Article
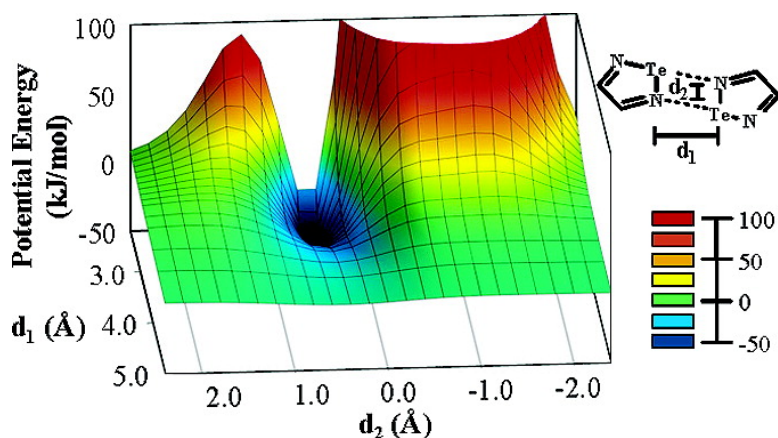
The Nature of the Supramolecular Association of 1,2,5-Chalcogenadiazoles

Anthony F. Cozzolino, Ignacio Vargas-Baca, Sarah Mansour, and Amir H. Mahmoudkhani

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 19 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

The Nature of the Supramolecular Association of 1,2,5-Chalcogenadiazoles

Anthony F. Cozzolino, Ignacio Vargas-Baca,* Sarah Mansour, and
Amir H. Mahmoudkhani

*Contribution from the Department of Chemistry, McMaster University,
1280 Main Street West, Hamilton, Ontario L8S 4M1*

Received October 1, 2004; E-mail: vargas@chemistry.mcmaster.ca

Abstract: Organochalcogen−nitrogen heterocycles such as the 1,2,5-chalcogenadiazoles have a distinct tendency to establish intermolecular links in the solid state through secondary bonding interactions E···N (E = S, Se, Te). The association of these molecules was examined in detail using relativistic density functional theory. Although there is an important electrostatic component, the interaction between these molecules is dominated by contributions arising from orbital mixing, which can be interpreted as the donation of a nitrogen lone pair into the chalcogen-centered antibonding orbitals. Because of its more polar character and lower-lying antibonding orbitals, the tellurium derivatives possess the strongest association energies; these are so large that the binding strength is comparable to that of some hydrogen bonds. In the absence of steric constraints, telluradiazoles associate in a coplanar fashion forming ribbon polymers. However, bulky susbstituents could be used to direct the formation of either helical chains or discrete dimers. In addition to its strength, the coplanar dimer is characterized by being rigid, yet no activation barrier is expected for the association/dissociation process. These attributes strongly indicate that tellurium−nitrogen heterocycles have great potential as building blocks in supramolecular architecture.

Introduction

The last two decades have witnessed remarkable progress in the construction of complex structures by the spontaneous assembly of small building blocks. Most of these achievements in supramolecular chemistry have been accomplished through the use of two types of interactions: hydrogen bonding and coordination of metal ions.[1−3] The use of other supramolecular forces would grant access to unique structures with unusual properties. In this context, aurophilic interactions are receiving increasing attention.[4−7] Heavy main-group elements often display short interatomic contacts that can be attributed to secondary bonding interactions (SBIs), attractive interactions between atoms that had previously satisfied their main valence. Some recent publications illustrate the ability of SBIs of heavy p-block elements to tailor the properties of materials and elicit unique chemistry. Dipolar molecules connected by −NO₂···I− Ar SBIs formed a noncentrosymmetric lattice capable of optical second-harmonic generation,[8] a chiral fluorocarbon was resolved thanks to the formation of an infinite helix through Br−···Br−
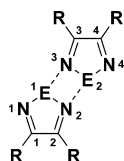
C SBIs,[9] chalcogen−chalcogen SBIs in tellurium- and selenium-substituted acetylenes assembled nanotubes that host organic solvents,[10−14] and the addition of a selenenyl halide to olefins was stereochemically controlled by the intramolecular SBI of Se with a chiral amine.[15] More examples in organochalcogen compounds are collected in a detailed review.[16]

More frequently than in hydrogen bonding and coordination chemistry, attempts to control the organization of molecules containing heavy main-group elements have resulted in unexpected structures, with absent SBIs in some instances. This led to the premature conclusion that SBIs centered on heavy main-group atoms are too weak and poorly directional to be reliably applied in supramolecular chemistry. It has been pointed out[17,18] that the actual problem is that the most effective SBI supramolecular synthons (the basic units that can be assembled by supramolecular forces) are yet to be identified. One way to accomplish this is through the systematic survey of published crystallographic data; using this method, Starbuck et al. have examined crystal structures of Sb(III) and Bi(III) compounds

(1) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: New York, 1995.
(2) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
(3) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383.
(4) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319.
(5) Desiraju, G. R. *Dalton* **2000**, 3745.
(6) Mohr, F.; Jennings, M. C.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 969.
(7) Vicente, J.; Chicote, M.-T.; Saura-Llamas, I.; Lagunas, M.-C.; De Arellano, M. C. R.; Gonzalez-Herrero, P.; Abrisqueta, M.-D.; Guerrero, R. *Met. Clust. Chem.* **1999**, *1*, 493.
(8) Sarma, J. A. R. P.; Allen, F. H.; Hoy, V. J.; Howard, J. A. K.; Thaimattam, R.; Biradha, K.; Desiraju, G. R. *Chem. Commun.* **1997**, 101.

(9) Farina, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G.; Vecchio, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2433.
(10) Gleiter, R.; Werz, D. B.; Rausch, B. J. *Chem. Eur. J.* **2003**, *9*, 2676.
(11) Werz, D. B.; Staeb, T. H.; Benisch, C.; Rausch, B. J.; Rominger, F.; Gleiter, R. *Org. Lett.* **2002**, *4*, 339.
(12) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Org. Chem.* **2002**, *67*, 4290.
(13) Werz, D. B.; Rausch, B. J.; Gleiter, R. *Tetrahedron Lett.* **2002**, *43*, 5767.
(14) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Am. Chem. Soc.* **2002**, *124*, 10638.
(15) Fujita, K.-i.; Murata, K.; Iwaoka, M.; Tomoda, S. *Tetrahedron* **1997**, *53*, 2029.
(16) Vargas-Baca, I.; Chivers, T. *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *164*, 207.
(17) Desiraju, G. R. *J. Mol. Struct.* **2003**, *656*, 5.
(18) Desiraju, G. R. *Chem. Commun.* **1997**, 1475.

Scheme 1

Scheme 2

Table 1. SBI Distances (Å) in 1,2,5-Chalcogenadiazoles

E	S	Se	Te
$r_{EvdW} + r_{NvdW}$[47]	3.26	3.36	3.54
E⋯N$_{(Average)}$	3.20	2.95	2.77

in search for the factors that favor supramolecular association with Lewis bases.[19] However, this approach is limited because it does not provide quantitative information on the inherent stability of the SBIs. The ideal supramolecular synthon should have a large bonding energy to provide thermodynamic stability, be strongly directional to guide the molecular arrangement, and be reversible to permit error self-correction in complex structures. Of course, all those attributes would be meaningless unless the building blocks are synthetically accessible.

With hydrogen bonds, the most effective supramolecular synthons are based on the paradigm of complementary units joined at multiple points of attachment; therefore, the corresponding precursors contain combinations of H-donor and H-acceptor groups. Greater stability is conferred by alternating the local dipole moments; this has afforded synthons so strong that bifunctional molecules assemble chains in solution that share the properties of true macromolecules.[20] Application of the same principles should lead to effective main-group supramolecular synthons. Heterocyclic molecules containing divalent chalcogens atoms in combination with other heteroatoms are well suited for this purpose. This concept was explored by Miyashi[21] and Yamahita[22] using heteropolycyclic molecules appended with auxiliary functional groups. Although the approach was successful in promoting intermolecular association to form extended two-dimensional lattices, the tight packing left no room for any pendant substituents that may confer functionality to the structure. One of the limiting factors in this case is that the removal of any attachment points weakens the structure, which causes the competing packing forces to strongly influence the arrangement in the crystal.

In search for more effective main-group supramolecular synthons based on SBIs, we have examined published structural data and used DFT computational modeling to evaluate prospective supramolecular synthons, with the intention of identifying the best candidates and applying them in future experimental investigations. Here, we report a detailed study of the nature of the supramolecular association of five-membered C_2N_2E heterocyles.

Results and Discussion

The crystal structures of compounds containing the 1,2,5-chalcogenadiazole ring often display intermolecular contacts that can be ascribed to SBIs. Of particular interest are those cases in which two rings are associated by two antiparallel E⋯N SBIs (E = S, S, Te), forming a four-membered cyclic supramolecular synthon (Scheme 1); this synthon may be repeated to link another molecule. A ribbon polymer is grown by repeating this operation (Scheme 2). The arrangement of these heterocycles

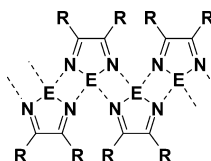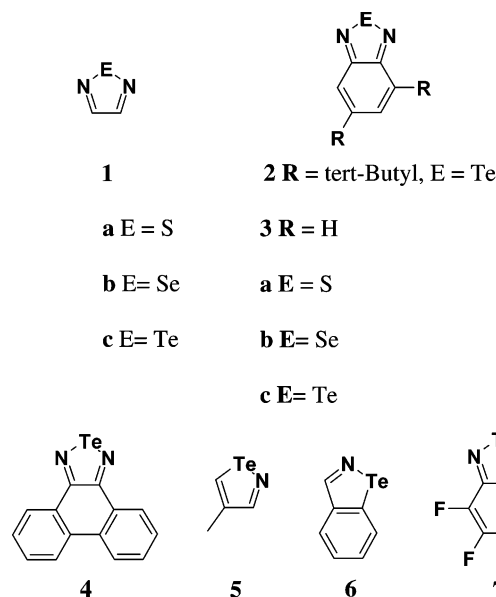is especially attractive as it leaves room for pendant functional groups. A survey of the Cambridge Structural Database (CSD)[23,24] was performed to identify those crystals where these features are observed.[21,22,25−46] This provided the average SBI distances that are compared in Table 1 to the sum of the corresponding van der Waals radii. The two sets of data follow opposite trends, suggesting that the tellurium SBIs are the strongest. The CSD survey also found that, while the selena- and telluradiazoles are more frequently associated in dimers and polymers, thiadiazoles most often do not appear to be associated, and those that do associate only make dimers.

A computational study using density functional theory was performed to understand the factors that control the association of these molecules, the influence of the nature of the chalcogen, and the viability of the 1,2,5-chalcogenadiazoles as building blocks for supramolecular structures. Models of the three parent 1,2,5-chalcogenadiazoles **1** (Chart 1) were fully optimized using all-electron basis sets. The zero order regular approximation

(19) Starbuck, J.; Norman, N. C.; Orpen, A. G. *New J. Chem.* **1999**, *23*, 969.
(20) Sijbesma, R. P.; Meijer, E. W. *Chem. Commun.* **2003**, 5.
(21) Suzuki, T.; Fujii, H.; Yamashita, Y.; Kabuto, C.; Tanaka, S.; Harasawa, M.; Mukai, T.; Miyashi, T. *J. Am. Chem. Soc.* **1992**, *114*, 3034.
(22) Ono, K.; Tanaka, S.; Yamashita, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1977.

(23) Allen, F. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 31.
(24) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, J. *J. Chem. Inf. Comput. Sci.* **1987**, *31*, 187.
(25) Esteban-Calderon, C.; Martinez-Ripoll, M.; Garcia-Blanco, S. *Acta Crystallogr., Sect. C* **1984**, *40*, 80.
(26) Barclay, T. M.; Cordes, A. W.; George, N. A.; Haddon, R. C.; Itkis, M. E.; Mashuta, M. S.; Oakley, R. T.; Patenaude, G. W.; Reed, R. W.; Richardson, J. F.; Zhang, H. *J. Am. Chem. Soc.* **1998**, *120*, 352.
(27) Yamashita, Y.; Eguchi, J.; Suzuki, T.; Kabuto, C.; Miyashi, T.; Tanaka, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 643.
(28) Bagryanskaya, I. Y.; Gatilov, Y. V.; Miller, A. O.; Shakirov, M. M.; Zibarev, A. V. *Heteroat. Chem.* **1994**, *5*, 561.
(29) Klimasenko, N. L.; Chetkina, L. A.; Ginzburg, S. L.; Neigauz, M. G.; Smelyanskaya, E. M. *Zh. Strukt. Khim.* **1973**, *14*, 108.
(30) Kane, J.; Schaeffer, R. *Cryst. Struct. Commun.* **1981**, *10*, 1403.
(31) Gieren, A.; Betz, H.; Hubner, T.; Lamm, V.; Neidlein, R.; Droste, D. *Z. Naturforsch., B* **1984**, *39*, 485.
(32) Yamashita, Y.; Saito, K.; Suzuki, T.; Kabuto, C.; Mukai, T.; Miyashi, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 434.
(33) Yamashita, Y.; Ono, K.; Tanaka, S.; Imaeda, K.; Inokuchi, H.; Sano, M. *Chem. Commun.* **1993**, 1803.
(34) Yamashita, Y.; Ono, K.; Tomura, M.; Tanaka, S. *Tetrahedron* **1997**, *53*, 10169.
(35) Hatta, T.; Kawano, M.; Imaizumi, Y.; Tsuge, A.; Moriguchi, T.; Maeda, H.; Tsuge, O. *Heterocycles* **1997**, *46*, 651.
(36) Fukushima, T.; Okazeri, N.; Miyashi, T.; Suzuki, K.; Yamashita, Y.; Suzuki, T. *Tetrahedron Lett.* **1999**, *40*, 1175.
(37) Richardson, C.; Steel, P. J. *Acta Crystallogr., Sect. C* **2001**, *57*, 197.
(38) Suzuki, T.; Fukushima, T.; Miyashi, T.; Tsuji, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2495.
(39) Mellini, M.; Merlino, S. *Acta Crystallogr., Sect. B* **1976**, *32*, 1074.
(40) Tian, W.; Grivas, S.; Olsson, K. *J. Chem. Soc., Perkin Trans. 1* **1993**, 257.
(41) Klimasenko, N. L.; Chetkina, L. A.; Gol'der, G. A. *Zh. Strukt. Khim.* **1973**, *14*, 515.
(42) Bertini, V.; Dapporto, P.; Lucchesini, F.; Sega, A.; Munno, A. D. *Acta Crystallogr., Sect. C* **1984**, *40*, 653.
(43) Neidlein, R.; Knecht, D.; Gieren, A.; Ruiz-Perez, C. *Z. Naturforsch., B* **1987**, *42*, 84.
(44) Chivers, T.; Gao, X.; Parvez, M. *Inorg. Chem.* **1996**, *35*, 9.
(45) Hanasaki, Y.; Watanabe, H.; Katsuura, K.; Takayama, H.; Shirakawa, S.; Yamaguchi, K.; Sakai, S.; Ijichi, K.; Fujiwara, M.; Konno, K.; Yokota, T.; Shigeta, S.; Baba, M. *J. Med. Chem.* **1995**, *38*, 2038.
(46) Mikhno, O. A.; Ezhkova, Z. I.; Zhdanov, G. S. *Kristallografiya* **1973**, *18*, 99.

Chart 1

1

2 R = tert-Butyl, E = Te

a E = S **3** R = H

b E= Se **a** E = S

c E= Te **b** E= Se

c E= Te

4   **5**   **6**   **7**

Table 2. Optimized Bond Lengths (Å) and Angles (°) for the Model Structures of 1,2,5-Chalcogenadiazoles and Their Dimers

E	S		Se		Te	
	1a	**1a$_2$**	1b	**1b$_2$**	1c	**1c$_2$**
E$_1$−N$_1$	1.653	1.658	1.837	1.835	2.053	2.071
E$_1$−N$_2$	1.653	1.658	1.837	1.845	2.053	2.064
N$_1$=C$_1$	1.331	1.331	1.314	1.317	1.309	1.303
N$_2$=C$_2$	1.331	1.332	1.314	1.317	1.309	1.304
C$_1$−C$_2$	1.423	1.421	1.440	1.437	1.453	1.456
C$_1$−H$_1$	1.089	1.089	1.092	1.093	1.096	1.098
C$_2$−H$_2$	1.089	1.089	1.092	1.092	1.096	1.095
E$_1$···N$_3$		3.199		2.924	2.604	
N$_1$−E$_1$−N$_2$	99.2	98.8	93.2	92.2	86.4	83.3
C$_1$=N$_1$−E$_1$	106.1	106.5	105.6	106.7	105.6	108.2
C$_2$=N$_2$−E$_1$	106.1	106.2	105.6	106.3	105.6	108.9
N$_1$=C$_1$−C$_2$	114.3	114.1	117.8	117.3	121.2	120.2
N$_2$=C$_2$−C$_1$	114.3	114.3	117.8	117.5	121.2	119.2
C$_1$−C$_2$−H$_2$	125.8	126.0	123.5	123.5	121.0	120.1
C$_2$−C$_1$−H$_1$	125.8	125.9	123.5	123.5	121.0	121.5

(ZORA) was used to account for relativistic effects. Although this is only essential for tellurium, the approach was applied to all molecules to ensure consistency. ZORA causes a small mismatch of total energy and gradients that may result in changes of molecular dimensions involving no heavy atoms at all. Test nonrelativistic calculations for all three molecules with the largest basis set available (frozen up to 4p for tellurium) produced structures that were marginally different, less than 0.003 Å in bond lengths and 0.2° in bond angles; the largest deviations were as expected in the Te−N distance and the N−Te−N angle which changed by 0.036 Å and 0.4°, respectively. The calculated molecular dimensions using relativistic corrections are gathered in Table 2. Along the **1a**−**1c** series, the C−C−N angle becomes progressively wider for the planar ring to accommodate the larger atoms and the N−E−N angle becomes more acute.

These "monomers" were used to construct models of supramolecular aggregates, beginning with the dimers, which were fully optimized. All three dimers converged to centrosymmetric coplanar structures with the two expected SBIs (Scheme 1), even in those cases where the optimization was started from two heterocycle molecules oriented arbitrarily from each other and

Table 3. Contributions to the Energy of Interaction between Two Chalcogenadiazole Molecules

E	contribution		
	reorganization	binding	ZPE
S	−0.08	−5.05	2.39
Se	0.43	−19.56	3.16
Te	4.17	−67.10	4.87
Te^a	4.12	−65.45	4.95
Te^b	2.64	−50.67	

[a] Core electrons frozen up to 4p. [b] Core electrons frozen up to 4d.

without any geometric constraints. These pairs are in principle stable because their energies are lower than those of the two isolated molecules and all their vibrational frequencies are real. The minimized structures of the rings in the dimers are compared to those of the isolated molecules in Table 2. The E···N SBI distances are in agreement with the average of the distances experimentally observed. The calculated structural modifications of the rings upon supramolecular association are small but significant and most noticeable in the chalcogen-centered dimensions. The largest changes pertain to the telluradiazole case, where the N−Te−N and the Te−N−C angles change as much as 3.1 and 3.2°. In view of the magnitude of these changes, it would not be appropriate to compare the calculated structure of the dimer with that of the polymer determined experimentally, such an analysis is left for models of the polymers themselves (vide infra).

The total interaction energy between two heterocycle molecules forming a dimer can be split in three contributions (eq 1): reorganization of the structure to adopt the geometry attained in the dimer, binding of the two fragments, and the zero-point energy correction. These contributions are presented in Table 3 for the three chalcogenadiazole rings. The magnitude of the total interaction energy increases in the same order observed for the E···N distances: **1a$_2$** (−2.82 kJ/mol) < **1b$_2$** (−15.54 kJ/mol) < **1c$_2$** (−53.85 kJ/mol). The last value is comparable to the strength of some hydrogen bonds. These calculations cannot account for London dispersion forces, but in any case these would only provide a small attractive contribution that would not significantly modify the results. A similar trend has been obtained using HF/3-21+G(dp) calculations for the dimers of chalcogen diamides.[83] Using VT NMR, Tomoda has estimated that Se···N interaction energies lie between −31.8 and −79.5 kJ/mol for intramolecularly coordinated amino-selenides.[48]

$$\Delta E_{\text{Total}} = 2\Delta E_{\text{Reorganization}} + \Delta E_{\text{Binding}} + \Delta \text{ZPE} \quad (1)$$

The reorganization energies are modest because all the structural changes are small; the largest such contribution is, as expected, for the tellurium case. The calculated reorganization energy for the thiadiazole dimer is very small and negative; this is likely an error due to the mismatch of energy and overlap in ZORA. The equivalent nonrelativistic calculation afforded a reorganization energy of just +0.01 kJ/mol.

The most straightforward interpretation of the binding energy is twice the energy of the individual SBI. A more complete description of the stability of the dimers is obtained by plotting the binding energy as a function of the EN distance as the rings

(47) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(48) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1996**, *118*, 8077.
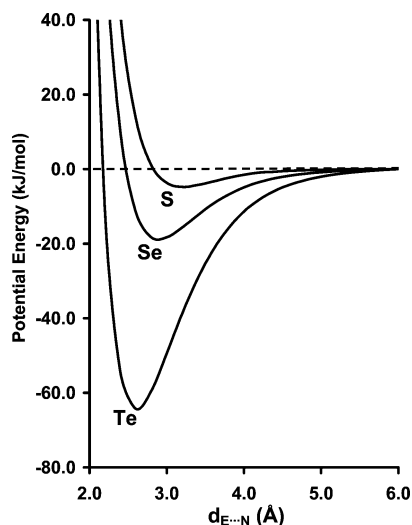
Figure 1. Potential energy curves for the in-plane dimerization of the 1,2,5-chalcogenadiazole rings trough two simultaneous antiparallel E···N (E = S, Se, Te) SBIs as a function of the intermolecular distance.
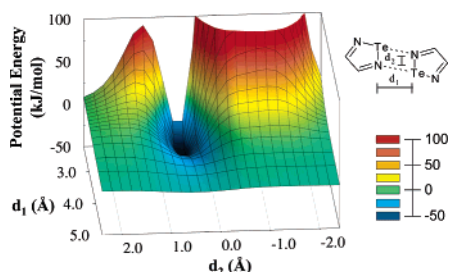
Figure 2. Potential energy surface for the in-plane deformation of the 1,2,5-telluradiazole ring.

are displaced along the direction of the E···N axes; such potential energy curves are displayed in Figure 1. This analysis reveals that the three heterocycle pairs sit in well-defined potential minima, and there is no activation barrier expected for the processes of association and dissociation of these molecular aggregates. Not only is the telluradiazole pair more stable than the selena- and thiadiazole cases, but it is also more difficult to deform by elongation of the SBIs. On the other extreme, the sulfur heterocycle dimers are very weakly bonded and have shallow potential wells.

For the most stable dimer, $1c_2$, the potential surface was explored in two dimensions with the use of a nonrelativistic basis set, a core frozen up to 4p and neglecting the relaxation energy at each point. Although this underestimated the binding energy by 16 kJ/mol, it was computationally much less expensive than the all-electron relativistic method. The potential surface calculated for the "in-plane" deformation of the dimers is presented in Figure 2. The potential well that corresponds to the formation of a stable dimer appears well defined. There are two large potential barriers that prevent the lateral movement of the rings with respect to each other because of the repulsion between lone pairs of nitrogen and tellurium. Similar calculations were performed to evaluate the cost of energy of shifting one ring away from the plane of the other and rotation of the one ring about the E···N axis. In both cases, the planar conformation was the most stable and steep slopes prevent any distortions. Additional calculations considered the possibility of face-to-face interactions driven by the molecular dipole moments but they failed to produce a minimum of potential

energy. All these results provide a semiquantitative view of the stability of the telluradiazole pair which, once formed, is a remarkably rigid structure and there should be no competing orientations for molecular association.

The position of the minima in the potential surfaces is dictated by the balance of three distance-dependent contributions:[49,50] the Pauli repulsion that arises from the interaction of completely occupied orbitals, the electrostatic that results from the local dipole moments created by differences of atomic electronegativity, and the interaction of empty and occupied orbitals. Figure 3 shows graphically the decomposition analysis for the dimers of the three heterocycles. Both the electrostatic and occupied-empty orbital contributions are stabilizing, the latter being always the most important. All three interactions are strengthened as the intermolecular separation decreases. The three plots are similar, the main difference being that at any distance, the magnitudes of the interactions increase with the weight of the chalcogen. Coulombic interactions in this case take place mainly between the negative nitrogen and the positive chalcogen atoms; the difference of electronegativity and the strength of the interactions is greatest in the tellurium molecules.

However, the most important contribution to the stabilization of the dimers results is the result of the interaction between empty and occupied molecular orbitals; in other words, the E···N SBI has a strong donor–acceptor character. In the single molecules, the lone pairs of the nitrogen atom are in the vicinity of the HOMO while the LUMO+1 and LUMO+2 consist of combinations of the σ^*_{E-N} orbitals (Figure 4). Therefore, the nitrogen atom can donate a lone pair into low-lying empty orbitals which are polarized toward the chalcogen. This interaction is well exemplified by the HOMO-12 of the tellurium dimer (Figure 5). This interpretation is consistent with the model of three-center four-electron bonding that has gained increasing acceptance in the interpretation of main-group SBIs.[51–53] The essential character of these donor–acceptor interactions was confirmed by performing a constrained-space orbital variation (CSOV)[54–59] analysis removing the virtual orbitals of the monomers (Table 4). The previous discussion is primarily focused on σ interactions only and ignores the intense repulsion that exists between the lone pairs of nitrogen and the chalcogen atom. Studies of the intramolecular "coordination" of chalcogen atoms in diazenes indicated that π interactions can substantially contribute to alleviate such repulsion and in one case are indispensable to stabilize the secondary S···N interaction.[60] In the 1_2 dimers, the σ and π orbitals are easily distinguished by symmetry. The corresponding extension of the CSOV analysis is presented in Table 4. The π (A_u, B_g) interactions are indeed stabilizing, but their contribution is in all instances 1 order of

(49) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.
(50) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.
(51) Landrum, G. A.; Hoffmann, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1887.
(52) Tani, K.; Kato, S.; Kanda, T.; Inagaki, S. *Org. Lett.* **2001**, *3*, 655.
(53) Iwaoka, M.; Komatsu, H.; Katsuda, T.; Tomoda, S. *J. Am. Chem. Soc.* **2004**, *126*, 5309.
(54) Bagus, P. S.; Illas, F. *Phys. Rev. B* **1990**, *42*, 10852.
(55) Hermann, K.; Bagus, P. S. *Appl. Phys. A* **1987**, *A44*, 63.
(56) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W., Jr. *Ber. Bunsen-Ges.* **1984**, *88*, 302.
(57) Bagus, P. S.; Nelin, C. J.; Bauschlicher, C. W., Jr. *J. Vac. Sci. Technol., A* **1984**, *2*, 905.
(58) Hermann, K.; Hass, H. J.; Bagus, P. S. *Z. Phys. D* **1986**, *3*, 159.
(59) Bauschlicher, C. W., Jr.; Bagus, P. S.; Roos, B. O. *J. Chem. Phys.* **1986**, *85*, 354.
(60) Chivers, T.; Krouse, I.; Parvez, M.; Vargas-Baca, I.; Ziegler, T.; Zoricak, P. *Inorg. Chem.* **1996**, *35*, 5836.
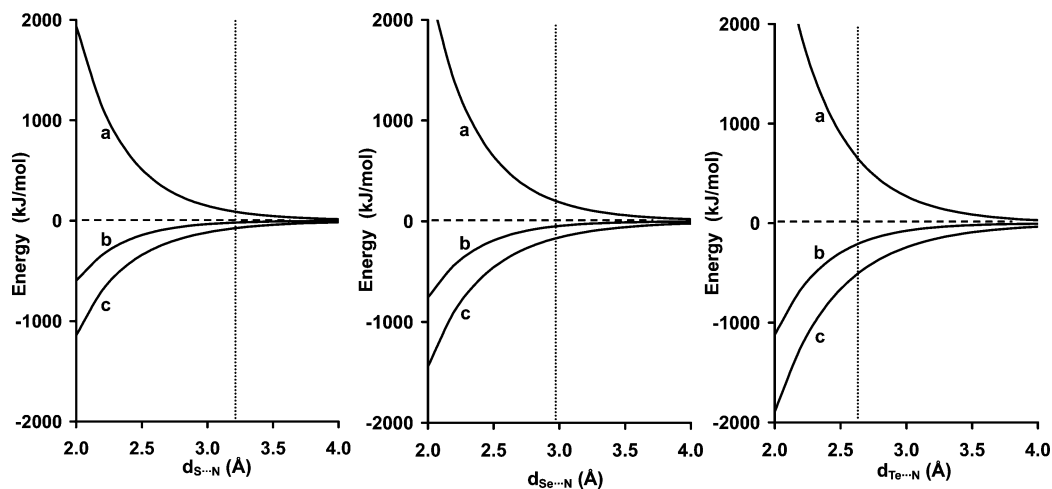
Figure 3. Contributions to the binding energy of the 1_2 dimers. (a) Pauli repulsion, (b) electrostatic interaction, (c) orbital interaction. The dotted lines are traced at the equilibrium distances.
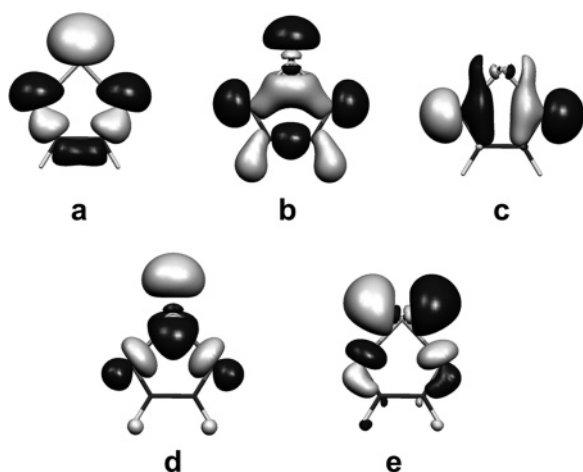
Figure 4. Selected molecular orbitals of **1c**. $LP\sigma_{Te}$: (a) HOMO-4 ($18A_1$). $LP\sigma_N$: (b) HOMO-2 ($19A_1$), (c) HOMO-1 ($11B_2$). σ^*_{Te-N}: (d) LUMO+1 ($12B_2$), (e) LUMO+2 ($20A_1$). Isosurfaces plotted at 0.05.
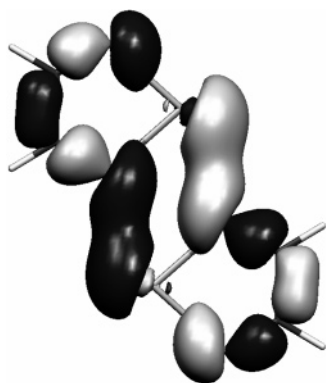
Figure 5. Calculated composition of the HOMO-12 ($27\ B_u$) of **1c**$_2$. Isosurface plotted at 0.04.

magnitude smaller than the σ (A_g, B_u). All the dimers are stable in calculation where the π virtual orbitals are removed but not when the σ acceptor orbitals are excluded.

A more detailed picture of the effect of the SBI arose from mapping the change of electron density upon dimerization in the internuclear E···N axis, as shown in Figure 6. The maps do show an enhancement of electron density between the two atoms that scales up with the size of the chalcogen. Not only is the

electron cloud of nitrogen polarized toward the SBI, but the vicinity of the chalcogen is also depleted of electron density. This observation is not in contradiction with the donor–acceptor concept; it is rather consequence of the difference of electronegativity of the participating atoms and highlights the covalent character of the SBI.

The study of the association of chalcogenadiazoles was extended to consider the infinite one-dimensional arrays observed in the solid state (Scheme 2). This analysis was confined to tellurium heterocycles since they are the most strongly associated and thus have the best potential as supramolecular building blocks. An estimate of the "polymerization energy" was obtained by building model heterocycle chains of increasing length and plotting the association energy as a function of the chain length (Figure 7); ZPE corrections were not considered in this case for computational efficiency. The slope of each linear plot corresponds to the association energy per molecule of telluradiazole. The calculated interaction energy per SBI in the polymer **1c**$_n$ (-29.7 kJ/mol) is less than in the dimer (-31.5 kJ/mol). In this particular case, the decrease of the SBI energy is mostly due to reorganization energy, and significant changes of bond distances and angles were calculated for the central unit of **1c**$_3$ with respect to the dimer **1c**$_2$. Steric interactions should be more significant for larger molecules. To explore this effect, models of benzotelluradiazole oligomers, **3c**$_n$, were optimized. Here, the repulsion between the ortho hydrogen atoms causes an additional decrease in the SBI association energy. More intense steric interactions would further destabilize the ribbon structure and induce a structural distortion in the molecule or in the chain. The crystal structure of **4** displays a telluradiazole ring puckered to enable the four Te···N SBIs; this leads to a staircase ribbon.[43] While the optimized structure of monomeric **4** is essentially planar, its calculated reorganization energy is only 14.29 kJ/mol; this is easily compensated by the strength of the SBI supramolecular links. Even stronger steric repulsion would prevent formation of a ribbon. In the sterically hindered compound **2**, a dimeric structure was observed[44] but an alternative helicoidal chain (Scheme 3), analogous to those formed by 4-methyltellurazole (**5**)[61] and 1,2-benzotellurazole (**6**),[62] is a plausible alternative.

(61) Munno, G. D.; F. Lucchesini *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 1437.

Table 4. Contributions to the Binding Energy (kJ/mol) and CSOV Analysis for the Dimers in the Equilibrium Geometries

| | Pauli repulsion | electrostatic interaction | orbital interactions | | | | CSOV analysis | | |
| | | | s | | p | | | | |
			A_g	B_u	A_u	B_g	no virtual	no p	no s
$1a_2$	28.0	−23.0	−4.0	−5.5	−0.4	−0.2	5.0	−4.5	4.3
$1b_2$	78.9	−62.6	−13.3	−20.0	−1.7	−0.9	16.3	−16.7	13.7
$1c_2$	330.5	−242.0	−63.9	−78.3	−8.9	−4.5	88.5	−51.1	76.4
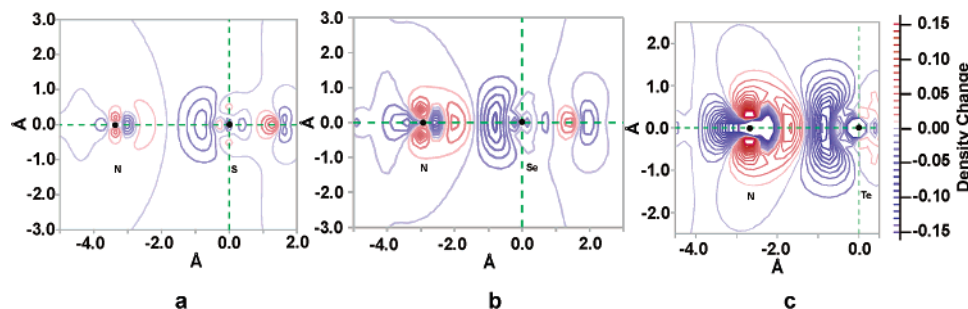
Figure 6. Calculated maps of electron density change along the E···N axis for (a) dimer of thiadiazole **$1a_2$**, (b) selenadiazole **$1b_2$**, (c) telluradiazole **$1c_2$**.
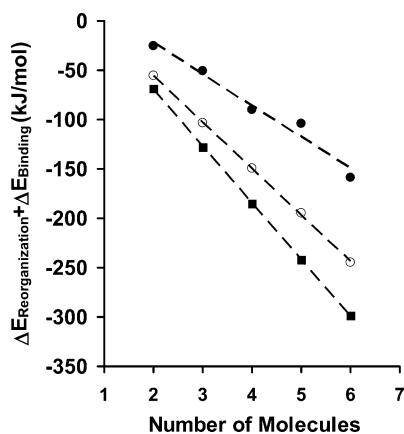
Figure 7. Total association energy of model telluradiazole oligomers. ■ ribbon **$1c_n$**, −57.4 kJ/mol; ○ ribbon **$3c_n$**, −46.9 kJ/mol; ● helicoidal **$1c_n$**, −31.9 kJ/mol.

Scheme 3
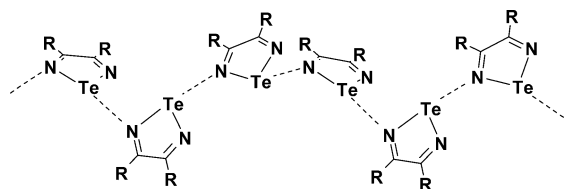
This was modeled and had approximately the same interaction energy per SBI and presumably the same stability of the discrete dimer. Even stronger steric repulsions, or alternatively much weaker SBIs, would result in monomeric species. Such a situation is observed in the isomorphic crystal structures of the benzothia- and benzo selenadiazole, **3a** and **3b**,[63−65] in which there are no evident SBIs; instead, each chalcogen atom sits at distances longer than the sum of van der Waals radii from the four closest nitrogen atoms of neighboring molecules. This study, however, predicts a polymeric structure for the structure

of the tellurium analogue **3c**. Interestingly, a monomeric perfluorinated derivative **7** has been claimed but not backed up with XRD data.[66]

Conclusions and Outlook

While previous attempts to apply chalcogen-centered SBIs in supramolecular chemistry have been mostly focused on molecules containing fused sulfur heterocycles and electron-rich functional groups, the results of this computational study strongly suggest that more attention should be devoted to compounds of the heaviest chalcogens. In the chalcogenadiazoles, there is a progression of SBI strength as the weight of the chalcogen increases. This is a result of both electrostatic and orbital contributions; most prominent is the donation of a lone pair of the nitrogen into the antibonding orbitals of the heavy atom. The thiadiazoles are so weakly bonded, and the S···N distance is so long, that the SBI in that case is little more that a van der Waals contact. In contrast, the selenium and tellurium heterocycles associate more strongly, and the heaviest atom leads to association energies that are as strong as hydrogen bonds.

The perturbations of molecular geometry and electron density upon supramolecular association together with the possibility of steric interactions imply that the total energy gain due to formation of infinite ribbon chains of heterocycles in the solid state cannot be obtained by simple addition of the SBI energies calculated for the dimers. This is specially true for telluradiazoles, which have the shortest E···N distances and experience the most significant structural reorganization.

The telluradiazole dimer constitutes a promising supramolecular synthon that, in addition to being stable, is fairly rigid yet should be labile enough to form and dissociate reversibly. An additional feature of chalcogen−nitrogen SBIs is that they enable electron communication between molecules, which would be advantageous in conducting materials. The results of these investigations call for more synthetic and structural studies of these and related heterocycles and invite the design of supramolecules based on these interactions.

(62) Campsteyn, H.; Dupont, L.; Lamotte-Brasseur, J.; Vermeire, M. *J. Heterocycl. Chem.* **1979**, *15*, 745.
(63) Gomes, A. C.; Biswas, G.; Banerjee, A.; Duax, W. L. *Acta Crystallogr., Sect. C* **1989**, *45*, 73.
(64) Suzuki, T.; Tsuji, T.; Okubo, T.; Okada, A.; Obana, Y.; Fukushima, T.; Miyashi, T.; Yamashita, Y. *J. Org. Chem.* **2001**, *66*, 8954.
(65) Luzzati, V. *Acta Crystallogr.* **1951**, *4*, 193.
(66) Kovtonyuk, V. N.; Makarov, A. Y.; Shakirov, M. M.; Zibarev, A. V. *Chem. Commun.* **1996**, 1991.

Computational Methods

The structures considered in this study were fully optimized using the ADF DFT package (versions 2002.02 and 2003.01).[67−69] The adiabatic local density approximation (ALDA) was used for the exchange-correlation kernel,[70,71] and the differentiated static LDA expression was used with the Vosko−Wilk−Nusair parametrization.[72] The calculation of model geometries was gradient-corrected with the exchange and correlation functionals of the gradient correction proposed in 1988 by Becke[73] and Perdew.[74] Preliminary geometry optimizations were conducted using a small double-ζ basis set with frozen cores corresponding to the configuration of the preceding noble gas and no polarization functions; the resulting structures were refined using a triple-ξ all-electron basis set with one polarization function and applying the zero order relativistic approximation (ZORA)[75−79] formalism with the specially adapted basis sets, unless it is otherwise indicated. Symmetry constraints were used when a point group was applicable and in each case were followed by vibrational calculations[80,81] to verify that all the computed frequencies were real. This also provided zero-point energies for all minima. However, this contribution was omitted in all potential surface plots. Additional visualization of the computational results was performed using Cerius2 (Accelrys) supplemented by the ADF SDK (SCM) interface and Molekel.[82]

Supporting Information Available: Details of the CSD survey of chalcogenadiazole structures, optimized (nonrelativistic) molecular dimensions of **1** and **1₂**; optimized (ZORA) molecular dimensions of **1c**$_x$ (x = 3−6), **3c**$_x$ (x = 2−6), and **4**; potential energy surface for the out-of-plane distortion of **1c₂**; potential energy curves for the face-to-face interaction of two **1c** molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

JA044005Y

(67) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(68) Guerra, C. F.; Snijders, J. G.; Velde, G. t.; E J Baerends *Theor. Chem. Acc.* **1998**, *99*, 391.

(69) Baerends, E. J.; Autschbach, J.; Bérces, A.; Bo, C.; Boerrigter, P. M.; Cavallo, L.; Chong, D. P.; Deng, L.; Dickson, R. M.; Ellis, D. E.; Fan, L.; Fischer, T. H.; Guerra, C. F.; Gisbergen, S. J. A. v.; Groeneveld, J. A.; Gritsenko, O. V.; Grüning, M.; Harris, F. E.; Hoek, P. v. d.; Jacobsen, H.; Kessel, G. v.; Kootstra, F.; Lenthe, E. v.; McCormack, D. A.; Osinga, V. P.; Patchkovskii, S.; Philipsen, P. H. T.; Post, D.; Pye, C. C.; Ravenek, W.; Ros, P.; Schipper, P. R. T.; Schreckenbach, H. G.; Snijders, J. G.; Sola, M.; Swart, M.; Swerhone, D.; Velde, G. t.; Vernooijs, P.; Versluis, L.; Visser, O.; Wezenekker, E. v.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Ziegler, T., ADF: Amsterdam Density Functional versions 2002.02 and 2003.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

(70) van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. *Phys. Rev. Lett.* **1997**, *78*, 3097.

(71) van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1998**, *109*, 10644.

(72) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(73) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(74) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(75) van Lenthe, E.; Ehlers, A.; Baerends, E.-J. *J. Chem. Phys.* **1999**, *110*, 8943.

(76) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.

(77) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783.

(78) van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. *Int. J. Quantum Chem.* **1996**, *57*, 281.

(79) van Lenthe, E.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1996**, *105*, 6505.

(80) Fan, L. Y.; Ziegler, T. *J. Chem. Phys.* **1992**, *96*, 9005.

(81) Fan, L. Y.; Ziegler, T. *J. Phys. Chem.* **1992**, *96*, 6937.

(82) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.0*; Swiss Center for Scientific Computing: Manno, Switzerland, 2000.

(83) Kontopoulos, C.; Sigalas, M. P. *J. Mol. Struct. (THEOCHEM)* **1999**, *490*, 125.