

# The Crystal and Molecular Structure of *anti*-2,6-Dimethyl-4-chloro-*N*-methylbenzaldoxime

BY KAREN GRAM JENSEN\* AND BODIL JERSLEV

Chemical Laboratory C, The Royal Danish School of Pharmacy, Copenhagen, Denmark

(Received 30 May 1968)

*anti*-2,6-Dimethyl-4-chloro-*N*-methylbenzaldoxime,  $\text{ClC}_6\text{H}_2(\text{CH}_3)_2\text{CH}=\text{N}(\rightarrow\text{O})\text{CH}_3$ , crystallizes as monoclinic needles. The space group is  $C2/c$ ,  $Z=8$ ; the  $b$  axis is short. The structure determination was based on intensities of 1663 independent reflexions obtained with  $\text{Cu } K\alpha$  radiation at room temperature and measured by a Flying Spot Integrating Microdensitometer (Joyce-Loebl). The  $b$  axis projection was solved by comparison with that of the isomorphous bromine compound, and the  $y$  coordinates were found from the three-dimensional Patterson function and from packing considerations. Least-squares full-matrix refinements were carried out. The hydrogen atoms were located by a difference-Fourier synthesis. The side chain of the molecule is twisted  $55^\circ$  out of the plane of the benzene ring. The bond lengths and valency angles in the oxime moiety do not deviate significantly from values found in related planar molecules. A short intermolecular distance between oxygen and a methyl hydrogen is interpreted as a hydrogen bridge. The conformation of the methyl groups is discussed in relation to the molecular structure and to the packing of the molecules in the crystal lattice.

## Introduction

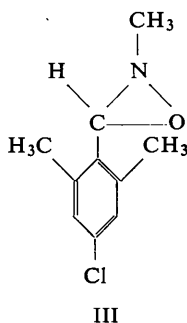
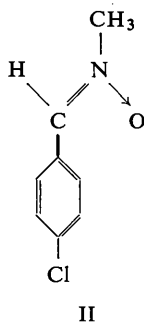
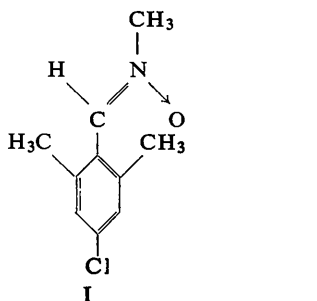
The present work is part of a research programme on the structure and chemistry of organic derivatives of hydroxylamine. In a previous crystal structure determination of *anti*-4-chloro-*N*-methylbenzaldoxime (II) the molecule was found to be approximately planar (Folting, Lipscomb & Jerslev, 1964). In *anti*-2,6-dimethyl-4-chloro-*N*-methylbenzaldoxime (I)

the molecule is sterically hindered in attaining a planar structure. The primary aim of studying the crystal structure of this compound has been to examine how the bonding system is affected by the non-coplanarity of the benzene ring and the side chain. Furthermore, the strongly polar oxygen atom could be expected to give rise to  $\text{C}-\text{H}\cdots\text{O}$  attractions of a similar type as previously found in 2-methyl-3-(2,6-dimethyl-4-chlorophenyl)oxaziridine (III) (Jerslev, 1967), and even this point might be elucidated by a crystal structure determination.

## Experimental

*anti*-2,6-Dimethyl-4-chloro-*N*-methylbenzaldoxime,  $\text{ClONC}_{10}\text{H}_{12}$ , previously prepared in this laboratory (Hjeds, Hansen & Jerslev, 1965) was used for the structure analysis. By slow evaporation of an alcohol-water solution bright crystals were obtained, which under the polarizing microscope were found to be monoclinic needles elongated in the  $b$  direction. The faces  $\{100\}$ ,  $\{10\bar{1}\}$  and  $\{001\}$  were observed, but the last mentioned form was well developed on only a few of the crystals. The interfacial angles were measured on a reflexion goniometer giving the  $\beta$  angle  $102.65^\circ$ . The density  $1.29 \text{ g.cm}^{-3}$  was found by flotation in a potassium iodide solution. The melting point was determined on a microscope hot-stage as  $177.5\text{--}178.5^\circ$ . The crystals slowly turn opaque when exposed to the air and to X-rays, but apart from this superficial change they appeared to be quite stable.

X-ray data were collected at room temperature using  $\text{Cu } K\alpha$  radiation and Weissenberg equi-inclination techniques. Multiple film exposures were made. The reflexions  $h0l$  were registered from a crystal with dimensions  $0.6 \times 0.5 \times 0.4 \text{ mm}^3$ , and the reflexions  $hkl$  with  $K=1\text{--}4$  from a crystal with dimensions  $0.5 \times 0.9 \times 0.5 \text{ mm}^3$ . A third crystal was cut by means of a razor



\* Present address: Chemical Laboratory B, Technical University of Denmark, Kgs. Lyngby, Denmark.

blade to dimensions  $0.3 \times 0.3 \times 0.3 \text{ mm}^3$  and was used for registration of the reflexions  $hkL$  with  $L=0-4$ . This registration covered 93 per cent of the reflexions obtainable within the sphere of reflexion ( $\xi < 1.97$ ). 1663 independent reflexions appeared as spots with measurable intensities, *i.e.* 72 per cent of the reflexions obtainable with  $\text{Cu K}\alpha$  radiation and 77 per cent of the reflexions observable on the photographs taken.

The intensities were measured by means of a Joyce-Loebl Flying Spot Integrating Microdensitometer. The values thus obtained include a certain compensation for spot-shape variations and further corrections for this type of error were not performed. Absorption and extinction corrections were neglected. Lorentz and polarization corrections and correlation of the data were performed with use of a scaling program for equi-inclination Weissenberg X-ray photographs (Hamilton, Rollett & Sparks, 1965).

Some preliminary two-dimensional Fourier series were calculated on the Frank analogue computer (Frank, 1957). Most calculations were performed on GIER computers or on the IBM 7090 computer at NEUCC, Lyngby, Denmark.

#### Unit cell and space group

The unit cell edges were obtained from zero-zone Weissenberg photographs taken with only one film in the camera and with aluminum powder lines superposed.  $a = 25.89 \text{ \AA}$ ,  $b = 5.050 \text{ \AA}$ ,  $c = 15.66 \text{ \AA}$ ,  $\beta = 102.65^\circ$  (from

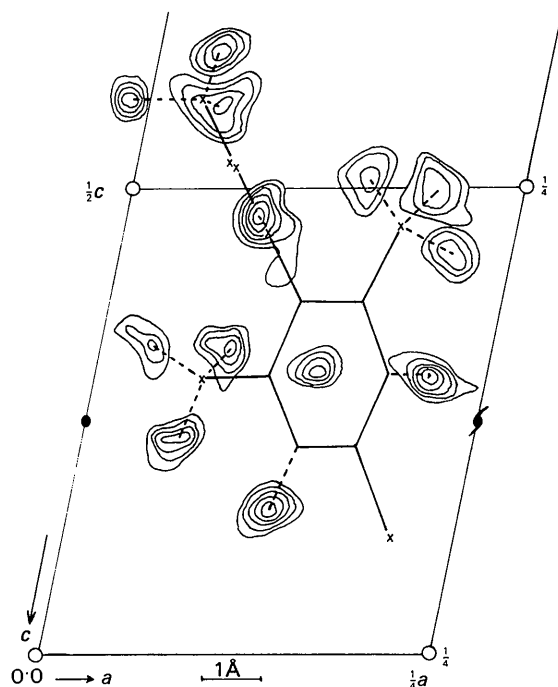


Fig. 1. Composite difference electron density map. Contours are at  $0.1 \text{ e.}\text{\AA}^{-3}$  intervals beginning at  $0.3 \text{ e.}\text{\AA}^{-3}$ . Some spurious peaks lower  $0.5 \text{ e.}\text{\AA}^{-3}$  are omitted. A molecular skeleton is superposed.

reflexion goniometer measurements).  $Z=8$  corresponds to the crystallographic density  $\rho_x = 1.31 \text{ g.cm}^{-3}$ . The absorption coefficient  $\mu_{\text{Cu K}\alpha}$  is  $30 \text{ cm}^{-1}$ .

The systematic absence of reflexions  $h0l$  with odd values of  $l$ , and of reflexions  $hkl$  with odd values of  $h+k$ , characterizes the centrosymmetric space group  $C2/c$  and the non-centrosymmetric  $Cc$ . A test for piezoelectric effect was performed with negative result, indicating the first mentioned as the most probable group. The refinement of the crystal structure determination confirmed that the space group is  $C2/c$ .

The analogous bromine compound, *anti*-2,6-dimethyl-4-bromo-*N*-methylbenzaldoxime,  $\text{BrONC}_{10}\text{H}_{12}$ , (Hjeds, Hansen & Jerslev, 1965) is isomorphous with the chlorine compound. Unit-cell dimensions were determined with less accuracy than the above mentioned, giving  $a = 26.5 \text{ \AA}$ ,  $b = 5.18 \text{ \AA}$ ,  $c = 16.1 \text{ \AA}$ ,  $\beta = 102.6^\circ$ ,  $Z=8$ ,  $\rho_x = 1.50 \text{ g.cm}^{-3}$ . Density determined by flotation was  $1.55 \text{ g.cm}^{-3}$ .  $\mu_{\text{Cu K}\alpha} = 55 \text{ cm}^{-1}$ .

#### Structure determination

The  $x$  and  $z$  coordinates were found from a study of the Patterson projections  $P(xz)$  of the chlorine compound and the isomorphous bromine compound. In the former map intramolecular vectors between the chlorine atom and the carbon atoms 1-9 were readily detected in the area around the origin, thus revealing the orientation of the planar part of the molecule (*cf.* Fig. 2). The halogen positions were detected from the  $P(xz)$  map of the bromine compound, and a subsequent Fourier synthesis  $\rho(xz)$  in which the signs of the structure factors were derived from the coordinates of the bromine atom, revealed all the non-hydrogen atoms. Two-dimensional refinements were performed by interpretation of electron density maps and by use of the  $R$ -minimization method of Bhuiya & Stanley (1963) programmed in ALGOL by Danielsen (1963). The bromine compound was not fully refined, and further work on that compound has not been carried out.

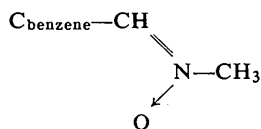
The  $y$  coordinates were obtained from the three-dimensional Patterson function  $P(xyz)$ , which was calculated with use of the Fourier program *ERFR 2* (Sly, Shoemaker & van den Hende, 1962). The Harker sections  $P(x0z)$  and  $P(x\frac{1}{2}z)$  made it possible to exclude two of the four sets of  $x, z$  coordinates, that are compatible with the  $\rho(xz)$  projection. Packing considerations led to the elimination of the third possibility. Finally an estimation of the tilt of the benzene ring based upon the  $x$  and  $z$  coordinates of the chlorine atom and of the carbon atoms 1-9 gave approximate  $y$  coordinates of all the non-hydrogen atoms.

Refinement of the positional parameters thus obtained was performed by the least-squares full-matrix program *ORFLS* (Busing, Martin & Levy, 1962) first using isotropic temperature factors and with all observed reflexions introduced in the calculations. No weighting scheme was used. The  $R$  value dropped to





values. Apart from the lengths of the N-C<sub>methyl</sub> bond, the geometry of the bonding system



was found to be identical in both compounds within the error of measurement. It may thus be inferred that the steric hindrance of coplanarity of the benzene ring and the side chain has had no measurable influence on the bond lengths and on the valency angles in this part of the molecule, and that the values found may be considered characteristic for this type of compound.

A marked difference between the two molecular structures is shown in the modes adopted to relieve the strain caused by interaction between the side chain

and the hydrogen atom, and the methyl group in the *ortho* position respectively. The molecule II is roughly planar, a plane through the non-hydrogen atoms of the side-chain forming an angle of 5° with the benzene plane. In this molecule the strain is compensated by an expansion to 127.8° of the appropriate angle between the side chain and the benzene ring [Fig. 4(II)]. In the present structure the corresponding angle is only slightly distorted [122.7°, Fig. 4(I)] and the strain has been relieved by the twisting of the side chain out of the plane of the benzene ring mentioned above.

Bond lengths and valency angles involving hydrogen atoms are listed in Table 4. Within the error of measurement the methyl groups have the expected tetrahedral configuration. The atoms H(2) and H(6) are placed in the benzene ring plane (see Fig. 2) and the corresponding valency angles C-C-H are about 120°. The atom H(9) is coplanar with C(9), C(4) and N as expected, the

Table 2. Atomic coordinates (*xyz*) with standard deviations ( $\sigma$ )

	<i>x</i>	$\sigma(x)$	<i>y</i>	$\sigma(y)$	<i>z</i>	$\sigma(z)$
Cl	0.21010	0.00006	0.18449	0.00034	0.87584	0.00008
C(1)	0.17637	0.00017	0.33143	0.00097	0.77896	0.00027
C(2)	0.13927	0.00018	0.52411	0.00098	0.78238	0.00027
C(3)	0.11102	0.00016	0.63600	0.00084	0.70496	0.00026
C(4)	0.12131	0.00016	0.55185	0.00083	0.62493	0.00025
C(5)	0.16092	0.00016	0.36245	0.00088	0.62280	0.00026
C(6)	0.18785	0.00017	0.24998	0.00098	0.70083	0.00030
C(7)	0.06989	0.00021	0.84375	0.00110	0.70833	0.00037
C(8)	0.17670	0.00020	0.28662	0.00125	0.53922	0.00031
C(9)	0.09122	0.00018	0.68370	0.00094	0.54561	0.00028
C(10)	0.03323	0.00022	0.70873	0.00112	0.40368	0.00032
N	0.06375	0.00014	0.55975	0.00070	0.47804	0.00023
O	0.05851	0.00014	0.30438	0.00063	0.47195	0.00023
H(7a)	0.0710	0.0022	0.8708	0.0122	0.7614	0.0038
H(7b)	0.0334	0.0023	0.7871	0.0116	0.6636	0.0034
H(7c)	0.0776	0.0021	1.0122	0.0128	0.6807	0.0035
H(8a)	0.2071	0.0023	0.1650	0.0118	0.5524	0.0034
H(8b)	0.1494	0.0022	0.1776	0.0118	0.4991	0.0035
H(8c)	0.1937	0.0021	0.4437	0.0119	0.5050	0.0034
H(10a)	0.0413	0.0021	0.6146	0.0120	0.3545	0.0036
H(10b)	-0.0112	0.0022	0.6700	0.0115	0.3956	0.0033
H(10c)	0.0485	0.0021	0.9181	0.0125	0.4138	0.0034
H(2)	0.1301	0.0020	0.5850	0.0114	0.8440	0.0034
H(6)	0.2168	0.0022	0.1446	0.0119	0.6977	0.0034
H(9)	0.0920	0.0021	0.8712	0.0126	0.5374	0.0034

Table 3. Thermal parameters ( $\beta_{ij}$ ) with standard deviations ( $\sigma$ )

The  $\beta_{ij}$  are defined by  $T = \exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \}$ .

	$\beta_{11}$	$\sigma \cdot 10^5$	$\beta_{22}$	$\sigma \cdot 10^5$	$\beta_{33}$	$\sigma \cdot 10^5$	$\beta_{12}$	$\sigma \cdot 10^5$	$\beta_{13}$	$\sigma \cdot 10^5$	$\beta_{23}$	$\sigma \cdot 10^5$
Cl	0.00217	3	0.05575	85	0.00269	5	0.00362	12	0.00011	3	0.00380	17
C(1)	0.00109	7	0.02708	210	0.00292	18	0.00046	30	0.00026	9	0.00151	52
C(2)	0.00130	7	0.02867	215	0.00248	17	-0.00067	32	0.00062	9	-0.00126	50
C(3)	0.00097	6	0.01611	173	0.00300	17	-0.00029	26	0.00027	8	-0.00158	46
C(4)	0.00098	6	0.01471	166	0.00263	17	-0.00061	26	0.00031	8	-0.00005	44
C(5)	0.00095	6	0.02348	194	0.00268	17	0.00005	28	0.00055	8	0.00062	47
C(6)	0.00091	7	0.02930	231	0.00360	20	0.00119	30	0.00050	9	0.00154	53
C(7)	0.00155	9	0.02506	236	0.00435	24	0.00139	36	0.00064	12	-0.00291	64
C(8)	0.00114	7	0.04901	288	0.00310	20	0.00099	39	0.00083	10	-0.00085	64
C(9)	0.00126	7	0.01589	179	0.00302	18	-0.00088	29	0.00027	9	0.00080	49
C(10)	0.00183	10	0.02749	230	0.00302	20	0.00090	39	-0.00035	11	0.00177	58
N	0.00119	6	0.01180	142	0.00324	16	-0.00001	23	0.00008	8	0.00018	39
O	0.00192	7	0.01183	128	0.00507	18	-0.00068	24	-0.00043	9	-0.00072	41

valency angle  $H(9)-C(9)-N$  ( $113^\circ$ ) is probably smaller than the angle  $H(9)-C(9)-C(4)$  ( $123^\circ$ ).

An impression of the molecular conformation can be obtained from Fig. 2. The conformation of the  $C(7)$ -

methyl group appears quite normal with one hydrogen atom approximately in the plane of the benzene ring and the other two placed symmetrically on either side of that plane. One of the hydrogen atoms [ $H(8a)$ ] of the

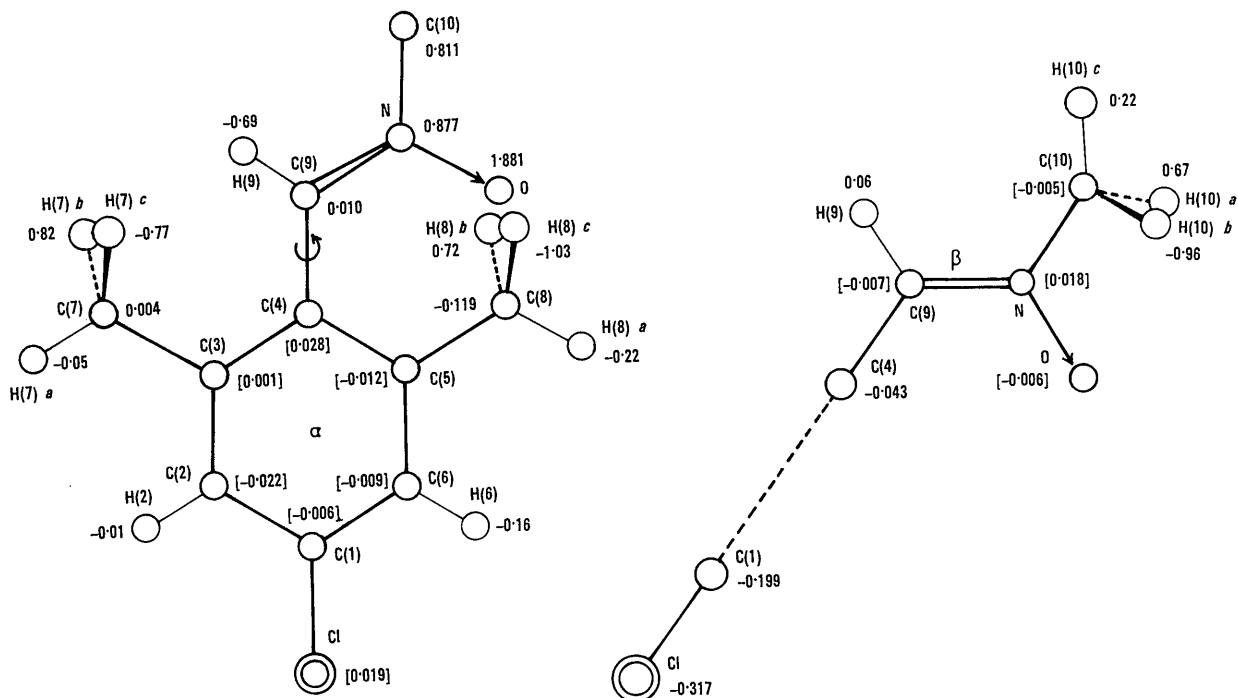


Fig. 2. Deviations, in Å units, from the best plane  $\alpha$  through the benzene ring and the chlorine atom, and from the best plane  $\beta$  through the side chain atoms  $C(9)$ ,  $N$ ,  $O$  and  $C(10)$ .

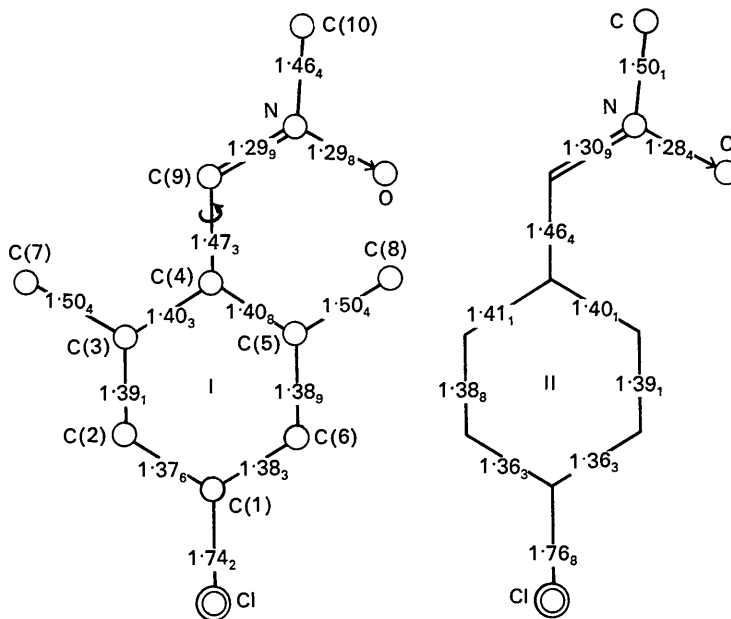


Fig. 3. Bond lengths in *anti*-2,6-dimethyl-4-chloro-*N*-methylbenzaldoxime (I), and *anti*-4-chloro-*N*-methylbenzaldoxime (II). Standard deviations in I, 0.004–0.007 Å and in II, 0.007–0.009 Å.

C(8)-methyl group is similarly placed near the benzene plane, but in this case the deviation of C(8) from the benzene plane and the close proximity with the oxygen atom complicates the pattern, and the atoms H(8*b*) and H(8*c*) are not symmetrically placed with respect to the benzene ring. One hydrogen atom [H(10*c*)] of the C(10)-methyl group is situated near the *trans* position with respect to the oxygen atom, a position which, considering the geometry of the bonds around the nitrogen atom, apparently gives the sterically most favourable arrangement. From the data of Foltz, Lipscomb & Jerslev (1964) it was calculated that the

conformation of the methyl group in the molecule II is practically identical with that of the C(10)-methyl group.

The short intramolecular distances observed (Table 5) show that the conformation of the C(7)-methyl group is fixed in the position described above by the steric hindrance exerted by the atom C(9). In the C(8)-methyl group the distance between a hydrogen atom [H(8*b*)] and the oxygen atom is probably significantly shorter than the sum of the Kitaigorodskii (1961) intermolecular atomic radii. A similar close contact between oxygen and a hydrogen atom [H(10*a*)] in the C(10)-

Table 4. Bond lengths and valency angles involving hydrogen atoms

Standard deviations:  $\sigma(\text{C-H}) \approx 0.06 \text{ \AA}$ ,  $\sigma(\angle \text{CCH})$  and  $\sigma(\angle \text{NCH}) \approx 3^\circ$ ,  $\sigma(\angle \text{HCH}) \approx 5^\circ$ .

C(2)—H(2)	1.09 Å	H(2)—C(2)—C(1)	122°	H(8 <i>a</i> )—C(8)—C(5)	110°
C(6)—H(6)	0.93	—C(3)	119	H(8 <i>b</i> )	113
C(9)—H(9)	0.96	H(6)—C(6)—C(1)	123	H(8 <i>c</i> )	117
		—C(5)	116		
C(7)—H(7 <i>a</i> )	0.84	H(9)—C(9)—C(4)	123	H(8 <i>a</i> )—C(8)—H(8 <i>b</i> )	102
—H(7 <i>b</i> )	1.08	—N	113	H(8 <i>a</i> )—      —H(8 <i>c</i> )	100
—H(7 <i>c</i> )	0.99			H(8 <i>b</i> )—      —H(8 <i>c</i> )	113
C(8)—H(8 <i>a</i> )	0.98	H(7 <i>a</i> )—C(7)—C(3)	106	H(10 <i>a</i> )—C(10)—N	102
—H(8 <i>b</i> )	1.00	H(7 <i>b</i> )	109	H(10 <i>b</i> )	111
—H(8 <i>c</i> )	1.10	H(7 <i>c</i> )	112	H(10 <i>c</i> )	105
C(10)—H(10 <i>a</i> )	0.97	H(7 <i>a</i> )—C(7)—H(7 <i>b</i> )	121	H(10 <i>a</i> )—C(10)—H(10 <i>b</i> )	103
—H(10 <i>b</i> )	1.20	H(7 <i>a</i> )—      —H(7 <i>c</i> )	109	H(10 <i>a</i> )—      —H(10 <i>c</i> )	116
—H(10 <i>c</i> )	1.13	H(7 <i>b</i> )—      —H(7 <i>c</i> )	100	H(10 <i>b</i> )—      —H(10 <i>c</i> )	119

Mean values: distance (H—methyl C) 1.03 Å  
 angle [H—methyl C—C (or N)] 109.4°  
 angle (H—methyl C—H) 109.2°

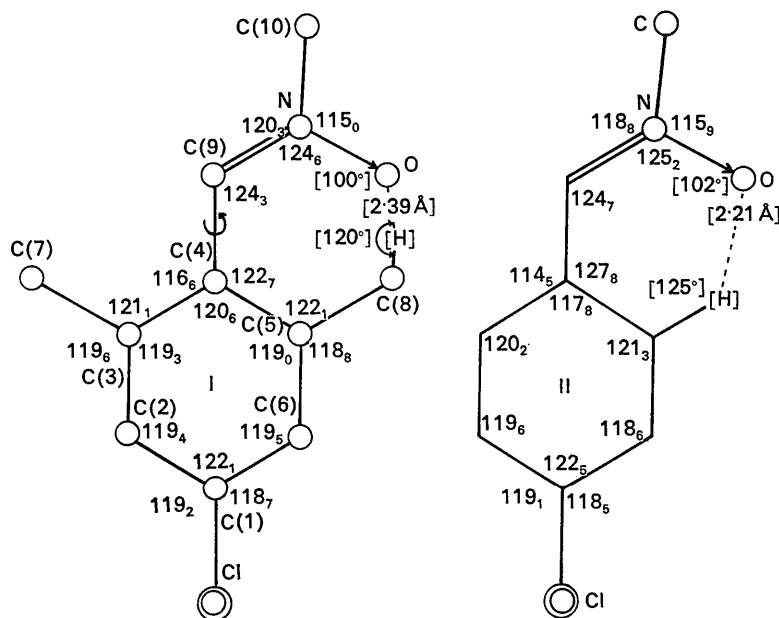


Fig. 4. Valency angles in *anti*-2,6-dimethyl-4-chloro-*N*-methylbenzaloxime (I) and *anti*-4-chloro-*N*-methylbenzaloxime (II). Standard deviations in I, 0.3–0.4° and in II, 0.5–0.6°. Short intramolecular O...H distances are shown.

Table 5. Short non-bonded intramolecular distances involving hydrogen atoms

Distances smaller than the sum of the Kitaigorodskii (1961) intermolecular radii  $R$  are given with the deviation  $\Delta$  from  $R_1 + R_2$ . Distances from methyl and benzene carbon atoms are omitted.

		$\Delta$
H(2)—Cl	2.86 Å	0.09 Å
H(6)—Cl	2.84	0.11
H(7b)—C(9)	2.67	0.30
H(7c)—C(9)	2.77	0.20
H(7a)—H(2)	2.29	0.05
H(8b)—O	2.39	0.14
H(8a)—H(6)	2.24	0.10
H(10c)—C(9)	2.43	0.54
H(10a)—O	2.38	0.15
H(10c)—H(9)	2.03	0.31

methyl group is also seen. Furthermore the atoms C(9) and H(9) make noticeable close contacts with the atom H(10c) in the latter methyl group.

Table 6. Short intermolecular distances

Distances smaller than the sum of the Kitaigorodskii (1961) intermolecular radii  $R$  are given with the deviations  $\Delta$  from  $R_1 + R_2$ . Molecular positions: (1)  $x, y, z$ . (1-)  $x, y-1, z$ . (2)  $x, 1-y, z+\frac{1}{2}$ . (3)  $\frac{1}{2}-x, \frac{1}{2}+y, 1\frac{1}{2}-z$ .

				$\Delta$
C(8)	(1)-Cl	(3)	3.56 Å	0.02 Å
O	(1)-H(10c)	(1-)	2.14	0.39
O	(1)-H(9)	(1-)	2.49	0.04
Cl	(1)-H(8c)	(2)	2.86	0.09
H(8b)	(1)-H(9)	(1-)	2.31	0.03

Short intermolecular distances (Table 6) include only one contact that is significantly shorter than the sum of the Kitaigorodskii intermolecular atomic radii, *i.e.*

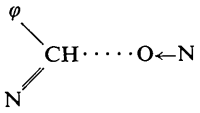
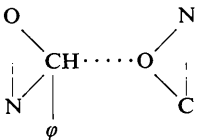
between the oxygen atom and the C(10)-methyl hydrogen atom H(10c) in a neighbour molecule.

Three short intra- or intermolecular contacts between methyl hydrogen atoms and oxygen thus appear in the structure. A short intermolecular CH...O contact was previously found in the crystal structure of the isomer molecule III. Calculations of intra- and intermolecular distances involving hydrogen atoms in the crystal structure of II disclosed two short distances of the same type. The results are summarized in Table 7. It deserves notice, that the angles associated with the intermolecular contact in the structure of compound III are in accordance with angular arrangements known from conventional hydrogen bonds, whereas this is not the case with the intermolecular contacts in the structures of molecule I and II. Cady (1967) has for a number of aromatic compounds reported short intermolecular distances between hydrogen atoms of benzene rings and oxygen atoms in nitro groups. The angular arrangements were in some cases in agreement with those of conventional hydrogen bonding systems, in other cases considerable deviations from such values were found. From the values in Table 7 and from Cady's results it seems justified to conclude that short C-H...O contacts may generally occur in crystal structures of organic molecules in which oxygen atoms are bonded to nitrogen, either by a coordinative bond or in a strained ring. A noteworthy feature in such contacts is that a pronounced polarization of the C-H bond is apparently not required, since methyl groups can take part in this type of hydrogen bridge formation.

The intra- and intermolecular O...H-C contacts which influence the conformations of the C(8)- and C(10)-methyl groups and which connect the molecules in the **b** direction are shown in Fig.5. In Fig.6 the

Table 7. Some short non-bonded distances CH...O

$\sigma$ - and  $\Delta$ -values defined as in Tables 4 and 5.  
 $\phi$  denotes a substituted phenyl group.

Compound	Type of contact		Distance H...O	$\sigma$	$\Delta$
I	N-CH <sub>3</sub> ...O←N	intermolecular	2.14 Å	0.06 Å	0.39 Å
II		—	2.15	—	0.38
III		—	2.30	0.10	0.23
I	N-CH <sub>3</sub> ...O←N	intramolecular	2.38	0.06	0.15
I	$\phi$ -CH <sub>3</sub> —	—	2.39	0.06	0.14
II	$\phi$ -H...O←N	—	2.21	—	0.32
Angles related to the intermolecular contacts					
I	C-H...O	157°	H...O-N	159°	
II	—	168	—	133	
III	—	168	—	103	



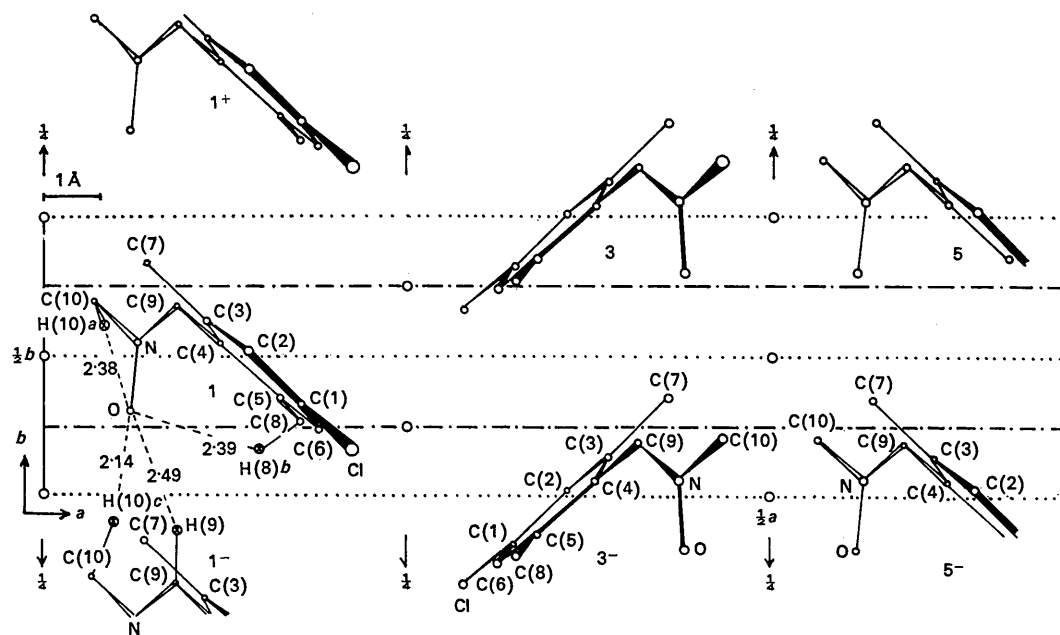


Fig. 5. The structure viewed along the *c* axis. Short O...H distances are shown.

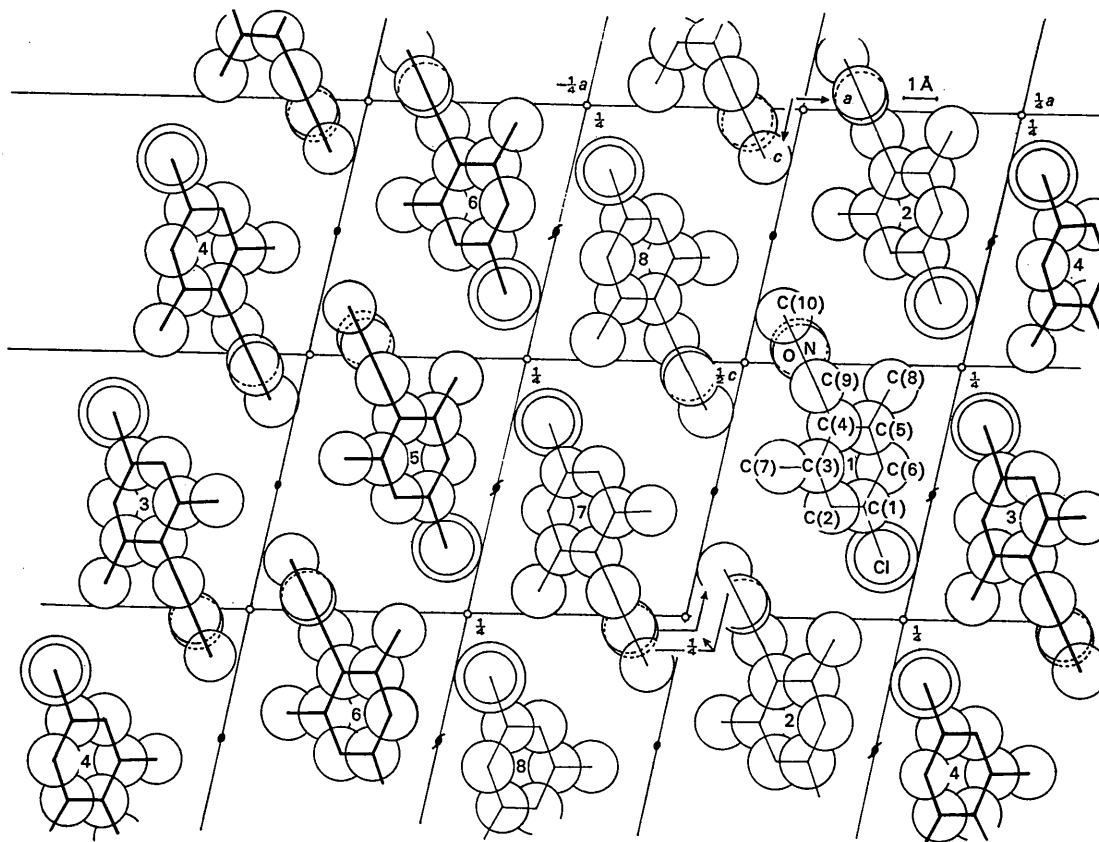


Fig. 6. The structure viewed along the *b* axis.

structure is viewed along the  $b$  axis. This projection illustrates very clearly that the external shape of a crystal – in this case the prominence of  $\{10\bar{1}\}$  – is a function of the packing of the molecules in the crystal lattice.

We are indebted to Professor R. W. Asmussen, Chemical Laboratory B, Technical University of Denmark for his kind interest and support during the final stages of this research.

#### References

- BHUIYA, A. K. & STANLEY, E. (1963). *Acta Cryst.* **16**, 981.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS: A FORTRAN Crystallographic Least-Squares Program*. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CADY, H. H. (1967). *Acta Cryst.* **23**, 601.  
 DANIELSEN, J. (1963). *ALGOL Program D45*. Univ. of Aarhus, Denmark.  
 FOLTING, K., LIPSCOMB, W. N. & JERSLEV, B. (1964). *Acta Cryst.* **17**, 1263.  
 FRANK, V. (1957). *J. Sci. Instrum.* **34**, 210.  
 HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129.  
 HJEDS, H., HANSEN, K. P. & JERSLEV, B. (1965). *Acta Chem. Scand.* **19**, 2166.  
 HUNT, D. J. (1965). *SFLS*. Imperial College of Science and Technology, London.  
 JERSLEV, B. (1967). *Acta Cryst.* **23**, 645.  
 KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau.  
 SLY, W. G., SHOEMAKER, D. P. & HENDE, J. H. VAN DEN (1962). *ERFR 2, Two and Three Dimensional Crystallographic Fourier Summation Program for the IBM 7090 Computer*. Massachusetts Institute of Technology.

*Acta Cryst.* (1969). **B25**, 925

## Effective Ionic Radii in Oxides and Fluorides\*

BY R. D. SHANNON AND C. T. PREWITT

*Central Research Department \* Experimental Station  
 E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, U.S.A.*

(Received 8 May 1968)

An empirical set of 'effective' ionic radii has been compiled by the use of techniques similar to those of Goldschmidt. The actual radius values were derived from: (1) 1000 experimental interatomic distances and (2) an approximately linear relationship between ionic volume and unit cell volume of over 60 isotopic series of oxides and fluorides. These radii take into account electronic spin state and the coordination of both cations and anions and have been found to reproduce closely the experimental interatomic distances in most oxides and fluorides. The choice of absolute values for anion radii and certain deviations from additivity are important and must be taken into consideration.

### Introduction

The traditional sets of ionic radii of Goldschmidt, Barth, Lunde & Zachariasen (1926), Pauling (1927), Zachariasen (1931), and Ahrens (1952) have been used with considerable success by chemists, physicists, mineralogists, and crystallographers alike. Ionic radii have been important to the crystal chemist because structure types and cation coordination numbers are determined principally by cation/anion radius ratios. The ability to substitute one cation for another in a particular structure is largely dependent upon matching ionic radii; thus, good values of ionic radii have been important to the chemist synthesizing inorganic compounds. The crystallographer has found radii helpful in comparing experimental interatomic distances with those

calculated for other structures.\* These interatomic distances in turn can help the chemist to infer oxidation states.

There are, however, several deficiencies in these traditional sets of radii: (1) they do not reproduce interatomic distances to the accuracy now possible in modern structural analyses; (2) although several papers (Pauling, 1927; Zachariasen, 1931) present techniques for calculating the effect of coordination number on *interatomic distances*, no provision is made for determining

\* Goldschmidt's & Pauling's radii and correction factors for coordination number (CN)  $\neq$  VI were included in Volume II of *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935). Interatomic distances in numerous inorganic compounds were published in Volume III of *International Tables for X-Ray Crystallography* (1962) and in *Tables of Interatomic Distances and Configuration in Molecules and Ions* (1958, 1965).

\* Contribution No. 1454.