

# A Neutron Diffraction Refinement of the Crystal Structure of Dimethylglyoxime\*

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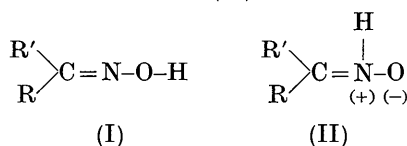
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Neutron diffraction data for two zones of dimethylglyoxime have been refined and the locations of all atoms, including hydrogen, determined. The structure has the normal O-H...N hydrogen bond rather than the zwitterion structure which has been proposed. The O-H bond length is  $1.02 \pm 0.04$  Å, and the O-H...N hydrogen bond angle is  $140 \pm 3^\circ$ , a significant departure from the usually assumed linear configuration. The methyl group may be somewhat distorted from the ideal tetrahedral shape. The other bond lengths and angles, although in some disagreement with the X-ray results, are in good agreement with those in related compounds. Of particular interest is the difference of 0.08 Å in the two C-C single bond lengths.

## Introduction

There has been some discussion in recent years as to whether normal oximes have the classical structure (I) or the zwitterion structure (II):



Based on the fact that the preliminary results of an X-ray investigation (Jerslev, 1950) of *syn-p*-chlorobenzaldoxime led to an O-N...O' angle of  $101.4^\circ$  and an N-O...N' angle of  $82^\circ$ , a suggestion was made by Pitt (1950) that the correct structure is the zwitterion structure. Under the assumption that the hydrogen bond is linear, such a structure would lead to a more satisfactory covalent bond angle in the molecule. A structure determination of acetoxime (Bierlein & Lingafelter, 1951), which is constructed of cyclic trimers, led to no further information on this point, as the two relevant angles are both larger than tetrahedral and thus compatible with either structure. The structure of dimethylglyoxime (Merritt & Lanterman, 1952), although cited by Dunitz & Robertson (1952) as supporting the zwitterion structure, is actually inconclusive, as the two angles involved are both near  $90^\circ$ , as was pointed out by Donohue (1956). The latter author also cites the structure of formamidoxime (Hall & Llewellyn, 1956) as supporting the classical non-polar structure. A recent infrared study (Orville-Thomas & Parsons, 1958) would seem to confirm the structure  $\text{H}_2\text{N}-\text{CH}=\text{N}-\text{O}-\text{H}$  for formamidoxime, as frequencies were observed which could be assigned to the O-H, C-H, and  $\text{NH}_2$  groupings.

In none of the above X-ray diffraction studies was the data of sufficient quality to determine hydrogen

atom positions unambiguously, although a small bump on the oxygen atom in a Fourier projection of dimethylglyoxime was interpreted as an indication that the bonding was O-H rather than N-H. It seemed clear that a neutron diffraction study of an oxime would provide valuable evidence on this question.

## Crystal structure

Crystals of dimethylglyoxime were reported by McCrone (1949) to be triclinic with  $Z=1$  and the cell constants indicated in Table I. A three-dimensional X-ray investigation was undertaken by Merritt & Lanterman (1952), who analyzed the structure on the basis of a centrosymmetric molecule and determined positions of the heavy atoms to an estimated accuracy of 0.01 Å. The quoted  $R$  factor was 0.196, with the calculated structure factors including hydrogen atom contributions; the hydrogen in the hydrogen bond was assumed to lie on the O...N line at a distance of 0.96 Å from oxygen, and the methyl group was assumed to be tetrahedral with a C-H bond length of 1.07 Å. Hydrogen bonds link the planar molecules in infinite chains, with the molecules approximately parallel to (101). Two overall temperature factors were determined,  $B=2.85$  Å<sup>2</sup> in the plane of the molecule and  $B=3.82$  Å<sup>2</sup> perpendicular to this plane. A standard deviation of 0.02 Å in the bond lengths with a maximum error of 0.05 Å was quoted.

## Experimental

Dimethylglyoxime crystals were obtained by slow evaporation of a saturated solution in ethanol. The cell constants given in Table I were obtained by a least squares fit to powder diffraction line positions obtained with a carefully calibrated X-ray diffractometer using Cu  $K\alpha$  radiation ( $\lambda=1.542$  Å). The crystal chosen for the collection of neutron diffraction data was an approximate rectangular parallelepiped with

\* Research performed under the auspices of the U.S. Atomic Energy Commission.

dimensions  $8.5 \times 2 \times 1$  mm., the long dimension being parallel to the  $c$  axis. (To reduce absorption, the crystal was cut approximately in half for collection of  $0kl$  data.)

Table 1. Cell constants for dimethylglyoxime

	McCrone (1949)	Merritt & Lanterman (1952)	Present work
$ a $	6.07 Å	6.10 Å	$6.053 \pm 0.015$ Å
$ b $	6.39	6.30	$6.292 \pm 0.015$
$ c $	4.48	4.48	$4.468 \pm 0.010$
$\alpha$	125°	122.52°	$122.37 \pm 0.2$ °
$\beta$	91	90.10	$91.56 \pm 0.1$
$\gamma$	79	79.02	$77.63 \pm 0.3$

The indicated errors in the cell constants are those estimated from the goodness of fit to the eleven well-resolved lines in the powder pattern; the true standard errors, particularly for the angles  $\alpha$  and  $\beta$ , may be somewhat larger. The bond distances and angles calculated for the structure are in any case relatively insensitive to the values of these angles, so that the discrepancies between the present values and those of Merritt and Lanterman are not serious.

Intensities for 77  $hk0$  and 53  $0kl$  reflections with  $d^* < 1.27$  Å<sup>-1</sup> were measured to an estimated accuracy of 10%,<sup>†</sup> using a monochromatized neutron beam with a wave length of 1.067 Å. The monochromatic neutron flux at the crystal was approximately  $10^5$  neutrons cm.<sup>-2</sup> sec.<sup>-1</sup>. Absorption corrections were calculated for the actual shape crystal used by a program for the IBM 704 computer which calculates combined extinction and absorption corrections for crystals of arbitrary shape.<sup>‡</sup> Examination of the data after refinement of the structure indicated that extinction was negligible. Structure factors were derived from the corrected intensities and placed on an absolute scale by the method of Wilson (1942).

### Refinement of the structure

#### (a) [001] zone

Structure factors were calculated omitting the hydrogen contributions, using the heavy-atom parameters from the X-ray investigation. The signs of the structure factors so obtained were used together with the experimental magnitudes in the calculation of a Fourier projection. This projection showed the approximate positions of all four hydrogen atoms and indicated clearly that the hydrogen bond is of the O-H...N type. (See Figs. 1 and 2.)

A series of least-squares refinements was carried out with an IBM 704 program which obtains the complete least-squares solution, including the off-diagonal terms which are frequently neglected. Weights were

<sup>†</sup> There is a greater uncertainty for some of the weak reflections due to the occasionally uneven incoherent peaks. This error was taken into account in the weighting.

<sup>‡</sup> The linear absorption coefficient of 2.18 cm.<sup>-1</sup> was calculated using effective atomic absorption cross sections of 38.4 barns for H, 1.1 barns for N, and 0 for O and C.

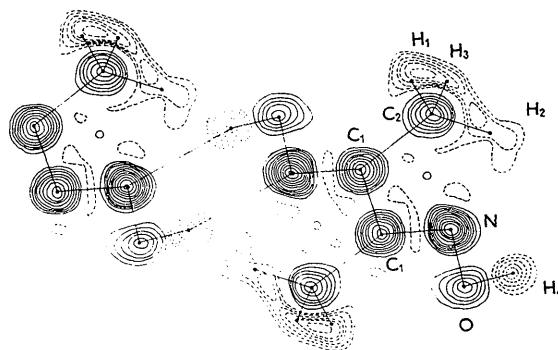


Fig. 1. Final Fourier projection along [001]. Arbitrary contour interval. Negative contours are dashed, and all contours but the zero contour are shown. The positions marked  $H_1$  and  $H_3$  are not the final positions shown in Fig. 2.

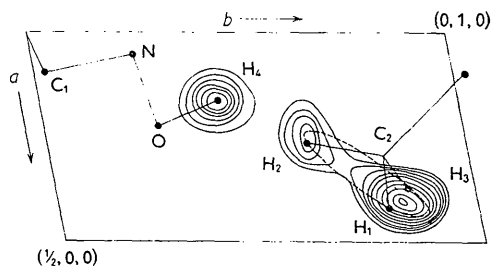


Fig. 2.  $(F_{OBS} - F_{CNO})$  Fourier projection along [001]. All contours are negative, the contour interval being approximately twice that in Fig. 1 with the lowest two contours omitted. Note the absence of heavy atom diffraction effects as compared with Fig. 1. The dashed ellipse indicates possible hydrogen positions for a tetrahedral methyl group.

chosen inversely proportional to the estimated variances of the observed structure factors. An individual isotropic temperature factor was assigned to each atom, and four cycles of least squares<sup>†</sup> reduced the quantity

$$R' = [\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2]^{\frac{1}{2}}$$

to 0.084. The corresponding value of

$$R = \sum w^{\frac{1}{2}} ||F_o| - |F_c|| / \sum w^{\frac{1}{2}} |F_o|$$

was 0.104. Further least-squares cycles in which the temperature factor on each atom was allowed to become anisotropic reduced  $R'$  to 0.036 and indicated significant vibrational anisotropy for the hydrogen atoms. There was also some improvement in the estimated standard deviations of the positional parameters.

#### (b) [100] zone

Trial values of the hydrogen atom parameters were obtained as for the [001] zone. The isotropic

<sup>†</sup> Refinement was stopped when the changes in positional parameters were approximately  $10^{-4}$  or  $10^{-5}$ , i.e. about  $0.01\sigma - 0.1\sigma$ .

refinement converged at  $R' = 0.098$ . Due to the limited amount of data collected for this zone, it was impossible to simultaneously refine all parameters, including anisotropic temperature factors, at this stage. However, subsequent refinement of positional and thermal parameters alternately brought the value of  $R'$  down to 0.023, without significantly improving the estimates of error on the positional parameters. The estimated errors of the thermal parameters were so large as to make it clear that no real improvement in the structure was being obtained, despite the low value of  $R'$ . The values of the  $y$  parameters obtained from this zone were within statistical error of those obtained from the [001] zone. Fouriers for this zone are shown in Fig. 3. It will be noted that  $H_3$  has a considerably lower peak height than the other hydro-

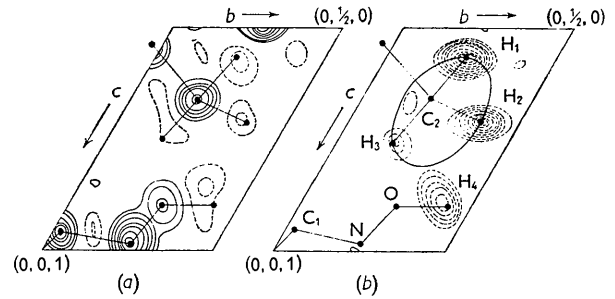


Fig. 3. (a) Fourier projection along [100]. Contour interval about half that in Fig. 1. Zero contour not shown. (b) Hydrogen density only projected along [100]. Contour interval comparable to that of Fig. 2. Note weakness of  $H_3$  as compared to  $H_1$  and  $H_2$ .

Table 2. Observed and calculated structure factors

$F_o$ 's are calculated for the parameters given in Table 4  
Atomic scattering factors used were N, 0.94; O, 0.58; C, 0.659; and H,  $-0.378 \times 10^{-12}$  cm.

(hkl)		$ F_o $	$F_c$	$\Delta F$	$ F_o $	$F_c$	$\Delta F$	$k$	$l$	$ F_o $	$F_c$	$\Delta F$		
0	1	2.11	2.34	-0.23*	6	3	0.94	1.03	-0.09	1	4	1.84	-1.32	-0.52
0	2	2.05	-2.06	0.01	6	4	0.56	-0.38	-0.19	2	0	2.05	-1.85	-0.20
0	3	0.44	0.59	-0.15	6	5	1.12	-1.16	0.04	2	1	0.72	-0.98	0.26
0	4	3.63	3.24	0.39	7	0	1.12	-0.97	-0.15	2	2	1.41	1.89	-0.48
0	5	1.16	0.99	0.17	1	-6	0.54	-0.59	0.04	2	3	1.34	-1.30	-0.04
0	6	0.41	0.05	0.37	1	-5	1.48	1.46	0.02	3	0	0.48	0.68	-0.20
1	0	3.42	3.44	-0.02	1	-4	3.42	3.68	-0.25	3	1	1.05	1.02	0.02
1	1	0.17	0.03	0.14	1	-3	0.28	0.03	0.25	3	2	0.62	-0.72	0.10
1	2	0.67	-0.79	0.12	1	-2	1.88	-1.87	-0.00	3	3	1.22	-1.35	0.12
1	3	1.50	1.55	-0.06	1	-1	3.22	3.14	0.08	4	0	3.80	3.35	0.45
1	4	0.51	0.65	-0.14	2	-6	0.27	0.18	0.09	4	1	2.46	2.62	-0.16
1	5	0.36	-0.27	-0.09	2	-5	1.41	1.06	0.36	4	2	0.52	0.72	-0.19
1	6	0.40	-0.23	-0.17	2	-4	1.08	0.82	0.26	5	0	1.22	0.85	0.36
2	0	0.54	0.65	-0.10	2	-3	0.15	-0.09	-0.06	5	1	1.30	1.36	-0.06
2	1	1.41	-1.35	-0.06	2	-2	1.60	1.67	-0.07	6	0	0.60	0.41	0.19
2	2	0.65	0.60	0.05	2	-1	0.44	0.61	-0.17	1	-5	0.73	-1.33	0.60
2	3	2.44	2.47	-0.03	3	-5	1.69	1.58	0.11	1	-4	0.36	-0.58	0.22
2	4	0.31	-0.25	-0.06	3	-4	0.51	-0.27	-0.25	1	-3	1.80	-1.50	-0.30
2	5	0.40	-0.75	0.35	3	-3	2.08	-1.91	-0.17	1	-2	2.78	-2.69	-0.09
2	6	1.46	-1.46	0.01	3	-2	1.10	0.92	0.18	1	-1	0.22	-0.05	-0.16
3	0	1.36	1.20	0.17	3	-1	1.53	1.34	0.18	2	-5	0.94	-1.45	0.50
3	1	2.12	-2.13	0.01	4	-5	0.81	0.86	-0.05	2	-4	1.70	-1.65	-0.05
3	2	2.42	-2.62	0.20	4	-4	0.89	0.72	0.17	2	-3	2.04	-2.06	0.02
3	3	0.29	0.09	0.20	4	-3	1.28	-0.88	-0.40	2	-2	1.02	-1.32	0.30
3	4	1.09	1.19	-0.11	4	-2	2.59	-2.21	-0.38	2	-1	0.63	-0.07	-0.56
3	5	0.12	-0.27	0.14	4	-1	0.56	-0.33	-0.24	3	-5	<0.35	0.10	0.25
3	6	1.45	-1.54	0.09	5	-4	0.64	-0.53	-0.11	3	-4	1.15	-1.24	0.09
4	0	1.08	0.93	0.15	5	-3	0.39	-0.58	0.19	3	-3	2.20	-2.38	0.18
4	1	0.38	-0.47	0.09	5	-2	0.53	-0.86	0.32	3	-2	3.29	3.29	0.01
4	2	1.40	-1.43	0.02	5	-1	0.57	0.38	0.20	3	-1	2.43	2.43	0.00
4	3	1.41	-1.75	0.34	6	-3	2.01	-1.91	-0.10	4	-5	<0.32	0.01	0.30
4	4	0.28	-0.24	-0.04	6	-2	0.11	-0.03	-0.08	4	-4	1.18	-1.08	0.09
4	5	1.62	-1.59	-0.03	6	-1	1.62	1.30	0.32	4	-3	1.70	1.36	0.34
4	6	0.89	-0.77	-0.12	7	-1	0.12	-0.05	-0.08	4	-2	0.91	1.59	-0.69
5	0	1.93	-1.80	-0.13	(0kl)					4	-1	<0.26	-0.05	-0.22
5	1	3.18	-3.23	0.05	$k$	$l$	$ F_o $	$F_c$	$\Delta F$	5	-5	2.53	-2.56	0.03
5	2	0.14	0.11	0.03	0	1	3.09	3.29	-0.20	5	-4	1.84	-1.19	-0.65
5	3	1.41	1.23	0.19	0	2	0.92	0.42	0.50	5	-3	0.71	0.29	0.42
5	4	0.28	-0.72	0.44	0	3	1.68	1.53	0.15	5	-2	1.38	-1.59	0.21
5	5	2.43	-2.92	0.49	0	4	0.62	0.43	0.19	5	-1	0.64	-0.42	-0.21
6	0	1.25	-1.32	0.07	1	0	2.27	2.35	-0.07	6	-5	1.64	-1.47	-0.16
6	1	2.62	-2.95	0.33	1	1	1.84	1.72	0.12	6	-4	1.82	-1.12	0.70
6	2	0.77	-1.09	0.32	1	2	1.94	1.91	0.03	6	-3	2.45	-2.24	-0.21
					1	3	1.95	1.85	0.11	6	-2	1.95	-2.12	0.17
										6	-1	0.50	-0.79	0.29

\*  $\Delta F$  may disagree by 0.01 with the difference between the tabulated  $F_o$  and  $F_c$ . All values were calculated to eight significant figures and then truncated to three.

gen atoms in this projection, in agreement with the high temperature factor obtained from the least-squares treatment. It is felt that this is due to systematic errors in the data rather than to anything real. Both Fourier projections and the least-squares refinements agree on the position of this atom.

(c) *Final refinement*

The data for both zones were combined, and all positional parameters, starting with the average of parameters from the separate refinements, were refined simultaneously. Again, an attempt to refine temperature factors anisotropically led to unrealistic values for these parameters in the [100] projection. The two zones of data were again refined separately, holding the  $y$  parameters fixed at the best values from the combined refinement. Separate isotropic temperature factors were obtained for each zone. The final values of  $R'$  and  $R$  are, for the [001] zone, 0.090 and 0.088 and for the [100] zone, 0.123 and 0.121. Values of observed and calculated structure factors and their differences are presented in Table 2.

### Results

The final parameter values and their least-squares-calculated standard deviations are presented in Table 3. The X-ray results are also listed. There is no clear correspondence between the positions of the methyl hydrogens assumed in the X-ray work and those found here. Only the isotropic temperature factor values are presented. For only the hydrogen atoms does the thermal anisotropy appear to be significant, but, as all components of the matrices have not been determined, no further discussion of the anisotropies will be given here other than to say that the motion comes nowhere near approaching free rotation of the methyl group. This will be apparent from inspection of the Fouriers, particularly that for the [100] zone. It will be noted that the methyl group temperature factors derived for the [100] zone do not appear altogether reasonable. This would seem to indicate further that there are in this zone unknown sources of experimental error, unfortunately reflected in the large standard deviations for the  $z$  parameters. It should be remarked that the correlation coefficients between positional and thermal parameters were generally small and that changing from isotropic to anisotropic temperature factors or vice versa did not change any coordinate by much more than the final standard deviations quoted.

The eight heavy atoms lie within statistical error on the plane

$$0.996x - 0.083y + z = 0.$$

The deviations of the atomic positions from this plane are  $C_1$ ,  $-0.03$  Å;  $C_2$ ,  $0.00$  Å;  $N$ ,  $-0.02$  Å; and  $O$ ,  $0.02$  Å.

Interatomic distances and bond angles are presented

Table 3. *Atomic positions and isotropic temperature factors in dimethylglyoxime*

	Position	Value	Standard deviation	X-ray
$C_1$	$x$	0.0907	0.0013	0.085
	$y$	0.0196	0.0014	0.016
	$z$	0.9016	0.0029	0.907
	$B_{001}$	1.55	0.20	
	$B_{100}$	0.66	0.55	
$C_2$	$x$	0.7062	0.0027	0.701
	$y$	0.1918	0.0022	0.194
	$z$	0.3086	0.0031	0.289
	$B_{001}$	1.89	0.33	
	$B_{100}$	1.67	0.65	
$N$	$x$	0.0526	0.0013	0.052
	$y$	0.2437	0.0016	0.238
	$z$	0.9623	0.0033	0.952
	$B_{001}$	2.24	0.19	
	$B_{100}$	2.50	0.65	
$O$	$x$	0.2187	0.0027	0.222
	$y$	0.2718	0.0035	0.266
	$z$	0.8104	0.0076	0.781
	$B_{001}$	3.61	0.40	
	$B_{100}$	4.42	1.10	
$H_1$	$x$	0.5881	0.0156	
	$y$	0.2149	0.0097	
	$z$	0.1423	0.0116	
	$B_{001}$	6.53	1.40	
	$B_{100}$	2.50	1.52	
$H_2$	$x$	0.7415	0.0110	
	$y$	0.3764	0.0082	
	$z$	0.3849	0.0087	
	$B_{001}$	5.27	0.80	
	$B_{100}$	1.95	1.04	
$H_3$	$x$	0.6374	0.0100	
	$y$	0.1647	0.0075	
	$z$	0.5098	0.0330	
	$B_{001}$	11.51	4.20	
	$B_{100}$	8.80	4.0	
$H_4$	$x$	0.1631	0.0046	0.118)*
	$y$	0.4304	0.0046	(0.456)*
	$z$	0.7952	0.0151	(0.845)*
	$B_{001}$	4.54	0.66	
	$B_{100}$	6.02	2.23	

\* Assumed.

in Table 4. The standard deviations were calculated using all the relevant correlation coefficients from the least squares error matrix.

Perhaps the most interesting feature of the structure is the hydrogen-bonding network (see Fig. 4). The  $O-H \cdots N$  angle of  $140^\circ$  departs greatly from the ideal linear hydrogen bond so often discussed in the literature. It shows clearly that other factors, such as the tendency of the covalent bond angles to remain undistorted and steric repulsion between hydrogen atoms, can outweigh any inherent tendency of the hydrogen bond to be linear. It would also seem to be important to have the hydrogen atom directed toward the lone-pair orbital of the nitrogen atom, which seems to be approximately the situation in this molecule. This result shows clearly the danger of making such arguments as those referred to in the introduction to

Table 4. *Interatomic distances in Å and bond angles in degrees in dimethylglyoxime*

In molecule			
C <sub>1</sub> -C <sub>1</sub>	1.562 ± 0.018	∗ C <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	120.0 ± 0.9
C <sub>1</sub> -C <sub>2</sub>	1.479 ± 0.015	∗ C <sub>1</sub> -C <sub>1</sub> -N	113.8 ± 0.9
C <sub>1</sub> -N	1.253 ± 0.011	∗ C <sub>2</sub> -C <sub>1</sub> -N	126.0 ± 1.0
N-O	1.321 ± 0.021	∗ H <sub>4</sub> -O-N	109.6 ± 2.1
C-H <sub>4</sub>	1.020 ± 0.036	∗ C <sub>1</sub> -N-O	111.4 ± 0.9
C <sub>2</sub> -H <sub>1</sub>	1.061 ± 0.072	∗ H <sub>1</sub> -C <sub>2</sub> -C <sub>1</sub>	111.8 ± 3.5
C <sub>2</sub> -H <sub>2</sub>	1.091 ± 0.061	∗ H <sub>2</sub> -C <sub>2</sub> -C <sub>1</sub>	109.4 ± 3.0
C <sub>2</sub> -H <sub>3</sub>	1.107 ± 0.065	∗ H <sub>3</sub> -C <sub>2</sub> -C <sub>1</sub>	109.3 ± 3.1
H <sub>1</sub> ...H <sub>4</sub>	2.842 ± 0.063	∗ H <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	88.1 ± 5.8
		∗ H <sub>1</sub> -C <sub>2</sub> -H <sub>3</sub>	115.8 ± 1.4
		∗ H <sub>2</sub> -C <sub>2</sub> -H <sub>3</sub>	121.0 ± 3.3
			Mean = 110.2 ± 1.4
			Mean = 108.3 ± 1.1
			Σ = 359.8 ± 0.2
In hydrogen-bond network			
O...N	2.766 ± 0.020	∗ O-H...N	140.0 ± 2.5
N...H <sub>4</sub>	1.906 ± 0.020	∗ O-N...H	106.2 ± 1.5
N...N	2.981 ± 0.019	∗ N-O...N	86.0 ± 0.7
O...O	3.147 ± 0.031	∗ O-N...O	94.0 ± 0.7

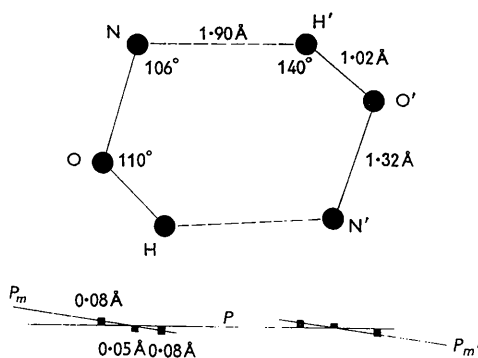


Fig. 4. Hydrogen bonding network in dimethylglyoxime. The line  $P$  at the bottom indicates the best plane through the six atoms; the deviation of the atoms from this plane are drawn to the same scale as is the upper drawing. The best molecular planes  $P_m$  and  $P'_m$  make angles of  $7^\circ$  with plane  $P$ .

this paper which depend explicitly on the assumption of a linear hydrogen bond. The O-H bond length is in excellent agreement with that found in heavy ice (Peterson & Levy, 1957) where the O...O distance is almost precisely the same as the O...N distance here. The present result is also in good agreement with the curve drawn by Lippincott & Schroeder (1955) giving O-H distance as a function of O...O distance, and also with that of Pimentel and McClellan (1960) for O-H...N hydrogen bonds.

It is interesting to note that the hydrogen-bonding network itself is approximately planar, the best least-squares plane through the atoms O, H, N, O', H', and N' being

$$x + 0.137y + 0.867z - 0.0685 = 0.$$

The deviations from planarity are here, however, statistically significant. This plane makes an angle of only  $7^\circ$  with the molecular plane (see Fig. 4). As Jerslev (1957) has pointed out, the hydrogen bond system in dimethylglyoxime is almost identical to that in *syn-p*-chlorobenzaldoxime. Indeed the N-O...N

and O-N...O angles are almost exactly the same, and the position of the hydrogen atom guessed by Jerslev on steric grounds is very close to that found here.

Although the C-H bond lengths and the C-C-H angles are closer to the ideal values than one might expect, the agreement between the H-C-H angles and the ideal tetrahedral value is far from pleasing. Each of these angles lies three to four standard deviations away from the ideal value. The data thus seem to indicate that there is some distortion of the methyl group. Attempts were made to refine structures with tetrahedral methyl groups; agreement was obtained for the [001] zone because of the partial overlap of H<sub>1</sub> and H<sub>3</sub>; however, the best value of  $R'$  obtained for the [100] zone was 0.29. The H<sub>1</sub>-C<sub>2</sub>-H<sub>2</sub> angle is the worst, and the sharpness of the H<sub>1</sub> and H<sub>2</sub> peaks in the difference synthesis (Fig. 2) would seem to rule out any large shifts in either of these positions.

The bond angles and distances found here are compared with the results for other oximes in Table 5. Also given are the X-ray results for dimethylglyoxime, with which the neutron diffraction results are unfortunately in disagreement for the C-C distances.\* *Cis* and *trans* are used to denote the location of the C-C bond relative to the N-O bond around the C-N axis. The neutron results are in agreement with the X-ray results for nickel and copper dimethylglyoximes as well as with the results for the similar bonding situation in acetoxime in indicating that the *trans* C-C bond has the normal C-C single bond length, while the *cis* bond is appreciably shortened. The difference between the two C-C bond lengths is  $0.083 \pm 0.027$  Å. This agreement lends some weight to

\* All distances and angles have also been calculated using the present parameters but using Merritt & Lanterman's cell constants. The differences are nowhere significant and exceed one standard deviation for only two functions in Table 4: 2.799 Å for the long O...N distance and 3.180 Å for the long O...O distance. The C<sub>1</sub>-C<sub>1</sub> and C<sub>1</sub>-C<sub>2</sub> distances are, for example, 1.551 and 1.491 Å if Merritt & Lanterman's cell constants are used.

Table 5. *Interatomic distances and bond angles in some oximes*

DMG(N), dimethylglyoxime, present work; DMG(X) dimethylglyoxime, Merritt & Lanterman (1952); NiDMG, nickel dimethylglyoxime, Godycki & Rund le(1953); CuDMG, copper dimethylglyoxime, Frasson, Bardi & Bezzi (1959); ACET, acetoxime, Bierlein & Lingafelter (1951); SYN and ANTIB, *syn*- and *anti-p*-chlorobenzaldoxime, Jerslev (1957); FORM, formamidoxime, Hall & Llewellyn (1956). The values for NiDMG and CuDMG are averages over two or four chemically, but not crystallographically, equivalent distances or angles

	DMG(X)	DMG(N)	NiDMG	CuDMG	ACET	SYNB	ANTIB	FORM
C <sub>1</sub> -C <sub>trans</sub>	1.44 Å	1.56 Å	1.53 Å	1.515 Å	1.55 Å	1.46 Å	—	—
C <sub>1</sub> -C <sub>cis</sub>	1.53	1.48	1.485	1.47	1.49	—	1.55 Å	—
C <sub>1</sub> -N	1.27	1.25	1.225	1.25	1.29	1.27	1.26	1.33, 1.30 Å
N-O	1.38	1.32	1.375	1.345	1.36	1.36	1.39	1.41
☆ C <sub>cis</sub> -C <sub>1</sub> -C <sub>trans</sub>	120.4°	120.0°	122.5°	122.3°	117°	—	—	—
☆ C <sub>trans</sub> -C <sub>1</sub> -N	115.1	113.8	111.0	112.8	113	123	—	—
☆ C <sub>cis</sub> -C <sub>1</sub> -N	124.6	126.0	126.5	124.9	131	—	130°	—
☆ N-O-H	—	109.6	(102)*	—	—	105†	—	—
☆ C <sub>1</sub> -N-O	113.9	111.4	121	119.5	111	112	118	110°
☆ N-O...N	—	86	—	—	111	84.7	—	—
☆ O-N...O	—	94	—	—	129	95.3	—	—
☆ O-N...H	—	106.2	—	—	—	106†	—	—
☆ O-H...N	—	140	—	—	—	160†	—	—

\* If O-H...O is linear.

† If position assumed a compromise between steric repulsion and geometrical effects.

the author's feeling that the present bond lengths are more realistic than those of the X-ray structure. The C-C bond lengths in the *p*-chlorobenzaldoximes are not really comparable, since one of the carbon atoms in the bond is aromatic. The C-N distance found is in agreement with that reported for all other oximes\* and with the value 1.265 Å calculated from the Pauling radii for a normal C-N double bond (Pauling, 1948). Although the present value for the N-O bond length at first sight looks somewhat low, it is less than two standard deviations away from the value of 1.36 Å which is quoted for two other oximes, and which is also the sum of the Pauling covalent radii (Pauling, 1948). The intramolecular bond angles for dimethylglyoxime and acetoxime are in good agreement, an agreement that persists in nickel and copper dimethylglyoximes, with the exception of the C-N-O angle, which is probably distorted in the complexes because of the adjacent metal atom and the somewhat different hydrogen-bonding situation.

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\* The bond lengths in formamidoxime are not directly comparable, because of the more complex resonance structure which must be used to describe it.

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