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The Crystal and Molecular Structure of Glyoxime

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Glyoxime, $H_2C_2(NOH)_2$, crystallizes in the monoclinic system, prismatic class, with two molecules per unit cell and belongs to space group $P2_1/c$. Unit-cell parameters are:

$$a_0=3\cdot868\pm0\cdot011,\ b_0=4\cdot414\pm0\cdot015,\ c_0=10\cdot949\pm0\cdot035\ \text{Å};\ \beta=91°\ 10'.$$

Optical properties: $\alpha=1\cdot482$; $\beta=1\cdot641$; $\gamma=1\cdot856$; optic axial plane parallel to (010); $2V=89°\ 30'$; $\widehat{zy}\simeq7°\ 30'$.

A three-dimensional analysis has been performed, based on all the reflexions accessible with Cu $K\alpha$ radiation, and the final R value, for 249 'observed' reflexions, is 6·9 %.

Glyoxime molecules are in the oxime form, planar and in the *anti-s-trans* configuration, therefore with symmetry C_{2h}; the molecular plane is sensibly parallel to $(1\bar{1}1)$. The molecules are linked by a net of hydrogen bonds, O–H - - - N, of length 2·811 Å; the successive sheets of molecules, along the x axis, are joined only by van der Waals forces.

In recent years several papers have been published on the structure of oximes and dioximes, since they have the interesting property of forming complexes with transition metals (*cf.* Hamilton, 1961). The authors therefore decided to undertake the study of the crystal structure of glyoxime and of some of its derivatives, also with the aim of integrating the long series of studies on α-dioximes published by G. Ponzio and coworkers in the Chemistry Institute of Turin.

In this paper the structure of glyoxime, $H_2C_2(NOH)_2$, on which Milone & Borello (1957) published an infrared spectrophotometric study, is described. Milone & Borello ascribed glyoxime to space group $P2_1/c$ and suggested that glyoxime molecules in the solid state are planar, in the *anti–s–trans* configuration and linked together by hydrogen bonds of medium strength, like dimethylglyoxime (Merritt & Lanterman, 1952).

Experimental

Preparation; goniometric and optical data

Glyoxime was prepared by reaction between hydroxylamine hydrochloride and glyoxal, made by acid hydrolysis of its bisulphite compound, by the method of Wittemberg & Meyer (1883) and recrystallized from water. The colourless transparent crystals (m.p. 178 °C) used in the present work were grown from either aqueous alcoholic or acetic acid solutions. From goniometric measurements we deduced that the crystals belong to the monoclinic system, prismatic class, with axial ratios $a:b:c = 0{\cdot}883:1:2{\cdot}489$ and $\beta = 91°\ 20'$. The combination of all the forms found is illustrated in Fig. 1, where: $a = (100)$; $b = (001)$; $c = (011)$; $d = (110)$; $e = (111)$; the commonest combination is formed by pinacoids {100} and {001} with prism {011}. It must be remarked that the crystals grown from acetic acid solutions are of three kinds; they can have either a tabular habit, in which case the most developed form may be the pinacoid {100} or the pinacoid {001}, or a prismatic habit, and in this latter case are elongated in the direction [100]. Crystals grown from aqueous alcoholic solutions are prismatic and elongated in the direction [010]; no twinned crystal has been found. Glyoxime crystals exhibit a distinct cleavage parallel to {100}.

An examination, under the polarizing microscope, of plates (100) and (001) revealed that the optic-axial plane is parallel to (010) and that the bisector of the optic-axial angle is almost normal to (001). Refractive indices have been measured by the Becke-line method on plates (100) and (001); for the yellow light of sodium at 21 °C, checking the refractive index of the liquid by a microrefractometer, the following values resulted:

$$\alpha' = 1{\cdot}489 \pm 0{\cdot}001 \quad \beta = 1{\cdot}641 \pm 0{\cdot}001 \quad \gamma' = 1{\cdot}850 \pm 0{\cdot}003.$$

By use of a universal stage it was possible to measure the optic-axial angle: $2V = 89°\ 30' \pm 1°$ (with negative optic sign). After also measuring the extinction angle $\widehat{zy} \simeq 7°\ 30'$ it was possible to calculate the principal refractive indices:

$$\alpha = 1{\cdot}482, \quad \gamma = 1{\cdot}856 \quad \text{and hence:} \quad 2V = 88°\ 54'.$$

a value which is in good agreement with the measured one.

From the optical data it seemed that the glyoxime molecules might form chains roughly parallel to the z axis. On the other hand the distinct cleavage parallel to {100} was consistent with the existence of molecular sheets approximately parallel to this pinacoid.

Roentgengraphic data

Unit-cell parameters and 'extinctions' were determined by Weissenberg photographs taken along the three crystallographic axes and superposing, on zero-layer photographs, lines due to a copper wire ($a_0 = 3{\cdot}6150$ Å). All X-ray measurements were made by Cu $K\alpha$ filtered radiation (λ taken as 1·54174 Å or 1·54434 and 1·54050 Å when α_1, α_2 separation occurred).

Monoclinic symmetry was confirmed and the systematically absent reflexions were: $0k0$ with k odd and $h0l$ with l odd, unambiguously indicating the space group $P2_1/c$. The unit-cell parameters obtained from Weissenberg photographs were refined by a least-squares procedure, using $2\theta_{hkl}$ values measured on a powder photograph taken with a camera of 45 cm circumference and with asymmetrical mounting. The refinement was performed by a program (Ferraris & Formia, 1965) which acts on reciprocal-cell parameters and takes into account also the corrections for absorption, eccentricity and divergence errors. The following values were deduced:

$$a_0 = 3{\cdot}868 \pm 0{\cdot}011, \quad b_0 = 4{\cdot}414 \pm 0{\cdot}015,$$
$$c_0 = 10{\cdot}949 \pm 0{\cdot}035\ \text{Å}; \quad \beta = 91°\ 10'.$$

The value of β was read directly on the φ circle of the Furnas goniostat (see below) and it was not refined. An angle β near 90° in fact hardly affects the calculation of d^*_{hkl}, and actually this angle, if allowed to vary during the refinement, proved to be subject to abnormal oscillations. Other data are: $V = 188{\cdot}171$ Å^3; M.W. 88·07; $D_{\text{meas}} = 1{\cdot}547$, $D_{\text{calc}} = 1{\cdot}555$ g.cm^{-3}; $Z = 2$; $F(000) = 92$; linear absorption coefficient for Cu $K\alpha$ radiation: $\mu = 12{\cdot}1$ cm^{-1}.

Intensity measurement

Intensities, on a relative scale, were collected by the General Electric manual single-crystal orienter, using a proportional counter tube, krypton filled. The crystal used for these measurements ($0{\cdot}30 \times 0{\cdot}37 \times 1{\cdot}80$ mm) was mounted with its y axis vertical and integrated intensities were measured by the moving-crystal moving-counter technique (Furnas, 1957), with a scanning speed of 2° per minute; background was of course considered. The computation of φ, χ and 2θ coordinates was made by a program written by one of us (Ferraris, 1965). Practically all the reciprocal-lattice portion accessible with Cu $K\alpha$ radiation was explored and altogether 393 reflexions were examined, of which 133 had intensity below the measurable minimum. We also checked the reflexions on long-exposure Weissenberg photographs, paying special attention to the 'unobserved' ones.

In view of the low absorption coefficient and the dimensions of the crystal, no correction for absorption was made. Correction for Lorentz-polarization effects and the computation of atomic scattering factors, by the interpolation formula of Forsyth & Wells (1953), were done with a program from the Olivetti repertoire. The constants, for neutral atoms, of the interpolation formula were taken from Moore (1963). A preliminary scaling factor for F_o^2 and an average vibrational parameter $B \simeq 2$ Å^2 were found by Wilson's method.

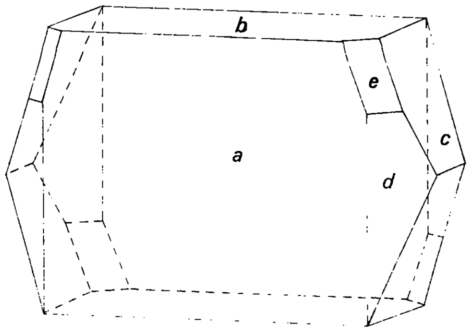
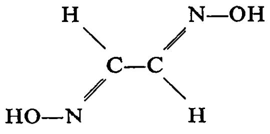


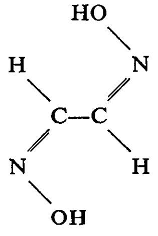
Fig. 1. Clinographic drawing of a glyoxime crystal showing all the forms observed.

Determination of the structure

*Patterson and Fourier syntheses**

Since the multiplicity of the set of equivalent general positions in space group $P2_1/c$ is four and in the unit cell there are only two molecules, the asymmetric unit must consequently be formed by only half a molecule; the molecule must therefore possess a centre of symmetry. Glyoxime molecules show a centre of symmetry either in form (I), *anti-s-trans*, or in form (II), *syn-s-trans*:


(I)


(II)

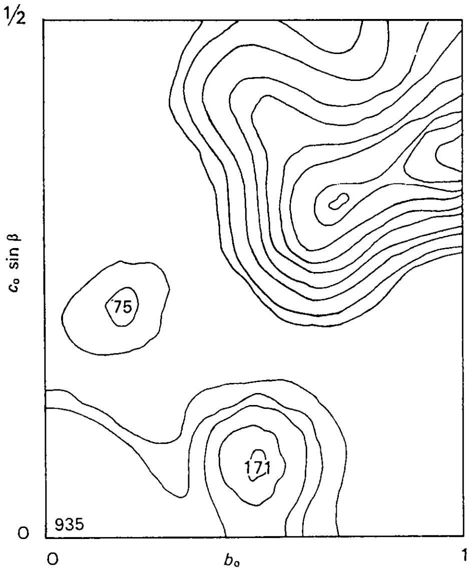


Fig. 2. Patterson projection along [100]; contour lines at arbitrary intervals. The relative heights of two peaks are marked (see text).

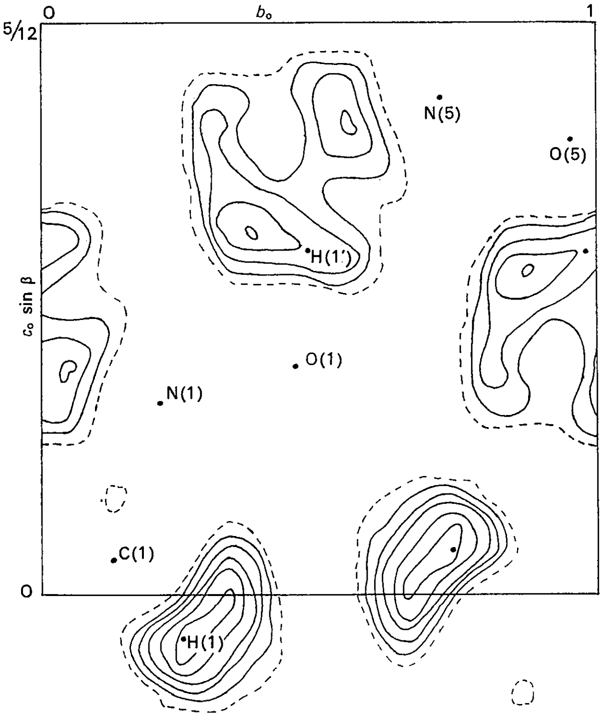


Fig. 3. Difference Fourier synthesis along [100]; contours which delimit areas of equal electron density are drawn at intervals of 0·1 e.Å^{-2}, zero lines broken. The final positions of C, N, O atoms are marked.

Remembering the physical properties of glyoxime crystals we could expect a Patterson projection along [100] to be the best resolved one. To solve the structure we therefore computed two Patterson projections, along [100] and [010]. It was possible to interpret the former by considering the position of peaks surrounding the origin and supposing, in accordance with Milone & Borello (1957), that the molecules were planar and in *anti-s-trans* configuration. In this instance, since C–C and N–O bonds are sensibly parallel, one should expect the appearance of a single peak in the direction of these bonds whose height should be approximately twice that of the peak in the direction of the C–N bond, in accordance with the atomic number of each atom. In fact the situation in the Patterson projection along [100] turned out to be of such a kind (Fig. 2). It was possible, on this ground, to reach a consistent interpretation of all the peaks appearing in the projection. The projection along [010], however, was much less precise, owing to the limited number of $h0l$ reflexions, so we decided to calculate a three-dimensional Patterson synthesis with sections normal to the x axis. On the basis of the results reached in two dimensions, the 3-D synthesis was easily interpreted and it was possible to obtain a set of coordinates which, with the use of an average vibrational parameter $B=2$ Å^2, yielded an $R=0\cdot40$ for all the 'observed' reflexions. By two cycles of electron density projections along [010] and [100] the improvement of coordinates led to an R value of 0·20. At this stage the lengths of the principal molecular bonds were: C–C 1·56, C=N 1·23 and N–O 1·34 Å.

Structure refinement

Since the coordinates drawn from the second electron density projections did not bring any further change in signs of the amplitudes, the refinement of the coordinates so far obtained was carried on by the least-squares method. With this aim we made use, first, of a full-matrix program written by F. Sgarlata of Rome University. The program refines the function: $\Sigma_{hkl}[|F_o|-|F_c|]^2$, with anisotropic vibrational parameters, after previously refining the scaling factor, and does not

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* Computed with Olivetti programs.

make use of any weighting system. After a first cycle we had $R=0{\cdot}14$ and principal bond lengths C–C 1·48, C=N 1·29 and N–O = 1·40 Å, while the molecule appeared to be practically planar. A second cycle reduced R to 0·086. At this stage we could ascribe the discrepancies Δ, between F_c and F_o, apart from experimental errors, to the absence of the contribution of the hydrogen atoms to F_c; hydrogen atom sactually contribute $\sim 8\%$ to the electronic content of the unit cell. We decided then to compute a difference synthesis with $0kl$ reflexions, making use of Δ_{0kl} corresponding to 'observed' F_o; from this Fourier synthesis (Fig. 3) it is clear that C, N, O atoms are in the right positions. In the projection, apart from minor and random undulations, positive peaks appear in positions which are likely to be occupied by hydrogen atoms. Accordingly we could draw a triad of coordinates, recorded in Table 1, for the hydrogen of the C–H group, under the conditions that the hydrogen atom was in the molecular plane and at a distance of about 1 Å from carbon and that the angle C–C–H was about 120°. We had then to place the other hydrogen atom of the asymmetric unit. The shortest intermolecular distance, 2·8 Å, turned out to be between O(1) and N(5) (Fig. 4); we inferred that this hydrogen atom was likely to be in such a position as to allow the formation of a hydrogen bond between these two atoms. Actually the positive region in the projection, indicating the presence of the hydrogen atom in question, is very diffuse and does not show definitely whether this atom is bound to oxygen or to nitrogen. Since there are several reasons, as explained afterwards, for the assumption that glyoxime molecules are in the oxime form (=N . OH) and not in the N-oxide-iminic one, $(=\underset{\substack{|\\ \mathrm{H}}}{\mathrm{N}} \rightarrow \mathrm{O})$ (Hodgkin & Pitt, 1950), we looked for the possibility of placing a hydrogen bridge O–H - - - N between O(1) and N(5). Considering the results obtained in some structural studies by neutron diffraction, we could also expect the angle O–H - - - N to be different from 180°. Having in mind these considerations we deduced for this hydrogen atom the set of coordinates listed in Table 1.

We then recalculated the structure factors assuming for the hydrogen atom of the C–H group an isotropic vibrational parameter of 1·5 Å^2 and for that of the O–H group, 3 Å^2; the new R value was slightly lower ($R=0{\cdot}080$). Encouraged by this result, we carried out a third least-squares cycle, allowing only the parameters of the C, N and O atoms to vary, and obtained an R value of 0·076. The values of the principal bond lengths were then C–C 1·462, C=N 1·294, N–O 1·403, C–H 1·072 and O–H 1·067 Å.

Since the program till then employed did not allow for the introduction of any weighting system we tried a further refinement using another program (Panattoni, *et al.* to be published) in which, for the solution, the system of normal equations is subdivided into partial systems of three equations for coordinates and six fos thermal anisotropic factors. With this program it is possible to make use of a rather flexible weighting function and the refined function is: $\Sigma w(hkl)[|F_o|-|F_c|]^2$. For a first cycle we used the following weighting system: $w=|\bar{F}|^2/|F_o|^2$ if $|F_o|>|\bar{F}|$ and $|F_o|^2/|\bar{F}|^2$ if $|\bar{F}|>|F_o|$, where $|\bar{F}|$ is the modulus of the average amplitude, which in our case has the value 6. Before the cycle a few reflexions were eliminated, namely those for which the discrepancy between F_o and F_c was greater than 20%; these reflexions are marked with an asterisk in Table 2. For fractional coordinates we observed variations of the fourth figures, while for thermal parameters we noticed a general rearrangement of B_{ij} terms with $i \neq j$, without any changes of sign. With a 0·8 'fudge factor' applied to shiftings of variables, R was reduced to 0·073. Nevertheless the average value of $w\Delta^2$ did not pass the test suggested by Cruickshank *et al.* (1961). After a careful examination of $w\Delta^2$ values, no weighting system was found which entirely satisfied the above mentioned test. However, the best scheme we could deduce was:

$$w=\frac{1}{0{\cdot}9|F_o|^2+|F_o|+1{\cdot}5} \quad \text{if } |F_o|\ge 2|F_{\min}|=3\,,$$
$$w=0{\cdot}1 \quad \text{if } |F_o|<2|F_{\min}|=3\,.$$

With such a weighting system, the average value of $w\Delta^2$, dividing the reflexions into groups of increasing $|F_o|$, was sufficiently constant, while, dividing the reflexions in groups according to the sequence in which they are recorded on the magnetic tape (increasing h values), the ratio between the lowest and the highest values of $w\Delta^2$ was 0·5. Another cycle with this weighting scheme and a 'fudge factor' of 0·8 gave an R value of 0·069. In this last cycle only the x coordinate of carbon varied appreciably; the others showed only slight variations of the same order as the standard

Table 1. *Final fractional coordinates and vibrational parameters with, below, the significant figures of the standard deviations*

	x/a_0	y/b_0	z/c_0	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0·1000	0·1278	0·0225	2·66	1·00	1·86	0·59	0·45	0·13
	8	6	2	13	11	13	9	10	8
N(1)	0·0613	0·2070	0·1342	2·75	0·78	2·00	0·34	0·39	0·20
	7	5	2	13	9	10	7	8	7
O(1)	0·2734	0·4529	0·1646	3·48	1·36	2·40	0·39 –	0·41	0·41 –
	6	5	1	13	8	11	8	9	7
H(1)	0·2774	0·2529	0·0333 –			$B=1{\cdot}50$			
H(1′)	0·1798	0·4786	0·2500			$B=3{\cdot}00$			

deviations, which meant that the function to be refined reached a minimum; a further cycle, in fact, gave no improvement. Besides, the refinement could be regarded satisfactory, since no percentage error Δ/F_o was abnormal and F_c computed for 'unobserved' reflexions, not introduced in the refinement, were satisfactorily small, except for a very few which did not change their magnitude throughout the refinement. In Table 2 all the 393 measured reflexions are listed; for 'unobserved' reflexions, in place of F_o values there is a dash. We must remark that using the second least-squares program we did not refine the scaling factor $K=\Sigma|F_c|/\Sigma|F_o|$, which was recalculated before each cycle, in order to avoid interference with vibrational parameters; R was calculated in the form $\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$.

Final parameters

Table 1 shows the final values, which gave $R=0{\cdot}069$ for 249 'observed' reflexions, of the fractional coordinates and vibrational anisotropic parameters, the latter expressed as coefficients B_{ij} of the expression:

$$\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*\right).$$

The significant figures of standard deviations are listed below the values of the pertinent parameters. To get an idea of the anisotropy of vibrations it is better to write the equation of vibrational ellipsoids, referred to their own axes, in the form (Rollett & Davies, 1955):

$$\sum_{i=1}^{3} q_i(g_{i1}ha^*+g_{i2}kb^*+g_{i3}lc^*)^2\,,$$

where q_i are the thermal-vibration parameters for the three principal axes of the ellipsoids of vibration and g_{ij} are the direction cosines of these principal axes with respect to a^*, b^*, c^* respectively. Our values of q_i and g_{ij} are listed in Table 3 together with the mean-square displacements along the three principal directions of

Table 2. *Observed structure amplitudes and calculated structure factors*

(10 times the true values for the whole unit cell)

HKL	F_o	$\lvert F_o \rvert$	
00L			
2	30	30	
4	−145	148	
6	245	262	
8	64	70	
10	−64	68	
12	7	–	
01L			
1	37	46	*
2	−292	293	
3	269	241	
4	48	46	
5	−31	30	
6	62	63	
7	−12	–	
8	−93	93	
9	86	87	
10	−60	57	
11	−27	27	
12	−2	–	
13	−26	28	
02L			
0	18	15	
1	18	20	
2	−80	79	
3	−85	98	
4	31	28	
5	−67	66	
6	55	54	
7	5	–	
8	−71	68	
9	−73	69	
10	−5	–	
11	−63	63	
12	54	53	
03L			
1	−148	146	
2	−26	34	*
3	73	88	
4	25	24	
5	−28	29	
6	−73	76	
7	−89	83	
8	−51	51	
9	13	–	
10	27	29	
11	22	22	
04L			
0	9	15	
1	110	119	
2	−70	75	
3	37	39	
4	−87	97	
5	−92	91	
04L (contd.)			
6	0	–	
7	25	20	*
8	0	–	
9	38	34	
05L			
1	4	–	
2	−47	41	
3	−62	63	
4	60	67	
5	−40	39	
6	32	35	
10L			
0	317	270	
2	−187	187	
−2	404	354	
4	97	114	
−4	−181	184	
6	71	77	
−6	40	40	
8	−28	26	
−8	216	205	
10	−11	–	
−10	−20	–	
12	−38	37	
−12	−32	–	
11L			
0	−221	204	
1	302	268	
−1	−48	42	
2	−197	184	
−2	−137	113	
3	−28	24	
−3	40	41	
4	10	–	
−4	−38	36	
5	−90	91	
−5	165	161	
6	−20	22	
−6	120	122	
7	97	98	
−7	−5	–	
8	−73	75	
−8	−33	32	
9	− 8	–	
−9	21	–	
10	−46	45	
−10	−83	87	
11	−58	58	
−11	51	52	
12L			
0	−118	134	
1	−102	113	
−1	−43	41	
12L (contd.)			
2	−55	52	
−2	89	84	
3	−167	163	
−3	44	60	*
4	162	161	
−4	18	20	
5	14	–	
−5	5	–	
6	−50	48	
−6	−16	–	
7	−40	34	
−7	−25	24	
8	−76	72	
−8	5	–	
9	−96	95	
−9	−17	–	
10	63	59	
−10	−20	–	
11	−12	–	
−11	−48	45	
12	15	17	
−12	19	16	
13L			
0	−80	90	
1	3	–	
−1	−161	198	
2	73	76	
−2	40	47	
3	33	32	
−3	−24	23	
4	−45	38	
−4	−37	38	
5	−40	43	
−5	43	46	
6	−114	112	
−6	0	–	
7	−6	–	
−7	−91	82	
8	24	22	
−8	−25	27	
9	16	–	
−9	−56	49	
10	1	–	
−10	−11	–	
11	19	13	
−11	29	27	
14L			
0	−16	–	
1	82	99	
−1	−19	20	
2	−72	80	
−2	−19	–	
3	−40	37	
−3	103	111	
4	−19	–	
14L (contd.)			
−4	−93	106	
5	−12	–	
−5	−49	49	
6	19	–	
−6	−51	53	
15L			
0	−34	34	
1	−2	–	
−1	15	–	
2	48	49	
−2	−39	42	
3	−56	58	
−3	−53	56	
4	54	53	
−4	−34	27	
5	−19	18	
−5	−54	51	
6	−7	–	
−6	51	44	
20L			
0	−41	44	
2	6	–	
−2	150	165	
4	−46	52	
−4	59	66	*
6	−45	48	
−6	−56	52	
8	20	28	*
−8	116	114	
10	−52	60	
−10	88	98	
12	−53	54	
−12	−34	34	
21L			
0	−120	121	
1	50	50	
−1	145	123	
2	−97	107	
−2	−1	–	
3	−136	142	
−3	−72	76	
4	−9	–	
−4	−36	46	*
5	48	51	
−5	32	36	
6	−1	–	
−6	71	67	
7	14	–	
−7	101	98	
8	−56	51	
−8	37	36	
9	−66	63	
−9	−6	–	
10	−27	33	
21L (contd.)			
−10	−52	–	
11	−8	–	
12	25	27	
−12	−14	17	
22L			
0	−133	131	
1	−169	168	
−1	20	17	
2	123	129	
−2	−20	18	
3	−43	44	
−3	−11	–	
4	58	60	
−4	112	117	
5	8	–	
−5	86	78	
6	−88	86	
−6	−31	25	
7	−70	67	
−7	17	–	
8	16	–	
−8	−32	32	
9	−30	30	
−9	−21	–	
10	41	41	
−10	20	19	
23L			
0	20	17	
1	13	–	
−1	−32	30	
2	25	25	
−2	121	125	
3	9	–	
−3	−56	55	
4	−113	107	
−4	12	–	
5	28	32	
−5	14	–	
6	−23	20	
−6	−38	33	
7	3	–	
−7	−20	15	
8	26	23	
−8	26	20	*
9	8	–	
−9	−74	66	
10	−29	27	
−10	3	–	
24L			
0	−21	25	
1	2	–	
−1	−32	30	
2	−13	–	
−2	−2	–	
24L (contd.)			
3	11	-	
−3	23	22	
4	12	–	
−4	−39	–	
5	−11	–	
−5	23	–	
6	20	21	
−6	−59	58	
7	−21	18	
−7	−59	51	
8	24	23	
−8	−18	15	
25L			
0	30	28	
1	−3	–	
−1	28	26	
2	51	44	
−2	7	–	
3	−44	36	*
−3	−29	–	
30L			
0	40	41	
2	−43	54	
−2	−11	–	
4	−102	110	
−4	11	–	
6	24	26	
−6	16	–	
8	−10	–	
−8	18	–	
10	−71	71	
−10	62	68	
31L			
0	−70	73	
1	−82	87	
−1	49	54	
2	−56	59	
−2	6	–	
3	12	–	
−3	34	38	
4	31	29	
−4	6	–	
5	13	–	
−5	−55	56	
6	5	–	
−6	47	46	
7	−47	41	
−7	40	42	
8	−40	33	
−8	44	50	
9	−16	–	
−9	47	49	
10	7	–	
−10	−7	–	
HKL	F_c	$\lvert F_o \rvert$	
32L			
0	3	–	
1	−67	63	
−1	80	79	
2	75	78	
−2	−84	71	*
3	4	–	
−3	−8	–	
4	−30	31	
−4	49	45	
5	−20	–	
−5	39	43	
6	−21	–	
−6	48	52	
7	−18	–	
−7	69	67	
8	20	–	
−8	−54	53	
9	2	–	
−9	0	–	
33L			
0	34	36	
1	−1	–	
−1	−4	–	
2	−48	–	
−2	11	34	
3	54	53	
−3	6	–	
4	−44	45	
−4	77	71	
5	26	26	
−5	−2	–	
6	11	–	
−6	−23	29	
7	−13	–	
−7	−5	–	
8	−3	–	
−8	−3	–	
34L			
0	14	–	
1	30	24	*
−1	19	15	
2	11	–	
−2	4	–	
3	11	–	
−3	3	–	
4	13	–	
−4	−8	–	
40L			
0	5		
2	−89	94	
−2	19	–	
4	−21	–	
−4	−50	55	
6	22	–	
40L (contd.)			
−6	−8	–	
8	−39	–	
−8	22	24	
41L			
0	−51	54	
1	−22	20	
−1	−35	35	
2	−4	–	
−2	5	–	
3	0	–	
−3	21	–	
4	34	30	
−4	−9	–	
5	−32	31	
−5	−8	–	
6	−7	–	
−6	36	32	
7	−10	–	
−7	−22	22	
42L			
0	24	26	
1	−9	–	
−1	35	35	
2	7	–	
−2	−24	–	
3	−4	–	
−3	22	23	
4	−6	–	
−4	−12	–	
5	5	–	
−5	8	–	
6	−3	–	
−6	43	41	
43L			
0	−5	–	
1	29	26	
−1	−13	–	
2	−19	17	
−2	−3	–	
3	44	37	
−3	17	14	

Table 3. *Vibrational parameters of the principal axes of vibration with the values of the angles* (φ) *which these axes make with the molecular plane*

	i	q_i(Å^2)	r.m.s.(Å)	g_{i1}	g_{i2}	g_{i3}	φ
	1	0·420	0·146	0·335	0·124	0·931	5°
C(1)	2	0·755	0·195	0·891	0·281	0·365	35°
	3	0·203	0·101	0·307 –	0·951	0·014	55° 30′
	1	0·461	0·153	0·387 –	0·043	0·917	3° 30′
N(1)	2	0·741	0·194	0·910	0·176	0·383	41°
	3	0·176	0·094	0·146 –	0·983	0·108 –	48° 30′
	1	0·584	0·172	0·373	0·224	0·897	6° 30′
O(1)	2	0·926	0·217	0·921 –	0·209	0·338 –	63° 30′
	3	0·298	0·123	0·114	0·952	0·285	25° 30′

vibration.† There is a remarkable anisotropy, since the three semi-axes are roughly in the ratio 1:1·5:2. The last column of Table 3 gives the values of the angles φ which the principal axes of vibration make with the molecular plane, the equation of which is given later; the intermediate semi-axes lie almost in the molecular plane and are practically orthogonal to the C–C bond. From an examination of Table 3 one can deduce that, apart from the lengths of the axes, the ellipsoids are sensibly iso-orientated; this suggests the existence of an oscillation of the molecule as a whole.

Description and discussion of the structure

In Table 4 the most interesting bond-lengths and bond-angles are included, together with the standard deviations for some of them; as can easily be seen, none of the values are abnormal. The bonds C–C and C=N are respectively 1·449 ± 0·006 and 1·284 ± 0·005 Å; the former, according to Pauling (1960) has about 20% of double-bond character and so there is a certain degree of conjugation between C=N bonds.

Table 4. *Bond lengths and bond angles*

Bond lengths	
C(1)–C(2)	$1·449 \pm 0·006_1$ Å
C(1)–N(1)	$1·284 \pm 0·004_9$
N(1)–O(1)	$1·397 \pm 0·004_5$
C(1)–H(1)	1·080 Å
O(1)–H(1′)	1·016
O(1)–N(5)	2·811
H(1′)–N(5)	1·882
Angles	
C(2)–C(1)–N(1)	117°40′ ± 17′
C(1)–N(1)–O(1)	111 04 ± 14
H(1)–C(1)–N(1)	119 11
C(2)–C(1)–H(1)	123 09
N(1)–O(1)–H(1′)	95 01
O(1)–H(1′)–N(5)	150 32

The length of the N–O bond, 1·397 ± 0·004 Å, which is even longer than in dimethylglyoxime (Merritt & Lanterman, 1952), indicates the presence of a classical oxime configuration, already confirmed for dimethylglyoxime by a neutron diffraction analysis (Hamilton, 1961). Milone & Borello (1957), moreover, found in the infrared spectrum of glyoxime a shift of the stretching frequency of O–H of about 350 cm^{-1}, which, according to Nakamoto *et al.* (1955), indicates the presence of a hydrogen bond of about 2·8 Å. Such a shift, in the case of an *N*-oxide-iminic configuration, with a hydrogen bridge of the type N–H - - - O, should presuppose an appreciably longer hydrogen bond (> 2·9 Å), whereas our intermolecular distance between O(1) and N(5) is 2·811 Å. The oxime form, besides, agrees with the low frequency, 977 cm^{-1}, found for N–O stretching by Borello & Colombo (1957). On the basis of these data we concluded that the correct configuration of the glyoxime molecule is the classical oxime one, despite the fact that the difference Fourier synthesis alone might give rise to some ambiguity in placing the hydrogen of N–O–H group, owing to the halving of the pertinent zonal maximum of electron density. Consideration of the data in our possession therefore induced us, as already mentioned, to place the hydrogen of the hydroxyimino group in the position specified by the coordinates of Table 1; this hydrogen atom is not aligned with oxygen and nitrogen atoms, but the angle O–H - - - N turns out to be 150° 32′, a value not in contrast with the results of recent neutron diffraction investigations. As a check we computed a difference synthesis with Δ_{0kl}, obtainable from the final F_c, including the contribution of the hydrogen atoms. This Fourier synthesis confirmed the correctness of our positions, including those of the hydrogen atoms.

Apart from the hydrogen bond, the shortest intermolecular distance is that between C(1) and O(4), 3·096 Å, with interposition of a hydrogen atom; it must be remarked, however, that the angle C(1)–H(1) · · · O(4) is 67° 15′, so that there is no steric hindrance.

Between successive layers of molecules translated along x, the shortest distance occurs between O(1) and nitrogen of the molecule in position (1, 0, 0), and it is equal to 3·258 Å, so that no intermolecular contact takes place in this direction. The mean plane through the molecule has, in integer coordinates and with reference to the monoclinic triad of axes, the following least-squares equation:

$$-1·5051x + 1·2755y - 0·5229z = 0\,.$$

This equation has been deduced under the condition that the plane passes through the origin and that the

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† For the evaluation of the orientation of ellipsoids we made use of a program worked out in the Institute of Mineralogy of Pavia.

distances of C, N and O from it are the least ones. From this plane, nearly parallel to (1$\bar{1}$1), the calculated distances are respectively 0·004 Å, 0·019 Å, 0·008 Å, while for the hydrogen atoms of groups C–H and O–H they are −0·00007 and 0·10 Å. We can deduce that glyoxime molecule is planar, within the limits of experimental errors. The deviation of the nitrogen atom from the mean least-squares plane, though greater than the mean standard deviation of this atom, does not indicate, in our opinion, a significant distortion of the molecule. We can conclude that the symmetry of the glyoxime molecule is C_{2h}.

We record finally that the angle between the C–C bond and the y axis is 38° 51′.

Fig. 4 is a drawing of the molecular pattern projected onto the (100) plane; it is characterized by hydrogen bonds, O–H - - - N, linking a molecule with its centre in (0, 0, 0) to one with its centre in (0, $\frac{1}{2}$, $\frac{1}{2}$). Each molecule is therefore affected by four hydrogen bonds. The pattern exhibits, along the z axis, spirals of molecules linked by hydrogen bonds; these chains are, in turn, also connected by hydrogen bonds, so generating a network structure. Such a packing then appears rather different from that of dimethylglyoxime. The tridimensional pattern is given by the repetition along the x axis of the layer projected in Fig. 4; since between successive layers one can expect the action of van der Waals forces only, the reason for the distinct cleavage parallel to {100} is quite obvious. The strong birefringence of glyoxime, as well as the high value of γ and the measured $\widehat{z\gamma}$ angle, agrees with the fact that the molecules form chains roughly parallel to the z axis.

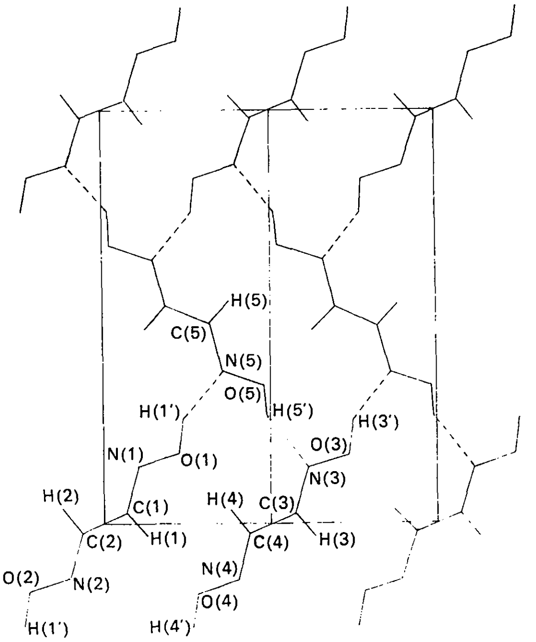

Fig. 4. Projection of the content of two unit cells onto the plane (100). Broken lines represent hydrogen bonds.

Standard deviations for coordinates, for thermal-vibration parameters and for cell constants have been evaluated by standard methods. With regard to the evaluation of standard deviations for bond lengths and angles we thought it better to make use of the full formula quoted by Templeton (1959), extended to angles too, since the standard deviations of coordinates are somewhat anisotropic (see Table 5). Anyway the values so deduced are in good agreement with those evaluated by the formulae suggested by Cruickshank & Robertson (1953), using an average $\bar{\sigma}$ for each of the three atoms C, N, O, as reported in Table 5, together with the standard deviations for integer coordinates.

Table 5. *Standard deviations* (σ) *and their mean values* ($\bar{\sigma}$) *for integer coordinates*

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\bar{\sigma}$
C	0·0033	0·0033	0·0023	0·0030
N	0·0028	0·0038	0·0052	0·0039
O	0·0038	0·0071	0·0059	0·0056

The computations were done on Olivetti ELEA 6001 computers of the Institute of Theoretical Physics of Turin and of the Impresa di Cristallografia del C.N.R., Rome.

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Riassunto

La gliossima, $H_2C_2(NOH)_2$, cristallizza nel sistema monoclino, classe prismatica, con due molecole per cella elementare ed appartiene al gruppo spaziale $P2_1/c$. Le costanti reticolari sono:

$$a_0=3{\cdot}868\pm0{\cdot}011,\ b_0=4{\cdot}414\pm0{\cdot}015,$$
$$c_0=10{\cdot}949\pm0{\cdot}035\ \text{Å};\ \beta=91°\ 10'\ .$$

Proprietà ottiche: $\alpha=1{\cdot}482$; $\beta=1{\cdot}641$; $\gamma=1{\cdot}856$; P.A.O. parallelo a (010); $2V=89°\ 30'$; $\widehat{z\gamma}\simeq7°\ 30'$.

E' stato eseguito uno studio strutturale basato su tutti i riflessi misurabili con la radiazione Cu $K\alpha$; il valore finale di R, per 249 riflessi con ampiezza diversa da zero, è risultato 6·9%. Le molecole della gliossima sono nella forma ossimica classica, sono planari e nella configurazione ***anti-s-trans***. La loro simmetria è C_{2h}; il piano molecolare è praticamente parallelo al piano (1$\bar{1}$1). Le molecole sono concatenate da legami idrogeno, del tipo O–H - - - N, di lunghezza 2·811 Å. Lungo l'asse delle x vengono a formarsi degli strati successivi di molecole legati solo da forze di van der Waals.

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Structure of *cis*-1,2,3-Tricyanocyclopropane

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A three-dimensional X-ray diffractometric study of $(CHCN)_3$, space group $R3c$, yields an endocyclic bond length (1·518 Å) and adjacent angles virtually duplicating those in cyclopropyl chloride. Other bond lengths are: exocyclic C–C, 1·449 Å, C≡N, 1·144 Å; these two bonds make an angle of 178·1°. The molecule departs slightly from $3m$ symmetry because of close N · · · H and N · · · C contacts in the crystal.

The difference electron density has a peak of $+0{\cdot}06$ e.Å^{-3} at the midpoint of the exocyclic C–C bond and one of $+0{\cdot}05$ e.Å^{-3} displaced 0·32 Å in the expected direction from the axis of the endocyclic bond. At the midpoint of the C≡N bond is a trough of $-0{\cdot}03$ 3.Å^{-3}.

In preparation for the study, by X-ray diffraction at low temperature, of the electron-density distributions in small organic molecules, we have determined, at room temperature (26° ± 1 °C), the crystal structure of *cis*-1,2,3-tricyanocylopropane $(CHCN)_3$ (Sadeh & Berger, 1958; Griffin & Peterson, 1963). The space group is $R3c$ and the hexagonal unit cell, with dimensions $a = 9{\cdot}8815 \pm 0{\cdot}0020$ Å and $c = 10{\cdot}4185 \pm 0{\cdot}0012$ Å (based on $\lambda = 1{\cdot}54050$ Å for Cu $K\alpha_1$), contains six molecules; $d_{\text{calc}} = 1{\cdot}324$. The molecule lies on a threefold rotation axis and the asymmetric unit comprises four atoms in general positions.

The crystal grows from aqueous ethanol as thin needles, elongated along the polar c axis. Cutting with a stream of abrasive powder (Pepinsky, 1953) yielded a hexagonal prism whose largest dimension was 0·5 mm. The reflexion intensities were measured with nickel-filtered Cu $K\alpha$ radiation on a General Electric single-crystal orienter (Furnas, 1957) with stationary crystal and counter and a 10° take-off angle, which provided a convergent beam 0·6° wide at the crystal. At low and medium Bragg angles ($2\theta < 130°$) the α_1–α_2 doublet was recorded; at higher angles the α_1 component alone was recorded, with the counter aperture set to exclude the α_2 reflexion. Of the 225 independent reflections accessible within the instrumental range of $2\theta < 165°$, one – 550 – gave no detectable intensity above a rather high background, due to Fe $K\alpha$ contamination, and was treated as unobserved but with low statistical weight and high threshold value; a second – 0,5,10 – could not be properly measured because of this same contamination and was given zero weight.

The measured intensities were corrected for absorption (Coppens, Leiserowitz & Rabinovich, 1965) and, towards the end of the refinement, for extinction (Zachariasen, 1963) with a computer program written by Mr L. Leiserowitz. The absorption factor varied between 0·76 and 0·84; the largest extinction correction amounted to 13% of the observed intensity. Comparison of the absorption-corrected intensities of sixteen pairs of symmetry-related reflexions led to an estimated random error in intensity of about 1·1% superimposed on the statistical counting error, *i.e.*

$$\sigma^2(F_o^2) \sim K^2(I+B+2)/10 + (0{\cdot}011\ F_o^2)^2\,,$$

where I and B are the reflexion and background counts, respectively, after reduction by an invisible first decade scaler, and $K = F_o^2/(I-B)$ includes scaling, Lorentz, polarization, absorption, and extinction corrections. The estimated standard deviations of the stronger reflexions were increased above this estimate to allow for a 10% uncertainty in the extinction correction.