

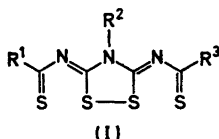
Structures of Linear Multisulfur Systems. XII. The Crystal and Molecular Structure of 3-(*N*-Diisopropylthiocarbamoylimino)-5-(thiobenzimino)-4-methyl-1,2,4-dithiazolidine, C₁₇H₂₂N₄S₄

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Crystals of the title compound, C₁₇H₂₂N₄S₄, are monoclinic, space group *P*2₁/*c*, with cell dimensions *a* = 10.603(3) Å, *b* = 14.434(2) Å, *c* = 13.866(2) Å, β = 109.60(2)°. 3538 independent reflections were recorded on an off-line four-circle diffractometer employing the θ–2θ scan technique. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares to an *R* of 0.051. The four sulfur atoms are arranged in a nearly linear row, with S–S distances in the region between a single bond and van der Waals distance; S(1)–S(2) = 2.815(2), S(2)–S(3) = 2.181(2), S(3)–S(4) = 2.620(3) Å.

The present structure determination is part of a program of X-ray crystallographic investigations of linear multisulfur compounds. So far four different symmetrically substituted 1,2,4-



dithiazolidine derivatives of type (I) have been studied.^{1–3} This is the first structure report of an unsymmetrically substituted derivative (R¹ ≠ R³).

EXPERIMENTAL

A sample of the compound was provided by Dr. J. Goerdeler, University of Bonn. Single crystals, deep green in colour, were grown by slow evaporation from a chloroform/light petroleum mixture at room temperature. The crystal used for data collection had dimensions

0.40 × 0.12 × 0.10 mm³ and was mounted along the *a*-axis. The space group was determined from Weissenberg and precession photographs. Cell dimensions were calculated based on diffractometer measurements of the 2θ values [λ(MoKα₁) = 0.70926 Å] for 15 reflections with 2θ > 60° using an ω-scan procedure.⁴ Within a sphere of reflection limited at sin θ/λ = 0.595 (2θ_{max} = 50°) the intensities of 3538 independent reflections were recorded on a four-circle diffractometer using the θ–2θ scan technique and niobium filtered MoKα radiation. Scan ranges were calculated according to the relationship Δ2θ = A + B tan θ,⁵ Δ2θ varying between 1.14° at 2θ = 0° and 1.32° at 2θ = 50°. Two reference reflections, measured for each 50 reflections recorded, indicated no deterioration of the crystal. Standard deviations in the intensities were calculated as σ_I = [σ_c² + (0.014N_{net})²]^{1/2}, where σ_c is the error due to counting statistics, and the “instability factor” of 0.014 were calculated in the data processing program, based on the variation in scale factors. Standard deviations in structure factors were calculated as σ_F = σ_I/2(*ILp*)^{1/2}. 1566 of the reflections had net counts less than 2σ_c. These reflections were assigned the threshold value of 2σ_c, and were later included in the refinement only if |*F*_c| > *F*_{threshold}. Data were corrected for Lorentz and polarization effects and for absorption.

CRYSTAL DATA

C₁₇H₂₂N₄S₄; *M.W.* = 410.65; crystal system monoclinic; space group *P*2₁/*c*; cell dimensions (20°C):

a = 10.603(3) Å, *b* = 14.434(2) Å, *c* = 13.866(2) Å, β = 109.60(2)°. *V* = 1999.1(7) Å³, *D_x* = 1.365 g cm^{–3}, *D_m* = 1.36(1) g cm^{–3}, *Z* = 4, *F*₀₀₀ = 864, μ_{MoKα} = 4.7 cm^{–1}.

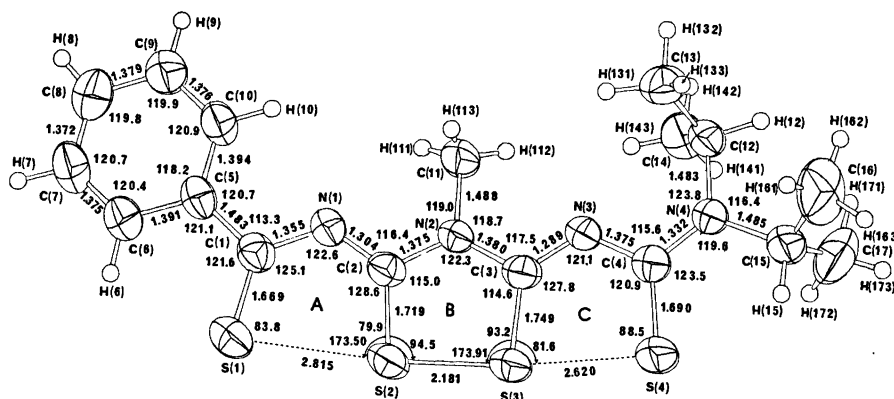


Fig. 1. Intramolecular distances and angles. Standard deviations as calculated from the least-squares inverse matrix are for S—S, S—C and C—N(C) bonds 0.002, 0.004 and 0.005–0.009 Å, respectively. Standard deviations in S—S—S and C—S—S angles are 0.07 and 0.2°; and 0.3–0.5° in angles at C and N. The thermal ellipsoids for non-hydrogen atoms are plotted at the 50 % probability level, hydrogen atoms are plotted with a fixed radius.

Table 1. Fractional coordinates and thermal parameters for non-hydrogen atoms with the corresponding standard deviations in parentheses. Thermal parameters are of the form $T_i = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, and the values are multiplied by a factor of 10^4 .

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.04311(15)	0.21917(8)	0.56414(10)	1060(12)	493(7)	859(10)	170(7)	465(8)	4(7)
S(2)	0.16626(13)	0.18811(7)	0.41604(9)	878(10)	366(6)	601(8)	79(6)	278(7)	-8(6)
S(3)	0.25500(14)	0.14763(7)	0.30141(9)	1115(12)	363(6)	695(8)	69(7)	459(8)	64(6)
S(4)	0.35187(19)	0.08128(8)	0.16484(11)	2052(19)	452(7)	1050(12)	187(10)	1067(13)	180(7)
N(1)	0.15854(34)	0.05536(19)	0.55415(24)	615(25)	442(19)	495(21)	23(17)	239(19)	-54(16)
N(2)	0.25574(32)	0.01777(19)	0.43584(23)	663(26)	338(17)	493(20)	67(17)	258(19)	30(16)
N(3)	0.33560(33)	-0.03326(19)	0.31147(23)	728(27)	367(17)	507(21)	6(18)	293(20)	-12(16)
N(4)	0.40735(34)	-0.09923(20)	0.18878(23)	736(27)	415(18)	455(20)	18(18)	284(19)	9(15)
C(1)	0.09356(40)	0.11126(25)	0.60047(28)	500(30)	498(24)	526(27)	-42(22)	167(23)	-106(21)
C(2)	0.19085(40)	0.08195(24)	0.47565(28)	542(30)	380(21)	483(25)	-19(21)	148(22)	-46(19)
C(3)	0.28759(41)	0.03461(23)	0.34873(29)	652(33)	381(21)	484(26)	-33(22)	196(24)	-8(19)
C(4)	0.36734(44)	-0.02267(25)	0.22375(30)	802(36)	459(23)	549(28)	4(24)	315(26)	5(21)
C(5)	0.07306(42)	0.06820(27)	0.69122(30)	531(32)	542(26)	473(26)	13(24)	157(24)	-142(22)
C(6)	0.02852(47)	0.12029(29)	0.75787(36)	785(40)	602(29)	620(30)	-18(27)	317(29)	-140(25)
C(7)	0.01396(54)	0.08007(36)	0.84341(40)	957(46)	790(36)	795(38)	54(33)	474(34)	-214(31)
C(8)	0.03976(54)	-0.01243(38)	0.86317(37)	1046(47)	906(39)	653(34)	-19(36)	465(33)	-12(31)
C(9)	0.08047(50)	-0.06585(30)	0.79656(36)	937(43)	622(30)	668(32)	87(29)	375(31)	19(26)
C(10)	0.09786(45)	-0.02581(29)	0.71180(33)	685(36)	576(28)	588(31)	77(26)	274(27)	-103(24)
C(11)	0.28977(50)	-0.07407(27)	0.48665(34)	1108(45)	470(25)	756(33)	264(28)	549(32)	183(24)
C(12)	0.43043(43)	-0.18909(25)	0.24384(29)	594(31)	428(22)	493(26)	-4(23)	197(24)	-63(21)
C(13)	0.30197(47)	-0.23517(28)	0.24254(32)	775(38)	553(27)	717(32)	-152(26)	277(28)	-19(23)
C(14)	0.53564(65)	-0.18336(43)	0.34901(39)	689(44)	691(35)	524(33)	142(35)	140(30)	47(30)
C(15)	0.44328(53)	-0.09495(27)	0.09419(32)	944(42)	491(25)	558(28)	102(27)	358(28)	58(22)
C(16)	0.36714(59)	-0.16938(40)	0.01899(35)	1450(55)	1458(51)	528(32)	-150(44)	383(35)	-326(34)
C(17)	0.59217(64)	-0.10009(38)	0.12013(42)	1031(51)	1213(46)	1088(46)	-53(39)	724(41)	147(37)

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by application of the symbolic addition procedure. An *E*-map based

on 283 reflections revealed the eleven atoms of "rings" A+B+C (Fig. 1). The remaining non-hydrogen atoms were localized in a subsequent Fourier map. The structure was refined by full-matrix least-squares, minimizing the

Table 2. Fractional coordinates and thermal parameters for hydrogen atoms with the corresponding standard deviations. Thermal parameters are of the form: $\exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$ and are multiplied by 10^3 .

Atom	X/a	Y/b	Z/c	U
H(6)	0.013(4)	0.189(2)	0.741(2)	72(11)
H(7)	-.016(4)	0.116(2)	0.893(3)	77(12)
H(8)	0.025(3)	-.043(2)	0.912(3)	75(12)
H(9)	0.098(3)	-.132(2)	0.810(2)	68(11)
H(10)	0.132(3)	-.062(2)	0.668(2)	55(10)
H(11)	0.299(5)	-.073(3)	0.551(4)	130(16)
H(112)	0.356(5)	-.100(3)	0.470(3)	119(16)
H(113)	0.217(6)	-.105(4)	0.464(5)	173(26)
H(12)	0.468(3)	-.229(2)	0.201(2)	52(10)
H(131)	0.260(4)	-.207(3)	0.292(3)	83(13)
H(132)	0.317(4)	-.301(3)	0.272(3)	92(13)
H(133)	0.235(4)	-.243(3)	0.172(3)	103(13)
H(141)	0.624(6)	-.155(4)	0.350(4)	145(30)
H(142)	0.561(5)	-.243(3)	0.378(3)	106(19)
H(143)	0.504(4)	-.152(3)	0.396(3)	86(17)
H(15)	0.415(3)	-.036(2)	0.061(3)	57(11)
H(161)	0.260(7)	-.165(5)	-.003(5)	225(29)
H(162)	0.401(7)	-.238(5)	0.038(5)	239(30)
H(163)	0.388(4)	-.154(3)	-.040(3)	107(14)
H(171)	0.628(5)	-.167(4)	0.148(4)	133(19)
H(172)	0.645(7)	-.047(4)	0.176(6)	218(30)
H(173)	0.622(4)	-.101(3)	0.069(3)	121(15)

function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. Anisotropic temperature factors were introduced for the non-hydrogen atoms. Hydrogen atoms were localized from a difference Fourier map, and positional and isotropic thermal parameters were refined. The sulfur atoms exhibit high thermal parameters with pronounced anisotropy. This may possibly indicate disorder in the sulfur chain, hence a model with split sulfur atoms was tested. But during the refinement the partial sulfur atoms in each pair moved constantly closer. Thus in the last refinement cycles only one position was refined for each of the atoms. The final S(4) thermal

parameters are unusually high with the main axis of vibration in a direction almost normal to the plane of rings A + B + C (Fig. 1). A difference map calculated at the end of the refinement showed no peaks around the sulfur atoms above the background level.

The refinement converged at an R ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.051, R_w being 0.032 and the standard deviation of an observation of unit weight being 1.71. No sign of secondary extinction was detected at the conclusion of the refinement. Scattering factors used were for C, N and S those of Cromer and Mann,⁶ and for H those of Stewart *et al.*⁷

The final coordinates and thermal parameters are listed in Tables 1 and 2. Lists of observed and calculated structure factors may be obtained from one of the authors (J.S.).

All calculations have been carried out on a UNIVAC 1110 computer. The programs concerning data collection and initial handling of the intensity data have been written by cand. real. K. Maartmann-Moe of this Department. For all other calculations the X-ray 72 system was used.⁸

RESULTS AND DISCUSSION

Intramolecular distances and angles involving non-hydrogen atoms are shown in Fig. 1 and in Table 3. The C—H distances lie in the region 0.86–1.10 Å with a mean value of 0.96 Å for $C(sp^2)$ —H and 0.98 Å for $C(sp^3)$ —H bonds. Standard deviations in the individual C—H bonds are in the range 0.03–0.07 Å. The four sulfur atoms are arranged in an almost linear row, the S—S—S angles being similar to those found in analogous compounds.^{1–3} The central S—S distance is significantly longer than the S—S bonds generally found in five-membered cyclic disulfides,⁹ and the terminal S—S

Table 3. Bond distances and angles in the isopropyl groups.

Distances	(Å)	Angles	(°)
C(12)–C(13)	1.511(7)	N(4)–C(12)–C(13)	112.7(3)
C(12)–C(14)	1.512(6)	N(4)–C(12)–C(14)	112.9(3)
C(15)–C(16)	1.526(6)	C(13)–C(12)–C(14)	114.0(4)
C(15)–C(17)	1.499(9)	N(4)–C(15)–C(16)	109.9(4)
		N(4)–C(15)–C(17)	110.3(4)
		C(16)–C(15)–C(17)	113.7(5)

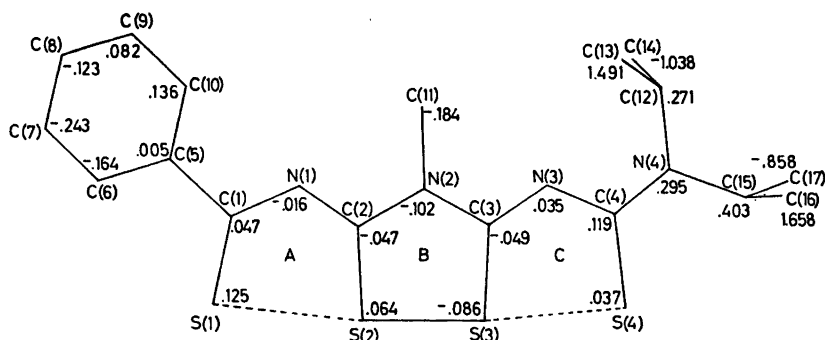


Fig. 2. Atomic deviations from the best least-squares plane through rings A + B + C.

distances are appreciably shorter than van der Waals distance. The bonding along this sulfur sequence may be described in terms of delocalized σ -bonding in a 4-center 6-electron linear system. According to CNDO/2 calculations the energy difference between a sulfur sequence with two-fold symmetry and an asymmetric sulfur sequence is small in this type of compounds.¹⁰ Relatively weak *intra*- as well as *inter*-molecular forces may affect the S–S distances significantly. Hence, it is not surprising that in this unsymmetrically substituted compound a relatively large asymmetry in the sulfur row is found.

The short intramolecular, non-bonding contacts $S(1) \cdots H(6) = 2.62(4)$ Å, $S(4) \cdots H(8) =$

$2.46(4)$ Å and $H(112) \cdots H(143) = 2.28(6)$ Å are of lengths similar to corresponding contacts in the compounds previously studied.^{1,2} In Fig. 2 the molecule is plotted in the best least-squares planes through rings A + B + C. This part of the molecule deviates slightly, but significantly from planarity. The molecule is slightly bent around $S(2) - C(2)$ and $S(3) - C(3)$, the dihedral angles between A and B; A and C; B and C being 3.2, 7.1 and 3.9°, respectively. The angles between the plane of the phenyl group and A is 11.4°.

In Fig. 3 the packing of molecules in the crystal is illustrated. Molecules related by a centre of symmetry (*e.g.* x, y, z and $-x, -y, 1-z$) overlap slightly, such that the phenyl group

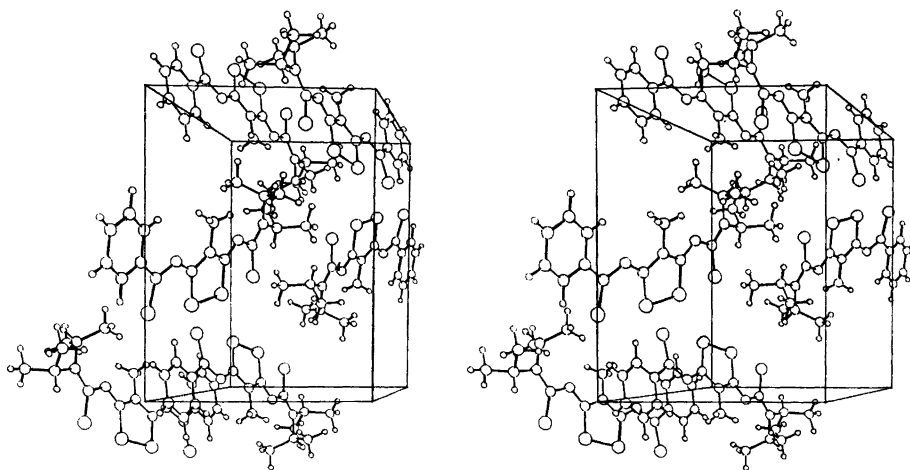


Fig. 3. Stereo drawing showing the molecular packing in the crystal. The *a*-axis runs along the interocular line left to right, the *b*-axis vertically, bottom to top, and the *c**-axis points towards the viewer. Figs. 1 and 3 have been prepared using the ORTEP program.¹¹

of one molecule is situated above ring B of the other molecule at an average distance of 3.5 Å. There are no intermolecular contacts shorter than van der Waals distance.

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