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Insight Into the Intermolecular Factors Responsible for the *Z*,*Z* Configuration of Ar–X–N=S=N–X–Ar (X = S, Se) Derivatives in the Solid State

Karla Tersago,[a] Irina Yu. Bagryanskaya,[b] Yuri V. Gatilov,[b] Sergey A. Gromilov,[c] Alexander Yu. Makarov,[b] Marcos Mandado,[a] Christian Van Alsenoy,[a] Andrey V. Zibarev,*[b,d] and Frank Blockhuys*[a]

Dedicated to Prof. Dr. Dr. h. c. Rüdiger Mews on the occasion of his 65th birthday

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The molecular and crystal structures of three new derivatives of Ph–S–N=S=N–S–Ph (**1**), with 2,4,6-(*tert*-$C_4H_9)_3C_6H_2$ (**4**), C_6F_5 (**5**) and 4-$CF_3C_6F_4$ (**6**) as peripheral rings, respectively, and one new derivative of Ph–Se–N=S=N–Se–Ph (**2**), with C_6F_5 (**7**) as peripheral rings, are reported and discussed in connection with those of the two parent structures **1** and **2** and those of the previously studied derivative of **1** containing 4-ClC_6H_4 (**3**) as peripheral rings. For these seven compounds the Z,Z configuration is the only one of the three theoretically possible configurations observed in the solid state and this configurational preference can not be explained by intramolecular stereoelectronic effects. Calculation of the packing energies and densities for the six most common space groups revealed that the crystal packing of the parent structure **1** in the Z,Z configuration has a systematic preference over the corresponding packing of **1** in the Z,E configuration by 0.3–4.9 kJ mol^{-1}. As a result, packing forces are most likely responsible for the dominance of the Z,Z configuration of the title compounds in the crystal.

1. Introduction

The molecular structures of chalcogen-nitrogen compounds are extremely diverse and continue to present a serious challenge to chemical theory in general.[1,2] Accurately predicting and rationalising these structures, both for isolated molecules and those arranged regularly in a crystal structure, remain of obvious fundamental interest.[3–5] This is particularly true when it comes to identifying and understanding the correlations that exist between molecular shape and the precise nature of the packing in the crystal. Within the family of chalcogen-nitrogen compounds, the oligomeric analogues of catenated sulfur nitride, $(SN)_x$, a metallic polymer and superconductor,[6] attract special attention due to possible applications as molecular wires in the field of molecular electronics. For this purpose, understanding the factors controlling molecular conformations is of the utmost importance.

Recently, we have shown[3] that the *Z*,*Z* configuration of C_6H_5–S–N=S=N–S–C_6H_5 (**1**)[7] and C_6H_5–Se–N=S=N–Se–C_6H_5 (**2**)[3] – and consequently that of 4-ClC_6H_4–S–N=S=N–S–C_6H_4Cl-4 (**3**)[8] – in the crystal can not be explained by the stabilising *intra*molecular interaction between the X^{II} (X = S, Se) atoms, which had been suggested in the literature, and that *inter*molecular forces in the crystal must be the driving force behind the observed configuration. In particular, we have demonstrated that in the gas phase or in solution the *Z*,*Z* configuration is not stabilised to a greater extent than the *Z*,*E* configuration.

In this work we report the preparation and analysis of the crystal structures of four new substituted derivatives of **1** and **2**, including 2,4,6-(*tert*-$C_4H_9)_3C_6H_2$–S–N=S=N–S–C_6H_2(*tert*-$C_4H_9)_3$-2,4,6 (**4**), C_6F_5–S–N=S=N–S–C_6F_5 (**5**), 4-$CF_3C_6F_4$–S–N=S=N–S–$C_6F_4CF_3$-4 (**6**), and C_6F_5–Se–N=S=N–Se–C_6F_5 (**7**); see Figure 1 for structural formulas. For all these compounds only the *Z*,*Z* configuration is observed in the solid state.[9] Based on the results of quantum chemical calculations (i.e. energy differences, bond orders

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[a] Department of Chemistry, University of Antwerp,
Universiteitsplein 1, 2610 Wilrijk, Belgium
Fax: +32-3-820-23-10
E-mail: frank.blockhuys@ua.ac.be
[b] Institute of Organic Chemistry, Russian Academy of Sciences,
630090 Novosibirsk, Russia
Fax: +7-383-330-97-52
E-mail: zibarev@nioch.nsc.ru
[c] Institute of Inorganic Chemistry, Russian Academy of Sciences,
630090 Novosibirsk, Russia
[d] Department of Physics, Novosibirsk State University,
630090 Novosibirsk, Russia

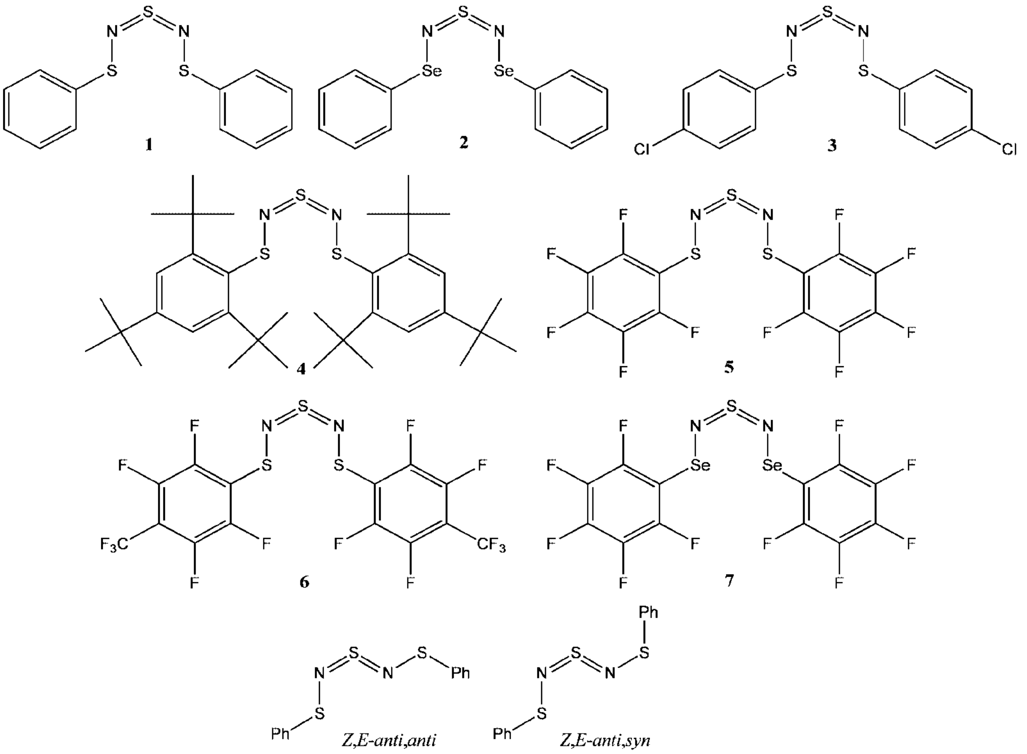

Figure 1. Structural formulas of the *Z*,*Z-anti*,*anti* conformers of the compounds under consideration; representative formulas of the *Z*,*E-anti*,*anti* and *Z*,*E-anti*,*syn* conformers have also been given.

and a topological analysis of the electron density) on 2,6-$(CH_3)_2C_6H_3$–S–N=S=N–S–$C_6H_3(CH_3)_2$-2,6 (**4′**) (as a model system for compound **4**) and **5**, using the same approach as we applied earlier,[3] *intra*molecular interactions can again be excluded as the reason for the observed *Z*,*Z* configurations. In order to shed more light on the possible *inter*molecular factors responsible for these observations, a number of simulations of the crystal packing of parent compound **1** were performed using the OPiX software.[10] The calculations show that for the six most common space groups ($P\bar{1}$, $P2_1/c$, $C2/c$, $Pbca$, $P2_1$, and $P2_12_12_1$) the crystal packing of **1** in the *Z*,*Z* configuration has a systematic preference over the packing of **1** in the *Z*,*E* configuration by 0.3–4.9 $kJ\,mol^{-1}$ and 0.010–0.025 $g\,cm^{-3}$ in energy and density, respectively. Based on this, we propose that the packing effects in the solid state are the driving force behind the observed *Z*,*Z* configuration of Ph–X–N=S=N–X–Ph (X = S, Se) and their derivatives.

2. Results and Discussion

2.1 Solid-State Molecular Structures

Previously, it was found that compounds **1**–**3** adopt the *Z*,*Z* configuration in the crystal.[3,7,8] This configuration features a virtually planar chalcogen-nitrogen fragment in which the $X^{II}\cdots X^{II}$ (X = S, Se) distance is significantly shorter than the sum of the van der Waals radii.[3,7,8] According to the XRD data we present here,[9] compounds **4**–**7** also exist in the *Z*,*Z* configuration in the crystal; see Figures 2, 3, 4, and 5 and Table 1 for geometrical data. For compound **4**, the –N=S=N– fragment is disordered over two sites (see Figure 2) in a ratio of 55:45. The chalcogen–nitrogen chain is planar to within ±0.012 and 0.032 Å for

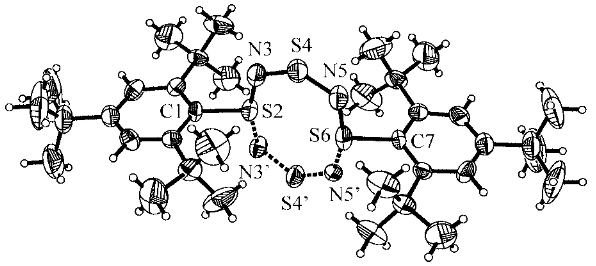

Figure 2. Molecular structure and partial numbering scheme of compound **4**. Displacement ellipsoids are at the 50% probability level; hydrogens are represented by spheres of arbitrary radius. Note that, for convenience, a unified numbering scheme has been used for compounds **4**–**7** in Figures 2, 3, 4, and 5; atoms S4 and S4′ of compound **4** actually lie on the C_2 symmetry axis.

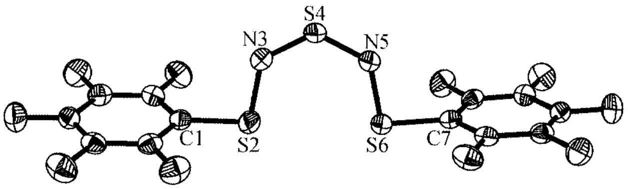

Figure 3. Molecular structure and partial numbering scheme of compound **5**. Displacement ellipsoids are at the 50% probability level.

Table 1. Selected solid-state geometrical data of compounds **4**–**6** (X = S) and **7** (X = Se); bond lengths in Å and angles in degrees.

	4[a]		**5**[b]		**6**	**7**
C1–X2	1.777(4)		1.763(5)	1.756(6)	1.765(4)	1.909(7)
X2–N3	1.816(6)	1.845(7)	1.668(5)	1.683(5)	1.684(3)	1.830(8)
N3–S4	1.550(7)	1.633(7)	1.543(5)	1.528(5)	1.537(3)	1.555(8)
S4–N5	1.550(7)	1.633(7)	1.525(5)	1.536(5)	1.537(3)	1.519(9)
N5–X6	1.816(6)	1.845(7)	1.684(5)	1.679(6)	1.684(3)	1.843(8)
X6–C7	1.777(4)		1.757(5)	1.761(6)	1.765(4)	1.911(8)
X2···X6	3.274(2)		3.370(2)	3.220(2)	3.212(2)	3.321(4)
C1–X2–N3	100.0(3)	95.8(3)	97.3(2)	96.8(2)	98.7(2)	94.1(3)
X2–N3–S4	125.6(4)	131.1(4)	128.4(3)	127.2(3)	126.2(2)	125.6(5)
N3–S4–N5	125.3(5)	114.2(5)	125.2(3)	124.4(3)	124.4(3)	126.0(4)
S4–N5–X6	125.6(4)	131.1(4)	128.6(3)	125.8(3)	126.2(2)	126.2(5)
N5–X6–C7	100.0(3)	95.8(3)	97.9(2)	97.1(3)	98.7(2)	93.9(3)
C1–X2–N3–S4	159.1(4)	–154.1(4)	174.0(5)	–169.6(5)	175.7(3)	–146.9(7)
X2–N3–S4–N5	–1.0(3)	–2.7(3)	–0.1(8)	2.3(8)	–0.4(2)	–9.6(10)
N3–S4–N5–X6	–1.0(3)	–2.7(3)	0.6(8)	–0.1(8)	–0.4(2)	2.4(10)
S4–N5–X6–C7	159.1(4)	–154.1(4)	170.7(5)	–160.0(6)	175.7(3)	–147.6(7)

[a] The –N=S=N– fragment is disordered over two sites in a ratio of 55:45. The abnormally long S2–N3 bond lengths obtained are attributed to the disorder. [b] Two crystallographically independent molecules.

the two disordered molecules of **4**, ±0.004 and 0.017 Å for the two crystallographically independent molecules of **5**, ±0.005 Å for **6** and ±0.055 Å for **7**. The bond lengths and angles in compounds **4**–**7** given in Table 1 are typical[11] and quite similar to those found for compounds **1**–**3**.[3,7,8] The intramolecular $X^{II}\cdots X^{II}$ distances are again significantly shorter than the sums of corresponding van der Waals radii, which are 3.60 Å for the S···S and 3.80 Å for the Se···Se contacts.[12,13]

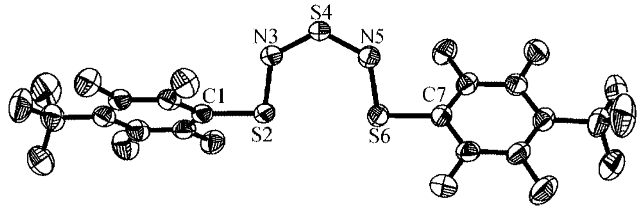

Figure 4. Molecular structure and partial numbering scheme of compound **6**. Displacement ellipsoids are at the 50% probability level.

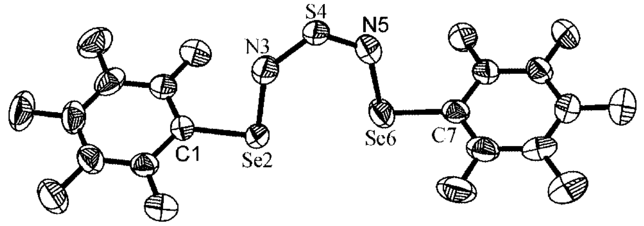

Figure 5. Molecular structure and partial numbering scheme of compound **7**. Displacement ellipsoids are at the 50% probability level.

Despite the fact that the seven compounds display the same *Z*,*Z* configuration, their particular molecular conformations are somewhat different. Molecules of compound **3** possess approximate C_{2v} symmetry, while those of compound **1** display C_2 symmetry, since both phenyl rings are twisted away from the plane of the sulfur-nitrogen moiety by about 30°; the molecular conformation of **2** is very similar to that of **1**.[3] In contrast, the aromatic rings of compounds **4** and **5** are practically perpendicular to the plane of sulfur-nitrogen fragment: the corresponding dihedral angles in **4**, which displays C_2 symmetry, are 89.3(1)°. For the two crystallographically independent molecules of **5**, which possess C_1 symmetry, they are 79.9(1) and 76.6(1), and 73.7(1) and 71.5(1)°. For compound **6**, which also displays C_2 symmetry, the angles are 53.1(1)°, i.e. significantly smaller. The dihedral angles between the planes of the two aromatic rings are 10.6(1)° in **4**, 9.6(3)° and 9.3(3)° in **5**, and 10.4(5)° in **7**. Thus, the conformational changes observed on going from **2** to **7** are similar to those on going from **1** to **5**.

The above observations on compounds **1**–**7** provide clear evidence that the *Z*,*Z* configuration is the one which is generally favoured in the solid state, and that this configuration is stable towards intramolecular perturbations such as significant variations in the stereoelectronic demand of the terminal aromatic groups or the substitution of S^{II} by Se^{II} atoms. At the same time, the observed solid-state molecular conformations vary from practically coplanar to severely non-coplanar and it seems that these do depend greatly on the nature of the aromatic groups.

2.2 Gas-Phase Molecular Structures

The calculated relative energies of the three lowest-energy conformers [*Z*,*Z*-*anti*,*anti* (C_2), *Z*,*E*-*anti*,*anti* (C_1) and *Z*,*E*-*anti*,*syn* (C_1), see Figure 1] of compounds **4′** and **5** have been compiled in Table 2. We note that all other possible conformers have energies which are considerably higher (> 20 kJ mol^{-1}), based on which they can be confidently excluded. The data in Table 2 indicate that the *Z*,*Z*-*anti*,*anti* conformer is the lowest-energy one; this is also the conformer that is found in the crystal. In analogy with the situation for the parent compounds **1** and **2**,[3] there are two *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 the calculations the equilibrium conformer compositions at 293 K are 87% C_2-*Z*,*Z*-*anti*,*anti*, 8% C_1-*Z*,*E*-*anti*,*anti* and 5% C_1-*Z*,*E*-*anti*,*syn* for compound **4′** and 73% C_2-*Z*,*Z*-*anti*,*anti*, 24% C_1-*Z*,*E*-*anti*,*anti*, and 3% C_1-*Z*,*E*-*anti*,*syn* for compound **5**.

Table 2. Calculated energies *E* [H] and relative energies Δ*E* [kJ mol^{-1}] of the three lowest-energy conformers [*Z*,*Z*-*anti*,*anti* (C_2), *Z*,*E*-*anti*,*anti* (C_1) and *Z*,*E*-*anti*,*syn* (C_1)] of compounds **4′** and **5** at the B3LYP/6-311+G* level of theory. See text for details.

	Conformer	*E*	Δ*E*
4′	C_2-*Z*,*Z*-*a*,*a*	–1924.7753	0.00
	C_1-*Z*,*E*-*a*,*a*	–1924.7731	5.98
	C_1-*Z*,*E*-*a*,*s*	–1924.7727	6.87
5	C_2-*Z*,*Z*-*a*,*a*	–2760.0944	0.00
	C_1-*Z*,*E*-*a*,*a*	–2760.0934	2.65
	C_1-*Z*,*E*-*a*,*s*	–2760.0914	7.78

The molecular geometries of the three conformers are given in Table 3. 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, i.e. S(4)–N(5), N(5)–S(6) and the three angles in the SNSNS fragment: differences of up to 0.056 Å for N(5)–S(6) and 15.7° for N(3)–S(4)–N(5) in **5** are found. These results are analogous to the ones found previously for the parent compounds **1** and **2**.[3] The changes in the non-bonded distances when going from one conformer to the other will be discussed in section 2.3. We note that conformational changes similar to the ones found in the solid state can be observed in the results of the calculations: while in the parent compounds **1** and **2** the benzene rings are twisted away from the plane of the XSNSX fragment by a mere 10.6 and 10.0°, respectively, for **4′** and **5** values of 70.1 and 69.1°, respectively, are found.

Comparing the XRD data of compounds **4** and **5** in Table 1 with those of the relevant gas-phase conformer (i.e. *Z*,*Z*-*anti*,*anti*) of compounds **4′** and **5** in Table 3 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 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_a-type distances while the $r_{\text{calcd.}}$ are r_e distances by definition.[14,15]

Table 3. Selected calculated geometrical data of the three lowest-energy conformers of compounds **4′** and **5**; bond lengths in Å and angles in degrees.

	4′			**5**		
	Z,*Z*-*a*,*a*	*Z*,*E*-*a*,*a*	*Z*,*E*-*a*,*s*	*Z*,*Z*-*a*,*a*	*Z*,*E*-*a*,*a*	*Z*,*E*-*a*,*s*
C1–S2	1.795	1.797	1.796	1.781	1.783	1.781
S2–N3	1.712	1.709	1.710	1.708	1.705	1.712
N3–S4	1.570	1.574	1.574	1.568	1.564	1.569
S4–N5	1.570	1.588	1.586	1.568	1.600	1.580
N5–S6	1.712	1.728	1.705	1.708	1.744	1.692
S6–C7	1.795	1.793	1.807	1.781	1.780	1.795
S2···S6	3.509	4.702	4.678	3.424	4.667	4.619
C1–S2–N3	99.7	98.5	98.5	98.1	96.8	96.6
S2–N3–S4	129.1	119.8	120.2	128.4	119.6	119.4
N3–S4–N5	125.8	110.8	111.1	124.9	109.2	110.8
S4–N5–S6	129.1	119.6	124.8	128.4	113.9	127.0
N5–S6–C7	99.7	99.0	107.1	98.1	99.2	107.5
C1–S2–N3–S4	166.9	178.6	–177.0	154.8	178.1	–179.4
S2–N3–S4–N5	–2.2	0.2	–0.2	–1.2	–0.5	–0.1
N3–S4–N5–S6	–2.2	179.1	–178.9	–1.2	–173.1	179.0
S4–N5–S6–C7	166.9	–179.5	–4.9	154.8	–120.4	–1.1

2.3 Intramolecular S···S Interactions

As mentioned before, both in the crystal and in the lowest-energy conformer in the gas phase the distances between S(2) and S(6) [3.274(2) in **4** and 3.509 Å in **4′**, respectively, and 3.370(2)/3.220(2) and 3.424 Å in **5**, respectively] are well below the sum of the van der Waals radii (3.60 Å). This does suggest some sort of bonding interaction between those atoms. However, the energy difference between the conformer which has the interaction, i.e. C_2-*Z*,*Z*-*anti*,*anti*, and one which does not, e.g. C_1-*Z*,*E*-*anti*,*anti*, is only of the order of 5.98 kJ mol^{-1} for **4′** and 2.65 kJ mol^{-1} for **5** (Table 2). That the C_1-*Z*,*E*-*anti*,*anti* conformers do not display an interaction between S(2) and S(6) can be clearly seen from the S···S distances in Table 3 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 interactions do not play an important stabilising role.

Additional evidence comes from the calculated Hirshfeld bond orders of the different bonds in both molecules; the results are given in Table 4. The data reproduce the different types of bonding in the molecules equally well for the three conformers of **4′** and **5**: the XC bonds are clearly single while the S=N bonds are virtually double. The values for the S···S contacts are negative for all conformers of both compounds, which is a result of the scaling procedure,[16] and this indicates that the bond orders of these bonds are very small. The unscaled values for the *Z*,*Z*-*anti*,*anti* conformers of **4′** and **5** are 0.03 and 0.04, respectively, and these can be directly compared to the unscaled values for the XC bonds which are 0.38 and 0.39, respectively. The bonding in the S···S contacts is about thirteen and ten times lower, respectively, than in a regular single bond; the interaction between the two atoms must therefore be extremely

Table 4. Hirshfeld bond orders for the three lowest-energy conformers of compounds **4′** and **5**. See text for details.

	4′			**5**		
	Z,*Z*-*a*,*a*	*Z*,*E*-*a*,*a*	*Z*,*E*-*a*,*s*	*Z*,*Z*-*a*,*a*	*Z*,*E*-*a*,*a*	*Z*,*E*-*a*,*s*
C1–S2	1.02	1.01	1.01	1.09	1.07	1.08
S2–N3	1.18	1.15	1.15	1.20	1.17	1.15
N3–S4	1.83	1.76	1.77	1.83	1.80	1.79
S4–N5	1.83	1.66	1.67	1.83	1.59	1.69
N5–S6	1.18	1.11	1.25	1.20	1.07	1.30
S6–C7	1.02	1.03	0.99	1.09	1.11	1.06
S2···S6	–0.53	–0.68	–0.68	–0.51	–0.68	–0.68

weak. These values are of the same order of magnitude as for **1**, for which the scaled and unscaled bond orders are –0.52 and 0.04, respectively.[3]

Finally, a topological analysis of the total molecular electron density was performed using the Atoms In Molecules (AIM) theory.[17] The electron densities $\rho(r)$ of a number of relevant bond critical points (BCPs) and ring critical points (RCPs) of the three lowest-energy conformers of compounds **4′** and **5** were calculated and the results are given in Table 5. The topological analyses of **4′** and **5** show that there is an interaction between S(2) and S(6) but that this interaction is extremely weak. This conclusion is based on the fact that for **4′** the density in the BCP of the S···S bond is about 27 times lower than in the BCP of the SC single bond; for **5** this is 22 times. Moreover, the densities in the BCPs are 2.3 to 2.8 times lower than those found [calculated at the RI-BP86/TZVP level of theory] for the intermolecular S···S contacts (with a contact distance of about 3.0 Å) in a series of bis(thiocarbamoyl)disulfides.[18] The values of the density correlate well with those calculated for the parent compound **1**,[3] even though it seems that in compound **4′** the S···S interaction is slightly weaker than in **1** (0.0071 vs. 0.0078); in compound **5** the interaction seems slightly stronger (0.0087). The values of the RCPs confirm that the interaction should be very weak: the values of the phenyl rings are about three times larger those of the NSNS···S ring, for both compounds.

Table 5. Values of the electron density $\rho(r)$ (in au) of the relevant BCPs and RCPs for the three lowest-energy conformers of compounds **4′** and **5**. See text for details.

		4′			**5**		
		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	S2–C1	0.1887	0.1888	0.1889	0.1911	0.1911	0.1912
	CH···N3	0.0081	0.0085	0.0086			
	CH···N5	0.0081	0.0091				
	S2···S6	0.0071			0.0087		
RCP	C_6Y_5	0.0213	0.0213	0.0214	0.0192	0.0192	0.0193
	SCCCH···N	0.0080	0.0083	0.0082			
	NSNS···S	0.0064			0.0074		

The combination of the above mentioned three criteria confirms the conclusion which was drawn for the parent compound: the proposed stabilising *intra*molecular interaction might not exist or at least be extremely weak, and *inter*molecular forces are the main cause of the observed *Z*,*Z* configuration in the solid.

2.4 Crystal Packing

Previously, it was hypothesized that in the crystal the *Z*,*Z* configuration of the title compounds allows a larger number of short intermolecular contacts per molecule, particularly via X···X (X = S, Se) contacts, than the corresponding *Z*,*E* configuration.[3] Naturally, this implies a closer packing. At present, though, the reliable ab initio prediction of a crystal packing remains practically very difficult, in particular for conformationally flexible molecules.[19–23] Still, we have been able to substantiate the idea that intermolecular (packing) forces are responsible for the preference of the *Z*,*Z* configuration, by performing simulations of the crystal packing of the parent compound **1** in both the *Z*,*Z* and *Z*,*E* configurations, using the OPiX software.[10] Starting from the atomic coordinates of a single molecule, this program generates[24–28] the solid-state packing for the six most common space groups ($P\bar{1}$, $P2_1/c$, $C2/c$, $Pbca$, $P2_1$, and $P2_12_12_1$), covering about 84% of the crystal structures deposited at the Cambridge Structural Database.[29,30] One limitation of the procedure, however, is the fact that the molecular geometry can not change during the optimization.[10] Even so, the energies of intermolecular interactions in molecular crystals are significantly smaller than the typical energies of intramolecular covalent interactions and, due to this, packing-induced molecular distortions are often limited.[31] Molecular structures calculated on higher levels of theory therefore often provide a good approximation to the structures observed in the crystal, and crystal structure predictions based on rigid calculated molecular structures is generally assumed to be reasonable.[32,33]

Also in the case of the parent Ph–S–N=S=N–S–Ph (**1**), the calculated gas-phase geometry of the *Z*,*Z*-*anti*,*anti* configuration seems to provide a useful model for the experimental geometry.[3] Therefore, the calculated molecular geometries of both configurations of **1** in the *anti,anti* conformation (i.e., *Z*,*Z*-*anti*,*anti* and *Z*,*E*-*anti*,*anti*, see Figure 1) were used in the OPiX calculations. However, to validate the simulation procedure and to investigate how well the method is able to reproduce experimentally observed unit cell dimensions, a first OPiX calculation was performed starting from the experimental geometry of **1** as it was reported by Leitch et al.[7] In the crystal (space group $C2/c$ and $Z = 4$) the molecules of **1** lie on C_2 axes. The OPiX software[10] allows using the corresponding subgroup which, in this case, is $P\bar{1}$. For this space group, the simulated unit cell of Ph–S–N=S=N–S–Ph (**1**) has a packing energy of –170.0 kJ mol^{-1} and the following parameters: a = 5.419 Å, b = 7.584 Å, c = 15.50 Å, α = 69.56°, β = 79.94°, and γ = 90.00°. The reduced unit cell parameters, calculated from the reported data,[7] are a = 5.601(5) Å, b = 7.792(8) Å, c = 14.95(1) Å, α = 78.82(1)°, β = 79.20(1)°, and γ = 90.00°. As can be seen, there is a good agreement between calculated and experimental data.

The relevant results of the OPiX calculations performed using the molecular geometries of both the *Z*,*Z*-*anti*,*anti* and *Z*,*E*-*anti*,*anti* configurations of **1**, obtained from the quantum chemical calculations, are given in Table 6. From the packing energies and densities, given in Table 6, it can be seen that for all considered space groups the crystal packing of **1** in the *Z*,*Z* configuration has a systematic preference over the packing of **1** in the *Z*,*E* configuration by 0.3–4.9 kJ mol^{-1} and 0.010–0.025 g cm^{-3}, respectively. In particular for the space group in which **1** crystallises, $C2/c$, the differences are 2.5 kJ mol^{-1} and 0.012 g cm^{-3} for the energy and density, respectively, in favour of the *Z*,*Z* configuration. It is interesting to note that for this space group the unit cell parameters simulated using the calculated *Z*,*Z* geometry (a = 6.113 Å, b = 6.848 Å, c = 15.466 Å, α = 77.25°, β = 83.10°, γ = 87.20°) are likewise acceptably close to the experimental values given above. Furthermore, the calculated packing energy of the crystal based on **1** in its experimental geometry is 10.0 kJ mol^{-1} lower than that of the crystal based on **1** in its gas-phase geometry, at least for the $P\bar{1}$ space group (see Table 6); it is 8.8 kJ mol^{-1} lower than the most favourable packing based on the gas-phase geometry, i.e. that in the $P2_12_12_1$ space group.

Table 6. Packing energies (E in kJ mol^{-1}) and densities (D in g cm^{-3})[a] of the crystal structures simulated by the OPiX suite of programs for the Z,E and Z,Z configurations of Ph–S–N=S=N–S–Ph **1**.

Space group	*Z*,*Z*-*a*,*a* *E*	*D*	*Z*,*E*-*a*,*a* *E*	*D*
$P\bar{1}$	–160.0	1.495	–156.4	1.476
$P2_1/c$	–158.7	1.496	–158.4	1.486
$C2/c$	–154.5	1.445	–152.0	1.433
$Pbca$	–152.0	1.459	–150.2	1.437
$P2_1$	–158.6	1.487	–153.7	1.462
$P2_12_12_1$	–161.2	1.501	–158.8	1.489

[a] The experimental value is 1.471 g cm^{-3}.[7]

These findings can be considered as the manifestation of a trend to approach a close-packing regime via the Z,Z configuration. In turn, this very favourable way of organising the crystal structure must then be largely responsible for the observed Z,Z configurations of the title compounds **1**–**7**. Indeed, our theoretical and experimental work on isolated molecules of Ar–X–N=S=N–X–Ar (X = S, Se, and their derivatives) – in this work and in ref.[3] – suggests that even in the absence of stabilizing stereoelectronic interactions between the X^{II} atoms the Z,Z configuration has a minor thermodynamic preference over the Z,E configuration (at least for the method/basis set combination used). As a consequence, both configurations coexist in the corresponding equilibria in the gas phase and in solution, but in the solid state only the Z,Z configuration exists. Our OPiX calculations then suggest that the crystal packing of the discussed derivatives in the Z,Z configuration has a further minor thermodynamic preference over that of the compounds in the Z,E configuration. Both the intramolecular and the intermolecular effects seemingly act in the same direction, i.e., towards the packing of Ar–X–N=S=N–X–Ar (X = S, Se) in the Z,Z configuration. Whereas in the gas phase or in solution the energy differences between the different isomers allows for the presence of the less stable isomer, the intermolecular (packing) forces seem to be critically important for the total domination of the Z,Z configuration in the solid state. The idea that rather than *intra*molecular factors *inter*molecular ones (i.e. packing forces) are the main driving force behind the experimentally observed configurations, which was until now based on the results of the quantum chemical calculations, has thus been strengthened by the simulations of the crystal packing.

3. Conclusions

For Ph–S–N=S=N–S–Ph (**1**) and Ph–Se–N=S=N–Se–Ph (**2**) and their derivatives **3**–**7** the Z,Z configuration is the only one of the three theoretically possible configurations observed in the solid state and this configurational preference can not be explained by intramolecular stereoelectronic effects, which is shown by three theoretical arguments at the B3LYP/6-311+G* level of theory. The analysis of the properties of the simulated crystal structures of two conformers of the parent compound Ph–S–N=S=N–S–Ph (**1**) strengthens the idea that rather than *intra*molecular factors *inter*molecular ones (that is packing forces) are the main driving force behind the experimentally observed Z,Z configurations.

Experimental Section

Compounds **4**[34] and **5**[35] were synthesized from $(Me_3SiN=)_2S$ and the corresponding ArSCl as described before. ^{15}N and ^{77}Se NMR spectra were recorded on a Bruker DRX-500 spectrometer at frequencies of 50.68 and 95.38 MHz, respectively, with NH_3 (liq.) and Me_2Se as standards. ^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer at a frequency of 188.20 MHz with C_6F_6 as the standard (the chemical shift of C_6F_6 with respect to $CFCl_3$ is –162.2 ppm). High-resolution mass spectra (EI, 70 eV) were recorded on a Finnigan MAT MS-8200 instrument. UV/Vis spectra were recorded on a Hewlett–Packard 8453 spectrophotometer. Synthetic procedures were carried out under an argon atmosphere in dried solvents with stirring. The reagents were added dropwise and solvents were always distilled off under reduced pressure.

Syntheses

1,5-Bis(heptafluoro-4-methylphenyl)-2,4-diaza-1,3,5-trihia-2,3-pentadiene (6): Over a period of 1 h, a solution of $4\text{-}CF_3C_6F_4SCl$[36] (2.85 g, 0.01 mol) in CH_2Cl_2 (15 mL) was added to a solution of $(Me_3SiN=)_2S$[37] (1.03 g, 0.005 mol) in CH_2Cl_2 (10 mL) at –30 °C. The reaction mixture was slowly warmed up to 20 °C, the solvent was distilled off and the residue was recrystallized from hexane. Compound **6** was obtained as bright yellow crystals in a yield of 2.23 g (80%), m.p. 75–76 °C. MS *m*/*z*: 557.9022 [M$^+$, calculated for $C_{14}F_{14}N_2S_3$ 557.9000]. NMR (C_6D_6): δ = ^{19}F 106.5, 31.1, 23.7 ppm. UV/Vis (heptane) λ_{max} (nm) (logε): 412 (3.97). $C_{14}F_{14}N_2S_3$ (558.34): calcd. C 30.12, F 47.64, N 5.01, S 17.23; found C 30.09, F 47.62, N 4.84, S 17.35.

1,5-Bis(pentafluorophenyl)-2,4-diaza-3-thia-1,5-diselena-2,3-pentadiene (7): Over a period of 1 h, a solution of C_6F_5SeCl[38] (0.90 g, 0.0032 mol) in hexane (10 mL) was added to a solution of $(Me_3SiN=)_2S$[37] (0.32 g, 0.0016 mol) in hexane (20 mL) at 20 °C. After an additional hour the solvent was distilled off and the residue was recrystallized from hexane. Compound **7** was obtained as orange crystals in a yield of 0.56 g (62%), m.p. 42–43 °C. MS *m*/*z*: 553.8034 [M$^+$, calculated for $C_{12}F_{10}N_2SSe_2$ 553.7952]. NMR ($CDCl_3$): δ = ^{15}N 302.1; ^{19}F 36.5, 13.7, 2.7; ^{77}Se 775 (broad, cf. ref.[2]) ppm. UV/Vis (heptane) λ_{max} (nm) (logε): 422 (3.68, sh), 370 (3.92). $C_{12}F_{10}N_2SSe_2$ (552.11): calcd. C 26.11, F 34.41, N 5.07; found C 25.93, F 34.45, N 5.11.

Crystallographic Analyses

The single-crystal X-ray structure determinations (Table 7) were carried out on a Bruker P4 for compound **4**, a Stoe Stadi4 for compound **5** and a Syntex P2$_1$ diffractometer for compounds **6** and **7**, with graphite-monochromated Mo-K_α (λ = 0.71073 Å) or Cu-K_α (λ = 1.54178 Å) radiation. The structures were solved by direct methods using SHELXS-97[39] and refined by least-squares methods in the full-matrix anisotropic (isotropic for hydrogen atoms)

Table 7. Crystal and refinement data of compounds **4**–**7**.

	4	**5**	**6**	**7**
Formula	$C_{36}H_{58}N_2S_3$	$C_{12}F_{10}N_2S_3$	$C_{14}F_{14}N_2S_3$	$C_{12}F_{10}N_2SSe_2$
M	615.02	458.32	558.34	552.12
T [K]	296	200	296	296
λ [Å]	0.71073	0.71073	1.54178	1.54178
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$Ccca$	$P2_1/n$	$Pbcn$	$P2_1/c$
a [Å]	20.179(5)	10.1269(6)	6.086(2)	4.531(4)
b [Å]	20.830(5)	9.8234(6)	9.550(2)	10.791(7)
c [Å]	17.917(3)	30.4702(14)	31.650(10)	31.96(2)
β [°]	90	92.422(5)	90	91.26(14)
U [Å^3]	7531(3)	3028.5(3)	1839.5(9)	1562(2)
Z	8	8	4	4
D_c [g cm^{-3}]	1.085	2.010	2.016	2.348
μ [mm^{-1}]	0.222	0.604	5.107	8.291
F(000)	2688	1792	1088	1040
Crystal size [mm]	$0.44 \times 0.41 \times 0.18$	$1.04 \times 0.64 \times 0.16$	$1.50 \times 0.40 \times 0.15$	$0.60 \times 0.40 \times 0.25$
θ range [°]	1.81–25.00	2.09–25.01	2.79–69.94	2.77–69.92
Index range	$0 \le h \le 23$	$-12 \le h \le 12$	$-7 \le h \le 0$	$0 \le h \le 5$
	$0 \le k \le 24$	$0 \le k \le 11$	$-2 \le k \le 11$	$0 \le k \le 13$
	$0 \le l \le 21$	$0 \le l \le 36$	$-2 \le l \le 38$	$-38 \le l \le 38$
Reflections collected	3310	5409	1862	3312
Independent reflections	3310	5301	1746	2923
		[R_{int} = 0.0239]	[R_{int} = 0.0359]	[R_{int} = 0.0417]
Completeness to θ (%)	99.6	93.3	84.8	98.5
Absorption correction	none	0.63–0.76	0.85–1.00	0.06–0.25
Refinement method	full-matrix least squares on F^2			
Data/restraints/parameter	3310/0/199	5301/0/488	1746/0/151	2923/0/245
Goodness-of-fit on F^2	1.032	1.080	1.053	1.065
Observed reflections	1260	4126	1260	1903
Final R indices	R_1 = 0.0671	R_1 = 0.0577	R_1 = 0.0557	R_1 = 0.0690
[$I > 2\sigma(I)$]	wR_2 = 0.1616	wR_2 = 0.1827	wR_2 = 0.1435	wR_2 = 0.1929
R indices (all data)	R_1 = 0.1434	R_1 = 0.0770	R_1 = 0.0774	R_1 = 0.0928
	wR_2 = 0.1703	wR_2 = 0.2092	wR_2 = 0.1601	wR_2 = 0.2105
Largest diff. peak	0.737	1.063	0.326	1.154
and hole [e Å^{-3}]	–0.263	–0.804	–0.411	–0.588

approximation using SHELXL-97.[39] Hydrogen atoms were located geometrically.

CCDC-185941 (for **4**), -185939 (for **5**), -185940 (for **6**) and -604700 (for **7**) contain 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.

Calculations

The DFT calculations were performed using Gaussian 03[40] applying standard gradient techniques at the B3LYP level of theory using the 6-311+G* basis set on all atoms; the basis set was used as it is implemented in the program. Calculations to determine the stability of the wave functions (or rather the mathematical constructions based on the Kohn–Sham orbitals) were performed 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. Bond orders (or rather overlap populations; see ref.[16]) were calculated according to the Hirshfeld Scheme.[16] QTAIM bond and ring properties were calculated using the AIMPAC suite of programs.[41] Crystal packing simulations were performed with the OPiX suite of programs[10] starting from the calculated (DFT/B3LYP/6-311+G*) geometries of the *Z*,*Z*-*anti,anti* and *Z*,*E*-*anti,anti* conformers of **1** (Figure 1). Initially, the recommended parameters were used in the optimizations, but in subsequent calculations these values were modified. In particular, the *energy threshold* parameter was lowered from the recommended value of 0.5 to 0.3 to obtain more detailed results. In the case of the *Pbca* space group the recommended values of the *energy threshold* and *step resolution* parameters were modified to 0.9 and 0.7, and 0.7 and 0.5 for the *Z*,*E* and *Z*,*Z* configurations, respectively.

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