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Structures of Linear Multisulfur Systems. VIII. The Crystal and Molecular Structure of 3,5-Bis(*N*,*N*-diisopropylthiocarbamoylimino)-4-(4-nitrophenyl)-1,2,4-dithiazolidine, $C_{22}H_{32}N_6O_2S_4$

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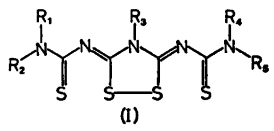
The structure of $C_{22}H_{32}N_6O_2S_4$ has been determined by X-ray crystallographic methods. 7456 independent reflections were measured on a diffractometer using the $\theta-2\theta$ scan technique and Mo$K\alpha$ radiation. The crystals are monoclinic, space group $P2_1/c$ with cell dimensions $a=12.643(6)$ Å, $b=24.365(6)$ Å, $c=27.147(6)$ Å, $\beta=99.67(4)°$. There are three molecules per asymmetric unit, giving a total of 12 formula units in the cell. The structure was solved by direct methods and refined by full-matrix least-squares to an R of 0.035. The three crystallographically independent molecules show only minor differences in their geometry. The four sulfur atoms in each molecule are approximately collinear, the average distances being S(1)–S(2) = 2.747 Å, S(2)–S(3) = 2.194 Å, S(3)–S(4) = 2.683 Å. Standard deviations in the individual S–S bond length are 0.001 Å.

The present structure determination was carried out as part of a program of X-ray crystallographic investigations of linear multisulfur compounds. In most of these compounds studied so far, the molecular skeleton connecting the sulfur atoms, has been made up of carbon atoms. Recently structure reports on similar compounds, where nitrogen atoms have been introduced into the frame, have been published.[1,2]



(I)

The present paper reports on the structure of a 1,2,4-dithiazolidine derivative, (I), where $R_1=R_2=R_4=R_5=$ isopropyl and $R_3=p$-nitrophenyl.

EXPERIMENTAL

A sample of the compound, consisting of orange, prismatic crystals was generously supplied by Goerdeler and Ulmen.[3] A single crystal of dimensions $0.25\times0.43\times0.42$ mm (along a, b, and c, respectively) mounted along the crystallographic b-axis, was used for all X-ray measurements. The experimental procedure for determination of cell dimensions and data collection are described elsewhere.[1] Standard deviations in intensities were calculated as $\sigma_I=[\sigma_c^2+(0.02N_{net})^2]^{\frac{1}{2}}$ where σ_c is the error due to counting statistics, and N_{net} is the net count of the reflections. Standard deviations in structure factors were evaluated as $\sigma_F=\sigma_I/2(I\,Lp)^{\frac{1}{2}}$. Out of a total of 7456 reflections with $2\theta\lesssim40°$ 1677 were less than $2\sigma_c$. These reflections were given a threshold value of $2\,\sigma_c$ and were later included in the refinement only if $|F_{calc}|>|F_{threshold}|$. Data were corrected for Lorentz and polarization effects according to standard procedures, and for absorption by the method described by Coppens *et al.*[4]

CRYSTAL DATA

$C_{22}H_{32}N_6O_2S_4$; M.W. = 540.80.
Crystal system monoclinic; space group $P2_1/c$; cell dimensions: $a=12.643(6)$ Å, $b=24.365(6)$ Å, $c=27.147(6)$ Å.

$\beta = 99.67(4)°$.
$V = 8244(1)$ Å^3; $D_x = 1.308$ g cm^{-3}; $D_m = 1.300$ g cm^{-3}.
$Z = 12$; $F_{000} = 3432$; $\mu_{MoK\alpha} = 3.7$ cm^{-1}.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by a symbolic addition procedure programmed by Long.[5] Signs for 360 reflections with $|E| \geq 1.70$ were derived by

Table 1. Atomic coordinates and thermal parameters for S, O, N, C with the corresponding standard deviations, referring to the last decimal places, listed in parentheses. Values for the coordinates are multiplied by 10^5, the thermal parameters by 10^4. $T_i = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.

Atom	Molecule	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	a	48790(8)	15023(5)	12514(4)	386(6)	813(9)	810(8)	-80(6)	254(7)	165(6)
	b	57677(8)	48030(5)	13882(4)	388(7)	987(10)	917(9)	0(6)	406(8)	189(6)
	c	52228(7)	80882(5)	12074(4)	350(6)	744(8)	718(8)	-74(5)	183(6)	134(5)
S(2)	a	67741(7)	10052(4)	16578(4)	441(6)	484(7)	634(7)	-79(5)	124(6)	177(5)
	b	76296(7)	43013(4)	18326(4)	402(6)	545(7)	574(7)	-67(5)	147(6)	142(5)
	c	70999(7)	75843(4)	16369(4)	373(6)	473(7)	567(7)	-81(5)	88(5)	150(5)
S(3)	a	83681(7)	6616(4)	19363(4)	501(6)	407(7)	552(7)	-38(5)	109(5)	170(5)
	b	91988(7)	39455(4)	21349(4)	451(6)	456(7)	459(6)	-28(5)	118(5)	146(5)
	c	86810(7)	72428(4)	19392(3)	427(6)	410(7)	495(6)	-56(5)	76(5)	149(5)
S(4)	a	103870(8)	3270(4)	22441(4)	618(7)	570(8)	621(7)	74(6)	207(6)	154(6)
	b	112125(8)	35768(4)	24446(4)	512(7)	668(8)	615(7)	44(6)	280(6)	94(6)
	c	106876(8)	69124(4)	22815(4)	517(7)	519(7)	483(6)	9(5)	141(5)	122(5)
O(1)	a	106382(27)	30982(14)	266(14)	1144(29)	1185(31)	1020(27)	-258(21)	315(24)	557(24)
	b	116322(25)	60935(14)	271(13)	1005(26)	1199(30)	750(24)	-234(20)	239(22)	418(21)
	c	111119(28)	94917(16)	-721(15)	1066(29)	1327(35)	1163(31)	-183(23)	432(27)	590(26)
O(2)	a	106970(28)	36250(15)	6658(14)	1189(29)	657(25)	1427(34)	-375(22)	186(24)	281(24)
	b	117580(31)	66682(17)	6236(14)	1548(37)	1086(32)	1107(31)	-766(28)	80(25)	397(25)
	c	112142(31)	100502(16)	5331(16)	1216(33)	794(29)	1693(41)	-384(24)	257(27)	547(27)
N(1)	a	52191(21)	23966(12)	7319(11)	395(18)	508(22)	594(21)	-14(16)	64(18)	113(16)
	b	61619(22)	55869(13)	7515(11)	390(19)	611(23)	616(22)	101(16)	152(19)	90(16)
	c	56184(21)	89737(13)	6865(11)	345(18)	607(23)	551(21)	58(16)	99(19)	118(15)
N(2)	a	67375(23)	19380(12)	10804(10)	355(20)	460(22)	489(20)	23(16)	50(17)	98(15)
	b	76520(23)	51401(12)	11583(11)	327(21)	508(22)	502(20)	49(16)	90(17)	76(16)
	c	71118(22)	84976(12)	10413(10)	319(21)	431(21)	470(20)	9(15)	27(16)	77(15)
N(3)	a	83705(22)	15546(11)	13898(10)	396(20)	357(20)	392(18)	-32(16)	78(15)	121(15)
	b	92578(22)	47716(11)	15141(10)	349(20)	409(20)	412(19)	-10(16)	102(16)	107(16)
	c	87214(21)	80989(11)	13529(10)	330(20)	356(20)	397(18)	-27(16)	50(15)	111(15)
N(4)	a	100596(25)	12359(11)	16726(10)	400(21)	426(20)	469(20)	55(16)	71(15)	136(16)
	b	109279(24)	44629(11)	18471(10)	314(20)	475(21)	445(19)	26(16)	79(16)	98(16)
	c	103949(24)	77857(11)	16668(10)	328(20)	409(20)	449(19)	14(16)	43(15)	102(15)
N(5)	a	118192(23)	9955(12)	19326(10)	453(21)	628(22)	545(21)	89(17)	87(17)	146(16)
	b	126742(23)	42559(12)	21763(10)	391(20)	633(22)	420(19)	34(16)	60(16)	63(15)
	c	121524(23)	75365(11)	19448(10)	404(21)	491(21)	490(20)	33(15)	102(15)	80(15)
N(6)	a	104402(27)	32022(17)	4409(17)	562(24)	654(31)	937(34)	-39(22)	249(29)	191(24)
	b	114626(27)	62365(18)	4322(15)	578(24)	834(34)	630(29)	-202(22)	208(27)	36(22)
	c	109074(29)	96280(19)	3296(18)	493(26)	855(36)	1022(37)	59(24)	411(34)	209(26)
C(1)	a	56381(29)	19675(15)	10086(13)	421(27)	489(28)	472(25)	-40(20)	-39(21)	130(19)
	b	65559(30)	51981(16)	10842(14)	434(29)	616(30)	536(27)	45(22)	53(22)	116(21)
	c	60070(29)	85443(15)	9667(13)	403(27)	494(29)	461(25)	-11(20)	-75(21)	122(20)
C(2)	a	72559(29)	15449(15)	13447(12)	415(26)	401(26)	395(23)	-80(20)	-29(20)	164(19)
	b	81437(29)	47819(15)	14652(13)	377(27)	460(27)	395(24)	-46(20)	9(20)	112(20)
	c	76077(28)	81055(15)	13117(12)	334(25)	390(26)	377(23)	-65(20)	-83(19)	109(18)
C(3)	a	90340(31)	11693(13)	16580(12)	497(28)	330(25)	351(22)	13(20)	-4(18)	144(19)
	b	99045(31)	44067(14)	18252(12)	454(27)	383(25)	377(24)	8(20)	-15(19)	142(20)
	c	93756(30)	77254(14)	16479(12)	393(26)	348(25)	377(23)	-18(20)	-14(19)	123(19)
C(4)	a	107858(31)	8766(15)	19362(13)	500(27)	511(28)	397(23)	31(22)	-29(20)	182(20)
	b	116317(30)	41233(15)	21460(12)	409(26)	589(28)	350(23)	23(22)	21(20)	97(20)
	c	111137(30)	74377(15)	19504(12)	406(26)	446(26)	383(23)	-12(21)	-46(19)	88(20)

Table 1. Continued.

C(5)	a	58758(35)	28169(18)	5253(17)	462(27)	483(29)	782(34)	9(24)	133(27)	-27(26)
	b	68542(35)	59495(18)	5019(16)	550(28)	510(30)	646(31)	46(25)	175(26)	38(25)
	c	63036(32)	93770(16)	4685(15)	428(25)	468(28)	656(30)	44(22)	103(25)	49(24)
C(6)	a	65959(56)	31419(26)	9246(30)	820(44)	551(41)	1156(56)	-115(35)	54(40)	-230(43)
	b	75696(51)	63196(25)	8574(25)	880(42)	567(39)	907(45)	-127(33)	-11(36)	-141(37)
	c	70286(45)	97054(24)	8614(23)	628(36)	584(39)	1017(45)	-47(31)	-10(35)	-100(35)
C(7)	a	64302(46)	25959(25)	1118(21)	632(36)	744(41)	863(42)	37(34)	298(34)	265(33)
	b	74394(48)	56368(26)	1459(21)	769(40)	852(44)	607(37)	11(36)	83(35)	246(34)
	c	68726(44)	91267(23)	748(20)	596(34)	730(38)	698(37)	96(31)	17(32)	246(31)
C(8)	a	40378(31)	24781(20)	6238(18)	405(26)	719(36)	829(38)	74(24)	144(30)	115(25)
	b	49894(35)	57155(25)	6601(21)	489(31)	961(45)	991(45)	170(30)	358(37)	183(30)
	c	44426(31)	90702(22)	5714(19)	417(27)	882(39)	821(38)	137(26)	265(32)	137(26)
C(9)	a	37227(60)	29952(40)	8747(34)	656(49)	1524(81)	1285(67)	347(55)	-371(57)	200(48)
	b	47916(84)	62466(64)	9170(36)	942(61)	2404(99)	1084(65)	979(84)	-400(68)	81(50)
	c	41499(58)	96136(38)	7874(27)	686(45)	1559(79)	819(49)	587(50)	-90(47)	97(37)
C(10)	a	36182(48)	24662(27)	638(22)	605(39)	784(46)	980(48)	23(32)	34(37)	-109(32)
	b	45091(48)	57324(28)	1057(25)	606(38)	781(44)	1148(54)	66(36)	44(41)	-164(35)
	c	40360(46)	90279(28)	127(23)	485(36)	920(47)	1007(49)	48(32)	-82(39)	-135(32)
C(11)	a	88608(25)	19918(15)	11443(14)	362(22)	411(28)	422(27)	-14(19)	59(23)	117(19)
	b	97880(25)	51607(16)	12302(14)	324(22)	421(29)	369(25)	-45(19)	88(22)	61(19)
	c	92301(25)	85136(15)	10843(14)	314(22)	402(28)	401(26)	2(19)	55(23)	90(19)
C(12)	a	92717(30)	24475(17)	14123(16)	544(27)	419(30)	473(29)	-66(21)	-32(26)	151(23)
	b	100222(29)	56767(18)	14134(15)	529(26)	522(34)	412(28)	-55(22)	-23(26)	147(21)
	c	96074(29)	89887(17)	13179(16)	529(26)	475(31)	425(28)	-81(22)	-38(26)	129(23)
C(13)	a	97718(32)	28466(19)	11752(19)	548(28)	379(31)	720(38)	-92(23)	-23(30)	101(25)
	b	105683(31)	60408(19)	11490(17)	580(28)	431(32)	606(33)	-124(24)	7(28)	116(24)
	c	101384(31)	93645(19)	10619(19)	517(28)	446(32)	727(37)	-107(24)	80(30)	102(25)
C(14)	a	98504(28)	27872(17)	6823(17)	407(24)	465(30)	574(31)	-49(21)	162(26)	130(22)
	b	108622(27)	58588(19)	7137(15)	390(24)	564(34)	420(28)	-82(22)	171(25)	96(20)
	c	102734(28)	92453(18)	5866(18)	339(24)	562(33)	671(34)	-42(22)	283(28)	160(23)
C(15)	a	94185(30)	23483(18)	4055(17)	469(26)	619(34)	496(30)	-24(23)	82(28)	147(23)
	b	106426(31)	53429(20)	5333(16)	507(28)	616(38)	384(29)	-46(24)	-13(29)	123(23)
	c	98631(31)	87831(20)	3419(17)	457(26)	669(35)	500(31)	0(24)	119(29)	175(23)
C(16)	a	89201(29)	19386(17)	6432(15)	501(25)	433(30)	502(31)	-89(22)	15(25)	150(21)
	b	100891(29)	49907(18)	7910(14)	526(26)	385(31)	378(28)	-90(22)	20(25)	83(21)
	c	93382(28)	84061(18)	5962(15)	381(24)	542(31)	447(30)	-41(21)	35(25)	119(21)
C(17)	a	121821(35)	14286(18)	16127(15)	407(28)	700(36)	563(31)	22(23)	52(24)	169(23)
	b	130834(33)	46545(18)	18346(14)	380(28)	770(38)	506(30)	-13(23)	50(24)	112(22)
	c	125478(31)	79980(16)	16633(14)	327(26)	562(32)	584(30)	6(20)	78(22)	121(21)
C(18)	a	120288(48)	20018(22)	18091(24)	698(40)	681(41)	841(44)	-60(30)	-50(33)	255(35)
	b	128384(51)	52423(22)	19398(26)	761(42)	655(43)	1011(50)	-135(32)	16(35)	335(35)
	c	123488(46)	85539(21)	18791(26)	609(37)	567(38)	1032(50)	-1(28)	-55(34)	260(34)
C(19)	a	117463(44)	13592(26)	10614(17)	612(36)	974(46)	528(34)	-81(31)	73(31)	224(28)
	b	127768(43)	44927(28)	12914(17)	556(35)	1101(52)	427(33)	48(32)	61(30)	110(27)
	c	121866(42)	79527(27)	11004(17)	492(33)	992(45)	548(34)	39(31)	140(31)	149(26)
C(20)	a	126754(36)	6598(21)	22337(19)	476(29)	844(38)	953(39)	166(27)	307(33)	73(29)
	b	135030(35)	39559(20)	25305(16)	454(28)	918(37)	573(30)	38(27)	204(29)	11(25)
	c	129939(35)	71877(20)	22400(18)	422(28)	800(36)	807(36)	14(26)	330(31)	44(27)
C(21)	a	134807(60)	10164(35)	25689(30)	891(50)	1632(71)	970(55)	123(50)	222(55)	-336(46)
	b	142399(69)	43611(40)	28483(27)	1013(57)	1746(81)	791(49)	-400(60)	411(54)	-481(47)
	c	135929(71)	75080(38)	26695(30)	1081(55)	1405(69)	958(53)	-21(56)	348(54)	-443(45)
C(22)	a	132023(66)	2974(33)	18804(35)	967(55)	988(57)	1631(74)	559(46)	72(57)	173(56)
	b	140617(99)	35347(54)	22579(39)	1310(77)	1803(94)	1203(73)	1004(74)	168(75)	155(70)
	c	136740(71)	69109(45)	19022(38)	1092(56)	1189(71)	1560(80)	824(58)	299(60)	306(51)

reiterative application of Sayres equation, starting with three origin determining reflections (1 3 $\bar{6}$, 3 6 $\bar{10}$, 5 12 $\bar{11}$) and three reflections with variable signs (0 3 4, 8 10 1, 0 9 12). The most probable set of phases had an internal consistency [5] of 0.87. The corresponding E-map revealed clearly only the twelve sulfur atoms, arranged in three almost parallel rows, separated by approximately 1/3 of a unit cell in the b-axis direction. A sub-cell with $b' = b/3$ is also indi-

Table 2. Coordinates and thermal parameters for hydrogen atoms with the corresponding standard deviations in parentheses. Values for coordinates are multiplied by a factor of 10^4, and thermal parameters by 10^3.

	Molecule	X/a	Y/b	Z/c	U
H(5)	a	5350(24)	3039(12)	384(11)	32(10)
	b	6370(24)	6177(12)	302(11)	32(10)
	c	5789(26)	9619(13)	272(11)	44(11)
H(61)	a	6174(42)	3250(22)	1189(20)	147(29)
	b	7147(42)	6509(23)	1131(20)	157(26)
	c	6534(34)	9884(18)	1091(16)	105(18)
H(62)	a	6833(37)	3398(20)	784(18)	93(22)
	b	7807(37)	6596(20)	723(18)	100(22)
	c	7375(35)	9999(19)	742(16)	101(19)
H(63)	a	7182(33)	2935(17)	1110(15)	86(16)
	b	8127(35)	6145(17)	1123(17)	102(18)
	c	7525(32)	9479(16)	1081(14)	78(15)
H(71)	a	5850(39)	2392(19)	-166(17)	123(20)
	b	6958(33)	5436(17)	-80(15)	89(18)
	c	6365(33)	8951(17)	-220(16)	95(17)
H(72)	a	6774(31)	2910(17)	-36(15)	85(15)
	b	7749(31)	5891(17)	-42(15)	80(16)
	c	7226(31)	9414(17)	-89(14)	83(15)
H(73)	a	6900(30)	2329(16)	194(14)	72(16)
	b	8038(38)	5373(20)	337(17)	119(19)
	c	7402(31)	8880(16)	212(15)	69(15)
H(8)	a	3764(28)	2143(16)	773(13)	73(13)
	b	4662(29)	5399(16)	758(14)	70(15)
	c	4114(30)	8781(16)	767(14)	85(15)
H(91)	a	3003(38)	2978(19)	850(16)	107(19)
	b	4095(43)	6254(21)	887(19)	119(22)
	c	3424(36)	9649(17)	727(15)	91(16)
H(92)	a	4070(39)	3256(19)	779(19)	85(24)
	b	5095(58)	6509(31)	884(30)	183(54)
	c	4491(45)	9916(23)	688(22)	129(33)
H(93)	a	4109(50)	2983(25)	1252(23)	182(31)
	b	5046(56)	6184(29)	1273(28)	215(39)
	c	4361(46)	9598(24)	1159(23)	175(29)
H(101)	a	2851(36)	2492(16)	3(15)	89(16)
	b	3702(45)	5762(21)	102(19)	147(23)
	c	3321(38)	9062(18)	-7(17)	108(19)
H(102)	a	3838(37)	2778(20)	-104(18)	103(22)
	b	4833(40)	6072(22)	-68(19)	146(23)
	c	4301(43)	9342(24)	-198(20)	158(27)
H(103)	a	3894(36)	2094(20)	-75(17)	115(19)
	b	4727(39)	5444(20)	-47(18)	113(23)
	c	4174(42)	8665(23)	-139(20)	158(27)
H(12)	a	9182(25)	2484(13)	1753(13)	51(12)
	b	9859(24)	5794(13)	1732(12)	52(12)
	c	9507(24)	9059(13)	1641(13)	44(11)
H(13)	a	10052(24)	3136(13)	1347(11)	36(12)
	b	10802(27)	6389(15)	1289(12)	59(13)
	c	10412(28)	9697(16)	1227(13)	65(14)
H(15)	a	9416(26)	2300(14)	39(14)	66(13)
	b	10826(22)	5227(12)	254(11)	30(10)
	c	9947(25)	8668(14)	-15(14)	61(12)
H(16)	a	8624(24)	1621(14)	469(11)	44(11)
	b	9946(20)	4623(12)	684(9)	14(9)
	c	9044(27)	8059(15)	428(13)	66(13)
H(17)	a	12902(27)	1376(13)	1632(12)	49(12)
	b	13848(25)	4611(11)	1927(10)	32(9)
	c	13305(26)	7975(12)	1726(10)	35(10)
H(181)	a	12387(33)	2051(18)	2148(16)	97(19)
	b	13038(38)	5366(20)	2274(18)	117(23)
	c	12636(36)	8591(19)	2247(18)	118(21)
H(182)	a	12392(37)	2250(19)	1611(17)	111(19)
	b	13203(33)	5509(18)	1749(15)	97(17)
	c	12641(39)	8794(21)	1685(19)	126(24)
H(183)	a	11290(35)	2062(16)	1827(15)	86(16)
	b	12075(36)	5335(18)	1916(15)	99(18)
	c	11601(33)	8644(15)	1847(13)	75(14)
H(191)	a	11833(38)	939(22)	940(19)	139(23)
	b	12975(40)	4116(22)	1257(19)	127(25)
	c	12421(38)	7602(20)	950(18)	127(22)
H(192)	a	12112(31)	1586(16)	865(15)	79(15)
	b	13120(33)	4669(17)	1066(16)	97(18)
	c	12542(36)	8236(19)	942(17)	112(19)
H(193)	a	10999(36)	1407(17)	955(15)	96(18)
	b	12013(33)	4531(16)	1159(14)	84(15)
	c	11465(31)	8014(14)	995(13)	67(14)
H(20)	a	12291(34)	391(18)	2444(16)	111(17)
	b	13086(25)	3759(12)	2732(11)	40(11)
	c	12568(28)	6938(15)	2383(13)	63(13)
H(211)	a	13971(41)	782(21)	2814(20)	133(21)
	b	14667(36)	4167(18)	3042(17)	87(18)
	c	14099(36)	7240(18)	2842(17)	100(17)
H(212)	a	13901(44)	1224(23)	2334(21)	156(29)
	b	14707(43)	4526(23)	2604(20)	149(26)
	c	13955(45)	7821(27)	2544(22)	150(30)
H(213)	a	13100(46)	1208(24)	2841(22)	165(30)
	b	13711(55)	4642(30)	2982(25)	208(44)
	c	13200(60)	7764(33)	2850(27)	213(49)
H(221)	a	13609(43)	64(22)	2090(19)	136(23)
	b	14480(44)	3347(23)	2515(21)	143(25)
	c	13960(42)	6657(22)	2065(19)	98(22)
H(222)	a	13555(48)	536(26)	1565(24)	198(32)
	b	14556(42)	3749(22)	2035(22)	149(27)
	c	14245(78)	7277(39)	1908(40)	230(50)
H(223)	a	12677(47)	96(24)	1696(22)	154(33)
	b	13621(57)	3368(33)	2064(28)	167(48)
	c	13439(57)	6835(31)	1497(30)	212(44)

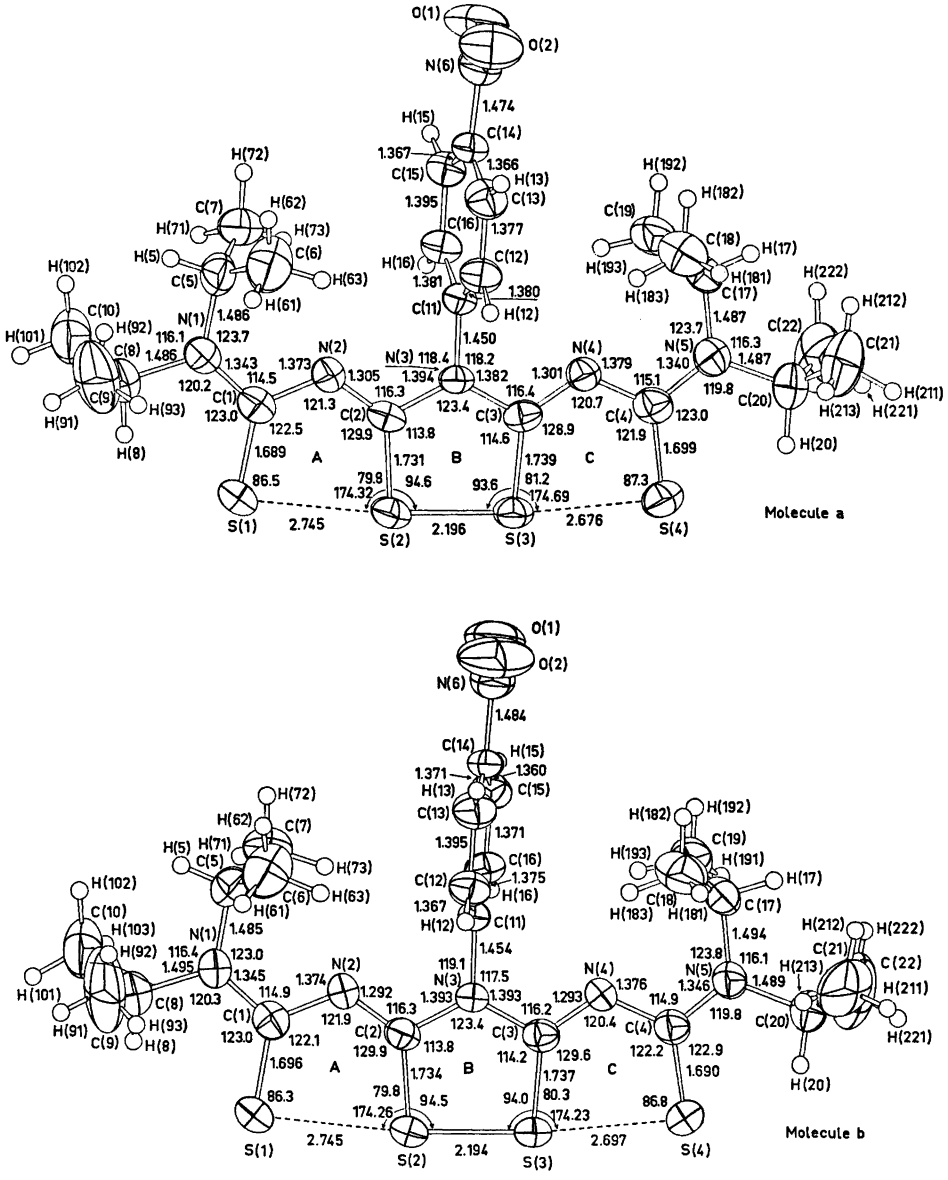
cated by the precession 0*kl* photograph where the 0, 3*n*, *l* lines are appreciably stronger than the other lines. Structure factor calculation based on sulfur only, gave an R of 0.56 ($R = \sum||F_o| - |F_c||/\sum|F_o|$). All 102 non-hydrogen atoms were located in four subsequent Fourier maps. The structure was initially refined using 3700 low order reflections. Later all reflections were included, and anisotropic thermal parameters were introduced on all non-hydrogen atoms. The 92 hydrogen atoms were located from a difference map, and included in the refinement with isotropic temperature factors. The refinement converged at an R of 0.035, the weighted R is 0.034 and the standard deviation of an observation of unit weight, $([\sum w(F_o - F_c)^2/$

$(n-m)]^{\frac{1}{2}}$) is 1.61. The function minimized in the refinement was $\sum w(|F_o|-|F_c|)^2$, where $w = 1/\sigma_F^2$. At the end of the refinement the shifts in atomic parameters were less than 0.7σ. No indication of secondary extinction was observed. In a residual difference map no regions significantly above the noice level were found.

The scattering factors used were for sulfur, oxygen, and carbon those of Hanson *et al.*[6] and for hydrogen those of Stewart *et al.*[7] Final coordinates and thermal parameters are listed in Tables 1 and 2. Lists of observed and calculated structure factors may be obtained from the author.

THERMAL ANALYSIS

The thermal parameters of the 11 atoms of rings $A+B+C$ (Fig. 1) of each molecule were analyzed in terms of rigid body motion using



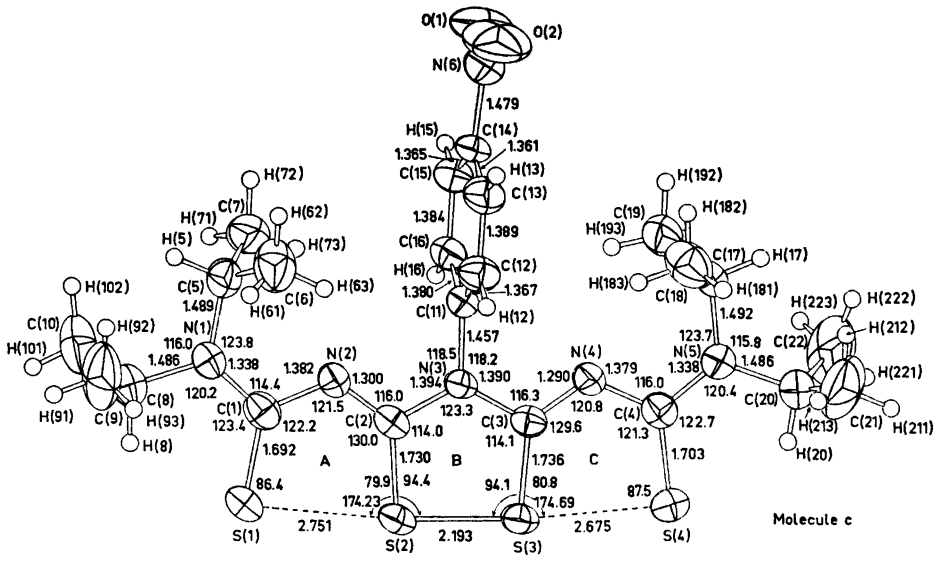


Fig. 1. Bond distances and angles in the three independent molecules (not corrected for rigid body motion). Standard deviations are 0.001 Å in S – S, 0.004 Å in S – C and 0.005 Å in N – C and C – C bonds. In the bond angles the standard deviations are 0.05° in S – S – S angles, 0.1° in S – S – C angles and 0.3° in the angles at C and N. For S, O, N, C the thermal ellipsoids are plotted at the 50 % probability level; H atoms are plotted with a fixed radius.

the method of Schomaker and Trueblood.[8] The observed mean-squares amplitude of vibration and the corresponding values calculated from the molecular **T**, **L**, **S** tensors, agree reasonably well, the r.m.s. ΔU being 0.0032, 0.0041, and 0.0026 Å^2 for molecules **a**, **b**, and **c**, respectively. In each case the axis of maximum libration was found to lie approximately parallel to the linear sulfur row, the angles of vibration being 7.3 (molecule **a**), 6.7 (**b**), and 6.7° (**c**). Corrections in bond distances were calculated according to Cruickshank's method.[9] The corrections are not significantly different in the three molecules, and amount to 0.004 Å in S – S, 0.012 – 0.014 Å in S – C, and 0.005 Å in C – N bond lengths.

RESULTS AND DISCUSSION

Bond distances and angles involving non-hydrogen atoms are shown in Fig. 1 and in

Table 3. Bond distances (Å) not shown in Fig. 1. Standard deviations in N – O distances are 0.006 Å and in C – C bonds of the isopropyl groups 0.010 Å.

Bond	Molecule **a**	Molecule **b**	Molecule **c**
N(6) – O(1)	1.219	1.207	1.209
N(6) – O(2)	1.214	1.204	1.201
C(5) – C(6)	1.516	1.506	1.513
C(5) – C(7)	1.519	1.517	1.513
C(8) – C(9)	1.517	1.511	1.519
C(8) – C(10)	1.524	1.516	1.521
C(17) – C(18)	1.519	1.503	1.513
C(17) – C(19)	1.515	1.513	1.523
C(20) – C(21)	1.519	1.522	1.498
C(20) – C(22)	1.536	1.508	1.517

Table 4. Bond angles (°) not shown in Fig. 1. Standard deviations are in the range 0.3 – 0.6°.

Angle	Molecule **a**	Molecule **b**	Molecule **c**
N(3) – C(11) – C(12)	120.1	119.9	120.3
N(3) – C(11) – C(16)	118.8	118.9	118.2
C(12) – C(11) – C(16)	121.1	121.2	121.5
C(11) – C(12) – C(13)	118.9	119.6	119.1
C(12) – C(13) – C(14)	119.8	117.9	118.8
C(13) – C(14) – C(15)	122.2	122.7	122.7
C(13) – C(14) – N(6)	119.2	118.6	118.5
C(15) – C(14) – N(6)	118.5	118.6	118.9
C(14) – C(15) – C(16)	118.4	119.0	118.7
C(15) – C(16) – C(11)	119.5	119.6	119.1
C(14) – N(6) – O(1)	117.7	118.3	117.9
C(14) – N(6) – O(2)	118.1	117.9	118.8
O(1) – N(6) – O(2)	124.2	123.8	123.3
N(1) – C(5) – C(6)	113.4	113.6	113.0
N(1) – C(5) – C(7)	113.0	112.3	113.0
C(6) – C(5) – C(7)	114.7	113.8	114.0
N(1) – C(8) – C(9)	110.7	109.8	110.9
N(1) – C(8) – C(10)	111.4	112.9	111.0
C(9) – C(8) – C(10)	113.0	111.3	112.4
N(5) – C(17) – C(18)	112.2	113.4	112.6
N(5) – C(17) – C(19)	113.6	112.1	112.9
C(18) – C(17) – C(19)	113.8	114.0	114.3
N(5) – C(20) – C(21)	111.6	110.2	110.1
N(5) – C(20) – C(22)	109.0	110.7	110.8
C(21) – C(20) – C(22)	112.7	115.3	116.0

Tables 3 and 4. The C – H distances all lie in region from 0.76 to 1.18 Å with a mean value of 0.97 Å both for C_{sp^2} – H and C_{sp^3} – H bonds. Standard deviations in the individual C – H distances range from 0.03 to 0.10 Å.

Corresponding bond distances in the three crystallographically independent molecules are identical within the experimental error, except for the S(3) – S(4) distance which is significantly longer in molecule **b** than in **a** and **c**. Molecule **b** also differs slightly, but significantly, from the two other molecules by showing a somewhat larger deviation from planarity in "rings" $A+B+C$ (Fig. 2.) The phenyl groups are oriented almost perpendicular to the main molecular planes. The twist angles in molecules **a** and **c** are 98 and 95° while the corresponding angle in **b** is 83°. There are short intramolecular contacts between the planes of the phenyl rings and the isopropyl groups (Table 5).

The asymmetry in the sulfur sequence of each molecule is reflected in different crystallographic

Table 5. Intramolecular contacts, distances in Å units. (ph···H) refers to the distance from a hydrogen atom to the plane of the phenyl group.

	Molecule **a**	Molecule **b**	Molecule **c**
S(1)···H(8)	2.34	2.49	2.38
S(4)···H(20)	2.38	2.41	2.35
ph···H(63)	2.89	2.56	2.85
ph···H(73)	2.73	2.83	2.75
ph···H(183)	2.70	2.85	2.72
ph···H(193)	2.92	2.66	2.85

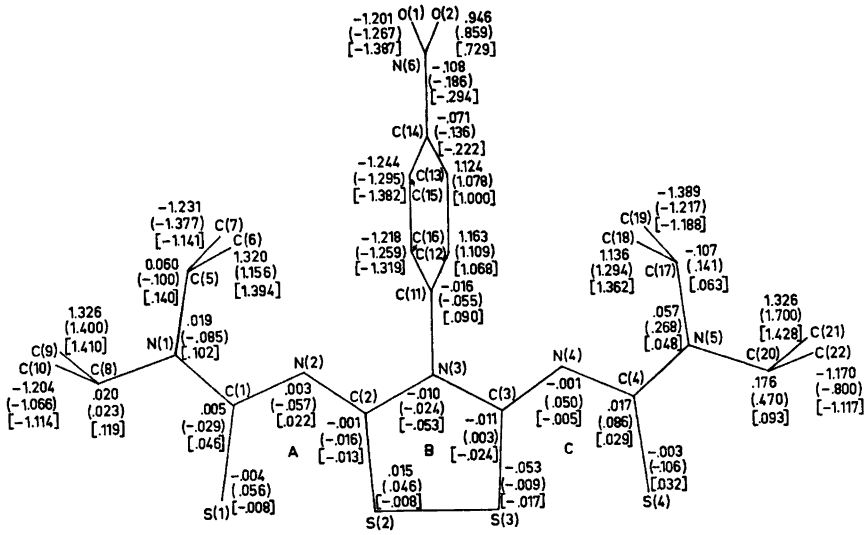


Fig. 2. Atomic deviations from the least-squares plane through rings $A+B+C$. Values for all three molecules are given; values for molecule **b** in parentheses, for molecule **c** in square brackets.

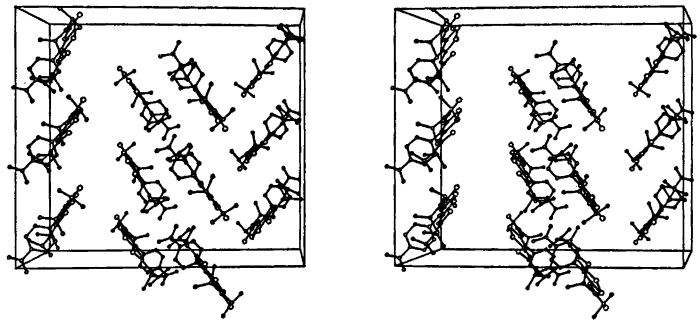
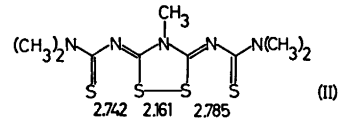


Fig. 3. Stereo drawing showing the packing of molecules in the crystal. The a^* axis is pointing towards the viewer, the b-axis is running top to bottom and the c-axis horisontally left to right. Hydrogen atoms have been omitted. Figs. 1 and 3 were drawn by computer using the ORTEP program.[14]

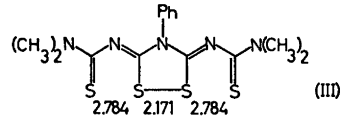
environment for atoms S(1) and S(4). This is best illustrated in the stereo drawing in Fig. 3. The molecules are arranged in columns running parallel to the crystallographic b-axis; molecules **a**, **b**, and **c** alternating through the column at a separation of approximately 1/3 unit cell. While there are no intermolecular short distances to S(1) of any molecule, the S(4) atoms have fairly short contacts to the molecules in the neighbouring stack related by a two-fold screw axis. S(4)**a** lies 3.40 Å above the molecular plane of molecule **b**′ (primed molecule at position $2-x$, $y-\frac{1}{2},\frac{1}{2}-z$); S(4)**b** is situated 3.25 Å above the plane of molecule **c**′; and S(4)**c** lies 3.35 Å from the plane of molecule **a**″ (double prime referring to position $2-x,y+\frac{1}{2},\frac{1}{2}-z$).

In one of the other dithiazolidine structures (II) determined, a similar asymmetry in the sulfur sequence is observed.[2] In two other analogous compounds (III, IV) the molecules possess a crystallographic twofold axis.[1,2]

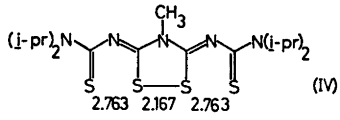
In the present structure the central S–S bond is significantly longer than in molecules II, III, and IV. The sum of the three S–S



(II)



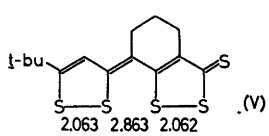
(III)



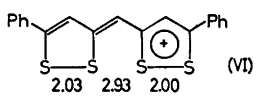
(IV)

bond lengths in each molecule is shorter in the present structure than in those previously studied; the values are 7.617, 7.636, and 7.619 Å for molecules **a**, **b**, and **c** respectively, compared to 7.688, 7.738, and 7.693 Å for II, III, and IV. The shorter overall S···S distances in the present compound may be caused by intramolecular strain; *i.e.* by repulsion between the *p*-nitrophenyl group and the closest isopropyl groups.

The sulfur–sulfur distances within each molecule are all in the region between single bond of 2.10 Å [10] and van der Waals distance. In other linear four-sulfur compounds (V and VI), however, the terminal S–S bonds have been found to be of the same length as those in isolated cyclic disulfides.[11,12] In these compounds (V, VI) the σ-bonding in the sulfur rows may be considered as four-centre four-electron bonding, giving two essentially localized bonds as the energetically most favourable arrangement. In the 1,2,4-dithiazolidine derivatives (I), where nitrogen atoms have been introduced into the ring system, the σ-bonding between the sulfur atoms may formally be regarded as four-centre six-electron bonding. The excess electrons populate non-bonding or weakly antibonding orbitals, resulting in partial σ-bonding between the sulfur atoms. Semi-empirical MO calculations on these systems will be published.



(V)



(VI)

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