Acta Cryst. (1983). C**39**, 1134–1136

(*E*)-4-Chloro-2,6-dimethylbenzaldehyde *O*-Methyloxime, $C_{10}H_{12}ClNO$, at 93 K

BY BODIL JERSLEV, JYTTE LERCHE AND INGRID KJØLLER LARSEN

Department of Chemistry BC, Royal Danish School of Pharmacy, 2 Universitetsparken, DK-2100 Copenhagen, Denmark

(*Received* 27 *January* 1983; *accepted* 3 *May* 1983)

Abstract. $M_r = 197{\cdot}67$, triclinic, $P\bar{1}$, $a = 10{\cdot}668$ (7), $b = 12{\cdot}151$ (8), $c = 4{\cdot}042$ (2) Å, $\alpha = 98{\cdot}85$ (5), $\beta = 100{\cdot}06$ (5), $\gamma = 71{\cdot}36$ (6)°, $V = 486$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}351$ (3), D_m (293 K) = 1·27 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}35$ mm^{-1}, $F(000) = 208$. Final $R = 0{\cdot}045$ for 3278 unique observed reflections. The oxime moiety is nearly planar and forms an angle of 23·3 (2)° with the benzene plane. There are no short *inter*molecular contacts in the crystal structure.

Introduction. The structure determination was undertaken in order to obtain reliable molecular dimensions of an *O*-methylated, aromatic aldoxime. The initial plan was to study the structure of 4-chlorobenzaldehyde *O*-methyloxime (m.p. 301 K) (*cf.* Folting, Lipscomb & Jerslev, 1964), but this was given up after preliminary X-ray photographs had indicated a disordered structure (Folting, unpublished data). The title compound was subsequently chosen in order to compare the structure with the corresponding *N*-methylated oxime (Jensen & Jerslev, 1969). The crystal structure at *ca* 233 K was initially determined from 975 photographically recorded reflections. The low-melting, volatile crystals were enclosed in a Lindemann-glass capillary during the exposure. The structure was solved by the Patterson method and refined to $R = 0{\cdot}11$. All hydrogen positions were located in a difference map except those of the *O*-methyl group, but the standard deviations on bond lengths and angles were large, 0·01–0·02 Å and 1° for bonds and angles, respectively (Udsen, 1970).

Experimental. Compound used for present structure determination prepared as described by Hjeds, Hansen & Jerslev (1965); suitable crystals for X-ray study obtained by very slow evaporation of a solution in ethanol–water (4:1) to which was added a small amount of acetone. D_m measured by flotation consistent with $Z = 2$. Crystals tend to grow as very long, rather flat needles, elongated in **c** direction, m.p. 309·5–310·0 K, crystal fragment 0·40 × 0·32 × 0·16 mm used. Picker FACS-2 diffractometer equipped with a graphite monochromator and a modified Nonius low-temperature device (Bernth, Larsen & Larsen, 1981). Temperature during data collection kept constant within ± 0·3 K, but actual temperature may deviate 2–3 K from that indicated in title. Cell parameters determined by least-squares calculations from θ values of 13 reflections. Intensities measured using θ–2θ scan method in range $2{\cdot}4 < 2\theta < 68°$. Four standard reflections, measured every 75 reflections, showed no significant variation. 4429 reflections measured over a hemisphere of intensity (h ±16, k ±18, l +6), 3963 of which unique ($R_{int} = 0{\cdot}02$), 3278 considered observed ($I_o > 2\sigma I_o$). Intensities corrected for Lorentz and polarization factors, but not for absorption. Atomic coordinates obtained by Udsen (1970) for non-H atoms used as starting point in refinement. After least-squares refining of positional and individual anisotropic thermal parameters of non-H atoms, a difference Fourier synthesis gave well defined maxima for all H atoms with peak heights 0·7–1·0 e Å^{-3}; background within ± 0·3 e Å^{-3} except in vicinity of Cl atom, where larger fluctuations occurred. Further refinement including positional parameters and individual isotropic thermal parameters of H atoms converged at $R = wR = 0{\cdot}045$ for 3278 unique observed reflections, $R = 0{\cdot}053$ for all 3963 unique reflections, $S = 2{\cdot}5$. Mean and max. shift/e.s.d. 0·04 and 0·2 respectively. All reflections given same weight which gave a flat distribution of $w(\Delta F)^2$. Refinements performed using XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

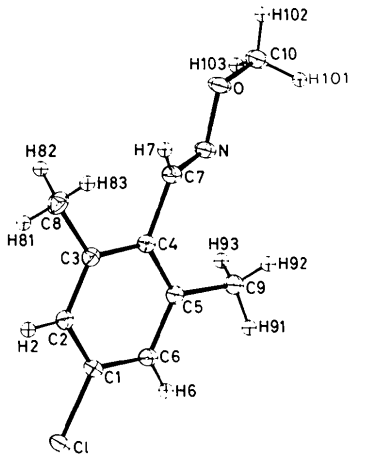

Fig. 1. *ORTEP* (Johnson, 1976) drawing of the title compound giving numbering of the atoms. The ellipsoids enclose 50% probability. H atoms are represented by spheres of arbitrary radius.

0108-2701/83/081134-03$01.50 © 1983 International Union of Crystallography

Table 1. *Atomic coordinates in fractions of the axial lengths and isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	U_{eq}/U_{iso} ($Å^2 \times 10^2$)
C(1)	0·2940 (2)	0·9506 (1)	1·0740 (4)	1·9 (1)*
C(2)	0·3964 (1)	0·8704 (1)	1·2529 (4)	1·9 (1)*
C(3)	0·3860 (1)	0·7596 (1)	1·2659 (4)	1·7 (1)*
C(4)	0·2718 (1)	0·7298 (1)	1·0943 (4)	1·6 (1)*
C(5)	0·1675 (1)	0·8131 (1)	0·9159 (4)	1·6 (1)*
C(6)	0·1801 (2)	0·9239 (1)	0·9099 (4)	1·8 (1)*
C(7)	0·2681 (2)	0·6107 (1)	1·1144 (4)	1·9 (1)*
C(8)	0·5016 (2)	0·6727 (1)	1·4531 (4)	2·1 (1)*
C(9)	0·0423 (2)	0·7881 (1)	0·7292 (4)	2·0 (1)*
C(10)	0·1391 (2)	0·3891 (1)	0·7321 (5)	2·4 (1)*
N	0·1982 (1)	0·5588 (1)	0·8947 (4)	2·0 (1)*
O	0·2188 (1)	0·4452 (1)	0·9799 (3)	2·1 (1)*
Cl	0·30957 (4)	1·08784 (3)	1·0508 (1)	2·49 (3)*
H(2)	0·474 (2)	0·893 (2)	1·380 (6)	2·8 (6)
H(6)	0·109 (2)	0·980 (2)	0·761 (6)	3·0 (6)
H(7)	0·313 (3)	0·575 (2)	1·321 (6)	3·1 (6)
H(81)	0·567 (2)	0·708 (2)	1·570 (6)	3·1 (6)
H(82)	0·546 (2)	0·607 (2)	1·302 (6)	2·5 (6)
H(83)	0·473 (2)	0·646 (2)	1·642 (6)	2·6 (6)
H(91)	−0·025 (2)	0·862 (2)	0·642 (7)	3·0 (6)
H(92)	0·001 (2)	0·756 (2)	0·876 (6)	2·2 (6)
H(93)	0·062 (2)	0·738 (2)	0·512 (6)	2·9 (6)
H(101)	0·043 (3)	0·427 (2)	0·743 (7)	4·0 (7)
H(102)	0·163 (3)	0·308 (2)	0·784 (6)	3·1 (6)
H(103)	0·156 (2)	0·392 (2)	0·494 (6)	2·1 (6)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsional angles* (°)

E.s.d.'s are in parentheses.

Cl–C(1)	1·746 (2)	C(5)–C(9)	1·511 (3)
C(1)–C(2)	1·388 (2)	C(4)–C(7)	1·475 (2)
C(2)–C(3)	1·395 (2)	C(7)–N	1·280 (2)
C(3)–C(4)	1·416 (2)	N–O	1·414 (2)
C(4)–C(5)	1·417 (2)	O–C(10)	1·433 (2)
C(5)–C(6)	1·399 (2)	C–H mean	0·99 (1)
C(6)–C(1)	1·388 (3)	$C-C_{benzene}$ mean	1·4005 (10)
C(3)–C(8)	1·515 (2)		
C(6)–C(1)–Cl	119·2 (1)	C(6)–C(5)–C(9)	117·9 (1)
C(2)–C(1)–Cl	119·2 (1)	C(3)–C(4)–C(7)	116·9 (1)
C(6)–C(1)–C(2)	121·6 (1)	C(5)–C(4)–C(7)	123·1 (1)
C(1)–C(2)–C(3)	119·5 (1)	C(4)–C(7)–N	123·3 (1)
C(2)–C(3)–C(4)	119·7 (1)	C(7)–N–O	109·7 (1)
C(3)–C(4)–C(5)	120·0 (1)	N–O–C(10)	108·7 (1)
C(4)–C(5)–C(6)	119·0 (1)	$C/N-C_{trigonal}-H$ mean	119 (1)
C(5)–C(6)–C(1)	120·1 (1)	$C/O-C_{methyl}-H$ mean	111 (1)
C(2)–C(3)–C(8)	118·2 (1)	$H-C_{methyl}-H$ range	101–114
C(4)–C(3)–C(8)	122·0 (1)	$H-C_{methyl}-H$ mean	108
C(4)–C(5)–C(9)	123·1 (1)		
C(3)–C(4)–C(7)–N	−156·3 (2)	C(6)–C(5)–C(9)–H(91)	−7 (2)
C(5)–C(4)–C(7)–N	24·1 (3)	N–O–C(10)–H(102)	174 (2)
C(2)–C(3)–C(8)–H(81)	7 (2)		

Discussion. The numbering of the atoms is shown in Fig. 1. Positional and thermal parameters are given in Table 1.* Bond lengths and angles and selected torsional angles are given in Table 2.

* Lists of structure factors, anisotropic thermal parameters and data of best planes α and β have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38560 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The benzene ring is nearly planar with a slight tendency towards a boat shape. Deviations from a calculated best plane, α, through the ring atoms are for C(1)–C(6): +7, −4, −7, +7, −3, −7 (2) Å $\times 10^{-3}$. The attached non-H atoms deviate considerably from that plane [Cl +55, C(7) +19, C(8) +34 and C(9) +3 (2) Å $\times 10^{-3}$]. The non-H atoms of the oxime side chain are approximately coplanar, maximum deviation from a best plane, β, defined by C(4), C(7), N and O being 0·011 (2) Å. The dihedral angle αβ is 23·3 (2)°. The magnitude of this angle varies considerably in crystal structures of aromatic aldoximes without *ortho* substituents (values from 1 to 33° have been found) presumably owing to packing conditions. In the present structure the minimum value is determined by the *intra*molecular contact distance between the N atom and the *ortho cis* methyl group [N···C(9) = 2·863 (2) Å].

The dimensions of the benzene ring agree well with those found for the *N*-methylated oxime of 4-chloro-2,6-dimethylbenzaldehyde (Jensen & Jerslev, 1969); this structure determination, based on data collected at room temperature, is, however, of lower accuracy (σ = 0·004–0·007 Å and 0·3–0·4° for bonds and angles, respectively). The ring angle *ortho cis* to the oxime chain is in the present structure 0·7 (2)° smaller than the *ortho trans* angle, and the *meta cis* angle is 0·5 (2)° larger than the *meta trans* angle. Similar angular deviations from C_{2v} symmetry were observed in the low-temperature study of (*E*)-benzaldehyde oxime (Jerslev, 1983), in which the dihedral angle αβ is of the same magnitude, but contrary to the present structure significant deviations from C_{2v} symmetry of the benzene bond lengths were observed in the (*E*)-benzaldehyde oxime molecules.

The dimensions of the oxime moiety agree with those of the only crystal structure published of an *O*-alkylated aldoxime (Gilman, Blount & Sternbach, 1972); the accuracy of these data is low. Direct comparison with accurate data from room-temperature studies cannot be made; but from a survey of such data for aromatic aldoximes (Jerslev, 1983), in which data for (*E*)-benzaldehyde oxime at 100 K are also included, some indirect conclusions may be drawn. The bond lengths found for (*E*)-benzaldehyde oxime at 100 K deviate appreciably from the values obtained at room temperature for a number of benzenoid (*E*)-aldoximes, whereas an excellent agreement with the well defined mean value of the angles C=N–O was observed. Based upon these results it is concluded, that the angle C=N–O found in the present study is probably within 1° characteristic for *O*-alkylated, aromatic (*E*)-oximes; furthermore it may be inferred that the length of the C=N bond in an *O*-alkylated, aromatic (*E*)-oxime does not, within an accuracy like that of the present determination, differ significantly from that of the corresponding unalkylated (*E*)-oxime, whereas the N–O bond as expected is longer, probably by *ca* 0·006 Å.

There are no *inter*molecular contacts shorter than the sum of the van der Waals radii in the crystal structure, in good accordance with the low melting point and the volatility of the compound.

The authors are grateful to Mr Flemming Hansen for collecting the data for the structure determination.

References

BERNTH, N., LARSEN, E. & LARSEN, S. (1981). *Tetrahedron*, **37**, 2477–2484.
FOLTING, K., LIPSCOMB, W. N. & JERSLEV, B. (1964). *Acta Cryst.* **17**, 1263–1275.
GILMAN, N. W., BLOUNT, J. F. & STERNBACH, L. H. (1972). *J. Org. Chem.* **37**, 3201–3206.
HJEDS, H., HANSEN, K. P. & JERSLEV, B. (1965). *Acta Chem. Scand.* **19**, 2166–2174.
JENSEN, K. G. & JERSLEV, B. (1969). *Acta Cryst.* B**25**, 916–925.
JERSLEV, B. (1983). *Acta Cryst.* C**39**. In the press.
JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
UDSEN, J. (1970). Thesis, Royal Danish School of Pharmacy.

Acta Cryst. (1983). C**39**, 1136–1138

Structure du Dithiosalicylide,* $C_{14}H_8O_2S_2$

PAR J.-M. MEDARD ET N. RODIER

Laboratoire de Chimie Minérale, Faculté des Sciences Pharmaceutiques et Biologiques, rue J.-B. Clément, 92290 *Châtenay-Malabry, France*

ET P. REYNAUD, J. D. BRION ET NGUYEN TRI XUONG

Laboratoire de Pharmacie Chimique, Faculté des Sciences Pharmaceutiques et Biologiques, rue J.-B. Clément, 92290 *Châtenay-Malabry, France*

(*Reçu le* 15 *septembre* 1982, *accepté le* 23 *mai* 1983)

Abstract. $M_r = 272{\cdot}3$, monoclinic, $P2_1/b$ (first setting), $a = 16{\cdot}224$ (9), $b = 24{\cdot}02$ (1), $c = 7{\cdot}933$ (3) Å, $\gamma = 127{\cdot}73$ (5)°, $V = 2446$ (5) Å^3, $D_x = 1{\cdot}48$ Mg m^{-3}, $Z = 8$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å (monochromator), $\mu = 0{\cdot}41$ mm^{-1}, $F(000) = 1120$, $T = 294$ (1) K, final $R = 0{\cdot}034$ for 2493 independent reflections. The molecules form layers parallel with the (100) plane and they are linked together by van der Waals interactions. The dihedral angle between the planes of the benzene rings *A* and *C* measures 69° in the first molecule and 63° in the second. In both cases, the intermediate *B* ring resembles a boat. Each molecule has an approximate twofold axis and a geometry compatible with a dipole moment.

Introduction. Les valeurs citées dans la littérature pour la température de fusion du dithiosalicylide sont fort peu concordantes. En effet, ce composé fond à 442–443 K (Anschütz & Rhodius, 1914), à 449–450 K (Baker, El-Nawawy & Ollis, 1952), entre 452 et 455 K (Fanning, Bickford & Roberts, 1972) ou vers 497 K (Gaitonde & Hosangadi, 1977). L'étude structurale du dithiosalicylide a été entreprise dans le but de déterminer la géométrie de sa molécule laquelle présente, selon Baker, El-Nawawy & Ollis, un moment dipolaire de 6,39 debye (1 debye = 3,34 × 10^{-30} C m). Elle a eu aussi pour objectif de contribuer à la mise en évidence d'un polymorphisme cristallin ou moléculaire susceptible d'expliquer la dispersion des températures de fusion.

Partie expérimentale. Préparation: acide thiosalicylique + mélange d'acide et d'anhydride propionique ou butyrique au reflux. Recristallisation dans l'acétate d'éthyle. T(fusion) = 455–456 K. Pas de mesure de la masse volumique. Cristal utilisé: tronc de pyramide, 0,20 × 0,35 × 0,45 mm. Dimensions de la maille déterminées sur monocristal avec 15 réflexions pour lesquelles $7{,}23 \le \theta \le 15{,}14°$. Diffractomètre Enraf–Nonius CAD-4; $\sin\theta/\lambda \le 0{,}527$ Å^{-1}; $-17 \le h \le 17$, $0 \le k \le 25$, $0 \le l \le 8$. Réflexions de contrôle des intensités: $\bar{9}$,12,2, 064 et 32$\bar{2}$, $\sigma(I)/I$ moyen = 0,035. 2935 réflexions indépendantes mesurées, 462 réflexions inobservées [$I \le 2\sigma(I)$]. Pas de correction d'absorption. Méthodes directes: programme *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Localisation des atomes d'hydrogène: synthèse ($F_o - F_c$). Paramètres affinés: x, y, z de tous les atomes, β_{ij} de S, O et C. $R_w = 0{,}036$, $S = 0{,}032$, $w = 1/\sigma^2(F)$. Valeur maximale du rapport variation/écart-type: 0,97. Densité électronique maximale et minimale de la différence Fourier finale: 0,091 et −0,108 e Å^{-3}. Pas de

* Dibenzo[*b*,*f*][dithiocin-1,5]dione-5,11.

0108-2701/83/081136-03$01.50 © 1983 International Union of Crystallography