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# *N*-Benzyloxycarbonyl-*N'*-(2,6-dichlorophenyl)-*N*-(5-methyl-1,3-thiazolin-2-yl)hydrazine, a Compound Containing a CO···S Single-Bond No-Bond System

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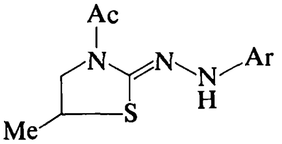
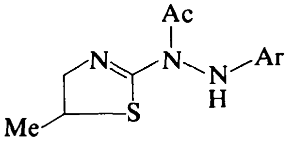
**Abstract.** $C_{18}H_{17}Cl_2N_3O_2S$, $M_r = 410{\cdot}3$, triclinic, $P\bar{1}$, $a = 12{\cdot}606\ (10)$, $b = 10{\cdot}090\ (3)$, $c = 8{\cdot}230\ (8)$ Å, $\alpha = 112{\cdot}96\ (2)$, $\beta = 95{\cdot}52\ (5)$, $\gamma = 94{\cdot}48\ (4)°$, $V = 952{\cdot}6$ Å$^3$, $D_c = 1{\cdot}43$, $Z = 2$, $D_m = 1{\cdot}47$ Mg m$^{-3}$, $F(000) = 424$. The structure was solved by the direct method and refined by block-diagonal least squares to a final $R = 0{\cdot}055$ for 2387 intensities. The acyl group is bound to the exocyclic nitrogen of the thiourea group. The compound possesses a short intramolecular C=O···S contact of 2·72 Å, with a C–S···O angle of 161°, suggesting a 'single-bond no-bond' resonance.

**Introduction.** The crystal structure determination of the title compound was carried out in order to reveal which of the possible isomers (I or II) had been yielded in a reaction acylating 5-methyl-1,3-thiazolidin-2-one (2,6-dichlorophenyl)hydrazone (Stanković, Ribár, Kálmán, Argay, Toldy, Tóth & White, 1980) with benzyloxycarbonyl chloride. The predominant tautomeric form of the parent molecule (Ac = H in I) suggested isomer (I), though a migration of the acyl group could not be excluded. Intensities were collected on a Philips PW 1100 diffractometer equipped with a graphite monochromator using Cu $K\bar{\alpha}$ radiation ($\lambda = 1{\cdot}5418$ Å). Cell constants were determined by least-squares refinement from the setting angles of 15 reflexions; 25 of the total 2412 independent reflexions with $I < 3\sigma(I)$ were taken as unobserved. No absorption correction was applied. The phases for 270 reflexions having $E \geq 1{\cdot}35$ were obtained with *SHELX* (Sheldrick, 1976). The *E* map revealed the positions of 19 of the 26 non-hydrogen atoms, which were used to phase an additional Fourier synthesis ($R = 0{\cdot}32$). Block-diagonal least-squares refinement of the positional parameters, anisotropic thermal parameters for the non-hydrogen atoms and isotropic for the H atoms gave a final *R* of 0·055 for the observed reflexions ($R_{\text{total}} = 0{\cdot}056$). The final weighting scheme was $w = (6{\cdot}0 + F_o + 0{\cdot}0017F_o^2)^{-1}$. The H atom positions, except those of H(22)–H(26), were located in a difference electron density map. The coordinates of H(22)–H(26) were generated from assumed geometries. Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962). The final fractional coordinates for the non-hydrogen atoms are given in Table 1 and for the H atoms in Table 2.†



(I)



(II)

Ac = $C_6H_5CH_2OCO$ Ar = $C_6H_3Cl_2$

**Discussion.** The structure depicted in formula (II) has been established in this structure analysis. Bond lengths, valency and relevant torsion angles together with the numbering scheme are given in Fig. 1. The short bond distance of 1·271 (5) Å between C(2) and N(3) is evidence for an almost completely localized double-bond in the thiazoline ring. As shown also by the analogous 2-[(2,6-dichlorophenyl)mesylamino]- and 2-[(2,6-dimethylphenyl)methylamino]-1,3-thiazines [$C{=}N_{\text{endo}}$ distances are 1·281 (8) and 1·254 (8) Å, respectively] (Kálmán, Argay & Vassányi, 1977; Argay, Kálmán, Kapor & Ribár, 1980), the N-acylated or alkylated 2-arylamino moieties cannot enter significantly into conjugation with the endocyclic C(2)=N(3) double bonds of the heterocyclic rings. It is worth noting that significant delocalization of such an endocyclic C=N double bond belonging to the thiourea group of a thiazoline ring has been found only in the

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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 35021 (16 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. *Positional parameters* ($\times 10^4$) *and* $B_{eq}$ ($Å^2$) *values of non-hydrogen atoms with their e.s.d.'s in parentheses*

|  | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| S(1) | 3909 (1) | 1426 (1) | 642 (2) | 5·2 (1) |
| C(2) | 4035 (3) | 3237 (4) | 2235 (5) | 4·3 (1) |
| N(3) | 4761 (3) | 4152 (3) | 2163 (5) | 4·8 (1) |
| C(4) | 5391 (4) | 3448 (5) | 742 (6) | 5·6 (2) |
| C(5) | 4738 (4) | 2074 (5) | −663 (7) | 5·9 (2) |
| N(6) | 3328 (3) | 3674 (3) | 3502 (4) | 4·6 (1) |
| N(7) | 3270 (3) | 5167 (3) | 4396 (4) | 4·6 (1) |
| C(8) | 2887 (3) | 5907 (4) | 3365 (5) | 4·6 (1) |
| C(9) | 3297 (4) | 7374 (4) | 3919 (6) | 5·2 (1) |
| C(10) | 2936 (4) | 8252 (4) | 3115 (6) | 6·8 (1) |
| C(11) | 2141 (5) | 7686 (5) | 1702 (7) | 7·9 (2) |
| C(12) | 1685 (4) | 6245 (5) | 1091 (6) | 6·8 (2) |
| C(13) | 2056 (4) | 5382 (4) | 1962 (6) | 5·2 (2) |
| Cl(14) | 1362 (1) | 3648 (1) | 1243 (2) | 6·7 (1) |
| Cl(15) | 4287 (1) | 8156 (1) | 5759 (2) | 6·0 (1) |
| C(16) | 4030 (5) | 2386 (6) | −2039 (7) | 7·8 (3) |
| C(17) | 2708 (4) | 2708 (4) | 3956 (6) | 5·5 (2) |
| O(18) | 2726 (3) | 1418 (3) | 3236 (5) | 7·2 (1) |
| O(19) | 2145 (3) | 3370 (3) | 5240 (4) | 6·1 (1) |
| C(20) | 1391 (4) | 2406 (6) | 5691 (7) | 7·7 (2) |
| C(21) | 351 (4) | 2026 (5) | 4459 (6) | 5·6 (2) |
| C(22) | −328 (4) | 3059 (5) | 4630 (7) | 6·7 (2) |
| C(23) | −1277 (5) | 2770 (7) | 3511 (8) | 8·7 (3) |
| C(24) | −1574 (5) | 1454 (7) | 2270 (9) | 8·7 (3) |
| C(25) | −955 (6) | 378 (7) | 2021 (9) | 8·5 (3) |
| C(26) | 49 (5) | 656 (5) | 3166 (8) | 7·7 (3) |

Table 2. *Positional parameters* ($\times 10^3$) *and isotropic thermal parameters* ($Å^2$) *of the* H *atoms*

|  | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| H(41) | 609 (4) | 326 (5) | 138 (7) | 4·4 (11) |
| H(42) | 568 (5) | 407 (6) | 18 (8) | 5·2 (12) |
| H(5) | 527 (4) | 131 (6) | −131 (7) | 5·8 (14) |
| H(7) | 397 (5) | 557 (6) | 515 (7) | 5·1 (12) |
| H(10) | 330 (4) | 933 (6) | 357 (7) | 7·0 (17) |
| H(11) | 184 (4) | 832 (6) | 97 (7) | 6·8 (16) |
| H(12) | 109 (4) | 577 (5) | 8 (7) | 4·3 (11) |
| H(161) | 345 (4) | 317 (5) | −137 (6) | 3·3 (9) |
| H(162) | 449 (5) | 262 (6) | −276 (8) | 8·0 (17) |
| H(163) | 359 (5) | 150 (7) | −282 (8) | 8·3 (16) |
| H(201) | 177 (5) | 144 (6) | 559 (8) | 9·0 (18) |
| H(202) | 112 (5) | 303 (6) | 691 (8) | 8·4 (17) |
| H(22) | −8 (4) | 406 (5) | 567 (6) | 6·6 (14) |
| H(23) | −177 (4) | 369 (5) | 359 (6) | 9·9 (17) |
| H(24) | −236 (4) | 135 (5) | 144 (6) | 10·7 (18) |
| H(25) | −110 (4) | −59 (5) | 109 (6) | 11·6 (20) |
| H(26) | 55 (4) | −8 (5) | 303 (6) | 6·2 (14) |

presence of an electron-withdrawing moiety such as a C=O group, *e.g.* in 2-amino-4,3-thiazolin-4-ones (*cf.* Table 3 of Argay, Kálmán, Lazar, Ribár & Tóth, 1977).

The bond angles around the central C(2) atom and at N(3) of the coplanar amidine moiety are in accordance with the predicted values for the amino forms of 2-arylamino(imino)-1,3-thiazoli(di)nes and analogous 1,3-thiazines (Kálmán, Argay, Ribár & Toldy, 1977, and references therein). The $S^{II}—C(sp^2)$

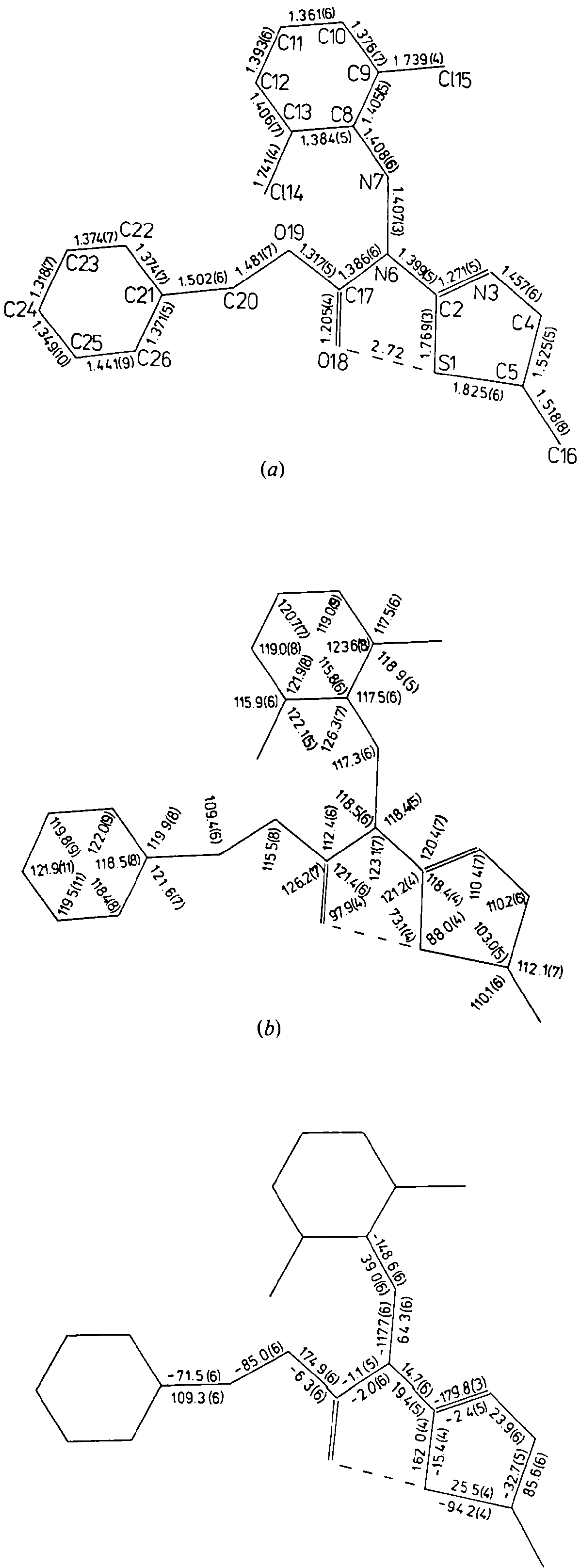

Fig. 1. (*a*) Bond distances (Å), (*b*) valency angles (°) and (*c*) relevant torsion angles (°), with their e.s.d.'s in parentheses.

and $S^{II}$—$C(sp^3)$ distances, 1·769 (3) and 1·825 (3) Å, agree well with the corresponding data found in the literature (*cf.* Argay, Kálmán, Lazar, Ribár & Tóth, 1977, and references therein).

The thiazoline ring has a distorted envelope conformation with C(5) at the flap (the pseudorotation phase angle is 171° with a maximum puckering amplitude $\varphi_m$ = 33°, if $\varphi_o$ is assigned to the rotation about C(2)—N(3), *cf.* Altona, Geise & Romers, 1968). As revealed by the torsion angles C(2)—S(1)—C(5)—C(16) = −94·2 (4) and N(3)—C(4)—C(5)—C(16) = 85·6 (6)°, the methyl group is axially bound to C(5) (Fig. 2). The entering acyl group has considerably altered the conformation of the parent molecule, as shown especially by the torsion angles:

| | Parent molecule | Title compound |
|---|---|---|
| S(1)–C(2)–N(6)–N(7) | 4·9 (7)° synperiplanar | −162·7 (4)° antiperiplanar |
| C(2)–N(6)–N(7)–C(8) | −175·8 (4) antiperiplanar | 64·3 (6) synclinal. |

This rearrangement enables the C=O group to assume a favourable position in front of the S atom, thus forming a 'single-bond no-bond' interaction characterized by a short intramolecular S···O approach of 2·72 Å and a C—S···O angle of 161·0°. According to Hamilton & La Placa (1964), the near linearity of the *X*—S···O configuration is a favourable situation for sulphur *p*- and *d*-orbital participation. The existence of such a close S···O approach together with the quasi-linear C(5)—S(1)···O(18) arrangement involves a five-atom conjugated system [S(1), C(2), N(6), C(17) and O(18)]. The best plane of this additional hetero ring, given by $0{\cdot}7874x - 0{\cdot}1531y + 0{\cdot}5972z - 3{\cdot}5072 = 0$ (where *x*,*y*,*z* are coordinates referred to orthogonal axes **a***, **c** × **a***, **c**) makes a dihedral angle of 14·5° with that of the thiazoline ring ($0{\cdot}6240x - 0{\cdot}3015y + 0{\cdot}7209z - 2{\cdot}4634 = 0$) computed only for the four coplanar atoms ($\Delta_{\rm mean}$ = 0·009 Å). The fifth atom, C(5), which is −0·534 (4) Å out of this best plane (*P*), is opposed on the other side by O(18) at a distance of 0·666 (3) Å. As shown by the dihedral angle of −177·9 (5)°, formed by the planes through C(2)—S(1)—C(5) and C(2)—S(1)—O(18), this arrangement with S in the centre is an optimal *X*—S···O configuration provided by the puckering of the thiazoline ring and the torsion angles about the C(2)—N(6) and N(6)—C(17) bonds. Accordingly, it is apparent that the observed 'single-bond no-bond' resonance (Lozac'h, 1971) is the dominant factor determining the conformation of the molecule which, as shown above, differs significantly from that of the parent compound, though the S···O distance is nearer to the sum of the van der Waals radii (3·25–3·35 Å) than those found in 3-benzoylimino-4-methylperhydro-1,2,4-oxathiazine (2·26 Å; Sólyom, Sohár, Toldy, Kálmán & Párkányi, 1977) and in other molecules (2·03–2·55 Å) possessing an *X*—S···O configuration with an angle about 173°, where *X* = S, O or N (Pinel, Mollier, Llaguno & Paul, 1971; Gieren & Dederer, 1978, and references therein). Our S···O contact distance of 2·72 Å with C—S···O = 161·0° fits, however, into the ranges 2·64–2·78 Å and 156–164° observed in various compounds in which *X* is also a C atom (Kapecki, Baldwin & Paul, 1968; Mellor & Nyburg, 1971; Cohen-Addad & Viallet, 1978; Kálmán & Párkányi, 1980).

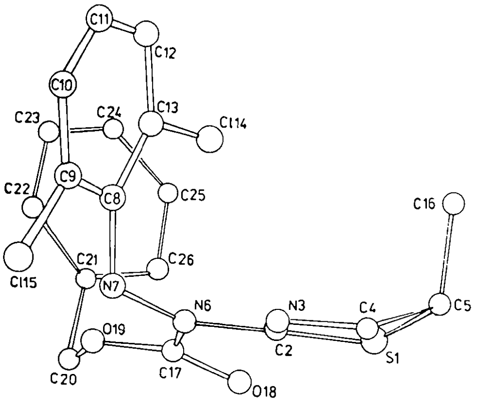

Fig. 2. A perspective view of the molecule with the atomic numbering. The H atoms have been omitted for clarity.

The phenyl rings are twisted out of the plane of the thiazoline moiety and its environment (Fig. 2). The best plane through the atoms C(8)–C(13) (given by $-0{\cdot}6776x + 0{\cdot}3633y + 0{\cdot}6394z + 0{\cdot}5330 = 0$) is almost perpendicular (94·1°) to the thiazoline ring plane *P* while the second ring formed by the atoms C(21)–C(26) ($-0{\cdot}4673x - 0{\cdot}2074y + 0{\cdot}8594z - 1{\cdot}8556 = 0$) makes a dihedral angle of 67·0° with *P* and 37·7° with the first phenyl ring. The molecules related by a centre of symmetry form dimers through pairs of weak hydrogen bonds [N(7)···N(3) = 3·39, H(7)···N(3) = 2·51 Å, ∠NH···N = 149·3°].

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# Structure of 7-Chloro-2-methylamino-5-phenyl-3*H*-1,4-benzodiazepin-3-ol

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**Abstract.** $C_{16}H_{14}ClN_3O$, $M_r = 299.76$, monoclinic, $P2_1/c$, $a = 14.29$ (1), $b = 20.72$ (2), $c = 10.27$ (1) Å, $\beta = 93.30$ (5)°, $U = 3034$ Å$^3$, $Z = 8$, $D_c = 1.312$ Mg m$^{-3}$, $F(000) = 1248$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu$(Mo $K\alpha$) = 0.21 mm$^{-1}$. Final $R = 6.1$% for 2302 observed counter amplitudes. E.s.d.'s average 0.009 Å for bond lengths and 0.55° for bond angles not involving H atoms. The angles between the 5-phenyl ring and the C(6)–(11) phenyl moiety of the 1,4-benzodiazepine system are 60.8 (5) and 65.4 (5)° for the two independent molecules.

**Introduction.** The crystal structure of the title compound (Sternbach, Reeder, Stempel & Rachlin, 1964) has been determined as part of an investigation of structure–activity relationships for 1,4-benzodiazepine derivatives. Certain of these compounds exhibit marked anxiolytic and anti-convulsant activity in man (Randall, Schallek, Sternbach & Ning, 1974).

A crystal 0.4 × 0.3 × 0.2 mm was mounted along the direction of elongation which coincided with *c*. Cell dimensions and intensities were measured on a Stoe Stadi-2 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. For layers 0–2, 140 counts of 1 s at intervals of 0.01° in $\omega$ were taken, backgrounds being measured for 30 s at each end of the scan. For the higher layers (3–10), the scan range was calculated from $[A + (B \sin\mu/\tan\theta')]$ where $\mu$ is the equi-inclination angle, $2\theta'$ is the azimuth angle and $A$ and $B$ were assigned values of 1.0 and 0.6, respectively. 2302 independent reflexions in the range $0.10 < \sin\theta/\lambda < 0.59$ Å$^{-1}$ were considered to be observed $[I > 2.5\sigma(I)]$. The intensities of four zero-layer reflexions were remeasured after each layer and showed no significant variation.

The structure was solved by direct methods with *SHELX* (Sheldrick, 1976) and refined by least squares until all calculated shifts were $<0.1\sigma$ and $R = 6.1$% for the 2302 observed reflexions. H atoms were included in the calculations but their coordinates were not refined. The H atoms bonded to N(12) and O(3) were located from a difference synthesis and the others were placed in theoretical positions. Anisotropic temperature factors were used for the heavier atoms and one overall isotropic temperature factor for H.

The weighting scheme was $w = 1/[\sigma^2(F)]$ where $\sigma(F)$ is the e.s.d. in the observed amplitudes derived from counting statistics. Final atomic coordinates are listed in Table 1.*

Computations were carried out on the CDC 7600 computer at the University of Manchester Regional Computer Centre and on the Birmingham University ICL 1906A.

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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 35032 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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