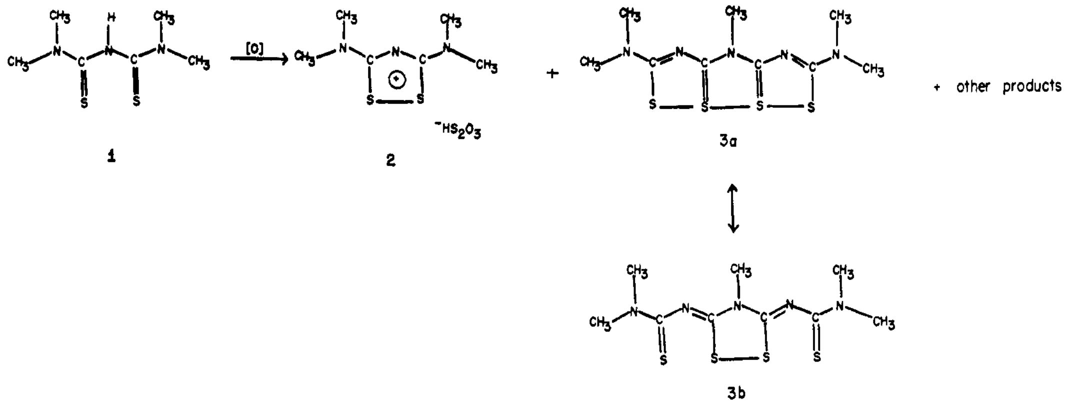
Structures of Two Dithiazolidines Containing Four Colinear Sulfur Atoms: $C_7H_{15}N_5S_4$ and $C_{12}H_{17}N_5S_4$

Judith L. Flippen

Contribution from the Laboratory for the Structure of Matter,
Naval Research Laboratory, Washington, District of Columbia 20375.
Received January 18, 1973

Abstract: The structures of two dithiazolidines, I and II, which are being investigated as possible insect sterilants, have been determined by X-ray analysis. Both materials crystallize in the monoclinic space group $C2/c$ with $a = 11.355$ (8) Å, $b = 9.077$ (6) Å, $c = 27.531$ (5) Å, $\beta = 97.8$ (1)°, and $Z = 8$ for the methyl analog (I) and $a = 17.805$ (8) Å, $b = 10.827$ (6) Å, $c = 9.664$ (6) Å, $\beta = 100.3$ (1)°, and $Z = 4$ for the phenyl analog (II). The X-ray data were collected on an automatic diffractometer and refined to a final R factor of 0.055 for I and 0.045 for II. Both structures were solved using the symbolic addition procedure. In both molecules the central S–S bond length is ~2.2 Å and the outer S–S distances are on the order of 2.8 Å. These distances place the molecules intermediate between the "bond, no-bond" thiathiaphthene systems and multilinear sulfur systems in which there is no attraction between the nonbonded sulfur atoms.

Several 1,1,5,5-tetraalkyldithiobiurets (**1**) are capable of sterilizing male house flies, *Musca domestica* L.[1] Most of these compounds slowly oxidize in air, with shelf-lives ranging from only a few days to a few weeks. However, some of the most active dithiobiurets retained rather high biological activity even after several months, and their decomposition products have been studied.[2-4] One of the products (**3**) was identified as a 3,5-bis(thiocarbamoyl)-1,2,4-dithiazolidine. From spectral results it was not possible to distinguish between the two forms, **3a** and **3b**, and it was to resolve this point that the X-ray analysis was undertaken. The methyl derivative exhibits only slight activity as an insect sterilant. However, the phenyl analog of **3**, which has recently been synthesized,[5] has shown some sterilant activity. As shown in the present work, both compounds have structure **3b**. A note on the chemistry of these molecules and a preliminary report of the structures have been published.[5]



Experimental Section

Crystals of both materials, 3,5-bis(*N*,*N*-dimethylthiocarbamoyl)-4-methyl-1,2,4-dithiazolidine (I) and 3,5-bis(*N*,*N*-dimethylthiocarbamoyl)-4-phenyl-1,2,4-dithiazolidine (II), were provided by Dr. J. E. Oliver of the U. S. Department of Agriculture. Information on data collection and physical quantities for both molecules are listed in Table I. Lorentz and polarization corrections were applied and normalized structure factor magnitudes $|E|$ as well as structure factor magnitudes $|F|$ were derived.

The structures were solved by routine application of the symbolic addition procedure[6] using computer programs written by Gilardi and Brenner of this laboratory.

Coordinates and thermal factors for both molecules were refined on F values using a full-matrix least-squares procedure which included a correction for isotropic secondary extinction.[7] The function minimized was $\Sigma W(|F_o| - |F_c|)^2$ where the weighting function W was calculated according to eq 1, where Q = attenuator factor,

$$W^{-1} = \sigma_{|F|}{}^2 = \left[\frac{Q(P - t_t(B_1 + B_2))}{4LP}\right] \times \left[\frac{P + C^2P^2 + t_t{}^2(B_1 + B_2 + C^2B_1{}^2 + C^2B_2{}^2)}{(P - t_t(B_1 + B_2))^2} + \left(\frac{\sigma_Q}{Q}\right)^2\right] \quad (1)$$

P = peak count, B_1, B_2 = background counts, t_t = time factor to put background and peaks on same scale, and C = instrumental reliability factor (0.01). A detailed derivation of the weighting function is given by Gilardi.[8] Atomic scattering factors used were those listed in the "International Tables for X-Ray Crystallography." All the hydrogen atoms were located in difference maps and their

---

[1] J. E. Oliver, S. C. Chang, R. T. Brown, and A. B. Borkovec, *J. Med. Chem.*, **14**, 772 (1971).

[2] J. Goerdler and J. Ulmen, *Chem. Ber.*, **103**, 3393 (1970).

[3] J. Goerdler and J. Ulmen, *Chem. Ber.*, **105**, 1568 (1972).

[4] J. E. Oliver and J. B. Stokes, *Int. J. Sulfur Chem., Part A*, 2, 105 (1972).

[5] J. E. Oliver, J. L. Flippen, and J. Karle, *J. Chem. Soc., Chem. Commun.*, 1153 (1972).

[6] J. Karle and I. L. Karle, *Acta Crystallogr.*, 21, 849 (1966).

[7] W. R. Busing, K. O. Martin, H. A. Levy, R. D. Ellison, W. C. Hamilton, J. A. Ibers, C. K. Johnson, and W. E. Thiessen, ORXFLS3, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1971.

[8] R. D. Gilardi, *Acta Crystallogr.*, submitted for publication.

Table I

	Molecule I	Molecule II
Molecular formula	$C_7H_{15}N_5S_4$	$C_{12}H_{17}N_5S_4$
Color	Yellow	Yellow
Crystal size	~(0.43 mm × 0.20 mm × 0.20 mm)	~(0.81 mm × 0.45 mm × 0.35 mm)
Space group	*C*2/*c*	*C*2/*c*
a	11.355 (8) Å	17.805 (8) Å
b	9.077 (6) Å	10.827 (6) Å
c	27.531 (5) Å	9.664 (6) Å
β	97.8 (1)°	100.3 (1)°
Z	8	4
No. of molecules per asymmetric unit	1	1/2
Density (calcd)	1.53 g/ml	1.39 g/ml
μ	6.47 cm⁻¹	5.07 cm⁻¹
Source of data	Automatic diffractometer	
Radiation	Mo Kα (λ 0.71069 Å) Zr filter	
Data collection technique	θ–2θ scan	
Scan width	$1.0° + 2\theta(\alpha_2) - 2\theta(\alpha_1)$	$1.3° + 2\theta(\alpha_2) - 2\theta(\alpha_1)$
Maximum sin θ/λ	0.515	0.595
No. of independent reflections	1588	1644

Table II. Fractional Coordinates and Thermal Parameters[a] with Standard Deviations[b] for Molecule I

Atom	*X*	*Y*	*Z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	0.16010 (11)	−0.01618 (14)	−0.11320 (4)	5.69 (7)	5.16 (6)	4.33 (6)	1.43 (5)	0.69 (5)	−0.90 (5)
S(2)	0.21996 (10)	−0.06313 (12)	−0.01455 (4)	5.01 (6)	3.67 (5)	4.23 (6)	1.22 (5)	0.74 (4)	−0.44 (4)
S(3)	0.25941 (10)	−0.08173 (12)	0.06423 (4)	4.90 (6)	3.64 (5)	4.29 (6)	1.42 (5)	0.63 (4)	0.03 (4)
S(4)	0.29952 (11)	−0.07900 (13)	0.16629 (4)	5.90 (7)	4.81 (6)	4.53 (6)	1.53 (5)	0.72 (5)	0.73 (5)
N(1)	0.02826 (28)	0.22304 (37)	−0.12827 (12)	3.95 (16)	4.54 (19)	3.74 (18)	0.63 (15)	0.42 (14)	0.08 (15)
N(2)	0.08448 (26)	0.17206 (33)	−0.04830 (12)	3.55 (16)	3.55 (16)	3.52 (18)	0.58 (13)	0.42 (12)	−0.18 (14)
N(3)	0.12784 (24)	0.14611 (32)	0.03417 (11)	3.26 (15)	2.79 (15)	3.60 (15)	0.51 (13)	0.64 (12)	−0.15 (13)
N(4)	0.16501 (26)	0.13092 (33)	0.11703 (12)	3.81 (17)	3.60 (16)	3.36 (18)	0.29 (13)	0.58 (12)	−0.15 (14)
N(5)	0.17766 (29)	0.13938 (38)	0.19890 (12)	5.29 (18)	4.48 (18)	3.21 (18)	0.23 (16)	0.49 (14)	−0.30 (15)
C(1)	0.02509 (46)	0.19935 (67)	−0.18056 (18)	5.54 (31)	7.28 (34)	4.03 (27)	0.18 (26)	0.39 (22)	0.12 (22)
C(2)	−0.03809 (42)	0.34722 (58)	−0.11446 (17)	5.64 (23)	5.33 (28)	4.79 (24)	1.69 (22)	0.93 (19)	0.82 (21)
C(3)	0.08761 (32)	0.13238 (44)	−0.09621 (15)	3.19 (19)	4.09 (21)	4.19 (24)	−0.24 (17)	0.75 (16)	−0.17 (18)
C(4)	0.13662 (31)	0.09622 (39)	−0.01227 (15)	3.06 (18)	3.02 (19)	4.14 (21)	−0.20 (15)	0.72 (15)	−0.38 (17)
C(5)	0.05831 (46)	0.27916 (51)	0.04091 (17)	5.94 (28)	4.19 (25)	4.16 (24)	2.03 (21)	0.58 (20)	−0.29 (19)
C(6)	0.18066 (30)	0.07428 (40)	0.07545 (14)	2.62 (18)	3.14 (18)	4.20 (21)	−0.21 (15)	0.40 (15)	0.10 (17)
C(7)	0.21079 (32)	0.06868 (43)	0.16054 (15)	3.57 (20)	3.66 (19)	4.24 (21)	−0.35 (17)	0.46 (17)	0.36 (18)
C(8)	0.21465 (67)	0.08880 (56)	0.24850 (19)	8.98 (42)	5.47 (27)	4.00 (24)	1.06 (35)	−0.29 (23)	−0.68 (22)
C(9)	0.09863 (48)	0.26548 (58)	0.19220 (19)	5.98 (30)	5.46 (28)	5.38 (27)	1.25 (25)	1.03 (23)	−1.21 (21)
H(1A)	0.088 (4)	0.183 (5)	−0.187 (2)						
H(1B)	0.013 (4)	0.284 (5)	−0.197 (2)						
H(1C)	−0.032 (4)	0.145 (5)	−0.192 (2)						
H(2A)	−0.047 (4)	0.422 (5)	−0.137 (2)						
H(2B)	−0.103 (4)	0.332 (5)	−0.106 (2)						
H(2C)	−0.011 (4)	0.389 (5)	−0.084 (2)						
H(5A)	0.033 (4)	0.320 (5)	0.012 (1)						
H(5B)	0.102 (4)	0.343 (5)	0.061 (2)						
H(5C)	0.002 (4)	0.260 (5)	0.064 (1)						
H(8A)	0.208 (5)	0.158 (5)	0.267 (2)						
H(8B)	0.213 (4)	−0.005 (5)	0.251 (2)						
H(8C)	0.321 (4)	0.084 (4)	0.257 (1)						
H(9A)	0.086 (4)	0.306 (5)	0.222 (2)						
H(9B)	0.136 (4)	0.345 (5)	0.174 (2)						
H(9C)	0.020 (4)	0.237 (5)	0.180 (2)						

[a] The thermal parameters of the form $T = \exp[{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Standard deviations are based solely on least-squares parameters.

positional parameters were refined. The hydrogen atoms were assigned thermal parameters equal to the final isotropic values for the atoms to which they were bonded and these parameters were included in the refinement as constants. All data were included in the refinement; no data were considered unobserved. The final R factors, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, were 0.055 for molecule I and 0.045 for molecule II. The final weighted R factors, where $R_W = [\Sigma W(|F_o| - |F_c|)^2/\Sigma W F_o^2]^{1/2}$, were 0.037 for I and 0.038 for II. Coordinates and thermal parameters are listed in Tables II and III for molecules I and II, respectively.[9]

Discussion

The stereoconfiguration of the methyl derivative (I) is illustrated in Figure 1. The entire molecule is planar to within ±0.087 Å. Deviations of individual atoms from the plane are shown in Figure 2. Bond distances and angles for molecule I are depicted in Figure 3. It should be noted that the systematic name of the molecule is based on the chemical numbering system and not on the crystallographic numbering system (see Figures 3 and 4) which is arbitrary. Even though

---

[9] See paragraph at end of paper regarding supplementary material.

Table III. Fractional Coordinates and Thermal Parameters[a] with Standard Deviations[b] for Molecule II

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	0.54899 (3)	0.59687 (4)	0.33499 (5)	5.12 (2)	2.73 (2)	5.10 (3)	−0.35 (2)	0.56 (2)	−0.39 (2)
S(2)	0.67335 (3)	0.57024 (5)	0.55227 (6)	6.03 (4)	3.98 (3)	5.99 (3)	−0.97 (2)	−0.73 (2)	−0.90 (2)
N(1)	0.50000	0.37617 (17)	0.25000	3.50 (9)	2.56 (8)	4.40 (10)	0.00	−0.07 (8)	0.00
N(2)	0.59866 (8)	0.36931 (13)	0.43426 (16)	3.63 (6)	3.38 (7)	4.20 (7)	−0.18 (5)	0.15 (6)	−0.16 (5)
N(3)	0.69417 (9)	0.33406 (15)	0.61795 (16)	3.97 (7)	4.57 (8)	4.36 (8)	−0.30 (6)	−0.24 (6)	−0.16 (6)
C(1)	0.55329 (9)	0.43709 (16)	0.34753 (18)	3.85 (9)	3.05 (7)	4.20 (9)	−0.34 (6)	0.80 (7)	−0.33 (6)
C(2)	0.65434 (10)	0.41860 (17)	0.53433 (19)	3.69 (7)	4.25 (9)	4.12 (9)	−0.48 (7)	0.61 (7)	−0.62 (7)
C(3)	0.75844 (16)	0.36730 (27)	0.72486 (30)	5.94 (14)	7.00 (14)	6.14 (15)	−0.30 (10)	−1.67 (11)	−0.54 (10)
C(4)	0.67182 (16)	0.20555 (23)	0.61502 (28)	6.31 (54)	4.48 (11)	5.84 (12)	−0.10 (9)	−0.51 (11)	0.64 (10)
C(5)	0.50000	0.24248 (22)	0.25000	3.65 (11)	2.82 (10)	4.74 (13)	0.00	−0.80 (10)	0.00
C(6)	0.54009 (12)	0.18105 (18)	0.16231 (24)	4.96 (10)	3.69 (9)	5.68 (11)	0.57 (8)	0.09 (8)	−0.53 (8)
C(7)	0.54012 (15)	0.05413 (22)	0.16341 (30)	6.49 (14)	3.90 (10)	8.14 (16)	1.10 (9)	−0.66 (11)	−1.43 (10)
C(8)	0.50000	−0.00942 (31)	0.25000	7.51 (21)	2.68 (13)	9.80 (26)	0.00	−1.79 (19)	0.00
H(3A)	0.747 (2)	0.409 (3)	0.788 (3)						
H(3B)	0.792 (2)	0.307 (3)	0.749 (3)						
H(3C)	0.789 (2)	0.432 (3)	0.689 (3)						
H(4A)	0.667 (2)	0.182 (2)	0.700 (3)						
H(4B)	0.634 (2)	0.185 (2)	0.543 (3)						
H(4C)	0.716 (2)	0.149 (2)	0.614 (3)						
H(6)	0.567 (1)	0.228 (2)	0.106 (3)						
H(7)	0.569 (2)	0.012 (2)	0.098 (3)						
H(8)	0.500	−0.099 (3)	0.250						

[a] The thermal parameters are of the form $T = \exp[{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Standard deviations are based solely on least squares parameters.

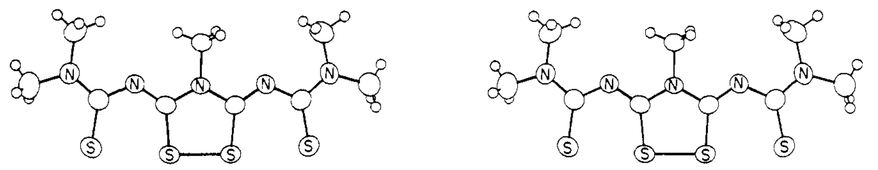
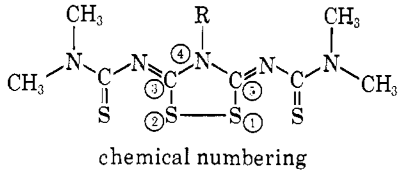


Figure 1. A stereodrawing of the methyl derivative including the refined positions of the hydrogen atoms.



chemical numbering

I, R = CH_3
II, R = C_6H_5

molecule I lies in a general position in the unit cell it does possess an approximate twofold axis with respect to bond lengths and angles. Excluding the bonds and angles associated with the methyl groups C(2), C(5), and C(9) the maximum deviations are on the order of 2σ for equivalent bonds and angles. The C(2)–N(1) and C(9)–N(5) bonds differ by 3σ. The angles involving the three methyl groups C(2), C(5), and C(9) differ by 4–5σ. The stereoconfiguration of the phenyl analog (II), which lies on a crystallographic twofold axis, is shown in Figure 5. The benzene ring is planar to within ±0.003 Å and the remainder of the molecule (excluding methyl groups) is planar to within ±0.116 Å. Deviations of individual atoms from this plane (see Figure 2) indicate a slight torsion about the twofold axis. The benzene ring is twisted out of this plane by 93.8°. Comparable distances and angles in the two molecules (I and II) agree quite well. Using average values for the equivalent bonds in the methyl derivative, the agreement between the two molecules is on the order of a maximum of 2σ for distances and a maximum of 3σ for the angles.

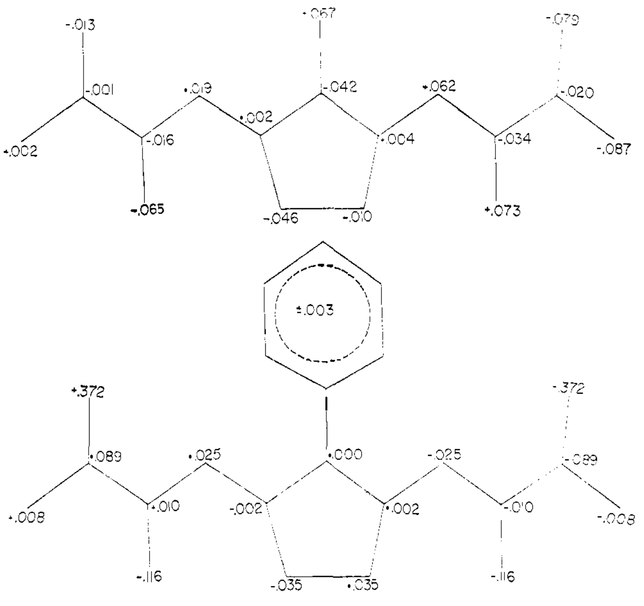


Figure 2. Deviations from least-squares planes for molecule I (top) and molecule II (bottom).

In both molecules there are significant differences between C—N and C═N bond lengths and between C—S and C═S bond lengths. Excluding N—CH_3 distances, the average C—N length is 1.349 (5) Å and the average C═N length is 1.286 (5) Å. The average C—S distance is 1.731 (3) Å and the average C═S distance is 1.676 (3) Å. The average N—CH_3 distance is 1.446 (5) Å.

Other multilinear sulfur systems containing four

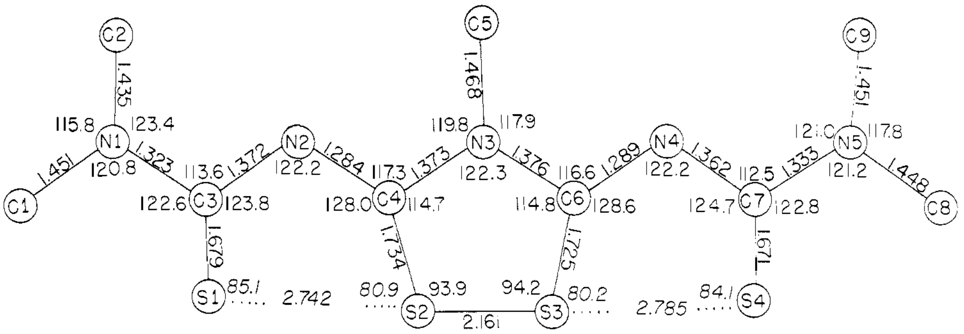


Figure 3. Bond distances and angles for molecule I. Standard deviations estimated from the least-squares refinement are ±0.005 Å for bonds and ±0.4° for angles.

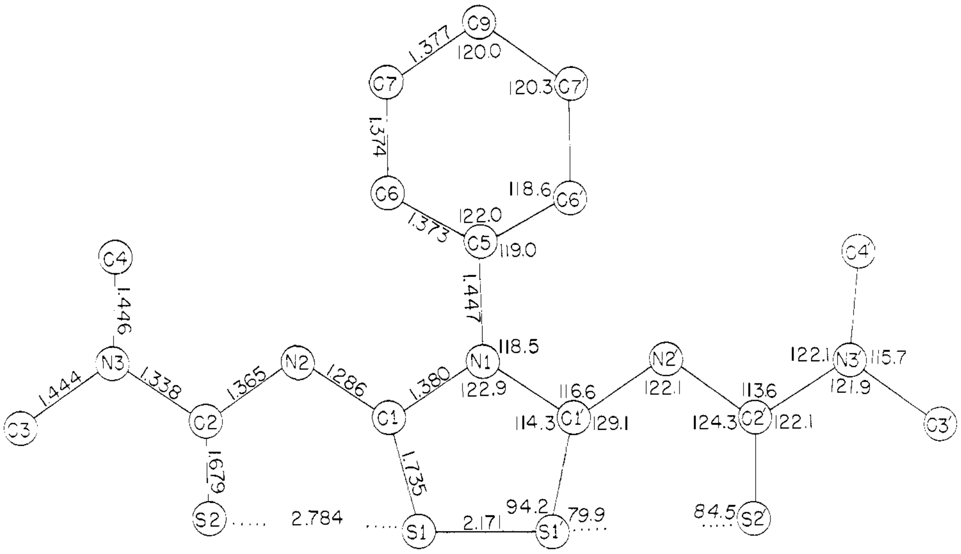


Figure 4. Bond distances and angles for molecule II. Standard deviations estimated from the least-squares refinement are ±0.003 Å for bonds and ±0.2° for angles.

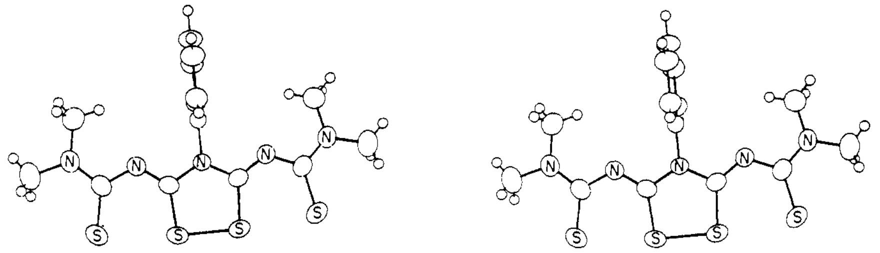


Figure 5. A stereodrawing of the phenyl derivative including the refined positions of the hydrogen atoms.

colinear sulfur atoms have been reported,[10,11] and one molecule with a multilinear system of five sulfur atoms has been studied.[12] In these systems, a correlation between formally nonbonded and bonded S–S distances is often reported; very short "nonbonded" distances are accompanied by lengthened bonded distances. In molecules III[10] and IV[11a] there are two five-membered disulfide rings which are quite similar to isolated dithiolium rings in which the S–S bond distance ranges from 2.00 to 2.06 Å.[13–15] The central S–S approaches in III and IV, while significantly shorter than van der Waal's separations (3.7 Å for two sulfur atoms), do not seem to be short enough to have any effect on the outer S–S bond lengths. In V,[11b] the two fused five-membered rings act like an isolated thiathiaphthene system[16–19] and the fourth sulfur atom, at a distance of 2.965 Å, does not have any apparent effect on the thiathiaphthene system. The position of the isolated disulfide ring seems to be more influenced by S–S and S–C repulsive forces. In VI the outer S–S single bonds are

---

(10) A. Hordvik, *Acta Chem. Scand.*, **19**, 1253 (1965).

(11) (a) J. Sletten, *Acta Chem. Scand.*, 26, 873 (1972); (b) *ibid.*, **25**, 3577 (1971).

(12) J. Sletten, *Acta Chem. Scand.*, **24**, 1464 (1970).

(13) A. Hordvik, *Acta. Chem. Scand.*, 20, 754 (1966).

(14) A. Hordvik, *Acta Chem. Scand.*, 20, 1874 (1966).

(15) A. Hordvik and J. Sletten, *Acta Chem. Scand.*, **20**, 1907 (1966).

(16) A. Hordvik and K. Julshamn, *Acta Chem. Scand.*, **23**, 3611 (1969).

(17) A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, **23**, 1852 (1969).

(18) P. L. Johnson and I. C. Paul, *Chem. Commun.*, 1014 (1969).

(19) S. M. Johnson, M. G. Newton, add I. C. Paul, *J. Chem. Soc. B*, 986 (1969).

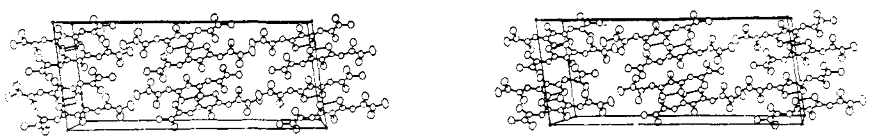


Figure 6. A stereodrawing of the packing of the methyl derivative. It is viewed looking down the *b* axis with *c* → and *a* ↑.

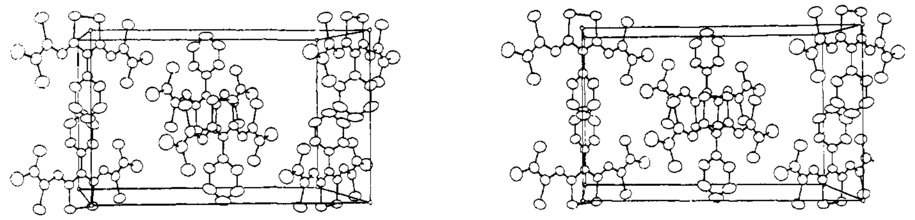
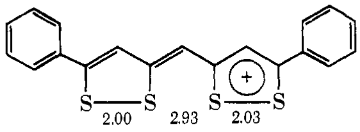
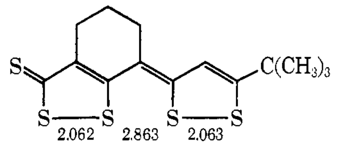


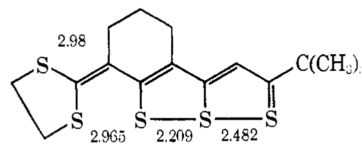
Figure 7. A stereodrawing of the packing of the phenyl derivative. It is viewed looking down the *c* axis with *a* → and *b* ↑.



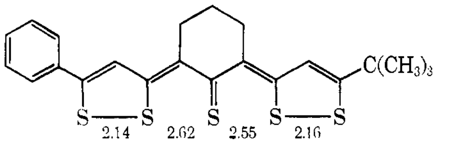
III



IV



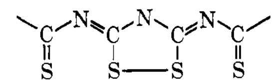
V



VI

longer than the S–S ring bonds in III and IV. This bond lengthening may be attributed to the attractive forces between the central sulfur atom and its two adjacent sulfur atoms. The sulfur–sulfur system in the molecules described by the present study (I and II) lies intermediate between the "bond, no-bond" systems in thiathiaphthene molecules[11b,16–19] and the multilinear sulfur systems having little or no attraction between nonbonded sulfur atoms.[10,11] Both analogs contain a five-membered disulfide ring which is similar to the dithiolium rings in VI. The outer S–S nonbonded distances in I and II, 2.74–2.78 Å, are longer than the nonbonded S–S distances in VI, 2.55–2.62 Å, and shorter than the nonbonded S–S distances in III–V, 2.86–2.93 Å. It would seem that in I and II, as in VI, the nonbonded sulfur atoms are close enough to the bonded sulfur atoms for the S–S interactions to have caused a lengthening of the central S–S single bond. However, there is also some repulsion between the nonbonded sulfur atoms, which is not found in VI, as evidenced by the large internal angles at C(3), N(2), C(4), C(6), N(4), and C (7) in the methyl derivative (av angle = 124.9°) and at C(2), N(2), and C(1) in the phenyl derivative (av angle = 125.2°).

Stereodiagrams of the molecular packing are shown in Figure 6 for the methyl derivative (I) and in Figure 7 for the phenyl derivative (II). Figures 1, 5, 6, and 7 were drawn by a computer program (ORTEP) written by Johnson.[20] In I the molecules are arranged in infinite columns along the *a* direction. Within a column all the molecules are parallel to one another but are rotated by 180° from the molecules in an adjoining column. The only intermolecular contact less than the sum of van der Waal's radii is S(2)···S(3) at 3.52 Å. The perpendicular distance between the planes of the closest molecules in a column is 3.64°. In II the molecules are assembled in pairs across a center of symmetry, with their



groupings arranged such that the C–S bonds in the two molecules are antiparallel. The perpendicular distance between two such planes is 3.72 Å. The closest intermolecular approaches of atoms in II are C(7)···C(7) at 3.44 Å, N(3)···C(4) at 3.59 Å, C(3)···C(6) at 3.61 Å, and S(1)–N(3) at 3.69 Å.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6073.

---

(20) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Analysis," U. S. Atomic Energy Commission Report ORNL-3794, 1965.