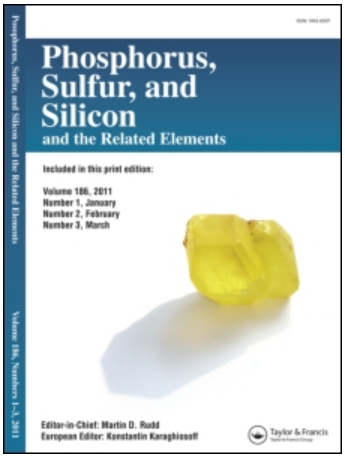


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# THE CRYSTAL STRUCTURES OF TWO IMINO-1,2,4- DITHIAZOLES FORMED BY THERMAL DECOMPOSITION OF 5-(DIALKYLAMINO)-3-(SUBSTITUTED IMINO)-1,2,4-DITHIAZOLES

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**To cite this Article** Flippen, Judith L.(1977) 'THE CRYSTAL STRUCTURES OF TWO IMINO-1,2,4- DITHIAZOLES FORMED BY THERMAL DECOMPOSITION OF 5-(DIALKYLAMINO)-3-(SUBSTITUTED IMINO)-1,2,4-DITHIAZOLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 3: 2, 185 — 189
**To link to this Article: DOI:** 10.1080/03086647708077710
**URL:** http://dx.doi.org/10.1080/03086647708077710

*Phosphorus and Sulfur*
1977, Vol. 3, pp. 185–189



# THE CRYSTAL STRUCTURES OF TWO IMINO-1,2,4-DITHIAZOLES FORMED BY THERMAL DECOMPOSITION OF 5-(DIALKYLAMINO)-3-(SUBSTITUTED IMINO)-1,2,4-DITHIAZOLES

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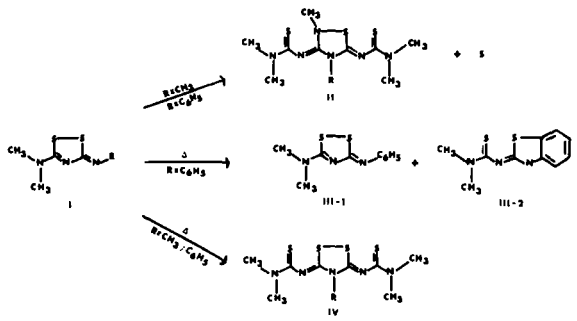
(*Received September 2, 1976*)

The thermal decomposition products of two substituted imino-1,2,4-dithiazoles have been studied by single crystal x-ray analysis. Both products crystallize in space group $P2_1/c$ with four molecules per unit cell. The first product, obtained from 5-(dimethylamino)-3-(methylimino)-1,2,4-dithiazole has cell dimensions of $a$ = 9.922(8) A, $b$ = 12.052(11) A, $c$ = 13.358(12) A and $\beta$ = 104.9(1)°. The molecule is made up of two planar segments related by an extremely large twist (~154°) about a C=N double bond. The results from this study have also contributed further information in the area of nonbonded interactions between ring and thione sulfur atoms. The second product, from 5-(dimethylamino)-3(phenylimino)-1,2,4-dithiazole was shown to be an ordered 1:1 complex of the starting material and one of its isomers. The cell dimensions are $a$ = 12.420(6) A, $b$ = 8.840(9) A, $c$ = 22.276(22) A and $\beta$ = 112.2(1)°. The different molecules are linked by an intermolecular NH · · · N hydrogen bond.



## INTRODUCTION

Several amino-substituted 1,2,4-dithiazole derivatives (e.g. **I**) have been studied as insect sterilants.[1] Related studies have dealt with the thermal decomposition of some of these dithiazoles[2] and it has been noted that alkylamino compounds appear to decompose via a dimeric cycloadduct with the accompanying release of elemental sulfur (e.g. **II**) while the phenylimino-



dithiazole decomposes by attack on a ring sulfur by the benzene ring. **I** can also be autoxidized in solution,[3] or reacted with isothiocyanate,[4] to give **IV** which has an interesting bond no-bond system of 4 colinear sulfur atoms. The structure of **IV** has been determined by x-ray single crystal analysis.[5] X-ray analyses have also been performed on **II** and **III** both to confirm the configuration of the products from the thermal decomposition reactions and to continue the study of bond no-bond sulfur-sulfur interactions.

## EXPERIMENTAL

Crystals of both materials were provided by Dr. J. E. Oliver of the U.S. Department of Agriculture. Details of data collection and physical quantities describing both crystals are listed in Table I. Lorentz and polarization corrections were applied and normalized structure factor magnitudes $|E|$ as well as structure magnitudes $|F|$ were derived. The structures were solved by the symbolic addition procedure for centrosymmetric crystals.[6] Computer programs written by R. D. Gilardi and S. A. Brenner of this laboratory, were used to facilitate application of the $\Sigma_2$ formula. Both structures were refined by full-matrix least-squares methods which included a correction for isotropic secondary extinction.[7] However, no absorption corrections were applied. Scattering factors used were those listed in the International Tables for X-Ray Crystallography.[8] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ in which the weight ($w$) was calculated according to Gilardi[9] and all data were included in the refinement, i.e. no reflections were considered unobserved. All hydrogen atoms on both molecules were located in difference maps and assigned thermal parameters equal to the final isotropic value for the atoms to which they were bonded. The hydrogen atom parameters were then included in the final cycles of refinement as constants. The final

TABLE I

| | Molecule II | Molecule III |
|---|---|---|
| Molecular formula | $C_{10}H_{18}N_6S_3$ | $C_{10}H_{11}N_3S_2$:$C_{10}H_{11}N_3S_2$ |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $a$ | 9.922(8) A | 12.420(16) A |
| $b$ | 12.052(11) | 8.840(9) |
| $c$ | 13.358(12) | 22.276(22) |
| $\beta$ | 104.9(1)° | 112.2(2)° |
| $z$ | 4 | 4 |
| Density (calc.) | 1.37 gm/cc | 1.27 gm/cc |
| $\mu$ | 4.63 | 4.17 |
| Source of data | automatic computer controlled diffractometer | |
| Radiation | Mo $K\alpha$ $\lambda = 0.7107$ A Zr filter | |
| Collection technique | moving crystal moving counter ($\theta$-$2\theta$ scan) | |
| Scanning speed | 2 deg/min | |
| Background time | 10 sec. | |
| Max sin $\theta/\lambda$ | 0.481 | 0.538 |
| No. of independent reflections | 1442 | 2129 |



TABLE II
Atomic coordinates and thermal parameters for molecule II

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S(1) | 0.3164 | 0.5816 | 0.4817 | 4.6 | 4.0 | 3.7 | −0.5 | 0.7 | 0.4 |
| S(2) | 0.1514 | 0.5315 | 0.3069 | 5.3 | 5.9 | 4.3 | −0.4 | 0.3 | 1.3 |
| S(3) | 0.4559 | 0.7088 | 0.8537 | 5.5 | 4.9 | 4.7 | 0.8 | 0.5 | −0.8 |
| N(1) | 0.2775 | 0.4552 | 0.6271 | 4.1 | 3.7 | 3.4 | −0.6 | 0.8 | 0.2 |
| N(2) | −0.0187 | 0.3631 | 0.3137 | 4.7 | 5.2 | 4.8 | −0.2 | 0.4 | −0.0 |
| N(3) | 0.4179 | 0.5944 | 0.6132 | 5.0 | 4.2 | 3.7 | −0.9 | 0.7 | 0.4 |
| N(4) | 0.1287 | 0.4102 | 0.4697 | 4.0 | 4.0 | 3.5 | −0.2 | 0.4 | −0.1 |
| N(5) | 0.4474 | 0.5016 | 0.7763 | 5.2 | 4.4 | 3.3 | −0.4 | 0.5 | −0.2 |
| N(6) | 0.6284 | 0.5389 | 0.9167 | 5.1 | 4.8 | 3.9 | 0.5 | 0.4 | 0.2 |
| C(1) | −0.0689 | 0.3681 | 0.1992 | 6.5 | 8.8 | 3.6 | −0.3 | −1.1 | 0.2 |
| C(2) | −0.0789 | 0.2763 | 0.3677 | 5.6 | 5.4 | 6.2 | −1.0 | 0.0 | −0.3 |
| C(3) | 0.0842 | 0.4300 | 0.3671 | 3.8 | 4.0 | 4.8 | 0.3 | 0.5 | 0.1 |
| C(4) | 0.2296 | 0.4721 | 0.5235 | 4.1 | 3.5 | 4.0 | 0.3 | 0.8 | 0.3 |
| C(5) | 0.2212 | 0.3679 | 0.6800 | 5.6 | 4.7 | 4.1 | −0.8 | 1.0 | 0.4 |
| C(6) | 0.3881 | 0.5225 | 0.6791 | 4.6 | 3.8 | 4.1 | 0.1 | 1.1 | −0.3 |
| C(7) | 0.5436 | 0.6632 | 0.6329 | 4.6 | 4.6 | 5.4 | −1.3 | 1.0 | −0.2 |
| C(8) | 0.5152 | 0.5771 | 0.8459 | 4.8 | 4.5 | 3.9 | −0.1 | 1.7 | −0.0 |
| C(9) | 0.6814 | 0.4259 | 0.9110 | 6.1 | 4.5 | 5.5 | 0.4 | 0.8 | 0.4 |
| C(10) | 0.7024 | 0.6049 | 1.0067 | 6.6 | 6.6 | 4.6 | 0.0 | −1.1 | −1.4 |

The thermal parameters are of the form

$$T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$$

TABLE III
Atomic coordinates and thermal parameters for molecule III

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S(1-1) | 0.1815 | 0.2310 | 0.1231 | 5.3 | 5.8 | 4.0 | −0.2 | 2.7 | −0.2 |
| S(1-2) | 0.0390 | 0.3421 | 0.0605 | 5.9 | 5.7 | 3.1 | −0.8 | 2.0 | 0.2 |
| C(1-3) | −0.0282 | 0.3513 | 0.1179 | 4.6 | 3.8 | 4.1 | −1.2 | 1.8 | −1.1 |
| N(1-4) | 0.0252 | 0.2960 | 0.1758 | 4.2 | 4.9 | 3.3 | 0.1 | 1.4 | −0.4 |
| C(1-5) | 0.1330 | 0.2411 | 0.1905 | 4.1 | 4.2 | 3.7 | −0.6 | 1.6 | −1.0 |
| N(1-6) | 0.1974 | 0.2051 | 0.2487 | 3.8 | 4.7 | 3.7 | −0.1 | 1.6 | −0.6 |
| C(1-7) | 0.3076 | 0.1387 | 0.2663 | 4.5 | 4.0 | 3.5 | −0.6 | 2.2 | −0.5 |
| C(1-8) | 0.3314 | 0.0208 | 0.2321 | 5.0 | 4.6 | 5.1 | 0.3 | 1.6 | −0.8 |
| C(1-9) | 0.4410 | −0.0463 | 0.2552 | 6.8 | 4.8 | 6.2 | 0.0 | 3.0 | −1.2 |
| C(1-10) | 0.5252 | 0.0006 | 0.3124 | 4.4 | 5.3 | 7.6 | 0.0 | 2.7 | 0.0 |
| C(1-11) | 0.5021 | 0.1165 | 0.3480 | 3.7 | 5.3 | 6.4 | −0.9 | 2.2 | −0.5 |
| C(1-12) | 0.3941 | 0.1840 | 0.3249 | 4.5 | 5.2 | 4.2 | −0.7 | 2.3 | −0.5 |
| N(1-13) | −0.1324 | 0.4158 | 0.0995 | 4.5 | 5.0 | 4.7 | −0.0 | 1.1 | −0.2 |
| C(1-14) | −0.1875 | 0.4903 | 0.0364 | 6.5 | 4.9 | 5.2 | −0.1 | −0.0 | 0.4 |
| C(1-15) | −0.1909 | 0.4233 | 0.1450 | 5.0 | 8.0 | 6.4 | 0.3 | 2.6 | −1.3 |
| S(2-1) | 0.9004 | 0.9544 | 0.0568 | 4.5 | 4.4 | 3.6 | −0.4 | 1.9 | 0.5 |
| S(2-2) | 0.6839 | 1.1212 | −0.0077 | 5.7 | 6.0 | 4.6 | 0.1 | 1.6 | 1.9 |
| C(2-3) | 0.6614 | 1.0839 | 0.0613 | 3.8 | 4.0 | 4.6 | −0.5 | 1.0 | 0.0 |
| N(2-4) | 0.7289 | 0.9907 | 0.1097 | 4.0 | 4.3 | 4.0 | 0.7 | 1.8 | 0.7 |
| C(2-5) | 0.8259 | 0.9313 | 0.1106 | 4.6 | 3.5 | 3.3 | −0.8 | 1.7 | −0.3 |
| N(2-6) | 0.8862 | 0.8365 | 0.1592 | 4.2 | 4.5 | 3.2 | 0.6 | 1.8 | 1.4 |
| C(2-7) | 0.9918 | 0.7826 | 0.1585 | 3.6 | 3.7 | 3.8 | −0.0 | 1.6 | −0.5 |
| C(2-8) | 1.0141 | 0.8389 | 0.1059 | 4.3 | 4.1 | 3.3 | −0.8 | 1.7 | −0.9 |
| C(2-9) | 1.1149 | 0.7979 | 0.0964 | 3.7 | 5.7 | 4.4 | −0.5 | 1.8 | −1.0 |
| C(2-10) | 1.1904 | 0.7008 | 0.1403 | 4.2 | 5.5 | 5.4 | −0.9 | 2.0 | −1.7 |
| C(2-11) | 1.1679 | 0.6440 | 0.1933 | 4.1 | 3.9 | 5.9 | 0.1 | 1.0 | −0.9 |
| C(2-12) | 1.0677 | 0.6842 | 0.2035 | 4.4 | 4.3 | 3.7 | 0.0 | 0.8 | 0.4 |
| N(2-13) | 0.5720 | 1.1443 | 0.0733 | 4.3 | 4.6 | 5.2 | 0.6 | 1.2 | 0.1 |
| C(2-14) | 0.5529 | 1.1157 | 0.1333 | 6.9 | 7.2 | 4.7 | 2.1 | 2.8 | 0.2 |
| C(2-15) | 0.4901 | 1.2473 | 0.0281 | 5.1 | 5.9 | 7.1 | 1.4 | 0.5 | 1.6 |

The thermal parameters are of the form:

$$T = \exp[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$$

TABLE IV
Hydrogen atom coordinates from a difference map—Molecule II

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| H-2A | −0.043 | 0.202 | 0.363 |
| H-2B | −0.178 | 0.273 | 0.329 |
| H-2C | −0.067 | 0.298 | 0.446 |
| H-5A | 0.242 | 0.296 | 0.662 |
| H-5B | 0.249 | 0.382 | 0.751 |
| H-5C | 0.123 | 0.369 | 0.662 |
| H-7A | 0.641 | 0.625 | 0.671 |
| H-7B | 0.560 | 0.680 | 0.558 |
| H-7C | 0.533 | 0.743 | 0.675 |
| H-9A | 0.639 | 0.391 | 0.845 |
| H-9B | 0.659 | 0.368 | 0.965 |
| H-9C | 0.789 | 0.435 | 0.918 |

$R$-factors (agreement between observed and calculated structure factors) where $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$ were 0.055 for II and 0.060 for III. The final weighted $R$-factors where $Rw = (\Sigma w(|F_o| - |F_c|)^2/(\Sigma wF_o^2)^{1/2}$ were 0.067 for II and 0.043 for III. Atomic coordinates and thermal parameters are listed in Tables II and III for molecules II and III respectively. Hydrogen coordinates are listed in Tables IV and V. Tables comparing observed and calculated structure factors are available.

## RESULTS AND DISCUSSION

The results of the structure analysis on II are displayed in the stereo-diagram[10] in Figure 1 and bond distances and angles are shown in Figure 2. This compound is very similar to molecule IV with the only chemical difference being the substitution of an $-NCH_3$ for one of the ring sulfur atoms. However, this substitution has dramatically altered the molecular geometry as well as the S · · · S interactions IV (with R = $-CH_3$) is essentially planar[5] while molecule II is composed of two planar sections with a twist of −154.1° about the C(6)—N(5) double bond (as measured by the

TABLE V
Difference map coordinates for hydrogen atoms—Molecule III

| Atom | x | y | z |
|---|---|---|---|
| H(1-8) | 0.268 | −0.011 | 0.192 |
| H(1-9) | 0.443 | −0.138 | 0.221 |
| H(1-10) | 0.612 | −0.052 | 0.328 |
| H(1-11) | 0.579 | 0.183 | 0.384 |
| H(1-12) | 0.368 | 0.248 | 0.355 |
| H(1-14A) | −0.184 | 0.406 | 0.002 |
| H(1-14B) | −0.160 | 0.629 | 0.043 |
| H(1-14C) | −0.274 | 0.455 | 0.008 |
| H(1-15A) | −0.262 | 0.407 | 0.140 |
| H(1-15B) | −0.148 | 0.457 | 0.195 |
| H(1-15C) | −0.184 | 0.291 | 0.159 |
| H(2-6(N)) | 0.864 | 0.790 | 0.196 |
| H(2-9) | 1.116 | 0.844 | 0.043 |
| H(2-10) | 1.285 | 0.687 | 0.135 |
| H(2-11) | 1.221 | 0.548 | 0.221 |
| H(2-12) | 1.050 | 0.636 | 0.246 |
| H(2-14A) | 0.519 | 0.977 | 0.121 |
| H(2-14B) | 0.495 | 1.187 | 0.143 |
| H(2-14C) | 0.608 | 1.082 | 0.175 |
| H(2-15A) | 0.522 | 1.351 | 0.022 |
| H(2-15B) | 0.476 | 1.194 | −0.020 |
| H(2-15C) | 0.403 | 1.212 | 0.017 |

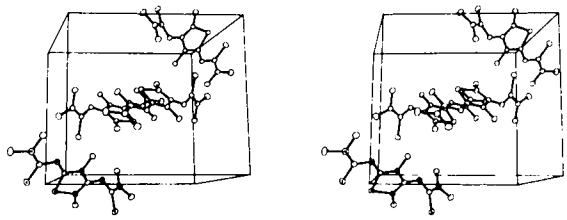


FIGURE 2 Contents of one unit cell for molecule II. The stereoview is shows with $b\rightarrow$, $a\uparrow$ and $c$ coming up out of the paper.

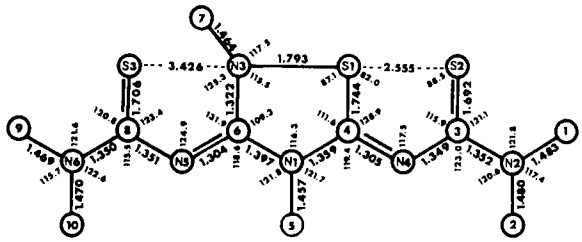


FIGURE 3 Bond lengths and angles for molecule II. Based solely on least-squares deviations the standard deviations are on the order of 0.006 Å for the bond lengths and 0.4° for the angles.

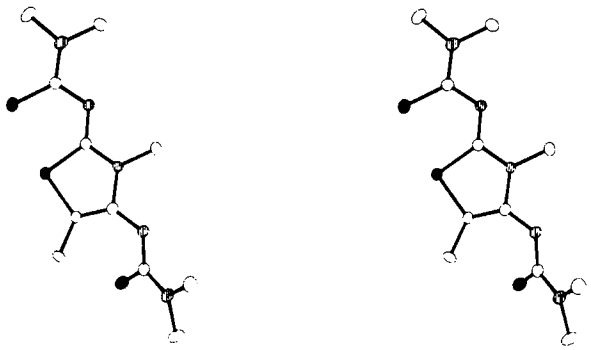


FIGURE 1 Stereodiagram of results of analysis on molecule. II. The nitrogen atoms are labeled ◍ and the sulfur atoms are labeled ⊛.

N(1)—C(6)—N(5)—C(8) torsion angle). This twist is probably due to the repulsive forces (mainly steric hindrance) between S(3) and the $CH_3$ group on N(3) which was not present in IV. The repulsive force between S(3) and N(3) has increased the values for the angles at C(6), N(5) and C(8); 131.9, 124.9 and 123.4° respectively. On the other hand, the angles for a similar moiety, C(4), N(4) and C(3) are 128.9, 117.5 and 115.9° respectively showing the influence of the attraction between S(1) and S(2). In addition, the colinear S · · · S bonding system in IV was such that the covalent S—S ring bond at 2.161 Å was longer than normal due to some attractive forces between the ring and outer sulfur atoms and at the same time the non-bonded S · · · S attractions at 2.74 and 2.78 Å were also weakened.[5] In II there is no covalent S—S bond and the non-bonded S · · · S attraction is stronger, with the two sulfur atoms being only 2.555 Å apart. This distance falls within the range of S · · · S approaches found in thiathiaphthene systems.[11] The S(1)—N(3) bond has also been affected by the S · · · S interaction such that, at 1.793 Å, it is ~0.05 Å longer than would be expected from normal covalent radii.[12] The packing of this molecule (see Figure 3) is influenced only by van der Waals' forces with the only intermolecular approach less than van der Waals' separations being an S(1) · · · S(3) approach of 3.53 Å

The second material studied was shown to be a 1 : 1 complex of the original starting material and one of its isomeric products. The two different molecules are linked in the crystal by an intermolecular N(2-6)H · · · N(1-6) hydrogen bond (see Figure 4). The parameters describing the hydrogen bond are the N · · · N distance of 2.87°, the H · · · N distance of 1.83 Å and the N—H · · · N angle of 171.1°. The stereoconfigurations of the two molecules and the packing of the unit cell are illustrated in Figure 4. Bond distances and angles for the two isomers are illustrated in Figure 5. Most of the covalent N—C and S—C bond lengths agree

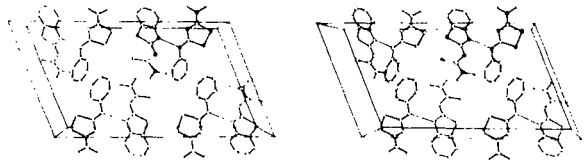


FIGURE 4 Stereodiagram of the contents of one unit cell for molecule **III**. The hydrogen bond linking molecules of **III**-1 and **III**-2 into pairs is indicated. The view is seen with *a* ↑, *c* → and *b* coming out of the paper.

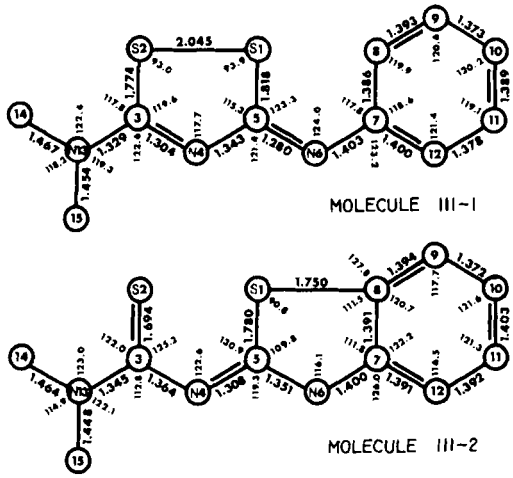



FIGURE 5 Bond lengths and angles for molecules **III**-1 and **III**-2. Standard deviations are the same as those quoted for molecule **II**.

quite well among the molecules **II**–**IV**. However, the C—S single bond distances in **III** are somewhat longer than the C—S distances in the other molecules (avg. = 1.781 Å for **III** and 1.734 Å for **II** and **IV**). There do not seem to be any significant S · · · S or S · · · C interactions in either **III**-1 or **III**-2. In **III**-2, the S(2-2) · · · S(2-1) distance at 2.924 Å and the large angles at C(2-5), N(2-4) and C(2-3); 130.9, 122.6, and 125.2° respectively, may indicate some slight repulsion between the two sulfur atoms. The entire molecule (**III**-2) is planar to within ±0.2 Å. However, it can be more precisely described as consisting of two planar segments (the fused rings planar to within ±0.02 Å and the remaining atoms planar to within ±0.01 Å) with an angle of 10.4° between the planes.

Molecule **III**-1 (the starting material) is also made up of two planar segments (the phenyl group planar to within ±0.01 Å and the remaining atoms planar to within ±0.15 Å) with an angle of 49.9° between the planes. In this molecule the two planes are related by a rotation about the C(7)–N(6) single bond whereas in molecule **II** the two planes were related by a rotation about a C=N double bond. In both molecules the deviations from planarity are due to steric hindrance between a sulfur atom and a hydrogen atom, on C(7) for molecule **II** and on C(8) for molecule **III**-1.

The three independent molecules investigated in this study all have different S · · · S environments which have provided interesting additional information in the area of non-bonded S · · · S interactions. In addition molecule **II** contains a significantly non-planar C=N double bond and molecules **III**-1 and **III**-2 provided an opportunity to study a 1 : 1 complex of isomers in the solid state.

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