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The Crystal and Molecular Structures of 4-Ethyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine and 2-Ethyl-4-phenyl-5-phenylimino-1,2,4-thiadiazolidin-3-thione

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The molecular structures of title compounds, two of the three isomeric products in the reaction of 2-ethyl-3-phenyloxaziridine with phenyl isothiocyanate, have been determined by means of X-ray diffraction. 4-Ethyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine (**6b**), orthorhombic, space group *Pcab*, a=27.171(1), b=10.213(2), c=11.421(1) Å, Z=8; 2-Ethyl-4-phenyl-5-phenylimino-1,2,4-thiadiazolidin-3-thione (**8b**), monoclinic, space group $P2_1/n$, a=9.278(1), b=27.525(3), c=5.826(1) Å, β=92.74(1)°, Z=4. Both structures were solved by the heavy atom method, and refined anisotropically by the block-diagonal least-squares procedure (R=0.066 and 0.060, respectively). The results corrected the reaction scheme proposed for the reaction of *N*-alkyloxaziridine with phenyl isothiacyanate.

It has been reported that the reaction of *N*-alkyloxaziridine (**1**) with phenyl isothiocyanate (**2**) gave heterocyclic compounds with incorporation of alkylnitrene.[1] However, stimulated by extensive studies by L'Abbé and co-workers on similar reactions of alkyl azides with isothiocyanates,[2,3] the structures of the cyclic adducts (R≠*t*-Bu) were reexamined by ^{13}C NMR. It indicated that the former assignment for **3** and **4** structures was not correct. In order to obtain the exact information on the molecular structures of the cyclic products, **6b** and **8b** (previously assigned as **3b** and **4b**), have been determined by means of X-ray diffraction.

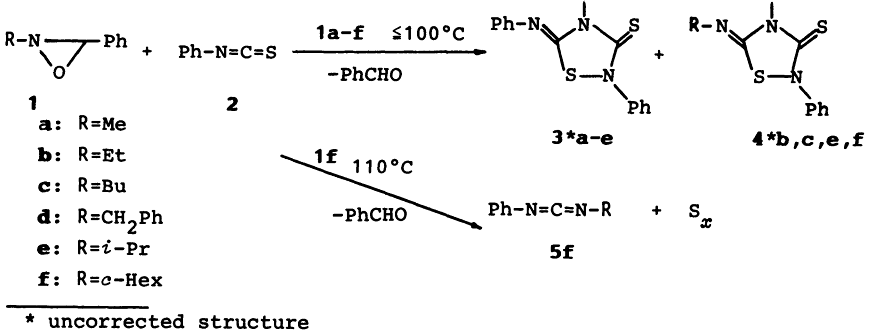
Experimental

Crystal Data. **6b**, $C_{16}H_{15}N_3S_2$, M 313.3, orthorhombic, space group *Pcab* (No. 61, absent reflections, $0kl$: $l=2n+1$, $h0l$: $h=2n+1$, $hk0$:$k=2n+1$), a=27.171(1), b=10.213(2), c=11.421(1) Å, D_m=1.30 g cm^{-3}, D_c=1.31 g cm^{-3} for Z=8, μ(Mo $K\alpha$)=3.3 cm^{-1}; **8b**, $C_{16}H_{15}N_3S_2$, M 313.3, monoclinic, space group $P2_1/n$ (No. 14, absent reflections, $h0l$:$h+l=2n+1$, $0k0$:$k=2n+1$), a=9.278(1), b=27.525(3), c=5.826(1) Å, β=92.74(1)°, D_m=1.33 g cm^{-3}, D_c=1.34 g cm^{-3} for Z=4, μ(Cu $K\alpha$)=29.6 cm^{-1}.

A Rigaku automated, four-circle diffractometer equipped with graphite monochromator was used for X-ray experiments. The crystals used had approximate dimensions of 0.2×0.2×0.2 (**6b**) and 0.2×0.2×0.3 mm (**8b**). Unit-cell dimensions of both crystals were determined by the least-squares fit of 2θ values of higher order feflections. Integrated intensities were measured on the diffractometer by the θ-2θ scan technique at a 2θ rate of 4° min^{-1}. Scan width for **6b** was $\Delta 2\theta=(2.0+0.7\tan\theta)°$ for Mo$K\alpha$ radiation (λ=0.71069 Å) and for **8b** $\Delta 2\theta=(2.0+0.3\tan\theta)°$ for Cu$K\alpha$ (λ=1.5418 Å). Backgrounds were counted for 7.5 s at both ends of a scan. Three standard reflections were measured after every 60 reflections, which showed no intensity decrease during intensity measurements on both crystals. Totals of 3470 and 2342 reflections were measured, of which 1292 and 2044 were observed ($|F_o|>3\sigma(F_o)$) for **6b** and **8b**, respectively. The usual Lorentz and polarization corrections were applied ignoring absorption correction. Densities were measured by flotation method in carbon tetrachloride-hexane mixed solutions.

Structure Solution and Refinement

Both structures were solved by the heavy atom method, and refined anisotropically by the block-diagonal least-squares procedure minimizing $\sum w(\Delta F)^2$ (*HBLS* V).[4] All hydrogen atoms were located on the difference Fourier map, which were refined isotropically. Three



* uncorrected structure

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reflections (020, 002, and 302), which were considered affected by the extinction largely, were excluded at the final stage. Final *R* values are 0.066 and 0.060 for **6b** and **8b**, respectively. Unit weights were employed only at the early stage of the refinement and the weighting schemes used at the final cycles were $w=\{\sigma^2(F_o)-1.1709|F_o|+0.0518|F_o|^2\}^{-1}$ for **6b** and $w=\{\sigma^2(F_o)-0.0762|F_o|+0.0095|F_o|^2\}^{-1}$ for **8b**, where σ is the standard deviation obtained by the counting statistics. Atomic scattering factors used were taken from International Tables for X-Ray Crystallography[5] for non-hydrogen atoms and from Stewart and coworkers[6] for hydrogen atoms. Final atomic coordinates are given in Table 1.[††]

Computations were done on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research Center, Osaka University.

Results and Discussion

Reaction Scheme. The conclusive evidence for the structure of the molecules formerly assigned as **3** and **4** has been obtained by the present X-ray crystal structure analysis. As is clearly seen in Fig. 1, the molecule assigned as **3b** (R=Et) is found to be 4-ethyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine (**6b**) and that as **4b** (R=Et) is 2-ethyl-4-phenyl-5-phenylimino-1,2,4-thiadiazolidin-3-thione (**8b**). Therefore, the reaction scheme proposed formerly[1] should be corrected as follows.[8]

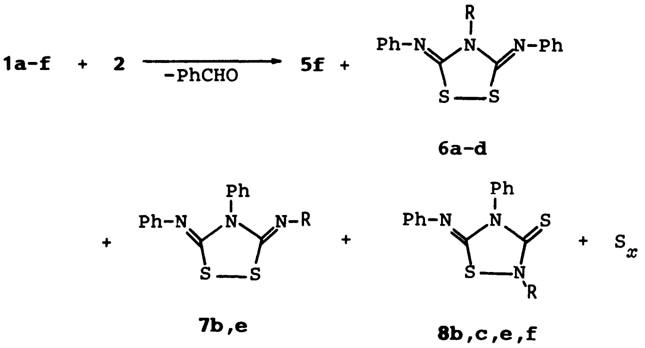


Table 1. Final Atomic Coordinatesof Non-Hydrogen Atoms with Estimated Standard Deviation in Parentheses

	Atom	*x*	*y*	*z*	B_{eq}[7]/Å^2
6b	S(1)	0.40347(4)	0.20928(12)	0.59890(12)	4.6
	S(2)	0.47677(4)	0.22428(12)	0.55385(13)	4.9
	C(3)	0.46558(12)	0.2698(4)	0.4063(5)	3.2
	N(4)	0.41605(10)	0.2740(3)	0.3767(3)	3.2
	C(5)	0.38041(13)	0.2420(4)	0.4594(4)	3.3
	N(6)	0.33527(10)	0.2377(3)	0.4320(4)	4.2
	N(7)	0.49907(10)	0.2958(3)	0.3338(4)	4.1

Table 1. (Continued)

	Atom	*x*	*y*	*z*	B_{eq}[7]/Å^2
	C(41)	0.40279(12)	0.3081(4)	0.2559(5)	4.5
	C(42)	0.40261(15)	0.4533(5)	0.2342(6)	7.3
	C(61)	0.30124(12)	0.1999(4)	0.5209(4)	3.6
	C(62)	0.27841(13)	0.0781(4)	0.5107(5)	3.9
	C(63)	0.24395(13)	0.0415(4)	0.5943(5)	4.6
	C(64)	0.23200(13)	0.1214(5)	0.6850(5)	5.4
	C(65)	0.25397(13)	0.2419(5)	0.6946(6)	6.0
	C(66)	0.28896(14)	0.2820(4)	0.6123(5)	5.0
	C(71)	0.54859(12)	0.2853(4)	0.3730(5)	3.8
	C(72)	0.57224(13)	0.1657(4)	0.3692(5)	4.9
	C(73)	0.62135(15)	0.1585(4)	0.4009(5)	6.0
	C(74)	0.64716(14)	0.2685(5)	0.4359(5)	6.0
	C(75)	0.62319(15)	0.3852(5)	0.4392(5)	6.9
	C(76)	0.57381(14)	0.3960(4)	0.4067(5)	5.8
8b	S(1)	0.14872(9)	0.19651(3)	0.31987(16)	3.9
	N(2)	0.0284(3)	0.21323(9)	0.1112(5)	4.2
	C(3)	−0.0520(4)	0.17739(12)	0.0252(6)	3.7
	N(4)	−0.0173(3)	0.13411(9)	0.1341(5)	3.5
	C(5)	0.0952(3)	0.13538(11)	0.2911(6)	3.3
	N(6)	0.1496(3)	0.09826(10)	0.3840(5)	3.6
	S(7)	−0.17358(10)	0.18346(4)	−0.18110(19)	5.2
	C(21)	0.0161(4)	0.26509(12)	0.0466(7)	5.3
	C(22)	0.1004(6)	0.27888(17)	−0.1456(8)	7.7
	C(41)	−0.0916(3)	0.08958(11)	0.0895(5)	3.1
	C(42)	−0.1796(4)	0.07389(13)	0.2528(7)	4.6
	C(43)	−0.2499(5)	0.03070(14)	0.2137(7)	5.4
	C(44)	−0.2313(4)	0.00474(13)	0.0167(7)	4.9
	C(45)	−0.1452(4)	0.02043(12)	−0.1436(6)	4.5
	C(46)	−0.0734(4)	0.06388(12)	−0.1091(6)	4.0
	C(61)	0.2641(4)	0.10519(11)	0.5412(6)	3.5
	C(62)	0.3835(4)	0.07940(14)	0.5032(6)	4.6
	C(63)	0.4965(4)	0.08360(16)	0.6570(7)	5.6
	C(64)	0.4900(4)	0.11249(15)	0.8507(6)	5.0
	C(65)	0.3713(4)	0.13734(14)	0.8881(6)	4.9
	C(66)	0.2589(4)	0.13370(13)	0.7347(6)	4.2

Table 2. Selected Bond Lengths and Bond Angles in **6b** and **8b** with Estimated Standard Deviations in Parentheses

6b		**8b**	
Bond length [*l*/Å]			
S(1)-S(2)	2.063(2)	S(1)-N(2)	1.711(3)
S(1)-C(5)	1.744(4)	S(1)-C(5)	1.767(3)
S(2)-C(3)	1.775(5)	S(7)-C(3)	1.654(3)
C(3)-N(4)	1.388(5)	C(3)-N(2)	1.341(4)
C(5)-N(4)	1.392(5)	C(3)-N(4)	1.384(4)
C(3)-N(7)	1.258(6)	C(5)-N(4)	1.393(4)
C(5)-N(6)	1.267(6)	C(5)-N(6)	1.261(4)
Bond angles [ϕ/°]			
S(2)-S(1)-C(5)	96.1(2)	N(2)-S(1)-C(5)	90.0(2)
S(1)-S(2)-C(3)	95.2(2)	S(1)-N(2)-C(3)	115.8(3)
S(2)-C(3)-N(4)	113.9(4)	N(2)-C(3)-N(4)	109.7(3)
S(2)-(3)-N(7)	123.8(4)	N(2)-C(3)-S(7)	125.5(3)
N(4)-C(3)-N(7)	112.3(5)	N(4)-C(3)-S(7)	124.8(3)
S(1)-C(5)-N(4)	114.5(3)	S(1)-C(5)-N(4)	107.8(3)
S(1)-C(5)-N(6)	124.6(4)	S(1)-C(5)-N(6)	128.0(3)
N(4)-C(5)-N(6)	120.9(4)	N(4)-C(5)-N(6)	124.2(3)
C(3)-N(4)-C(5)	120.1(4)	C(3)-N(4)-C(5)	116.5(3)

[††] Tables of anisotropic thermal parameters, coordinates of hydrogen atoms and tables of observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8624.

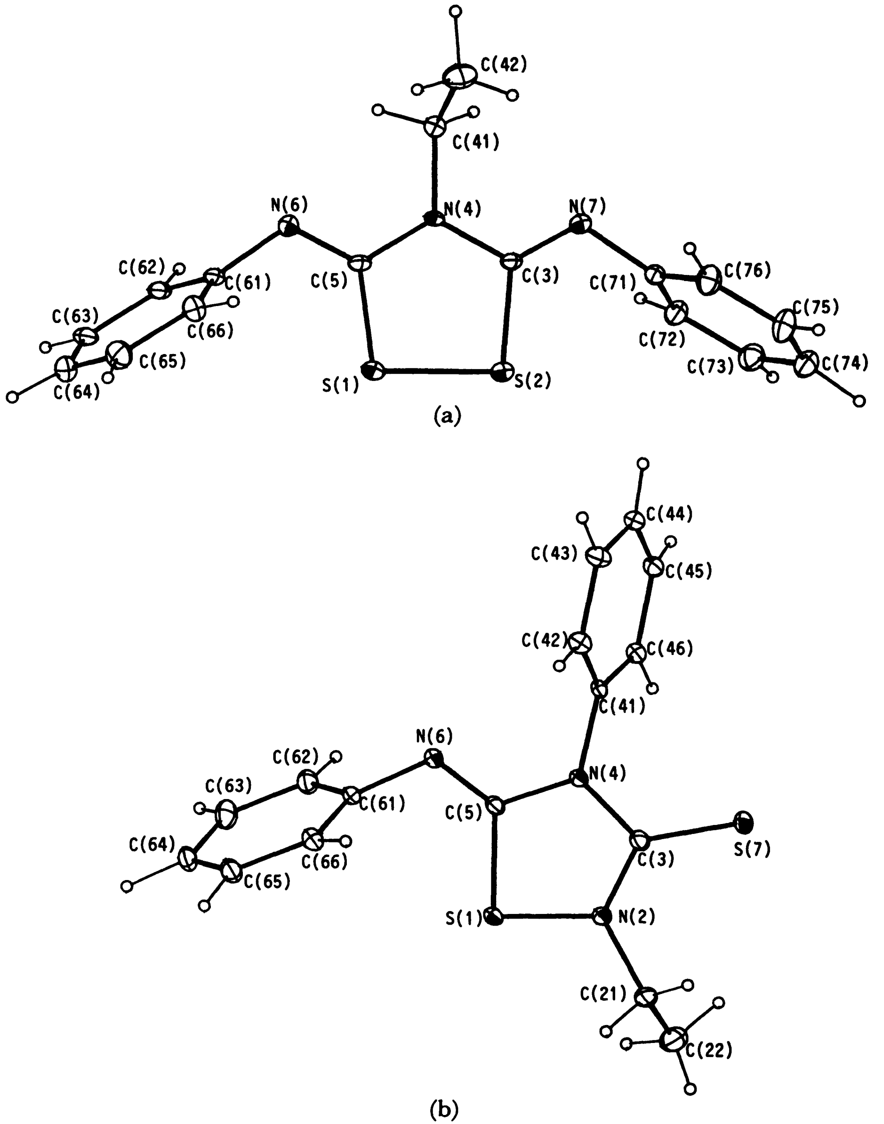
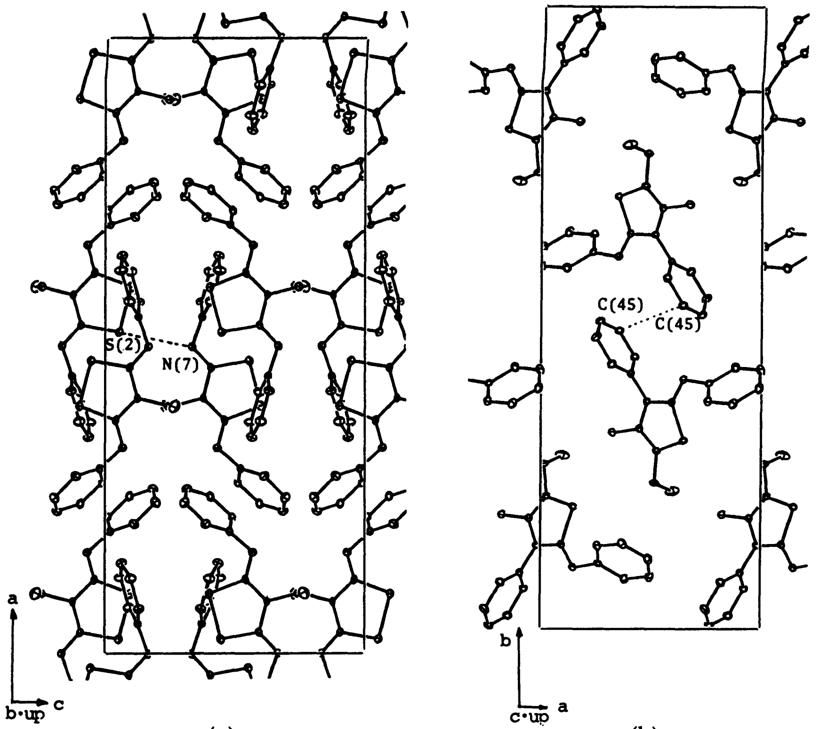


Fig. 1. Molecular structures.[9]
Non-hydrogen atoms are expressed as thermal ellipsoids with 10% probability level and hydrogen atoms as spheres with B=1.0 Å^2.
(a) **6b**, (b) **8b**.

Molecular Structure. Selected bond lengths and bond angles in the **6b** and **8b** molecules are given in Table 2.

The symmetrical **6b** molecule has an approximate two-fold axis except the ethyl group attached to the N(4) atom. 1,2,4-Dithiazolidine ring is planar, the maximum deviation of the atoms from the plane being 0.033 Å at the C(5) atom. In the ring, the S–S bond has a single bond length, 2.063(2) Å. Two C–N bonds are equal in length [1.388(5) and 1.392(5) Å], however, the S(1)–C(5) bond [1.744(4) Å] is slightly shorter than the S(2)–C(3) bond [1.775(5) Å]. Two S–S–C [96.1(2) and 95.5(2)°] and two S–C–N [114.5(3) and 113.9(4)°] bond angles are equal to each other. This structural feature is very similar to that of the dithiazolidine ring in 4-benzyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine[10] except for the S(1)–C(5) bond length, but differs from those of the 1,2,4-dithiazolidines containing four colinear sulfur atoms.[11,12] In the phenylimino groups attached to the dithiazolidine ring of **6b**, two C=N bond lengths [1.267(6) and 1.258(6) Å] and C=N–C(Ph) angles [117.4(4) and 117.5(4)°] are respectively equal. Two phenyl groups make different angles of 106.1 and 94.8° with the dithiazolidine ring.

The 1,2,4-thiadiazolidine ring of **8b** is also planar, maximum deviation of the atom from the plane being 0.030 Å at C(5). The S(1)–N(2) bond length is 1.711(3) Å, which seems to be an intermediate value among those in 1,2,4-thiadiazolidines[13–15] and 2,4-dimethyl-1,2,4-thidiazolidin-3,5-dithione.[16] This bond length is comparable with those in 2,3,3,5-tetraphenyl-1,2,5-thiadiazolidin-4-one [1.726(11) and 1.701(9) Å][17] and also to one of the S–N bonds in 2-diphenylmethylene-3,5,7,7-tetraphenyl-2,3,6,7-tetrahydro-5H-1,4,3,5-



(a) (b)

Fig. 2. Crystal structures.[9]
Non-hydrogen atoms are expressed as thermal ellipsoids with 10% probability level. Hydrogen atoms are omitted for clarity.
(a) **6b**, projected along the *b* axis, (b) **8b**, projected along the *c* axis

oxathiadiazepin-6-one [1.718(8) Å].[18] The S(1)–C(5) bond length of 1.767(3) Å is equal to those in the 1,2,4-thiadiazolidines and also equal to the S(2)–C(3) length in **6b**. Of the three C–N bonds in the ring, the C(3)–N(4) and C(5)–N(4) bonds have equal lengths [1.384(4) and 1.393(4) Å], which can be compared with the corresponding lengths in **6b**. The C(3)–N(2) [1.341(4) Å] and the C(3)=S(7) [1.654(3) Å] lengths are respectively equal to those in the 1,2,4-thiadiazolidin-3,5-dithione [1.347(5) and 1.655(4) Å]. The N(2)–S(1)–C(5) angle [90.0(2)°] is smaller than those in the 1,2,4-thiadiazolidines and the 1,2,4-thiadiazolidin-3,5-dithione. Bond angles around the N(2) and C(3) atoms are respectively equal to the corresponding angles in the 1,2,4-thiadiazolidin-3,5-dithione, and those around the N(4) and C(5) are equal to the corresponding angles in the 1,2,4-thiadiazolidines.

Crystal Structure. The packing modes of molecules in both crystals are shown in Fig. 2. In the **6b** crystal molecules are packed rather tightly (Fig. 2a), the closest intermolecular contact between non-hydrogen atoms being 3.272(4) Å(N(7)(x, y, z)···S(2)($1-x, 0.5-y, -0.5+z$)). The loose packing of molecules are observed in the **8b** crystal (Fig. 2b), the shortest contact being 3.405 Å between the C(45)(x, y, z) and C(45)($\bar{x}$, $\bar{y}$, $\bar{z}$) atoms (Table 3).

Table 3. Close Intermolecular Atomic Contact [l/Å] Less than 3.6 Å with Estimated Standard Deviation in Parentheses

6b		
N(7)···S(2)^a	3.272(4)	key: a, $1-x$, $0.5-y$, $-0.5+z$;
C(71)···S(1)^a	3.391(5)	key: b, $0.5-x$, y, $0.5+z$;
C(72)···S(1)^a	3.406(5)	key: c, x, $0.5+y$, $0.5+z$.
C(64)···N(6)^b	3.566(6)	
C(42)···N(4)^c	3.531(7)	
8b		
C(44)···C(46)^a	3.534(5)	key: a, $-x$, $-y$, $-z$;
C(45)···C(45)^a	3.405(7)	key: b, $0.5+x$, $0.5-y$, $-0.5+z$.
C(45)···C(46)^a	3.432(5)	
N(6)···C(45)^a	3.554(4)	
C(22)···S(7)^b	3.560(5)	

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