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## The Crystal Structure of Formamidoxime

BY D. HALL AND F. J. LLEWELLYN

*Department of Chemistry, Auckland University College, Auckland, New Zealand*

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Formamidoxime is orthorhombic,  $P2_12_12_1-D_2^2$ , with four molecules of  $\text{CH}_4\text{N}_2\text{O}$  in a unit cell of dimensions  $[a] = 8.22$ ,  $[b] = 7.36$ ,  $[c] = 4.78$  Å. The planar molecules, which are arranged in a series of hydrogen-bonded interlocking spirals, may be described in terms of the resonance structures  $\text{NH}_2-\text{CH}=\text{N}-\text{OH}$  (formamidoxime) and  $\text{NH}=\text{CH}-\text{NH}-\text{OH}$  (hydroxyformamidine). The formamidoxime contributor probably predominates.

### Introduction

Geometric isomerism to be expected in amidoximes has never been observed; Brady & Perkin (1929) suggest that in solution the tautomers  $\text{NH}_2-\text{CR}=\text{N}-\text{OH}$  (an amidoxime) and  $\text{NH}=\text{CR}-\text{NH}-\text{OH}$  (a hydroxyamidine) coexist in equilibrium. In the solid state such an equilibrium, involving the migration of a proton, is not possible unless, as in the case of isatin (Goldschmidt & Llewellyn, 1950), more than one molecule is involved in a resonance mechanism through a system of hydrogen bonds. In this investigation the structure of the first member of the series, formamidoxime  $\text{NH}_2-\text{CH}=\text{N}-\text{OH}$ , is reported.

### Experimental

Formamidoxime was prepared by treating hydroxylamine hydrochloride in methanol with sodium cyanide (Tiemann, 1884). Recrystallization from ethanol gave colourless deliquescent orthorhombic needles, m.p.  $105^\circ\text{C}$ .; very slow crystallization from the same solvent gave more evenly developed prisms, m.p.  $114^\circ\text{C}$ ., exhibiting  $\{011\}$  and various terminal faces. Both melting points have been recorded previously (Lossen & Schifferdecker, 1873; Nef, 1894). The optical properties and cell dimensions of these two crystal forms are identical. The forms differ only in the direction of maximum growth and in face development; the prisms

were used in all subsequent work. Optical examination was difficult because of the rapid deliquescence, but the crystals were shown to be biaxial and positive. Unit-cell dimensions were obtained from rotation photographs; all reflexions obtainable with Cu  $K\alpha$  radiation were recorded on equi-inclination Weissenberg photographs, using the multiple-film technique, and their intensities were estimated visually. The crystals were enclosed in perspex capsules during photography (Llewellyn, 1951). The cell dimensions are

$$[a] = 8.22, [b] = 7.36, [c] = 4.78 \text{ \AA}.$$

The density, measured by flotation, is  $1.365 \text{ g.cm.}^{-3}$ ; that calculated for 4 molecules of  $\text{CH}_4\text{N}_2\text{O}$  per cell is  $1.380 \text{ g.cm.}^{-3}$ . Absent spectra are  $\{h00\}$  when  $h \neq 2n$ ,  $\{0k0\}$  when  $k \neq 2n$ ,  $\{00l\}$  when  $l \neq 2n$ , whence the space group is  $P2_12_12_1$ . Intensities were made absolute by direct comparison with a few diffracted beams from *p*-dinitrobenzene crystals; the scaling factor was subsequently confirmed using Harker's procedure (Harker, 1948).

The Fourier summations were computed using Robertson's strips; in the three-dimensional difference Fourier sections and lines three-figure accuracy at intervals of  $6^\circ$  was achieved.

### Structure determination

By means of Harker-Kasper (1948) inequalities the following phase relationships in the  $\{hk0\}$  zone were obtained:

$$\begin{aligned} S_{200} = S_{600} = S_{800} = -S_{020} = -S_{220} = -S_{420} = -S_{040} \\ = S_{440} = -S_{640} = -S_{840} = S_{060} = S_{260} = S_{860} \\ = -S_{480} = +; \end{aligned}$$

$$S_{710} = S_{910} = -S_{130} = -S_{730} = -S_{930};$$

$$S_{210} = S_{810} = S_{230} = -S_{430} = -S_{250};$$

$$S_{170} = S_{770};$$

$$S_{320} = S_{360}.$$

To define the origin it was assumed that  $S_{710} = +$ , and  $S_{210} = -$ , and the phases of the 24  $\{hk0\}$  planes

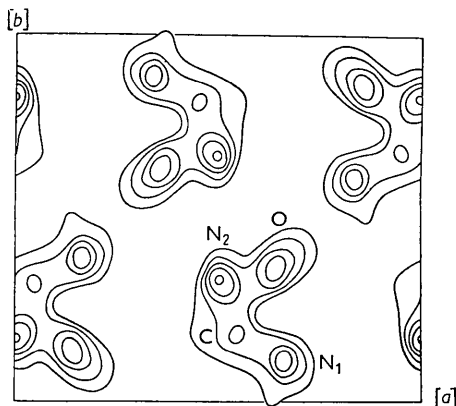


Fig. 1. Fourier projection on (001) using 24  $hk0$  planes whose phases were determined from inequalities. Contours are at arbitrary intervals.

thus determined were included in a Fourier projection on to 001 (Fig. 1). The accuracy of the  $x, y$  coordinates from this very limited Fourier synthesis proved extraordinarily good. Structure amplitudes calculated from the coordinates obtained from this projection (assuming  $Z = 7$  for all the atoms) agreed well with the observed values and a second synthesis was evaluated, using further  $\{hk0\}$  planes. From the relative heights of the peaks thus obtained it was possible to assign each peak to the appropriate atom in the molecule. Structure amplitudes were now calculated with the atoms correctly weighted, using a carbon scattering curve derived by McWeeny (1951) and a temperature factor  $B = 3.0 \text{ \AA}^2$ ; it was assumed that  $f_N = 1.16f_C$  and  $f_O = 1.33f_C$ . One further Fourier projection produced a stable phase pattern and completed the refinement of the  $x, y$  coordinates.

The  $z$  coordinates were readily obtained from the Harker-Patterson sections  $P_{x, \frac{1}{2}, z}$  and  $P_{\frac{1}{2}, y, z}$ , and these satisfied very closely those obtained from fitting a planar molecule with conventional bond distances and angles on to the  $x, y$  coordinates. The  $\{h0l\}$  structure amplitudes showed reasonable agreement with the observed values, but since neither the projection down  $[a]$  nor down  $[b]$  could possibly resolve all the atoms the coordinates were refined by means of three-dimensional Fourier sections and lines parallel, respectively, to (001) and [001] through each of the atoms. Very little change in atomic coordinates occurred; the temperature factor remained unaltered; the reliability factor  $\Sigma|F_o - F_c| \div \Sigma F_o$  was 0.17.

Two cycles of three-dimensional difference Fourier sections and lines passing through the coordinates of each atom reduced the reliability factor to 0.145. The final coordinates are:

Atom	$x$	$y$	$z$
C	0.294	0.297	0.242
N <sub>1</sub>	0.426	0.401	0.225
N <sub>2</sub>	0.256	0.160	0.083
O	0.379	0.134	-0.120

Difference Fourier projections on to (001), (010) and (100) gave evidence of a number of maxima, some of which could reasonably be ascribed to hydrogen; for others no explanation could be found. Three-dimensional difference Fourier sections and lines passing through the coordinates of all of these maxima were calculated, and, finally, bounded difference Fourier projections (Booth, 1948) parallel to (010) and of thickness  $0.1 [b]$  were evaluated throughout the whole of the molecular environment in order to ensure that none of the maxima was overlooked. Four, and only four, large maxima appeared with  $\rho_{\text{max}}$  between  $0.6$ – $0.85 \text{ e. \AA}^{-3}$  and within  $1.2 \text{ \AA}$  of a heavy atom. A general undulating background seldom exceeded  $0.25 \text{ e. \AA}^{-3}$  and once exceeded  $0.4 \text{ e. \AA}^{-3}$  at a distance greater than  $2 \text{ \AA}$  from any heavy atom. The unexplained maxima in the difference projections were due to superposition of two or more discrete smaller maxima. The coordinates of

Table 1. *Measured C-N bond lengths*

$R_{C-N}$ (Å)	Compound	Reference
1.39	Glycine	Albrecht & Corey, 1939
1.465	Methylamine hydrochloride	Hughes & Lipscomb, 1946
(cf. 1.47	Methylamine	Schomaker, 1950
1.48	Methylamine	Atoji & Lipscomb, 1953)
1.48 and 1.50	Hydroxy-L-proline	Donohue & Trueblood, 1952
1.48 and 1.51	$\beta$ -Glycyl glycine	Hughes & Moore, 1949
1.49	Geranylamine hydrochloride	Jeffrey, 1945
1.49	L <sub>s</sub> -Threonine	Shoemaker <i>et al.</i> , 1950
1.49	DL-Serine	Shoemaker <i>et al.</i> , 1953
1.50	DL-Alanine	Donohue, 1950
1.50	$\beta$ DL-Methionine	Mathieson, 1952
1.50	DL-Norleucine	Mathieson, 1953
1.50	Glycyl-L-tyrosine hydrochloride	Smits & Wiebenga, 1953
1.51	L-Glutamine	Cochran & Penfold, 1952
1.52	Hexamethylenediamine dihydrochloride	Binnie & Robertson, 1949
(cf. 1.51	Hexamethylenediamine	Binnie & Robertson, 1950)
1.52	$\alpha$ DL-Methionine	Mathieson, 1952
1.52	DL-Glutamic acid hydrochloride	Dawson, 1953

the four largest peaks with  $q_{\max.} > 0.6 \text{ e.}\text{\AA}^{-3}$  are designated  $H_1, H_2, H_3, H_4$  in the following table.

Peak	$x$	$y$	$z$	$q_{\max.} (\text{e.}\text{\AA}^{-3})$
$H_1$	0.518	0.391	0.082	0.60
$H_2$	0.202	0.317	0.396	0.65
$H_3$	0.376	0.068	-0.130	0.80
$H_4$	0.358	0.180	-0.147	0.85

It was assumed that these represent the coordinates of the four hydrogen atoms, and their contributions to the structure amplitudes were calculated; the reliability factor was reduced to 0.125. For reasons to be discussed later, it became obvious that the two maxima labelled  $H_3$  and  $H_4$  could not be caused by hydrogen atoms, but were in fact due to anisotropic vibration of the oxygen atom. The reliability factor with the inclusion of  $H_1$  and  $H_2$  maxima as hydrogen atoms is 0.13. Observed and calculated structure amplitudes are listed in Table 2.\*

### Discussion

The bond lengths  $C-N_1 = 1.330 \text{ \AA}$  and  $C-N_2 = 1.301 \text{ \AA}$  indicate that both are involved in single-bond-double-bond resonance. Cox & Jeffrey (1951) quote a large number of measured C-N single bonds and conclude that the best value is 1.47-1.48 Å, in agreement with Pauling's estimate. The bonds involved in this structure may, however, include C-N<sup>-</sup> and/or C-N<sup>+</sup> contributors. Pauling (1940) estimates that the C-N<sup>-</sup> single bond will be approximately 0.03 Å longer than the C-N single bond and that the C-N<sup>+</sup> will be correspondingly shorter. Table 1 includes a number of measured C-N<sup>+</sup> bonds in amine hydrochlorides and amino acid zwitterions; excepting only glycine there

is no evidence of any shortening, and where values are available for the amine and its hydrochloride there appears to be no significant difference. It was not possible to test the hypothesis that C-N<sup>-</sup> is longer than C-N, and it has therefore been assumed that C-N, C-N<sup>+</sup> and C-N<sup>-</sup> are all 1.475 Å. Various values have been quoted for C=N: 1.265 Å (Pauling, 1940), 1.27 Å (Gordy, 1947), 1.28 Å (Cox & Jeffrey, 1951), 1.24 Å (Vaughan & Donohue, 1952). Godycki & Rundle (1953) report values of 1.21 Å and 1.25 Å in nickel dimethyl glyoxime, supporting the smaller value of Vaughan & Donohue, but calculation (following Cruickshank, 1949) shows that the shortest bond in dimethyl glyoxime (1.21 Å), with standard deviation 0.03 Å, is not definitely significantly different from the longest bond (1.28 Å). Other carbon-nitrogen separations which involve considerable but not pure double-bond character are: 1.27 Å in 2-amino-4,6-dichloropyrimidine (Clews & Cochran, 1948), 1.27 Å in dimethyl glyoxime (Merritt & Lanterman, 1952), 1.29 Å in acetoxime (Bierlein & Lingafelter, 1951); all these values favour the lower figure (1.265 Å) for pure C=N.

Taking the bond lengths C-N = 1.475 Å and C=N = 1.265 Å, the C-N<sub>1</sub> bond in formamidoxime is 40% double bond and the C-N<sub>2</sub> bond is 60% double bond. If Vaughan & Donohue's values, 1.48 Å and 1.24 Å respectively, are used, a less satisfactory result is obtained: C-N<sub>1</sub> = 35% double bond, C-N<sub>2</sub> = 50% double bond.

Consideration of the standard deviations shows that the difference in the observed lengths of the bonds C-N<sub>1</sub> and C-N<sub>2</sub> is significant only if the length of a C-N bond with 50% double-bond character lies outside the range 1.30-1.33 Å. This is most improbable since of the values quoted for the single- and double-bond distances, only the shortest (1.465 and 1.24 Å respectively) lead to a value outside this range. Thus it cannot be asserted that the formamidoxime-type structure is the major contributor but it is highly probable that its contribution is not less than 50%.

\* Table 2 has been deposited as Document No. 4737 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Pauling (1940) estimates the N–O single-bond length to be 1.36 Å, but this differs considerably from that of Schomaker & Stevenson (1941) of 1.435 Å. Measured N–O bonds, which are predominantly single, range between 1.37 Å and 1.45 Å: 1.37 Å and 1.38 Å in nickel dimethyl glyoxime (Godycki & Rundle, 1953), 1.38 Å in dimethyl glyoxime (Merritt & Lanterman, 1952), 1.41 Å in nitric acid (Maxwell & Moseley, 1940), 1.43 Å in *O*-methyl hydroxylamine (Schomaker & Stevenson, 1941), 1.45 Å in hydroxylamine hydrochloride and hydroxylamine hydrobromide (Jerslev, 1948). The N<sub>2</sub>–O bond in formamidoxime is 1.414 Å, and is probably predominantly of single-bond character.

The heavy atom coordinates indicate, therefore, resonance between the two bond systems, N<sub>1</sub>–C=N<sub>2</sub>–O and N<sub>1</sub>=C–N<sub>2</sub>–O, probably in proportion 60:40. The N<sub>1</sub>–C–N<sub>2</sub> bond angle 127°, and the C–N<sub>2</sub>–O bond angle 109½° are consistent with this view, and in reasonable agreement with bond angles in other compounds containing the *cis* planar R–C=N–R' grouping, unrestricted by ring formation (see Bierlein & Lingafelter (1951), Merritt & Lanterman (1952), and also Holmes & Powell (1953)).

The only intermolecular separations worthy of comment are N<sub>2</sub>–O' = 2.81 Å, N<sub>1</sub>–O' = 3.01 Å and N<sub>1</sub>–N<sub>2</sub>' = 3.12 Å. These represent the principal cohesive forces within the crystal constituting interlocking spirals of hydrogen bonds parallel to [c].

The atoms C, N<sub>1</sub>, N<sub>2</sub>, O, H<sub>1</sub> and H<sub>2</sub> are effectively coplanar; if their coordinates are expressed in Ångström units the equation of the plane through the atoms N<sub>1</sub>, N<sub>2</sub> and O is

$$0.904x - 1.160y + 1.170z = 1$$

and the displacements of the other atoms from this

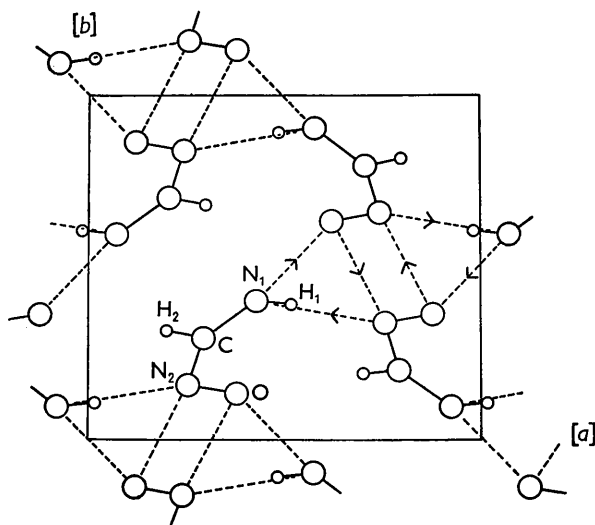


Fig. 2. The structure projected on (001). Short intermolecular separations indicated by broken lines; arrows indicate positive direction in [c].

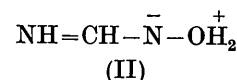
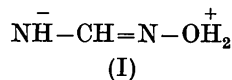
plane are: C, 0.001 Å; H<sub>1</sub>, 0.017 Å; H<sub>2</sub>, 0.005 Å. The general configuration of the heavy atoms is that of the *anti* oxime (it should be noted that the terms *syn* and *anti* refer to the position of the oxygen atom relative to the simplest substituent on the carbon atom). The standard deviations in the coordinates of the heavy atoms, and in the bond lengths and bond angles, were calculated by Cruickshank's method (Cruickshank, 1949). A projected view of the structure is shown in Fig. 2. Bond lengths and bond angles, with their standard deviations in parentheses, are:

N <sub>1</sub> –C	1.330 Å	(0.011 Å)
N <sub>2</sub> –C	1.301 Å	(0.010 Å)
N <sub>2</sub> –O	1.414 Å	(0.009 Å)
N <sub>1</sub> –C–N <sub>2</sub>	127° 21'	(41')
C–N <sub>2</sub> –O	109° 31'	(34')

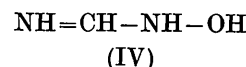
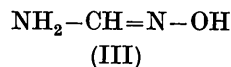
Other distances and angles involving the difference Fourier maxima H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub> and H<sub>4</sub> for which no standard deviations were calculated are:

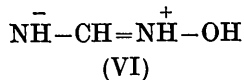
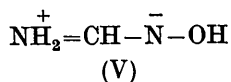
N <sub>1</sub> –H <sub>1</sub>	1.02 Å	C–N <sub>1</sub> –H <sub>1</sub>	127°
C–H <sub>2</sub>	1.06	N <sub>1</sub> –C–H <sub>2</sub>	123
O–H <sub>3</sub>	0.40	N <sub>2</sub> –C–H <sub>2</sub>	110
O–H <sub>4</sub>	0.49	N <sub>2</sub> –O–H <sub>3</sub>	100
		N <sub>2</sub> –O–H <sub>4</sub>	78
		H <sub>3</sub> –O–H <sub>4</sub>	142

If H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub>, H<sub>4</sub> represent hydrogen atoms the two principal structures must be (I) and (II):

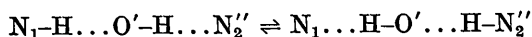


Considerable doubt is cast, however, on the identification of H<sub>3</sub> and H<sub>4</sub> with hydrogen atoms, because (a) the relative electronegativities of oxygen and nitrogen suggest that neither of the resonance hybrids (I) and (II) will be very stable, (b) the distances O–H<sub>3</sub> (0.49 Å) and O–H<sub>4</sub> (0.40 Å) are abnormally short, (c) the bond distribution about the oxygen atom is inconsistent with hybrid bonds (*sp*<sup>2</sup> or *sp*<sup>3</sup>) or pure *p* bonds for the oxygen linkages. Inspection of the various difference Fourier syntheses showed that the two maxima H<sub>3</sub> and H<sub>4</sub> occur along with two minima, the four being arranged approximately at the corners of a square with the oxygen atom at the intersection of the diagonals; it is reasonable to interpret this in terms of anisotropic vibration of the oxygen atom. No such doubts occur with H<sub>1</sub> and H<sub>2</sub>, and these maxima are ascribed to hydrogen atoms. A satisfactory explanation of the observed bond distances is obtained in terms of (III) and (IV) as the major contributors, with (V) and (VI) possibly contributing to a lesser extent.





The location of  $\text{H}_1$  near the intermolecular line  $\text{N}_1 \dots \text{N}'_2$  (see Fig. 2) and the  $\text{N}_1 \dots \text{N}'_2$  separation of 3.12 Å indicate weak hydrogen bonding. Hydrogen atoms corresponding to the stronger  $\text{N}_1-\text{O}'$  (2.81 Å) and  $\text{N}_2-\text{O}'$  (3.01 Å) hydrogen bridges have not been detected. If the resonance mechanism involving (III) and (IV) can be explained in terms of a two-step process



it is possible that the hydrogen atoms concerned are non-localized, as has been reported in the structure of orthoboric acid (Cowley, 1953). Simple resonance may then be postulated additionally between (III) and (V) and between (IV) and (VI), but the extent is not determinable by crystallographic methods.

It is, however, equally feasible that the accuracy of this analysis is scarcely sufficient for hydrogen atom location, and that it is of no significance that only two such atoms have been detected. The most suitable description would then be in terms of (III) and (V).

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