SHORT STRUCTURAL PAPERS

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2-Phenyliminothiazolidine

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Abstract. $C_9H_{10}N_2S$, monoclinic, $P2_1/c$, $a = 7{\cdot}750$ (4), $b = 11{\cdot}870$ (5), $c = 11{\cdot}620$ (5) Å, $\beta = 123{\cdot}1$ (1)°, $Z = 4$, $D_c = 1{\cdot}32$, $D_m = 1{\cdot}28$ g cm^{-3}. The structure was solved by direct methods. An R of 0·039 was obtained for 755 observed reflexions after least-squares refinement. The molecular geometry shows that the imino form is the predominant tautomer as in 2-(2,6-dimethylphenyl)iminothiazolidine [Argay, Kálmán, Lazar, Ribár & Tóth, *Acta Cryst.* (1977), **B33**, 99–105]. Molecules related by a centre of symmetry form dimers through pairs of N(1)–H · · · N(2) hydrogen bonds.

Introduction. 1250 independent reflexions were collected on an Enraf–Nonius CAD-4 computer-controlled diffractometer with Mo $K\bar{\alpha}$ radiation ($\bar{\lambda} = 0{\cdot}7107$ Å) from a graphite monochromator. After data reduction only 901 reflexions with $F_o > \sigma(F_o)$ were accepted. The structure was solved by direct methods with a program written by Dr P. Engel (Bern) and with 240 reflexions having $E \geq 1{\cdot}20$. Isotropic and anisotropic least-squares refinement with a limited number of reflexions (560) reduced R to 0·047. Further refinement with all 901 reflexions, including isotropic refinement for H atoms, gave a final R of 0·039 for 755 observed [$F_o > 2{\cdot}0\sigma(F_o)$] and 0·049 for all 901 reflexions. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The refinement was carried out on a Varian 73 computer at the University of Novi Sad. The final coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1, the parameters of the H atoms and the X–H

Table 1. *Fractional coordinates and anisotropic thermal parameters* (× 10^4)

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are given in the form:
$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	634 (2)	859 (1)	3421 (1)	329 (2)	133 (1)	111 (1)	−153 (3)	285 (1)	−110 (2)
N(1)	−924 (4)	−265 (3)	1196 (3)	238 (5)	77 (3)	88 (2)	−111 (7)	178 (5)	−53 (5)
N(2)	1785 (4)	810 (3)	1564 (2)	214 (5)	59 (3)	66 (2)	−32 (7)	125 (5)	−21 (4)
C(1)	−1618 (6)	61 (5)	2912 (4)	435 (8)	153 (6)	201 (3)	−259 (11)	489 (6)	−167 (8)
C(2)	−2244 (6)	−558 (5)	1645 (4)	401 (9)	186 (7)	144 (3)	−279 (13)	350 (7)	−127 (9)
C(3)	605 (4)	455 (4)	1943 (3)	184 (6)	61 (3)	60 (2)	16 (7)	119 (5)	0 (5)
C(4)	3479 (4)	1529 (3)	2369 (3)	198 (6)	51 (3)	77 (2)	20 (8)	160 (5)	1 (5)
C(5)	3850 (5)	2363 (4)	1693 (3)	264 (7)	70 (4)	84 (3)	−26 (9)	177 (6)	4 (6)
C(6)	5532 (6)	3061 (4)	2400 (4)	345 (7)	67 (4)	138 (3)	−92 (9)	309 (6)	−26 (6)
C(7)	5898 (5)	2937 (4)	3797 (4)	245 (7)	88 (4)	150 (4)	−121 (10)	232 (7)	−88 (7)
C(8)	6553 (5)	2121 (4)	4472 (4)	210 (8)	99 (4)	73 (3)	−46 (11)	91 (7)	−30 (7)
C(9)	4865 (5)	1409 (4)	3774 (3)	203 (7)	69 (4)	85 (3)	14 (9)	131 (6)	6 (6)

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* Contribution No. 292.

distances in Table 2, the bond distances and angles in Fig. 1.*

Discussion. The aim of this analysis was to obtain further information concerning the tautomerism of 2-arylaminothiazolines which has been studied up to the present only by spectroscopic methods. Contrary to the conclusions deduced from these spectroscopic investigations (*e.g.* NMR: Rabinowitz, 1969; Toldy, Sohár, Faragó, Tóth & Bartalits, 1970; MS: Tamás & Toldy, 1970; UV: Toldy & Lipták, 1970; IR: Sohár & Toldy, 1973) the short C(3)–N(2) distance of 1·284 (5) Å and the large bond angle of 118·7 (4)° at the endocyclic N atom [which indicates, even better than the difference map, the location of the H atom on N(1)] show that the predominant tautomer of the title compound, which can be regarded as the basic molecule of the 2-arylaminothiazolines, is the imino form; *i.e.* the C=N double bond is exocyclic. The structure analysis of a related compound 2-(2,6-dimethylphenyl)iminothiazolidine (preceding paper) shows that the predominant tautomer is similarly the imino form.

The five-membered ring is almost planar [mean deviation from the best plane (Table 3) is 0·017 Å] with three shorter than expected bond distances: S^{II}–C(1) 1·778 *vs* 1·81, C(1)–C(2) 1·470 *vs* 1·54, C(2)–N(1) 1·423 *vs* 1·47 Å. This unusual phenomenon suggests that C(1) and C(2) gain partial sp^2 character, which cannot, however, be explained. It might perhaps be correlated with the limited number of observed reflexions. The S^{II}–C(3) distance of 1·771 Å agrees well, however, with the value expected for a S^{II}–C(sp^2) single bond (Argay, Kálmán, Nahlovski & Ribár, 1975; Párkányi, Kálmán & Nógrádi, 1975). No anomalous features were found for the phenyl ring [mean bond length 1·380 Å, mean deviation from the

Table 2. *Fractional coordinates* (×10^3), *isotropic temperature parameters* (Å^2) *and bond distances* (Å) *for the hydrogen atoms*

	x	*y*	*z*	*B*	Bond length
H(11)	–250 (9)	41 (6)	291 (6)	9·9 (20)	0·80 (7)
H(12)	–157 (9)	–47 (6)	350 (7)	11·2 (22)	0·91 (7)
H(21)	–162 (11)	–128 (9)	201 (8)	10·4 (30)	0·96 (10)
H(22)	–341 (6)	–84 (4)	108 (4)	4·2 (11)	0·84 (5)
H(N1)	–121 (5)	–49 (3)	45 (3)	1·7 (8)	0·81 (4)
H(5)	291 (4)	247 (3)	76 (3)	0·8 (7)	0·93 (3)
H(6)	581 (5)	369 (4)	194 (3)	2·8 (9)	1·01 (4)
H(7)	807 (4)	339 (3)	424 (3)	1·2 (7)	0·93 (3)
H(8)	743 (5)	200 (3)	542 (3)	2·5 (9)	0·94 (4)
H(9)	458 (4)	90 (4)	423 (3)	1·2 (7)	0·91 (3)

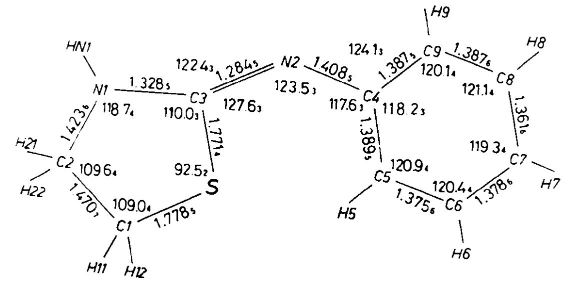

Fig. 1. Atomic numbering, bond distances and angles with their e.s.d.'s.

Table 3. *Equations of the atomic planes of the title compound*; *X*, *Y*, *and Z are in* Å *and are related to the orthogonal axes a*, *b*, *c**

P(1) for ring *A*

$$0\cdot3669X-0\cdot7717Y+0\cdot5195Z=0\cdot3025$$

P(2) for ring *B*

$$0\cdot7485X-0\cdot6432Y-0\cdot1613Z=-0\cdot6440$$

Angle formed by these least-squares planes: 46·6°

Atomic deviations from the planes

S	0·022† Å	C(4)	–0·003† Å
N(1)	0·003†	C(5)	0·002†
C(1)	–0·026†	C(6)	0·002†
C(2)	0·018†	C(7)	0·002†
C(3)	–0·018†	C(8)	–0·003†
		C(9)	0·003†
N(2)	–0·110		
H(N1)	–0·076	N(2)	0·072

† Atoms defining the planes.

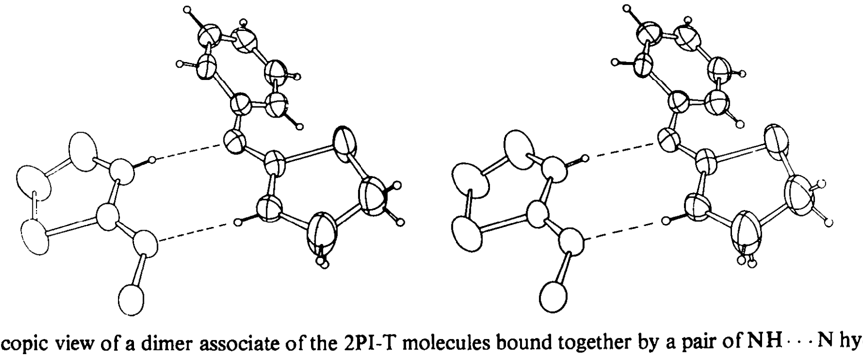

Fig. 2. Stereoscopic view of a dimer associate of the 2PI-T molecules bound together by a pair of NH···N hydrogen bonds.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31983 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

best plane (Table 3) 0·0025 Å]. The angle between the best planes of the five- and six-membered rings is only 46·6°, much less than those in 2-(2,6-dimethylphenyl)-iminothiazolidine and its N(1)-acylated (with 2-methylbenzoic acid) derivative (Argay, Kálmán, Nahlovski & Ribár, 1975) (83·0, 82·2 and 86·4° respectively). The steric hindrance of the *ortho*-methyl groups cannot permit a stronger interaction of the dimethylphenyl moieties with the p_z orbital of the N(2) atoms. Their π-electron sextet can interact with the lone pair of N(2). The π-electron cloud of the unsubstituted phenyl ring of the title compound interacts simultaneously with both the p_z orbitals and the lone pair of the N atom thus forming a slightly stronger C_ϕ—N(2) = 1·408 Å multiple bond than those in dimethylphenyl-substituted derivatives. This partly explains the relatively longest (1·284 Å) C=N double bond in the compounds discussed [1·276 (5), 1·264 (5) and 1·250 (7) Å respectively].

The C(3)—N(2)—C(4) bond angle (123·5°), as expected, is somewhat greater than in 2-(2,6-dimethylphenyl)iminothiazolidine (119·6, 118·3°).

The imino form can exist as two geometrical isomers *Z* and *E* (*syn–anti*). Nevertheless, the formation of dimers around the centres of symmetry (Fig. 2), maintained by an NH···N bond [N(1)···N(2) = 2·97, N(H1)···N(2) = 2·17 Å, ∠NH···N = 170°], permits only the *Z* isomers. Further details on this point are discussed in the preceding paper.

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(5*SR*, 6*SR*, 7*RS*)-7-Phenylacetamino-3-methyl-4,4,7-trimethoxycarbonyl-Δ2-cephem

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Abstract. Triclinic, $P\bar{1}$, $a = 14·42$ (2), $b = 8·081$ (9), $c = 12·19$ (1) Å, $\alpha = 108·87$ (8), $\beta = 121·45$ (8), $\gamma = 91·8$ (1)°; $C_{21}H_{22}N_2O_8S$, $Z = 2$, $M_r = 462·2$, $D_x = 1·382$ g cm^{-3}, m.p. 169 °C. The S atom and the phenylacetamino group are *cis* to the β-lactam ring. The N atom of the β-lactam ring is only 0·030 Å above the plane of its ligands.

Einführung. Die Kristalle wurden von Herrn Dr Kühlein (Hoechst AG) hergestellt (Kühlein & Jensen, 1974).

Die Röntgenintensitäten erfassten wir auf einem rechnergesteuerten Einkristalldiffraktometer der Fa. Siemens [Fünfwertmessung (Hoppe, 1965); Mo $K\alpha$-Strahlung; $\theta_{\max} = 28°$; 2764 Reflexe wurden vermessen, weitere 2800 infolge einer zu geringen Intensität nicht weiter berücksichtigt]. Das Strukturproblem konnte mit den Methoden der direkten Phasenbestimmung (Germain & Woolfson, 1968; Germain, Main & Woolfson, 1970) gelöst werden. Die Strukturparameterverfeinerung wurde nach der Methode der kleinsten Quadrate mit vollständiger Matrix durchgeführt. Die Verfeinerung wurde abgebrochen, als die grösste Änderung eines Parameters kleiner als 10% der jeweiligen Standardabweichung war. Keiner der 10 grössten Peaks einer Differenzfouriersynthese der Elektronendichte (0,4 bis 0,6 e Å^{-3}) konnte chemisch sinnvoll als Lage eines Wasserstoffatoms gedeutet werden. Der R-Wert ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100\%$) beträgt 7,4% (2764 Reflexe). Die Atomform-