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The Crystal Structure of Dimethylglyoxime*

By Lynne L. Merritt, Jr. and Elma Lanterman†

Department of Chemistry, Indiana University, Bloomington, Indiana, U.S.A.

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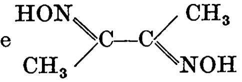
The crystal structure of dimethylglyoxime  $\mathrm{HON(CH_3)C{-}C(CH_3)NOH}$ has been determined by single-crystal methods. The unit cell is triclinic with $a=6{\cdot}10$, $b=6{\cdot}30$, $c=4{\cdot}48$ Å, $\alpha=122°\,31'$, $\beta=90°\,6'$, $\gamma=79°\,1'$. The space group is $P\bar{1}-C_i^1$ and there is one molecule per unit cell.

Atomic positions were determined by two-dimensional Fourier refinement and by further three-dimensional refinements by the method of least squares. Structure factors were obtained from visually estimated intensities on Weissenberg photographs taken with Cu $K\alpha$ radiation.

The crystal is composed of chains of essentially planar, centro-symmetric dimethylglyoxime molecules joined together by a network of hydrogen bonds. The bond lengths are normal except for the central carbon–carbon bond (1·44 Å).

Introduction

The determination of the crystal structures of some organic reagents of analytical importance and the complexes they form with metallic atoms is part of a long-range investigation of the factors involved in chelation which is being carried out in these Laboratories. The study of the crystal structure of dimethylglyoxime is reported here as part of this program. This compound is of special interest because of its high selectivity for nickel and palladium atoms.

Experimental technique, unit cell and space group

Dimethylglyoxime (Eastman Kodak Company) was recrystallized from 50% alcohol–50% water (by volume) at room temperature. The lines in the X-ray powder photographs of these crystals agree with the lines reported by McCrone (1949).

Morphological examination by McCrone has shown that these crystals are triclinic with

$$a:b:c = 0{\cdot}950:1:0{\cdot}703$$

and

$$\alpha = 125°,\ \beta = 91°,\ \gamma = 79° .$$

He measured the crystal density with a pycnometer and reported 1·353 g.cm.$^{-3}$. McCrone also reported the refractive indices to be

$$\alpha = 1{\cdot}40\pm0{\cdot}01,\ \beta = 1{\cdot}54\pm0{\cdot}01,\ \gamma = 1{\cdot}85\pm0{\cdot}01\ ,$$

and gave the following optical properties:

Optic axial angle (5893 Å; 25° C.): $2V = 80°$.
Optic axial plane: approximately parallel to (100).
Sign of double refraction: (+).
Acute bisectrix: approximately parallel to b.
Extinction: 1° on (100) with γ almost parallel to b.

McCrone determined the axial lengths by X-ray diffraction to be $a = 6{\cdot}07$, $b = 6{\cdot}39$, $c = 4{\cdot}48$ Å.

A brief optical examination gave results in agreement with those of McCrone, although no accurate measurements were attempted. The dimensions of the real cell were obtained from oscillation photographs, and the reciprocal cell angles were found from Weissenberg photographs by the method of ω separations (Buerger, 1942). The values of axial lengths were

$$a = 6{\cdot}10,\ b = 6{\cdot}30,\ c = 4{\cdot}48\ \text{Å}\ .$$

The values of the reciprocal cell angles were

$$\alpha^* = 57°\,1',\ \beta^* = 95°\,55',\ \gamma^* = 102°\,25'\ .$$

The cell angles were then calculated from relations of the type

$$\cos\alpha = \frac{\cos\beta^*\ \cos\gamma^*\ - \cos\alpha^*}{\sin\beta^*\ \sin\gamma^*} .$$

The values of the real cell angles were

$$\alpha = 122°\,31',\ \beta = 90°\,6',\ \gamma = 79°\,1'\ .$$

Using the density reported by McCrone and the volume of the cell calculated from the above data, the number of molecules per unit cell was found to be 0·99, i.e. one molecule per unit cell.

The piezo-electric and pyro-electric properties were measured to determine whether or not the crystal was centrosymmetric. The results of these tests were

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† Present address: Department of Physics, North Carolina State College, Raleigh, North Carolina, U.S.A.

negative, and, therefore, the crystal was assumed to possess a center of symmetry. From the above data it was concluded the space group was $P\bar{1}$–C_i^1.

Complete sets of equi-inclination Weissenberg photographs about the [010] and [001] axes were taken for intensity estimation. The two crystals used were roughly cylindrical in shape and small enough (about 1 mm. × 0·5 mm. × 0·5 mm.) so that differences in absorption for different planes were not large enough to be significant. Nearly the entire range of reflections which can be observed with Cu $K\alpha$ radiation (λ = 1·5418 Å) was explored.

The reflections were indexed and the value of sin θ for each spot was measured graphically. Relative intensities were estimated visually by comparison with standard intensity strips. The standard intensity strips were prepared by taking a timed series of 5° Weissenberg exposures of a prominent reflection of the same crystal which was used to make the complete set of Weissenberg films about the [001] axis. The multiple-film technique (Robertson, 1943) was employed both for the Weissenberg films and in the preparation of the standard intensity strips. Four sheets of Eastman No-screen film were used. Intensities were corrected for Lorentz and polarization factors to obtain relative $|F_{hkl}|^2$ values. Intensities on levels other than the equatorial level were also corrected for oblique penetration of the film by the X-rays and by the application of a time factor according to Cox & Shaw (1930). The zero-layer Weissenberg photograph around [001] was taken as the standard film and by cross calibration all relative $|F_{hkl}|^2$ values were reduced to this common level.

Determination of atomic positions

It was assumed that the important features of the structure would be revealed by the projection on the (001) plane, which could be calculated from the (hk0) data. This assumption was based on the following considerations: (a) The strong indications from the optical data that the crystal has a chain or ribbon structure, namely the fact that the crystal is optically positive with γ approximately parallel to b and α inclined about 90° to [010], of course, and about 50° from [100]; i.e. nearly perpendicular to the (101) plane and suggesting that the plane of the ribbon is parallel to the (101) plane of the crystal. (b) The pronounced fibrous cleavage parallel to [010]. (c) The perpendicular distance between the (001) planes is only 3·75 Å, hence the chains or ribbons are just one molecule thick and can not be tipped far out of the (001) plane. (d) The unit cell contains one molecule. (e) The molecule has a center of symmetry.

A paper model of the molecule was rotated on a drawing of the (001) plane of the unit cell so as to try to satisfy the conditions for strong or weak reflections for a few selected planes as well as to satisfy the symmetry requirements of the space group. It was possible to select a probable trial structure for further examination.

Structure factors, F_{hk0}, were calculated for this trial structure. A Fourier projection (001) of the electron density in the unit cell was calculated with the observed values of F_{hk0} for which the signs were fairly certain. The resulting projection exhibited a recognizable but poorly resolved picture of the molecule. Improved atomic parameters were measured from the above projection. From these parameters new structure factors were calculated. The agreement with observed magnitudes was better and more signs of F_{hk0} could be assigned correctly. Further Fourier refinements yielded better agreement.

It was necessary to determine the temperature factor to be applied in the computation of F_c and the scale factor which places F_o on the absolute scale. The relationship between F_o and F_c may be expressed by

$$k|F_o| = |F_c| \exp\left[-B\,(\sin\theta/\lambda)^2\right], \qquad (1)$$

where $\exp[-B\,(\sin\theta/\lambda)^2]$ is the temperature factor, B is a constant for a particular crystal, k is the scale factor, θ is the Bragg angle, and λ is the wavelength of the X-radiation. Scale and temperature factors were obtained simultaneously from equation (1) by the method of least squares.

When the first set of Fourier projections had converged the disagreement between $|F_c|$ and $|F_o|$ was still quite large. At this point it was decided to calculate a Patterson projection on (001). The Patterson projection (Fig. 1) indicated that the structure was essentially correct except that the molecule was tipped more toward the (101) plane than had been anticipated. The origin peak of this projection has been removed by using as coefficients $|F_{(hk0)}|^2 - \sum_m |f_m|^2$.

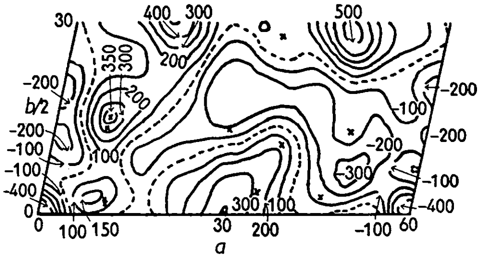


Fig. 1. Patterson projection of dimethylglyoxime on (001). Peak at origin removed. Zero contour broken.

The contour lines are arbitrarily drawn at intervals of 100. The crosses represent the ultimate positions of projected interatomic vectors within one molecule. A new series of Fourier refinements, using values of the parameters modified according to the results of the Patterson projection, rapidly converged. The value of

$$R = \Sigma(|F_o| - |F_c|) \div \Sigma|F_o|$$

at this point was 0·25. The contributions of the hydrogen atoms were not included. Centers of atoms were located by the method of Carpenter & Donohue (1950).

Further refinement was carried out by the method of least squares (Hughes, 1941). After each least-squares refinement, new values of the constant in the exponent of the temperature factor and of the scale factor were determined by the method of least squares. A trial calculation of all of the (*hkl*) structure factors, assuming that the molecule was lying on the (101) plane, gave such good agreement with the observed values that it was decided to refine these parameters further by the method of least squares. At first, those few reflections for which the sign of F_c was uncertain were omitted from the least-squares treatment. In the second refinement all terms were included. R was 0·21. When the contributions of the hydrogen atoms were included R fell to 0·20. The hydrogen atoms were placed in a tetrahedral arrangement around the methyl carbon, initially at distances of 1·07 Å from the carbon, and along the line between nitrogen and oxygen of adjacent molecules at 0·96 Å from the oxygen atom. Some indication of an anisotropic temperature factor was noted and therefore the constants A and B in the expression $\exp\left[-(A+B\cos^2\varphi)\sin^2\theta/\lambda^2\right]$ and the scale factor k were determined by the method of least squares. The angle φ between the direction of maximum vibration of the atoms and the normal to the reflecting plane was taken as the angle between the normal to the planes and the normal to the (101) plane. Recalculation of all the F_c values, using an anisotropic temperature factor and including hydrogen atom contributions, yielded an R value of 0·196 (reflection (101) was omitted since F_o for this, the strongest reflection, is obviously low owing to extinction). A final least-squares refinement, after readjusting the values of A and B in the anisotropic temperature factor expression and of k, the scale factor, produced shifts in parameters averaging less than 0·007 Å with a maximum of 0·013 Å and no appreciable change in R. Final parameters are given in Table 1. The final values of $|F_o|$ and F_c are given in Table 2 along with the final values of A and B in the anisotropic temperature factor. Fig. 2 is a Fourier projection on (001). The contour lines are drawn at intervals of 1 e.Å^{-2}, commencing at 1 e.Å^{-2}.

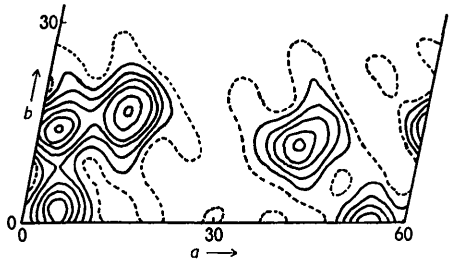


Fig. 2. Fourier projection of dimethylglyoxime on (001). Contours at 1 e.Å^{-2}; broken contour = 1 e.Å^{-2}.

The calculations of the Fourier projections and of the structure factors were carried out with the aid of I.B.M. machines (Donohue & Schomaker, 1949; Shaffer, Schomaker & Pauling, 1946).

Table 1. *Atomic parameters of dimethylglyoxime*

(Parameters are expressed as fraction of cell edge)

	x	y	z
C_1	0·085	0·016	0·907
C_2	0·701	0·194	0·289
N	0·052	0·238	0·952
O	0·222	0·266	0·781

Positions assigned to hydrogen atoms

	x	y	z
H_1	0·530	0·305	0·679
H_2	0·683	0·353	0·745
H_3	0·699	0·196	0·464
H_4	0·118	0·456	0·845

Discussion of structure

The dimensions of a single molecule are presented in Fig. 3 and Table 3. The displacements of the atoms from the average plane of the molecule are all within the limits of probable error, which is estimated to be about ±0·01 Å for the position of an atom and about ±0·02 Å for the length of a bond, except in the case of carbon atom, C_1, which cannot be located so precisely. The errors in the case of C_1 are probably two or three times as great. It is unlikely that the length of any given bond is in error by more than 0·05 Å. The corresponding probable error in a bond angle is about 2·0°. The root-mean-square amplitude of the thermal vibrations of the atoms is 0·19 Å in the plane of the molecule and 0·22 Å in the direction perpendicular to the plane of the molecule.

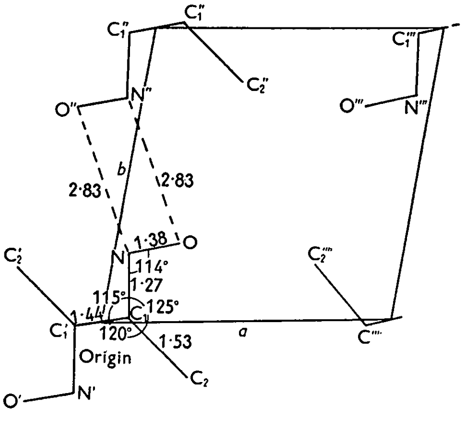


Fig. 3. Projection of dimethylglyoxime molecule on (001) showing angles and intermolecular distances.

The atoms of a single molecule, exclusive of hydrogen atoms, are within ±0·04 Å of the least-squares best plane passing through the origin. Atom C_1 is 0·04 Å

Table 2. *Observed and calculated structure factors*

In each column, the left hand column is the h index, the middle column is the observed structure factor, and the right hand column is the calculated structure factor. All structure factors have been multiplied by ten and hydrogen atoms are included. $A = 2{\cdot}79$, $B = 0{\cdot}99$ Å^2

$h00$

1	136	172
2	69	−58
3	33	27
4	34	42
5	17	−23
6	27	−28
7	20	−20

$h10$

0	107	90
1	6	− 4
2	129	−119
3	3	7
4	10	9
5	83	−76
6	69	−65
7	3	− 3

$h20$

0	152	−169
1	39	30
2	49	59
3	79	−59
4	91	−67
5	32	−25
6	3	−11
7	3	6

$h30$

0	15	12
1	97	76
2	58	62
3	40	−44
4	22	−22
5	39	40
6	18	18
7	12	−15

$h40$

0	84	93
1	19	14
2	10	6
3	23	23
4	3	4
5	11	− 5
6	12	−11
7	16	−19

$h50$

0	34	29
1	20	−22
2	18	−15
3	9	18
4	22	−20
5	52	−47
6	26	−18

$h60$

0	8	− 6
1	4	7
2	13	−11
3	27	−19
4	24	−17
5	19	−19

$h\bar{1}0$

1	105	−125
2	149	141
3	28	28
4	28	−31
5	10	15
6	28	31

$h\bar{2}0$

1	47	−51
2	91	77
3	3	13
4	49	−52
5	14	−15

$h\bar{3}0$

1	3	−19
2	22	−19
3	21	−18
4	3	− 2
5	26	−18

$h\bar{4}0$

1	85	84
2	5	− 5
3	11	−16
4	22	18

$h\bar{5}0$

1	47	43
2	30	24
3	33	19

$h\bar{6}0$

1	26	−17

$h01$

0	178	156
1	232	365
2	130	111
3	27	−32
4	16	18
5	18	25
6	16	−16
7	16	−17
$\bar{1}$	82	−62
$\bar{2}$	48	30
$\bar{3}$	48	45
$\bar{4}$	25	−21
$\bar{5}$	33	−36
$\bar{6}$	22	−25
$\bar{7}$	17	−20

$h11$

0	110	89
1	70	61
2	22	−26
3	42	−52
4	4	1
5	9	4
6	40	−46
7	22	−38
$\bar{1}$	130	129
$\bar{2}$	33	21
$\bar{3}$	32	−34
$\bar{4}$	37	16

$h21$

0	38	−38
1	97	−102
2	19	16
3	14	33
4	34	−34
5	34	−34
6	12	−12
$\bar{1}$	54	62
$\bar{2}$	5	8
$\bar{3}$	44	−51
$\bar{4}$	13	−19

$h31$

0	3	− 6
1	7	9
2	48	48
3	33	35
4	15	−21
5	8	−13
6	11	21
$\bar{1}$	7	−17
$\bar{2}$	16	−15
$\bar{3}$	3	− 3
$\bar{4}$	15	−18

$h41$

0	51	59
1	51	60
2	9	8
3	41	6
4	10	13
5	3	0
6	5	− 4
$\bar{1}$	3	− 2
$\bar{2}$	8	−13
$\bar{3}$	11	15
$\bar{4}$	7	0

$h51$

0	24	30
1	17	20
2	3	−13
3	6	− 8
4	6	9
$\bar{1}$	17	18

$h\bar{1}1$

1	81	68
2	139	114
3	101	88
4	23	22
5	16	−20
6	3	10
7	11	20

$h\bar{2}1$

0	29	−13
1	125	−143
2	41	−50
3	58	67
4	3	11
5	36	−38
6	11	−10
$\bar{1}$	60	72
$\bar{2}$	70	−89

Table 2 (*cont.*)

	$h\bar{3}1$	
0	88	100
1	11	10
2	3	−25
3	12	− 9
4	15	−15
5	3	− 1
6	13	−14
$\bar{1}$	71	73
$\bar{2}$	46	−65
	$h\bar{4}1$	
0	23	24
1	87	104
2	68	92
3	3	− 7
4	6	−13
5	15	16
$\bar{1}$	4	3
$\bar{2}$	27	33
$\bar{3}$	15	10
	$h\bar{5}1$	
0	29	−33
1	32	34
2	47	48
3	24	27
4	19	20
$\bar{1}$	18	−21
$\bar{2}$	17	27
$\bar{3}$	10	−28
	$h\bar{6}1$	
0	6	8
1	12	− 9
2	22	−20
3	17	14
$\bar{1}$	4	−14
$\bar{2}$	9	−29
$\bar{3}$	10	−28
	$h\bar{7}1$	
0	31	22
$\bar{1}$	10	− 5
	$h02$	
0	22	−43
1	95	91
2	172	156
3	63	52
4	8	−13
5	8	14
6	3	9
7	8	− 9
$\bar{1}$	20	14
$\bar{2}$	43	40
$\bar{3}$	18	−16
$\bar{4}$	34	−38
$\bar{5}$	25	−26
$\bar{6}$	18	−21
	$h12$	
0	66	67
1	54	52
2	33	32
3	3	−10
4	19	−25
5	7	1
6	8	1
$\bar{1}$	25	19
$\bar{2}$	26	−27
$\bar{3}$	8	12
$\bar{4}$	30	34
	$h22$	
0	25	39
1	18	−26
2	33	−37
3	7	12
4	3	12
5	16	−17
6	12	−14
$\bar{1}$	8	5
$\bar{2}$	29	−41
$\bar{3}$	13	−18
$\bar{4}$	27	4
	$h32$	
0	3	− 8
1	3	0
2	7	0
3	23	27
4	16	19
5	3	−10
	$h42$	
0	3	− 1
1	28	37
2	25	32
3	6	5
	$h\bar{1}2$	
0	93	−63
1	18	−27
2	74	34
3	61	63
4	51	52
5	12	13
6	4	−11
$\bar{3}$	96	−100
	$h\bar{2}2$	
1	15	−11
2	72	−87
3	21	−25
4	26	47
5	3	5
6	16	−22
$\bar{1}$	111	−70
	$h\bar{3}2$	
0	59	55
1	75	80
2	5	5
3	3	−11
4	3	−12
5	13	−10
$\bar{1}$	40	−54
$\bar{2}$	36	−36
	$h\bar{4}2$	
0	3	− 1
1	26	21
2	66	92
3	50	72
4	3	− 5
5	3	− 7
6	27	12
$\bar{1}$	38	31
$\bar{2}$	26	20
$\bar{3}$	11	4
	$h\bar{5}2$	
0	21	−23
1	26	−24
2	36	32
3	43	41
4	26	24
$\bar{1}$	18	28
$\bar{2}$	27	−29
$\bar{3}$	81	−97
	$h\bar{6}2$	
0	14	−15
1	6	9
2	13	−12
3	21	−18
$\bar{1}$	36	−37
$\bar{2}$	42	−39
$\bar{3}$	38	−38
	$h\bar{7}2$	
0	3	− 6
1	48	−34
$\bar{1}$	39	22
	$h03$	
0	9	6
1	3	−21
2	50	46
3	58	73
4	26	22
5	3	− 4
$\bar{1}$	20	28
$\bar{2}$	18	−15
$\bar{3}$	29	−29
$\bar{4}$	20	−20
$\bar{5}$	16	−17
	$h04$	
0	6	14
1	7	4
2	3	−10
3	21	20
4	19	34
5	11	9
$\bar{1}$	14	−12
$\bar{2}$	20	−20
$\bar{3}$	15	−14

from this plane while the other atoms are within 0·014 Å. This may indicate either that the C_1 atom is not truly in the plane of the rest of the molecule or that its position is in error by about 0·04 Å. It is difficult to decide in this case. This plane makes an angle of 8·9° with the (101) plane of the unit cell. The

Table 3. *Bond lengths and angles in dimethylglyoxime structure*

(*a*) Between atoms of a single molecule

Bond	Length	Angle	Value
C_1–C_2	1·53 Å	C_1'–C_1–C_2	120·4°
C_1–N	1·27	C_1'–C_1–N	115·1
C_1–C_1'	1·44	C_2–C_1–N	124·6
N–O	1·38	C_1–N–O	113·9

(*b*) Between atoms of neighboring molecules

Bond	Length	Angle	Value
N–O″	2·83 Å	N–O · · · (H) · · · N″	75·9°
O–N″	2·83	O″–N″ · · · (H) · · O	75·9
O–C_2''''	3·44		
O–O‴	4·63		
O–C_2''	3·69		
O–N^V	3·76		

equation of the plane of the molecule is, in terms of the unit-cell vectors,

$$0·978x+0·004y+z = 0 .$$

The bond lengths found were not significantly different from the expected values except for the central C–C bond, which was 1.44 Å. In 1,3-butadiene and cyclopentadiene (Schomaker & Pauling, 1939) the value found for the C–C bond between the conjugated double bonds is 1·46 Å. This corresponds to 18% double-bond character. From the length of the central C–C bond in dimethylglyoxime one must conclude that there is about 25% double-bond character in this bond (Pauling, 1948).

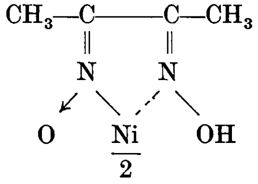
The C–C bond in oxalic acid has been reported (Dunitz & Robertson, 1947) as 1·46 Å but three-dimensional analysis of the urea–oxalic acid compound has shown this bond to have the normal single-bond length of 1·54 Å (Sturdivant, Schuch & Merritt, 1950; see also Brill, Herman & Peters, 1942). It is believed that further refinement of the parameters of dimethylglyoxime would not appreciably lengthen the C–C bond using the present observations, although certainly the error in this bond length is greater than that of other bonds.

One attempt was made to adjust the parameters so as to lengthen this bond to the normal single-bond length. A least-squares refinement immediately indicated a change back to the value reported, 1·44 Å. Further observations, using data available from molybdenum radiation, would be of interest.

The strongest attractive forces between adjacent molecules in the crystal of dimethylglyoxime are the hydrogen bonds formed between the oxygen atom of one molecule and the nitrogen atom of the next molecule. These hydrogen bonds lie in the plane of the molecule and form an angle of 75·9° with the N–O bond. It is not possible to say, from this determination, whether the hydrogen is closer to the oxygen or the nitrogen atom. There were weak, diffuse tails on the electron-density map near the oxygen atom and in the direction of the hydrogen bond, so the hydrogen was arbitrarily assigned a position 0·96 Å from the oxygen atom. Similar hydrogen bonds between a nitrogen atom and an oxygen atom are found in diketopiperazine (Corey, 1938), glycine (Albrecht & Corey, 1939) and hydrazonium sulfate (Nitta, Sakurai & Tomiie, 1951). The N–O distances in these molecules vary from 2·76 to 3·03 Å. From these data the 2·83 Å N–O hydrogen bond in dimethylglyoxime would seem to be a rather strong hydrogen bond. The high melting point of dimethylglyoxime (240–246° C.) is probably a result of this strong hydrogen bonding.

The hydrogen bonds tie the molecules together to form infinite chains parallel to [010]. The crystal can be easily cleaved parallel to the [010] axis without breaking any hydrogen bonds. The chains are apparently bound to one another by van der Waals forces to form the three-dimensional crystal.

The work of Pfeiffer (1930) has shown that the complex compound formed between a nickel atom and dimethylglyoxime is



which must result from the 'anti' configuration of the dimethylglyoxime. When dimethylglyoxime is dissolved in a solvent, the molecules must rotate around the central C–C bond and the structure reported in this paper would result in the necessary 'anti' configuration for preparation of the nickel complex. After this rotation occurs, the distance between the nitrogen atoms would be 1·70 Å. A preliminary report of the structure of nickel dimethylglyoxime has appeared (Godycki, Rundle, Voter & Banks, 1951). This latter structure investigation apparently has not proceeded far enough to fix the bond angles accurately. Considerable distortion of the dimethylglyoxime molecule would have to occur if the N–Ni–N bond angle is 90°. Depending on the radius of the nickel atom, this bond angle could lie between 54° and 75° with no distortion of the organic molecule (the radius of the nickel ion could conceivably vary from 0·70 Å for the purely ionic radius to about 1·24 Å when it has a coordination number of four). A comparison of the interatomic distances in the two structures shows good agreement for the C–N distance but we find a somewhat longer (0·04 Å) N–O bond, a somewhat longer (0·03 Å) C–CH_3 bond and a considerably shorter (0·06 Å) C–C bond. It will be interesting to compare results when the nickel dimethylglyoxime structure is complete and it is hoped that such comparisons will throw light on the problems associated with the formation and stability of this type of chelate complex, in particular, the unusual selectivity of the dimethylglyoxime molecule for nickelous and palladous ions.

A preliminary report of the space group of a copper dimethylglyoxime crystal has recently appeared (Bua & Schiavinato, 1951). The space group is reported to be $P2_1/n$ with four molecules in the unit cell. It would not be necessary, then, to have a centro-symmetrical molecule in the copper dimethylglyoxime structure.

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The Molecular Structure of 1,1,2,2-Tetramethylcyclopropane*

By H. P. Lemaire† and R. L. Livingston

Department of Chemistry and Purdue Research Foundation, Purdue University, Lafayette, Indiana, U.S.A.

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The structure of 1,1,2,2-tetramethylcyclopropane has been investigated by electron diffraction. The results indicate an average C–C bond distance of 1·52 ± 0·03 Å and an external angle (CH_3–C–CH_3) of 114 ± 6°.

Introduction

The two main points of interest in connection with the structure of cyclopropane or of its derivatives are the C–C bond distance in the ring and the value of the external angle (the H–C–H angle in cyclopropane and the corresponding angle in its derivatives). There is evidence that the C–C distance is shorter than in most hydrocarbons and that the external angle is greater than tetrahedral. In cyclopropane Pauling & Brockway (1937) have given 1·53 ± 0·03 Å and 109·5° for these parameters; more recently Bastiansen & Hassel (1946) found values of 1·535 Å and 118·2 ± 2°. In 1,1-dichlorocyclopropane O'Gorman & Schomaker (1946) have found a C–C distance of 1·52 ± 0·02 Å and a Cl–C–Cl angle of 112 ± 4°. Smith (1941), from infra-red data, arrived at an exterior angle of 136° in cyclopropane, assuming a C–H bond distance of 1·09 Å and a C–C bond distance of 1·53 Å. However, it was later shown by Skinner (1947) that the moment of inertia determined by Smith is compatible with the model of Bastiensen & Hassel.

The results of this work indicate that in 1,1,2,2-tetramethylcyclopropane the average C–C bond distance is 1·52 ± 0·03 Å and the external angle (CH_3–C–CH_3) is 114 ± 6°.

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* From the Ph.D. Thesis of H. P. Lemaire, Research Corporation Fellow in Chemistry, Purdue University, 1949–50.

† Present address: Department of Chemistry, St. Michael's College, Winooski Park, Vermont, U.S.A.