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Structures of Linear Multisulfur Systems. XIII. The Crystal and Molecular Structure of 3,5-Bis(*N*,*N*-diisopropylthiocarbamoylimino)-4-isopropyl-1,2,4-dithiazolidine, $C_{19}H_{35}N_5S_4$

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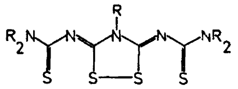
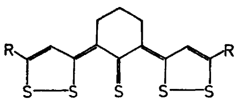
The title compound crystallizes in space group $P\bar{1}$ with a unit cell of dimension $a = 18.726(6)$ Å, $b = 8.204(2)$ Å, $c = 8.794(2)$ Å, $\alpha = 103.08(2)°$, $\beta = 81.81(4)°$, $\gamma = 107.12(2)°$. X-Ray intensity data were recorded on a four-circle diffractometer. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to an R of 0.035. The four sulfur atoms are almost collinearly arranged, the intramolecular S···S distances being 2.729(1), 2.161(1) and 2.721(1) Å, respectively.

A series of compounds containing almost linear sequences of four and five sulfur atoms have been investigated. It has been shown that the S – S σ-bonding in compounds like I and II may be described in terms of delocalized 4-centre-6-electron bonding and 5-centre-6-electron bonding, respectively.[1] These weak bonds, of lengths between a single bond and van der Waals distance, are easily influenced by *intra*- as well as *inter*-molecular effects. In the present investigation a compound of type I with relatively bulky substituents (R = isopropyl) is studied.



(I)



(II)

EXPERIMENTAL

The crystals grew as orange prisms from pyridine solution at room temperature. The space group was determined from Weissenberg and precession photographs. A crystal of dimension 0.27 mm × 0.20 mm × 0.50 mm mounted along c^* was used throughout the data collection. Cell dimensions were calculated from the 2θ-values $[\lambda(\mathrm{Mo}K\alpha_1) = 0.70926$ Å$]$ of 27 reflections with $2\theta > 36°$ as measured on a four-circle diffractometer with an ω-scan procedure.[2] The intensities of 4892 unique reflections were recorded on the diffractometer employing the $\theta - 2\theta$ scan technique. Scan ranges were calculated according to the Alexander and Smith equation,[3] $\Delta 2\theta$ varying between 1.2 and 1.7°. No sign of crystal deterioration was found by remeasuring two reference reflections for every 50 reflections recorded. These measurements were used to bring the data on a common relative scale. Standard deviations in the intensities were evaluated as $\sigma_I = [\sigma_c^2 + (0.01N_{\mathrm{Net}})^2]^{\frac{1}{2}}$, where σ_c is the error due to counting statistics, N_{Net} is the net count of the reflection, and 0.01 is an "instability factor" evaluated from the variation in the reference reflections. 1118 reflections had a net count less than a threshold value of $2\sigma_I$. These reflections were assigned an intensity of $2\sigma_I$ and coded unobserved, and were later included in the refinement only if $|F_{\mathrm{calc}}| > |F_{\mathrm{threshold}}|$. The data were corrected for Lorentz and polarization effects according to standard procedures. Absorption correction was carried out, A^* varying between 1.06 and 1.10.

CRYSTAL DATA

$C_{19}H_{35}N_5S_4$; M.W. = 461.78; crystal system triclinic; space group $P\bar{1}$ (or $P1$); cell dimen-

Table 1. Final atomic coordinates and thermal parameters with corresponding standard deviations, referring to the last decimal places, in parentheses. Thermal parameters are defined by $T_i = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ and are multiplied by a factor of 10^4.

Atom	X/a	Y/b	Z/c	U_{11}(Å^2)	U_{22}(Å^2)	U_{33}(Å^2)	U_{12}(Å^2)	U_{13}(Å^2)	U_{23}(Å^2)
S(1)	0.38719(4)	0.09664(7)	−.20895(7)	924(4)	544(3)	917(4)	358(3)	401(3)	432(3)
S(2)	0.30292(3)	0.18728(6)	0.05931(6)	707(3)	345(2)	717(4)	201(2)	127(3)	242(2)
S(3)	0.23265(3)	0.23876(6)	0.27183(6)	786(4)	318(2)	669(3)	233(2)	64(3)	137(2)
S(4)	0.14137(3)	0.27490(6)	0.53991(6)	902(4)	427(3)	631(3)	307(3)	59(3)	42(2)
N(1)	0.41101(8)	−.21041(18)	−.21921(18)	543(10)	458(8)	700(11)	209(7)	204(8)	249(8)
N(2)	0.32789(8)	−.13342(17)	−.01895(17)	469(9)	376(8)	574(10)	156(7)	91(7)	191(7)
N(3)	0.24817(8)	−.08083(15)	0.20004(16)	506(9)	288(7)	504(9)	139(6)	56(7)	128(6)
N(4)	0.17653(8)	−.02738(16)	0.43050(16)	525(9)	359(7)	434(9)	151(7)	−8(7)	50(6)
N(5)	0.10560(8)	−.01140(17)	0.66481(16)	566(10)	447(8)	394(8)	167(7)	−24(7)	12(7)
C(1)	0.37557(10)	−.09070(22)	−.14686(22)	470(11)	415(10)	657(13)	128(8)	82(9)	204(9)
C(2)	0.29498(9)	−.02518(20)	0.07376(21)	447(11)	323(8)	558(11)	112(8)	1(9)	150(8)
C(3)	0.21544(9)	0.03143(19)	0.31119(20)	480(11)	303(8)	494(11)	120(8)	−63(8)	71(8)
C(4)	0.14090(10)	0.07123(21)	0.54760(20)	514(11)	410(9)	441(10)	133(8)	−99(9)	−4(8)
C(5)	0.39806(11)	−.38122(23)	−.17249(23)	609(13)	450(10)	723(14)	262(9)	161(10)	219(9)
C(6)	0.42261(12)	−.36601(27)	−.01209(27)	703(15)	684(14)	891(17)	295(12)	−4(12)	299(12)
C(7)	0.31963(12)	−.49609(24)	−.19936(26)	692(14)	446(11)	875(16)	137(10)	53(12)	188(11)
C(8)	0.46684(12)	−.17867(25)	−.35549(26)	736(15)	578(12)	866(16)	299(11)	362(12)	314(11)
C(9)	0.54470(13)	−.15927(34)	−.31372(32)	572(15)	1049(20)	1090(21)	−22(14)	240(14)	33(16)
C(10)	0.44567(13)	−.31666(34)	−.50048(28)	804(17)	1185(21)	720(16)	438(15)	113(13)	321(14)
C(11)	0.23677(10)	−.26482(20)	0.22061(21)	607(12)	283(8)	580(12)	169(8)	130(10)	148(8)
C(12)	0.27428(12)	−.26827(25)	0.36002(27)	679(14)	499(11)	926(17)	214(10)	−71(12)	303(11)
C(13)	0.15546(11)	−.36847(22)	0.21412(23)	697(14)	354(10)	608(13)	33(9)	−21(10)	53(9)
C(14)	0.10928(11)	−.19056(23)	0.66658(21)	713(14)	487(11)	442(11)	210(10)	48(10)	92(9)
C(15)	0.15804(14)	−.18711(30)	0.79089(27)	970(18)	829(16)	753(16)	362(14)	−157(14)	228(13)
C(16)	0.03205(14)	−.31530(27)	0.68091(29)	847(17)	529(13)	955(19)	32(12)	−41(14)	83(12)
C(17)	0.06439(11)	0.07061(24)	0.80390(21)	642(13)	565(12)	415(11)	174(10)	6(10)	−32(9)
C(18)	0.11457(13)	0.22878(28)	0.90225(24)	888(17)	750(15)	521(13)	171(13)	−86(12)	−165(11)
C(19)	−.00604(12)	0.10275(30)	0.76331(26)	656(15)	873(16)	762(16)	348(13)	−9(12)	−8(12)

sions: $a=18.726(6)$ Å, $b=8.204(2)$ Å, $c=8.794(2)$ Å, $\alpha=103.08(2)°$, $\beta=81.81(4)°$, $\gamma=107.12(2)°$. $V=1253.5(6)$ Å^3, $Z=2$, $D_x=1.224$ gcm^{-3}, $D_m=1.22(1)$ gcm^{-3}, $F_{000}=496$, $\mu(\mathrm{Mo}K\alpha)=3.8$ cm^{-1}.

STRUCTURE DETERMINATION AND REFINEMENT

The distribution of E-values clearly indicated centrosymmetry, thus space group $P\bar{1}$ was tentatively selected. The positions of the four sulfur atoms were derived from a Patterson map. The remaining non-hydrogen atoms were located in two subsequent Fourier maps. Full-matrix least-squares refinement, introducing anisotropic thermal parameters on all atoms in the final cycles, reduced R to 0.067 ($\mathrm{R}=\sum||F_\mathrm{o}|-|F_\mathrm{c}||/\sum|F_\mathrm{o}|$). A difference map calculated at this stage revealed the hydrogen atoms, which were included in the refinement with isotropic thermal parameters. The refinement converged at an R of 0.035, the weighted R_w being 0.031. At the end of the refinement correction for secondary extinction was attempted, the correction gave, however, no significant changes in F_c, and was thus abolished. The quantity minimized in the refinement was $\sum w||F_\mathrm{o}|-|F_\mathrm{c}||^2$, where $w=1/\sigma_F{}^2$. Scattering factors for non-hydrogen atoms were taken from Ref. 4, and that for hydrogen was from Ref. 5. Final atomic coordinates and thermal parameters are listed in Tables 1 and 2. Lists

Table 2. Coordinates and thermal parameters of the hydrogen atoms with the corresponding standard deviations. Thermal parameters are defined by $T_i=\exp(-8\pi^2U\sin^2\theta/\lambda^2)$, and are multiplied by 10^3.

Atom	X/a	Y/b	Z/c	U (Å^2)
H(5)	0.4312(9)	−.4359(20)	−.2465(18)	56(5)
H(61)	0.4232(12)	−.4833(28)	0.0027(24)	99(7)
H(62)	0.3902(12)	−.3201(29)	0.0725(25)	106(7)
H(63)	0.4732(12)	−.2895(26)	0.0023(22)	88(7)
H(71)	0.3063(12)	−.5076(27)	−.3095(26)	106(7)
H(72)	0.2824(11)	−.4607(25)	−.1261(23)	87(6)
H(73)	0.3166(11)	−.6157(26)	−.1950(24)	93(7)
H(8)	0.4653(11)	−.0788(25)	−.3770(22)	83(6)
H(91)	0.5531(14)	−.0646(34)	−.2307(32)	143(10)
H(92)	0.5791(13)	−.1344(30)	−.4052(29)	116(8)
H(93)	0.5480(14)	−.2688(35)	−.2938(30)	140(10)
H(101)	0.4523(14)	−.4245(32)	−.4878(28)	124(9)
H(102)	0.4793(12)	−.2861(28)	−.5949(26)	106(8)
H(103)	0.3923(16)	−.3371(35)	−.5232(32)	152(10)
H(11)	0.2635(8)	−.3118(18)	0.1257(17)	42(4)
H(121)	0.3291(12)	−.2053(28)	0.3522(25)	100(7)
H(122)	0.2567(13)	−.2143(30)	0.4572(27)	115(8)
H(123)	0.2743(11)	−.3833(27)	0.3654(23)	92(7)
H(131)	0.1230(11)	−.3333(25)	0.2981(24)	89(7)
H(132)	0.1343(11)	−.3677(25)	0.1157(23)	85(6)
H(133)	0.1530(11)	−.4932(25)	0.2100(22)	84(6)
H(14)	0.1330(9)	−.2245(21)	0.5684(19)	55(5)
H(151)	0.2087(14)	−.1047(33)	0.7807(29)	130(9)
H(152)	0.1359(12)	−.1419(27)	0.8973(24)	99(7)
H(153)	0.1636(12)	−.3033(29)	0.7872(26)	107(8)
H(161)	−.0003(13)	−.3125(31)	0.6099(30)	126(9)
H(162)	0.0035(14)	−.2904(32)	0.7906(30)	129(9)
H(163)	0.0355(11)	−.4319(25)	0.6675(22)	85(6)
H(17)	0.0474(9)	−.0234(21)	0.8643(19)	63(5)
H(181)	0.1622(14)	0.2126(31)	0.9166(29)	127(9)
H(182)	0.0900(13)	0.2503(30)	0.9926(27)	113(8)
H(183)	0.1264(13)	0.3297(30)	0.8564(27)	130(9)
H(191)	−.0375(13)	−.0017(30)	0.7041(26)	115(8)
H(192)	−.0316(13)	0.1453(30)	0.8563(27)	112(8)
H(193)	0.0063(12)	0.2008(29)	0.7030(26)	110(8)

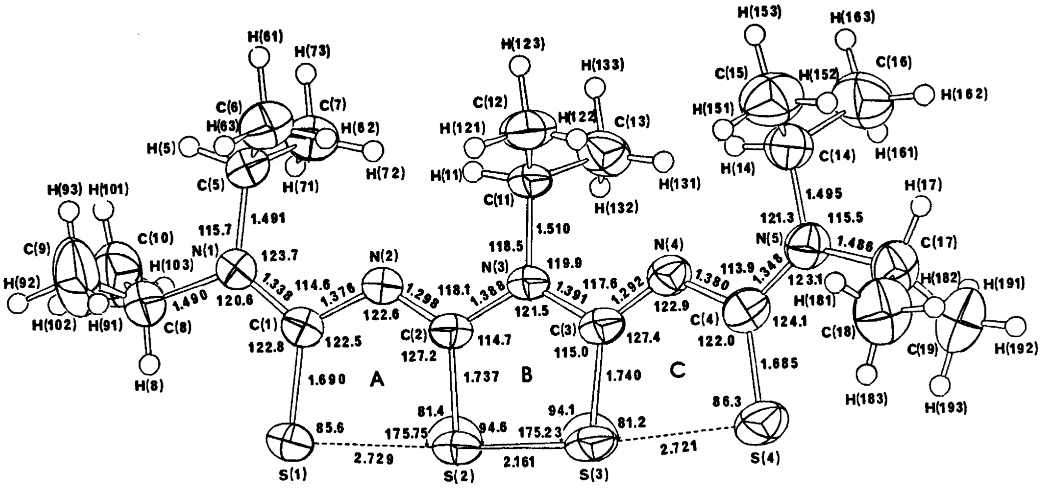


Fig. 1. Bond distances and angles. Standard deviations in S – S, S – C and C – N(C) distances are 0.001, 0.002 and 0.002 – 0.004 Å, respectively. Standard deviations in angles are: ∠S – S – S 0.03°, ∠C – S – S 0.1°, angles at C and N 0.1 – 0.2°. The thermal ellipsoids are plotted at the 50 % probability level; hydrogens are plotted with a fixed, arbitrary set radius.

of observed and calculated structure factors may be obtained from one of the authors (JS).

All calculations have been carried out on a UNIVAC 1110 computer utilizing the X-ray 72 system, except when otherwise noted.

RESULTS AND DISCUSSION

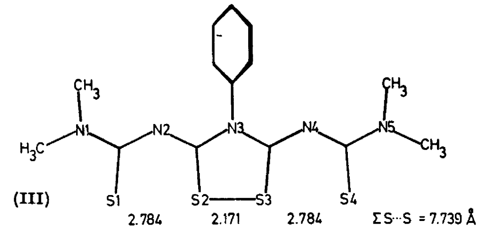
Bond distances and angles involving non-hydrogen atoms are shown in Fig. 1 and in Table 3 and 4. The C – H bond lengths are in the range 0.87 – 1.04 ($\sigma = 0.01 - 0.03$) Å with a mean value of 0.97 Å. The four sulfur atoms are arranged in an almost linear row with all three S···S distances longer than the corresponding bond in isolated cyclic disulfides[6] and shorter than van der Waals distance. The sulfur sequence has approximately two-fold symmetry. In the analogous derivatives previously studied, symmetrical sulfur rows have been found only when required by crystallographic symmetry.[7–10] The results of two previous investigations have shown that there is a significantly shorter total S···S sequence in

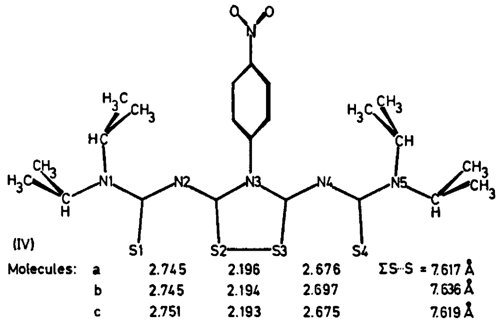
Table 3. Bond distances in the isopropyl groups.

Bond	(Å)
C(5) – C(6)	1.513(3)
C(5) – C(7)	1.511(3)
C(8) – C(9)	1.508(4)
C(8) – C(10)	1.514(3)
C(11) – C(12)	1.507(3)
C(11) – C(13)	1.512(3)
C(14) – C(15)	1.512(4)
C(14) – C(16)	1.513(3)
C(17) – C(18)	1.523(3)
C(17) – C(19)	1.523(4)

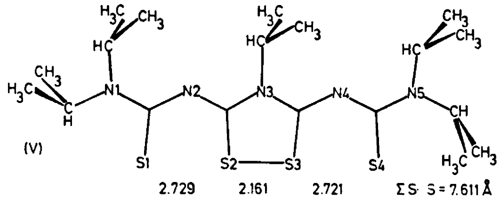
Table 4. Bond angles in the isopropyl groups.

Angle	(°)
N(1) – C(5) – C(6)	113.7(1)
N(1) – C(5) – C(7)	111.9(2)
C(6) – C(5) – C(7)	114.5(2)
N(1) – C(8) – C(9)	110.6(2)
N(1) – C(8) – C(10)	112.0(2)
C(9) – C(8) – C(10)	112.3(2)
N(3) – C(11) – C(12)	111.3(1)
N(3) – C(11) – C(13)	111.8(2)
C(12) – C(11) – C(13)	115.7(2)
N(5) – C(14) – C(15)	111.0(1)
N(5) – C(14) – C(16)	111.9(2)
C(15) – C(14) – C(16)	112.7(2)
N(5) – C(17) – C(18)	113.2(2)
N(5) – C(17) – C(19)	112.6(2)
C(18) – C(17) – C(19)	113.7(2)


(III)


(IV)

IV than in III.[7,9] This might possibly be due to repulsion between the bulky substituent in the "upper" part of the molecule, squeezing the sulfur atoms together. Introducing an isopropyl substituent at the central nitrogen, N(3), further increases the crowding in the "upper" part of the molecule relative to compound IV. However, the results of the present investigation show that the steric tension has been relieved through a 180° rotation around N–C of the isopropyl groups at N(5), (V), relative to the orientation in IV, and the total S···S sequence is not significantly shortened as compared to IV. The H···H contacts in the upper part of the molecule are: H(62)···H(11) = 2.37 Å, H(72)···H(11) = 2.31 Å; H(131)···H(14)


(V)

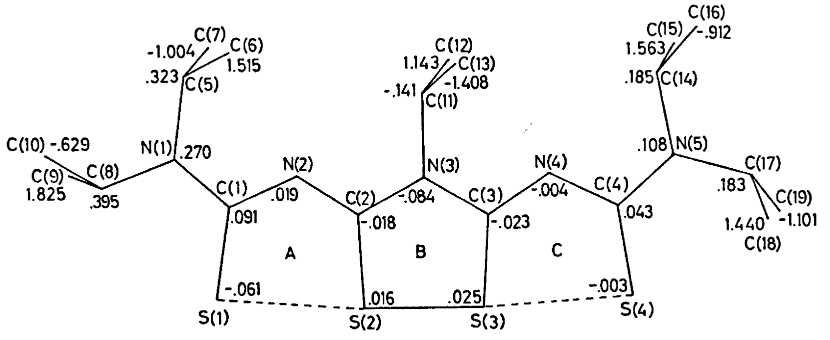


Fig. 2. Atomic deviations from the least-squares plane through rings A + B + C.

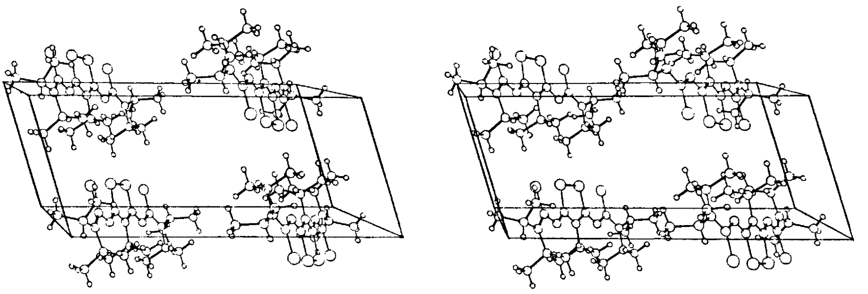


Fig. 3. Stereoscopic view as seen down the c^*-axis; the a-axis runs from left to right, the b-axis from bottom to top.

= 2.36 Å; H(122)···H(14) = 2.37 Å ($\sigma = 0.02 - 0.03$ Å).

Fig. 2 shows the atomic deviations from the best least-squares plane through rings A + B + C. The rings deviate slightly but significantly from planarity; and the substituents at C(1) and C(4) are bent out of the plane to one side, while the N(3) substituent is bent to the opposite side.

In Fig. 3 the three dimensional arrangement of molecules in the crystal is illustrated. There are no intermolecular contacts shorter than van der Waals distance.

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