

The Crystal and Molecular Structure of 2-Amino-4-phenylthiazole Hydrobromide Monohydrate

BY G. R. FORM AND E. S. RAPER

Department of Chemistry, Newcastle-upon-Tyne Polytechnic, Newcastle-upon-Tyne, NE1 8ST, England

AND T. C. DOWNIE

School of Chemistry, Thames Polytechnic, London SE1, England

(Received 20 June 1973; accepted 2 October 1973)

2-Amino-4-phenylthiazole hydrobromide monohydrate is monoclinic with $a=12.425$, $b=9.477$, $c=10.339$ Å, $\beta=110.55^\circ$, $Z=4$. Intensities were collected on a Hilger-Watts four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations. R for 1094 observed reflexions was 0.085. The compound consists of a protonated heterocyclic molecule, a bromide ion and a water molecule. The phenyl and thiazole rings are planar (within experimental error), with an interplanar angle of 19.1° and an interring distance of 1.51 Å. The heterocyclic molecule is described in terms of resonance between protonated aminothiazole and protonated iminothiazoline forms, with a larger contribution from the latter. The negative charge on the bromide ion is modified by eight contacts to neighbouring atoms. Two at 3.547 and 3.722 Å are to neighbouring sulphur atoms. The rest are hydrogen bonds. Two are N-H...Br⁻ bonds at 3.34 and 3.64 Å, which are formed by symmetry-related exocyclic amino nitrogen atoms. A C-H...Br⁻ bond at 3.64 Å is formed from C(5) and H(5) atoms. Each water molecule forms three bonds to two bromide ions. Two H...Br⁻ distances of 2.7 and 2.8 Å involve the same bromide ion while a third H...Br⁻ distance of 3.1 Å is to a symmetry-related ion. This situation suggests that one of the water hydrogen atoms is asymmetrically bifurcated.

Introduction

2-Amino-4-phenylthiazole hydrobromide monohydrate (2-APT) reduces the corrosion rate of mild steel in 0.1 M hydrochloric acid. The extent of this corrosion inhibition ranges from 30% at 0.03×10^{-3} M to 87% at the solubility limit of the inhibitor, 1.1×10^{-3} M (Donnelly, Downie & Grzeskowiak, unpublished). The related compound, 2-aminothiazole, also inhibits the corrosion of mild steels as well as copper alloys and is used as a brightener in the electroplating industry.

Hudson & Warning (1970) have demonstrated that the addition of a small amount of inorganic halide together with organic molecules, such as pyrrole, to sulphuric acid solutions of low-carbon steels considerably reduces both the rate of dissolution and hydrogen absorption by the steel. It is possible that corrosion inhibition in this case is caused by coordination of the organic molecule and the halide to cations on the metal surface. Poling (1970) has provided evidence for the formation of complexes on metal surfaces by demonstrating that the corrosion inhibition of copper, in dilute sulphuric acid solution, by benzotriazole (BTZ) occurs by the formation of polymeric $[\text{Cu(I)BTZ}]_n$ layers several thousand ångströms thick on the metal surface. The coordination of 2-aminothiazole to the M^{II} ions of cobalt, nickel, and copper has been studied by Duff, Hughes & Rutt (1972) who report nitrogen-bonded rather than sulphur-bonded complexes for this monodentate ligand.

The coordination chemistry and structure of the inhibitor provide useful information towards the understanding of corrosion inhibition processes and the structure of 2-APT has been undertaken as part of a continuing program of work in this field.

Experimental

Crystal data

Anhydrous 2-APT was obtained from the Aldrich Chemical Company. Single crystals, suitable for X-ray analysis, were obtained by evaporation from aqueous ethanolic solution.

Comparison of the infrared spectra of the original and the recrystallized material indicated the retention of water following recrystallization. This was confirmed by a density determination by the flotation method.

The crystals grew as thin needles elongated along [100] and were allocated to space group $P2_1/c$ from Weissenberg and precession photographic data. Unit-cell dimensions were determined on a Hilger-Watts four-circle diffractometer with Mo $K\alpha$ ($\lambda=0.7107$ Å) radiation (Table 1).

Data collection and reduction

A crystal of dimensions $0.40 \times 0.23 \times 0.11$ mm, with Mo $K\alpha$ radiation and a 3.5 mm collimator, was used to collect the data on the diffractometer. A θ - 2θ scan technique was employed out to $2\theta=40^\circ$ in the hkl and $\bar{h}k\bar{l}$ octants. Each scan consisted of 70 steps at inter-

Table 1. *Crystal and experimental data*

Formula	C ₉ H ₁₁ ON ₂ SBr
F.W.	275.17
Unit cell	
<i>a</i>	12.425 (3) Å
<i>b</i>	9.477 (4)
<i>c</i>	10.339 (3)
β	110.55 (2)°
<i>V</i>	1139.97 Å ³
Systematic absences	0 <i>kl</i> : <i>k</i> = 2 <i>n</i> + 1 <i>h</i> 0 <i>l</i> : <i>l</i> = 2 <i>n</i> + 1
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>D</i> _c	1.60 g cm ⁻³
<i>D</i> _m	1.60
<i>Z</i>	4
μ (Mo <i>K</i> α)	39.71 cm ⁻¹
<i>F</i> (000)	552

vals of 0.01°, the total counting time for each reflexion being 210 s plus 35 s for each of two background counts performed before and after the scan. The 300, 004 and 152 reflexions were measured as internal standards every 40 reflexions. 2312 unique reflexions were measured and of these 1097 were greater than 3 σ 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. In the later stages of refinement the weighting scheme used was:

$$\sqrt{\omega} = 1/[P_1 + |F_o| + P_2|F_o|^2 + P_3|F_o|^3]^{1/2}$$

with $P_1 = 10.8$, $P_2 = 0.011$ and $P_3 = 1 \times 10^{-4}$.

With $R = 0.089$ a difference synthesis was calculated with only those reflexions having $\sin^2 \theta \leq 0.11$. Eleven peaks ranging from 0.35 to 0.65 Å⁻³ were observed and assigned to hydrogen atoms. Some residual electron density, 1.0 e Å⁻³, was also observed around the bromine atom. Each hydrogen atom was given a temperature factor equal to that of the atom to which it was attached and refined isotropically. The non-hydrogen atoms were refined by full-matrix least-squares calculations to $R = 0.085$. At this stage no shift was greater than one-third of the corresponding standard deviation and refinement was stopped. A weighting scheme showed that $\sum \omega \Delta^2 / N$ was independent of both $|F_o|$ and $\sin^2 \theta$.

Atomic scattering factors for Br⁻, Br, S, N, O and C were taken from Volume III of *International Tables for X-ray Crystallography* (1962). A dispersion correc-

Table 2. *Atomic coordinates and thermal parameters*

(a) Non-hydrogen atomic parameters ($\times 10^5$)

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

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₂₃	<i>b</i> ₁₃	<i>b</i> ₁₂
Br(1)	112552	24442	21595	1260	800	1049	-148	1361	86
S(1)	90479	11167	35327	1067	814	1020	-61	1188	241
O(1)	75914	58328	48677	1190	838	1404	101	1607	56
N(2)	93289	38794	33433	1077	870	1435	16	1495	371
N(3)	80621	30511	44051	790	862	782	138	752	354
C(2)	88363	28743	37943	658	1032	735	605	468	679
C(4)	76685	17573	47538	755	914	712	-106	674	-33
C(5)	80928	6458	43584	850	1062	929	-261	813	-29
C(6)	67810	18214	54388	805	1014	770	99	764	-127
C(7)	61301	29823	54053	1097	1384	1357	207	1513	643
C(8)	52642	29454	59752	1257	1781	1594	-55	1864	321
C(9)	51118	17910	66555	1218	1810	1135	-155	1538	-340
C(10)	57305	5908	66483	867	2079	813	-2	574	-973
C(11)	66094	5800	60685	834	1404	795	275	610	-110

Table 2 (cont.)

(b) Hydrogen-atom coordinates ($\times 10^5$) and thermal parameters (Å² $\times 10^3$)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
H(1)	73934	67140	43866	5444
H(2)	91936	47824	33531	2916
H(3)	79236	40998	47052	7867
H(4)	99008	36317	28864	3194
H(5)	77826	-3463	40603	4873
H(6)	82952	61514	49604	3071
H(7)	60658	42036	48939	5988
H(8)	49333	37303	57639	6250
H(9)	45715	17665	71533	4199
H(10)	54454	-4842	68486	4731
H(11)	71301	-4279	61488	7440

tion of -0.3 e was added to the Br⁻ and Br scattering curves (Templeton, 1962). Although calculations involving both Br⁻ and Br were performed there were no observable differences in the coordinates of the atoms; the results quoted are for the Br⁻ ion since this is chemically more sensible.

The scattering curve for hydrogen was that of Stewart, Davidson & Simpson (1965). Reflexions 100, 210 and 310 were omitted from the final stages of refinement as they appeared to be subject to extinction. The final positional and thermal parameters are shown in Table 2(a) and (b) and the observed and calculated structure amplitudes in Table 3.

Table 4 (cont.)

(b) Bond angles with e.s.d.'s in parentheses

C(2)—S(1)—C(5)	90.2 (7)°
H(1)—O(1)—H(6)	103 (14)
C(2)—N(2)—H(2)	127 (9)
C(2)—N(2)—H(4)	120 (7)
H(2)—N(2)—H(4)	114 (11)
C(2)—N(3)—C(4)	113 (1)
C(2)—N(3)—H(3)	118 (9)
C(4)—N(3)—H(3)	129 (9)
S(1)—C(2)—N(2)	122 (1)
S(1)—C(2)—N(3)	112 (1)
N(2)—C(2)—N(3)	126 (1)
N(3)—C(4)—C(5)	114 (1)
N(3)—C(4)—C(6)	117 (1)
C(5)—C(4)—C(6)	128 (1)
S(1)—C(5)—C(4)	111 (1)
S(1)—C(5)—H(5)	110 (9)
C(4)—C(5)—H(5)	133 (9)
C(4)—C(6)—C(7)	116 (1)
C(4)—C(6)—C(11)	123 (1)
C(7)—C(6)—C(11)	120 (1)
C(6)—C(7)—C(8)	117 (1)
C(6)—C(7)—H(7)	124 (9)
C(8)—C(7)—H(7)	118 (9)
C(7)—C(8)—C(9)	122 (2)
C(7)—C(8)—H(8)	114 (8)
C(9)—C(8)—H(8)	123 (8)
C(8)—C(9)—C(10)	119 (2)
C(8)—C(9)—H(9)	118 (8)
C(10)—C(9)—H(9)	123 (8)
C(9)—C(10)—C(11)	121 (2)
C(9)—C(10)—H(10)	135 (13)
C(11)—C(10)—H(10)	104 (13)
C(6)—C(11)—C(10)	121 (2)
C(6)—C(11)—H(11)	135 (7)
C(10)—C(11)—H(11)	105 (7)

Bond lengths within the thiazole ring are compared with the corresponding values from some related molecules in Table 6. Excellent agreement is observed between Fehlmann's (1970) data and those of 2-APT. A comparison of the theoretical data for the thiazole molecule with the other results in Table 6 indicates that the largest differences occur in the C-S bond lengths, the observed values being generally the greater. Fehlmann considers the C-S bonds in 2-methylamino-benzothiazole to be pure single bonds if shortening due to hybridization is taken into account.

Table 6. A comparison of some thiazole ring dimensions

Molecule and reference	S(1)—C(2)	C(2)—N(3)	N(3)—C(4)	C(4)—C(5)	C(5)—S(1)
M-O calculations. Thiazole (Vincent, Phan-Tan-Luw & Metzger, 1966)	1.70 Å	1.32 Å	1.37 Å	1.35 Å	1.71 Å
2-APT (This investigation)	1.763	1.297	1.381	1.391	1.739
2-Methylaminobenzothiazole (Fehlmann, 1970)	1.763	1.297	1.381	1.391	1.739
Phenylthiazolidinedione (Matthews, 1964)	1.776	1.338	1.322	1.527	1.813
2-(<i>O</i> -Hydroxy-phenyl) benzothiazole (Stenson, 1970)	1.749	1.280	1.404	1.372	1.757
<i>N</i> -Benzyl-4-methylthiazolium bromide (Power <i>et al.</i> , 1970)	1.671	1.308	1.398	1.334	1.712
Sulphathiazole II (Kruger & Gafner, 1971)	1.742	1.332	1.375	1.315	1.720
2-Amino-4-thiazolidinone-5-acetic acid (Amirthalingham & Muralidharan, 1972a)	1.726	1.361	1.413	1.515	1.863
2-Imino-4-thiazolidinone (Amirthalingham & Muralidharan, 1972b)	1.777	1.336	1.369	1.554	1.765
2-Amino-4-phenylthiazoline-4-one (Mornon & Raveau, 1970)	1.771	1.338	1.357	1.527	1.839

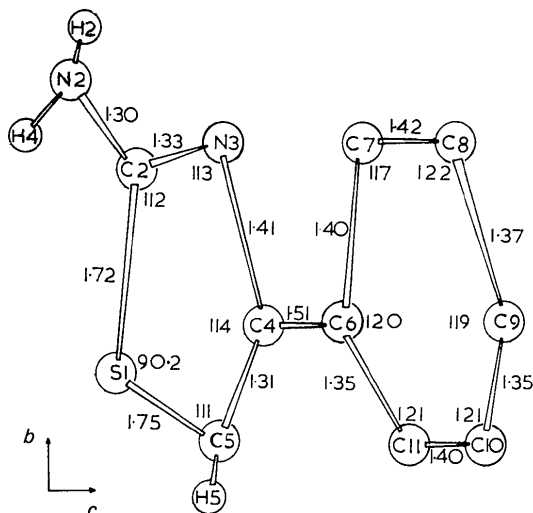
Fig. 1. Labelled perspective drawing of the molecule in a^* projection.

Table 5. Equations of the mean planes and displacements of atoms from these planes

Each plane is represented by an equation of the type $lX + mY + nZ - P = 0$, referred to an orthogonal system of axes, which has X along the a axis, Y in the (a, b) plane and Z along the c^* axis.

(a) Phenyl ring

$$-0.3916X - 0.3062Y - 0.8677Z + 7.6187 = 0$$

Atomic displacements and e.s.d.'s (Å)

C(4)	+0.060 (13)	C(9)	-0.033 (17)
C(6)	-0.005 (13)	C(10)	+0.033 (21)
C(7)	-0.001 (14)	C(11)	-0.002 (17)
C(8)	-0.019 (15)		

(b) Aminothiazole ring

$$-0.4741X + 0.0150Y - 0.8804Z + 7.7178 = 0$$

Atomic displacements and e.s.d.'s (Å)

S(1)	+0.001 (4)	C(4)	-0.008 (13)
C(2)	-0.027 (13)	C(5)	-0.005 (15)
N(2)	+0.004 (14)	C(6)	+0.050 (13)
N(3)	+0.016 (11)		

The internal bond angles all show the characteristic reduction from 120° which is usual in five-membered heterocyclic molecules. The angle at the sulphur atom, 90.2°, is common for substituted thiazole molecules.

The exocyclic, C(2)–N(2), and heterocyclic, C(2)–N(3), bonds possess 60 and 40% double-bond character respectively, on Wheatley's (1955) scale. This is indicative of amino–imino tautomerism in the neutral molecule. These tautomers are illustrated in Fig. 2, together with an ionic aminothiazole form. Mornon & Raveau (1970) report a similar tautomeric system in 2-amino-5-phenylthiazoline-4-one and suggest that approximately equal proportions of amino, imino and ionic forms are present. Tautomers I and III (Fig. 2) indicate atoms N(2) and N(3) to be likely binding sites for the proton from the HBr molecule. The location of two hydrogen atoms on N(2) and one on N(3), together with the significant delocalization of the $p\pi$ electrons in the N(2)–C(2)–N(3) region of the protonated molecule, indicate that it is best described in terms of the canonical forms illustrated in Fig. 3. The very short exocyclic C–N distance suggests that form II is probably the more significant.

(c) Molecular packing and hydrogen bonding

The unit-cell contents are illustrated in a^* projection in Fig. 4. The hydrogen bonding scheme is illustrated in Fig. 5, also in a^* projection. Only the relevant molecules are included in this Figure and each is labelled by the symmetry code used in Table 8. The bromide ion and water molecules used are symmetry-related to those whose coordinates appear in Table 2. All the shortest non-bonding contacts are listed in Table 7 and the hydrogen-bonded distances and angles are shown in Table 8.

Table 7. Shortest ($<4.0 \text{ \AA}$) non-bonding intermolecular contacts in 2-APT (*e.s.d.*'s in parentheses)

Equivalent position			Symmetry code
x	y	z	I
\bar{x}	\bar{y}	\bar{z}	II
x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	III
x	$\frac{1}{2}+y$	$\frac{1}{2}-z$	IV

Br(1) \cdots S(1 ^{IV})	3.547 (4) \AA
Br(1) \cdots S(1 ^I)	3.722 (5)
Br(1) \cdots C(2 ^{III})	3.73 (1)
S(1) \cdots S(1 ^{II})	3.774 (5)
O(1) \cdots N(2 ^{II})	3.63 (2)
O(1) \cdots C(8 ^{II})	3.54 (3)
O(1) \cdots C(10 ^{III})	3.58 (2)
O(1) \cdots H(4 ^{II})	3.2 (1)
O(1) \cdots H(8 ^{II})	3.0 (2)
N(2) \cdots C(4 ^{III})	3.61 (2)
N(2) \cdots C(6 ^{III})	3.58 (2)
N(2) \cdots C(11 ^{III})	3.41 (2)
N(3) \cdots C(10 ^{III})	3.52 (2)
N(3) \cdots C(11 ^{III})	3.53 (2)
C(2) \cdots C(6 ^{III})	3.52 (2)
C(2) \cdots C(11 ^{III})	3.50 (2)
C(7) \cdots C(9 ^{III})	3.64 (2)
C(9) \cdots C(11 ^{III})	3.65 (2)
C(10) \cdots C(10 ^{III})	3.44 (2)
C(10) \cdots C(11 ^{III})	3.44 (2)

Table 8. Hydrogen-bond distances and angles involving a bromide ion (*e.s.d.*'s in brackets)

Equivalent position			Symmetry code
x	y	z	I
\bar{x}	\bar{y}	\bar{z}	II
x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	III
\bar{x}	$\frac{1}{2}+y$	$\frac{1}{2}-z$	IV
$1+x$	y	z	V
\bar{x}	$\frac{3}{2}+y$	$\frac{1}{2}-z$	VI

Br(1) \cdots O(1 ^{II})	3.33 (1) \AA
Br(1) \cdots O(1 ^{IV})	3.30 (1)
Br(1) \cdots H(1 ^{IV})	2.8 (2)
Br(1) \cdots H(6 ^{II})	3.1 (2)
Br(1) \cdots H(6 ^{IV})	2.7 (2)
Br(1) \cdots N(2 ^V)	3.34 (2)
Br(1) \cdots N(2 ^{VI})	3.46 (1)
Br(1) \cdots H(2 ^{VI})	2.6 (1)
Br(1) \cdots H(4 ^V)	2.4 (1)
Br(1) \cdots C(5 ^{IV})	3.64 (2)
Br(1) \cdots H(5 ^{IV})	2.9 (2)

Br(1)–H(1)–O(1)	115 (13) $^\circ$
Br(1)–H(6 ^{II})–O(1)	95 (13)
Br(1)–H(6 ^{IV})–O(1)	122 (13)
Br(1)–H(2)–N(2)	168 (12)
Br(1)–H(4)–N(2)	164 (10)
Br(1)–H(5)–C(5)	129 (11)

The molecules are stacked head to tail along c . There are no direct inter-ring hydrogen bonds but an extensive hydrogen-bonded network exists which involves bromide ions, amino-nitrogen atoms, C(5) atoms and water oxygen atoms. It can be seen from Fig. 5 that the negative charge on the bromide ion is modified by eight contacts. There is no regular coordination about the ion, and its proximity to both the screw axis

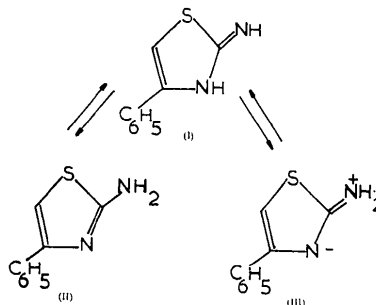


Fig. 2. Tautomeric forms of the 2-APT molecule. I=Iminothiazoline, II=aminothiazole, III=aminothiazole (ionic form).

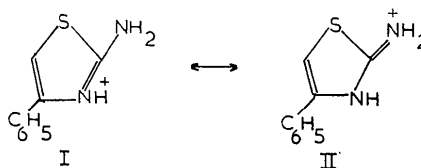


Fig. 3. Canonical forms of the protonated 2-APT molecule. I=Protonated aminothiazole, II=protonated iminothiazoline.

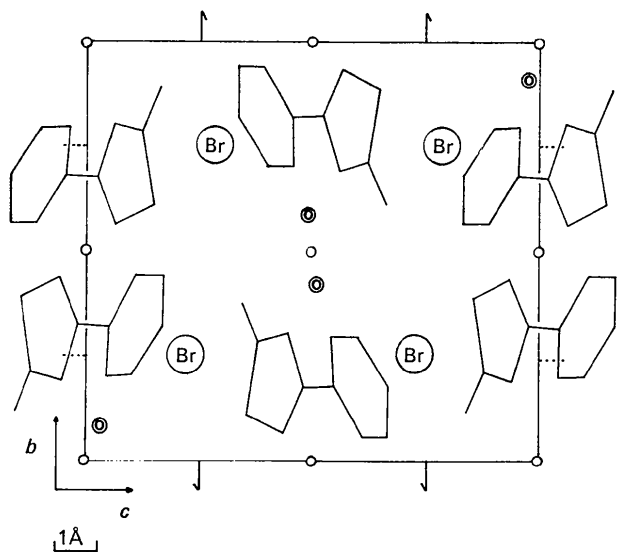
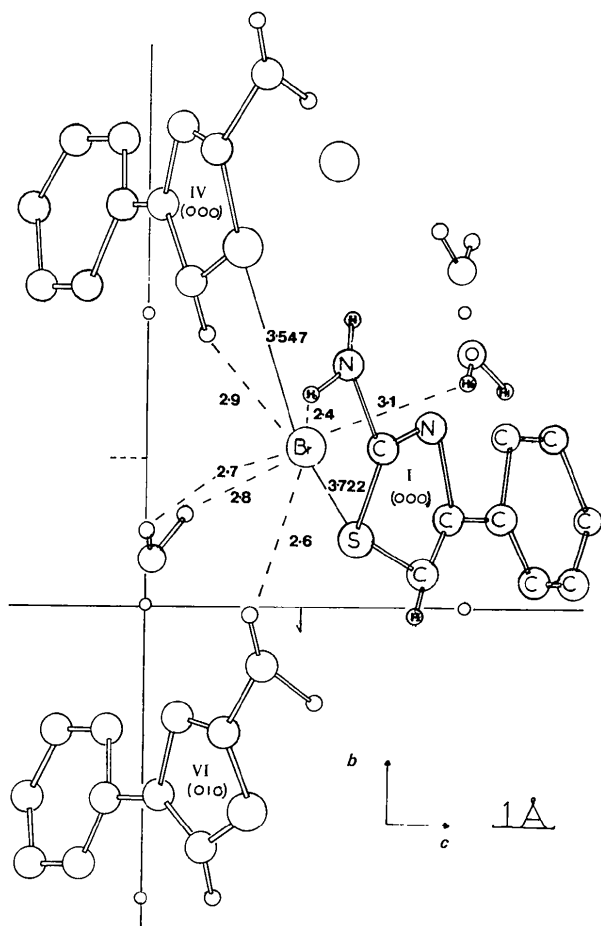
Fig. 4. Molecular packing in a^* projection.

Fig. 5. Hydrogen-bonding scheme for a bromide ion.

and the glide plane is related to the large number of contacts.

The $S \cdots Br^-$ distances of 3.547 and 3.722 Å are shorter than the sum of the van der Waals radii, 3.80 (Pauling, 1960). Similar reductions, 3.476 and 3.491 Å, have been observed by Power, Pletcher & Sax (1970) and interpreted in terms of weak $S \cdots Br^-$ interactions. Such interactions seem likely in 2-APT as part of the process of neutralizing the charge on the bromide ion. The same workers suggest a $C-H \cdots Br^-$ distance of 3.62 Å consisting of a C-H distance of 1.64 Å and a 1.98 Å acceptor radius for the Br^- ion. The 3.64 Å for the $C(5)-H(5) \cdots Br^-$ contact in 2-APT is in good agreement with this computed distance and it is reasonable to classify this contact as a weak, non-linear hydrogen bond.

In hydrated halogeno organic crystals, water molecules tend to direct their hydrogen atoms toward halide ions rather than heterocyclic hydrogen-bond acceptor atoms (Clark, 1963). This preference is strong and often results in spiral chains of hydrogen-bonded water molecules. Such features are present in this structure. Each water molecule forms three hydrogen bonds to two bromide ions. The $H(1) \cdots Br^-$ and $H(6) \cdots Br^-$ distances of 2.7 and 2.8 Å respectively are to the same bromide ion and display significant shortening from the sum of the van der Waals radii ($H = 1.2$ and $Br^- = 1.98$ Å). They must be regarded as definite hydrogen bonds. The 3.1 Å $H(6) \cdots Br^-$ contact is to a symmetry-related bromide ion and must obviously be weaker than the other two. On Donohue's (1968) classification it is a doubtful hydrogen bond. However, in the asymmetric bifurcation of hydrogen atoms, it is not uncommon for one contact to be longer than the other and for the corresponding angles to exhibit differing degrees of distortion from linearity. This situation is observed in H(6) with $H(6) \cdots Br^-$ contacts of 3.1 and 2.7 Å and corresponding $O-H \cdots Br^-$ angles of 95 and 122° respectively. Consequently, it seems reasonable to classify H(6) as a possibly asymmetrically bifurcated hydrogen atom. The $O(1) \cdots Br^-(1)$ contacts of 3.30 and 3.33 Å compare favourably with a series of $O \cdots Br^-$ values reported by Lundgren (1970) for the mono-, di- and trihydrates of hydrogen bromide.

The exocyclic amino group forms $N-H \cdots Br^-$ bonds. Two contacts, to the same bromide ion, are formed by the amino groups from two molecules which are related by the screw axis (Fig. 5). The $H(4) \cdots Br^-$ distance of 2.4 Å and the $H(2) \cdots Br^-$ distance of 2.6 Å both show significant shortening from the sum of the corresponding van der Waals radii and must be classified as definite hydrogen bonds. The $N(2) \cdots Br^-$ distances and angles are compatible with some recent data which are listed in Table 9. The observed values are not unexpected in view of the polarity of the N(2) atom and indicate that the protonated imino-phenyl-thiazoline form is the major contributing canonical form in this structure. The remaining non-bonded distances are of the normal van der Waals type.

Table 9. Nitrogen-bromide hydrogen-bond distances (Å) and angles°

N-H...Br ⁻ (distance)	H...Br ⁻	N-H...Br ⁻ (angle)	
3.31	2.53	—	2-Methyl-3-phenyl-4-(N-methyl-N-hydroxyamidin)-isoxazolin-5-one hydrobromide; Fanfani, Nunzi, Zanazzi & Zanazzi (1972)
3.44	2.42	169	10-Methylisoalloxazine hydrobromide trihydrate; Trus & Fritchie (1969)
3.45	2.61	165.5	N-Methyl-DL-leucylglycine hydrobromide; Chandrasekharan & Subramanian (1969)
3.34	2.40	168	This investigation
3.46	2.60	164	

All the calculations were performed on the IBM 360/67 computer at the University of Newcastle-upon-Tyne. The programs used throughout the analysis, in addition to small local programs, were from the integrated set devised for the IBM 360 by Dr F. R. Ahmed and his group at N.R.C., 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.

We are grateful to the S.R.C. for the provision of a research grant to G.R. Form, and to Dr H.M.M. Shearer and the Chemistry Department, University of Durham, for the use of their diffractometer.

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