gle-crystal polarized spectroscopic studies are needed to clarify the molecular orbital scheme.

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Molecular, Electronic, and Crystal Structure of Naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine

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Abstract: Naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine (**1**) crystallizes in the form of long, thin, lustrous, metallic green needles. The unit cell is monoclinic ($Z = 2$) with the $P2_1/a$ space group, and the lattice parameters are $a = 14.935$ (8) Å, $b = 8.304$ (6) Å, $c = 3.794$ (4) Å, $\beta = 91.53$ (7)°. In fact the molecule adopts the higher D_{2h} point group symmetry. The molecular geometry shows that **1** is heavily cross conjugated with a relatively small contribution from the structure corresponding to a naphthalene nucleus with peri-fused sulfurdiimide bridges. Strong bond-length alternation is found in **1**, particularly around the periphery of the molecule. The molecules form stacks in the *c* direction with a pseudohexagonal packing. Along the stacks the molecular planes are within a distance of 3.40 Å and the atoms are positioned similarly to those in the rhombohedral modification of graphite. The stacks are connected by two pairs of short intermolecular S⋯N contacts (3.104 Å), which leads to a ribbon-like array of nearly coplanar molecules. The intermolecular interaction takes the form of a parallelogram with sides composed of the intramolecular S–N bond (1.649 Å) and the S⋯N intermolecular contact (3.104 Å). Reference to the literature shows that short intermolecular chalcogen–nitrogen contacts occur in many compounds containing the –NSN– linkage. Furthermore, there is found to be a strong inverse correlation between the lengths of the intramolecular S–N bonds and the intermolecular S⋯N contacts, and possible reasons for this behavior are discussed.

Introduction

Recently the synthesis and the chemical and physical properties of naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine (**1**) have been reported.[1] The compound has a chemical stability indicative of aromatic character. On the other hand, physicochemical results (electrochemical behavior, electronic spectrum, and ^{1}H NMR chemical shift) suggest antiaromatic character. On this basis it was concluded that **1** is a compound of ambiguous aromatic character. In order to further elucidate the molecular and electronic structure of **1** we have carried out

an X-ray structure analysis in the course of a systematic study[2a-k] on sulfur–nitrogen multiple bond systems.

Experimental Section

The title compound crystallizes from 1,2-dichloroethane in the form of long, thin, lustrous, metallic green needles. On the basis of Weissenberg and precession photographs the monoclinic space group $P2_1/a$ was determined from the 2/*m* symmetry of the reflections and the systematic absences ($h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$). The photographs show that the compound tends to form twinned crystals with (100) as the twinning plane. In order to determine the lattice parameters and to measure the intensities we used a punch-tape controlled automatic single crystal diffractometer (Siemens AED).
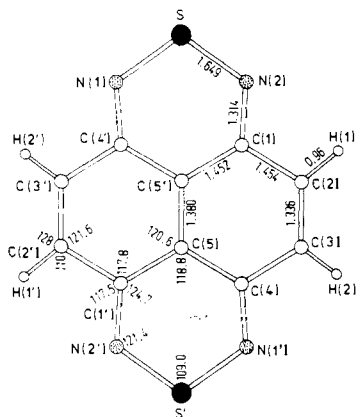
† Bell Laboratories.

Figure 1. Molecular structure of naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]-thiadiazine (1). The given bond lengths and angles are mean values averaged over the molecular symmetry.

Table I. Fractional Coordinates and Thermal Parameters of All Atoms

atom	Coordinates[a]		
	x	y	z
S	0.3975 (1)	0.8545 (2)	0.9195 (5)
N(1)	0.5039 (3)	0.8371 (6)	0.8187 (15)
N(2)	0.3443 (3)	0.6883 (6)	0.8036 (16)
C(1)	0.3862 (4)	0.5671 (7)	0.6553 (16)
C(2)	0.3335 (4)	0.4253 (8)	0.5608 (19)
C(3)	0.3709 (4)	0.2977 (8)	0.4088 (20)
C(4)	0.4656 (4)	0.2928 (7)	0.3317 (17)
C(5)	0.5194 (4)	0.4343 (7)	0.4210 (16)
H(1)	0.270 (5)	0.445 (9)	0.622 (17)
H(2)	0.343 (6)	0.201 (13)	0.355 (26)

atom	Thermal Parameters[b]					
	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	2.9 (1)	2.1 (1)	4.6 (1)	0.5 (1)	0.3 (1)	−0.8 (1)
N(1)	2.9 (2)	2.0 (2)	4.6 (3)	0.1 (2)	0.1 (2)	−0.6 (2)
N(2)	2.7 (2)	2.5 (2)	5.0 (3)	0.2 (2)	0.1 (2)	−0.6 (2)
C(1)	2.4 (2)	2.5 (2)	3.5 (3)	0.1 (2)	0.1 (2)	−0.3 (2)
C(2)	2.3 (2)	2.8 (3)	4.8 (3)	−0.2 (2)	0.2 (2)	−0.3 (2)
C(3)	2.7 (3)	2.5 (3)	5.0 (3)	−0.6 (2)	0.2 (2)	−0.6 (2)
C(4)	2.8 (2)	1.9 (2)	4.0 (3)	−0.3 (2)	−0.1 (2)	−0.2 (2)
C(5)	2.5 (2)	2.0 (2)	3.3 (3)	−0.1 (2)	−0.4 (2)	−0.2 (2)
	b					
H(1)	3.8 (15)					
H(2)	7.6 (26)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and the following table. [b] The form of the anisotropic thermal ellipsoid is $\exp\{-\frac{1}{4}(b_{11}h^2a^{*2} + b_{22}k^2b^{*2} + b_{33}l^2c^{*2} + 2b_{12}hka^*b^* + 2b_{13}hla^*c^* + 2b_{23}klb^*c^*)\}$.

The lattice parameters are $a = 14.935$ (8) Å, $b = 8.304$ (6) Å, $c = 3.794$ (4) Å, $\beta = 91.53$ (7)°. The crystallographic c axis is identical with the long growth direction (needle axis) of the crystals. From the volume of the unit cell (470.4 Å³) together with the molecular weight (244.3) and a measured density $D_m = 1.72$ g cm⁻³ ($D_x = 1.725$ g cm⁻³) a unit cell content of two molecules ($Z = 2$) was calculated. This requires that the molecules occupy a twofold special position of the space group $P2_1/a$ with the point symmetry $\bar{1}$.

The intensities of the reflections were collected with an untwinned crystal with the dimensions 0.16 × 0.16 × 0.85 mm³. By the procedure of five-point measurement using $\theta/2\theta$ scan mode (Cu Kα radiation, Ni filter, $\theta_{max} = 70°$) 901 independent reflections were measured. Of these, 54 were considered to be unobserved ($I \leqslant 2\sigma_I$, $|F_o| = 4\sigma_F$). Lp corrections were applied to the data in the normal way but no absorption correction ($\mu_{Cu K\alpha} = 47.2$ cm⁻¹). The statistics of the E values proved the existence of a centrosymmetric space group.
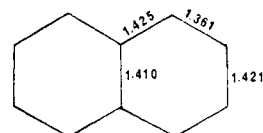

Figure 2. Bond lengths of naphthalene (ref 15)

Table II. Bond Distances and Angles[a]

Bond Distances (Å)			
S–N(2)	1.647 (6)	S–N(1)	1.652 (5)
N(2)–C(1)	1.320 (8)	N(1)–C(4')	1.308 (8)
C(1)–C(2)	1.456 (9)	C(3)–C(4)	1.452 (9)
C(1)–C(5')	1.447 (8)	C(4)–C(5)	1.458 (8)
C(2)–H(1)	1.00 (7)	C(3)–H(2)	0.93 (10)
C(2)–C(3)	1.336 (10)		
C(5)–C(5')	1.380 (8)		

Bond Angles (deg)			
N(1)–S–N(2)	109.0 (3)		
S–N(2)–C(1)	121.4 (4)	S–N(1)–C(4)	121.4 (4)
N(2)–C(1)–C(2)	117.5 (5)	N(1)–C(4')–C(3')	117.5 (5)
N(2)–C(1)–C(5')	124.6 (5)	N(1)–C(4')–C(5')	124.8 (5)
C(2)–C(1)–C(5')	117.9 (5)	C(3)–C(4)–C(5)	117.7 (5)
C(1)–C(2)–C(3)	121.2 (6)	C(2)–C(3)–C(4)	122.0 (6)
C(4)–C(5)–C(5')	120.2 (5)	C(1')–C(5)–C(5')	121.0 (5)
C(1)–C(2)–H(1)	109 (4)	C(4)–C(3)–H(2)	111 (6)
C(3)–C(2)–H(1)	130 (4)	C(2)–C(3)–H(2)	127 (6)

[a] Two values within a line are equivalent by molecular symmetry.

Structure Determination and Refinement. The positional coordinates of the sulfur atom of the asymmetric unit were found by Patterson synthesis. The following Fourier synthesis phased by the S atoms showed all nonhydrogen atoms. We also tried to solve the structure by direct methods, using the program PHASDT.[3] For this the 80 reflections with the highest E values were taken into account to calculate the sign relationships. Three reflections were given signs to define the origin. Together with four additional permuted reflections 16 permutations resulted. From the most significant solution according to the Q criterion an E-Fourier synthesis was calculated. Although the correct structure could not be found in this way, a fragment of the molecule with shifted origin was seen. This led to a correlation, which in principle had been observed several times before,[4] between the strongest maximum ($x = 0.4503$, $y = 0.8508$, $z = 1.3659$) of this E-Fourier synthesis and the strongest non-Harker vector V ($u = 0.1050$, $v = 0.0$, $w = 0.9106$) of the Patterson synthesis. Shifting the maximum of the E-Fourier synthesis by the vector $-V/2$ gives the sulfur position. The structure has been refined first with isotropic, then anisotropic temperature factors according to the least-squares method (full matrix, unit weights). A difference Fourier synthesis calculated at an R value ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.094 showed the coordinates of the hydrogen atoms. These were included with isotropic temperature factors in the refinement which yielded $R = 0.070$ (observed reflections). The unobserved reflections were not included in the calculation of the parameter shifts unless $|F_o| < |F_c|$. Moreover, in the last cycles of the refinement, 11 reflections with $\Delta F = ||F_o| - |F_c|| > 5$ were not taken into account for the calculation of the parameter shifts.

Computer calculations were carried out by a Siemens 4004/150, using a modified version of the X-RAY-67 program system.[5,6] The scattering factors for C, N, and S were taken from the International Tables for X-ray Crystallography,[7] and those for H were taken from Stewart, Davidson, and Simpson.[8] Table I contains the fractional coordinates and temperature factors of all atoms. A list of the observed and calculated structure factors may be obtained from A. Gieren and V. Lamm.

Results and Discussion

Molecular Structure. The structure of **1** is shown in Figure 1. The molecule is planar within the limits of error. Its centrosymmetry is derived from the crystallographic symmetry, but the compound has the higher symmetry $mmm(D_{2h})$. As
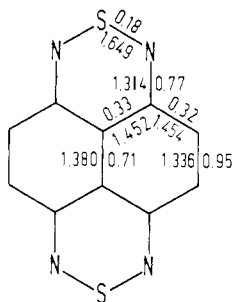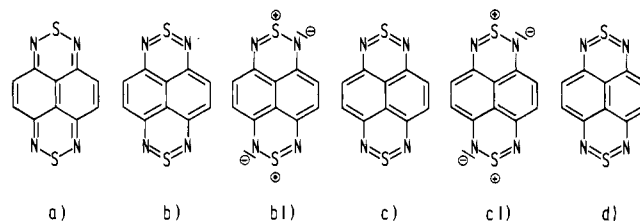
Figure 3. Bond lengths and derived π bond orders.

shown in Table II, none of the bond lengths or bond angles has significant deviations from this symmetry. The differences between values equivalent by symmetry are always <2σ. Therefore the distances and angles given in Figure 1 are averaged according to *mmm* symmetry.

The S–N distance is 1.649 Å. It is somewhat closer to the S—N single bond distance of 1.73 Å[2d,9] than to the S=N double bond distance found in sulfur diimides (ca. 1.53 Å[21]) and somewhat longer than the S(IV)—N bond distance in structures of the sulfilimine type (R[1]R[2]S=NSO₂R[3]) with a value of 1.62-1.64 Å.[10] With a length of 1.314 Å the C—N bond is shorter than that found in conjugated N-heterocycles (1.339 Å[11a]), and approaches the C=N double bond length. The C—C bond lengths in the naphthalene skeleton also point to intermediate bond orders. The shortest bond length is C(2)–C(3) with a length of 1.336 Å, which is very close to a pure (unconjugated) C=C double bond distance (1.335 Å[11b]). This bond distance is significantly shorter than that of the central bond C(5)–C(5') in the naphthalene fragment, which has a length of 1.380 Å. The bond lengths C(1)–C(2) and C(1)–C(5') are the longest in the naphthalene system. With lengths of 1.454 and 1.452 Å, respectively, they are equal within the limits of experimental error. Summarizing, the C–N, C(2)–C(3) and C(5)–C(5') bonds are principally double in character but the S–N, C(1)–C(2), and C(1)–C(5') bonds shows a predominantly single bond character. On the other hand, the intermediate bond order of all bonds (perhaps with the exception of C(2)–C(3)) indicates a partial delocalization of the π electrons. A similar situation prevails in the antiaromatic [16]annulene where the presence of bond length alternation[12] does not totally suppress the development of a paramagnetic ring current,[13] and the same behavior has also been observed[1] for **1**. The bond distances found for **1** can be ap-

propriately described by the resonance formulas a–c. The prevailing single- and double-bond character of the bonds as derived from the interatomic distances suggests the dominance of resonance formula a. The compound therefore has far more of the character of a naphthoquinone thiooxime ether (cf. the structure[14] of 5,8-dihydroxy-1,4-naphthoquinone) than of a sulfur diimide bridged naphthalene. The influence of resonance formula a is also shown by the fact that the bond lengths C(2)–C(3) and C(5)–C(5') are shortened in comparison with the corresponding bond lengths of naphthalene[15] (Figure 2) whereas the bond distances C(1)–C(2) and C(1)–C(5') are increased. On the other hand, the resonance formulas b and c, whose part in the overall electronic structure involves aromatic character in the naphthalene nucleus, effectively describe the partial double bond character found in **1**. In addition b and c help to explain the fact that the C(2)–C(3) bond in the naphthalene fragment is 0.04 Å shorter than the central C(5)–C(5') bond. In this connection it is interesting to note that the resonance structure d (Erlenmeyer formula) does not play any significant role as its participation in **1** would require the C(5)–C(5') bond to be shorter than the C(2)–C(3) bond, in analogy to naphthalene itself. In fact the case is quite the reverse. In addition, d would require unequal C(1)–C(2) and C(1)–C(5') bond lengths, which is also not observed.

The resonance formulas a–c deduced from the geometry found by X-ray determination confirm that the compound is predominantly described by resonance structure a but still has a partial delocalization of the π electrons. The description of **1** as a molecule of ambiguous aromatic character (as previously derived[1]) is therefore confirmed by the X-ray structure analysis.

The application of suitable regression analyses to the measured bond lengths of **1** results in the π-electron bond orders shown in Figure 3. The following equations were used: R_{rs} (Å) = $1.514 - 0.188p_{rs}$ for C–C bonds and R_{rs} (Å) = $1.443 - 0.167p_{rs}$ for C–N bonds.[16] The bond order of the S–N bond is derived from a table given by Glemser et al.[17] This description also shows the predominance of resonance formula a, al-
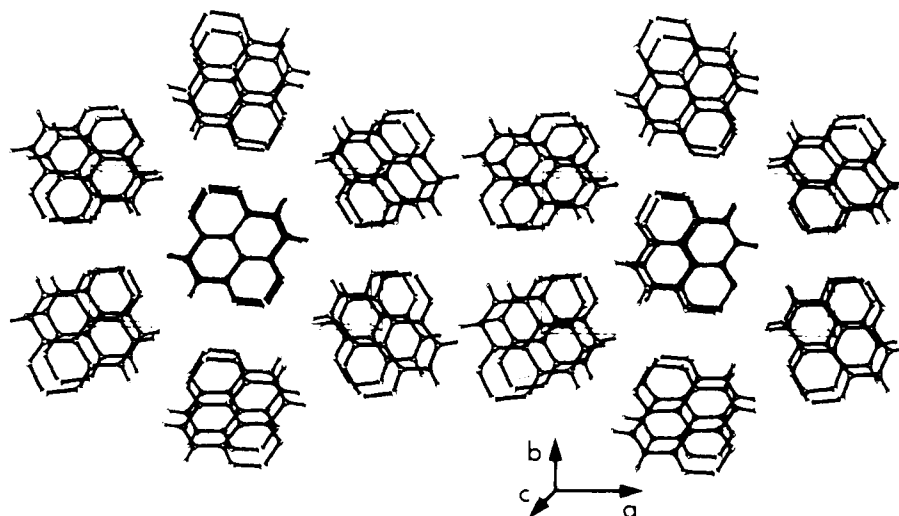

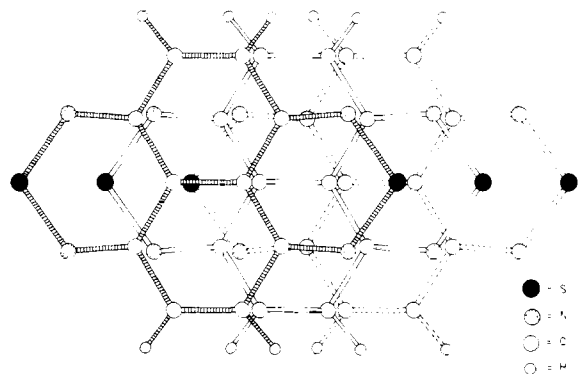**Figure 4.** Stereoscopic view of the crystal packing.

Figure 5. Three adjacent molecules within a stack projected on the molecular plane show a similar structure to that of rhomobohedral graphite.

Table III. Bond Lengths and Shortest Intermolecular S···N Contact Distances (Å) in Structures with -NSN- Units

compd	intramolecular S–N bond length	intermolecular S···N contact distance	ref
S_2N_2	1.654	2.890	27
1	1.649	3.104	
6	1.617	3.16	23
S_4N_4	1.617	3.16	28
$(SN)_x$	1.610[a]	3.256	27
4	1.60[b]	3.27[b]	21
3	1.632	3.68	3
sum of the van der Waals radii		3.35	26

[a] Average value of S–N bond lengths (1.593, 1.628). [b] Probable error of ±0.03 Å.

though a significant delocalization of π-electron density is evident.

The bonding in the —C≡NSN≡C— unit can be compared with the analogous molecular fragment in 1,2,5-thiadiazole (**2**)[18,19] (S–N, 1.631 Å; C–N, 1.328 Å; S–N, 1.632 Å; C–N, 1.329 Å), 3,4-diphenyl-1,2,5-thiadiazole[20] (**3**) (S–N, 1.632
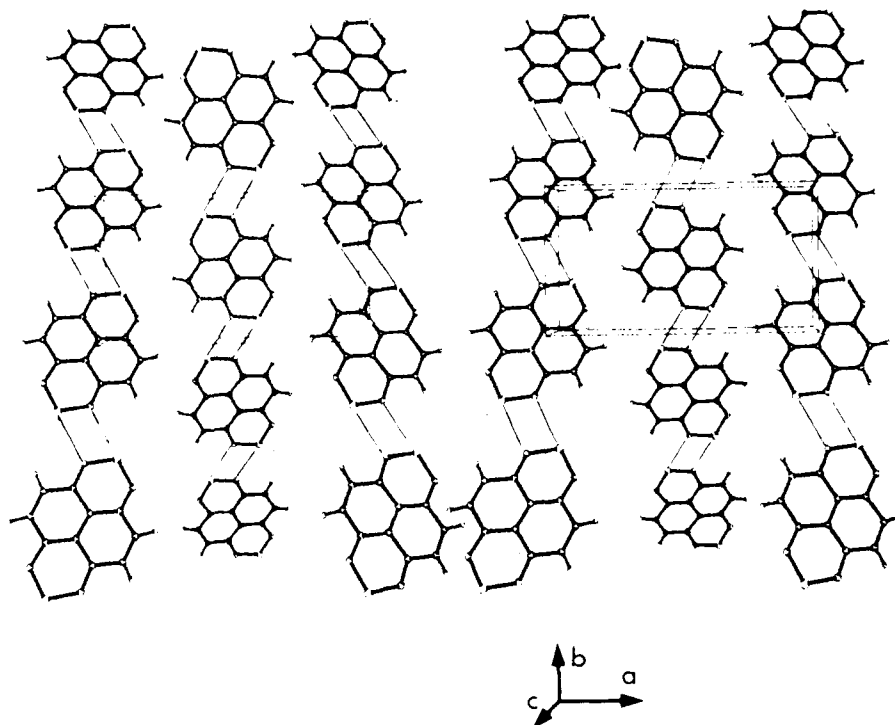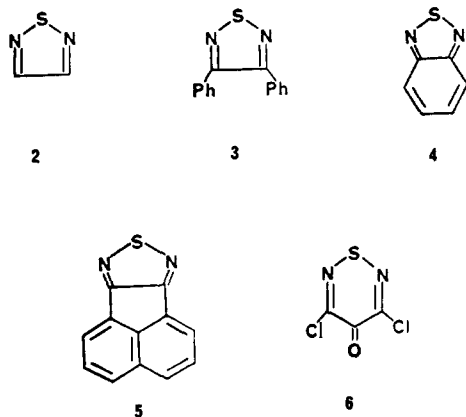

Å; C–N, 1.335 Å (mean values)), and 3,4-benzo-1,2,5-thiadiazole[21] (2,1,3-benzothiadiazole, **4**) (S–N, 1.60 Å; C–N, 1.34 Å). In all these model compounds the S–N bond lengths are shorter and the C–N bond lengths are correspondingly longer than those found in **1**, showing a stronger delocalization of the π electrons. The bond lengths in acenaphtho[1,2-c]-1,2,5-thiadiazole[22] (**5**) (S–N, 1.65 Å; C–N, 1.31 Å (mean values)) are comparable to those found for **1**. In contrast to the compounds where the –NSN– units are integrated into five-membered 1,2,5-thiadiazole rings, 3,5-dichloro-4H-1,2,6-thiadiazin-4-one[23] (**6**) has this unit as part of a six-membered thiadiazine ring, comparable to **1**. Here as well, the averaged S—N bond length of 1.617 Å is shorter than in **1**, but, in contrast to the compounds mentioned above, the average C≡N bond length of 1.274 Å is shorter than the analogous bond lengths in **1**. The angles at sulfur and nitrogen (108.8, 121.8°) in **6** are identical with the values found for **1** (109.0; 121.4°). Although these angles at the twofold coordinated S and N atoms within both compounds are identical, the S–N distances are clearly different.

Molecular Packing. Figure 4 shows the arrangement of **1** in the crystal structure. The molecules form stacks in the *c* direction with a pseudohexagonal packing. Along the stacks

Figure 6. Stereoscopic view of the ribbons within the crystal.

the molecular planes are within a distance of 3.40 Å equal to the layer spacing in graphite.[24] Not only the distance between the planes but also the entire packing arrangement within the stacks is analogous to graphite. Figure 5 shows the projection of three adjacent molecules within a stack projected on the molecular plane. There can be clearly recognized the ABC sequence of the rhombohedral modification of graphite.[25] Above and beneath the center of every ring there is a nonhydrogenic atom of the neighboring molecule. The six-membered rings are positioned so that alternating above and beneath each atom in the molecular plane there is an atom of the neighboring molecules—with the exception of the sulfur atoms. Therefore, with this exception, all atoms within a stack have a close neighbor which is situated at a distance corresponding roughly to the layer spacing mentioned before, e.g., $C(5)\cdots C(5') = 3.411$ Å and $N(1)\cdots C(4') = 3.418$ Å. At the sulfur atoms the sequence analogous to graphite is interrupted. Owing to the greater van der Waals radius, they have no neighbor atoms vertically above or beneath the molecular plane. The $S\cdots S$ contact between the molecules within a stack results from the cell translation in the c direction and so it is equal in length with the c axis (3.794 Å) and only slightly longer than the sum of the van der Waals radii[26] (3.70 Å).

In the unit cell the molecules are oriented in such a way that the vector $C(1)-C(2')$ is nearly parallel to the a direction and the vector $N(1)-N(1')$ points to the [011] or [01$\bar{1}$] direction, and is roughly parallel to (100). The angular divergences between the intramolecular vectors and the directions mentioned above are 11 and 2°, respectively. This arrangement of the molecules leads to a very short intermolecular $S\cdots N$ contact distance of 3.104 Å between the stacks, which is significantly shorter than the sum of the van der Waals radii (3.35 Å[26]). As a result of the crystallographic and molecular symmetry this contact distance leads to a ribbon-like connection of the molecules (Figure 6). The ribbons are in the directions [011] and [01$\bar{1}$]. Because the molecules within a ribbon are transformed into one another by centers of symmetry, all the molecules are arranged parallel to one another. In addition, the displacement of the planes between two neighboring molecules in a ribbon is extremely small (0.16 Å). Thus the molecules in a ribbon are nearly coplanar. Every molecule has four short $S\cdots N$ contact distances. As a result, it is connected to two neighboring molecules within the ribbon, thus leading to a linear ribbon. The short $S\cdots N$ contact distances between pairs of molecules lead to a centrosymmetrical parallelogram whose sides are the $S-N(1)$ bond and the 3.104 Å $S\cdots N(1)$ intermolecular contact. Apparently the angles in this parallelogram are correlated with the van der Waals radii of the S and N atoms. The S atoms with the greater van der Waals radii form the long diagonal of the parallelogram ($S\cdots S$: 3.936 Å) and the N atoms the short one ($N\cdots N$: 3.038 Å). The $S\cdots S$ and the $N\cdots N$ contacts are near the sum of the van der Waals radii. The ribbons are stacked in the c direction with a layer distance comparable to that in graphite. The transition from graphite to our structure can be approximated by cutting the graphite structure into slices perpendicular to the graphite layers, by rotating them around an axis vertical to the section plane, and by changing the graphite structure so that covalent bonds in a modified symmetry are substituted for $S\cdots N$ contacts The growth of crystals twinned on (100) is energetically easy because the formation of the twins changes neither the ribbons nor the stacks.

Some other compounds in the literature that contain the $-NSN-$ linkage evidence short intermolecular $S\cdots N$ distances in the solid state. Relevant parameters of such compounds (which exhibit a parallelogram-like structure of N and S atoms) are given in Table III. Furthermore (with the exception of 3 and such compounds as $S_4N_4\cdot SO_3$[2d] which involve an $S\cdots N$ contact distance greater than the sum of the van der Waals

radii), there is a strong inverse correlation between the lengths of the intramolecular S–N bonds and the intermolecular $S\cdots N$ contact distances. That is, as the intramolecular S–N bonds lengthen the intermolecular $S\cdots N$ contacts shorten. Taking the $-NSN-$ unit as an example, it is clear that the development of the $-N{=}S{=}N-$ configuration will strengthen (shorten) the $N{-}S$ bond, the admixture of the $=NSN=$ configuration will weaken (lengthen) the $N{-}S$ linkage, while the $-\bar{N}{-}\overset{+}{S}{=}N-$ configuration will lead to intermediate character. It seems reasonable to suppose that in situations where the intramolecular $S{-}N$ double bond is less developed there will be greater opportunities for intermolecular electrostatic interactions between $-\bar{N}{-}\overset{+}{S}{=}N-$ dipoles and/or weak intermolecular bonding involving a partial rehybridization at sulfur with d-orbital participation. Such an effect would explain the trend which is apparent in Table III. It is also possible that donor–acceptor interactions could be important, and indeed the colors of the solution and solid states of 1 are clearly different.

References and Notes

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