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Does a Stabilising Interaction Favouring the *Z*,*Z* Configuration of −S-N=S=N-S− Systems Exist?

Karla Tersago,[a] Marcos Mandado,[a] Christian Van Alsenoy,[a] Irina Yu. Bagryanskaya,[b] Mikhail K. Kovalev,[c] Alexander Yu. Makarov,[b] Yuri V. Gatilov,[b] Makhmut M. Shakirov,[b] Andrey V. Zibarev,*[b, d] and Frank Blockhuys*[a]

Abstract: The existence of the orbital interaction presented in the literature as being the cause for the stabilisation of the *Z*,*Z* configuration of Ph-S-N=S=N-S-Ph (**1**) and its derivatives in the crystal phase, has been investigated. The results of theoretical calculations at the DFT/B3LYP/6-311+G* level of theory suggest that such a stabilising interaction might not exist or be extremely weak and that packing forces must be the main cause of the observed *Z*,*Z* configuration in the solid. To reach this conclusion structural and energetic parameters were combined to study the bonding in these -S-N=S=N-S- systems. For the analogous Ph-Se-N=S=N-Se-Ph (**2**) in particular the isomeric equilibrium in solution found in the variable-temperature ^{77}Se NMR spectrum indicates that, in the gas phase or in solution, the observed *Z*,*Z* configuration is not stabilised to a greater extent than the *Z*,*E* configuration.

Keywords: chalcogen–nitrogen chains · density functional calculations · intramolecular interactions · X-ray diffraction

Introduction

Polyconjugated sulfur–nitrogen compounds of the type Ar-S$_k$-(N=S=N-S)$_l$-N=S=N-S$_m$-Ar, where $k, m \in [0, 1]$ and $l \in [0, 1, 2, 3, \ldots]$ and in particular the extended chains with $l \geq 1$,[1–4] are oligomeric analogues of poly(sulfur nitride) or $(SN)_x$, a molecular metal and low-temperature superconductor.[5,6] These materials have possible applications as molecular wires in the field of molecular electronics.[2,7,8] It is known that the molecular geometry of catenated sulfur–nitrogen compounds, based on the three possible orientations of the substituents at each N=S=N fragment—*Z*,*E*, *Z*,*Z* and *E*,*E*, of which the *Z*,*E* configuration usually is the most stable[9,10]—depends on the stereoelectronic demand of the α,ω-substituents in an unpredictable way. In many cases severely nonplanar molecular conformations were observed[11,12] which are in effect useless for molecular electronics due to the broken π-conjugation.

Previously, it was found for derivatives of 1,5-diaryl-2,4-diaza-1,3,5-trithia-2,3-pentadiene (Ar-S-N=S=N-S-Ar, $k = m = 1$ and $l = 0$) for which the peripheral aryl groups are C_6H_5 and 4-ClC_6H_4, that in the crystal they adopt the *Z*,*Z* configuration featuring a planar sulphur–nitrogen fragment in which the $S^{II}\cdots S^{II}$ distance is significantly shorter than the sum of the van der Waals radii of the atoms.[13,14] This configuration was later rationalised by Rzepa et al. in terms of MO theory: according to the data of MNDO and HF/6-31G* calculations on model compounds such as H-S-N=S=N-S-H, the *Z*,*Z* configuration was said to be stabilised by the interaction of the *n*(N) orbitals with the *n*[S^{II}] orbitals.[15,16] This σ,σ interaction should logically lead to the presence of bonding electron density in the area between the two S^{II} atoms due to which the $S^{II}\cdots S^{II}$ distance is shortened to about 3.20 Å,[13,14] while the sum of the van der

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[a] K. Tersago, Dr. M. Mandado, Prof. C. Van Alsenoy,
Prof. F. Blockhuys
Department of Chemistry, University of Antwerp
Universiteitsplein 1, 2610 Wilrijk (Belgium)
Fax: (+32) 382-02-310
E-mail: frank.blockhuys@ua.ac.be

[b] Dr. I. Y. Bagryanskaya, Dr. A. Y. Makarov, Prof. Y. V. Gatilov,
Dr. M. M. Shakirov, Prof. A. V. Zibarev
Institute of Organic Chemistry
Russian Academy of Sciences, 630090 Novosibirsk (Russia)
Fax: (+7) 383-230-9752
E-mail: zibarev@nioch.nsc.ru

[c] M. K. Kovalev
Department of Natural Sciences
Novosibirsk State University, 630090 Novosibirsk (Russia)

[d] Prof. A. V. Zibarev
Department of Physics
Novosibirsk State University, 630090 Novosibirsk (Russia)

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Waals radii is 3.60 Å; for a minireview of weakly bonding interactions in organochalcogen chemistry, see reference [17].

It is interesting to note that in a number of the more recent publications[7,10–12] regarding the conformation of similar systems, the authors consistently refer to Rzepa's work[15,16] for the explanation of the S···S interaction determining the conformational preference, even though this information is now over a decade old and the conclusions were based on the results of low-level quantum chemical methods. Additionally, Leitch suggested in his original paper on the crystal structure of 1,5-diphenyl-2,4-diaza-1,3,5-trithia-2,3-pentadiene from 1973, that "the outer sulfur atoms open out the systems rather than pull it together";[13] his conclusion was based on a careful interpretation of the valence angles in the -S-N=S=N-S- fragment and almost suggests a repulsive effect. To deal with these apparent inconsistencies we have thoroughly re-investigated the different possible configurations and conformations of 1,5-diphenyl-2,4-diaza-1,3,5-trithia-2,3-pentadiene, Ph-S-N=S=N-S-Ph (**1**) (see Figure 1), by means of high-level quantum chemical calculations at the DFT/B3LYP/6-311+G* level of theory. The suggested interaction between the sulfur atoms has been studied by combining structural and energetic parameters but no definitive proof of its existence was found. Investigation of the bonding in the diselena derivative of **1**, 1,5-diphenyl-2,4-diaza-1,5-diselena-3-thia-2,3-pentadiene, Ph-Se-N=S=N-Se-Ph (**2**) (see Figure 1), in combination with variable-temperature ^{77}Se NMR in solution strengthens the idea that the proposed[15,16] stabilising interaction might not exist and that packing forces are the main cause of the observed *Z*,*Z* configuration in the solid.

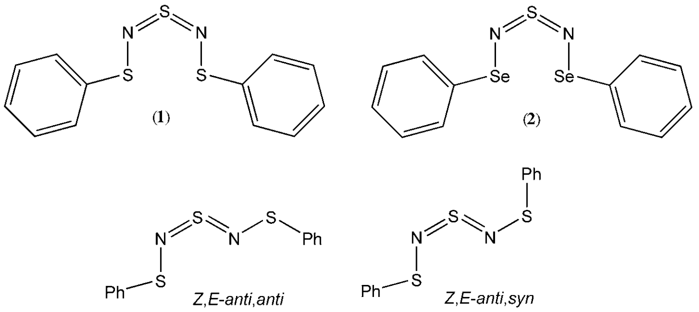

Figure 1. Structural formulas of the *Z*,*Z*-*anti*,*anti* conformers of compounds **1** and **2**; representative formulas of the *Z*,*E*-*anti*,*anti* and *Z*,*E*-*anti*,*syn* have also been given.

Results and Discussion

X-ray molecular structures: As is the case for the parent compound **1**, for derivative **2** the conformer with the *Z*,*Z* configuration is found in the crystal as can be seen in Figure 2 and from the data in Table 1; the chalcogen–nitrogen moiety is nearly planar to within 0.021 Å. The dihedral angles between the -Se-N=S=N-Se- plane and the two planes of the aromatic rings are 28.03(14) and −28.03(14)°, while the dihedral angle between the planes of the phenyl rings is 55.33(14)°. The lengths of the Se−N and S−N bonds are 1.833(5) and 1.520(4) Å, respectively; based on these values the former can be described as a single and the latter as a double bond. The latter value is close to the one found for the dithia analogue **1** of which the experimental geometrical data[13] can be found in Table 2; yet the S=N distance is longer by about 0.01 Å (XRD) in the parent compound **1**. The nonbonded Se···Se distance of 3.418(1) Å is considerably shorter than the sum of the van der Waals radii (3.80 Å). The N=S=N bond angle is 125.7(4)° and is also compatible with the value of the sulfur system. The angles in the SeNSNSe fragment in the diselena derivative **2** are consistently larger than in the corresponding SNSNS fragment in **1**; in contrast, the angles with the phenyl rings are smaller in **2** than in **1**. The conformations of these peripheral phenyl rings, expressed by the torsion angles, are similar for both compounds.

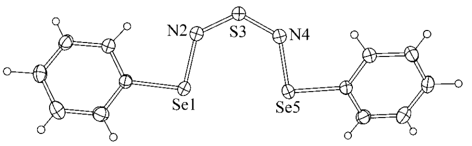

Figure 2. X-ray molecular structure of compound **2**. For selected bond lengths and bond angles see Table 1.

Table 1. Selected data comparing solid-state (XRD) and calculated (B3LYP, r_e) geometries of compound **2**; bond lengths in Å and bond angles in degrees. Computational results for the three lowest-energy conformers [*Z*,*Z*-*anti*,*anti* (C_2), *Z*,*E*-*anti*,*anti* (C_1) and *Z*,*E*-*anti*,*syn* (C_1)] are given. See text for details.

	Z,*Z*-*a*,*a*	*Z*,*E*-*a*,*a*	*Z*,*E*-*a*,*s*	XRD
Se1−N2	1.851	1.842	1.848	1.833(5)
N2−S3	1.566	1.564	1.570	1.520(4)
S3−N4	1.566	1.597	1.581	1.520(4)
N4−Se5	1.851	1.888	1.870	1.833(5)
Se1−C	1.938	1.937	1.935	1.912(5)
Se5−C	1.938	1.936	1.945	1.912(5)
Se1···Se5	3.523	4.880	4.854	3.418(1)
C-Se1-N2	96.7	96.1	96.1	95.9(2)
Se1-N2-S3	128.5	119.1	118.8	128.3(3)
N2-S3-N4	125.7	110.1	110.8	125.7(3)
S3-N4-Se5	128.5	112.8	123.3	128.3(3)
N4-Se5-C	96.7	98.2	104.6	95.9(2)
C-Se1-N2-S3	156.5	176.3	180.0	176.2(3)
Se1-N2-S3-N4	−3.6	0.7	0.0	2.2(5)
N2-S3-N4-Se5	−3.6	−170.6	−180.0	2.2(5)
S3-N4-Se5-C	156.5	−123.6	−0.1	176.2(3)

Overall, the substitution of S^{II} by Se^{II} atoms does not seem to affect the *Z*,*Z* configuration and conformation of the parent Ph-S-N=S=N-S-Ph (**1**) to any great extent. A possible reason for this may be the close similarity of the electronic (the energies of valence atomic orbitals) and the spatial (van der Waals radius) characteristics of sulfur and selenium atoms. Furthermore, all other structurally character-

Table 2. Selected data comparing solid-state (XRD, taken from ref. 13) and calculated (B3LYP, r_e) geometries of compound **1**; bond lengths in Å and bond angles in degrees. Computational results for the three lowest-energy conformers [*Z*,*Z*-*anti*,*anti* (C_2), *Z*,*E*-*anti*,*anti* (C_1) and *Z*,*E*-*anti*,*syn* (C_1)] are given. See text for details.

	Z,*Z*-*a*,*a*	*Z*,*E*-*a*,*a*	*Z*,*E*-*a*,*s*	XRD
S1−N2	1.688	1.681	1.688	1.659(6)
N2−S3	1.571	1.570	1.574	1.530(4)
S3−N4	1.571	1.599	1.585	1.530(4)
N4−S5	1.688	1.718	1.700	1.659(6)
S1−C	1.789	1.788	1.786	1.758(7)
S5−C	1.789	1.785	1.802	1.758(7)
S1···S5	3.471	4.682	4.648	3.231(6)
C-S1-N2	100.4	99.8	99.7	101.0(2)
S1-N2-S3	129.3	120.9	120.4	126.6(3)
N2-S3-N4	124.7	109.8	110.5	124.8(3)
S3-N4-S5	129.3	115.6	125.7	126.6(3)
N4-S5-C	100.4	100.6	107.2	101.0(2)
C-S1-N2-S3	162.2	176.3	179.5	−173.5(4)
S1-N2-S3-N4	−3.3	−0.8	−1.1	1.4(6)
N2-S3-N4-S5	−3.3	−172.8	177.5	1.4(6)
S3-N4-S5-C	162.2	−141.1	5.6	−173.5(4)

ised derivatives of Ar-S-N=S=N-S-Ar (with Ar = 4-ClC_6H_4[14] and 2,4,6-(*tert*-$C_4H_9)_3C_6H_2$, C_6F_5 and 4-$CF_3C_6F_4$)[18] and Ar-Se-N=S=N-Se-Ar (with Ar = C_6F_5[18]) as well as derivatives of R-S-N=S=N-S-R (with R = Ph_2C=N)[19] possess the same *Z*,*Z* configuration in the crystal. Thus, in the solid state this configuration seems to be intriguingly stable towards significant variations in the stereoelectronic demand of the α,ω-substituents.

Calculated gas-phase structures: Calculations on all possible conformers and isomers of **1** were performed to assess which are energy minima and which are transition states. In order to have a complete list of minimum-energy conformers of Ph-S-N=S=N-S-Ph (**1**) the full potential energy surface was scanned at discrete points by calculating the energy, the geometry and the force field of every possible conformer of this compound in every possible symmetry. An overview of the 25 calculated conformers and the number of imaginary frequencies can be found in Table 3. The entries under the heading "configuration" determine the two configurations of the two consecutive S=N bonds, while the entries under the heading "conformation" determine the two conformations around the two peripheral S−N bonds: *anti* denotes an antiperiplanar conformation, while *syn* a synperiplanar one. The structures with D_{2h}, D_{2d} and D_2 symmetry contain a linear -S-N=S=N-S- chain, and the two conformers with C_{2h} symmetry, contain a linear -N=S=N- fragment, which is clearly unacceptable. Of the 20 remaining possibilities only seven are energy minima—these are the *Z*,*Z*-*anti*,*anti* and *Z*,*Z*-*syn*,*syn* forms with C_2 symmetry and the C_1-*E*,*E*-*anti*,*syn*, C_1-*Z*,*E*-*anti*,*anti*, C_1-*Z*,*E*-*syn*,*syn*, C_1-*Z*,*E*-*anti*,*syn* and C_1-*Z*,*E*-*syn*,*anti* conformers with C_1 symmetry. The relative energies of these seven conformers have been compiled in Table 4.

The data for **1** in Table 4 indicate that the *Z*,*Z*-*anti*,*anti* conformer with C_2 symmetry is indeed the lowest-energy one and this is the one that is found in the crystal. Nevertheless, there are two other *Z*,*E* conformers with an energy low enough so that they will be present in the gas phase (or in solution) at room temperature. Based on the results of our calculations the equilibrium conformer composition at 293 K is 89% C_2-*Z*,*Z*-*anti*,*anti*, 10% C_1-*Z*,*E*-*anti*,*anti* and 1% C_1-*Z*,*E*-*anti*,*syn*. Importantly Rzepa's previous work[15,16] does not mention the possibility of other low-energy conformers besides the *Z*,*Z* conformer.

For the diselena derivative only six of the seven conformations found for **1** were calculated and their relative energies are also given in Table 4; the C_2-*Z*,*Z*-*syn*,*syn* conformer

Table 3. Overview of the B3LYP/6-311+G* calculations on all possible configurations and conformations of compound **1**: the configuration, conformation, symmetry and number of imaginary frequencies *n* for each are given. See text for details.

Symmetry	Configuration	Conformation	*n*
D_{2h}	–	–	5
D_{2d}	–	–	8
D_2	–	–	7
C_{2h}	–	–	3
	–	–	3
C_{2v}	*Z*,*Z*	*anti*,*anti*	1
	Z,*Z*	*syn*,*syn*	3
	E,*E*	*anti*,*anti*	4
	E,*E*	*syn*,*syn*	3
C_2	*Z*,*Z*	*anti*,*anti*	0
	Z,*Z*	*syn*,*syn*	0
	E,*E*	*anti*,*anti*	1
C_s	*Z*,*Z*	*anti*,*anti*	1
	E,*E*	*syn*,*syn*	1
	E,*E*	*anti*,*syn*	3
	Z,*E*	*anti*,*anti*	1
	Z,*E*	*syn*,*syn*	3
	Z,*E*	*anti*,*syn*	1
	E,*E*	*anti*,*anti*	1[a]
C_1	*E*,*E*	*anti*,*syn*	0
	Z,*E*	*anti*,*anti*	0
	Z,*Z*	*anti*,*syn*	0[b]
	Z,*E*	*syn*,*syn*	0
	Z,*E*	*anti*,*syn*	0
	Z,*E*	*syn*,*anti*	0

[a] Converts to C_s-*E*,*E*-*syn*,*syn*. [b] Converts to C_2-*Z*,*Z*-*anti*,*anti*.

Table 4. Calculated energies *E* (H) and relative energies Δ*E* [kJ mol^{-1}] of the different conformers of compounds **1** and **2** at the B3LYP/6-311+G* level of theory.

	Conformer	*E*	Δ*E*
1	C_2-*Z*,*Z*-*a*,*a*	−1767.4825	0.00
	C_1-*Z*,*E*-*a*,*a*	−1767.4805	5.18
	C_1-*Z*,*E*-*a*,*s*	−1767.4779	12.07
	C_1-*Z*,*E*-*s*,*a*	−1767.4712	29.62
	C_1-*Z*,*E*-*s*,*s*	−1767.4697	33.69
	C_2-*Z*,*Z*-*s*,*s*	−1767.4655	44.56
	C_1-*E*,*E*-*a*,*s*	−1767.4613	55.73
2	C_2-*Z*,*Z*-*a*,*a*	−5774.1506	0.00
	C_1-*Z*,*E*-*a*,*a*	−5774.1505	0.38
	C_1-*Z*,*E*-*a*,*s*	−5774.1491	4.00
	C_1-*Z*,*E*-*s*,*s*	−5774.1407	26.08
	C_1-*Z*,*E*-*s*,*a*	−5774.1400	27.81
	C_1-*E*,*E*-*a*,*s*	−5774.1325	47.57

was not calculated since the three lowest-energy conformers had already been found and since it would also be a higher-energy conformer, as for **1**. The results of these calculations lead to the following conclusions. Again the *Z*,*Z-anti*,*anti* conformer with C_2 symmetry is the lowest-energy one and is found in the crystal, and again there are two other low-energy conformers present with even lower relative energies than in the case of **1**. Based on these values the equilibrium conformer composition at 293 K for **2** is 49% C_2-*Z*,*Z-anti*, *anti*, 42% C_1-*Z*,*E-anti*,*anti* and 9% C_1-*Z*,*E-anti*,*syn*. It is clear that in the case of the diselena derivative **2** due consideration has to be given to the presence of two conformers in almost equal abundance. The energies of the other four possible conformers of both compounds are quite high and these can be confidently excluded from further consideration.

The calculated geometries of the three lowest-energy conformers of both the parent (**1**) and the diselena derivative (**2**) have been compiled in Tables 1 and 2, respectively. A comparison of the different calculated stable conformations of the two compounds reveals that when changing the conformation and/or configuration of the molecule the geometrical changes are quite substantial for the parameters directly involved in the change, that is, S3–N4, N4–X5 and the three angles in the XNSNX fragment (X = S,Se): differences of up to 0.037 Å for N4–Se5 and 15.6° for N2-S3-N4 in **2** have been found. Of particular importance to the rest of discussion are the changes in the nonbonded distances when going from one conformer to the other; this will be discussed in the Section on the Intramolecular S···S and Se···Se Interactions.

Comparing the XRD data in Tables 1 and 2 with those of the relevant gas-phase conformers (i.e., *Z*,*Z-anti*,*anti*) it is clear that the qualitative agreement between the calculated and experimental structures is quite good: the differences between single and double bonds are well reproduced as are the different angles and torsion angles (disregarding the signs) in the heteroatomic fragment. A quantitative comparison indicates that the calculations overestimate the bond lengths but this is mainly due to the fact that r_{XRD} are r_{α}-type distances while the r_{calcd} are r_{e} distances by definition.[20,21] The deviations are larger for the non-bonded Se···Se and S···S distances but since these are more sensitive to the crystal environment than the bonded ones, this is to be expected.

Variable-temperature ^{77}Se NMR spectroscopy: The presence of two NMR-active selenium nuclei in **2** makes it possible to verify the presence of more than one isomer in solution. Even though solvent effects can not be ruled out and one must be very careful when transferring the calculated energy differences to a different aggregation state, we assumed, based on the values of the latter, that more than one isomer should be visible in the ^{77}Se NMR spectrum of **2**. The ^{77}Se NMR spectra of Ph-Se-N=S=N-Se-Ph (**2**) in toluene at 353, 323 and 203 K are given in Figure 3. At 353 K there is just one relatively narrow signal at 936 ppm which significantly broadens at 323 K and splits into three well-resolved signals at 999, 960 and 902 ppm, at 203 K. The relative intensities of the latter three signals are 1.4, 2.2 and 1.0, respectively. Similarly, Table 5 compiles the calculated chemical shifts of the selenium atoms of the three lowest-energy conformers of **2**. At 203 K the calculated equilibrium conformer composition is 53% C_2-*Z*,*Z-anti*,*anti*, 42% C_1-*Z*,*E-anti*,*anti* and 5% C_1-*Z*,*E-anti*,*syn*.

Based on the calculated chemical shifts in Table 5 it is reasonable to assign the signal at 960 ppm to the *Z*,*Z-anti*,*anti* conformer. The signals at 999 and 902 ppm would then be assigned to the *Z*,*E-anti*,*anti* and *Z*,*E-anti*,*syn* conformers: both selenium nuclei of the *Z*,*E-anti*,*syn* and one [Se1] of the *Z*,*E-anti*,*anti* conformer would then jointly contribute to

Table 5. Calculated ^{77}Se NMR chemical shifts of the three lowest-energy conformers of compound **2** [in ppm vs $(CH_3)_2Se$].

	Z,*Z-a*,*a*	*Z*,*E-a*,*a*	*Z*,*E-a*,*s*
Se1	939	1076	1010
Se5	939	873	1044

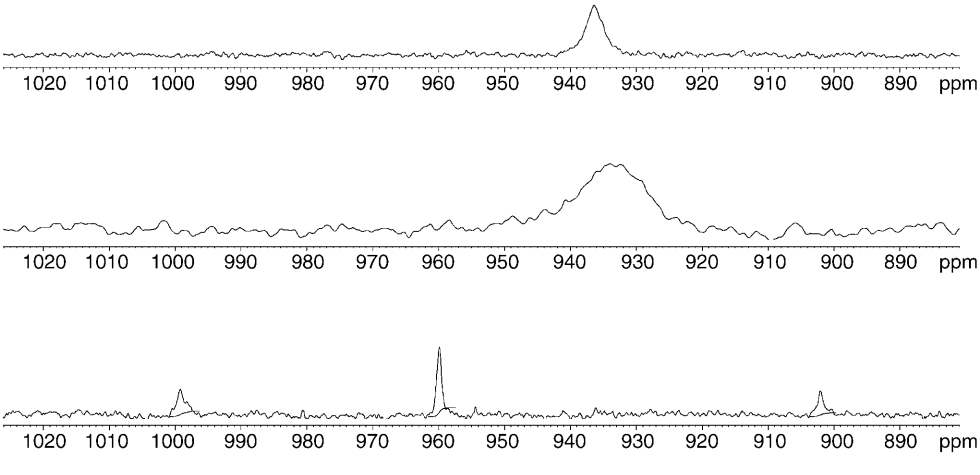

Figure 3. ^{77}Se NMR spectrum of Ph-Se-N=S=N-Se-Ph (**2**) at 353 (top), 323 (middle) and 203 K (bottom).

the low-field signal at 999 ppm while the remaining one [Se5] of the *Z*,*E-anti*,*anti* conformer would generate the signal at 902 ppm. It is quite reasonable to assume that the three selenium nuclei contributing to the signal at 999 ppm would not be able to be resolved. We note that for the signal of the *Z*,*Z* isomer (960 ppm) and the high-field signal of the *Z*,*E* isomers (902 ppm, for which direct comparison of experiment and theory is possible) the difference between experimental and calculated ^{77}Se chemical shifts is only 21 and 29 ppm, respectively; these are deviations of 2 and 3 %, respectively. The combination of theory and experiment leads to conclusion that both in solution and in the gas phase the *Z*,*Z* and the lowest-energy *Z*,*E* isomer of **2** are present in a (roughly) 1:1 equilibrium.

There is no reason to assume that a similar equilibrium does not exist for the parent compound **1**. Even though it is shifted more to the *Z*,*Z-anti*,*anti* conformer due consideration has to be given to the presence of a considerable amount of *Z*,*E-anti*,*anti* conformer.

Intramolecular S···S and Se···Se interactions: The information presented above can now be applied to the issue of the stabilising interaction between S1 and S5 in **1** and between Se1 and Se5 in **2**. As was mentioned before, both in the crystal and in the lowest-energy conformer in the gas phase the distances between S1 and S5 [3.231(6) and 3.471 Å, respectively] and between Se1 and Se5 [3.418(1) and 3.523 Å, respectively] are well below the sum of the van der Waals radii (3.60 and 3.80 Å, respectively). This does suggest some sort of bonding interaction between those atoms. However, the energy difference between the conformer which has the interaction, that is, C_2-*Z*,*Z-anti*,*anti*, and one which does not, for example, C_1-*Z*,*E-anti*,*anti* is only of the order of 5.18 kJ mol^{-1} for **1** and 0.38 kJ mol^{-1} for **2** (Table 4). That the C_1-*Z*,*E-anti*,*anti* conformer does not display an interaction between S1 and S5 or Se1 and Se5 can be clearly seen from the S···S and Se···Se distances in Tables 1 and 2 which are well above the sum of the van der Waals radii. These small energy differences suggest that the observed *Z*,*Z* configuration is not stabilised to a greater extent than the lowest-energy *Z*,*E* configuration and that the supposed S···S and Se···Se interactions do not play an important stabilising role.

Additional evidence comes from a plot of the deformation electron density of **1** in the plane of the N=S=N fragment which is given in Figure 4a. The Figure contains all the expected features: the bond maxima for the two S–C, the two S–N and the two S=N bonds and the free electron pairs on the five heteroatoms. What it does not contain is any electron density between S1 and S5. Again, this does not suggest any bonding interaction between these two atoms. Similar conclusions can be drawn for the diselena derivative **2**; its deformation electron density plot is given in Figure 4b.

Thirdly, the Hirshfeld bond orders of the different bonds in both molecules were calculated and the results are given in Table 6. The data reproduce the different types of bonding in the molecules equally well for the six conformers of **1** (X = S) and **2** (X = Se): the XC bonds are clearly single while the S=N bonds are virtually double. For the parent compound **1** some of the electron density of the latter has flowed to the neighbouring SN bonds which are clearly stronger than regular single bonds; in **2** the SeN bonds remain single. It seems that within the SNSNS fragment some delocalisation of π density has taken place. Of greater importance here is the value for the S···S and Se···Se contacts. For all conformers of both compounds these values are negative, which is a result of the scaling procedure,[22] and this indicates that the bond orders of these bonds are very small. The unscaled values for the *Z*,*Z-anti*,*anti* conformers for **1** and **2** are 0.04 and 0.06, respectively, and these can be directly compared to the unscaled values for the XC bonds which are 0.39 and 0.36, respectively. The bonding in the S···S and Se···Se contacts is about ten and six times lower, respectively, than in a regular single bond; the inter-

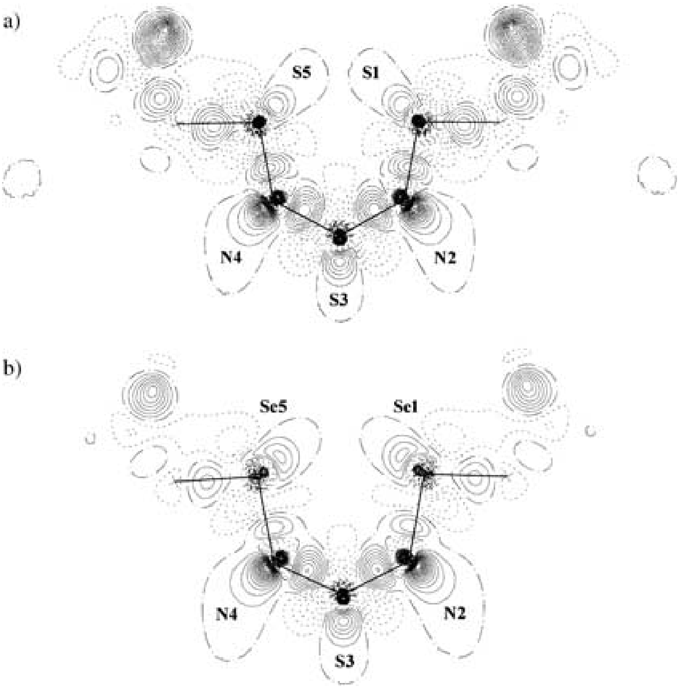

Figure 4. Deformation electron density of a) compound **1** and b) compound **2** in the plane of the N=S=N fragment. ——: positive electron density, -----: electron density and •••••: zero electron density. Isodensity lines were plotted every 0.05 e Å^{-3}.

Table 6. Hirshfeld bond orders for the three lowest-energy conformers of compounds **1** (X = S) and **2** (X = Se). See text for details.

	1			2		
	Z,*Z-a*,*a*	*Z*,*E-a*,*a*	*Z*,*E-a*,*s*	*Z*,*Z-a*,*a*	*Z*,*E-a*,*a*	*Z*,*E-a*,*s*
X1–N2	1.25	1.24	1.22	1.03	1.02	1.01
N2–S3	1.81	1.77	1.76	1.85	1.81	1.79
S3–N4	1.81	1.60	1.68	1.85	1.61	1.70
N4–X5	1.25	1.14	1.28	1.03	0.91	1.04
X1–C	1.07	1.07	1.08	0.93	0.93	0.94
X5–C	1.07	1.09	1.03	0.93	0.94	0.91
X1···X5	–0.52	–0.68	–0.68	–0.43	–0.68	–0.68

action between the two atoms must therefore be extremely weak.

Finally, a topological analysis of the total molecular electron density was performed using the atoms-in-molecules (AIM) theory.[23] The quantum theory of atoms in molecules (QTAIM)[23,24] provides a definition of the chemical bond based on physical observables. Two atoms are bonded when there is a (3,−1) critical point of the molecular charge density (a so-called bond critical point or BCP) that gives rise to a bond path connecting these atoms.[25] A similar definition can be formulated for a ring and a ring critical point (RCP). The electron densities $\rho(\boldsymbol{r})$ of a number of relevant BCPs and RCPs of the three lowest-energy conformers of compounds **1** and **2** were calculated and the results are given in Table 7. The topological analysis of **1** shows that there is an interaction between S1 and S5 but that this interaction is extremely weak. This conclusion is based on the fact that the density in the BCP is about two times lower than in the BCP of the N···H contact. The latter can even be considered very weak in comparison with hydrogen interactions such as the O···H contact in creatine for which a value of 0.0350 au was found.[26] The density in the BCP of the S···S bond is thus about five times lower than in the latter contact and about 25 times lower than in the BCP of the SC single bond. The situation for **2** is similar even though the Se···Se contact seems a bit stronger as it is only 15 times weaker than the SeC single bond; this observation corroborates the conclusion regarding the bond orders. The values of the RCPs confirm that the interaction should be very weak: the values for the phenyl rings and even the weakly bound XCCH···N rings are about three and two times larger, respectively, for both compounds. We conclude by noting that in the case of very low values for the electron density in a BCP associated with an intramolecular bond, these BCPs tend to disappear when the basis set is enlarged.[27] We have not tested this for the compounds studied here due to computational restrictions, but it suggests that the BCP we found may be artifacts of the basis set used.

Table 7. Values of the electron density $\rho(r)$ (in au) of the relevant BCPs and RCPs for the three lowest-energy conformers of compounds **1** (X = S) and **2** (X = Se).

		1			**2**		
		Z,Z-a,a	*Z,E-a,a*	*Z,E-a,s*	*Z,Z-a,a*	*Z,E-a,a*	*Z,E-a,s*
BCP	X1−C	0.1914	0.1922	0.1926	0.1495	0.1506	0.1508
	CH···N2	0.0137	0.0136	0.0137	0.0128	0.0128	0.0127
	CH···N4	0.0137	0.0140	–	0.0128	0.0128	–
	X1···X5	0.0078	–	–	0.0099	–	–
RCP	C_6H_5	0.0216	0.0216	0.0216	0.0217	0.0217	0.0217
	XCCH···N	0.0133	0.0133	0.0133	0.0118	0.0116	0.0117
	NSNX···X	0.0069	–	–	0.0078	–	–

The combination of the above mentioned four criteria leads to the logical conclusion that the proposed stabilising *intra*molecular interaction might not exist or at least be extremely weak. Therefore, it must be *inter*molecular forces that are the main cause of the observed *Z*,*Z* configuration in the solid.

Intermolecular S···S and S···Se interactions: A reasoned examination of the forces working in the solid state—as we have just done for an isolated molecule in the gas phase—is virtually impossible: short intermolecular contacts can be observed but not readily quantified. Nevertheless, as the final part of this work, we would like to present a concise description of the intermolecular contacts that may possibly be the cause of the observed configuration in 1,5-diphenyl-2,4-diaza-1,3,5-trithia-2,3-pentadiene (**1**) and its derivatives. A closer look at the crystal packing of seven structurally characterised Ar-X-N=S=N-X-Ar (X = S, Se) compounds (this work and refs. [13,14,18]) reveals the general tendency of the chalcogen atoms to enlarge their coordination number via short intermolecular contacts. For compounds **1** and **2** these have been represented in Figure 5. In all crystal lattices the molecules seem to form ribbons or layers connected by short X···X (X = S,Se) intermolecular contacts (details will be given elsewhere).[18] As said, whether or not these contacts stabilise the overall structure can not be easily determined.

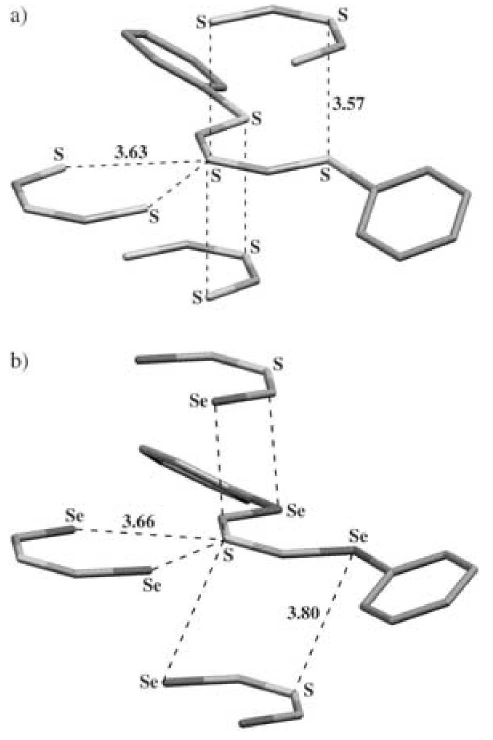

Figure 5. Short intermolecular contacts (distances in Å) in the crystal structure of a) the parent compound **1** and b) compound **2**. The atoms involved in the contacts have been labeled.

The only comment that can be made about them is that probably the *Z*,*Z* configuration allows for a larger number of stabilising intermolecular contacts per molecule compared to the *Z*,*E* configuration.

Conclusions

1,5-Diphenyl-2,4-diaza-1,5-diselena-3-thia-2,3-pentadiene, Ph-Se-N=S=N-Se-Ph, crystallises in the *Z*,*Z* configuration with a nearly planar heteroatomic fragment; this configuration is identical to those of 1,5-diphenyl-2,4-diaza-1,3,5-trithia-2,3-pentadiene, Ph-S-N=S=N-S-Ph, and its derivatives. To investigate the existence of the orbital interaction presented in the literature as being the cause for the stabilisation of the *Z*,*Z* configuration all possible conformations and configurations of the parent Ph-S-N=S=N-S-Ph were studied theoretically by quantum chemical calculations at the DFT/B3LYP level of theory with the 6-311+G* basis set. The occurrence of the *Z*,*Z* configuration in the crystal can not be explained by stabilising intramolecular interaction between the S^{II} atoms but is more likely due to packing forces in the crystal. Four arguments have been presented which suggest that such a stabilising interaction does not exist or is extremely weak and can not be the cause of the occurrence of the Z,Z configuration in the solid. The logical conclusion is that the observed configuration is the result of packing forces or *inter*molecular effects rather than of *intra*molecular effects. Since the former can not easily be quantified at this moment the final proof of this conclusion will have to wait until they can.

Experimental and Computational Details

Theoretical calculations were performed by using Gaussian 03[28] applying standard gradient techniques at the DFT/B3LYP level of theory using the 6-311+G* basis set on all atoms; the basis set was used as it was implemented in the program. Calculations to determine the stability of the wave functions were performed by using the same level and basis set and all wave functions were found to be stable. Force field calculations were used to ascertain whether the resulting structures were energy minima. All subsequent calculations of molecular properties were performed at the B3LYP/6-311+G* geometries. Deformation densities were calculated by subtracting the pro-molecular density from the total molecular density. Chemical shielding factors were calculated at all atomic positions at the DFT/B3LYP/6-311+G* level of theory by using the GIAO method implemented in Gaussian 03. The chemical shift for the selenium atom was obtained by subtracting the chemical shielding value of this atom from the one calculated for dimethylselenide which is 1623.1500 ppm at the B3LYP/6-311+G* level of theory, based on the corresponding geometry (C_{2v} symmetry, *anti*,*anti*-conformer). Bond orders were calculated according to the Hirshfeld scheme.[22] QTAIM bond and ring properties were calculated using the AIMPAC suite of programs.[29]

1,5-Diphenyl-2,4-diaza-1,5-diselena-3-thia-2,3-pentadiene (**2**) was prepared as described previously.[30] Its ^{77}Se NMR spectra were recorded on a Bruker DRX-500 spectrometer at a frequency of 95.38 MHz in [D$_8$]toluene; chemical shifts δ are given in ppm referenced to Me_2Se. The single-crystal X-ray structure determination of compound **2** was carried out at 23 °C on a Bruker P4 diffractometer by using $Mo_{K\alpha}$ radiation and a graphite monochromator. The structure was solved by direct methods using SHELXS-86[31] and refined by a least-squares method in the full-matrix anisotropic (isotropic for the hydrogen atoms) approximation by using SHELXL-97.[31] The parameters of the hydrogen atoms were given geometrically. The structure obtained was analysed for short contacts between nonbonded atoms with the PLATON program.[32,33]

CCDC-261563 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Crystal data for 1,5-diphenyl-2,4-diaza-1,5-diselena-3-thia-2,3-pentadiene (2): $C_{12}H_{10}N_2SSe_2$, $M_w=372.20$, monoclinic, $a=30.263(4)$, $b=5.7280(8)$, $c=7.6217(9)$ Å, $\beta=100.295(7)°$, $V=1299.9(3)$ Å^3, space group $C2/c$, $Z=4$, $\rho_{\text{cald}}=1.902\ \text{g cm}^{-3}$, $\mu(Mo_{K\alpha})=5.817\ \text{mm}^{-1}$, 1491 unique reflections ($R_{\text{int}}=0.0366$) measured. Final R_1 [1108 $F=2\sigma(I)$] = 0.0451, wR(all F^2) = 0.1323.

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