2-Ethyl-5-ethylimino-3-*p*-methoxyphenylimino-4-*p*-methoxyphenyl-1,2,4-thiadiazolidine

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Abstract. $C_{20}H_{24}N_4O_2S$, monoclinic, $P2_1/c$, $Z = 4$, $M_r = 384 \cdot 5$, $a = 12 \cdot 24\,(1)$, $b = 15 \cdot 45\,(1)$, $c = 11 \cdot 14\,(1)$ Å, $\beta = 103 \cdot 3\,(4)°$, $D_x = 1 \cdot 23$, $D_m = 1 \cdot 22$ g cm^{-3} (by flotation). Final residual $R = 0 \cdot 085$.

Introduction. This work is part of a systematic investigation of the oxidation products of thiourea derivatives (Kinoshita & Tamura, 1969; Kinoshita, Sato & Tamura, 1971; Sato, Kinoshita, Hata &

Table 1. *Fractional coordinates and thermal parameters*

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form:
$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \times 10^{-4}]$. Fractional coordinates are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for H atoms.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S(1)	−385 (2)	5827 (2)	928 (2)	80 (2)	37 (1)	107 (3)	−4 (1)	−5 (2)	−8 (1)
N(2)	855 (6)	5415 (4)	1785 (6)	77 (6)	30 (3)	70 (7)	−10 (4)	8 (5)	−3 (4)
C(3)	1551 (8)	6055 (5)	2393 (7)	72 (7)	35 (4)	71 (8)	2 (4)	17 (6)	1 (5)
N(4)	1095 (5)	6867 (4)	2105 (6)	63 (5)	33 (3)	79 (7)	7 (4)	5 (5)	2 (4)
C(5)	31 (7)	6905 (5)	1349 (8)	83 (8)	36 (4)	98 (9)	7 (5)	29 (7)	−5 (5)
C(6)	692 (8)	4638 (5)	2477 (9)	85 (8)	36 (4)	148 (12)	−8 (5)	40 (8)	7 (6)
C(7)	250 (9)	4830 (7)	3616 (10)	143 (12)	54 (4)	155 (14)	−18 (7)	62 (11)	−3 (7)
N(8)	2507 (6)	5993 (4)	3118 (6)	89 (7)	23 (6)	114 (8)	5 (4)	10 (6)	2 (4)
C(9)	3085 (7)	5203 (6)	3289 (8)	60 (7)	45 (3)	114 (10)	−17 (5)	16 (7)	−11 (6)
C(10)	3368 (8)	4753 (7)	2359 (9)	98 (9)	65 (4)	123 (12)	22 (6)	24 (8)	28 (7)
C(11)	3976 (9)	3988 (7)	2576 (10)	107 (10)	69 (6)	149 (13)	14 (7)	36 (9)	−18 (8)
C(12)	4295 (8)	3666 (6)	3745 (10)	69 (8)	52 (6)	210 (16)	11 (6)	9 (9)	18 (8)
C(13)	4043 (8)	4100 (7)	4695 (9)	94 (9)	65 (5)	149 (13)	−1 (6)	−7 (9)	25 (7)
C(14)	3446 (8)	4864 (6)	4468 (9)	93 (9)	51 (6)	123 (11)	−3 (6)	0 (8)	−6 (6)
O(15)	4883 (7)	2893 (5)	3801 (10)	124 (8)	69 (5)	354 (17)	37 (5)	25 (10)	45 (8)
C(16)	5331 (10)	2578 (9)	4987 (17)	115 (13)	70 (5)	447 (34)	−2 (8)	−24 (17)	58 (13)
C(17)	1652 (6)	7653 (5)	2626 (7)	60 (7)	29 (8)	82 (9)	6 (4)	2 (6)	3 (4)
C(18)	1506 (7)	7950 (5)	3730 (8)	69 (7)	42 (3)	86 (9)	−5 (5)	20 (7)	−1 (5)
C(19)	2037 (7)	8692 (6)	4196 (8)	67 (7)	57 (4)	90 (9)	−5 (5)	33 (7)	−14 (6)
C(20)	2700 (7)	9130 (5)	3602 (8)	65 (7)	39 (5)	98 (9)	0 (5)	10 (6)	−7 (5)
C(21)	2850 (8)	8827 (6)	2505 (9)	113 (10)	56 (4)	117 (11)	−27 (6)	53 (9)	14 (6)
C(22)	2324 (8)	8064 (6)	2013 (8)	131 (10)	55 (5)	72 (9)	−27 (6)	34 (7)	−20 (6)
O(23)	3183 (6)	9877 (4)	4157 (6)	111 (7)	48 (5)	152 (9)	−20 (4)	28 (6)	−16 (4)
C(24)	3732 (11)	10420 (7)	3477 (12)	177 (15)	56 (3)	222 (19)	−44 (8)	45 (13)	−29 (9)
N(25)	−507 (6)	7575 (5)	1014 (8)	68 (7)	52 (6)	151 (10)	13 (5)	−4 (6)	7 (5)
C(26)	−1614 (9)	7499 (7)	214 (12)	98 (10)	58 (4)	205 (17)	7 (7)	0 (10)	1 (8)
C(27)	−1717 (10)	7847 (9)	−1007 (12)	121 (12)	104 (6)	196 (18)	−16 (9)	−12 (12)	−14 (11)

	x	y	z	B_i (Å^2)	X–H		x	y	z	B_i (Å^2)	X–H
H(C6a)	140 (5)	438 (4)	269 (6)	3·4 (1·6)	0·94 (6)	H(C18)	105 (6)	763 (5)	420 (7)	4·8 (1·9)	0·98 (8)
H(C6b)	18 (7)	445 (5)	246 (7)	6·0 (2·1)	0·68 (8)	H(C19)	193 (5)	890 (4)	499 (6)	2·8 (1·5)	0·98 (7)
H(C7a)	11 (6)	426 (4)	394 (6)	4·3 (1·7)	0·98 (7)	H(C21)	332 (6)	905 (5)	206 (6)	4·6 (1·8)	0·90 (8)
H(C7b)	−45 (6)	517 (5)	342 (7)	6·6 (2·1)	0·99 (8)	H(C22)	240 (6)	790 (4)	123 (7)	4·7 (1·8)	0·94 (8)
H(C7c)	80 (6)	519 (5)	421 (7)	5·2 (1·9)	1·00 (7)	H(C24a)	376 (6)	1097 (5)	385 (7)	5·5 (1·9)	0·94 (8)
H(C10)	313 (6)	496 (5)	154 (6)	4·2 (1·7)	0·94 (7)	H(C24b)	327 (6)	1049 (5)	255 (7)	6·2 (2·1)	1·06 (7)
H(C11)	412 (6)	374 (5)	189 (7)	5·3 (1·9)	0·90 (8)	H(C24c)	446 (7)	1015 (5)	358 (7)	6·9 (2·2)	0·97 (9)
H(C13)	431 (7)	387 (5)	561 (7)	6·7 (2·1)	1·06 (8)	H(C26a)	−219 (6)	780 (5)	59 (7)	5·7 (2·0)	1·02 (8)
H(C14)	329 (5)	521 (4)	518 (6)	3·9 (1·7)	1·01 (7)	H(C26b)	−189 (5)	691 (4)	13 (6)	3·6 (1·6)	0·96 (7)
H(C16a)	584 (7)	211 (6)	510 (8)	9·2 (2·7)	0·95 (9)	H(C27a)	−252 (6)	774 (5)	−149 (7)	5·8 (2·0)	1·02 (7)
H(C16b)	474 (6)	241 (5)	546 (7)	5·9 (2·1)	1·03 (9)	H(C27b)	−120 (6)	750 (5)	−137 (7)	4·9 (1·8)	0·98 (8)
H(C16c)	571 (6)	304 (5)	563 (7)	6·1 (2·1)	1·05 (8)	H(C27c)	−151 (6)	844 (5)	−92 (6)	4·6 (1·8)	0·95 (7)

Tamura, 1972; Kinoshita, Sato, Furukawa & Tamura, 1975; Kinoshita, Sato & Tamura, 1976). The oxidation reaction of 1-alkyl-3-arylthioureas with benzoyl peroxide in dichloromethane possibly produces several isomers involving the 1,2,4-thiadiazolidine ring; so far three isomers have been isolated. The structure determination of one of these (2,4-dimethyl-3,5-diphenylimino-1,2,4-thiadiazolidine; hereinafter designated as 2,4ME3,5PH) has already been published [Sato *et al.* (1972), Kinoshita *et al.* (1976); and an independent analysis by Christophersen, Ottersen, Seff & Treppendahl (1975)].

The crystals were obtained as colourless needles from an ethanol solution. 1639 independent reflexions [$F \geq 3\sigma(F)$] were collected on a Rigaku four-circle automatic diffractometer with Mo $K\alpha$ radiation and the ω–2θ scanning technique. Intensities were corrected for Lorentz–polarization effects but not for absorption. The structure was solved by the three-dimensional

Patterson method, and all positional parameters of non-hydrogen atoms were obtained through successive Fourier syntheses. After refinement by a block-diagonal least-squares method, all the H atoms were obtained on a difference Fourier map. With anisotropic thermal parameters assigned to all heavy atoms and isotropic ones to H atoms, block-diagonal least-squares refinement was carried out. The final conventional R value was 0.085.* The final positional and thermal parameters are given in Table 1, together with their estimated standard deviations.

Discussion. The stereo pair in Fig. 1 illustrates the geometrical aspects of the molecule and the atomic numbering. The bond lengths and angles are shown in Table 2 together with their standard deviations. The deviations from the least-squares planes through the three rings are given in Table 3 and dihedral angles in Table 4.

Table 2. Bond lengths (Å) and angles (°)

Standard deviations are in parentheses.

S(1)–N(2)	1.719 (6)	N(2)–S(1)–C(5)	92.2 (3)
S(1)–C(5)	1.773 (8)	S(1)–N(2)–C(3)	112.0 (5)
N(2)–C(3)	1.377 (9)	S(1)–N(2)–C(6)	112.7 (5)
N(2)–C(6)	1.464 (11)	C(3)–N(2)–C(6)	118.3 (6)
C(3)–N(4)	1.381 (10)	N(2)–C(3)–N(4)	111.5 (6)
C(3)–N(8)	1.263 (10)	N(2)–C(3)–N(8)	129.6 (7)
N(4)–C(5)	1.379 (10)	N(4)–C(3)–N(8)	118.9 (7)
N(4)–C(17)	1.448 (9)	C(3)–N(4)–C(5)	117.1 (6)
C(5)–N(25)	1.238 (11)	C(3)–N(4)–C(17)	122.8 (6)
C(6)–C(7)	1.519 (16)	C(5)–N(4)–C(17)	120.0 (6)
N(8)–C(9)	1.402 (10)	S(1)–C(5)–N(4)	107.2 (6)
C(9)–C(10)	1.358 (14)	S(1)–C(5)–N(25)	127.3 (6)
C(9)–C(14)	1.389 (13)	N(4)–C(5)–N(25)	125.5 (7)
C(10)–C(11)	1.387 (15)	N(2)–C(6)–C(7)	113.4 (7)
C(11)–C(12)	1.356 (15)	C(3)–N(8)–C(9)	121.1 (7)
C(12)–C(13)	1.347 (16)	N(8)–C(9)–C(10)	123.5 (8)
C(12)–O(15)	1.389 (13)	N(8)–C(9)–C(14)	119.8 (8)
C(13)–C(14)	1.381 (14)	C(10)–C(9)–C(14)	116.6 (8)
O(15)–C(16)	1.396 (20)	C(9)–C(10)–C(11)	121.6 (9)
C(17)–C(18)	1.363 (12)	C(10)–C(11)–C(12)	120.1 (10)
C(17)–C(22)	1.344 (13)	C(11)–C(12)–C(13)	120.1 (9)
C(18)–C(19)	1.361 (12)	C(11)–C(12)–O(15)	112.9 (13)
C(19)–C(20)	1.342 (13)	C(13)–C(12)–O(15)	127.0 (10)
C(20)–C(21)	1.361 (14)	C(12)–C(13)–C(14)	119.2 (9)
C(20)–O(23)	1.375 (10)	C(9)–C(14)–C(13)	122.4 (10)
C(21)–C(22)	1.393 (13)	C(12)–O(15)–C(16)	115.4 (11)
O(23)–C(24)	1.402 (16)	N(4)–C(17)–C(18)	119.8 (7)
N(25)–C(26)	1.446 (12)	N(4)–C(17)–C(22)	118.7 (8)
C(26)–C(27)	1.440 (19)	C(18)–C(17)–C(22)	121.5 (7)
		C(17)–C(18)–C(19)	118.5 (8)
		C(18)–C(19)–C(20)	121.8 (9)
		C(19)–C(20)–C(21)	119.4 (8)
		C(19)–C(20)–O(23)	116.6 (8)
		C(21)–C(20)–O(23)	124.0 (8)
		C(20)–C(21)–C(22)	119.9 (9)
		C(17)–C(22)–C(21)	118.8 (9)
		C(20)–O(23)–C(24)	118.0 (8)
		C(5)–N(25)–C(26)	118.4 (8)
		N(25)–C(26)–C(27)	114.7 (10)

Table 3. Deviations (Å) from least-squares planes

Deviations of atoms not included in the calculations are given in parentheses.

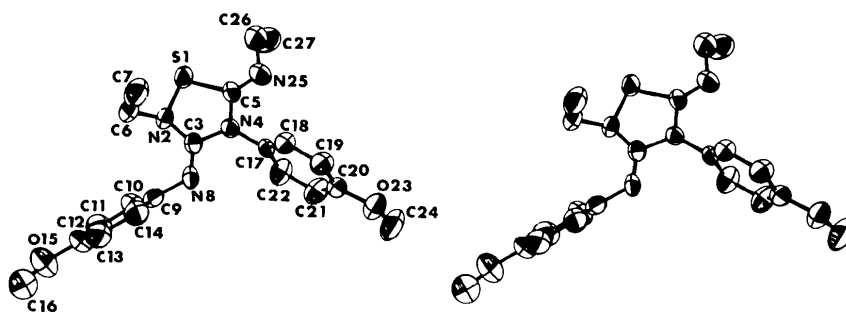|		Phenyl ring	
		A	B
S(1)	–0.003		
N(2)	0.012		
C(3)	–0.018		
N(4)	0.016		(0.014)
C(5)	–0.007		
C(6)	(–0.890)		
C(7)	(–2.354)		
N(8)	(–0.046)	(–0.035)	
C(9)	(0.130)	0.008	
C(10)		–0.001	
C(11)		–0.008	
C(12)		0.008	
C(13)		–0.001	
C(14)		–0.007	
O(15)		(0.018)	
C(16)		(–0.106)	
C(17)	(–0.015)		0.010
C(18)			–0.003
C(19)			–0.003
C(20)			0.002
C(21)			0.004
C(22)			–0.010
O(23)			(0.016)
C(24)			(0.234)
N(25)	(0.000)		
C(26)	(–0.024)		
C(27)			

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

Table 4. *Selected torsion angles* (°)

S(1)—N(2)—C(6)—C(7)	76·3	C(3)—N(4)—C(17)—C(22)	91·9
C(3)—N(2)—C(6)—C(7)	57·0	C(5)—N(4)—C(17)—C(18)	89·0
N(2)—C(3)—N(8)—C(9)	8·6	C(5)—N(4)—C(17)—C(22)	92·4
C(3)—N(8)—C(9)—C(10)	58·6	S(1)—C(5)—N(25)—C(26)	1·7
C(3)—N(4)—C(17)—C(18)	86·7	C(5)—N(25)—C(26)—C(27)	113·8

Table 5. *Intermolecular contacts less than* 3·7 Å

S(1)···S(1^i)	3·548	C(10)···O(23^{iv})	3·567
S(1)···N(2^i)	3·514	C(13)···C(13^v)	3·600
C(6)···N(25^{ii})	3·634	C(13)···C(14^v)	3·400
C(7)···C(7^{iii})	3·320	C(16)···C(20^v)	3·675
C(7)···N(25^{ii})	3·514		

Symmetry code

(i)	$-x$	$1-y$	$-z$	(iv)	x	$\frac{3}{2}-y$	$-\frac{1}{2}+z$
(ii)	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	(v)	$1-x$	$1-y$	$1-z$
(iii)	$-x$	$1-y$	$1-z$				

The five-membered thiadiazolidine ring is nearly planar with a maximum deviation of 0·018 Å at C(3). This is explained by the sp^2 hybridization in the ring system concerted with the peripheral double bond. A similar type of ring character is also found in hydantoin derivatives (Walker, Folting & Merritt, 1969; Camerman & Camerman, 1971). Significantly different atomic configurations of the two N atoms in the endocyclic thiadiazolidine ring are observed. The sums of the bond angles around N(2) and N(4) are 343·0 and 359·9° and the deviations of the N atoms from the planes consisting of the three adjacent atoms are 0·364 and 0·030 Å respectively. These data indicate that the atomic configuration of N(2) is sp^3 hybridized but that N(4) is sp^2 hybridized. S(1)—N(2) and S(1)—C(5) are 1·719 and 1·773 Å. These values are consistent with unconjugated S^{II}—N(sp^3) and S^{II}—C(sp^2) bonds. The intramolecular nonbonded distance C(6)···N(8) is 3·017 Å, whereas N(8)···C(17) and N(25)···C(17)

are 2·777 and 2·834 Å respectively. Also, the lone-pair electrons on N(8) and N(25) are directed toward C(17) in the phenyl ring. These observations indicate that some weak n–π interactions may be present in the direction normal to phenyl ring B. N(4)—C(17), 1·448 Å, almost equals the non-conjugated single-bond distance (Gropen & Skancke, 1970). In addition, the dihedral angle between the thiadiazolidine ring and the phenyl ring B is 89·7°. These values therefore imply that the overlapping of the π electrons at the N(4)—C(17) bond may to some extent be at a minimum.

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