Acta Cryst. (1980). B**36**, 2282–2286

The Structures of 5-Methyl-1,3-thiazolidin-2-one (2,6-Dichlorophenyl)hydrazone and 1,3-Thiazolidin-2-one (2,6-Dimethylphenyl)hydrazone

By Slobodanka Stanković and Béla Ribár

Institute of Physics, Faculty of Sciences, Ilije Djuričića 4, 21000 *Novi Sad, Yugoslavia*

Alajos Kálmán and Gyula Argay

Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest, POB 17, *H*-1525, *Hungary*

Lajos Toldy and István Tóth

Institute of Drug Research, Budapest, POB 82, *H*-1325, *Hungary*

and David N. J. White

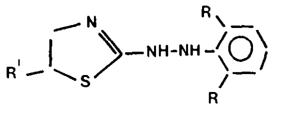
*Chemistry Department, University of Glasgow, Glasgow G*12 8*QQ, Scotland*

(*Received* 9 *October* 1979; *accepted* 10 *March* 1980)

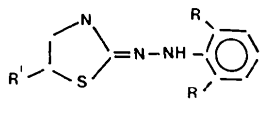
Abstract

The structures of the title compounds have been established by X-ray crystallography from diffractometer data. Crystals of $C_{10}H_{11}Cl_2N_3S$ (I) are monoclinic, space group $P2_1/n$, with cell dimensions a = 11·623 (7), b = 10·784 (5), c = 9·974 (8) Å, β = 90·89 (5)°, Z = 4. Crystals of $C_{11}H_{15}N_3S$ (II) are orthorhombic, space group *Pbca*, with cell dimensions a = 24·248 (10), b = 13·833 (5), c = 7·042 (4) Å, Z = 8. Both structures were solved by Patterson and Fourier calculations and refined by least-squares calculations to R values of 0·079 for 1798 reflections for (I) and 0·050 for 1762 reflections for (II). The difference electron density and the very short exocyclic double bonds [1·266 (7) and 1·283 (2) Å] show that the tautomeric H atom is bound to the endocyclic N(3). The characteristic features of the tautomerism of these compounds in comparison with those of the analogous 2-arylamino(imino)thiazoli(di)nes are discussed. A quantitative conformation analysis of the molecules has also been performed. The centrosymmetrically related pairs of molecules are linked together by hydrogen bonds. In these dimers the molecules should assume only the isomeric form Z (*syn*).

X-ray analysis of the tautomerism of 2-arylamino(imino)thiazoli(di)nes and analogous 1,3-thiazines (Argay, Kálmán, Lazar, Ribár & Tóth, 1977; Petrović, Ribár, Argay, Kálmán & Nowacki, 1977; Argay, Kálmán, Kapor & Ribár, 1977; Kálmán, Argay, Ribár & Toldy, 1977) has now been extended to *N*-aryl-*N'*-thiazolinylhydrazines which have been described as potential hypnotics (Toldy *et al.*, 1973). In order to reveal the influence of an additional NH moiety located between the aryl and 2-aminothiazoline groups upon the formation of the predominant tautomeric form (amino or imino) the structures of two representatives of these compounds [(I): R = Cl, R' = Me, and (II): R = Me, R' = H] have been determined.



AMINO (HYDRAZINO)



IMINO (HYDRAZONO)

The molecular conformations revealed in the crystalline state are accompanied by the results of a quantitative conformational analysis using empirical molecular force-field calculations.

Experimental

5-*Methyl*-1,3-*thiazolidin*-2-*one* (2,6-*dichlorophenyl*)-*hydrazone* (I)

Crystal data. $C_{10}H_{11}Cl_2N_3S$, M_r = 276·2, monoclinic, a = 11·623 (7), b = 10·784 (5), c = 9·974 (8) Å, β = 90·89 (5)°, V = 1250·2 Å^3, D_c = 1·47, Z = 4, D_m = 1·51 Mg m^{-3} (by flotation), $F(000)$ = 568, $\mu[\lambda(\text{Mo } K\alpha)$ = 0·7107 Å] = 0·68 mm^{-1}, space group $P2_1/n$ (from systematic absences).

Intensities of 1979 independent reflexions were collected on a Philips PW 1100 computer-controlled four-circle diffractometer equipped with a graphite

0567-7408/80/102282-05$01.00

monochromator. Cell constants were determined during the alignment procedure by least-squares refinement of the setting angles of 14 carefully centred reflexions. Data were not corrected for absorption. After data reduction, 181 reflexions with $F_o - 3{\cdot}0\sigma(F_o) < 0$ were considered unobserved.

Coordinates of two of the three heavy (S,Cl) atoms were determined by the Patterson method. A subsequent cycle of structure factor and Fourier electron density calculations revealed the positions of all the non-hydrogen atoms. At this stage R was 0·37. The structure was refined by block-diagonal least-squares calculations. The function minimized was $\varphi = \sum_{\mathbf{h}} w(|F_o| - 1/G|F_c|)^2$ with the weighting scheme $w = (4{\cdot}0 + F_o + 0{\cdot}0074F_o^2)^{-1}$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). After two cycles of refinement with anisotropic vibrational parameters ($R = 0{\cdot}12$) the positions of 10 H atoms were calculated geometrically. The tautomeric proton was located in the neighbourhood of N(3) by a difference electron density calculation. Three further cycles of anisotropic refinement of non-hydrogen atoms, with H atoms treated isotropically, gave a final residual of 0·079 for the 1798 observed reflexions ($R_{\text{tot}} = 0{\cdot}086$).

1,3-*Thiazolidin*-2-*one* (2,6-*dimethylphenyl*)*hydrazone* (II)

Crystal data. $C_{11}H_{15}N_3S$, $M_r = 221{\cdot}3$, orthorhombic, $a = 24{\cdot}248\,(10)$, $b = 13{\cdot}833\,(5)$, $c = 7{\cdot}042\,(4)$ Å, $V = 2353{\cdot}0$ Å^3, $D_c = 1{\cdot}249$ Mg m^{-3}, $Z = 8$, $F(000) = 944$, $\mu[\lambda(\text{Cu } K\bar{\alpha}) = 1{\cdot}5418$ Å$] = 0{\cdot}227$ mm^{-1}, space group *Pbca* (from systematic absences).

The intensities were again collected on the Philips diffractometer but with monochromated Cu *Kα* radiation in order to increase the accuracy of the intensities which was relatively poor in the case of (I) measured by Mo *Kα* radiation. 1762 of the total of 1769 independent reflexions with $F_o - 3{\cdot}0\sigma(F_o) > 0$ were taken as observed. No absorption correction was performed.

The fractional coordinates of the S atom were determined by the Patterson method. One cycle of structure factor and Fourier electron density calculation gave the positions of all non-hydrogen atoms. At this stage R was 0·25. Four cycles of isotropic ($R = 0{\cdot}15$) and four cycles of anisotropic refinement (using the same block-diagonal least-squares procedure described above) reduced R to 0·08. At this stage all H atoms could be located unambiguously in a difference electron density map. The tautomeric proton, similar to that in (I), was revealed in the surroundings of N(3). Three further cycles of anisotropic refinement of the non-hydrogen atoms with H atoms treated isotropically resulted in a final R of 0·05 for 1762 observed reflexions. The final weighting scheme was $w = (2{\cdot}0 + F_o + 0{\cdot}0055F_o^2)^{-1}$.

Table 1. *Positional parameters* ($\times 10^4$) *and isotropic thermal parameters of the non-hydrogen atoms for compound* (I) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{B}_{\text{iso}}$ (Å^2)
S(1)	2655 (1)	3828 (1)	2513 (1)	4·30 (5)
C(2)	3821 (4)	4423 (5)	3473 (5)	3·87 (19)
N(3)	3468 (4)	5320 (5)	4320 (5)	5·4 (2)
C(4)	2233 (5)	5463 (6)	4444 (7)	5·5 (3)
C(5)	1676 (5)	5031 (7)	3142 (7)	6·5 (3)
N(6)	4859 (4)	4083 (4)	3381 (5)	4·51 (18)
N(7)	5002 (4)	3212 (5)	2307 (5)	5·1 (2)
C(8)	6142 (4)	2764 (5)	2260 (6)	4·1 (2)
C(9)	6627 (5)	2045 (6)	3260 (6)	5·0 (2)
C(10)	7746 (6)	1609 (7)	3195 (9)	7·1 (3)
C(11)	8372 (6)	1908 (7)	2077 (10)	8·3 (4)
C(12)	7921 (6)	2577 (7)	1047 (8)	7·1 (3)
C(13)	6812 (5)	2986 (5)	1146 (6)	5·1 (2)
Cl(14)	6226 (2)	3812 (2)	−217 (2)	8·17 (9)
Cl(15)	5785 (2)	1606 (2)	4594 (2)	8·01 (9)
C(16)	480 (5)	4642 (8)	3178 (8)	6·6 (3)

Table 2. *Positional parameters* ($\times 10^4$) *and isotropic thermal parameters of the non-hydrogen atoms for compound* (II) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{B}_{\text{iso}}$ (Å^2)
S(1)	617 (1)	3377 (1)	−3821 (1)	5·13 (2)
C(2)	347 (1)	4026 (1)	−1905 (3)	3·68 (8)
N(3)	−202 (1)	4141 (2)	−2064 (3)	5·32 (8)
C(4)	−445 (1)	3889 (2)	−3830 (4)	5·24 (11)
C(5)	−53 (1)	3279 (2)	−4920 (5)	6·27 (13)
N(6)	620 (1)	4333 (1)	−458 (3)	4·34 (7)
N(7)	1200 (1)	4088 (1)	−535 (3)	4·45 (7)
C(8)	1515 (1)	4769 (1)	536 (3)	3·66 (8)
C(9)	1537 (1)	5728 (2)	−80 (4)	7·19 (9)
C(10)	1838 (1)	6384 (2)	989 (5)	5·52 (11)
C(11)	2124 (1)	6100 (2)	2610 (5)	5·54 (11)
C(12)	2113 (1)	5145 (2)	3145 (4)	4·95 (10)
C(13)	1812 (1)	4466 (2)	2138 (3)	3·99 (8)
C(14)	1823 (1)	3421 (2)	2757 (5)	5·68 (12)
C(15)	1265 (1)	6031 (2)	−1924 (5)	6·79 (14)

The scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962). All calculations were performed on a Varian 73 computer at the University of Novi Sad. The final fractional coordinates for non-hydrogen atoms for both compounds are given in Tables 1 and 2 and for H atoms in Tables 3 and 4.* The bond distances, valency angles and relevant torsion angles along with the atomic numbering are given in Figs. 1 and 2. The corresponding values obtained from the empirical molecular force-field calculations are given in square brackets.

---

* Lists of structure factors and anisotropic thermal parameters for both compounds, and Table 6 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35275 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Parameters* ($\times 10^3$; *U in* Å^2 $\times 10^3$) *of the hydrogen atoms of compound* (I)

	x	*y*	*z*	*U*
H(17)	403 (4)	570 (5)	504 (5)	2 (1)
H(18)	197 (5)	485 (6)	521 (7)	5 (2)
H(19)	209 (6)	632 (6)	480 (7)	6 (2)
H(20)	158 (8)	581 (9)	247 (10)	11 (3)
H(21)	15 (6)	447 (7)	225 (7)	7 (2)
H(22)	52 (6)	390 (6)	371 (7)	6 (2)
H(23)	7 (6)	518 (7)	368 (8)	7 (2)
H(24)	455 (6)	349 (7)	150 (8)	8 (3)
H(25)	792 (8)	115 (8)	405 (10)	11 (3)
H(26)	913 (8)	167 (8)	205 (10)	10 (3)
H(27)	831 (5)	285 (6)	26 (7)	5 (2)

Table 4. *Parameters* ($\times 10^3$; *U in* Å^2 $\times 10^3$) *of the hydrogen atoms of compound* (II)

	x	*y*	*z*	*U*
H(16)	−37 (1)	464 (2)	−129 (4)	58 (9)
H(17)	−50 (2)	455 (3)	−467 (7)	131 (17)
H(18)	−84 (2)	357 (2)	−365 (6)	84 (12)
H(19)	−16 (1)	259 (3)	−470 (6)	85 (11)
H(20)	−5 (2)	331 (3)	−626 (7)	112 (16)
H(21)	123 (1)	340 (2)	−15 (5)	59 (9)
H(22)	231 (1)	494 (2)	432 (4)	48 (8)
H(23)	236 (1)	653 (1)	334 (3)	63 (5)
H(24)	187 (1)	700 (2)	57 (5)	63 (10)
H(25)	133 (2)	552 (3)	−287 (7)	125 (16)
H(26)	135 (2)	665 (2)	−201 (5)	81 (12)
H(27)	86 (1)	610 (2)	−173 (6)	83 (12)
H(28)	204 (2)	332 (3)	389 (6)	84 (13)
H(29)	145 (1)	316 (2)	300 (5)	68 (10)
H(30)	201 (2)	301 (3)	192 (6)	106 (15)

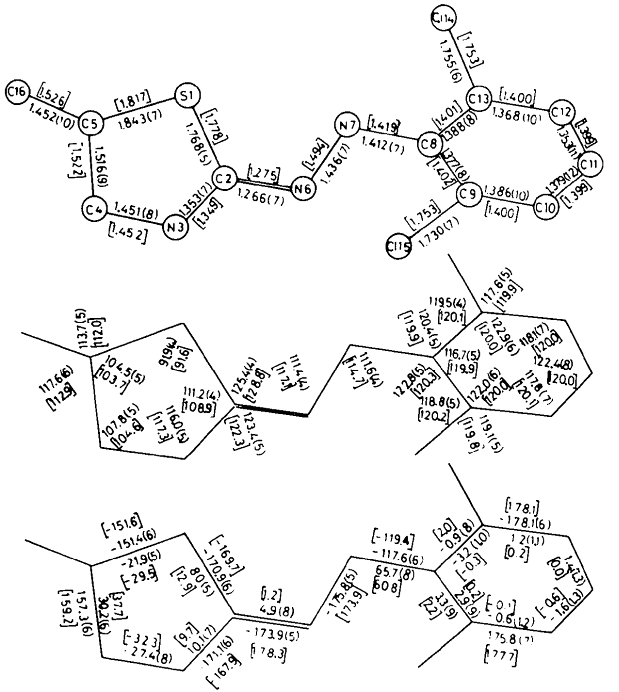


Fig. 1. (*a*) Bond distances (Å), (*b*) valency angles (°) and (*c*) torsion angles (°) with e.s.d.'s in parentheses for compound (I). The corresponding parameters obtained from the molecular force-field calculations are in square brackets.

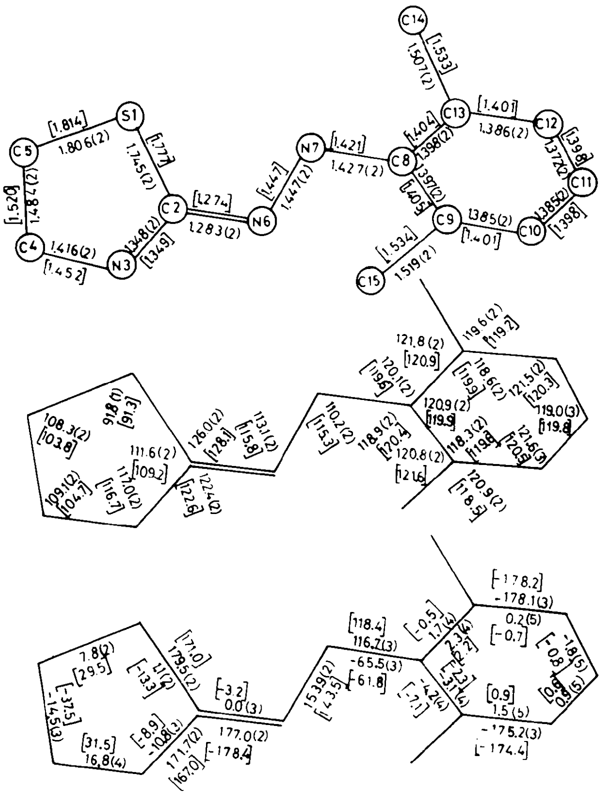


Fig. 2. (*a*) Bond distances (Å), (*b*) valency angles (°) and (*c*) torsion angles (°) with e.s.d.'s in parentheses for compound (II). The corresponding parameters obtained from the molecular force-field calculations are in square brackets.

Table 5. *The strain energy of compounds* (I) *and* (II)

	(I)	(II)
E_l	0·97 kJ mol^{-1}	1·29 kJ mol^{-1}
E_{vdW}	13·66	18·36
E_θ	18·56	16·56
E_ω	10·53	17·19
E_{opb}	0·56	0·64
E_{total}	44·28	54·04

Previous work has shown that useful results may be obtained from molecular-mechanics calculations using force fields which have not been subjected to the usual rigorous optimization routine (Tute, 1978; White & Guy, 1975; White & Sim, 1973). In the present case there is insufficient experimental data available with which to calibrate a precision force field. Nevertheless, it seems worthwhile to generate and calibrate an approximate force field for the class of compounds which is the subject of this, and future, investigations. The procedure for force-field development is described elsewhere (White & Bovill, 1977). The components of the total strain energy of compounds (I) and (II) due to bond stretching (E_l), bond-angle bending (E_θ), torsional strain (E_ω), out-of-plane bending ($E_{\rm opb}$) and repulsion (or attraction) between non-bonded atoms ($E_{\rm vdW}$) are shown in Table 5. The values for the various force constants k_l, k_θ, k_ω, and ε are listed in Table 6.*

Discussion

The short exocyclic C—N bond length in both molecules [I: 1·266 (7); II: 1·283 (2) Å] is accompanied by a significantly longer endocyclic C—N distance [I: 1·353 (7); II: 1·348 (2) Å], in agreement with the position of the tautomeric proton bound to the endocyclic N(3). These observations are supported by the values of the bond angles involving the NH—C(S)=N amidine groups for the analogous 2-arylamino(imino)thiazoli(di)nes and 1,3-thiazines (Kálmán, Argay, Ribár & Toldy, 1977). They are even more sensitive to the location of the H atom, as shown by Table 7. These observations indicate that the predominant tautomeric form of *N*-aryl-*N*′-thiazolinylhydrazines is the imino (hydrazono) form, similar to the analogous 2-arylimino-3*H*-thiazolidines, *etc.* This means that neither the additional NH group forming the hydrazono moiety nor the $R' = {\rm H}$ or Me at C(5) influences the formation of the predominant tautomeric form, at least in the crystalline state. The *R* (Cl or Me) substituents have even less effect upon the tautomerism through the extra bridging NH group, than in related compounds (Argay, Kálmán, Kapor & Ribár, 1980, and references therein). The N atoms of the hydrazono moieties are essentially single bonded while their linkage to the phenyl ring has the same weak multiple-bond character as in the corresponding 2-arylimino-3*H*-thiazolidines ($N—C_\varphi = 1{\cdot}42$ Å). The dihedral angle between the best plane of the thiourea group and the phenyl ring (Table 8) is 71·2° in (I) and 76·5° in (II).

Table 7. *Relevant bonding in* (I) *and* (II), *compared to the five corresponding inequalities obtained for the amino and imino forms of* 2-*arylamino*(*imino*)*thiazoli*-(*di*)*nes*

	(I)	(II)	Imino form	Amino form
C—N(*endo*)	1·353 (7) Å	1·348 (2) Å	1·37 Å	1·33 Å
C—N(*exo*)	1·266 (7)	1·283 (2)	1·27	1·32
S—C—N(*endo*)	111·2 (4)°	111·6 (2)°	110°	119°
S—C—N(*exo*)	125·4 (4)	126·0 (2)	127	118
C—N—C	116·0 (5)	117·0 (2)	117	111

Table 8. *Equations of the atomic planes in the form* $AX + BY + CZ = D$, *where X, Y and Z are orthogonal* (Å) *coordinates related to the axes a*, b, c*

Deviations (Å $\times 10^3$) of relevant atoms from the planes are in square brackets; values for molecule (I) precede those for molecule (II).

Plane (1): S(1), C(2), N(3), N(6)

$0{\cdot}1531X + 0{\cdot}6930Y - 0{\cdot}7045Z = 1{\cdot}5998$ (r.m.s.d. 0·0035)
$0{\cdot}1581X + 0{\cdot}8610Y - 0{\cdot}4834Z = 5{\cdot}5604$ (r.m.s.d. 0·0087)

[S(1) 2 (1), −4 (1); C(2) −6 (5), 15 (2); N(3) 2 (5), −5 (2); C(4) −214 (6), 201 (3); C(5) 272 (7), −5 (3); N(6) 2 (4), −6 (2); N(7) 133 (5), −49 (2)]

Plane (2): C(8) → C(13) phenyl rings

$0{\cdot}3331X + 0{\cdot}8356Y + 0{\cdot}4382Z = 5{\cdot}7862$ (r.m.s.d. 0·0118)
$0{\cdot}8020X - 0{\cdot}1930Y - 0{\cdot}5653Z = 1{\cdot}4770$ (r.m.s.d. 0·0113)

[C(8) 19 (5), −17 (2); C(9) −10 (6), 5 (2); C(10) −6 (8), 9 (3); C(11) 13 (8), −12 (3); C(12) −4 (7), 0 (3); C(13) −13 (6), 15 (3); N(7) 11 (5), −22 (2)]

The *conformation* of the molecules can be best described in terms of the torsion angles (Figs. 1*c* and 2*c*). The five-membered ring in (I) has a slightly deformed half-chair conformation, as shown by the asymmetry parameter $\Delta C_2[{\rm C(2)}] = 4{\cdot}2°$ (Duax, Weeks & Rohrer, 1976) and the pseudorotation phase angle of −9·3°, with the maximum amplitude of puckering $\varphi_m = 30{\cdot}9°$ [if φ_0 is assigned to the rotation about C(4)—C(5), *cf.* Altona, Geise & Romers (1968)]. The corresponding thiazolidine moiety in (II) assumes, however, an envelope form with C(4) at the flap. Its deviation from the best plane of the ring is 0·2 Å, as is also indicated by $\Delta C_s[{\rm C(4)}] = 2{\cdot}7°$ and $\Delta = -22{\cdot}5°$ with $\varphi_m = 16{\cdot}8°$ [φ_0 is assigned to N(3)—C(4)]. The molecular force-field calculations revealed a more pronounced half-chair conformation $\{\Delta C_2[{\rm C(2)}] = 3{\cdot}0°, \Delta = 0{\cdot}3°$ with $\varphi_m = 37{\cdot}7°\}$ for the ring in (I) and a half-chair conformation $\{\Delta C_2[{\rm C(2)}] = 4{\cdot}3°, \Delta = 5{\cdot}0°$ with $\varphi_m = 37{\cdot}6°$ [φ_0 is assigned to N(3)—C(4)]$\}$ for the ring in (II), instead of the envelope form found in the crystal lattice. It is worth noting that because of the generally good agreement between experiment and calculation for other parts of the molecule one might hypothesize that the thiazolidine ring shows a half-chair form in the isolated molecule, or in solution. In fact the barrier to pseudorotation is low and the thiazolidine ring may assume different forms between envelope and half-chair conformations depending on the circumstances {*e.g.* in 2-(2,6-dimethylphenyl)imino-3-mesylthiazolidine (Kálmán & Argay, 1978) where $\Delta C_2 = 8{\cdot}1°$, $\Delta C_s = 7{\cdot}4°$ in accordance with $\Delta = 17{\cdot}5°$, with $\varphi_m = 35{\cdot}3°$ [φ_0 is at C(4)—C(5)] indicating an intermediate form}. The root-mean-square discrepancies between the experimental (X-ray) and calculated (force-field) bond lengths and angles [0·007 Å and 0·5° for (I), 0·004 Å and 0·1° for (II)] are in the range of estimated standard deviations of the bond parameters, indicating that the experimental and

---

* See previous footnote.

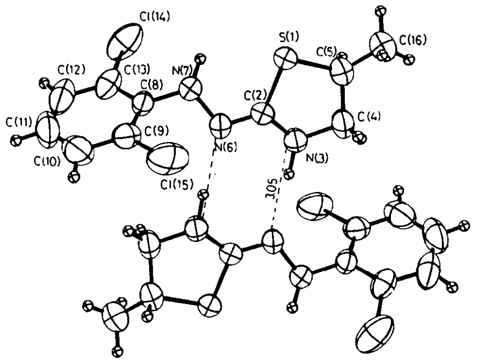


Fig. 3. A perspective view of the molecular associates linked together by a pair of hydrogen bonds (shown by dashed lines) for compound (I).

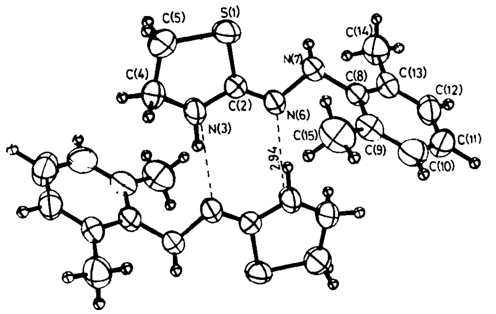


Fig. 4. A perspective view of the molecular associates linked together by a pair of hydrogen bonds (shown by dashed lines) for compound (II).

calculated structures are similar. A few significant differences in bond lengths can be regarded as the effect of thermal vibrations on the experimental values. The conformation of the hydrazono linkages between the five- and six-membered rings can be described by a synperiplanar [S(1)–C(2)–N(6)–N(7)] and an antiperiplanar [C(2)–N(6)–N(7)–C(8)] torsion angle. The latter, as shown by theoretical calculation (Fig. 2*c*), can assume an anticlinal conformation in (II). The 5-methyl group in (I) is bound to the ring pseudo-equatorially.

As we discussed earlier (Argay, Kálmán, Lazar, Ribár & Tóth, 1977), the imino (now hydrazono) tautomers can exist as the two geometrical isomers *syn* (*Z*) and *anti* (*E*), of which, due to the dimer formation (Figs. 3 and 4), only isomer *Z* has been found so far. These dimers can be characterized by the hydrogen-bond pairs:

	N···N	H···N	∠NH···N
(I) N(3)–H···N(6)|1 – *x*, 1 – *y*, 1 – *z*|	3·05 Å	2·04 Å	163·3°
(II) N(3)–H···N(6)|–*x*, 1 – *y*, –*z*|	2·94	1·97	172·7.

Conclusion

The X-ray analysis of the selected molecules has shown that they crystallize in the imino (hydrazono) form and are bound together by pairs of hydrogen bonds. These hydrogen bonds are maintained by the N atoms of the amidine groups. Thus the generalized structure interpretation of the potentially tautomeric cyclic amidine systems given by Jackman & Jen (1975) can also be extended to *N*-aryl-*N*′-thiazoli(di)nylhydrazines and thiazoli(di)none arylhydrazones.

The authors thank Dr B. Rezessy for the crystals. This study was supported by the Research Foundation of the Socialist Autonomous Province Voivodina (Yugoslavia).

References

Altona, G., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Argay, Gy., Kálmán, A., Kapor, Á. & Ribár, B. (1977). *Cryst. Struct. Commun.* **6**, 665–670.

Argay, Gy., Kálmán, A., Kapor, Á. & Ribár, B. (1980). *Acta Cryst.* B**36**, 363–368.

Argay, Gy., Kálmán, A., Lazar, D., Ribár, B. & Tóth, G. (1977). *Acta Cryst.* B**33**, 99–105.

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.

Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Top. Stereochem.* **9**, 271–383.

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

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

Kálmán, A. & Argay, Gy. (1978). *Cryst. Struct. Commun.* **7**, 659–662.

Kálmán, A., Argay, Gy., Ribár, B. & Toldy, L. (1977). *Tetrahedron Lett.* pp. 4241–4244.

Petrović, D., Ribár, B., Argay, Gy., Kálmán, A. & Nowacki, W. (1977). *Acta Cryst.* **33**, 106–108.

Toldy, L., Tóth, I., Rezessy, B., Borsy, J., Székely, J., Mankker, Cs., Polgáry, I. & Elekes, I. (1973). Hungarian Patent No. 168 777.

Tute, M. F. (1978). Private communication.

White, D. N. J. & Bovill, M. J. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1610–1623.

White, D. N. J. & Guy, M. H. P. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 43–46.

White, D. N. J. & Sim, G. A. (1973). *Tetrahedron*, **29**, 3933–3938.