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# The Crystal and Molecular Structure of 2-(2,6-Dimethylphenyl)iminothiazolidine, $C_{11}H_{14}N_2S$

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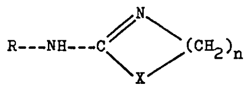
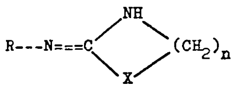
2-(2,6-Dimethylphenyl)iminothiazolidine, $C_{11}H_{14}N_2S$, is monoclinic, space group $P2_1/c$, with $a = 7{\cdot}390$, $b = 24{\cdot}004$, $c = 15{\cdot}344$ Å, $\beta = 123{\cdot}8°$, $Z = 8$. The structure was solved by direct methods and refined by least squares to $R = 0{\cdot}040$. In both symmetry-independent molecules the arylamino group is bound to the five-membered ring by a strong localized C=N double bond (1·264 and 1·276 Å) in accordance with the position of the tautomeric H atom on the endocyclic N(1). Characteristic features of the tautomerism, *i.e.* the amino and imino forms of various 2-aminothiazoline derivatives, are shown and discussed. Both $C(sp^3)$–$S^{II}$ and $C(sp^2)$–$S^{II}$ mean lengths (1·796 and 1·768 Å) indicate single bonds and agree well with the expected values. The symmetry-independent molecules are linked by two hydrogen bonds. In these dimers the molecules should assume only the isomeric form *Z* (*syn*). It is shown, however, by $^1H$ NMR measurements that in a solvent which destroys the dimer associations, equilibrium of isomers *E* and *Z* can be established.

## Introduction

The tautomerism of the cyclic amidines, which possess significant biological activities, has been extensively studied by spectroscopic methods:


(I)


(II)

(where X = C, N, O or S, while *n* is either 2 or 3).

Most of the spectroscopic data, however (Sohár & Toldy, 1973), 'in spite of including UV, IR and NMR investigations did not unambiguously distinguish the tautomers, as the different methods led to contradictions'. Jackman & Jen (1975) reported a comprehensive and critical NMR ($^1H$, $^{13}C$) study of several amidine derivatives [*e.g.* 2-arylaminopyrroles ⟷ 2-arylaminopyrrolidines (X = C, $n = 2$), cyclic guanidines (X = N, $n = 2$), 2-arylamino(imino)-1,3-thiazines (X = S, $n = 3$)] and concluded that the predominant tautomeric form is (II), where the C=N double bond is exocyclic. This conclusion is in agreement with the earlier result of Rabinowitz (1969) substantiated later by Toldy and coworkers (NMR: Toldy, Sohár, Faragó, I. Tóth & Bartalits, 1970; UV: Toldy & Lipták, 1970; MS: Tamás & Toldy, 1970; IR: Sohár & Toldy, 1973) concerning the 1,3-thiazine derivatives, but conflicts with their structure interpretation for the analogous 2-arylamino(imino)thiazoli(di)nes (X = S, $n = 2$) even though the tautomerism of thiazolines was not discussed by Jackman & Jen (1975). Rabinowitz (1969) on the basis of NMR studies, and also Toldy and coworkers using various spectroscopic methods (*cf.* references cited above) suggested that the predominant tautomer of the five-membered thiazoline rings is the amino (I) form. Even the association structures (dimers) formed by these thiazoline and analogous thiazine derivatives were believed to be different in the solid state (Sohár & Toldy, 1973).

Taking into account the criticism of Jackman & Jen (1975) upon the conflicting results and interpretations concerning the tautomerism of thiazines published by Tisler (1959), Najer, Giudicelli & Mennin (1965), Rabinowitz (1969), Toldy, Sohár, Faragó, I. Tóth & Bartalits (1970) and Sohár & Toldy (1972), it seemed worth while to throw light on the tautomerism of both 2-arylamino(imino)-1,3-thiazines and analogous thiazolines by X-ray diffraction. Application of X-ray analysis seemed to be encouraging after the solution of the problem arising in the interpretation of NMR and MS spectra concerning the acylation of 2-arylamino-(imino)-1,3-thiazines and analogous thiazolines with *ortho*-substituted benzoyl groups (Argay, Kálmán, G. Tóth & Toldy, 1972). The structure determination of 2-

phenylimino-1,3-thiazine with two molecules in the asymmetric unit (Argay, Kálmán, Ribár & Toldy, 1977) corroborated the predominance of the imino (II) tautomeric form (both exocyclic C—N distances [1·271 (6), 1·282 (6) Å] indicate strong double bonds). Similarly, the X-ray analysis of the analogous 2-phenyliminothiazolidine (hereinafter 2PI-T) (Petrović, Ribár, Argay, Kálmán & Nowacki, 1977) and that of the title compound (hereinafter 2DMPI-T) show that the predominant tautomer is the imino form, rather than the amino form, contrary to previous spectroscopic conclusions. Because of this, the structure determinations of thiazoline derivatives will first be published.

## Experimental

IR and melting point data showed that the product crystallized free from mother liquor. The lattice parameters were determined by single-crystal diffractometry. The density was measured by flotation.

*Crystal data*

$C_{11}H_{14}N_2S$, $M_r = 206{\cdot}30$, monoclinic; $a = 7{\cdot}390$ (4), $b = 24{\cdot}004$ (5), $c = 15{\cdot}344$ (5) Å; $\beta = 123{\cdot}8$ (1)°; $V = 2261{\cdot}87$ Å$^3$, $Z = 8$, $D_c = 1{\cdot}211$, $D_m = 1{\cdot}206$ g cm$^{-3}$, $F(000) = 688$; space group $P2_1/c$; $\mu$(Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}7107$ Å).

Intensities of 2688 independent reflexions were collected on an Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer with Mo $K\bar{\alpha}$ radiation from a graphite monochromator. The data were corrected for Lorentz and polarization effects, but not for absorption. After data reduction, 745 reflexions with $|F_o| = 5\sigma(F_o) < 0$ were taken as unobserved.

## Structure determination and refinement

The structure was solved with *SHELX* (Sheldrick, 1976) adapted on a CDC 3300 computer in Budapest. In this procedure 178 $E$'s $\geq 1{\cdot}1$ were used and $2^{10}$ sign permutations were expanded by the $\Sigma_2$ formula. Four $E$ maps were computed, one of which with best consistency gave the 28 non-hydrogen atoms out of the 35 highest peaks. A structure factor calculation, based on the coordinates obtained from the $E$ map, with an overall isotropic temperature factor resulted in an $R$ of 0·23 for the observed reflexions.

The structure was refined by least squares, minimizing the function $\Sigma w(|F_o| - 1/G|F_c|)^2$ with the weighting scheme $w = (5{\cdot}0 + F_o + 0{\cdot}0063F_o^2)^{-1}$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). Isotropic refinement reduced $R$ to 0·12. At this stage the positions of 14 out of 28 H atoms were located geometrically. Subsequent anisotropic refinement

Table 1. *Fractional coordinates and anisotropic thermal parameters* ($\times 10^4$)

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 | 2752 (2) | 4632 (1) | 1122 (1) | 498 (3) | 17 (0) | 81 (1) | 26 (1) | 273 (2) | 19 (1) |
| N(1) | 3254 (5) | 3644 (1) | 1866 (2) | 456 (8) | 13 (1) | 83 (2) | 22 (4) | 271 (5) | 3 (2) |
| N(2) | 2924 (5) | 4313 (1) | 2862 (2) | 333 (7) | 13 (1) | 66 (2) | 9 (4) | 197 (4) | 4 (2) |
| C(1) | 2935 (8) | 4074 (2) | 398 (3) | 578 (13) | 26 (1) | 95 (2) | 3 (7) | 351 (7) | 1 (3) |
| C(2) | 3148 (9) | 3544 (2) | 934 (4) | 670 (15) | 20 (1) | 88 (2) | 48 (7) | 321 (8) | 1 (3) |
| C(3) | 2978 (6) | 4177 (2) | 2081 (3) | 214 (8) | 13 (1) | 60 (2) | −3 (4) | 121 (5) | 1 (2) |
| C(4) | 2733 (6) | 4891 (2) | 3023 (3) | 339 (9) | 14 (1) | 58 (2) | −14 (4) | 181 (5) | −6 (2) |
| C(5) | 665 (7) | 5133 (2) | 2519 (3) | 416 (10) | 15 (1) | 88 (2) | 29 (5) | 256 (6) | 5 (2) |
| C(6) | 519 (9) | 5688 (2) | 2717 (4) | 649 (15) | 20 (1) | 123 (3) | 59 (7) | 377 (9) | 3 (3) |
| C(7) | 2340 (10) | 5985 (2) | 3388 (5) | 836 (19) | 20 (1) | 158 (4) | −39 (8) | 505 (10) | −36 (4) |
| C(8) | 4353 (9) | 5749 (3) | 3900 (4) | 603 (16) | 27 (1) | 110 (3) | −110 (7) | 315 (9) | −45 (3) |
| C(9) | 4603 (7) | 5187 (2) | 3721 (3) | 433 (11) | 24 (1) | 76 (2) | −50 (6) | 239 (7) | −18 (3) |
| C(10) | −1342 (8) | 4804 (3) | 1804 (5) | 307 (12) | 30 (1) | 127 (4) | 24 (7) | 196 (9) | 4 (4) |
| C(11) | 6771 (9) | 4929 (3) | 4239 (5) | 347 (15) | 44 (2) | 100 (4) | −39 (9) | 130 (11) | −13 (5) |
| S* | 379 (2) | 2379 (1) | 3691 (1) | 278 (2) | 21 (0) | 87 (1) | −11 (1) | 186 (1) | 26 (1) |
| N(1*) | 760 (4) | 3376 (1) | 3180 (2) | 386 (7) | 16 (1) | 113 (2) | 26 (4) | 332 (4) | 21 (2) |
| N(2*) | 3302 (5) | 2759 (2) | 3284 (3) | 292 (6) | 13 (1) | 73 (1) | 4 (3) | 207 (4) | 8 (2) |
| C(1*) | −1575 (7) | 2889 (2) | 3524 (4) | 351 (9) | 29 (1) | 128 (3) | 19 (6) | 314 (6) | 31 (3) |
| C(2*) | −753 (7) | 3446 (2) | 3484 (4) | 325 (9) | 28 (1) | 118 (3) | 25 (6) | 286 (6) | 14 (3) |
| C(3*) | 1709 (5) | 2866 (2) | 3365 (3) | 248 (8) | 16 (1) | 58 (2) | −3 (4) | 152 (5) | 11 (2) |
| C(4*) | 4335 (5) | 2229 (2) | 3605 (3) | 227 (7) | 13 (1) | 68 (3) | −11 (4) | 171 (5) | 2 (2) |
| C(5*) | 3978 (6) | 1830 (2) | 2865 (3) | 296 (8) | 17 (1) | 79 (3) | −11 (5) | 205 (5) | −4 (2) |
| C(6*) | 5149 (7) | 1335 (2) | 3222 (3) | 423 (10) | 18 (1) | 109 (3) | −14 (5) | 304 (6) | −20 (3) |
| C(7*) | 6630 (7) | 1238 (2) | 4277 (4) | 367 (11) | 19 (1) | 110 (3) | 42 (5) | 247 (7) | 19 (3) |
| C(8*) | 6977 (7) | 1635 (2) | 4996 (3) | 279 (10) | 21 (1) | 84 (3) | 11 (5) | 159 (7) | 18 (3) |
| C(9*) | 5855 (5) | 2134 (2) | 4675 (3) | 252 (8) | 17 (1) | 72 (3) | −14 (4) | 176 (5) | 6 (2) |
| C(10*) | 2417 (8) | 1944 (3) | 1712 (3) | 468 (14) | 32 (1) | 71 (3) | −9 (7) | 202 (8) | −15 (3) |
| C(11*) | 6323 (7) | 2574 (2) | 5469 (3) | 367 (11) | 25 (1) | 69 (3) | −40 (6) | 159 (7) | −18 (3) |

reduced $R$ to 0·053. The 14 missing H atoms were then located from a difference map. In the closing stage of refinement, the atomic parameters of each symmetry-independent molecule were refined separately. Refinement of the nonhydrogen atom parameters with the H atoms treated isotropically resulted in a final $R$ of 0·040 for the 1943 observed intensities (0·054 for all reflexions). The refinement was carried out on a Varian 73 computer at the University of Novi Sad. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1, the parameters for the H atoms and the X–H distances in Table 2, the bond distances and angles in Fig. 1.* A description of the structure of 2PI-T is given in the following paper.

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

| | $x$ | $y$ | $z$ | $B$ | Bond length |
|---|---|---|---|---|---|
| H(11) | 424 (7) | 412 (2) | 38 (4) | 5·0 (1·4) | 0·98 (5) |
| H(12) | 182 (9) | 408 (2) | −28 (4) | 7·0 (1·7) | 0·90 (6) |
| H(21) | 438 (10) | 335 (3) | 109 (5) | 9·6 (2·0) | 0·92 (7) |
| H(22) | 205 (10) | 328 (3) | 48 (5) | 11·4 (2·1) | 0·96 (8) |
| H(N1) | 337 (6) | 338 (2) | 228 (3) | 2·8 (1·1) | 0·86 (5) |
| H(6) | −95 (9) | 590 (2) | 235 (4) | 7·3 (1·7) | 1·04 (6) |
| H(7) | 208 (8) | 638 (2) | 344 (4) | 6·2 (1·5) | 0·99 (6) |
| H(8) | 563 (9) | 593 (3) | 438 (4) | 7·9 (1·8) | 0·92 (6) |
| H(101) | −153 (10) | 473 (3) | 111 (5) | 8·8 (1·9) | 1·00 (7) |
| H(102) | −267 (9) | 500 (3) | 150 (4) | 7·3 (1·7) | 0·95 (7) |
| H(103) | −157 (12) | 444 (4) | 198 (6) | 11·9 (2·7) | 0·96 (9) |
| H(111) | 754 (11) | 492 (3) | 491 (5) | 13·2 (2·6) | 0·85 (8) |
| H(112) | 706 (11) | 456 (3) | 418 (5) | 11·2 (2·4) | 0·93 (8) |
| H(113) | 774 (10) | 519 (3) | 424 (5) | 12·0 (2·3) | 0·95 (8) |
| H(11*) | −195 (8) | 282 (3) | 402 (4) | 7·1 (1·7) | 0·96 (6) |
| H(12*) | −292 (8) | 278 (3) | 280 (4) | 7·0 (1·6) | 1·03 (6) |
| H(21*) | 19 (8) | 359 (2) | 427 (4) | 6·5 (1·5) | 1·06 (6) |
| H(22*) | −183 (8) | 367 (3) | 305 (4) | 7·7 (1·7) | 0·89 (6) |
| H(N1*) | 142 (7) | 367 (2) | 309 (3) | 3·2 (1·1) | 0·92 (5) |
| H(6*) | 486 (8) | 107 (2) | 269 (4) | 5·9 (1·5) | 0·95 (6) |
| H(7*) | 740 (7) | 90 (2) | 452 (3) | 3·8 (1·2) | 0·93 (5) |
| H(8*) | 806 (6) | 156 (2) | 575 (3) | 2·9 (1·0) | 0·99 (5) |
| H(101*) | 112 (9) | 207 (3) | 152 (4) | 8·1 (1·8) | 0·88 (6) |
| H(102*) | 296 (10) | 202 (3) | 136 (5) | 10·5 (2·2) | 0·85 (7) |
| H(103*) | 190 (10) | 161 (3) | 134 (5) | 9·0 (2·1) | 0·92 (7) |
| H(111*) | 754 (9) | 251 (3) | 603 (4) | 8·0 (1·9) | 0·85 (7) |
| H(112*) | 638 (9) | 296 (3) | 518 (4) | 6·7 (1·7) | 1·05 (8) |
| H(113*) | 487 (9) | 262 (3) | 545 (4) | 7·4 (1·7) | 1·07 (6) |

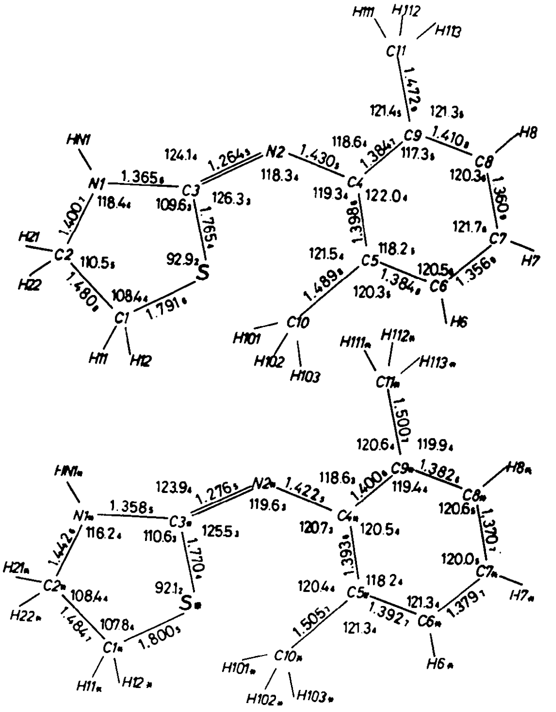


Fig. 1. Atomic numbering, bond distances and angles with their e.s.d.'s for both symmetry-independent molecules of the title compound.

Table 3. *Comparison of the bond lengths measured in various 2-amino(imino)thiazoli(di)nes* (Å)

See footnote to Table 4 for references.

| | S–C(3) | S–C(1) | C(1)–C(2) | C(2)–N(1) | N(1)–C(3) | N(1)–X | C(3)–N(2) |
|---|---|---|---|---|---|---|---|
| 2A-5PTO I[a] | 1·756 (12) | 1·841 (12) | 1·535 (16) | 1·349 (16) | 1·336 (16) | | 1·303 (16) |
| | 1·771 (12) | 1·839 (12) | 1·527 (16) | 1·357 (16) | 1·338 (16) | | 1·301 (16) |
| 2A-5PTO II[a] | 1·755 | 1·812 | 1·542 | 1·357 | 1·337 | | 1·323 |
| | 1·737 | 1·813 | 1·531 | 1·354 | 1·342 | | 1·316 |
| 2PMA-5PTO[b] | 1·753 (8) | 1·807 (8) | 1·540 (11) | 1·354 (11) | 1·312 (10) | | 1·324 (10) |
| 2PA-5PTO[c] | 1·748 (9) | 1·813 (11) | 1·531 (15) | 1·393 (13) | 1·321 (13) | | 1·334 (13) |
| | 1·753 (10) | 1·826 (11) | 1·549 (14) | 1·364 (13) | 1·316 (13) | | 1·344 (13) |
| 2PI-3M-5PTO[d] | 1·764 (8) | 1·808 (8) | 1·537 (11) | 1·357 (10) | 1·388 (10) | 1·462 (12) (Me) | 1·257 (11) |
| | 1·764 (9) | 1·814 (8) | 1·520 (11) | 1·368 (11) | 1·377 (11) | 1·472 (12) (Me) | 1·273 (11) |
| 2DMPI-3MB-T[e] | 1·772 (5) | 1·796 (7) | 1·531 (10) | 1·462 (8) | 1·392 (7) | 1·386 (7) (Ac) | 1·250 (7) |
| 2DMPI-T[f] | 1·770 (4) | 1·800 (5) | 1·484 (7) | 1·442 (6) | 1·358 (5) | 0·86 (5) (H) | 1·276 (5) |
| | 1·765 (4) | 1·791 (6) | 1·480 (8) | 1·400 (7) | 1·365 (5) | 0·92 (5) (H) | 1·264 (5) |
| 2PI-T[g] | 1·771 (4) | 1·778 (5) | 1·470 (7) | 1·423 (6) | 1·328 (5) | 0·81 (4) (H) | 1·284 (5) |

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31982 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

## Discussion

The short exocyclic C=N bonds in both symmetry-independent molecules of 2DMPI-T as well as in 2PI-T show that the predominant tautomer of these compounds, contrary to the conclusion deduced from spectroscopic evidence, is the imino (II) form. This is confirmed by the location of the H atom on N(1).

In the course of the structure analysis of 2-(2,6-dimethylphenyl)imino-3-(2-methylbenzoyl)thiazolidine (Argay, Kálmán, Nahlovski & Ribár, 1975) we had summarized partly the parameters of the five-membered rings of the quasi-analogous 2-aminothiazolin-4-one–2-iminothiazolidin-4-one systems (Mornon & Raveau, 1971; Mornon & Bally, 1972; Bally, 1973; Bally & Mornon, 1973*a*,*b*). A comparison of these parameters revealed that the strong C(3)—N(2) exocyclic bonds (mean 1·260 Å), characteristic of the imino tautomers, are accompanied by low S—C(3)—N(1) angles (mean 110·1°) and long $S^{II}$—C($sp^2$) bonds [mean S—C(3) = 1·767 Å] relative to those in the dominantly amino forms. The C(2)—N(1) lengths were not comparable, owing to the acylation.

When this analysis was extended to further bond distances (Table 3) and angles (Table 4) belonging to the five-membered rings the following became apparent: The mean values of the N(1)—C(3) and C(3)—N(2) distances for the imino (1·368 and 1·267 Å) and the amino forms (1·329 and 1·321 Å) are significantly different. The imino tautomers can be characterized by a strong exocyclic double bond and a considerably weaker endocyclic multiple bond, while the amino structures are indicated by two equally strong multiple bonds. The C—N bond pairs in the desmotropic forms of *S*-methyl-5,5-diphenyl-2-thiohydantoin (Lempert, Nyitrai, Zauer, Kálmán, Argay, Duisenberg & Sohár, 1973) show similar effects. The 'conjugated' form exhibits two equally strong C—N multiple bonds (1·328 and 1·312 Å) while the 'non-conjugated' desmotrope possesses a strong C=N double bond and a considerably longer multiple bond (1·278 and 1·396 Å) which resemble the corresponding bonds in 2-(aryl)-amino(imino)thiazoli(di)nes.

The predominance of the imino form in the structures investigated can be confirmed not only by the significant differences in the C—N bond pairs, but also by several pairs of bond angles: (*a*) the lower S—C(3)—N(1) angles mentioned above (mean 110·1° *vs.* 118·6°), (*b*) the exocyclic S—C(3)—N(2) angles (mean 127·0° *vs.* 118·7°) and (*c*) the endocyclic C(2)—N(1)—C(3) angles (mean 117·2° *vs.* 111·0°) are considerably greater in the imino structures than in the amino tautomers. The significant differences can be explained in terms of the VSEPR theory (Gillespie, 1963), *e.g.* the bare N(1) atoms due to the repulsion of the lone pair (or pairs) of electrons localized on them should have the lowest angles, as found (mean 111·0°). If this

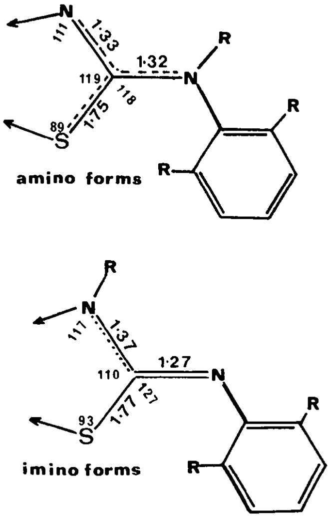

Fig. 2. Characteristically different mean bond distances and angles for the amino and imino tautomers of 2-arylamino(imino)-thiazoli(di)nes. R = H or $CH_3$ group.

Table 4. *Comparison of the bond angles measured in various 2-amino(imino)thiazoli(di)nes* (°)

| | C(3)—S—C(1) | S—C(1)—C(2) | C(1)—C(2)—N(1) | C(2)—N(1)—C(3) | N(1)—C(3)—S | S—C(3)—N(2) | N(1)—C(3)—N(2) |
|---|---|---|---|---|---|---|---|
| 2A-5PTO I[a] | 87·8 (25) | 106·2 (25) | 114·5 (25) | 111·8 (25) | 119·0 (25) | 118·3 (25) | 122·6 (25) |
| | 88·4 (25) | 105·8 (25) | 115·7 (25) | 111·5 (25) | 118·1 (25) | 118·8 (25) | 122·9 (25) |
| 2A-5PTO II[a] | 90·0 | 104·5 | 116·4 | 110·8 | 118·0 | 120·8 | 121·1 |
| | 89·7 | 104·4 | 117·1 | 109·7 | 118·9 | 121·0 | 120·1 |
| 2PMA-5PTO[b] | 89·7 (6) | 104·9 (10) | 115·5 (14) | 111·3 (14) | 118·6 (13) | 118·4 (13) | 123·1 (16) |
| 2PA-5PTO[c] | 90·1 (7) | 105·1 (13) | 115·2 (17) | 110·8 (16) | 118·5 (15) | 117·2 (15) | 124·4 (19) |
| | 89·5 (7) | 104·3 (12) | 115·7 (16) | 111·1 (16) | 119·0 (15) | 116·5 (14) | 124·4 (19) |
| 2PI-3M-5PTO[d] | 93·4 (6) | 106·0 (10) | 112·1 (13) | 118·2 (14) | 110·1 (10) | 128·1 (14) | 121·8 (15) |
| | 92·5 (6) | 106·8 (10) | 111·7 (14) | 117·9 (15) | 110·8 (12) | 128·4 (15) | 120·6 (17) |
| 2DMPI-3MB-T[e] | 92·6 (3) | 105·1 (5) | 104·6 (5) | 113·5 (5) | 109·4 (4) | 126·3 (4) | 124·2 (5) |
| 2DMPI-T[f] | 92·1 (2) | 107·8 (4) | 108·4 (4) | 116·2 (4) | 110·6 (3) | 125·5 (3) | 123·9 (4) |
| | 92·9 (2) | 108·4 (4) | 110·5 (5) | 118·4 (4) | 109·6 (3) | 126·3 (3) | 124·1 (4) |
| 2PI-T[g] | 92·5 (2) | 109·0 (4) | 109·6 (4) | 118·7 (4) | 110·0 (3) | 127·6 (3) | 122·4 (3) |

(*a*) 2-Amino-5-phenylthiazolin-4-one (Mornon & Raveau, 1971; Mornon & Bally, 1972). (*b*) 2-Phenylamino-5-phenylthiazolin-4-one (Bally, 1973). (*c*) 2-Phenylamino-5-phenylthiazolin-4-one (Bally & Mornon, 1973*a*). (*d*) 2-Phenylimino-3-methyl-5-phenylthiazolidin-4-one (Bally & Mornon, 1973*b*). (*e*) 2-(2,6-Dimethylphenyl)imino-3-(2-methylbenzoyl)thiazolidine (Argay, Kálmán, Nahlovski & Ribár, 1975). (*f*) Present work. (*g*) 2-Phenyliminothiazolidine (Petrović, Ribár, Argay, Kálmán & Nowacki, 1977).

N atom is substituted, the C(2)—N(1)—C(3) angle is increased. Even if this substituent is bound by a multiple bond, as in 2DMPI-3MB-T (1·386 Å), the C(2)—N(1)—C(3) angle is somewhat increased (113·5°). When the substituent is linked by a single bond, as for example a methyl group in 2PI-3M-5PTO, the bond angle at N(1) is as large (mean 118·1°) as in 2PI-T and 2DMPI-T (mean 117·8°). These characteristic bond parameters for both tautomeric forms are summarized in Fig. 2.

The lengths of the $S^{II}$—C($sp^3$) and $S^{II}$—C($sp^2$) bonds indicate single bonds and agree well with predicted values (Kálmán, 1973). It is somewhat peculiar that the C(1)—C(2) and N(1)—C(2) bonds are considerably shorter in both molecules than might be expected. Similarly to 2PI-T, C(2) belonging to a methylene group shows a virtual $sp^2/sp^3$ character, which cannot be explained, however. The most probable interpretation is that these molecules try to assume a coplanar conformation. This can be supported by the conformation of *N*-vinyl-2-thiopyrrolidone (Kálmán, Argay & Cser, 1976). The saturated five-membered ring, which is usually non-planar (*e.g.* 1,6-diazaspiro-[4.4]nonane-2,7-dione; Czugler, Kálmán & Kajtár, 1976), gains a mirror plane by the shortening of one of the C($sp^3$)—C($sp^3$) single bonds. In 2PI-T and 2DMPI-T both C(1)—C(2) and C(2)—N(1) single bonds are shortened by a few hundredths of an ångström in order to provide an energetically favourable quasi-coplanar conformation. As can be seen from Table 3, the sum of the lengths of C(1)—C(2) and C(2)—N(1) for each molecule is near to a mean of 2·897 Å (r.m.s. deviation 0·005 Å) except (2·99 Å) for the definitely non-planar 2DMPI-3MB-T molecule. The second greatest deviation (0·04 Å) is shown by one of the 2DMPI-T molecules (marked by an asterisk) which is markedly less planar than the other rings (Table 5). In the thiazolin-4-one derivatives listed in Table 3 there are comparatively short C(2)—N(1) multiple bonds (mean 1·35 Å) which could be accompanied by long C($sp^3$)—C($sp^2$) distances (mean 1·53 Å) according to the empirical rule observed. In 2PI-T and 2DMPI-T this condition can only be satisfied however by a proper shortening of both C(1)—C(2) and C(2)—N(1) single bonds.

The least-squares planes of the phenyl rings in the symmetry-independent 2DMPI-T molecules are nearly orthogonal (82·2 and 83·0°) to the best planes of the five-membered rings (Table 5), due to the steric hindrance of the *ortho–ortho'* methyl groups. The corresponding dihedral angle in 2PI-T is 46·6° in accordance with a somewhat stronger N(2)–phenyl interaction (Petrović, Ribár, Argay, Kálmán & Nowacki, 1977). The molecular pairs in asymmetric units are linked together by two NH···N hydrogen bonds:

| | N(1)···N(2) | H···N(2) | N(1)—H···N(2) |
|---|---|---|---|
| N···N* | 3·03 Å | 2·17 Å | 174·5° |
| N*···N | 2·95 | 2·04 | 175·5 |

forming rather twisted dimer associates (Fig. 3). The angle between the best planes of thiazolidine rings belonging to the same dimer is 45·2° (Table 5). Comparable dimer associates are formed around the centres of symmetry in 2PI-T, but both kinds of dimer differ from that which was predicted by Sohár & Toldy (1973) for 2-arylamino(imino)thiazoli(di)nes in the solid state.

Table 5. *Equations of the atomic planes of the two independent molecules of the title compound and atomic deviations*

*X*, *Y* and *Z* are in Å and related to orthogonal axes *a*, *b* and $c^*$.

Plane *P*(1) for ring *A*

$$0\cdot8430X + 0\cdot1076Y + 0\cdot5270Z = 2\cdot8532$$

Plane *P*(2) for ring *B*

$$-0\cdot5982X - 0\cdot2712Y + 0\cdot7541Z = 0\cdot0660$$

Plane *P*(1)′ for ring *A*′

$$0\cdot1297X + 0\cdot1653Y + 0\cdot9777Z = 5\cdot1153$$

Plane *P*(2)′ for ring *B*′

$$0\cdot9118X + 0\cdot4054Y - 0\cdot0648Z = 1\cdot9945$$

Dihedral angles (°) formed by the least-squares planes given above

| | | | |
|---|---|---|---|
| *P*(1)/*P*(2) | 82·2 | *P*(1)′/*P*(2)′ | 83·0 |
| *P*(1)/*P*(2)′ | 38·9 | *P*(1)′/*P*(2) | 52·1 |
| *P*(2)/*P*(2)′ | 45·2 | *P*(1)′/*P*(1) | 50·0 |

Atomic deviations (Å) from the planes

| | *P*(1) | *P*(1)′ | | *P*(2) | *P*(2)′ |
|---|---|---|---|---|---|
| S | 0·004† | 0·059 | C(4) | −0·007† | −0·005 |
| N | 0·027† | −0·091 | C(5) | 0·007† | 0·002 |
| C(1) | 0·008† | −0·116 | C(6) | 0·001† | 0·002 |
| C(2) | −0·021† | 0·139 | C(7) | −0·009† | −0·002 |
| C(3) | −0·018† | 0·009 | C(8) | 0·009† | −0·001 |
| | | | C(9) | 0·000† | 0·005 |
| N(2) | −0·053 | 0·027 | N(2) | 0·047 | 0·089 |
| H(N1) | 0·009 | −0·009 | C(10) | 0·055 | 0·052 |
| | | | C(11) | −0·027 | 0·065 |

† Atoms defining the planes

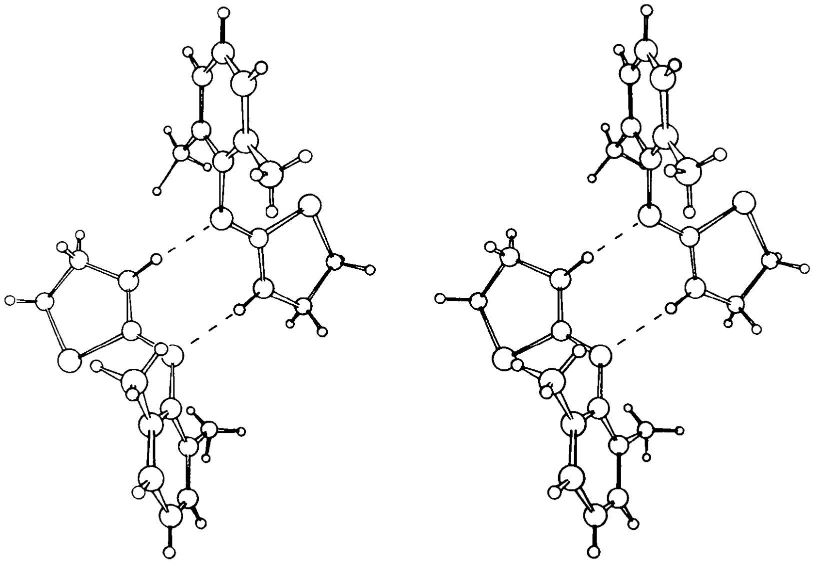

Fig. 3. Stereoscopic view of the molecules in the asymmetric unit linked together by two NH · · · N hydrogen bonds.

It is known that the imino tautomers (II) can exist as two geometrical isomers, *syn* (*Z*) and *anti* (*E*). In crystals of 2DMPI-T and 2PI-T, however, owing to the dimer formation only the *Z* isomers could be found. Even in solution only solvents with high polarity can destroy these dimer associates. After fruitless $^1$H NMR measurements in $CDCl_3$ down to −80 °C, only in a 1 : 1 mixture of $CD_3OD$ and $CDCl_3$ was it possible to show the simultaneous presence of both *Z* and *E* isomers of 2DMPI-T. The *Z*/*E* isomer ratio is 30:70 at −50 °C, while the activation free energy of interconversion of the *Z*/*E* isomers is $\Delta G^{\ddagger} \sim 12$ kcal mol$^{-1}$.

Further details of the NMR studies will be published by one of us elsewhere (G. Tóth, 1977). In any event the NMR confirmation of the *Z*/*E* isomer equilibrium of the title compound corroborates the predominance of the imino tautomeric form also in solution.

## Conclusion

The X-ray analysis of 2DMPI-T and 2PI-T and the $^1$H NMR study of 2DMPI-T performed in a proper solvent have shown unambiguously that the predominant tautomer of the 2-arylamino(imino)thiazoli(di)nes is the imino form. Thus the generalized structure interpretation for the potentially tautomeric cyclic amidine systems given by Jackman & Jen (1975) can also be extended to 2-arylamino(imino)thiazoli(di)nes. Reconsideration of the earlier interpretations inferred from NMR (Rabinowitz, 1969; Toldy, Sohár, Faragó, I. Tóth & Bartalits, 1970), UV (Toldy & Lipták, 1970), MS (Tamás & Toldy, 1970) and IR (Sohár & Toldy, 1973) spectra seems desirable in the light of the present crystallographic results accompanied by carefully performed NMR measurements. The differences encountered in various spectra of the corresponding thiazolines and thiazines might perhaps be explained by the different number of $CH_2$ groups in five- and six-membered rings.

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## References

Argay, Gy., Kálmán, A., Nahlovski, Á. & Ribár, B. (1975). *Acta Cryst.* **B31**, 1956–1961.

Argay, Gy., Kálmán, A., Ribár, B. & Toldy, L. (1977). To be published.

Argay, Gy., Kálmán, A., Tóth, G. & Toldy, L. (1972). *Tetrahedron Lett.* pp. 3179–3182.

Bally, R. (1973). *Acta Cryst.* **B29**, 2635–2637.

Bally, R. & Mornon, J. P. (1973*a*). *Acta Cryst.* **B29**, 1157–1159.

Bally, R. & Mornon, J. P. (1973*b*). *Acta Cryst.* **B29**, 1160–1162.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. Pepinsky, J. M. Robertson & J. C. Speakman. Oxford: Pergamon Press.

Czugler, M., Kálmán, A. & Kajtár, M. (1976). *Cryst. Struct. Commun.* **5**, 25–28.

Gillespie, R. J. (1963). *J. Chem. Educ.* **40**, 295–301.

*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

Jackman, L. M. & Jen, T. (1975). *J. Amer. Chem. Soc.* **97**, 2811–2818.

KÁLMÁN, A. (1973). *Proc. Yugosl. Cent. Crystallogr. (Zagreb)*, **8**, 5–15.

KÁLMÁN, A., ARGAY, GY. & CSER, F. (1976). *Acta Cryst.* B**32**, 2672–2674.

LEMPERT, K., NYITRAI, J., ZAUER, K., KÁLMÁN, A., ARGAY, GY., DUISENBERG, A. J. M. & SOHÁR, P. (1973). *Tetrahedron*, **29**, 3565–3569.

MORNON, J. P. & BALLY, R. (1972). *Acta Cryst.* B**28**, 2074–2079.

MORNON, J. P. & RAVEAU, B. (1971). *Acta Cryst.* B**27**, 95–108.

NAJER, H., GIUDICELLI, R. & MENNIN, J. (1965). *Bull. Soc. Chim. Fr.* pp. 2120–2122.

PETROVIĆ, D., RIBÁR, B., ARGAY, GY., KÁLMÁN, A. & NOWACKI, W. (1977). *Acta Cryst.* B**33**, 106–108.

RABINOWITZ, J. (1969). *Helv. Chim. Acta*, **52**, 255–261.

SHELDRICK, G. (1976). To be published.

SOHÁR, P. & TOLDY, L. (1972). *Magy. Kém. Foly.* (in Hungarian), **78**, 535–539.

SOHÁR, P. & TOLDY, L. (1973). *Acta Chim. (Budapest)*, **75**, 99–110.

TAMÁS, J. & TOLDY, L. (1970). *Tetrahedron Lett.* pp. 2173–2176.

TISLER, M. (1959). *Tetrahedron Lett.* (12), pp. 12–15.

TOLDY, L. & LIPTÁK, J. (1970). *Tetrahedron Lett.* pp. 4319–4322.

TOLDY, L., SOHÁR, P., FARAGÓ, K., TÓTH, I. & BARTALITS, L. (1970). *Tetrahedron Lett.* pp. 2167–2171.

TÓTH, G. (1977). *Acta Chim. (Budapest)*. In the press.