B:

$$D_{AB} = \frac{D_{AA} + D_{BB}}{2} \exp(-\lambda_A \lambda_B \Delta IP) \qquad \text{(eq.1)}$$

The pre-exponential factors λ_A and $\lambda_B$were obtained by fitting the computed value of D_{AB} to equation 1.

Direct application of this equation to the determination of the dissociation energy of the 2c-3e S-Se bonds in the cyclic radical cations of **3a-e** is hindered by two facts. First, λ_A values were not published for organoselenium compounds, and second, the ionization potentials needed for the calculation of ΔIP are those of the neutral compounds A and B. Since in this study an *intra*molecular 2c-3e bond formation is investigated, only one *global* ionization potential could be computed for neutral cyclic compounds **3a-e**, and it was not possible to determinate the difference ΔIP.

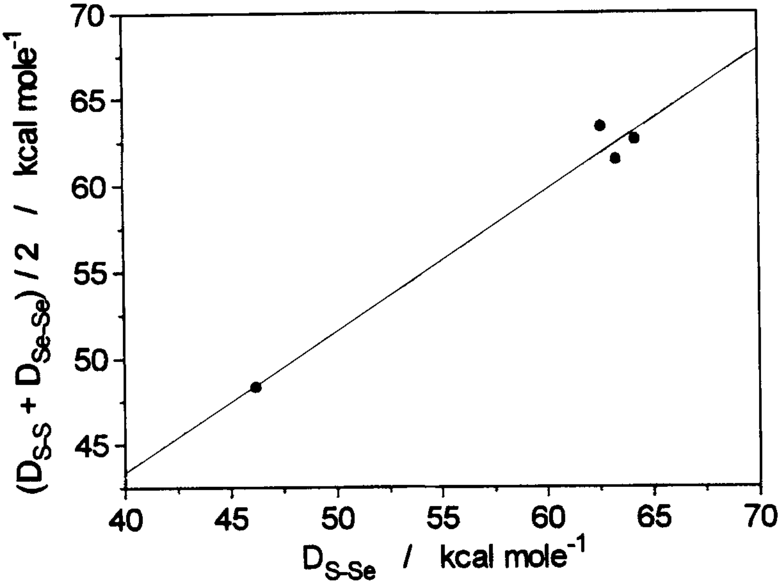


FIGURE 7 Linear correlation between the computed dissociation energy of 2c-3e S-Se bonds and the calculated dissociation energy according to equation 2

This last difficulty was circumvented by assuming that ΔIP can be approximated by computing the ionization potentials of model compounds. As shown by PM3 computations for $CH_3SeCH_2CH_3$ and $CH_3SCH_2CH_3$ which gave respectively -8.98 and -8.87 eV for the HOMO energy, the ionization potentials are likely very similar, and in consequence ΔIP should be close to zero. This is not surprising because electronegativities of the elements sulfur and selenium are nearly equal. Since furthermore all published λ values are between 0.057 and 0.190 (the value for H_2S is 0.132)[3], the exponential term finally tends to unity. Thus, in the case of sulfur (S) and selenium (Se) compounds, equation 1 may be rewritten as:

$$D_{S-Se} \approx \frac{D_{S-S} + D_{Se-Se}}{2} \qquad \text{(eq.2)}$$

This equation is in good agreement with the computed stabilization energies of *intra*molecular 2c-3e S-Se bonds (Fig. 7).

3.3. Strength of the intramolecular orbital interaction

The strength of the orbital interaction in a 2c-3e bond is, according to theoretical calculations[3,33], directly related to the σ/σ^* separation (Fig. 1). This has been experimentally investigated by characterization of the 2c-3e bond radical cations of **1–3**[18]. The most favorable orbital overlap (characterized by the highest σ/σ^* separation – and thus the lowest λ_{max} in optical absorption spectra) was found for the compounds with n = 3 (Table III)[18]. PM3 computations of the energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are also in good agreement with this theory. In the case of the cyclic radical cations of **1b-e, 2b-e** and **3b-e** it was generally the compound with three methylene carbons (n = 3) which exhibited the highest energetical difference $\Delta E = |E_{HOMO} - E_{LUMO}|$ (Table IV). Since the neutral cyclic conformers **2b-e** and **3b-e** are up to 36.6 kcal mole^{-1} more stable than their linear analogs (Table II), we also investigated the lone pair – lone pair interaction in the neutral cyclic compounds **1–3**. According to a previous paper[18], the strongest interaction between the electronic lone pairs was expected for the compounds with three methylene carbons (n = 3). Because the energy of the antibonding orbital (containing 2 electrons) is raised, ionization should be easier for the compound with n = 3 than for n = 1[18] (Fig. 8).

This hypothesis has been partly confirmed by the computing the energy of the HOMO for the neutral cyclic compounds **1–3**. In the case of the cyclic sulfur derivatives **1**, which were only very weekly stabilized by lone pair – lone pair interaction (1.3 kcal mole^{-1} for **1b**), ionization potentials (IP = – E_{HOMO}) show a minimum around n = 3 to 4. Corresponding values are 9.05, 9.07, 7.68, 7.63, and 7.70 eV for n = 1 to 5.

Contrary to the thioalkanes **1**, the cyclic conformations of the selenium analogs **2** were highly stabilized towards the linear forms (see above). Corresponding ionization energies are respectively 8.49, 7.86, 7.53, 7.65, and 7.40 eV for n = 1 to 5. In this case, the computed values agreed well with the hypothesis of a minimum at n = 3. The further decrease observed for n = 5 might be explained by an additional effect: by increasing the chain length the added methylene group increase slightly the electron density on the selenium atom by inductive effect, leading to a gradual diminution of the ionization energy.

TABLE III Reported values[18] of the maximum absorption wavelength (λ_{max}) of the 2c-3e bond radical cation in water, and of the oxidation peak potential (V vs. Ag/0.1 N $AgNO_3$) in acetonitrile / n-Et_4NClO_4 0.1N. (a) not indicated

	CH_3-S-$(CH_2)_n$-S-CH_3 (1)					CH_3-Se-$(CH_2)_n$-Se-CH_3 (2)					CH_3-S-$(CH_2)_n$-Se-CH_3 (3)				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*	*a) n = 1*	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*	*a) n = 1*	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
λ_{max}/nm	660	525	440	460	475	680	550	440	460	470	620	550	435	435	470
E_p/V	1.130	1.095	0.742	0.900	(a)	0.820	0.600	0.500	0.580	0.660	0.894	0.850	0.600	0.665	0.791

TABLE IV Energies of the HOMO and LUMO, as well as their difference $\Delta E=|E_{HOMO}-E_{LUMO}|$ for the derivatives **1–3**. All energies are expressed in eV. (a) same value as for the linear conformation (see text)

Structure	*Charge*		CH_3-S-$(CH_2)_n$-S-CH_3 (1)					CH_3-Se-$(CH_2)_n$-Se-CH_3 (2)					CH_3-S-$(CH_2)_n$-Se-CH_3 (3)				
			a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*	*a) n = 1*	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*	*a) n = 1*	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
Linear	0	E_{HOMO}	-9.05	-8.94	-8.94	-8.94	-8.92	-8.49	-9.02	-9.06	-9.05	-9.02	-9.04	-8.96	-8.96	-8.94	-8.92
		E_{LUMO}	-0.38	-0.16	+0.12	+0.23	+0.30	-1.09	-1.20	-0.78	-0.71	-0.63	-0.95	-0.87	-0.67	-0.63	-0.59
		ΔE	8.67	8.78	9.06	9.17	9.22	7.40	7.83	8.29	8.25	8.31	8.09	8.09	8.29	8.31	8.33
	+1	E_{HOMO}	-14.55	-12.35	-11.66	-11.20	-10.85	-15.22	-11.93	-11.23	-11.33	-10.98	-14.91	-12.46	-11.77	-11.31	-10.96
		E_{LUMO}	-6.43	-8.16	-8.16	-8.16	-8.14	-7.04	-8.63	-8.68	-8.08	-8.05	-6.82	-8.08	-8.13	-8.14	-8.08
		ΔE	8.13	4.19	3.50	3.04	2.71	8.28	3.30	2.55	3.25	2.93	8.12	4.38	3.64	3.17	2.88
Cyclic	0	E_{HOMO}	(a)	-9.07	-7.68	-7.63	-7.70	(a)	-7.86	-7.53	-7.65	-7.40	(a)	-8.50	-7.78	-7.74	-7.77
		E_{LUMO}	(a)	+0.23	+0.16	+0.06	0.00	(a)	-0.93	-0.37	-0.57	-0.26	(a)	-0.67	-0.43	-0.42	-0.17
		ΔE	(a)	9.30	7.84	7.68	7.71	(a)	6.93	7.16	7.09	7.14	(a)	7.93	7.31	7.27	7.59
	+1	E_{HOMO}	(a)	-14.07	-13.84	-13.78	-13.68	(a)	-14.59	-14.55	-14.16	-13.97	(a)	-14.48	-14.28	-14.00	-13.95
		E_{LUMO}	(a)	-5.81	-5.38	-5.58	-5.54	(a)	-6.49	-6.19	-6.05	-5.98	(a)	-6.28	-5.84	-5.77	-5.73
		ΔE	(a)	8.34	8.31	8.19	8.14	(a)	8.10	8.22	8.12	8.00	(a)	8.23	8.49	8.24	8.22

Similar considerations may also be valid for the sulfur-selenium derivatives, for which the neutral cyclic conformation is moderately stabilized (10.2 to 18.6 kcal mole^{-1}), and for which the ionization energies are respectively 9.04, 8.50, 7.78, 7.74, and 7.77 eV for n = 1 to 5. Thus, whereas lone pair – lone pair interactions could not be evidenced for sulfur compounds (**1**), this type of interaction is largely present in their selenium analogs (**2**) and the mixed sulfur-selenium derivatives (**3**), leading to a stabilization of the cyclic forms.

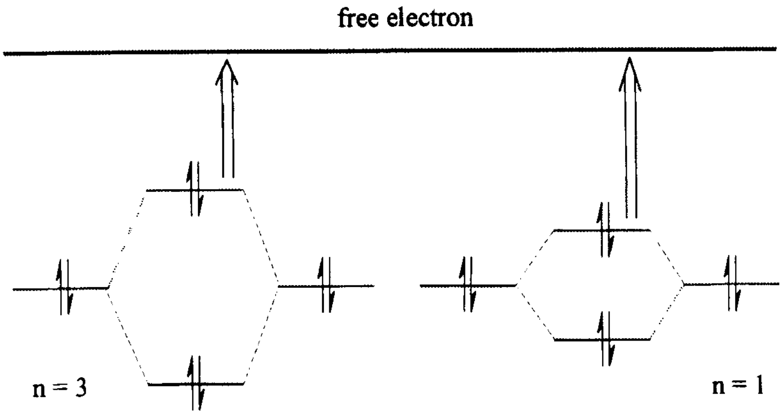


FIGURE 8 Ionization energies considering lone pair – lone pair interactions in cyclic neutral compounds **1–3** a and **c**

As during the electrochemical oxidation of a compound, (at least) one electron is withdrawn from the HOMO, it is often possible to establish a correlation between the electrochemical oxidation potentials and the ionization potentials within a series of compounds. In order to verify this relationship for organochalcogens **1–3**, linear regressions were realized between the published oxidation peak potentials[18] (Table III) and E_{HOMO} (Table IV) for the neutral linear and cyclic species. Under no circumstances, however, a linear relationship was observed. This result argues against the previously emitted hypothesis that the variation of the oxidation peak potentials within the series of compounds **1–3** can be rationalized by lone pair - lone pair interactions[18] and rather confirms another hypothesis emitted by the same authors, indicating that the common trend observed in the electrochemical oxidation potentials may reflect the thermodynamic stability of the 2c-3e *intra*molecular radical cations. Actually, the electrochemical oxidation peak potential in linear sweep and cyclic voltammetry depends also upon possible follow-up reactions of the formed product. When this product is consumed in a chemical reaction (for example *inter*molecular 2c-3e bonding with a neutral species, or dimerization of the radical cations) the corresponding oxidation peak is shifted towards less positive potentials[53,54]. In the case of compounds **1**–**3** this process could rationalize the shift of the oxidation potentials. However, it should not be forgotten that the heterogeneous electron transfer reaction is slow, because of the high geometric alterations[46], which results in shifting the oxidation peak towards more positive potentials as the scan rate is increased in cyclic voltammetry[53,54].

3.4. Follow-up reactions of the radical cations of 1–3

*Intra*molecular 2c-3e bond formation is only one type of stabilization mechanism which organosulfur and -selenium radical cations (**1**–**3**) can undergo. Further reaction pathways include complexation by a neutral species, yielding a 2c-3e *inter*molecular bond, and the dimerization reaction, leading to a dimeric dication. These reaction pathways were also investigated for compounds **1**–**3** by PM3 calculations. Results are given in the next two sections.

3.4.1. Reaction between a radical cation and a neutral species

Preliminary computations of the *inter*molecular 2c-3e bond formation between the radical cation of **2c** and neutral **2c** showed that at least four different structures could be formed. For the linear conformers the most stable complex was obtained with the chains facing each other as in a mirror, whereas for the cyclic compounds the corresponding structure involved a 4 center odd-electron interaction.

Total energies and bond dissociation energies of the *inter*molecular complex into the constituents (the cyclic radical cation + the cyclic neutral species) are given in Table V. As shown, all radical cations of **1**–**3**, either linear or cyclic, undergo coupling with the corresponding neutral molecule. Even cyclic radical cations, already stabilized by 2c-3e bonds, react readily with neutral molecules to form a complex radical cations. Assuming that the interactions are similar in solution (water), this means that under pulse radiolysis conditions (concentration ratio [neutral species] / [radical cation] ≈ 10 to 1000[12]), *intra*molecular 2c-3e bond formation can only be observed at low concentrations, whereas at high concentrations a multi-center odd-electron complex is formed.

TABLE V Total energies (kcal mole^{-1}) and dissociation energies (kcal mole^{-1}, in brackets) of the dimeric radical cation. Dissociation energies are reported towards the cyclic forms of the radical cations with 2c-3e *intra*molecular bond and the neutral organochalcogen. For the compounds **3**, first values are given for the isomer with two S-Se interactions, while the second values are those of the isomer with S-S and Se-Se interaction. (a) same values as for the "linear" conformation

Dimeric radical cation	*CH_3-S-$(CH_2)_n$-S-CH_3 (1)*				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
Linear	-39122.8 (+32.5)	–46016.5 (+14.3)	-52917.0 (+11.4)	–59814.9 (+10.8)	-66708.6 (+7.1)
Cyclic	(a) (a)	-46012,0 (+9.8)	–52921.4 (+15.8)	-59813.6 (+9.5)	–66716.0 (+14.5)

Dimeric radical cation	*CH_3-Se-$(CH_2)_n$-Se-CH_3 (2)*				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
Linear	–40100.3 (+113.2)	–47028.9 (+103.6)	-53866.7 (+20.0)	-60755.9 (+9.7)	–67658.8 (+9.5)
Cyclic	(a) (a)	-47025.4 (+100.1)	–53957.2 (+110.5)	-60835.2 (+89.0)	–67751.6 (+102.3)

Dimeric radical cation	*CH_3-S-$(CH_2)_n$-Se-CH_3 (3)*				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
Linear	-39630.0 (+89.5); -39601.9 (+61.4)	–46528.9 (+67.3); –46507.0 (+45.4)	-53395.0 (+16.7); -53389.4 (+11.1)	–60287.1 (+7.1); –60283.9 (+3.9)	-67183.8 (+4.1); -67183.5 (+3.8)
Cyclic	(a) (a) (a) (a)	-46528.1 (+66.2); -46517.9 (+56.0)	–53431.3 (+50.2); –53427.1 (+46.0)	-60327.7 (+47.7); -60324.4 (+44.4)	–67225.3 (+45.6); –67226.1 (+46.4)

It is also worth to note that in the case of the mixed sulfur-selenium compound **3** two different types of complexes can be built as the interactions may occur between the same type of chalcogen or not. As shown in Table V, odd-electron complexes with two S-Se interactions are up to 28 kcal mole^{-1} more stable than their isomers with S-S and Se-Se interactions. This energetical difference however decreases with increasing methylene chain length from the mentioned value (**3a**) to about 0 kcal mole^{-1} (**3e**).

3.4.2. Reaction between two radical cations

Since it has been experimentally shown that the radical cation of 1,4-bis(methylseleno)benzene dimerizes upon electrochemical oxidation in acetonitrile[45] (Fig. 3), computations were performed with the organochalcogens **1–3** in order to evidence similar bonding, leading to the formation of two 2c-3e bonds. As in the previous case (§ 3.4.1.), calculations were realized for the linear chains opposing each other, and for the cyclic chains in which all four chalcogens atoms are close to each other.

Results (Table VI) indicate that *only* the organoselenium compounds (**2a-e**) form 4 center dimeric dications, stabilized by about 5.6 to 31 kcal mole^{-1} towards the *cyclic* radical cations. In the case of the corresponding sulfur and sulfur-selenium radical cations the dimerization equilibrium is strongly directed towards the dissociation of the dimeric dication into the radical cation which is stabilized by a 2c-3e bond. Therefore, electrochemical measurements (characterized by a high concentration ratio [neutral species] / [radical cation] at the electrode surface), must lead under thermodynamic control to the *intra*molecular stabilized radical cation of **1a-e** and **3a-e**, whereas for the selenium analogs **2a-e** the more stable cyclic radical cations readily dimerize into dimeric dications at high concentrations !

3.4.3. Other complexes formed from three molecules

In order to evidence possible higher complexes of the radical cations of **1–3**, computations were realized for associations of three identical (cyclic) molecules, with total charges ranging from +1 to +3. Starting structures were obtained by disposing the three cyclic molecules as a triangle, with the chalcogen atoms pointing from outside to the comers. Then, after drawing *intra*molecular bonds between the chalcogens in each of the three cycles, each chalcogen was furthermore connected to the nearest chalcogen of the closest cycle. In the case of the mixed compounds **3**, only sulfur-selenium bonds were considered since corresponding 2c-3e bonds are more stabilized (see Table s V and VI). The obtained structures were then optimized by the MM+ method, and used as starting structures for PM3 calculations after deleting all six chalcogen-chalcogen bonds.

Results of computations (Table VII) show great differences between the compounds **1–3**. For bis(methylthio)alkanes **1**, the only stable trimolecular association was formed by a radical cation and two neutral molecules. Corresponding complexes with total charges of +2 and +3 where highly destabilized and underwent generally dissociation into a dimeric radical cation + a cyclic radical cation, and three cyclic radical cations, respectively. In the case of bis(methylseleno)alkanes **2**, and methylthio-methylselenoalkanes **3**, all trimolecular associations in their singly and doubly positively charged states are stabilized towards the isolated cyclic neutral molecules and radical cations. Only the triply charged complexes were unstable – with one exception: **2a**, for which the (highly polarizable) selenium atoms are so close one to the other that they interact strongly.

4. CONCLUSIONS

Radical cations of **1–3** were shown to undergo *intra*molecular cyclization by 2c-3e bond formation between the to involved chalcogen atoms. Dissociation energies of the 2c-3e S-Se bonds was given by the average of the corresponding values for S-S and Se-Se bonds. In the case of neutral and dicationic **2** and **3** the cyclic conformations were also stabilized by chalcogen-chalcogen interactions. Computation of the energetic difference between the HOMO and LUMO showed, in agreement with published results of pulse-radiolysis experiments, that the cyclic conformation of the radical cation with three methylene groups (n = 3) has the strongest orbital overlap in the series of 2c-3e bonds. Published electrochemical oxidation potentials of neutral compounds **1–3** could however not be linearly correlated to the energy of the HOMO, *indicating that they might reflect the* influence of follow-up reactions like the *intra*molecular 2c-3e bonding. Computations realized for bi- and trimolecular associations between radical cations and neutral species showed that even radical cations stabilized by an *intra*molecular 2c-3e chalcogen-chalcogen bond can undergo di- and trimerization! Although results were only computed *in the gas phase*, similar interactions are very likely to occur in solution (since the presence of solvent molecules increases the dielectric permittivity, leading for example to a decrease of the coulombic repulsion between two radical cations), and may be experimentally proven in the future.

TABLE VI Total energies (kcal $mole^{-1}$) and dissociation energies (kcal $mole^{-1}$, in brackets) of the dimeric dication. Dissociation energies are reported towards two cyclic radical cations with 2c-3e *intra*molecular bond. For the compounds **3**, first values are given for the isomer with two S-Se interactions, while the second values are those of the conformer with S-S and Se-Se interaction. (a) same values as for the "linear" conformation; (b) not converged – dissociation into two cyclic radical cations

Dimeric dication	CH_3-S-$(CH_2)_n$-S-CH_3 (1)				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
Linear	-38876.0 (-33.8)	–45761.3 (-71.3)	-52695.5 (-59.9)	–59605.4 (-49.0)	-66509.8 (-41.6)
Cyclic	(a) (a)	(b) (b)	(b) (b)	-59602.0 (-52.4)	–66503.8 (-47.7)

Dimeric dication	CH_3-Se-$(CH_2)_n$-Se-CH_3 (2)				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
Linear	-39827.2 (+11.8)	-46781.5 (+19.3)	–53642.8 (-47.6)	-60547.0 (-46.6)	-67450.7 (-46.3)
Cyclic	(a) (a)	-46789.4 (+27.2)	–53706.7 (+16.3)	-60599.2 (+5.6)	–67528.0 (+31.0)

Dimeric dication	CH_3-S-$(CH_2)_n$-Se-CH_3 (3)				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
Linear	–39363.3 (-2.7); -39338.1 (-27.0)	–46288.0 (-12.6); –46265.8 (-34.8)	–53172.6 (-56.4); –53165.3 (-63.7)	–60080.8 (-47.8); –60075.3 (-53.3)	–66982.3 (-46.5); –66981.7 (-47.1)
Cyclic	(a) (a) (a) (a)	-46278.9 (-21.8); -46278.9 (-21.7)	–53205.9 (-23.9); –53204.9 (-24.1)	-60103.8 (-24.8); -60085.1 (-43.6)	–67004.6 (-24.2); –66986.7 (-42.1)

TABLE VII Total energies (kcal mole^{-1}) and dissociation energies (kcal mole^{-1}, in brackets) of trimolecular associations at total positive charges of +1, +2, and +3. Dissociation energies are reported towards two cyclic radical cations with 2c-3e *intra*molecular bond. (a) not converged - dissociation into a dimeric radical cation and a cyclic radical cation; (b) not converged – dissociation into three cyclic radical cations; (c) conformer with only mixed (S-Se) interactions

Total charge	CH_3-S-$(CH_2)_n$-S-CH_3 (1)				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
+1	-58774.9 (+49.2)	-69116.2 (+28.1)	-79463.3 (+22.2)	-89803.7 (+15.1)	-100156.7 (+22.8)
+2	-58545.6 (-90.6)	(a)	(a)	(a)	(a)
+3	-58246.1 (-118.6)	(b)	(b)	(b)	(b)

Total charge	CH_3-Se-$(CH_2)_n$-Se-CH_3 (2)				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n= 5*
+1	−60284.7 (+218.2)	-70686.7 (+217.2)	-81087.2 (+239.0)	-91377.1 (+181.5)	-101773.4 (+223.3)
+2	-60061.6 (+166.8)	-70499.2 (+192.8)	-80838.7 (+146.8)	-91169.2 (+126.2)	−101573.1 (+175.3)
+3	-59736.0 (+12.9)	-70129.6 (-13.7)	-80526.6 (-9.0)	-90877.2 (-13.2)	−101227.5 (-18.0)

Total charge	CH_3-S-$(CH_2)_n$-Se-CH_3 (3) (c)				
	a) n = 1	*b) n = 2*	*c) n = 3*	*d) n = 4*	*e) n = 5*
+1	−59566.2 (+168.2)	-69901.6 (+128.1)	-80250.4 (+102.7)	-90582.9 (+87.2)	-100942.0 (+97.0)
+2	−59326.7 (+103.2)	-69688.6 (+76.4)	-80050.9 (+55.3)	-90391.1 (+46.8)	−100731.3 (+37.2)
+3	−59005.3 (-43.7)	-69371.2 (-79.7)	-79758.8 (-84.7)	-90108.8 (-84.1)	−100459.9 (-83.3)

Acknowledgements

Financial support is gratefully acknowledged from the Deutsche Forschungsgemeinschaft (Postdoctoral Fellowship R.M.) and the Fonds der Chemischen Industrie.

References

[1] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).
[2] N.C. Baird, J. Chem. Educ. **54**, 291 (1977).
[3] T. Clark, J. Am. Chem. Soc. **110**, 1672 (1988).
[4] B.C. Gilbert, D.K.C. Hodgeman, and R.O.C. Norman, J. Chem. Soc., Perkin Trans. 2, 1748 (1973).
[5] W.B. Gara, J.R.M. Giles, and B.P. Roberts, J. Chem. Soc. Perkin Trans. 2, 1444 (1979).
[6] W.K. Musker, T.L. Wolford, J. Am. Chem. Soc. **98**, 3055 (1976).
[7] W.K. Musker, T.L. Wolford, and P.B. Roush, J. Am. Chem. Soc. **100**, 6416 (1978).
[8] D.N.R. Rao, M.C.R. Symons, and B.W. Wren, J. Chem. Soc. Perkin Trans 2, 1681 (1984).
[9] M.C.R. Symons, J. Chem. Soc., Perkin Trans. 2, 1618 (1974).
[10] M. Bonifacic, H. Möckel, D. Bahnemann, and K.-D. Asmus, J. Chem. Soc., Perkin Trans. 2, 657 (1975).
[11] D. Bahnemann and K.-D. Asmus, J. Chem. Soc. Chem. Commun., 238 (1975).
[12] K.-D. Asmus, Acc. Chem. Res. **12**, 436 (1979).
[13] K.-D. Asmus, D. Bahnemann, Ch.-H. Fischer, and D. Veltwisch, J. Am. Chem. Soc. **101**, 5322 (1979).
[14] J. Mönig, R. Goslich, and K.-D. Asmus, Ber. Bunsenges. Phys. Chem. **90**, 115 (1986).
[15] K. Bobrowski and J. Holcman, J. Phys. Chem. **93**, 6381 (1989).
[16] K.-D. Asmus, NATO ASI Ser., Ser. A, 197 (Sulfur-Cent. React. Intermed. Chem. Biol.), 155 (1990).
[17] H. Mohan and J.P. Mittal, J. Chem. Soc., Perkin Trans. 2, 207 (1992).
[18] T. Tobien, H. Hungerbühler, and K.-D. Asmus, Phosph. Sulf. Sil. **95–96**, 249 (1994).
[19] S.A. Chaudhri, H. Mohan, E. Anklam, and K.-D. Asmus, J. Chem. Soc., Perkin Trans. 2, 383 (1996).
[20] H. Möckel, Fres. Z. Anal. Chem. **295**, 241 (1979).
[21] T. Drewello, C.B. Lebrilla, H. Schwarz, L.J. deKoning, R.H. Fokkens, N.M.M. Nibbering, E. Anklam, and K.-D. Asmus, J. Chem Soc. Chem. Commun., 1381 (1987).
[22] Y. Deng, A.J. Illies, M.A. James, M.L. McKee, and M. Peschke, J. Am. Chem. Soc. **117**, 420 (1995).
[23] M.A. James and A. J. Illies, J. Phys. Chem. **100**, 15794 (1996).
[24] R.S. Glass, M. Hijjatie, G.S. Wilson, S. Mahling, M. Göbl, and K.-D. Asmus, J. Am. Chem. Soc. **106**, 5382 (1984).
[25] K.-D. Asmus, M. Göbl, K.O. Hiller, S. Mahling, and J. Mönig, J. Chem. Soc., Perkin Trans. 2, 641 (1985).
[26] J. Mönig, M. Göbl, and K.-D. Asmus, J. Chem. Soc. Perkin Trans. 2, 647 (1985).
[27] W.K. Musker, A.S. Hirschon, and J.T. Doi, J. Am. Chem. Soc. **100**, 7754 (1978).
[28] R.A.J. Janssen, O.M. Aagaard, M.J. Van der Woerd, H.M. Buck, Chem. Phys. Lett. **171**, 127 (1990).
[29] H. Hungerbühler, S.N. Guha, and K.-D. Asmus, J. Chem. Soc. Chem. Commun., 999 (1991).
[30] K.-D. Asmus, D. Bahnemann, M. Bonifacic, and H.A. Gillis, Faraday Discuss. Chem. Soc. **63**, 213 (1977).
[31] M.C.R. Symons and R.L. Petersen, J. Chem. Soc. Faraday Trans. 2, 210 (1978).
[32] M. Bonifacic and K.-D. Asmus, J. Chem. Soc. Perkin Trans 2, 758 (1980).
[33] T. Clark, J. Comput. Chem. **3**, 112 (1982).

[34] E. Anklam, H. Mohan, and K.-D. Asmus, Helv. Chim. Acta **70**, 2110 (1987).

[35] E. Anklam, H. Mohan, and K.-D. Asmus, J. Chem. Soc., Chem. Commun., 629 (1987).

[36] E. Anklam, H. Mohan, and K.-D. Asmus, J. Chem. Soc. Perkin Trans 2, 1297 (1988).

[37] M.H. Champagne, M.W. Mullins, A.O. Colson, and M.D. Sevilla, J. Phys. Chem. **95**, 6487 (1991).

[38] K. Nishikada and Ff. Williams, Chem. Phys. Lett. **34**, 302 (1975).

[39] H. Fujihara, R. Akaishi, and N. Furukawa, Chem. Lett., 549 (1990).

[40] R. Müller, L. Lamberts, and M. Evers, Electrochim. Acta, **39**, 2507 (1994).

[41] R. Müller, Ph. D. Thesis, Facultés Universitaires N.D. de la Paix, 1995, Namur (Belgium).

[42] R. Müller, L. Lamberts, and M. Evers, J. Electroanal. Chem. **401**, 183 (1996).

[43] R. Müller, L. Lamberts, and M. Evers, J. Electroanal. Chem. **407**, 175 (1996).

[44] R. Müller, L. Lamberts, and M. Evers, J. Electroanal. Chem. **417**, 35 (1996).

[45] R. Müller, J. Heinze, L. Lamberts, and L. Christiaens, J. Electrochem. Soc. **145**, 541 (1998).

[46] A.J. Bard and L.R. Faulkner, "Electrochemical methods. Fundamentals and Applications.", Wiley (New York), 1980, p. 96.

[47] J.J.P. Stewart, J. Comput. Chem. **10**, 209 (1989).

[48] W.J. Hehre, R. Ditchfield, and J.A. Pople, J. Chem. Phys. 56, 2257 (1972).

[49] M.L. McKee, J. Phys. Chem. **96**, 1675 (1992).

[50] T. Clark, J. Comput. Chem. **2**, 261 (1981).

[51] H. Fujihara, R. Akaishi, A. Nakamura, and N. Furukawa, Tetrahed. Lett. **31**, 6375 (1990).

[52] H. Fujihara, Y. Ueno, J.-J. Chiu, and N. Furukawa, Chem. Lett., 1649 (1991).

[53] J. Heinze, Angew. Chem. Int. Ed. **23**, 831 (1984).

[54] G. Bontempelli, F. Magno, G.A. Mazzochin, and R. Seeber, Annali di Chimica, **79**, 102 (1989).