BRAUN, R. L. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **22**, 780.
BROWN, G. M. (1969). *Acta Cryst.* B**25**, 1338.
BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). *The Oak Ridge Computer-Controlled X-ray Diffractometer.* Report ORNL-4143, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
CALLERI, M., FERRARIS, G. & VITERBO, D. (1967). *Acta Cryst.* **22**, 468.
CHANG, S. C., PARK, D. Y. & LI, N. C. (1968). *Inorg. Chem.* **7**, 2144.
EVERETT, G. W., JR & HOLM, R. H. (1968). *Inorg. Chem.* **7**, 776.
FOX, M. R., ORIOLI, P. L., LINGAFELTER, E. C. & SACCONI, L. (1964). *Acta Cryst.* **17**, 1159.
FRASSON, E. & PANATTONI, C. (1960). *Acta Cryst.* **13**, 893.
GODYCKI, L. E. & RUNDLE, R. E. (1953). *Acta Cryst.* **6**, 487.
HALL, G. S. & SODERBERG, R. H. (1968). *Inorg. Chem.* **7**, 2300.
HOLIAN, B. L. & MARSH, R. E. (1970). *Acta Cryst.* B**26**, 1049.
HOLM, R. H., CHAKRAVORTY, A. & THERIOT, L. J. (1966). *Inorg. Chem.* **5**, 625.
HOLM, R. H., EVERETT, G. W., JR & CHAKRAVORTY, A. (1966). *Progress in Inorganic Chemistry.* Edited by F. A. Cotton. Vol. 7, pp. 83–214. New York: Interscience.
HOLM, R. H. & O'CONNOR, M. J. (1971). *Progress in Inorganic Chemistry.* Edited by S. J. LIPPARD. Vol. 14, pp. 241–401. New York: John Wiley.
IBERS, J. A. (1962). *International Tables for X-ray Crystallography.* Vol. III, p. 202. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1969). Vol. I, p. 149. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
SACCONI, L. (1968). *Transition Metal Chemistry.* Edited by R. L. CARLIN. Vol. 4, pp. 199–298. New York: Dekker.
SACCONI, L., PAOLETTI, P. & CIAMPOLINI, M. (1963). *J. Amer. Chem. Soc.* **85**, 411.
SACCONI, L., CIAMPOLINI, M. & NARDI, N. (1964). *J. Amer. Chem. Soc.* **86**, 819.
SACCONI, L., CIAMPOLINI, M. & CAMPIGLI, U. (1965). *Inorg. Chem.* **4**, 407.
SCHERINGER, C. (1963). *Acta Cryst.* **16**, 546.
SCHLEMPER, E. O. (1968). *Inorg. Chem.* **7**, 1130.
SMITH, D. L. (1962). *PLANE, A Least-Squares Plane Program for the CDC* 1604 *Computer.* Ph. D. Thesis (Appendix IV), Univ. of Wisconsin, Madison, Wisconsin.
TEMPLETON, D. H. (1962). *International Tables for X-ray Crystallography.* Vol. III, p. 214. Birmingham: Kynoch Press.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
WATKINS, S. F. (1966). *Rigid Body Mechanics.* Ph. D. Thesis (Appendix I), Univ. of Wisconsin, Madison, Wisconsin.
WEI, C. H. (1972*a*). *Inorg. Chem.* **11**, 1100.
WEI, C. H. (1972*b*). *Inorg. Chem*, In the press.
WEI, C. H. & DAHL, L. F. (1969). *J. Amer. Chem. Soc.* **91**, 1351.

Acta Cryst. (1972). B**28**, 2598

The Crystal Structure of 2-Methyl-3-phenyl-4-(*N*-methyl-*N*-hydroxyamidin)-isoxazolin-5-one Hydrobromide

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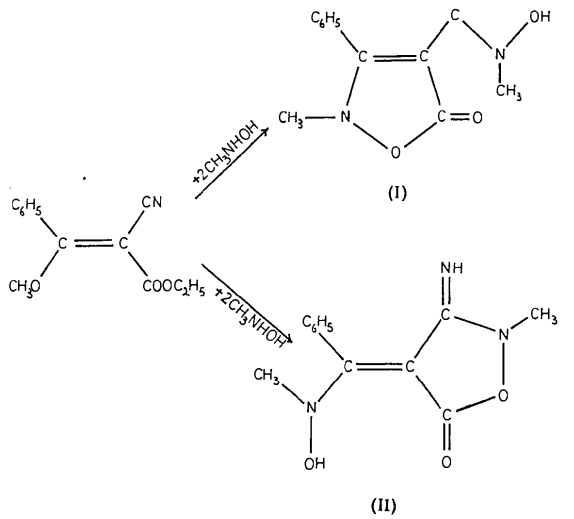
Crystals of 2-methyl-3-phenyl-4-(*N*-methyl-*N*-hydroxyamidin)isoxazolin-5-one hydrobromide are orthorhombic, space group *Pbca*, with $a = 19{\cdot}539$ (2), $b = 10{\cdot}676$ (2) and $c = 13{\cdot}418$ (2) Å. There are eight formula units per unit cell. The structure was solved by the heavy atom method employing 2954 intensity data collected on a Weissenberg apparatus. It was refined by least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms to an R index of 0·075 for 1452 independent observed reflexions. Bond distances are in reasonable agreement with the corresponding values for related substances. The nitrogen atom of the iminic group is protonated. The planarity of the *N*-methyl-*N*-hydroxyamidin chain indicates the occurrence of two mesomeric forms for this group.

Introduction

The present X-ray study was undertaken in order to determine the molecular structure of the product of the reaction between ethyl-α-cyano-β-methoxy-β-phenyl acrylate and an excess of methylhydroxylamine because spectroscopic data and chemical behaviour did not confirm which of the two stereoisomers (I) and

(II), among several possible compounds, was formed (Adembri & Tedeschi, 1967). The two chemical reactions can be sketched as it follows:



Experimental

Crystals of the hydrobromide of the reaction compound were kindly supplied by Professor Tedeschi of the Institute of Organic Chemistry of Florence University. They are short, prismatic in habit and colourless, but turn brown after a long exposure to the air and to X-rays. Their melting point is 204–206 °C.

From preliminary oscillation and Weissenberg photographs, crystals were assigned to the orthorhombic system, space group *Pbca*, and approximate lattice parameters were determined. Cell constants were refined by a least-squares method employing 2θ values of 37 high Bragg-angle reflexions, measured on *hk*0 and *h*0*l* Weissenberg photographs.

The density, measured by flotation in an aqueous solution of potassium iodomercurate, is 1·53 g.cm^{-3}, in agreement with the calculated value of 1·556 g.cm^{-3} if eight molecules are assumed present in the unit cell. Crystal data are reported in Table 1.

Table 1. *Crystal data for 2-methyl-3-phenyl-4-(N-methyl-N-hydroxyamidin)isoxazolin-5-one hydrobromide*

F.W.: 328·1
Melting point: 205 ± 1 °C
Systematic absences: 0*kl* $k=2n+1$; *h*0*l* $l=2n+1$; *hk*0 $h=2n+1$
Space group: *Pbca*

$a=19{\cdot}539\pm0{\cdot}002$ Å	$V=2799$ Å^3
$b=10{\cdot}676\pm0{\cdot}002$	$Z=8$
$c=13{\cdot}418\pm0{\cdot}002$	
$D_m=1{\cdot}53$ g.cm^{-3}	$D_x=1{\cdot}556$ g.cm^{-3}
$F(000)=1328$	μ(Cu $K\alpha$) = 45·0 cm^{-1}.

For the structural study, reflexions from the *hk*0 to *hk*10 layers were collected from a well formed crystal elongated in the **c** direction with dimensions 0·8 × 0·4 × 0·3 mm. Since this crystal turned brown during X-ray exposure, intensity data from the *h*0*l* to *h*7*l* layers were collected from a second crystal with a different shape and approximate dimensions 0·6 × 0·2 × 0·3 mm.

An integrating Weissenberg apparatus was used employing equiinclination and multiple-film techniques and Cu $K\alpha$ radiation. 2954 independent diffraction effects were obtained, of which 1502 were too weak to be measured. These reflexions were given an intensity value of zero.

Intensities were measured with a microdensitometer and converted to F^2 values, corrected by the Lorentz and polarization factors. An approximate cylindrical absorption correction was applied to the *hk*0 ~ *hk*10 data set. A correction according to the method of De Meulenaer & Tompa (1965) was applied to *h*0*l* ~ *h*7*l* data.

In order to obtain a unique set of data, the scaling of the F^2's from different layers was carried out by the correlation of the common reflexions, employing the least-squares method of Rae (1965).

Determination and refinement

The structure was solved by the heavy atom method; the coordinates of the bromine atom were determined from a three-dimensional Patterson function and a complete, but approximate, structural model, with the exclusion of the hydrogen atoms, was derived by means of successive electron density maps leading to a reliability index of 0·27. This model was consistent with the chemical formula (I).

The structure was refined by the least-squares method. The weighting scheme used in the refinement was $\sqrt{w}=1$ for observed reflexions with $|F_o|\leq 4|F_{min}|$, $\sqrt{w}=4|F_{min}|/|F_o|$ for observed reflexions with $|F_o|>4|F_{min}|$. After five cycles of calculation, using the block-diagonal approximation and individual isotropic thermal parameters, the R index dropped to 0·14. At this stage two more cycles, with anisotropic thermal parameters, were computed. The R index decreased to 0·12.

A difference Fourier synthesis was then computed, which revealed residual peaks at the positions expected for the hydrogen atoms. In the last cycle, the coordinates of all the atoms and the anisotropic thermal parameters of the Br, C, O, N atoms were refined (an isotropic value of 5 Å^2 was set for all the hydrogen atoms). The final R value was 0·075 for all the observed reflexions.

The atomic scattering factors used in the calculations were taken from *International Tables for X-ray Crystallography* (1962).

Observed and calculated structure factors are given in Table 2. Final atomic coordinates and thermal parameters with estimated standard deviations are listed in Tables 3 and 4 respectively.

Table 2. *Observed and calculated structure factors* ($\times 10$)

Unobserved reflexions were given zero intensities. The asterisks indicate reflexions affected by extinction.

Table 2 (*cont.*)

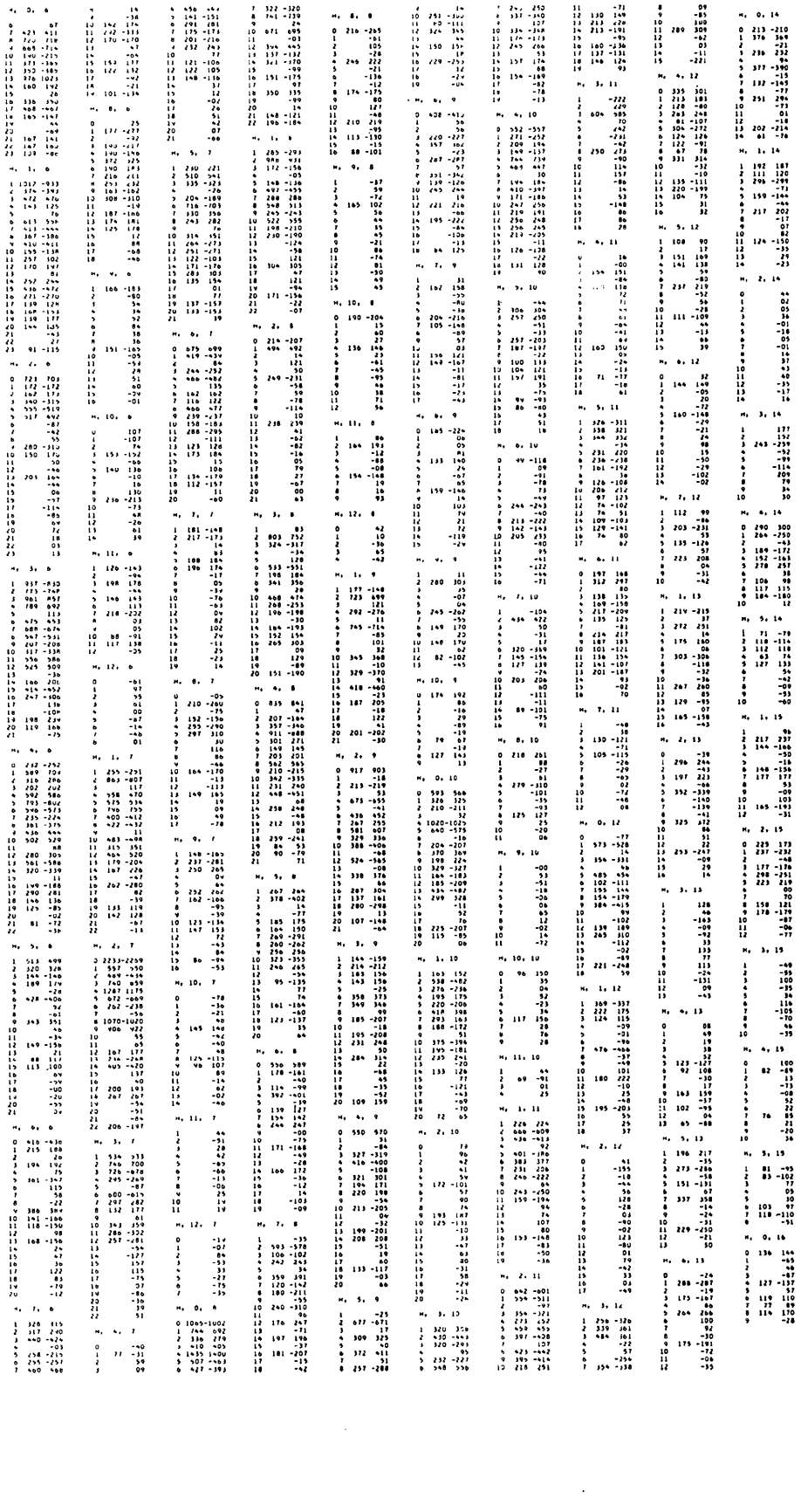


Table 3. *Fractional atomic coordinates with standard deviations in parentheses*

Atomic coordinates are ($\times 10^4$) for non-hydrogen and ($\times 10^3$) for hydrogen atoms.

	x	*y*	*z*
Br	1353 (1)	1123 (1)	1923 (1)
C(1)	1515 (5)	1624 (10)	4738 (8)
C(2)	984 (6)	792 (10)	4574 (9)
C(3)	950 (6)	−328 (11)	5052 (10)
C(4)	1471 (7)	−648 (12)	5751 (11)
C(5)	1980 (7)	176 (12)	5926 (10)
C(6)	2028 (6)	1319 (11)	5408 (9)
C(7)	1517 (5)	2820 (10)	4223 (8)
N(1)	2096 (4)	3352 (9)	3918 (7)
O(1)	1949 (3)	4537 (7)	3468 (6)
C(8)	1244 (5)	4736 (10)	3564 (9)
C(9)	983 (5)	3622 (9)	4036 (7)
C(10)	268 (5)	3525 (9)	4355 (7)
N(2)	102 (4)	3423 (8)	5304 (6)
N(3)	−217 (4)	3612 (8)	3672 (7)
C(11)	−133 (7)	3496 (13)	2581 (9)
O(2)	−886 (4)	3610 (7)	4006 (6)
C(12)	2716 (5)	2810 (12)	3503 (10)
O(3)	1004 (4)	5707 (7)	3314 (6)
H[C(2)]	60 (6)	89 (12)	408 (9)
H[C(3)]	64 (6)	−107 (11)	503 (10)
H[C(4)]	135 (6)	−167 (12)	615 (9)
H[C(5)]	230 (6)	−29 (12)	631 (9)
H[C(6)]	243 (7)	197 (12)	549 (9)
H(1)[N(2)]	55 (6)	319 (12)	554 (9)
H(2)[N(2)]	−36 (6)	355 (11)	546 (9)
H(1) [C(11)]	33 (6)	308 (12)	254 (10)
H(2) [C(11)]	−23 (6)	442 (12)	236 (11)
H(3) [C(11)]	−45 (6)	265 (12)	246 (10)
H[O(2)]	−109 (6)	465 (12)	398 (9)
H(1) [C(12)]	274 (6)	249 (13)	289 (9)
H(2) [C(12)]	269 (6)	199 (12)	370 (9)
H(3) [C(12)]	310 (6)	319 (12)	383 (9)

Results and discussion

The projection of the structure along the *b* axis is shown in Fig. 1. Bond distances and angles are reported in Fig. 2 and in Table 5.

The heterocyclic ring is planar in the limits of experimental error. The equation of the best plane (plane I) through the five atoms of the ring, referred to the crystallographic axes, is given in Table 6. Deviations from this plane are reported in the same table.

Table 5. *Interatomic distances and bond angles with standard deviations in parentheses*

(*a*) Distances

C(1)—C(2)	1·38 (1) Å
C(2)—C(3)	1·36 (2)
C(3)—C(4)	1·42 (2)
C(4)—C(5)	1·35 (2)
C(5)—C(6)	1·41 (2)
C(6)—C(1)	1·38 (2)
C(1)—C(7)	1·45 (2)
C(7)—N(1)	1·33 (1)
N(1)—C(12)	1·45 (1)
N(1)—O(1)	1·43 (1)
O(1)—C(8)	1·40 (1)
C(8)—O(3)	1·19 (1)
C(8)—C(9)	1·44 (1)
C(9)—C(7)	1·37 (1)
C(9)—C(10)	1·46 (1)
C(10)–N(2)	1·32 (1)
C(10)–N(3)	1·32 (1)
N(3)—O(2)	1·38 (1)
N(3)—C(11)	1·48 (2)
C(2)—H[C(2)]	1·01 (12)
C(3)—H[C(3)]	1·00 (12)
C(4)—H[C(4)]	1·24 (12)
C(5)—H[C(5)]	0·95 (12)
C(6)—H[C(6)]	1·05 (13)
N(2)—H(1) [N(2)]	0·97 (12)
N(2)—H(2) [N(2)]	0·93 (12)
C(11)–H(1) [C(11)]	1·00 (12)
C(11)–H(2) [C(11)]	1·05 (13)
C(11)–H(3)[C(11)]	1·11 (13)
O(2)—H[O(2)]	1·18 (13)
C(12)–H(1) [C(12)]	0·89 (12)
C(12)–H(2) [C(12)]	0·92 (13)
C(12)–H(3) [C(12)]	0·97 (13)

Table 4. *Anisotropic thermal parameters* ($\times 10^4$) *for non-hydrogen atoms*

Temperature factors are in the form

$$T=\exp(-h^2\beta_{11}-k^2\beta_{22}-l^2\beta_{33}-2hk\beta_{12}-2hl\beta_{13}-2kl\beta_{23}).$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	30 (1)	136 (1)	61 (1)	−7 (1)	−2 (1)	−6 (1)
C(1)	22 (3)	89 (11)	55 (6)	12 (4)	1 (3)	−5 (7)
C(2)	28 (3)	93 (12)	70 (8)	4 (5)	5 (4)	2 (7)
C(3)	34 (4)	99 (13)	85 (9)	0 (6)	11 (5)	6 (9)
C(4)	53 (5)	98 (13)	80 (9)	15 (7)	12 (6)	3 (9)
C(5)	41 (4)	114 (15)	73 (9)	21 (6)	−7 (5)	25 (9)
C(6)	28 (3)	104 (14)	76 (8)	19 (5)	−1 (4)	−16 (9)
C(7)	22 (3)	97 (12)	51 (6)	3 (4)	2 (3)	−11 (7)
N(1)	22 (2)	90 (10)	81 (7)	3 (4)	2 (3)	−16 (6)
O(1)	23 (2)	78 (8)	79 (6)	0 (3)	10 (3)	3 (5)
C(8)	30 (3)	80 (12)	59 (7)	6 (5)	9 (4)	−5 (7)
C(9)	21 (2)	77 (10)	49 (6)	0 (4)	0 (3)	−5 (6)
C(10)	27 (3)	63 (10)	52 (6)	6 (4)	0 (3)	−5 (6)
N(2)	25 (3)	101 (10)	54 (5)	4 (4)	5 (3)	18 (6)
N(3)	22 (2)	105 (11)	64 (6)	3 (4)	−4 (3)	2 (7)
C(11)	46 (5)	162 (18)	46 (7)	21 (7)	−6 (5)	−15 (9)
O(2)	22 (2)	113 (9)	88 (6)	0 (3)	−1 (3)	7 (6)
C(12)	28 (3)	112 (15)	103 (10)	8 (6)	12 (5)	−7 (10)
O(3)	32 (2)	88 (8)	77 (6)	8 (4)	12 (3)	19 (5)

Table 5 (*cont.*)

(*b*) Angles

C(1)—C(2)—C(3)	121·7 (1·1)°
C(2)—C(3)—C(4)	119·2 (1·1)
C(3)—C(4)—C(5)	119·0 (1·2)
C(4)—C(5)—C(6)	121·9 (1·2)
C(5)—C(6)—C(1)	118·4 (1·0)
C(6)—C(1)—C(2)	119·7 (1·0)
C(2)—C(1)—C(7)	119·4 (0·9)
C(6)—C(1)—C(7)	120·9 (0·9)
C(1)—C(7)—N(1)	121·6 (0·9)
C(1)—C(7)—C(9)	129·2 (0·9)
N(1)—C(7)—C(9)	108·9 (0·9)
C(7)—N(1)—O(1)	109·7 (0·8)
C(7)—N(1)—C(12)	131·0 (1·0)
C(12)–N(1)—O(1)	111·0 (0·8)
N(1)—O(1)—C(8)	107·0 (0·7)
O(1)—C(8)—C(9)	105·3 (0·8)
O(1)—C(8)—O(3)	119·7 (1·0)
O(3)—C(8)—C(9)	134·9 (1·0)
C(8)—C(9)—C(7)	109·0 (0·9)
C(8)—C(9)—C(10)	121·6 (0·9)
C(7)—C(9)—C(10)	128·9 (0·9)
C(9)—C(10)–N(2)	121·5 (0·9)
C(9)—C(10)–N(3)	118·4 (0·9)
N(2)—C(10)–N(3)	120·0 (0·9)
C(10)–N(3)—O(2)	116·9 (0·8)
C(10)–N(3)—C(11)	127·0 (0·9)
O(2)—N(3)—C(11)	115·2 (0·8)

C(1)————C(2)—H[C(2)]	127 (7)°
H[C(2)]——C(2)—C(3)	112 (7)
C(2)————C(3)—H[C(3)]	135 (8)
H[C(3)]——C(3)—C(4)	106 (7)
C(3)————C(4)—H[C(4)]	111 (6)
H[C(4)]——C(4)—C(5)	129 (6)
C(4)————C(5)—H[C(5)]	104 (8)
H[C(5)]——C(5)—C(6)	133 (8)
C(5)————C(6)—H[C(6)]	124 (7)
C(10)————N(2)—H(1) [N(2)]	97 (7)
C(10)————N(2)—H(2) [N(2)]	116 (8)
N(3)————O(2)—H[O(2)]	108 (6)
N(3)————C(11)–H(1) [C(11)]	101 (8)
N(3)————C(11)–H(2) [C(11)]	100 (8)
N(3)————C(11)–H(3) [C(11)]	98 (7)
N(1)————C(12)–H(1) [C(12)]	124 (7)
N(1)————C(12)–H(2) C(12)]	103 (7)
N(1)————C(12)–H(3) C(12)]	108 (7)
H(1) [N(2)]—N(2)—H(2) [N(2)]	147 (11)
H(1) [C(11)]–C(11)–H(2) [C(11)]	124 (10)
H(1) [C(11)]–C(11)–H(3) [C(11)]	98 (9)
H(2) [C(11)]–C(11)–H(3) [C(11)]	129 (10)
H(1) [C(12)]–C(12)–H(2) [C(12)]	84 (11)
H(1) [C(12)]–C(12)–H(3) [C(12)]	122 (11)
H(2) [C(12)]–C(12)–H(3) [C(12)]	109 (10)

Bond distances in the isoxazolin-5-one ring are comparable with those found in two other analogous compounds, *i.e.* in *N*-methyl-4-phenylisoxazolin-5-one (Sabelli & Zanazzi, 1969*a*) and in *N*-methyl-3-phenyl-4-bromoisoxazolin-5-one (Sabelli & Zanazzi, 1969*b*).

The phenyl ring is planar; the equation of the best plane (plane II) as well as the atomic deviations from this plane are listed in Table 6. The bonds C(1)–C(7) (1·45 Å) and C(9)–C(10) (1·46 Å) are significantly shorter than a single C–C bond while C(7)–C(9) is longer than a double C=C bond (1·37 Å). This seems to indicate a certain degree of conjugation between the phenyl ring and the atoms C(7), C(9) and (C10). However, the high value (39°45′) of the dihedral angle between plane I and plane II is consistent with only partial conjugation.

Table 6. *Least-squares planes*

(*a*) Least-squares plane of the heterocyclic ring

$$2{\cdot}542x + 4{\cdot}591y + 11{\cdot}987z - 6{\cdot}752 = 0$$

Atoms included in plane	Δ	Atoms not included in plane	Δ
C(7)	−0·01 Å	C(1)	+0·06 Å
N(1)	+0·02	C(10)	+0·15
O(1)	−0·02	O(3)	+0·10
C(8)	+0·01	C(12)	−0·57
C(9)	0·00		

(*b*) Least-squares plane of the phenyl ring

$$-10{\cdot}355x + 4{\cdot}608y + 9{\cdot}795z - 3{\cdot}818 = 0$$

C(1)	+0·00 Å	C(7)	+0·05 Å
C(2)	+0·01		
C(3)	−0·01		
C(4)	−0·01		
C(5)	+0·02		
C(6)	−0·01		

(*c*) Least-squares plane of the amidinic chain

$$1{\cdot}172x + 10{\cdot}656y + 0{\cdot}183z - 3{\cdot}818 = 0$$

N(2)	−0·06 Å	C(9)	+0·23 Å
C(10)	+0·05		
N(3)	+0·07		
O(2)	0·00		
C(11)	−0·06		

The proton of the hydrobromic acid has been found linked to the iminic nitrogen atom N(2).

In the amidinic chain, the distances C(10)–N(3) and C(10)–N(2) are equal; a resonance of the following type

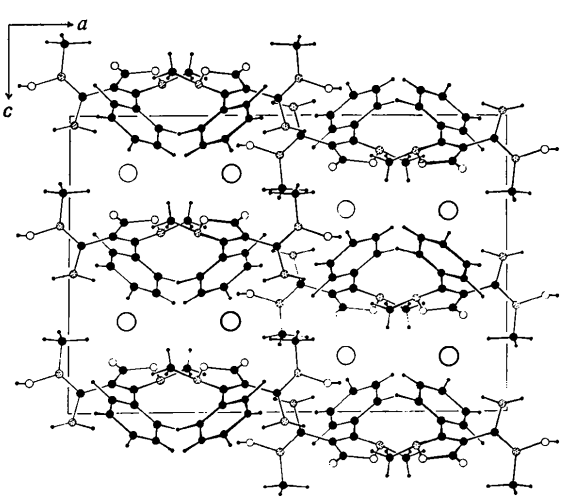


Fig. 1. Projection of the structure along the *b* axis.

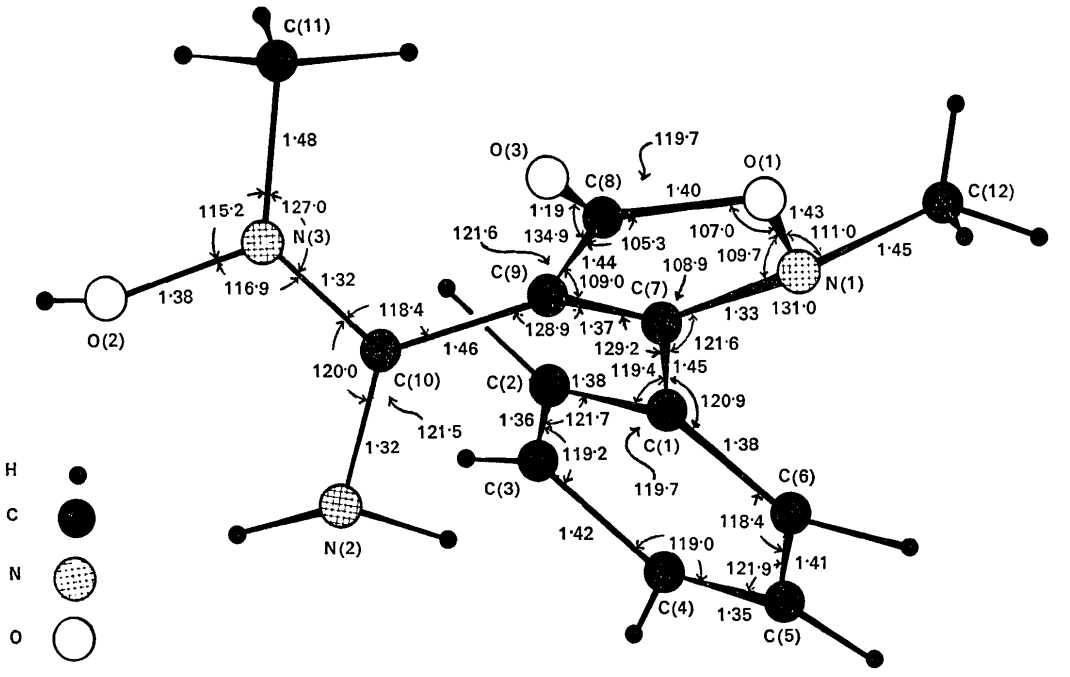
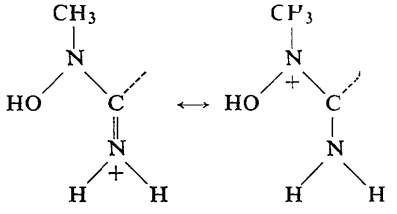


Fig. 2. Intramolecular bond distances and angles.



can account for this and for the approximate coplanarity of O(2), N(3) C(10), N(2) and C(9) (the equation of the least-squares plane – plane III – is given in Table 6, with the deviations of the atoms from the plane).

The C–H bond lengths have an average value of 1·02 Å. The mean N–H distance is 0·95 Å. Each bromide ion links two different molecules by hydrogen bonds to O(2) of one molecule and N(2) of another. The distance Br···O(2) is 3·09, Br··N(2) 3·31 Å. The corresponding bromine–hydrogen distances are Br···HO(2) 2·05 Å and Br···H(1) N(2) 2·53 Å.

References

ADEMBRI, G. & TEDESCHI, P. (1967). *Chim. Ind. (Milan)*, **49**, 879.

DE MEULENAER, J. & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

RAE, A. D. (1965). *Acta Cryst.* **19**, 683.

SABELLI, C. & ZANAZZI, P. F. (1969*a*). *Acta Cryst.* **B25**, 182.

SABELLI, C. & ZANAZZI, P. F. (1969*b*). *Acta Cryst.* **B25**, 192.