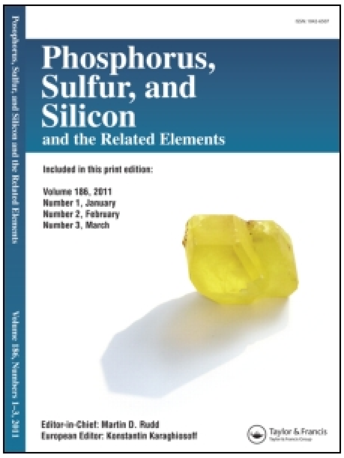

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WEAKLY BONDING INTERACTIONS IN ORGANOCHALCOGEN CHEMISTRY

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INTRODUCTION

Weakly bonding interactions are a subject of interest for many areas of chemistry. For example, these interatomic forces are central in the association processes that lead to molecular recognition, self-assembly of supramolecular structures, crystal packing and crystal growth. The activity of biological macromolecules is determined by the structures they adopt as a result of such forces and the interaction with their substrates. The useful macroscopic properties (electric, optical or magnetic) of some materials depend on organization at a molecular level and electronic communication between neighboring molecules.

The most widely recognized of such interactions is the hydrogen bond formed between groups containing acidic protons and electron-rich atoms, i.e. atoms which possess lone pairs. Closely related to the hydrogen bond is the formation of adducts by donation of electron density into the σ^* orbitals of halogen and interhalogen molecules; indeed the existence of a "chlorine bond" has been recently postulated.[1] Although the hydrogen bond is still the focus of intense research, the study of other weak interactions is receiving increasing attention.[2]

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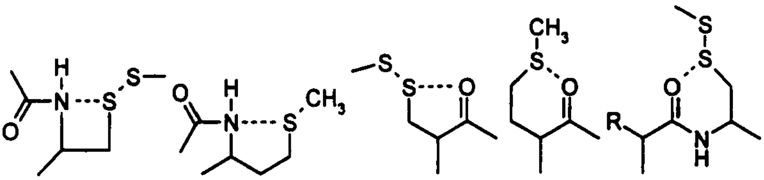
Divalent sulfur and, to a lesser extent, selenium are capable of participating in hydrogen bonds,[3] either in the role of H-donors or as H-acceptors. Because of their lone pairs they also form adducts with halogens.[4] These types of weak interactions can be readily detected and characterized by spectroscopic methods. However, the chalcogens S, Se and Te are also capable of participating in other weak interactions that were not recognized until X-ray structural characterization methods were widely available. In chalcogen compounds another heteroatom is often located at a distance longer than the standard single bond length, but substantially shorter than the sum of van der Waals radii. Some of these long bonds have been fully rationalized in terms of MO theory. For example, transannular chalcogen-chalcogen bonds arise from Jahn-Teller distortions and subsequent electron-pairing in π-electron rich heterocycles, e.g. 1,5-$(R_2P)_2N_4E_2$(E = S, Se).[5] Intermolecular chalcogen-chalcogen contacts are involved in the cofacial dimerization of π-delocalized radicals in the solid state.[6]

More intriguing are the short intramolecular contacts that occur between atoms that have closed shells. In recent years, several studies have identified consistent structural patterns and attributed at least a weakly bonding character to such interactions, promoting further investigations into their chemical and spectroscopic consequences. In this overview the growing importance of this phenomenon will be illustrated by selected examples beginning with a discussion of molecular structures. This will be followed by sections on isomerization processes, electronic structures, spectroscopic properties, and the modification of reactivity of these chalcogen compounds including the stabilization of reactive functional groups.

MOLECULAR STRUCTURES

Information in crystallographic databases reveals that close interatomic contacts involving chalcogen atoms are a recurrent phenomenon; a 1985 search on the Cambridge Structural Database found 755 cases of S···O contacts[7] Chalcogens also display this type of interaction with other electron-rich atoms, e.g. nitrogen, halogens and other chalcogen atoms. It is most frequently observed as an intramolecular phenomenon. Similar interactions can be found in large biomolecules; an analysis of results deposited at the Protein Data Bank revealed that 28% of S···O and S···N contacts in serine proteinases are shorter than 3.05 Å (see Table I).[8] Contacts to oxygen are more abundant than those to nitrogen. They may occur in the same residue or between neighbors of the peptide chain. Four-, five- and, occasionally, six-membered rings can be observed (Scheme 1). A feature that is unique to the proteins is the participation of sulfur atoms in bifurcated N···S···N or O···S···O contacts. It has been suggested that these interactions may play a role in protein structure and function.



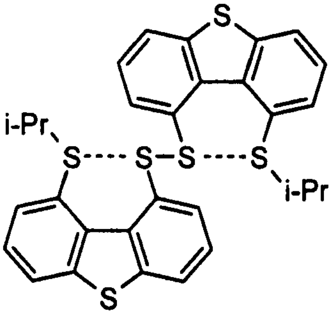
SCHEME 1

TABLE I Sums of Van der Waals Radii (Å)[a]

S···N	3.35	Se···N	3.45	Te···N	3.61
S···O	3.32	Se···O	3.42	Te···O	3.58
S···S	3.60	Se···Se	3.80	Te···Te	4.12
S···Se	3.70	Se···Te	3.96		
S···Te	3.86				

[a] Taken from Alcock, N.W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

The orientation of the atom in contact with a divalent sulfur atom falls into one of two categories.[9] Atoms that may be regarded as electron-acceptors or electrophiles (A), approach the chalcogen at ca. 20° from the plane X-S-Y (Scheme 2A). Other atoms that behave as electron-donors of nucleophiles (D) lie within the X-S-Y plane, preferably along the extension of one of the covalent bonds (Scheme 2B). Most short intramolecular contacts adopt the latter orientation. This anisotropy is a clear indication that these short contacts between chalcogen and electron-rich atoms have some bonding character, i.e. they are subject to the geometric restrictions of orbital overlap. Even in those cases where the chalcogen has a contact with another atom of the same element, this interpretation can be applied and the role of each atom inferred from the geometric arrangement.[10] In the structures of the sulfur and selenium compounds **1**[11] and **2**[12] the terminal chalcogens seem to act as donors towards the atoms in the dichalcogenide bridge. This geometry closely resembles that of **3**, in which the nitrogen lone pairs are clearly oriented towards the Se-Se link.[13] These geometric considerations help to clarify the nature of the weak Se···H interactions observed in the boat and chair conformers of the diselenocin **4**, d(Se···H) = 2.86 and 2.92 Å, respectively.[14] The relative orientation of the selenium bonds indicates that the chalcogen acts as an electron donor.



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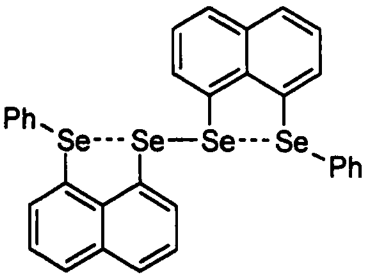

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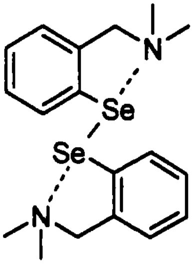

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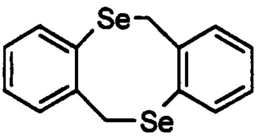
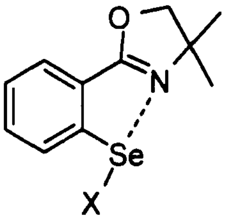
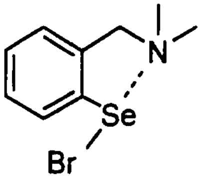


4

Several structural determinations indicate that the E···D interaction is highly influenced by the electronegativity of the opposite group X. In the series **5a-c** the Se···N distances are 2.05 Å for x = Cl, 2.06 Å for Br and 2.13 Å for I.[15] In the diselenide **3** the Se···N distance of 2.86 Å is much longer than that in the bromide **6** (2.14 Å).[13] The strength of the chalcogen-nitrogen interaction can also be enhanced by introducing substituents with an electron-withdrawing effect on sulfur, as demonstrated by comparison of the S···N distances in **7** (2.61 Å) and **8** (2.10 Å).[16]



5a, X = Cl
5b, X = Br
5c, X = I



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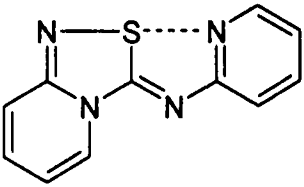

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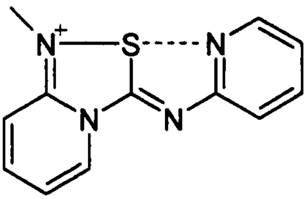

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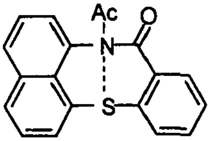
The heavier chalcogens seem more prone towards secondary interactions than sulfur. In particular, the chemistry of tellurium has plentiful examples of "intramolecular coordination" in derivatives such as diazenes, Schiff bases, pyridines, amines, and carbonylic compounds.[17] The oxidation state of the chalcogen is also influential; S(IV) centers have stronger interactions than S(II). The thiazocine derivative **9** displays a S···N distance longer than that of **10**, 2.968 Å and 2.753–2.832 Å respectively.[18]

A **B**

SCHEME 2

The S(IV) derivative **11** has a sulfurane-like trigonal bipyramidal geometry with d(S···O) = 2.68 Å and ∠ OSN = 171.0° indicating that S=N double bonds favor secondary contacts.[19]



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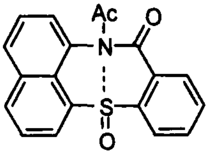

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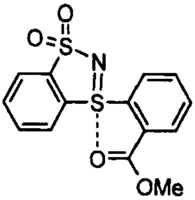

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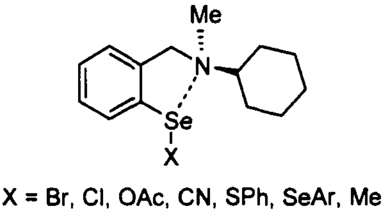
NMR STUDIES: ISOMERIZATION PROCESSES

The weak intramolecular interactions observed in the solid state for many chalcogen compounds may be reversibly broken in solution at moderate temperatures resulting in isomerization processes. In certain cases NMR solution studies can provide further insight into the nature of these interactions. For example, the rotational barrier for the exchange of the benzylic protons in 2-selenobenzylamine derivatives **12** includes the dissociation of the Se···N contact. The interaction energy estimated from VT NMR studies correlates with the electrophilicity of the substituent X. It ranges from > 79 kJ mol^{-1} for X = Cl or Br to < 32 kJ mol^{-1} for X = SeAr or CH_3.[20]



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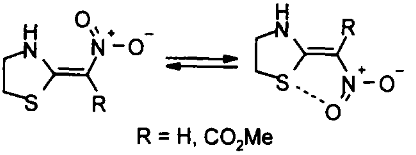

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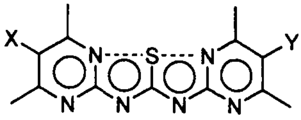

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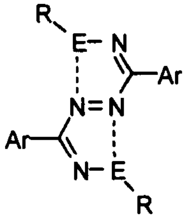
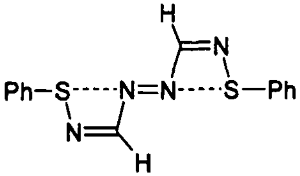
These isomerization processes can be dependent on the nature of the solvent. Compound **13**exists in the *E* configuration in $CHCl_3$, but it isomerizes to the *Z* form in DMSO with K = 4.[21] The rotational barrier of the tetrazathiapentalenes **14** (ca. 67 kJ mol^{-1}) is influenced by the donor/acceptor ability of the substituents x and Y through the S···N short contacts.[22] Solvents with acidic protons seem to increase the magnitude of the barrier. Solvents which are good Lewis bases decrease the magnitude of the barrier, due to solvation of the transition state. On the other hand, Lewis acids have no consistent effect.

Diazene derivatives of the type REN=C(R′)N=NC(R′)=NER have a rich structural chemistry.[23,24,25] The selenium derivatives **15a,b** display a *Z,E,Z* conformation with two short 1,5- Se···N contacts (2.65 Å). Several sulfur analogs **15c-g** have the same structure. A different *Z,E,Z* conformer **16** with two 1,4- S···N contacts (2.83 Å) has also been characterized.[24] A third type of diazene is the *E,E,E* isomer **17a,b**, with no intramolecular short contacts;[25] the oxygen analog **17c** also displays this structure. Compound **16** is the only member of this family that displays an equilibrium between different conformers.[24] At room temperature the ^1H NMR spectrum of **16** consists of four singlets in the region δ 8.5–9.5 ppm (Figure 1).



15a, E = Se, R = Me, Ar = Ph
15b, E = Se, R = Ar = Ph
15c, E = S, R = Ar = Ph
15d, E = S, R = Ph, Ar = 4-$CH_3C_6H_4$
15e, E = S, R = Ar = 4-$CH_3C_6H_4$
15f, E = S, R = Ph, Ar = 4-$CF_3C_6H_4$
15g, E = S, R = Ph, Ar= 4-BrC_6H_4



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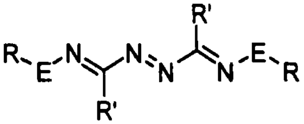


17a, E = S, R = Ph, R' = 2-BrC_6H_4
17b, E = S, R = Ph, R' = 2-$CF_3C_6H_4$
17c, E = O, R = R' = H

The relative intensities of these four resonances are independent suggesting that each one corresponds to the formamidinic proton of a symmetrical geometrical isomer. In toluene solution the middle two signals coalesce on heating to 330 K and the two other signals also broaden. At higher temperature all four resonances collapse to give a singlet. These observations may be attributed to exchange between the *E,E,E* rotamers **III** and **V** (via C-N bond rotation) and, subsequently, an exchange with the isomers **I** and **II**. The higher energy of this second exchange process is ascribed to the intramolecular S···N interactions in **I** and **II**. The ^1H NMR spectra in CH_2Cl_2 at low temperatures reveal a second exchange process (Figure 1). The outer resonances do not change upon cooling, consistent with the assignment of these signals to the thermodynamically most stable isomers. However, the middle two resonances coalesce and broaden on cooling to

210 K indicating that a very low energy exchange process is occurring even at this temperature.[24]

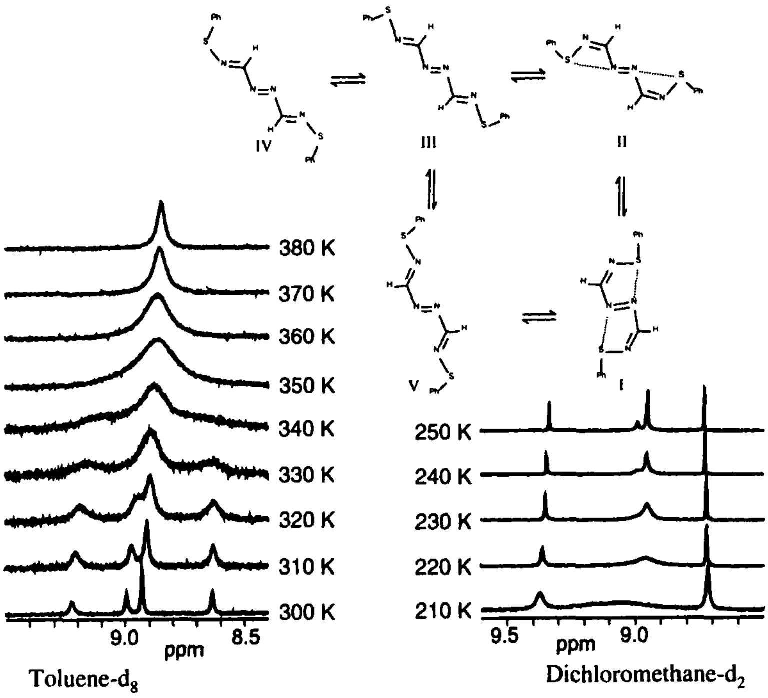
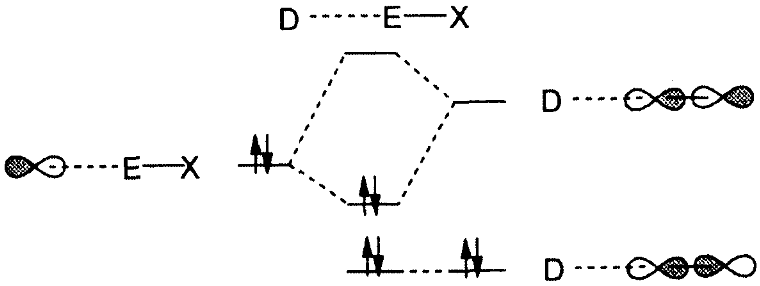


FIGURE 1 VT ^{1}H NMR spectra of **16**

MO CALCULATIONS: ELECTRONIC STRUCTURES

Early calculations were based on semiempirical methods and failed to identify any bonding character in these interactions. Therefore, it was common to consider them as "non-bonded interactions". The geometrical trends discussed above were interpreted in terms of nonspherical van der Waals surfaces, the large polarizabilities of chalcogen atoms or the diffuse nature of their orbitals. Occasionally *d* orbitals were invoked to explain these "secondary" bonds.

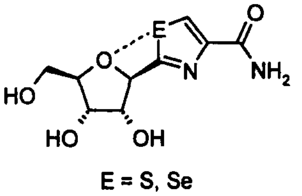
As more rigorous *ab initio* computational methods became applicable to heavy elements, better bonding descriptions became available. Calcula-



SCHEME 3

tions on a model compound for the S, Se interaction with the furanose oxygen in thiazole and selenazole nucleosides **18** suggested that the interaction of ca. 16 kJ mol^{-1}has a mainly electrostatic nature, due to the positive partial charge on the chalcogen.[26] However, this interpretation is incomplete. Adducts of sulfonium ions (R_3S^+) with water are formed by stronger electrostatic interactions, but the calculated S···O distance is 2.917 – 2.990 Å, even longer than that observed in many S···O intramolecular contacts.[27] Thus it is apparent that a contribution from covalent interactions is required to explain the E···D contacts.

In a computational study of 1,5 S···O interactions two conformations for the model X-S-A=B-Y(Z)=O, **19** and **20**, were considered.[28] The former was consistently more stable by 2.5 to 46 kJ mol^{-1}. A single bond character of 10–30% was attributed to these interactions.



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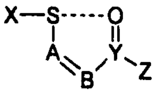

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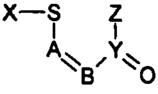

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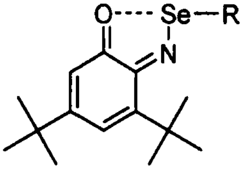
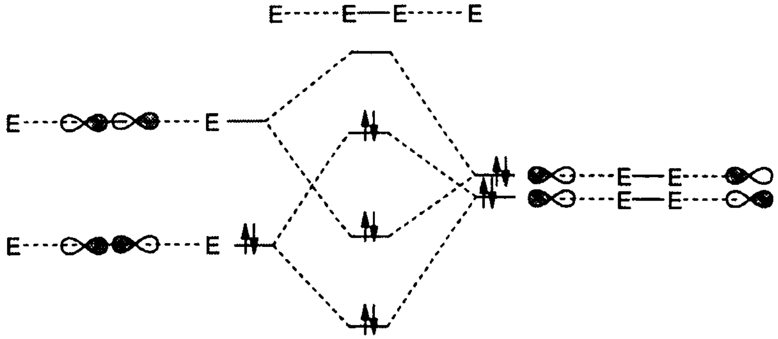
A very common interpretation of the interaction of chalcogens with nucleophiles considers donation of electron density from a lone pair into the σ^*_{SX} orbital. As the degree of covalency increases, a hypervalent three-center four-electron bond is formed (Scheme 3). This has been applied in a study of selenoquinones **21** with short Se···O contacts.[29] The concept explains and reproduces the trend observed for d(N···Se) as a function of the substituent X.[20] The three-center hypervalent bond description can be easily extended to explain the double contacts observed in disulfides and diselenides such as **1** and **2**, the linear arrangement implies a four-center six-electron bond model (Scheme 4).[12] Real systems fall somewhere between "secondary" (n-σ^*) interactions and hypervalent (3c-4e) bonds. The two extremes can be distinguished by the correlation of X-E and E···X′ distances.[30] In the hypervalent case both bond distances decrease simultaneously, whereas in the "secondary" bond the distances are anticorrelated.



R = Ph, Me

21



SCHEME 4

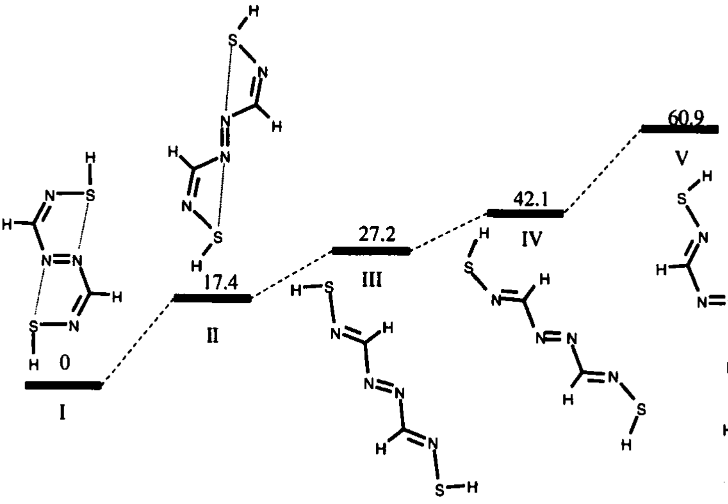


FIGURE 2 Energy level diagram for the geometric isomers of HSN=C(H)N=NC(H)=NSH

DFT calculations on model compounds allowed a thorough investigation of diazene-chalcogen interactions in **15**, **16** and other isomers.[25] Five different geometries were considered for HSN=C(H)-N=N-C(H)=NSH (Figure 2). A total bonding energy analysis showed that the isomer with 1,5-S···N interactions (**I**) is the most stable. However, the structure with 1,4-S···N contacts (**II**) is only 17.4 kJ mol^{-1} higher in energy. The other structurally characterized conformer **17a,b** corresponds precisely to the third most stable geometry (**III**). A symmetry-based analysis for **I** provides a detailed bonding description. It is evident that the simplistic n-σ^* scheme neglects the lone pair of the chalcogen, which has an orientation and energy suitable to interact repulsively with the donating lone pair of the -N=N- group. A second neglected interaction is "π-back donation" into a suitable acceptor orbital, such as $\pi^*_{N=N}$. The contributions to the total atomization energy between geometries **I** and **V** indicate that, while the σ interactions are destabilizing, the π interactions are stabilizing. Larger stabilization energies (74.4 and 144.4 kJ mol^{-1}) for the heavier chalcogens Se and Te, respectively, were found. A fragment analysis revealed that the chalcogen···diazene close contact is better described as a weak bonding interaction involving donation from a chalcogen lone pair π_{Elp} into $\pi^*_{N=N}$

(Figure 3). The resulting molecular orbital has an additional contribution from the carbon atoms (Figure 4). The interaction with the σ^* orbitals is less effective and only alleviates the repulsive forces. Delocalization of electron density onto two incipient five-membered rings provides additional stabilization. It follows that these intramolecular contacts will be favored by enhancing the orbital interactions in the π framework.

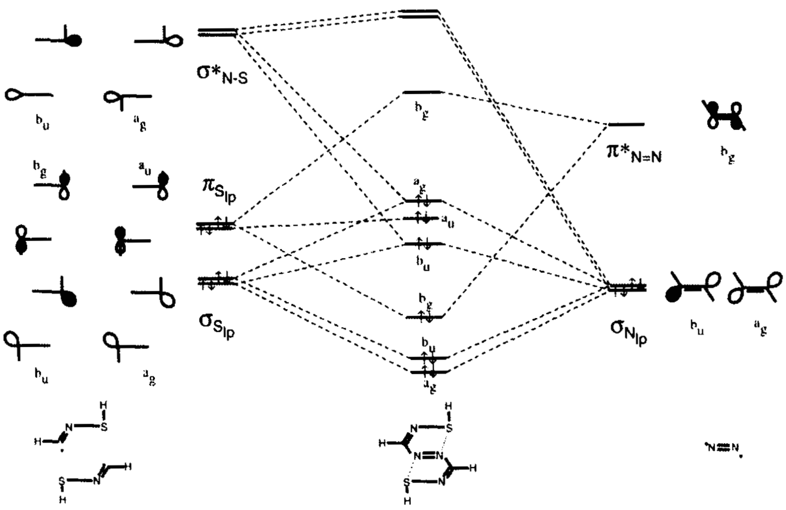
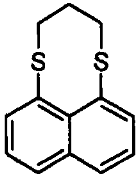


FIGURE 3 Orbital Interaction Diagram for the fragments ·N=N· and $(HSN{=}C(H){\cdot})_2$

SPECTROSCOPIC STUDIES

Unambiguous detection of intramolecular contacts requires structural determination by diffraction methods. In several cases the effect on the electronic structure is too small to be detected by spectroscopic means. Vibronic analysis derived from *ab initio* calculations on the family of compounds **22–26** indicates that, despite the short S···S separation in the sulfide-sulfoxide and bisdisulfoxide molecules (3.00 Å in **23**and 3.05 Å in **24**), there is no significant change in the frequencies of the normal vibrational modes of the molecules.[31]

The contact between a carbonyl oxygen atom and a chalcogen in **21** causes a decrease in the frequency of $\nu_{C=O}$ which has been correlated to



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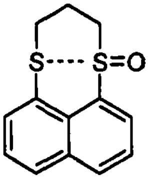

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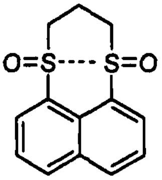

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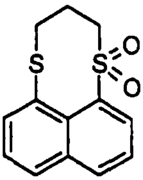

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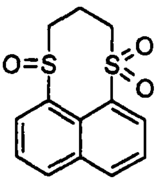
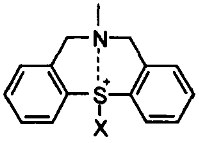


26

the strength of the interaction.[29] However, the ^{77}Se NMR chemical shifts do not seem to depend on the strength of the interaction. Coupling constants may be a better probe. Recently a weak intramolecular Se···F interaction in *o*-selenobenzyl fluoride derivatives was identified by measurement of $J(Se\cdots F) = 22.7–84.2$ Hz in solution.[32] The thiocine derivatives **27** display short S···N distances (2.09 – 2.60 Å)[33] and their ^{15}N and $^{1}H_{N\text{-}Me}$ NMR chemical shifts correlate with the electronegativity of X.[34]



X = Cl, OMe, Me, O^{-}

27

MODIFICATION OF REACTIVITY

Participation of a chalcogen atom in an intramolecular interaction influences its reactivity by steric or electronic effects. This may lead to unique reaction patterns, including stereochemical control. Such interactions may also stabilize reactive functional groups enabling the isolation of otherwise unstable species or their use as transient intermediates.

The sulfur (II) center involved in an interannular contact with nitrogen in **28** is remarkably resistant to oxidation. An excess of *m*-chloroperbenzoic acid reacts preferentially with the C=N double bond producing **29**.[35] As a

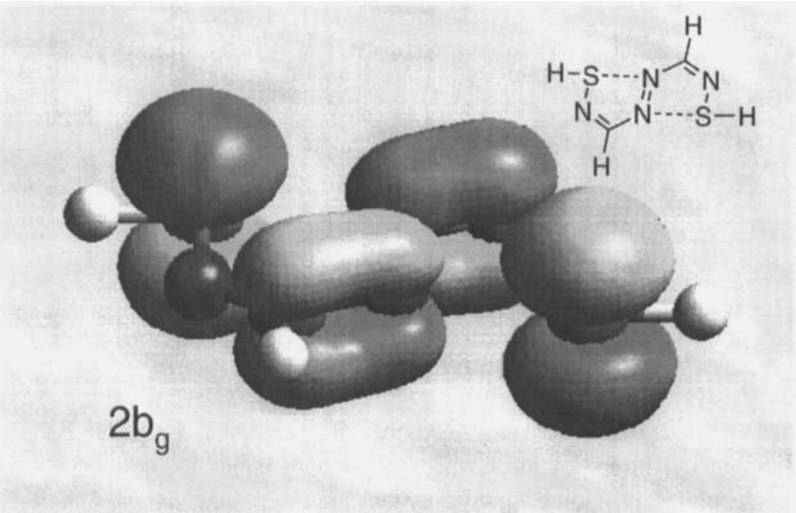
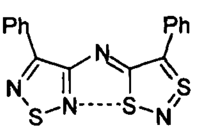
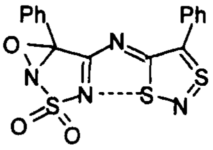


FIGURE 4 HOMO of HSN=C(H)N=NC(H)=NSH, conformer I

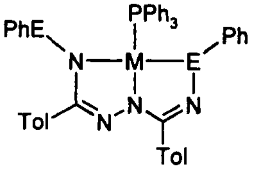
contrast, the two sulfur atoms of **15e** are oxidized readily to S(VI) with simultaneous reduction of the N=N double bond and formation of a thiatriazole ring to yield **30** (Scheme 5).[36] The reaction probably proceeds via the formation of a sulfoxide intermediate followed by immediate ring closure and sequential oxidation of the second S(II) center. Diazenes of the type **15** are remarkably resistant to protonation. However, the chalcogen···nitrogen linkages are readily disrupted upon oxidative addition with $Pd(PPh_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$ to produce the complexes **31** with N-N bond lengths of 1.40–1.42 Å indicating formal reduction of the diazene to an azine.[37]



28

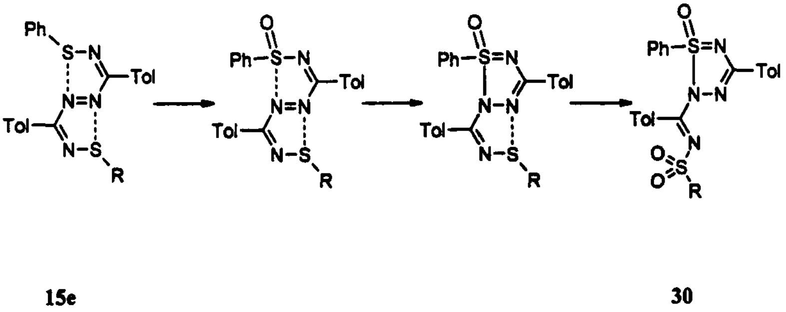


29



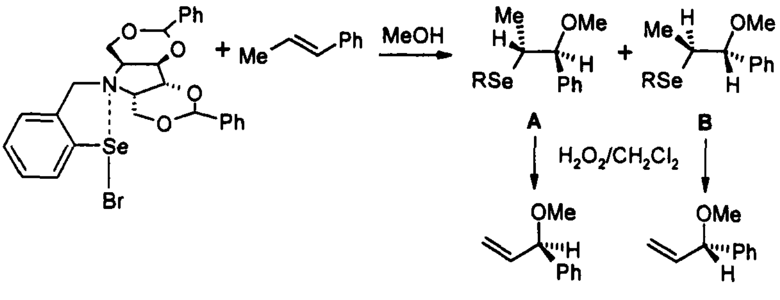
M = Pt, Pd
E = S, Se

31



SCHEME 5

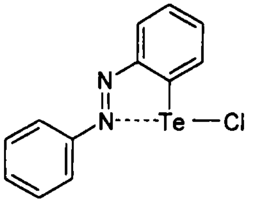
Selenenyl bromides react with C=C double bonds in the presence of nucleophiles, providing a convenient route to introduce various functional groups. The reaction proceeds with facility, but affords a racemic mixture. The modified reagent **32** contains a chiral amine in close interaction with the selenium atom. It reacts with olefins affording up to 97% ee of isomer A in Scheme 6.[38]



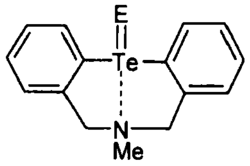
SCHEME 6

Te (II) compounds of the type ArTeCl are stabilized only when Ar is an azobenzene **33**.[17] Presumably intramolecular coordination hinders the disproportionation reaction. Transannular Te···N interactions have also been employed to stabilize compounds with Te=E (E = S, Se) double bonds,

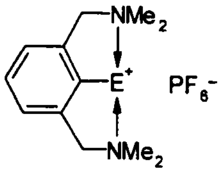
34,[39] and the first aryl-selenenium and -tellurenium cations (ArE$^+$, E = Se, Te)[40] **35**. In **34b** the Te-Se bond length is 2.445 Å (cf. 2.54 Å for a Te-S single bond) and d(Te···N) = 2.620 Å.[39]



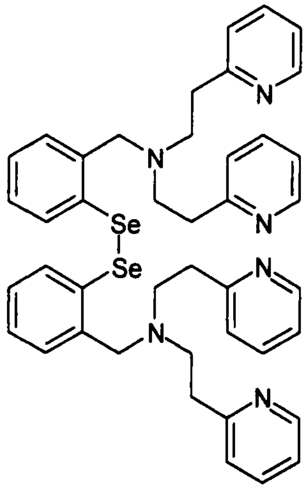
33



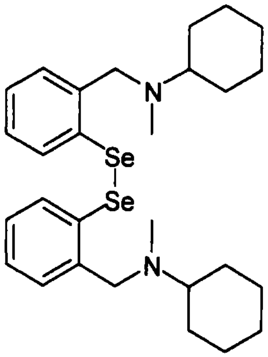
34a, E = S
34b, E = Se



35a, E = Se
35b, E = Te



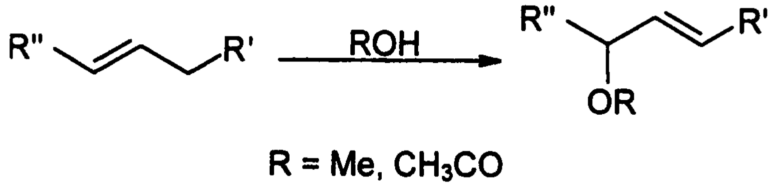
36



37

Before the report of **5c** the only known selenenyl iodide was stabilized by very bulky groups.[15] In a similar way, the Se···N interaction stabilizes a transient selenenic acid ArSeOH.[41] Through such a reactive intermediate, the diselenides **36** and **37** catalyze the reaction of oxidation of alkenes to allylic esters or ethers in the presence of sodium persulfate

(Scheme 7).[42] Compound **37** can also catalyze the oxidation of thiols to disulfides by hydrogen peroxide serving as a model to study the role of the amino nitrogens located at the active center of glutatione peroxidase.[43] Characterization of the intermediate steps by ^{77}Se NMR and kinetic studies indicate that the model behave in the same way as the enzyme, although the latter posseses two nitrogen atoms in proximity to the selenium of a selenocysteine. The proximal nitrogen is thought to play an additional role activating the selenol into selenolate.



SCHEME 7

CONCLUSIONS AND OUTLOOK

The availability of low-lying σ^* orbitals as well as lone pairs enables the chalcogens to engage in weak bonds, particularly with electron-rich atoms. The close contacts are influenced by a combination of factors including steric and electrostatic effects, as well as attractive and repulsive σ and π orbital interactions. The stabilizing contributions are stronger for the heavier chalcogens, especially when bonded to electron-withdrawing groups.

A better understanding of these structural features has begun to guide the design of systems that take advantage of the ability of weak bonding interactions to stabilize unusual functional groups and provide useful reagents for synthesis. It can be anticipated that similar strategies will lead to novel protective groups and synthons.

These interactions could be of particular advantage in materials science, although they have received limited attention. The expectation that careful design of a molecule will direct the processes of organization and crystal growth to generate functional structures has made self-assembly an area of intense research. An enormous amount of work has been devoted to the construction of self-assembled structures held together by noncovalent forces, mainly hydrogen bonds. As theoretical and experimental studies of the chalcogen-based weak interactions indicate that their binding energy values are comparable to those of some hydrogen bonds, it should be possible to build supramolecular entities based on organo-chalcogen molecules. Using noncovalent interactions other than hydrogen bonds would allow the incorporation into supramolecular structures of species and processes that are not compatible with acidic hydrogen atoms.

Although weakly bonding interactions of the chalcogens are observed most frequently as intramolecular contacts, there are important examples in the literature of intermolecular association. It has been shown that the electric conductivity of sulfur and selenium organic compounds in the solid state is favored by the formation of E···E networks.[44] In one attempt to direct the structure of a material, the 1,2,3,5-dithia- and diselenadiazolyl radicals $[NCC_6H_4CN_2E_2]\cdot(E = S, Se)$ were prepared. The dimer units form ribbon-like arrays connected by head-to-tail CN···E contacts that are packed in an antiparallel fashion with no close interdimer E···E contacts.[45]

Acknowledgements

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References

1. Legon, A. C. *Chem. Eur. J.* **1998**, *4*, 1890–1897.
2. Desiraju, G. R.; Sharma, C. V. K. in *The Crystal as a Supramolecular Entity, Perspectives in Supramolecular Chemistry*, Ed. Desiraju, G. R., John Wiley & Sons, Chichester, **1996**, *2*, 31–61.
3. Allen, F. H.; Bird, C. M.; Rowland, R. S., Raithby, P. R. *Acta Crystallogr. Sect. B* **1997**, *B53*, 696–701.
4. (a) Drozdova, Y.; Steudel, R.; Koch, W.; Miaskiewicz, K.; Topol, I.A. *Chem. Eur. J.* **1999**, *5*, 1936–1943.
   (b) Aragoni, M.C.; Arca, M.; Devillanova, F.A.; Garau, A.; Isaia, F.; Lippolis, V.; Verani, G. *Coord. Chem. Rev.* **1999**, *184*, 271–290.
   (c) Bock, H; Havlas, Z.; Rauschenbach, A.; Näther, C.; Kleine, M. *Chem. Commun.* **1996**, 1529–1530.
5. (a) Chivers T.; Doxsee, D. D.; Edwards, M.; Hilts, R. W. in *The Chemistry of Inorganic Ring Systems, Stud. Inorg. Chem.*, Ed. Steudel, R., Elsevier, Amsterdam, **1992**, *14*, 271–294.
   (b) Oakley, R.T. *Prog. Inorg. Chem.* **1988**, *36*, 299–421.
   (c) Chivers T. *Acc. Chem. Res.* **1984**, *17*, 166–171.
6. (a) Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S.H.; Haddon, R. C.; Oakley, R. T.; Palstra, T. T. M., Perel, A. S.; Schneemeyer, L. F.; Waszcak, J. V. *Nature* **1993**, *365*, 821–822.
   (b) Rawson, J. M.; Banister, A. J.; Lavender, I. *Adv. Heterocyclic. Chem.* **1995**, *62*, 137–245.

7. Kucsman, A.; Kapovits, I. in *Organic Sulfur Chemistry*, Ed. Bernardi, F; Csizmadia, I.G.; Mangini, A., Elsevier, Amsterdam, **1985**, 191–245.
8. Vajda, T. *J. Mol. Struct.* **1984**, *125*, 159–165.
9. Rosenfield, R. E.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 4860–4862.
10. Guru Row, T. N.; Parthasarathy, R. *J. Am. Chem. Soc.* **1981**, *103*, 477–479.
11. Kimura, T.; Izumi, Y.; Horn, E.; Furukawa, N. *Heteroatom Chem.* **1996**, *7*, 313–322.
12. Nakanishi, W.; Hayashi, S.; Toyota, S. *Chem. Commun.* **1996**, 371–372.
13. Kaur, R.; Singh, H. B.; Patel, R. P. *J. Chem. Soc. Dalton Trans.* **1996**, 2719–2726.
14. Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 4463–4464.
15. Mugesh, G.; Panda, A.; Singh, H. B.; Butcher, R. J. *Chem. Eur. J.* **1999**, *5*, 1411–1421.
16. L'abbe, G; Van Meervelt, L.; Emmers, S.; Dehaen, W.; Toppets, S. *J. Heterocycl. Chem.* **1992**, *29*, 1765–1768.
17. Sudha, N.; Singh, H. B. *Coord. Chem. Rev.* **1994**, *135/136*, 469–515.
18. Kuti, M.; Rábai, J.; Kapovits, I.; Jalsovski, I.; Argay, Gy.; Kálmán, A.; Párkány, L. *J. Mol. Struct.* **1996**, *382*, 1–11.
19. Kuti, M.; Rábai, J.; Kapovits, I.; Kucsman, A.; Párkány, L.; Argay, Gy.; Kálmán, A. *J. Mol. Struct.* **1996**, *382*, 13–21.
20. Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1996**, *118*, 8077–8084.
21. Rajappa, S.; Bhawal, B. M.; Deshmukh, A. R. A. S.; Manjunatha, S. G.; Chandrasekhar, J. *Chem. Commun.* **1989**, 1729–1730.
22. Ohkata, K.; Ohsugi, M.; Yamamoto, K.; Ohsawa, M.; Akiba, K. *J. Am. Chem. Soc.* **1996**, *118*, 6355–6359.
23. (a) Chandrasekhar, V.; Chivers, T.; Fait, J. F.; Kumaravel, S.S. *J. Am. Chem. Soc.* **1990**, *112*, 5373–5374.
    (b) Chandrasekhar, V.; Chivers, T.; Kumaravel, S. S.; Parvez, M.; Rao, M. N. S. *Inorg. Chem.* **1991**, *30*, 4125–30.
24. Chivers, T.; McGarvey, B.; Parvez, M.; Vargas-Baca, I.; Ziegler, T.; Zoricak, P. *Inorg. Chem.* **1996**, *35*, 3839–3847.
25. Chivers, T.; Krouse, I. H.; Parvez, M.; Vargas-Baca, I.; Ziegler, T.; Zoricak, P. *Inorg. Chem.* **1996**, *35*, 5836–5842.
26. Burling, F. T.; Goldstein, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 2313–2320.
27. Markham, G. D., Bock, C. W. *Struct. Chem.***1996**, 7, 281–300.
28. Angyan, J. G.; Poirer, R. A.; Kucsman, A.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1987**, *109*, 2237–2245.
29. Barton, D. H. R.; Hall, M. B.; Lin, Z.; Parekh, S. I.; Reibenspies, J. *J. Am. Chem. Soc.* **1993**, *115*, 5056–5059.
30. Landrum, G. A.; Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1887–1890.
31. Glass, R. S.; Adamowicz, L.; Broecker, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 1065–1072.
32. Iwaoka, M.; Komatsu, H.; Tomoda, S. *Chem. Lett.* **1998**, 969–970.
33. Akiba, K.; Takee, K.; Shimizu, Y.; Okhata, K. *J. Am. Chem.* Soc. **1986**, *108*, 6320–6327.
34. Ohkata, K.; Ohnishi, M.; Yoshinaga, K.; Akiba, K.-y.; Rongione, J. C.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 9270–9276.
35. Dunn, P. J.; Rees, C. W.; Slawin, A. M. Z.; Williams, D. J.; *Chem. Commun.* **1989**, 1134–1136.
36. Chandrasekhar, V.; Chivers, T.; Ellis, L.; Krouse, I.; Parvez, M.; Vargas-Baca, I. *Can. J. Chem.* **1997**, *75*, 1188–1194.
37. (a) Chivers, T.; McGregor, K.; Parvez, M. *Chem. Commun.* **1993**, 1021–1023.
    (b) Chivers, T.; McGregor, K.; Parvez, M. *Inorg. Chem.* **1994**, *33*, 2364–2369.
38. Fujita, K.-I.; Murata, K.; Iwaoka, M.; Tomoda, S. *Tetrahedron* **1997**, *53*, 2029–2048.
39. Fujihara, H.; Uehara, T.; Furukawa, N. *J. Am. Chem. Soc.* **1995**, *117*, 6388–6389.
40. Fujihara, H.; Mima, H.; Furukawa, N. *J. Am. Chem. Soc.* **1995**, *117*, 10153–10154.
41. Iwaoka, M.; Tomoda, S., *Phosphorus, Sulfur, Silicon Relat. Elem.* **1992**, *67*, 125–130.

42. Iwaoka, M.; Tomoda, S. *Chem. Commun.* **1992**, 1165–1167.
43. Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 2557–2561.
44. (a) Nishikawa, H.; Sato, T.; Kodama, T.; Ikemoto, I.; Kikuchi, K.; Anzai, H.; Yamada, J.-i. *J. Mater. Chem.* **1999**, *9*, 693–696.
(b) Tani, H.; Kawada, Y.; Azuma, N.; Ono, N. *Mol. Liq. Cryst.* **1997**, *296*, 19–30.
45. Cordes, A.W.; Haddon, R.C.; Hicks, R.G.; Oakley, R.T.; Palstra, T.T.M. *Inorg. Chem.* **1992**, *31*, 1802–1808.