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The Structure of 4-Ethyl-5-ethylimino-2-phenyl-3-phenylimino-1,2,4-thiadiazolidine

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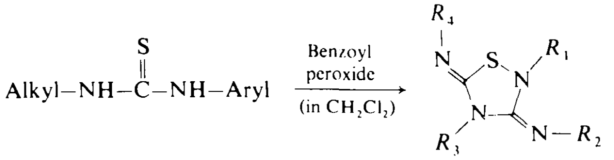
Abstract

The crystal and molecular structure of the title compound, the third isomer to be isolated from the oxidation products of 1-alkyl-3-arylthioureas, has been identified by X-ray analysis. The crystals are monoclinic, space group $P2_1/n$ with a = 12·995 (3), b = 11·522 (3), c = 12·016 (3) Å, β = 101·97 (6)°, Z = 4. The five-membered heterocyclic ring is almost planar with a maximum deviation of 0·025 Å. The two N atoms in the thiadiazolidine ring have different atomic configurations; one is sp^3 hybridized whereas the other is sp^2 hybridized. The dihedral angles made by the two phenyl groups are 35·0° relative to each other, and 72·0 and 78·1° relative to the thiadiazolidine ring.

Introduction

This work is part of the systematic structural investigations on the positional isomers produced from thiourea derivatives. Oxidation of 1-alkyl-3-arylthioureas (I) gave several isomers of 1,2,4-thiadiazolidine derivatives from which (II*a*), (II*b*) and (II*c*) could be isolated.



(I) (II)

(II*a*) $R_3 = R_4 =$ alkyl (−Et), $R_1 = R_2 =$ aryl (−Ph)

(II*b*) $R_1 = R_4 =$ alkyl (−Et), $R_2 = R_3 =$ aryl (−PhOMe)

(II*c*) $R_1 = R_3 =$ alkyl (−Me), $R_2 = R_4 =$ aryl (−Ph)

We have previously published crystallographic studies on (II*b*) (Kinoshita, Sato & Tamura, 1976) and (II*c*) (Sato, Kinoshita, Hata & Tamura, 1977). The results of these analyses may be useful in the determination of reaction mechanisms for the formation of isomers of the title compound; complete chemical studies and reaction mechanisms have already been published (Kinoshita, Sato & Tamura, 1979). The present paper deals with the structure of (II*a*).

Experimental

Colourless crystals of (II*a*) were obtained through evaporation of its ethanol solution. Preliminary diffraction photographs showed that the crystal system is monoclinic with the space group $P2_1/n$. Unit-cell dimensions and their associated standard deviations were derived from a least-squares refinement of 20 reflexions collected on a Rigaku four-circle automatic diffractometer. Crystal data are given in Table 1. Intensities were collected to a maximum 2θ of 55° with monochromatized Mo $K\alpha$ radiation, using the ω–2θ scanning technique. 2131 independent reflexions $[F \geq 2{\cdot}5\sigma(F)]$ were corrected for Lorentz and polarization factors but not for absorption.

The position of the S atom was determined from a three-dimensional Patterson synthesis, and the subsequent Fourier map allowed assignment of all the remaining heavy atoms. After refinement by the block-diagonal least-squares method, all the H atoms could be located on a difference Fourier map. Further refinements with anisotropic thermal parameters for all heavy atoms and isotropic thermal parameters for the H atoms gave a final conventional R value of 0·075. Atomic parameters are given in Table 2,* together with their estimated standard deviations.

Results and discussion

The stereo pair in Fig. 1 illustrates the geometrical aspects of the molecule and the atomic numbering. Bond lengths and angles are given in Tables 3 and 4 together with their estimated standard deviations.

The S(1)—N(2) and S(1)—C(5) bond lengths, 1·744 and 1·759 Å, are in good agreement with the expected values for $S^{II}-N_{sp^3}$ and $S^{II}-C_{sp^2}$ bonds, respectively. Of the three C—N bonds in the endocyclic thiadiazolidine ring, the C(3)—N(4) and N(4)—C(5) lengths of 1·370 and 1·376 Å are almost equal, whereas the N(2)—C(3) length, 1·399 Å, is slightly longer. Such a lengthening

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35486 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Crystal data*

Formula	$C_{18}H_{20}N_4S$	β (°)	101·97 (6)
M_r	324·5	Volume (Å^3)	1760·0
Space group	$P2_1/n$ ($Z = 4$)	D_{obs} (Mg m^{-3})	1·21
a (Å)	12·995 (3)	D_{calc} (Mg m^{-3})	1·22
b (Å)	11·522 (3)		
c (Å)	12·016 (3)		

Table 2. *Atomic parameters*

(a) Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms

	x	y	z	B_{eq}
S(1)	5178 (1)	3178 (1)	5205 (1)	3·83
N(2)	6403 (3)	2635 (4)	5876 (4)	3·17
C(3)	6448 (4)	2489 (5)	7042 (4)	3·20
N(4)	5511 (3)	2755 (4)	7334 (3)	3·37
C(5)	4702 (4)	3108 (5)	6471 (4)	3·29
C(21)	6723 (4)	1636 (5)	5289 (4)	4·17
C(22)	6371 (5)	541 (6)	5485 (5)	5·23
C(23)	6694 (6)	−396 (6)	4928 (6)	5·85
C(24)	7313 (6)	−217 (7)	4146 (6)	5·73
C(25)	7657 (5)	870 (7)	3953 (6)	4·39
C(26)	7354 (5)	1812 (6)	4536 (5)	2·95
N(30)	7252 (4)	2158 (4)	7777 (4)	3·64
C(31)	8254 (4)	2101 (5)	7490 (4)	3·62
C(32)	8759 (5)	1048 (5)	7490 (5)	3·96
C(33)	9773 (5)	1016 (6)	7290 (6)	5·17
C(34)	10276 (5)	2013 (7)	7104 (6)	5·65
C(35)	9775 (5)	3083 (7)	7124 (6)	5·48
C(36)	8760 (5)	3111 (6)	7305 (5)	4·41
C(41)	5391 (5)	2676 (6)	8518 (5)	4·41
C(42)	4954 (7)	1552 (8)	8774 (7)	7·20
N(50)	3809 (4)	3365 (5)	6625 (4)	4·40
C(51)	3039 (6)	3756 (8)	5602 (6)	6·92
C(52)	2529 (8)	4787 (8)	5761 (8)	8·71

(b) Fractional coordinates ($\times 10^3$), isotropic temperature parameters (Å^2) and bond distances (Å) for the H atoms

	x	y	z	B_{iso}	X—H
H(C22)	592 (4)	37 (5)	606 (4)	3·8 (1·3)	1·02 (5)
H(C23)	650 (5)	−122 (5)	515 (5)	5·5 (1·5)	1·04 (6)
H(C24)	753 (5)	−85 (5)	365 (5)	6·0 (1·5)	1·03 (6)
H(C25)	812 (5)	103 (5)	326 (5)	6·0 (1·6)	1·13 (5)
H(C26)	763 (4)	260 (5)	442 (5)	4·9 (1·4)	1·00 (6)
H(C32)	841 (4)	31 (5)	771 (4)	3·9 (1·2)	1·02 (5)
H(C33)	1021 (4)	22 (5)	738 (5)	5·3 (1·4)	1·07 (6)
H(C34)	1103 (4)	200 (5)	696 (5)	5·4 (1·4)	1·04 (5)
H(C35)	1019 (4)	387 (5)	704 (5)	5·6 (1·5)	1·07 (6)
H(C36)	838 (4)	390 (5)	732 (5)	5·3 (1·4)	1·03 (6)
H(C41*a*)	491 (4)	331 (5)	870 (5)	5·4 (1·4)	1·01 (5)
H(C41*b*)	616 (4)	283 (5)	912 (4)	4·0 (1·3)	1·12 (5)
H(C42*a*)	531 (5)	99 (5)	852 (5)	5·5 (1·4)	0·89 (6)
H(C42*b*)	417 (4)	147 (5)	834 (5)	5·5 (1·4)	1·04 (5)
H(C42*c*)	503 (5)	139 (5)	971 (5)	6·4 (1·6)	1·12 (6)
H(C51*a*)	239 (5)	311 (6)	538 (5)	7·0 (1·6)	1·11 (6)
H(C51*b*)	333 (5)	390 (6)	489 (5)	6·9 (1·6)	1·01 (6)
H(C52*a*)	191 (4)	438 (5)	596 (5)	5·7 (1·4)	1·01 (5)
H(C52*b*)	225 (5)	523 (6)	491 (5)	8·0 (1·8)	1·14 (7)
H(C52*c*)	292 (5)	531 (6)	651 (5)	8·0 (1·8)	1·11 (6)

may be attributed to differences in the atomic configurations of the N(2) and N(4) atoms and/or steric effects due to the bulky exocyclic phenyl and iminophenyl substituents attached to the N(2) and C(3) atoms. The sums of the three bond angles about the N(2) and N(4) atoms are 338·7 and 360·0°, and the deviations of the N atoms from the planes consisting of the three adjacent atoms are 0·411 and 0·005 Å, respectively. Thus, the atomic configuration of N(2) is sp^3 hybridized, whereas that of N(4) is sp^2 hybridized. Similar results were obtained for the corresponding N atoms of (II*b*) and (II*c*). It is of interest that the deviation of N(2) from the plane consisting of the

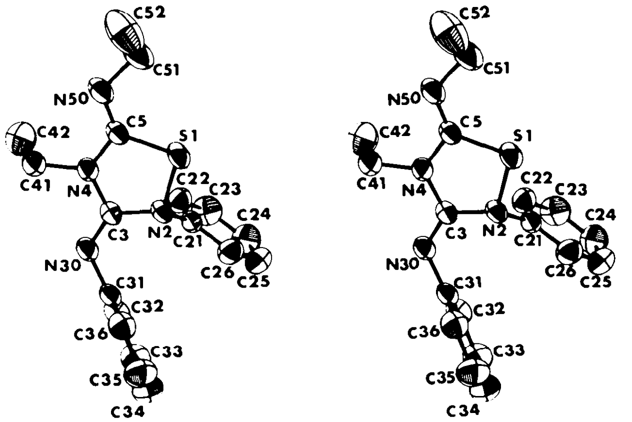


Fig. 1. Stereoscopic view of the molecule showing the atomic numbering.

Table 3. *Bond lengths* (Å)

Standard deviations are in parentheses.

S(1)—N(2)	1·744 (4)	C(24)—C(25)	1·367 (11)
S(1)—C(5)	1·759 (5)	C(25)—C(26)	1·393 (10)
N(2)—C(3)	1·399 (6)	N(30)—C(31)	1·416 (6)
N(2)—C(21)	1·456 (7)	C(31)—C(32)	1·379 (8)
C(3)—N(4)	1·370 (6)	C(31)—C(36)	1·378 (9)
C(3)—N(30)	1·279 (6)	C(32)—C(33)	1·388 (7)
N(4)—C(5)	1·376 (6)	C(33)—C(34)	1·363 (10)
N(4)—C(41)	1·465 (7)	C(34)—C(35)	1·396 (10)
C(5)—N(50)	1·247 (6)	C(35)—C(36)	1·380 (7)
C(21)—C(22)	1·379 (8)	C(41)—C(42)	1·472 (11)
C(21)—C(26)	1·355 (7)	N(50)—C(51)	1·486 (8)
C(22)—C(23)	1·381 (9)	C(51)—C(52)	1·392 (12)
C(23)—C(24)	1·374 (9)		

Table 4. *Bond angles* (°)

Standard deviations are in parentheses.

N(2)—S(1)—C(5)	92·0 (1)	C(31)—C(32)—C(33)	119·4 (5)
S(1)—N(2)—C(3)	110·5 (2)	C(32)—C(31)—C(36)	120·0 (4)
S(1)—N(2)—C(21)	112·6 (2)	N(30)—C(31)—C(36)	119·6 (5)
C(5)—N(4)—C(41)	122·1 (3)	N(30)—C(31)—C(32)	120·1 (5)
C(3)—N(4)—C(41)	120·9 (4)	C(24)—C(25)—C(26)	119·5 (5)
C(3)—N(4)—C(5)	117·0 (3)	C(23)—C(24)—C(25)	120·8 (7)
N(4)—C(3)—N(30)	122·1 (5)	C(22)—C(23)—C(24)	119·6 (6)
N(2)—C(3)—N(30)	125·9 (4)	C(21)—C(26)—C(25)	119·5 (6)
N(4)—C(5)—N(50)	123·2 (5)	C(21)—C(22)—C(23)	119·2 (4)
N(2)—C(3)—N(4)	112·0 (4)	C(22)—C(21)—C(26)	121·3 (5)
C(3)—N(2)—C(21)	115·7 (3)	N(2)—C(21)—C(22)	120·1 (3)
S(1)—C(5)—N(4)	108·3 (2)	N(2)—C(21)—C(26)	118·6 (4)
S(1)—C(5)—N(50)	128·5 (5)	C(3)—N(30)—C(31)	120·4 (4)
C(34)—C(35)—C(36)	119·2 (6)	N(4)—C(41)—C(42)	112·4 (5)
C(33)—C(34)—C(35)	120·0 (4)	C(5)—N(50)—C(51)	115·9 (4)
C(32)—C(33)—C(34)	120·8 (6)	N(50)—C(51)—C(52)	113·8 (6)
C(31)—C(36)—C(35)	120·6 (6)		

three adjacent atoms increases with increasing bulkiness of the exocyclic substituents on N(2): the N atom in (II*c*), with a methyl group, deviates by 0·292 Å; in (II*b*), with an ethyl group, it deviates by 0·364 Å; and in (II*a*), with a phenyl group, it deviates by 0·411 Å. However, for the N(4) atom such an effect cannot be clearly observed.

The rotation angle of the phenyl ring attached to N(2) of the thiadiazolidine ring is 72·0° which is significantly large, suggesting slight conjugation between the lone-pair electrons of the N(2) atom and the π electrons of the phenyl ring. The N atoms of compounds that have a small rotation angle around the N–phenyl bond are usually coplanar with the three adjacent atoms, *e.g.* *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (4·8°, 0·050 Å) (Hanson, 1965) and *N*,*N*-dimethyl-*m*-nitroaniline (8·6°, 0·034 Å) (Delugeard & Messager, 1975). In that sense, the large rotation angle in the present compound is probably due to steric hindrance between the two neighbouring phenyl rings, which are in the *cis* configuration with respect to one another. The other phenyl ring, attached to N(30) of the thiadiazolidine ring, also has a large angle of rotation of 78·1°, and the dihedral angle between the two phenyl rings is 35·0°.

The C=N bond lengths in the exocyclic imino groups are significantly different: C(3)=N(30), 1·279; C(5)=N(50), 1·247 Å. This may be because the substituents attached to the two N atoms are in somewhat different atomic configurations and the steric environments about the two C=N bonds are different. The C(3)=N(30) bond lies between the two exocyclic substituents attached to the N(2) and N(4) atoms, whereas the C(5)=N(50) bond has only one substituent. The torsion angles about the two C=N bonds indicate that the former bond is twisted to a greater degree than the latter. Such observations on the C=N bond have also been noted in the corresponding portions of the reports on (II*b*) and (II*c*). The short bond length of 1·392 Å in the ethyl group, C(51)–C(52), may be due to the effects of thermal motion.

The five-membered thiadiazolidine ring is almost planar with a maximum deviation of 0·025 Å at N(2), as shown in Table 5. Similar geometries were found in (II*b*) and (II*c*), where the corresponding deviations are 0·018 and 0·035 Å, respectively. The three molecules projected on the mean planes of each thiadiazolidine ring are shown in Fig. 2, and selected torsion angles are listed in Table 6. These results show that in spite of the

Table 5. *Deviations* (Å) *from the least-squares planes*

	Plane *A*		Plane *B*		Plane *C*
S(1)	−0·024 (3)	C(21)	−0·002 (8)	C(31)	0·003 (7)
N(2)	0·025 (6)	C(22)	0·013 (8)	C(32)	−0·006 (7)
C(3)	−0·012 (7)	C(23)	−0·017 (9)	C(33)	−0·001 (9)
N(4)	−0·013 (6)	C(24)	0·011 (9)	C(34)	0·006 (9)
C(5)	0·025 (7)	C(25)	0·000 (9)	C(35)	−0·009 (9)
C(21)	1·087 (8)	C(26)	−0·005 (8)	C(36)	0·005 (8)
N(30)*	−0·053 (6)	N(2)*	0·014 (7)	N(30)*	−0·107 (7)
C(41)*	−0·068 (8)				
N(50)*	0·040 (6)				

Angles (°) between the planes

A–*B* 72·0 (5), *A*–*C* 78·1 (5), *B*–*C* 35·0 (7)

* Not included in the calculations of the planes.

Table 6. *Selected torsion angles* (°) *of the three molecules*

	(II*a*)	(II*b*)	(II*c*)
C(5)–S(1)–N(2)–C(3)	3·9 (4)	−1·5 (6)	−4·0 (5)
S(1)–N(2)–C(3)–N(4)	−2·9 (6)	3·1 (5)	5·7 (7)
N(2)–C(3)–N(4)–C(5)	−0·2 (7)	−3·8 (7)	−5·1 (8)
C(3)–N(4)–C(5)–S(1)	3·1 (6)	2·5 (6)	2·0 (4)
N(4)–C(5)–S(1)–N(2)	−3·9 (4)	−0·6 (8)	1·2 (4)
C(21)–N(2)–C(3)–N(30)	−54·0 (8)	−44·8 (9)	−33·1 (7)
N(30)–C(3)–N(4)–C(41)	0·3 (9)	1·7 (9)	−9·6 (6)
C(41)–N(4)–C(5)–N(50)	1·3 (9)	3·1 (4)	3·2 (8)
C(3)–N(2)–C(21)–C(22)	−44·9 (7)	−57·0 (7)	–
N(2)–C(3)–N(30)–C(31)	−11·3 (9)	−8·6 (8)	−11·7 (6)
C(3)–N(30)–C(31)–C(32)	−69·3 (7)	−58·6 (5)	−54·3 (5)
C(5)–N(4)–C(41)–C(42)	86·2 (8)	89·0 (8)	–
S(1)–C(5)–N(50)–C(51)	−1·4 (10)	1·7 (9)	−5·3 (8)
C(5)–N(50)–C(51)–C(52)	130·1 (8)	113·8 (8)	118·6 (8)

Table 7. *Intermolecular contacts* (Å) *less than* 3·7 Å

S(1)···C(31)^{i}	3·690 (5)	S(1)···C(32)^{i}	3·514 (6)
S(1)···C(33)^{i}	3·556 (7)	C(5)···C(33)^{ii}	3·673 (9)
C(25)···N(50)^{iii}	3·547 (9)	N(30)···C(51)^{iv}	3·498 (8)
C(33)···N(50)^{iv}	3·665 (9)		

Symmetry code

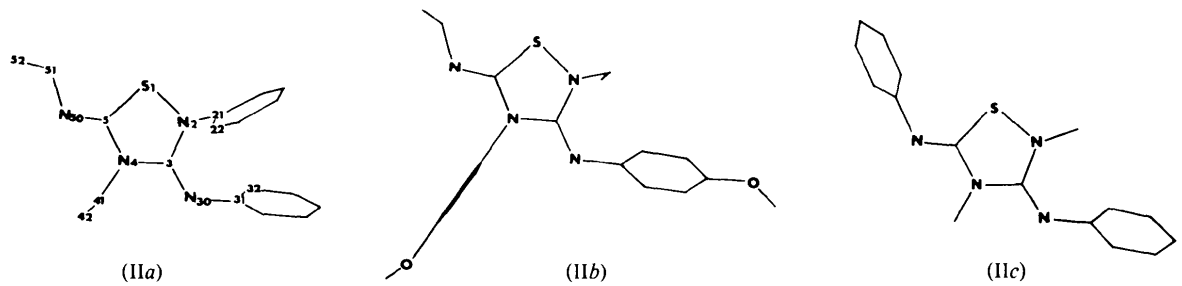
(i) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$

(ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$

(iii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$

(iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$

(v) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$



(II*a*) (II*b*) (II*c*)

Fig. 2. Projection of the three molecules on their thiadiazolidine mean planes.

different substituents in these isomers, most of the torsion angles are similar except those at the bonds related to the N(2) and N(30) atoms. The C(21)—N(2)—C(3)—N(30) and C(3)—N(30)—C(31)—C(32) torsion angles are distorted considerably by the hindrance of the substituent at N(2). Their respective values are −54·0 and −69·3°.

The short intermolecular distances, excluding those for H atoms, are given in Table 7. None of these are shorter than the sum of the van der Waals radii.

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The Structure of 3-Methyl-3-(3-methylaminopropyl)-1-phenyl-2-indolinone Hydrochloride

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Abstract

$C_{19}H_{23}N_2O^+.Cl^-$ is orthorhombic, space group *Pcab* (alternative setting of *Pbca*), with $a = 11{\cdot}105$ (1), $b = 34{\cdot}147$ (7), $c = 9{\cdot}563$ (1) Å, $Z = 8$. Final $R = 0{\cdot}078$ for 2396 observed reflections. The indoline group is nearly planar. The dihedral angle between the phenyl ring and indoline group is 49°. The N atom of the methylaminopropyl chain is protonated and forms hydrogen bonds with the Cl^- ion, the average $N\cdots Cl$ distance being 3·102 (6) Å.

Introduction

The discovery in 1957 of the therapeutic effect of imipramine in endogenous depression stimulated a search for other substances with similar properties, and several drugs which are structurally closely related to imipramine, known collectively as the tricyclic antidepressants, have become available. The spectrum of antidepressant effects of these drugs is fairly uniform, although some possess tranquillizing activity, which is useful for treating patients whose depression is complicated by agitation. But these substances have side effects which stem partly from anticholinergic and antihistaminic properties. In the past five years attempts have been made to depart from the tricyclic structures, and antidepressant activity has been claimed for iprindole, thiazesim and other compounds, but it is too early to assess their place in the therapy of depression.

Attempts to develop an antidepressant drug of novel structure which might display new pharmacological and clinical features were reported (Cañas-Rodriguez & Leeming, 1969). Medicinal chemical considerations led to the development of a series of aminoalkyl-substituted *N*-phenylindolines and -2-indolinones.

The compound was synthesized by treatment of 3-methyl-1-phenyl-2-indolinone with 3-(*N*-benzyl-*N*-methylamino)propyl chloride in the presence of sodamide and subsequent hydrogenolysis.

Experimental

Crystals were in the form of colourless prisms. Preliminary cell dimensions and space-group information were obtained from oscillation and Weissenberg photographs taken with Mo $K\alpha$ radiation. Accurate cell dimensions (Table 1) were obtained by least squares from the θ values of 50 reflections measured on a Philips PW 1100 automated four-circle diffractometer. Intensities were also collected on this instrument with graphite-monochromated Mo $K\alpha$ radiation and the ω–2θ step scanning mode. Intensities were collected over the range $2° < \theta < 30°$ to give 5199 independent reflections of which 2396 were considered as observed $[I > 2\sigma(I)]$.

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