The ammonium ion is surrounded by seven bromine atoms in the range 3·30 to 3·75 Å and three more bromine atoms if the range is extended to 4·31 Å (Table 4). The sum of the crystal radii of ammonium and bromine is 3·43 Å (Pauling, 1967).

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References

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.

Couch, T. W., Lokken, D. A. & Corbett, J. D. (1972). *Inorg. Chem.* **11**, 357–362.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Davis, M. F. & Whitaker, A. (1966). *Acta Cryst.* A**21**, 822–823.

Hjortås, J. (1970). *SCALER*, Report 09-RII-70, Institutt for røntgenteknikk, Norges tekniske høgskole, Trondheim.

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

Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Main, P., Woolfson, M. M. & Germain, G. (1971). *MULTAN*. Department of Physics, Univ. of York.

Pauling, L. (1967). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.

Rytter, E. (1974). Thesis, Institutt for uorganisk kjemi, Norges tekniske høgskole, Trondheim.

Rytter, E., Rytter, B. E. D., Øye, H. A. & Krogh-Moe, J. (1973). *Acta Cryst.* B**29**, 1541–1543.

Rytter, E., Øye, H. A., Cyvin, S. J., Cyvin, B. N. & Klaeboe, P. (1973). *J. Inorg. Nucl. Chem.* **35**, 1185–1198.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The X-RAY System, Version of June 1972, Computer Science Center, Univ. of Maryland.

Acta Cryst. (1975). B**31**, 2181

The Crystal and Molecular Structure of Thiazolidine-2,4-dione

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$C_3H_3O_2NS$ is orthorhombic, space group *Pbca*, with $a = 7{\cdot}393$ (1), $b = 9{\cdot}416$ (1), $c = 13{\cdot}251$ (1) Å, $Z = 8$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to $R = 0{\cdot}066$ for 622 counter reflexions. The predominant tautomer is the thiazolidine form. All the bonds in the molecule show significant multiple character, with the exception of those belonging to the saturated methylene carbon atom, C(5). A series of canonical forms are proposed to interpret the π electron distribution within the molecule. None of the ring atoms shows significant deviation from planarity. The molecules pack in the form of hydrogen-bonded dimers predominantly in the *ab* plane.

Introduction

Thiazolidinones are of physiological and industrial importance. Aravamudan, Krishnan & Udupa (1973) have related the physiological activity of 2-imino-4-oxo-1,3-thiazoline to its coordination chemistry and have shown that the compound forms pseudo-tetrahedral, nitrogen-bonded complexes with Co(II) halides.

Thiazolidine-2,4-dione is an inhibitor of the corrosion of mild steels in acidic solution. The extent of the inhibition, in 0·1 *M* HCl, ranges from 37% at an inhibitor concentration of $0{\cdot}03 \times 10^{-3}$ *M* to 92% at the solubility limit of the inhibitor, 4×10^{-3} *M* (Donnelly, Downie & Grzeskowiak, unpublished). The compound is also used as a 'brightener' in the electroplating industry. The molecule is potentially ambidentate and a possible explanation of its ability to inhibit metallic corrosion is in terms of its coordination at the metallic surface.

This analysis has been undertaken as part of a programme in which the structure and coordination chemistry of heterocyclic molecules, associated with corrosion inhibition, are being investigated.

Experimental

Crystal data

Single crystals, in the form of cuboid plates, were obtained by evaporation from methanolic solution.

Table 1. *Crystal and experimental data*

$C_3H_3O_2NS$
F.W. 117·13
$a = 7{\cdot}393$ (1) Å
$b = 9{\cdot}416$ (1)
$c = 13{\cdot}251$ (1)
$V = 922{\cdot}44$ Å^3
$D_c = 1{\cdot}69$ g cm^{-3}
$D_m = 1{\cdot}68$

Systematic absences
$0kl$: $k = 2n+1$
$h0l$: $l = 2n+1$
$hk0$: $h = 2n+1$
Space group: *Pbca*
$Z = 8$
μ(Mo $K\alpha$) $= 5{\cdot}25$ cm^{-1}
$F(000) = 480$

From systematic absences on Weissenberg and precession photographs the crystals were allocated to space group *Pbca*. Cell dimensions were determined on a Hilger–Watts four-circle diffractometer with Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation. The density was determined by flotation.

Table 1 contains the crystal and experimental data.

Data collection and reduction

A crystal of dimensions $0{\cdot}21\times0{\cdot}21\times0{\cdot}13$ mm with Mo $K\alpha$ radiation and a 3·5 mm collimator were used to collect the data on a Hilger–Watts four-circle diffractometer. A θ–2θ scan technique was used out to $2\theta=60°$. Each scan consisted of 70 steps at 0·01° intervals; the counting time for each reflexion was 140 s plus 30 s on each of two background counts performed before and after the scan. The 060, 210 and 104 reflexions were used as standards at intervals of 50 reflexions.

It had been intended to record data from both the *hkl* and the $\bar{h}kl$ octants. However, during the recording of the $\bar{h}kl$ data the intensities of the standards started to decline and data collection was stopped. A close examination of the crystal showed signs of decomposition. The values of the net intensities of the standard reflexions were used in the calculation of scale factors which were employed in placing all the data on a common scale. Reflexions collected after significant changes in the net intensities of the standard reflexions had occurred were rejected. Approximately one-third of the final data was actually obtained by the averaging of *hkl* and $\bar{h}kl$ reflexions.

Of the 1158 unique reflexions 622 had $I>3\sigma(I)$ and were considered observed.

The data were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

The coordinates of the non-hydrogen atoms were obtained by Patterson and Fourier methods and refined by least-squares calculations. The weighting scheme was: $\sqrt{w}=1/[P_1+|F_o|+P_2|F_o|^2+P_3|F_o|^3]^{1/2}$ with $P_1=7{\cdot}84$, $P_2=0{\cdot}012$ and $P_3=1\times10^{-4}$.

With $R=0{\cdot}075$ a difference map was computed from only those reflexions with $\sin^2\theta<0{\cdot}11$. The three H atoms in the structure were located from peak densities ranging from 0·50 to 0·76 e Å^3. Refinement was continued, with isotropic temperature factors allocated to the H atoms.

Calculation of the geometry of the CH_2 group showed that the bond lengths and angles associated with the refined H atoms were unacceptable. Re-examination of the difference map revealed residual electron density on C(5). This was attributed to the unresolved H atoms. At this stage full-matrix refinement was applied to the non-hydrogen atoms in the hope that better resolution of the methylene H atoms would ensue. This refinement was continued until no parameter shift was larger than 1×10^{-5} at which point $R=0{\cdot}069$. The difference map was recalculated but no improvement in the resolution of the methylene H atoms was achieved; they were subsequently removed from the refinement. At $R=0{\cdot}066$ and with no parameter shift greater than one-sixth of the corresponding standard deviation, refinement was terminated. A weighting analysis showed $\sum\omega\Delta^2/N$ to be independent of both $|F_o|$ and $\sin^2\theta$. 002, 021, 115 and 230 were removed from the final stages because they appeared to be subject to extinction.

Scattering factors for S, N, O and C were obtained from *International Tables for X-ray Crystallography* (1962). The curve for H was that of Stewart, Davidson & Simpson (1965).

The final positional and thermal parameters are shown in Table 2.*

Description and discussion of the structure

Bond lengths and angles are listed in Table 3.

Planarity in the molecule

The best plane through the molecule and the atomic displacements are given in Table 4. The average deviation is 0·006 Å.

Exclusion of the methylene H atoms from the calculations produces a planar molecule. Although in the related molecules, rhodamine (Van der Helm, Lessor

Table 2. *Positional and anisotropic thermal parameters* ($\times10^5$)

The values of b_{ij} are defined by the expression $\exp[-\frac{1}{4}(h^2a^{*}b_{11}+2hka^{*}b^{*}b_{12}+\ldots)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
S(1)	61290	13151	40812	1703	695	481	36	−168	428
O(2)	63349	34117	53953	1900	944	362	−204	−547	690
O(4)	30579	37949	25114	1860	874	532	−20	−879	−64
N(3)	46122	37862	39942	1044	623	355	−183	−136	167
C(2)	57164	29914	46052	1085	635	400	113	113	312
C(4)	40263	31750	31117	1024	634	402	−23	134	−178
C(5)	47520	16523	29448	596	348	216	−48	−51	8

	x	y	z	B (Å$^2\times10^3$)
H(3)	43097	45711	42688	6108

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30998 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

& Merritt, 1962) and phenylthiazolidinedione (Matthews, 1964) the methylene C atom shows a larger displacement from the ring than in this compound.

Table 3. *Bond lengths* (Å) *and angles* (°)

S(1)–C(2)	1·751 (7)	C(2)–S(1)–C(5)	94·2 (3)
S(1)–C(5)	1·845 (5)	C(2)–N(3)–C(4)	117·5 (5)
O(2)–C(2)	1·209 (8)	C(2)–N(3)–H(3)	112 (6)
O(4)–C(4)	1·219 (8)	C(4)–N(3)–H(3)	130 (6)
N(3)–C(2)	1·372 (8)	S(1)–C(2)–O(2)	124·9 (5)
N(3)–C(4)	1·373 (8)	S(1)–C(2)–N(3)	111·2 (5)
N(3)–H(3)	0·9 (1)	O(2)–C(2)–N(3)	123·9 (6)
C(4)–C(5)	1·547 (8)	O(4)–C(4)–N(3)	122·7 (6)
		O(4)–C(4)–C(5)	123·7 (6)
		N(3)–C(4)–C(5)	113·6 (5)
		S(1)–C(5)–C(4)	103·6 (4)

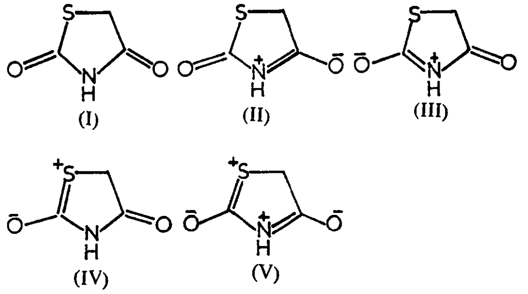

Fig. 1. Canonical forms of the molecule.

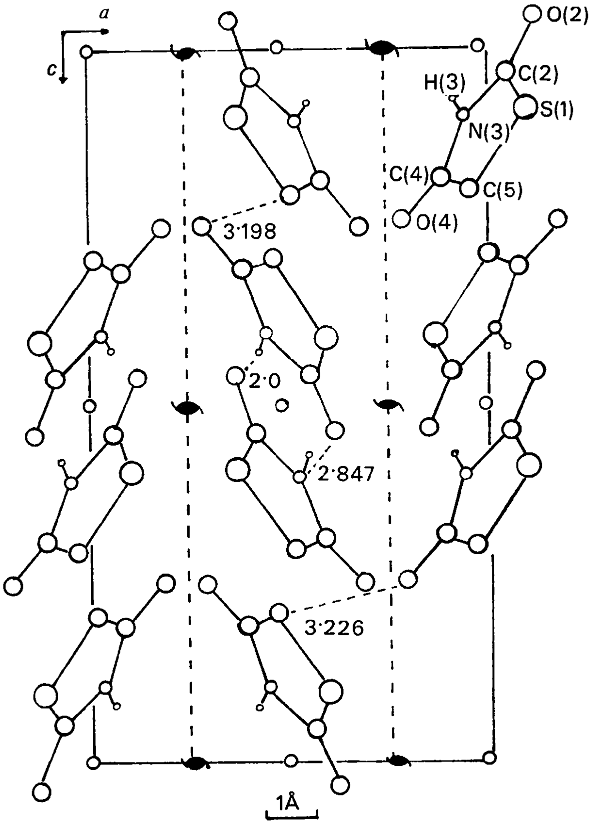

Fig. 2. Molecular packing diagram in **b** projection.

Table 4. *Equation of a mean plane with atomic displacements*

The equation of the plane is $lX+mY+nZ-P=0$, where X, Y and Z are fractional coordinates and P is the origin to plane distance in Å.

$$0{\cdot}8033X+0{\cdot}3610Y-0{\cdot}4738Z-1{\cdot}5257=0$$

S(1)	−0·001 (2) Å	C(4)	−0·009 (7) Å
C(2)	−0·005 (6)	O(4)	+0·004 (5)
O(2)	+0·009 (5)	C(5)	+0·009 (5)
N(3)	−0·007 (5)	H(3)	−0·092 (95)

Molecular dimensions

The bond lengths in the molecule indicate it to be the thiazolidine tautomer; there is no evidence supporting thiazoline or thiazole forms (Fig. 3). Neither C(5)–S(1) nor C(4)–C(5) show any evidence of multiple bonding. S(1)–C(2) indicates 40% double bonding on Abrahams's (1956) scale and the two C–N distances correspond to 25% double bonding on Wheatley's (1955) scale.

The bond lengths of the carbonyl groups are not significantly different from one another and agree well with known ketonic distances (Sutton, 1965). However, Parthasarathy (1969) does not regard carbonyl bond lengths of the order of 1·207 Å as representative of pure double bonds. This supports the contention of High & Kraut (1966) that five-membered rings induce an increased *s* character in the hybridized state of the ring C atom of the carbonyl group, with a resultant shortening of the bond. These authors report a value of 1·189 Å for a carbonyl group in androsterone and similar values have been found in γ-lactones. Consequently in this structure it would seem prudent to assume a C–O bond order of less than two.

Thus, with the exception of C(5), which is saturated, all the atoms in this structure are involved in multiple bonding. These bond lengths may be interpreted in a qualitative way by a combination of the canonical forms (I)–(V) illustrated in Fig. 1. The bond angles are typical of thiazoline derivatives with the smallest value occurring at the S atom (94·2°).

Molecular packing and hydrogen bonding

The molecular packing is illustrated in Fig. 2, in **b** projection.

The most significant molecular contacts are given in Table 5. The molecules pack as hydrogen-bonded dimers in the *ab* plane and are stacked in columns along **c**; N–H···O(2) bonds of 2·847 Å hold the molecules together. This intermolecular contact supports the resonance scheme for the molecule which suggests acidic character for the H atom attached to N(3) and a degree of negative charge on O(2). The methylene H atoms were not located with sufficient accuracy to be included in the structural details, but the two O(4)···C(5) distances of 3·198 and 3·226 Å suggest probable C–H···O bonds. Sutor (1962) in her considerations of the donor properties of CH groups points out that a suitable acceptor atom is frequently ketonic oxygen. C–H···O distances of 3·346 and 3·331 Å have been interpreted in terms of 'doubtful' hydrogen bonds in 6-mercaptopurine monohydrate (Sletten, Sletten & Jensen, 1969; Brown, 1969). A definite C–H···O bond length of 2·914 Å has been reported by Smith (1969).

Table 5. *Non-bonding* (<4·0 Å) *intermolecular contacts* (Å)

Equivalent positions and symmetry code

$\bar{x}, \bar{y}, \bar{z}$	(*a*)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	(*f*)
$\bar{x}, 1-y, \bar{z}$	(*b*)	$\bar{x}, \frac{3}{2}+y, \frac{1}{2}-z$	(*g*)
$\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$	(*c*)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	(*h*)
$\frac{3}{2}+x, \frac{1}{2}-y, \bar{z}$	(*d*)	$\frac{1}{2}+x, y, \frac{1}{2}-z$	(*i*)
$\frac{1}{2}-x, \frac{1}{2}+y, z$	(*e*)	$\frac{3}{2}+x, y, \frac{1}{2}-z$	(*j*)

S(1)–S(1)	(*b*)	3·853 (3)	*O(2)–H(3)	(*a*)	2·0 (1)
S(1)–O(4)	(*g*)	3·232 (5)	O(4)–N(3)	(*j*)	3·236 (8)
S(1)–O(4)	(*i*)	3·455 (5)	O(4)–C(2)	(*i*)	3·382 (8)
S(1)–N(3)	(*c*)	3·626 (6)	O(4)–C(4)	(*j*)	3·147 (9)
*O(2)–N(3)	(*a*)	2·847 (7)	†O(4)–C(5)	(*h*)	3·198 (7)
O(2)–N(3)	(*c*)	3·288 (7)	†O(4)–C(5)	(*i*)	3·226 (7)
O(2)–C(2)	(*d*)	3·498 (8)	O(4)–C(5)	(*e*)	3·447 (7)
O(2)–C(4)	(*c*)	3·179 (8)	N(3)–N(3)	(*a*)	3·558 (7)
O(2)–C(5)	(*f*)	3·576 (7)	N(3)–C(2)	(*a*)	3·565 (8)

* Hydrogen bond O(2)···H(3)–N(3).

† Possible hydrogen bond O(4)···H–C(5).

The remaining distances correspond to normal van der Waals values.

All the calculations were performed on the IBM 360/67 computer at the University of Newcastle upon Tyne. The programs, in addition to local programs, were from the integrated set derived by Dr F. R. Ahmed and his group at NRC, Ottawa, Canada. The SFLS block-diagonal refinement program, NRC-10, was modified for full-matrix refinement by Dr H. M. M. Shearer of Durham University.

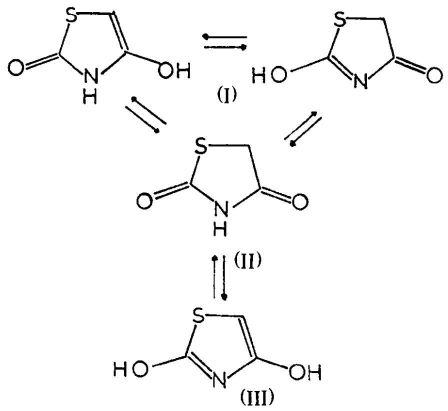

Fig. 3. Tautomeric forms of the molecule. (I) Thiazolines. (II) Thiazolidine. (III) Thiazole.

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References

Abrahams, S. C. (1956). *Quart. Rev.* **10**, 407–436.
Aravamudan, G., Krishnan, G. & Udupa, M. R. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 491–495.
Brown, G. M. (1969). *Acta Cryst.* B**25**, 1338–1353.
High, D. F. & Kraut, J. (1966). *Acta Cryst.* **21**, 88–96.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
Matthews, B. W. (1964). *Acta Cryst.* **17**, 1413–1420.
Parthasarathy, R. (1969). *Acta Cryst.* B**25**, 509–518.
Sletten, E., Sletten, J. & Jensen, L. H. (1969). *Acta Cryst.* B**25**, 1330–1338.
Smith, D. L. (1969). *Acta Cryst.* B**25**, 625–632.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Sutor, D. J. (1962). *Nature, Lond.* **195**, 68–69.
Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Spec. Publ. No. 18, pp. 20–22. London: The Chemical Society.
Van der Helm, D., Lessor, A. E. & Merritt, L. L. (1962). *Acta Cryst.* **15**, 1227–1232.
Wheatley, P. J. (1955). *Acta Cryst.* **8**, 224–226.