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The Crystal Structure of *syn-p*-Nitrobenzaldoxime

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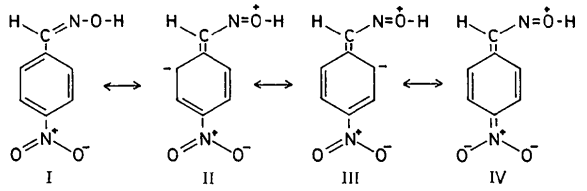
The crystal structure of *syn-p*-nitrobenzaldoxime, NO_2–C_6H_4–CH=NOH, has been determined from three-dimensional photographically recorded and visually estimated X-ray diffraction data by a symbolic addition procedure, and has been refined by Fourier and full-matrix least-squares methods. The final R is 0·100. The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a=6{\cdot}252\pm0{\cdot}009$, $b=4{\cdot}88\pm0{\cdot}01$, $c=24{\cdot}75\pm0{\cdot}03$ Å, $\beta=94{\cdot}66\pm0{\cdot}04°$. There are four molecules in the unit cell. The molecular geometry of the molecules has been compared with those found for other benzenoid aldoximes, especially with that for *syn-p*-chlorobenzaldoxime, and indicates that there is a small contribution from a quinonoid structure to the hybrid molecules. As in *syn-p*-chlorobenzaldoxime, the structure is built up of dimers formed by association through hydrogen bonds with O–H···N distances of 2·83 Å.

Introduction

The crystal structure of *syn-p*-nitrobenzaldoxime has been analysed firstly to compare the geometry of the oxime moiety of that molecule with the dimensions found for other benzenoid aldoximes, especially for *syn-p*-chlorobenzaldoxime (Jerslev, 1958; Folting, Jerslev & Lipscomb, 1964; Gram Jensen & Jerslev, 1969; Gram Jensen, 1969, 1970). It was possible in the latter case that the replacement of a chlorine atom with a nitro group might influence the geometry of the oxime group owing to a contribution from the quinonoid structure to the hybrid molecule. This is IV in the diagrams below, which show a few of the possible resonance molecules.



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Secondly, it was of interest to determine whether the structure is built up of dimers formed by association through hydrogen bonds, as in the structure of *syn-p*-chlorobenzaldoxime. This is indicated by the infrared spectroscopic data for the compounds.

Experimental

syn-p-Nitrobenzaldoxime was prepared by reacting *p*-nitrobenzaldehyde with hydroxylamine and purified by recrystallization from ethanol. After slow evaporation of a 90% ethanol–water solution colourless, elongated, needle-like crystals (m.p. 128–129 °C) were obtained.

Preliminary precession and Weissenberg X-ray diffraction photographs showed that the crystals were monoclinic with the unique axis parallel to the crystal needle axis. The space group was determined from systematically absent reflexions and the unit-cell parameters (see *Crystal data*) were measured from precession photographs taken at room temperature with Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation. The crystal density was measured by flotation in potassium iodide solution.

A crystal with dimensions $0{\cdot}18\times0{\cdot}16\times0{\cdot}4$ mm, placed in a Lindemann glass tube, was used to collect three-dimensional, multiple-film, equi-inclination Weissenberg diffraction photographs for layers hKl with $0\leq K\leq4$, using Cu $K\alpha$ X-radiation. Precession photographs from the same crystal and using Mo $K\alpha$ radiation were taken for the layers Hkl with $0\leq H\leq2$. All photographs were made at room temperature. The intensities of the diffracted spectra were estimated visually by comparison with a calibrated film strip. Lorentz and polarization factors, and corrections for spot-shape differences in the Weissenberg data (Phillips, 1956) were applied and the observations were placed on a common scale using the least-squares method of Hamilton, Rollett & Sparks (1965). The intensities measured from the precession photographs were not included in the observed data set, being used only to correlate the intensities observed on the Weissenberg photographs. No corrections for absorption or extinction were made. A total of 797 observed independent reflexions, about 60% of the number

within the copper sphere, were thus prepared for use in the structure analysis.

Crystal data

syn-p-Nitrobenzaldoxime, NO_2–C_6H_4–CH=NOH, $M=166{\cdot}14$. Monoclinic, $a=6{\cdot}252\pm0{\cdot}009$, $b=4{\cdot}88\pm0{\cdot}01$, $c=24{\cdot}75\pm0{\cdot}03$ Å, $\beta=94{\cdot}66\pm0{\cdot}04°$, $U=753\pm2$ Å^3. $D_m=1{\cdot}47\pm0{\cdot}01$ g.cm^{-3}, $Z=4$, $D_c=1{\cdot}464\pm0{\cdot}004$ g.cm^{-3}. Linear absorption coefficient for X-rays [λ(Cu $K\alpha$)$=1{\cdot}5418$ Å], $\mu=10{\cdot}2$ cm^{-1}. Number of electrons per unit cell, $F(000)=344$. Systematically absent reflexions: $h0l$ when l odd, $0k0$ when k odd; space group $P2_1/c$. Crystal needle axis parallel to **b**.

Structure determination

The structure was determined by a symbolic addition procedure (Zachariasen, 1952; Karle & Karle, 1966) using the computer program written for centrosymmetric crystals by Dewar and Stone, University of Chicago, U.S.A. The input to this program, apart from control parameters and basic crystal data for the compound to be analysed, is an approximate empirical formula, atomic scattering factors for those atoms comprising the structure and a set of structure amplitudes (or related quantities) for the crystal studied, and it can proceed without interruption to determine signs and conclude with sets of signed normalized structure factors which can be used as input to an appropriate Fourier program for calculation of E maps. Intervention is possible at various stages in the program if desired.

For the analysis described here this program was used in its fully automatic mode to perform the following sequence of operations: initially all reflexions within the experimental copper sphere of reflexion were used to compute a Wilson plot (Wilson, 1942). The overall temperature factor ($B=2{\cdot}2$ Å^2) and scale factor derived in this step were employed in the computation of the normalized structure amplitudes, $|E_h|$, from the expression

$$|E_h|^2 = |F_h|^2/\varepsilon \sum_{j=1}^{N} f_{jh}^2 .$$

$|F_h|^2$ is the square of the structure amplitude with indices h, placed on an absolute scale and corrected for vibrational motion, the multiplicity factor ε for space group $P2_1/c$ is 2 for the $h0l$ and $0k0$ reflexions and 1 for all others, f_j is the atomic scattering factor for the j^{th} atom and the summation is over the N atoms of the unit cell. The average distribution of $|E_h|$'s was calculated, after which the data were rescaled (the factor required was 1·026) so that the average value of $|E_h|^2$ was unity, and new distributions were calculated. The results are listed in Table 1.

The rescaled data were sorted in order of decreasing $|E_h|$ and the 400 largest of them (an input parameter) with $|E_h|\geq0{\cdot}97$ were selected to be employed in the sign determination, which was based exclusively on the satisfaction of the $\sum_2$ relationship,

$$\mathrm{s}\ E_h \approx \mathrm{s} \sum_k E_k \,.\, E_{h-k}$$

where s and $\approx$ have their usual meanings of 'the sign of' and 'probably equals' respectively. The 25 largest of the $|E_h|$'s ($\geq2{\cdot}55$) were then systematically tested in all possible pairs, used as E_k and E_{h-k}, for $\sum_2$ interactions producing E_h's from the other 398 data of the set. All the possible symmetry-equivalent indices were generated and used in this step. Symbols were assigned to five of these 25 largest reflexions using a selection rule based upon a combination of the following criteria (in decreasing order of weight): (i) as many symmetry groups as possible were included, (ii) reflexions having most interactions with other large $|E_h|$'s were favoured, and (iii) larger $|E_h|$'s were preferentially selected.

Starting with the set of five assigned reflexions the $\sum_2$ relationship was used to determine phases in terms of the symbols in the usual iterative procedure. After five cycles the phases of 176 reflexions (the number desired is an input parameter) had been assigned. In the first four of these a probability criterion (Woolfson, 1954; Cochran & Woolfson, 1955) requiring the overall probability corresponding to the summed product of all the pairs giving the same sign or symbol indication for a given unknown $|E_h|$ to be greater than 0·998 was used. For the last cycle this was reduced to 0·978. In addition, for the first three cycles a reflexion was not accepted as determined if there were any inconsistencies between the various symbol indications obtained for that reflexion from many combinations satisfying the $\sum_2$ relationship. Later, two such inconsistencies were permitted although, in fact, only rarely did any occur.

Three of the symbols used in the phasing process were then given plus signs to fix an origin (Hauptman & Karle, 1953). The two remaining symbols allowed four possible sign combinations and each of these was tested by substituting signs for the symbol combinations expressing the phase of each reflexion and computing an index which is a function of the inconsistencies generated by each sign combination. The indices

Table 1. *Distribution of* $|E_h|$*'s*

(*i*) Using the data scale factor obtained from the Wilson plot.
(*ii*) After rescaling to make $\langle|E_h|^2\rangle$ unity.

	Calculated (i) Wilson plot scale factor	Calculated (ii) Re-scaled	Theoretical (Centric)	Theoretical (Acentric)
$\langle\|E_h\|\rangle$	0·816	0·826	0·798	0·886
$\langle\|E_h^2\|\rangle$	0·975	1·000	1·000	1·000
$\langle\|E_h^2-1\|\rangle$	0·934	0·946	0·968	0·736
$\|E_h\|>1$ (%)	27·22	27·58	32·00	37·00
$\|E_h\|>2$ (%)	4·88	5·09	5·00	1·80
$\|E_h\|>3$ (%)	0·36	0·36	0·30	0·01

of two of these combinations were found to be equal and very much lower (corresponding to a greater likelihood of the sign combination being correct) than the others. Consequently two E maps, using signs for the 176 'known' E_h's based respectively on each of the more probable solutions, were computed and plotted. One of these clearly showed the full structure. Fig. 1 shows a composite projection along the b axis of the correct E map.

Refinement

Structure factors using the approximate coordinates for the twelve nitrogen, oxygen and carbon atoms obtained from the interpretable E map, and the overall isotropic temperature factor from the Wilson plot, were computed. The R value* for the 797 non-zero reflexions was 0·36.

Five cycles of Fourier refinement, still with an overall isotropic temperature factor but with individual scale factors dependent upon the index k appropriate to each datum (*viz.* layer scale factors) as additional parameters, reduced R to 0·195. Refinement then continued using the full-matrix least-squares method in blocks of four cycles. In two cycles of each block thermal parameters were varied while the scale factors were held, and in the other two cycles the layer scale factors were varied, keeping some appropriate thermal parameters fixed. This operation was necessary to avoid possible matrix singularities. Four cycles varying the atomic coordinates, scale factors and, now, individual atomic isotropic temperature factors in the manner just described were followed, at $R=0{\cdot}159$, by a further block of four cycles in which the thermal parameters were converted to anisotropic form, these additional parameters being refined with the others. Unit weights for all observed data were used. At this stage R was 0·140 and the shifts of all parameters were less than one tenth of their formal estimated standard deviations. After another block of four cycles of least-squares refinement employing only observed data with $\sin\theta/\lambda > 0{\cdot}35$ a three-dimensional difference synthesis (with all reflexions) was computed. The subsequent map showed maxima with peak heights of 0·5–0·7 e.Å^{-3} in positions expected for the hydrogen atoms. Although there were some spurious peaks, none had a magnitude greater than the lowest probable hydrogen peak, so there was little difficulty in postulating coordinates for all six hydrogen atoms. After another block of least-squares cycles in which the position parameters for all atoms, the scale factors and the anisotropic thermal parameters for the heavier atoms were varied (the thermal parameters of the hydrogen atoms were fixed at isotropic values with $B=3{\cdot}0$ Å^2), the nine strongest observations, which were considered to be affected by extinction or other factors, were omitted from the data set, and the analysis continued with four further cycles of full-matrix least-squares refinement of the same form as the previous block.

A graph of $1/\Delta^2$ against $|F_o|$, where $\Delta=||F_o|-|F_c||$ was plotted and, using this as a basis, a more realistic weighting scheme of the form

$$w=1/(A+|F_o|+B|F_o|^2)\,,$$

where w is the weight accorded each observation, $A=5$ electrons and $B=0{\cdot}007$ electron, was selected. The introduction of this weighting scheme was the only change made before the final block of four least-squares refinement cycles was computed. On the last cycle in this block shifts of all parameters were less than one tenth of their formal estimated standard deviations and the final R is 0·100. Tables 2 and 3 list the final atomic coordinates and the final thermal parameters (in the form of the mean-square-amplitude tensors, U_{ij}) respectively. From these parameters the terminal set of structure factors, listed with the observed data in Table 4, was computed. Comparison of the 176 signs determined by the symbolic addition procedure with the corresponding phases computed from the refined structure shows that all had been correctly assigned.

The computations described were performed firstly on an IBM 7094 computer using modifications of programs written by Tegenfeldt (see Liminga, 1965), (least-squares determination of unit-(cell parameters, Hamilton, Rollett & Sparks (1965, data reduction and scaling), Dewar & Stone (1968; symbolic addition), Sly, Shoemaker & van den Hende (1962; E, electron-density and difference electron-density maps) and Stewart & High (1964; *X-ray* 63 *crystallographic program system*) and later on an IBM 360/75 computer using

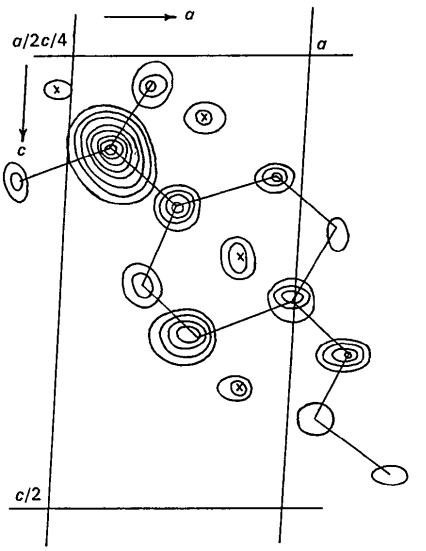

Fig. 1. Sections from the three-dimensional E map projected down the b axis. The contours are at equal intervals on an arbitrary scale. A skeleton of the molecule is superposed. The peaks marked with crosses are spurious.

* Defined, as usual, as $R=\sum||F_o|-|F_c||/\sum|F_o|$, where F_o and F_c are the observed and calculated structure factors and the summations are over all the reflexions (in this case non-zero reflexions only).

Table 2. *Atomic coordinates*

The estimated standard deviations ($\times 10^3$) of the coordinates are given in parentheses. The general positions are $\pm(x,y,z)$; $\pm(x,\frac{1}{2}-y,\frac{1}{2}+z)$.

	x/a	y/b	z/c
O(1)	1·2324 (1·0)	1·4858 (1·4)	0·4743 (0·2)
O(2)	0·4179 (0·8)	0·3198 (1·2)	0·3199 (0·2)
O(3)	0·6644 (0·9)	0·2580 (1·2)	0·2663 (0·2)
N(1)	1·0644 (1·0)	1·3119 (1·3)	0·4549 (0·3)
N(2)	0·5947 (0·9)	0·3764 (1·2)	0·3043 (0·2)
C(1)	0·7239 (1·1)	0·5789 (1·5)	0·3332 (0·3)
C(2)	0·9197 (1·1)	0·6538 (1·7)	0·3135 (0·3)
C(3)	1·0438 (1·1)	0·8425 (1·6)	0·3414 (0·3)
C(4)	0·9816 (1·1)	0·9724 (1·5)	0·3881 (0·3)
C(5)	0·7796 (1·1)	0·8915 (1·8)	0·4062 (0·3)
C(6)	0·6553 (1·2)	0·7032 (1·9)	0·3785 (0·3)
C(7)	1·1230 (1·2)	1·1681 (1·8)	0·4166 (0·3)
H(1)	1·177 (16)	1·610 (25)	0·493 (4)
H(2)	0·956 (15)	0·562 (23)	0·286 (4)
H(3)	1·163 (15)	0·913 (22)	0·327 (4)
H(5)	0·764 (14)	0·962 (22)	0·437 (4)
H(6)	0·576 (16)	0·628 (25)	0·389 (4)
H(7)	1·267 (16)	1·164 (22)	0·408 (4)

Table 3. *Mean square vibration amplitude tensors, $U_{ij}(\times 10^3)$ in* Å^2

The estimated standard deviations ($\times 10^3$) of the U_{ij} are given in parentheses. The U_{ij} are derived from the β_{ij}'s of the anisotropic temperature factor term $\exp\{-(\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j)\}$ using the relations $\beta_{ij}=2\pi^2U_{ij}a_i^*a_j^*$ where a_i and a_j are the appropriate unit cell dimensions:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
O(1)	66 (4)	37 (6)	57 (3)	−29 (3)	−17 (3)	4 (3)
O(2)	42 (3)	31 (6)	66 (3)	−26 (3)	4 (3)	12 (2)
O(3)	53 (3)	15 (6)	66 (3)	−6 (3)	−23 (3)	11 (3)
N(1)	52 (4)	4 (6)	56 (4)	−16 (3)	−4 (3)	2 (3)
N(2)	37 (3)	1 (6)	50 (3)	−10 (3)	4 (3)	2 (2)
C(1)	36 (3)	4 (6)	47 (4)	−2 (3)	12 (3)	3 (3)
C(2)	34 (4)	23 (5)	43 (4)	−5 (4)	−6 (4)	12 (3)
C(3)	35 (3)	15 (7)	46 (4)	−5 (4)	−5 (3)	10 (3)
C(4)	43 (4)	5 (6)	46 (4)	−3 (3)	11 (3)	7 (3)
C(5)	45 (4)	15 (7)	45 (4)	−2 (4)	2 (4)	11 (3)
C(6)	36 (4)	16 (7)	56 (5)	−6 (3)	2 (4)	10 (3)
C(7)	39 (4)	21 (7)	45 (4)	−7 (4)	−3 (4)	8 (3)

programs written by Stewart, Kundell & Baldwin (1970; *The X-ray System*). The X-ray atomic scattering factors used were taken from *International Tables for X-ray Crystallography*, (1962).

Discussion

As indicated by the infrared data the crystals of *syn-p*-nitrobenzaldoxime, like those of *syn-p*-chlorobenzaldoxime, are composed of dimers. Actually, the crystal structures of these two compounds are closely similar, the coordinates of most of the atoms of the nitro compound being approximately related to those published for their equivalents in the chloro compound (x_{Cl}, y_{Cl}, z_{Cl}) by the transformation ($\frac{1}{2}+x_{Cl}$, $\frac{1}{2}+y_{Cl}$, $\frac{1}{2}-z_{Cl}$). In other words, the differences between the two lead to a relative disposition of the symmetry elements such that the monoclinic cells have about the same size but an obtuse β angle for one compound and an acute β angle for the other. Projection diagrams illustrating the molecular packing of *syn-p*-nitrobenzaldoxime are shown in Fig. 2 and 3. The dimers result from the formation of two hydrogen bonds between two molecules related by a centre of symmetry. The lengths of the

Table 4. *Observed structure amplitudes $|F_o|$ and calculated structure factors $|F_c|$ (in electrons $\times 10$)*

Within each group of reflexions with constant h and k, the columns list, from left to right, l, $10|F_o|$, and $10F_c$. Reflexions marked with an asterisk were omitted from the final stages of the refinement.

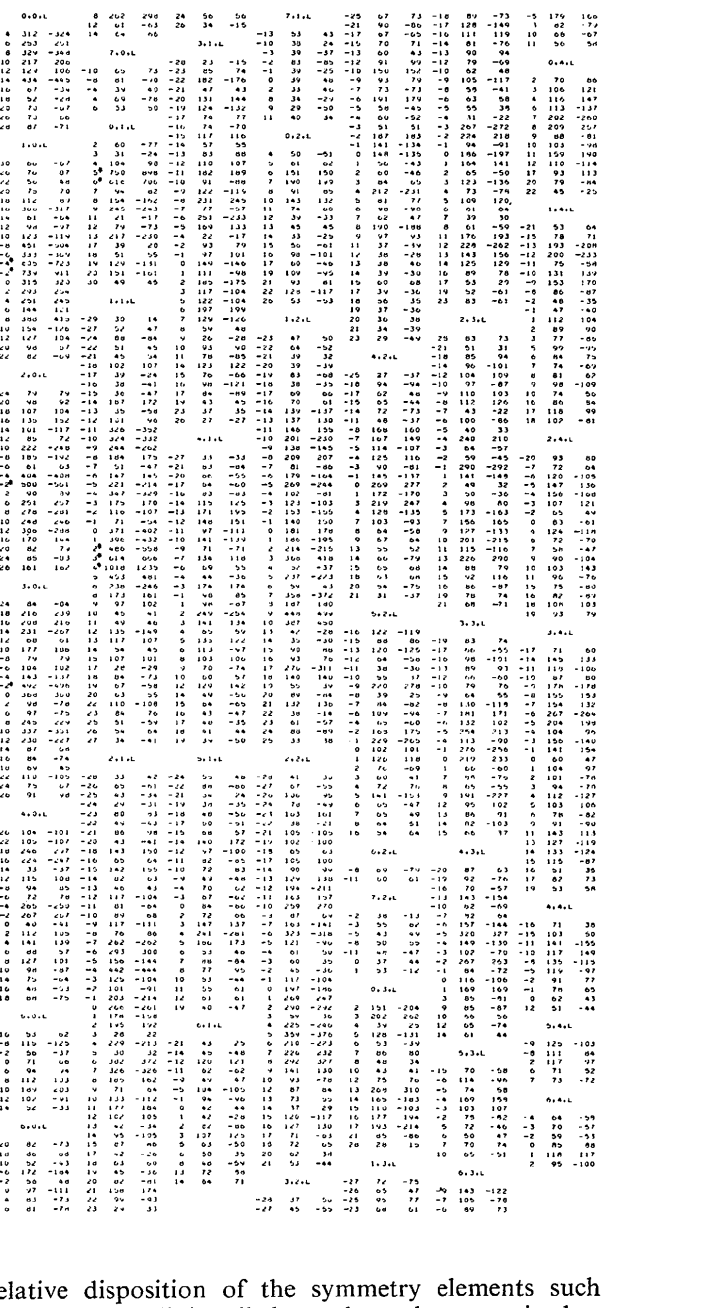

Table 5. *Comparison of hydrogen bonding systems*

	syn-p-Nitrobenzaldoxime	*syn-p*-Chlorobenzaldoxime	Dimethylglyoxime
N–O···N(II)	85·0 ± 0·4°	84·7°	86·0 ± 0·7°
O–N···O(II)	95·0 ± 0·4	95·3	94·0 ± 0·7
H–O–N	107 ± 7	(105–106)*	110·0
O–N···H(II)	104 ± 3	(105–107)*	106·2 ± 1·5
O–H···N(II)	144 ± 10	(147–150)*	140·0 ± 2·5
O···N(II)	2·833 ± 0·010 Å	2·825 ± 0·006 Å	2·766 ± 0·020 Å
O–H	0·85 ± 0·11	(0·96–1·06)*	1·020 ± 0·036
H···N(II)	2·10 ± 0·10	(1·90–1·99)*	1·906 ± 0·020
H···H(II)	2·51 ± 0·15	2·4*	
N···N(II)	3·050 ± 0·010		2·981 ± 0·019
O···O(II)	3·270 ± 0·010		3·147 ± 0·031

* Hydrogen atomic positions calculated from considerations of steric and geometrical factors.

O–H···N bonds are 2·83 Å, the same as the value found in the chloro compound. The least-squares plane through the two oxygen atoms and the two nitrogen atoms makes a angle of 11·2° with the plane through the benzene ring carbon atoms. In addition, the hydrogen atoms are 0·85 Å distant from the oxygen atoms but, to allow them to be sufficiently separated (Table 5) they are not on the line joining the nitrogen and oxygen atoms of bonded dimers. In fact, the O–H···N angle is 144 ± 10° (Fig. 4). This hydrogen bonding system is almost identical with that in dimethylglyoxime (Hamilton, 1961) and *syn-p*-chlorobenzaldoxime (Table 5) although, in the latter case, the hydrogen atoms were not located directly. Further intermolecular contacts are made by each molecule with eleven others. The shortest (2·95 Å) is about 0·5 Å less than any of the others and occurs between atoms [N(2) of one molecule and O(3) of the neighbouring molecule related to the first by a twofold screw axis] which in the resonance structures carry some charge. Such small residual charges, together with the hydrogen bonding, may have determined the packing in the crystal structure.

Tables 6 and 7 and Fig. 5 show the interatomic distances and angles found for molecules of *syn-p*-nitrobenzaldoxime.

Table 6. *Bond lengths*

The estimated standard deviations ($\times 10^2$ for bonds to hydrogen, $\times 10^3$ for others) of the distances are given in parentheses.

N(1)–O(1) Å	1·405 (9)	C(1)–N(2)	1·432 (9) Å
N(1)–C(7)	1·258 (10)	N(2)–O(2)	1·232 (8)
C(7)–C(4)	1·445 (11)	N(2)–O(3)	1·214 (8)
C(4)–C(5)	1·430 (10)	O(1)–H(1)	0·85 (11)
C(5)–C(6)	1·353 (11)	C(2)–H(2)	0·85 (10)
C(6)–C(1)	1·373 (11)	C(3)–H(3)	0·92 (10)
C(1)–C(2)	1·403 (10)	C(5)–H(5)	0·85 (10)
C(2)–C(3)	1·356 (11)	C(6)–H(6)	0·69 (11)
C(3)–C(4)	1·401 (10)	C(7)–H(7)	0·94 (10)

Using the *t* test, comparisons were made between the equivalent distances in this compound, *syn-p*-chlorobenzaldoxime, and other benzenoid compounds. These do, in fact, indicate that the quinonoid resonance structure makes a slight contribution to the hybrid molecule. C(3)–C(2) and C(5)–C(6), 1·356 and 1·353 Å respectively, both appear significantly shorter than the length in benzene when tested at the 1 % level, although it can be seen from the estimated standard deviations that the variations from the normal benzene C–C distances are of marginal significance when the pos-

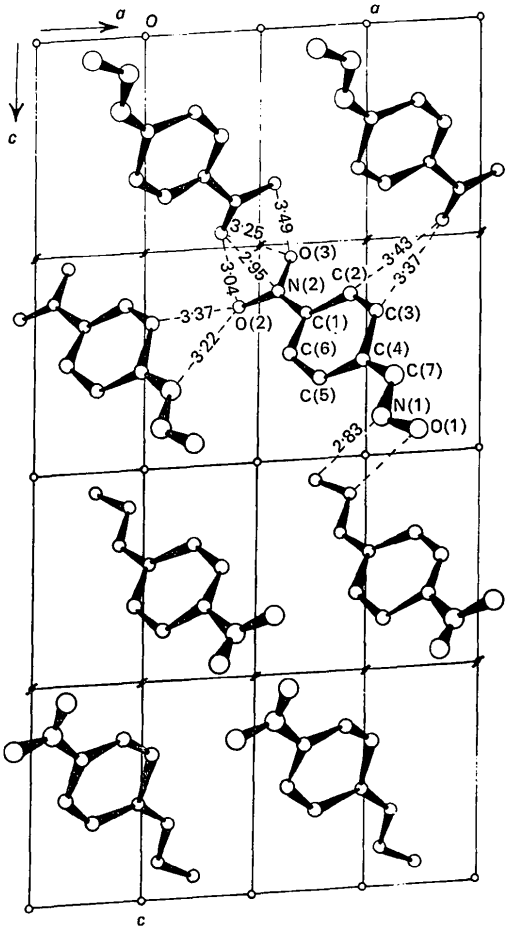

Fig. 2. Projection of the structure down the *b* axis. Some of the shorter intermolecular contacts are indicated.

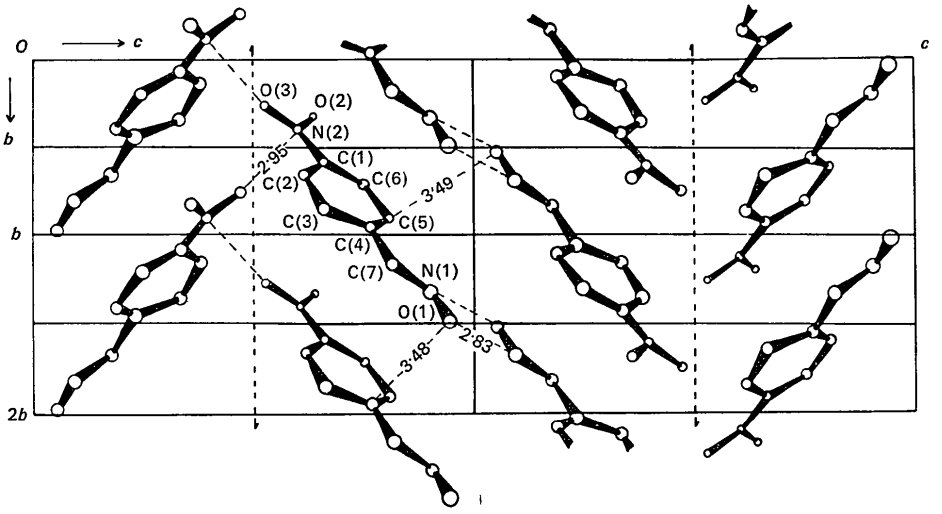

Fig. 3. Projection of the structure on the *bc* plane. Some of the shorter intermolecular contacts are indicated.

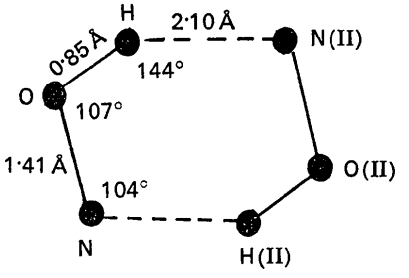

Fig. 4. Schematic diagram showing the geometry of the hydrogen bonding system.

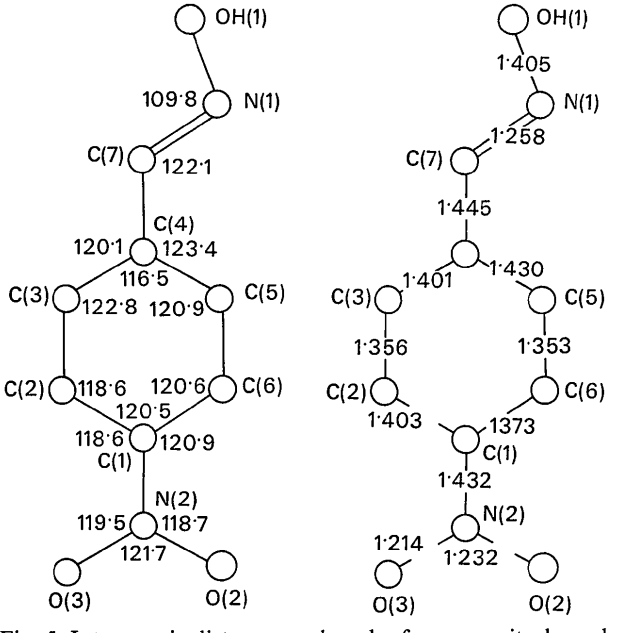

Fig. 5. Interatomic distances and angles for *syn-p*-nitrobenzaldoxime.

Table 7. *Valency angles*

The estimated standard deviations (×10 for angles not involving hydrogen) of the angles are given in parentheses.

O(1)–N(1)–C(7)	109·8 (6)°	C(1)–N(2)–O(2)	118·7 (6)°
N(1)–C(7)–C(4)	122·1 (7)	C(1)–N(2)–O(3)	119·5 (6)
C(7)–C(4)–C(5)	123·4 (6)	C(1)–C(2)–H(2)	116 (7)
C(7)–C(4)–C(3)	120·1 (6)	C(3)–C(2)–H(2)	126 (7)
C(3)–C(4)–C(5)	116·5 (6)	C(2)–C(3)–H(3)	121 (6)
C(4)–C(5)–C(6)	120·9 (7)	C(4)–C(3)–H(3)	116 (6)
C(5)–C(6)–C(1)	120·6 (7)	C(4)–C(5)–H(5)	110 (6)
C(6)–C(1)–C(2)	120·5 (7)	C(6)–C(5)–H(5)	129 (6)
C(1)–C(2)–C(3)	118·6 (7)	C(5)–C(6)–H(6)	125 (9)
C(2)–C(3)–C(4)	122·8 (7)	C(1)–C(6)–H(6)	111 (9)
N(2)–C(1)–C(6)	120·9 (6)	C(4)–C(7)–H(7)	116 (6)
N(2)–C(1)–C(2)	118·6 (6)	N(1)–C(7)–H(7)	122 (6)
O(3)–N(2)–O(2)	121·7 (6)	N(1)–O(1)–H(1)	107 (7)

sible effects of unaccounted systematic data errors are considered. Resonance contribution is probably also responsible for the significant shortening (1% level) of the C–NO_2 bond from the single bond value of 1·485 to 1·432 Å. This distance is close to the C–NO_2 length of 1·405 Å found in *N,N*-dimethyl-*p*-nitroaniline (Mark & Trotter, 1965) and that of 1·442 Å in α-*p*-nitrophenol (Coppens & Schmidt, 1965).

The geometry of the nitro group itself is quite normal.

The deviations from 120° of the valence angles in the benzene ring are probably not structurally real although one of them – the angle C(3)–C(4)–C(5) of 3·5° – appears significant on purely statistical grounds.

The only significant difference in the oxime groups of *syn-p*-nitrobenzaldoxime and *syn-p*-chlorobenzaldoxime is the length C(4)–C(7), the shortening of 0·041 Å to 1·445 Å in the former providing further evidence of a small quinonoid resonance contribution in the nitro compound.

The benzene ring is planar within the limits of

experimental error; Table 8 lists the displacements of some atoms from the least-squares plane through it. The nitrogen atom of the nitro group is in this plane, but the exocyclic carbon atom may be slightly out of it. The plane of the nitro group and that of the oxime group make angles of 4·7 and 9·1° respectively with the benzene ring plane; these twists are in the same sense and probably relieve some overcrowding between the oxime nitrogen atom and the benzene hydrogen atom *ortho* to the oxime group in one case and between the nitro group oxygen atoms and the benzene hydrogen atoms *ortho* to them in the other.

Table 8. *Distances of atoms from least squares planes* (Å)

The coordinates x, y and z are expressed parallel to the orthogonal axial directions **a**, **b** and **c***.

I. Benzene ring.

Equation: $0{\cdot}4070x - 0{\cdot}7209y + 0{\cdot}5610z - 4{\cdot}1320 = 0$

Atom	Deviation	Atom	Deviation
C(1)	0·012	C(7)†	0·040
C(2)	−0·010	N(1)†	−0·116
C(3)	0·005	N(2)†	0·019
C(4)	−0·002	O(1)†	−0·048
C(5)	0·005	O(2)†	−0·028
C(6)	−0·010	O(3)†	0·118

II. Oxime group.

Equation: $0{\cdot}2803x - 0{\cdot}7029y + 0{\cdot}6538z - 4{\cdot}4447 = 0$

C(4)† −0·020

III. Nitro group.

Equation: $0{\cdot}3786x - 0{\cdot}6810y + 0{\cdot}6269z - 4{\cdot}6299 = 0$

C(1)† 0·059

† These atoms were not included in the calculation of the least squares plane.

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