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(*E*)-4-Chloro-2,6-dimethylbenzaldehyde Oxime at 110 K

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Abstract. $C_9H_{10}ClNO$, $M_r = 183.6$, monoclinic, $P2_1/n$, $a = 6.8553\,(10)$, $b = 15.399\,(2)$, $c = 8.5628\,(9)$ Å, $\beta = 95.763\,(10)°$, $V = 899.3\,(3)$ Å^3, $Z = 4$, $D_x = 1.356$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54178$ Å, $\mu = 34.03$ cm^{-1}, $F(000) = 384$, $T = 110$ K, final $R = 0.036$ for 1715 unique reflexions. The molecules are dimerized by hydrogen bonds around centres of symmetry. Steric hindrance causes the nearly planar oxime side chain to deviate considerably, 50.5 (1)°, from coplanarity with the benzene ring.

Introduction. The structure determination was undertaken to enable a comparative study of the molecular dimensions and the intermolecular interactions of the present oxime and the *O*-methylated oxime (Jerslev, Lerche & Larsen, 1983) to be made, based on low-temperature diffraction data.

Experimental. The compound used for the present structure determination was prepared as described by Hjeds, Hansen & Jerslev (1965). A rod-like single crystal of size 0.15 × 0.20 × 0.40 mm was selected. An Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation was used for data collection. The crystal was cooled to *ca* 110 K by an Enraf–Nonius gas-flow low-temperature device. The temperature remained constant within 1 K. Cell parameters were obtained from least-squares refinement of the setting angles for 22 reflexions ($37{\cdot}5 < \theta < 46.4°$). The remeasurements of three standard reflexions every 10 000 s showed no significant changes during the exposure time. The orientation of the crystal was checked every 300 reflexions. Data were recorded by the ω–2θ scan mode for 3928 reflexions ($0 < h < 8$, $-19 < k < 19$, $-10 < l < 10$) with θ in the range 1–75°. Data reduction included corrections for Lorentz, polarization and absorption effects. Transmission factors were in the range 0.431–0.657. Symmetry-related reflexions were averaged ($R_{\rm int} = 0.021$) to give 1854 independent reflexions. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). The 1715 reflexions which had $I > \sigma(I)$ were used in the refinement by the full-matrix least-squares method minimizing $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma_{\rm cs}^2(F) + 6 \times 10^{-4}|F|^2$, $\sigma_{\rm cs}$ calculated from counting statistics. The positions of the H atoms were shown clearly in the $\Delta\rho$ maps. They were given a common fixed isotropic displacement parameter, $B = 2.00$ Å^2, and their positional parameters were included in the refinement. Anisotropic displacement parameters were used for all the non-H atoms. The number of variables was 139. After the final cycle of least-squares refinement the maximum shift was 0.04σ, $R = 0.036$, $wR = 0.053$, $S = 1.73$. The final $\Delta\rho$ map was featureless with values in the range −0.47 to 0.27 e Å^{-3}. All calculations except the structure solution were performed with the Enraf–Nonius *SDP* program system (Enraf–Nonius, 1985). Scattering factors including corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and used as included in the program.

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

The benzene ring is planar within ±0.002 (1) Å. Of the attached atoms only C9 and Cl are displaced significantly from this plane [0.045 (2) and 0.0584 (4) Å respectively]. The C4—C7—N—O side chain is planar within ±0.004 (1) Å, and the attached H atoms H7 and HO are displaced −0.05 (2) and −0.08 (2) Å respectively from the plane.

The differences between equivalent bond lengths in the (*E*)-*O*-methyl oxime and the parent (*E*)-oxime (e.s.d.'s 0.002–0.003 Å) (Jerslev, Lerche & Larsen, 1983) are, for most of the bonds, hardly significant, whereas significant differences in bond angles (e.s.d.'s 0.1–0.2°) are observed. The major differences are found in the region of the molecule which is most

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* Lists of anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54413 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0222]

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Table 1. *Positional and equivalent isotropic thermal parameters for the atoms with e.s.d.'s in parentheses*

$$B_{\text{iso}} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{iso} (Å^2)
C1	0.2306 (2)	0.33851 (8)	0.6001 (2)	1.32 (2)
C2	0.2447 (2)	0.42713 (8)	0.6294 (1)	1.32 (2)
C3	0.2455 (2)	0.48439 (8)	0.5041 (2)	1.19 (2)
C4	0.2325 (2)	0.45154 (8)	0.3504 (1)	1.23 (2)
C5	0.2175 (2)	0.36137 (8)	0.3219 (1)	1.28 (2)
C6	0.2174 (2)	0.30508 (8)	0.4493 (1)	1.34 (2)
C7	0.2326 (2)	0.51512 (8)	0.2207 (2)	1.51 (2)
C8	0.2635 (2)	0.58061 (8)	0.5369 (2)	1.57 (2)
C9	0.1966 (2)	0.32358 (9)	0.1585 (2)	1.79 (2)
N	0.3484 (2)	0.50626 (7)	0.1147 (1)	1.52 (2)
O	0.3263 (2)	0.57400 (6)	0.0032 (1)	2.07 (2)
Cl	0.22116 (6)	0.26783 (2)	0.75796 (4)	2.045 (7)
H2	0.252 (3)	0.449 (1)	0.739 (2)	2.0*
H6	0.203 (3)	0.243 (1)	0.433 (2)	2.0*
H7	0.151 (3)	0.565 (1)	0.220 (2)	2.0*
H8*A*	0.372 (3)	0.607 (1)	0.489 (2)	2.0*
H8*B*	0.152 (3)	0.610 (1)	0.489 (2)	2.0*
H8*C*	0.279 (3)	0.588 (1)	0.646 (2)	2.0*
H9*A*	0.111 (3)	0.358 (1)	0.088 (2)	2.0*
H9*B*	0.153 (3)	0.263 (1)	0.162 (2)	2.0*
H9*C*	0.323 (3)	0.324 (1)	0.110 (2)	2.0*
HO	0.421 (3)	0.562 (1)	−0.055 (2)	2.0*

* B_{iso} was fixed during refinement of the positional parameters.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsional angles* (°) *with e.s.d.'s in parentheses*

C1—C2	1.3892 (13)	C4—C7	1.4805 (13)
C2—C3	1.3896 (14)	C5—C9	1.5085 (14)
C3—C4	1.4043 (14)	C7—N	1.2721 (14)
C4—C5	1.4116 (13)	N—O	1.4118 (11)
C5—C6	1.3938 (14)	C—H range	0.94–1.00 (2)
C6—C1	1.3842 (14)	O—HO	0.88 (2)
C1—Cl	1.7418 (10)	N···O	2.823 (1)
C3—C8	1.5108 (13)	N···HO	2.01 (2)
C1—C2—C3	119.29 (9)	C6—C5—C9	118.59 (9)
C2—C3—C4	119.37 (9)	C3—C4—C7	117.38 (9)
C3—C4—C5	120.87 (9)	C5—C4—C7	121.75 (9)
C4—C5—C6	118.82 (9)	C4—C7—N	120.77 (9)
C5—C6—C1	119.59 (9)	C7—N—O	111.77 (9)
C6—C1—C2	122.07 (9)	N—O—HO	101.4 (10)
C2—C1—Cl	118.73 (8)	N···HO—O	154 (1)
C6—C1—Cl	119.16 (8)	H—C$_{\text{methyl}}$—H range	104–113 (1)
C2—C3—C8	119·03 (9)	H—C$_{\text{methyl}}$—H mean	108.4
C4—C3—C8	121.59 (9)	C—C$_{\text{methyl}}$—H range	107–112 (1)
C4—C5—C9	122.57 (9)	C—C$_{\text{methyl}}$—H mean	110.5
C3—C4—C7—N	129.60 (14)	C4—C7—N—O	−179.48 (11)
C5—C4—C7—N	−51.2 (2)	C7—N—O—HO	174.6 (12)

affected by the position of the oxime side chain relative to the benzene ring. With the plane of the side chain turned 50.5 (1)° out of the plane of the benzene ring in the oxime, only a weak conjugation between these parts of the molecule is expected, as compared to the *O*-methylated oxime. In that molecule the interplanar angle between the ring plane and that of the side chain is only 23.3 (2)°. This should result in a longer C4—C7 bond and a shorter C7—N bond in the oxime. The signs and magnitudes of the observed differences [+0·006 (2) and −0·008 (2) Å] strongly support this interpretation. The length of the N—O bond in the two structures is identical within the accuracy of the structure determinations; but the bond in the present oxime is considerably longer [by 0.011 (2) Å] than that found in the low-temperature structure determination of (*E*)-benzaldehyde oxime (Jerslev, 1983). The magnitudes of the angles Ar—C=N and C=N—O in the present structure do not deviate from those found in (*E*)-benzaldehyde oxime, but the C=N—O angle is 2.1 (1)° larger and the Ar—C=N angle is 2.5 (1)° smaller than found in the *O*-methylated oxime. The difference between the angles C3—C4—C7 and C5—C4—C7 is less notable in the oxime [−4.4 (1)°] than in the *O*-methylated oxime [−6.2 (1)°], clearly because some of the steric strain in this part of the oxime molecule is counteracted by the side chain being considerably turned out of the benzene plane.

Association to dimers by hydrogen bonds is observed in the present structure, as in most crystal structures of aromatic (*E*)-aldoximes. But the present study is the first in which the association exerts a steric hindrance for approximate coplanarity of the

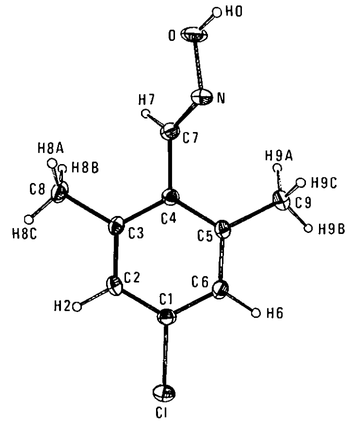

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound giving the numbering of the atoms. The ellipsoids enclose 50% probability. H atoms are represented by spheres of fixed radius.

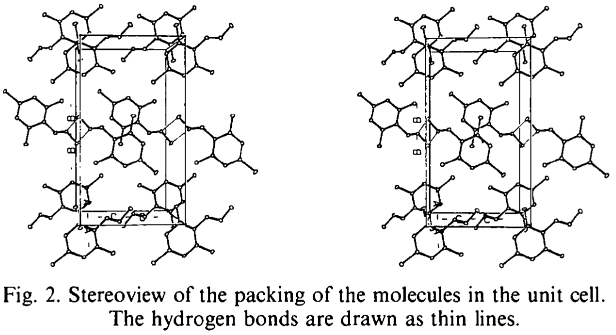

Fig. 2. Stereoview of the packing of the molecules in the unit cell. The hydrogen bonds are drawn as thin lines.

aromatic ring and the oxime side chain. The dimensions of the hydrogen bonds, O—H···N, are given in Table 2. The N···O distance is slightly longer (about 0.04 Å), and the angle O—H··N somewhat smaller, than hitherto met with in most oxime associates. The molecules are dimerized by hydrogen bonds around centres of symmetry (see Fig. 2, which shows the packing of the molecules in the crystal). Apart from the hydrogen bonds no unusual short intermolecular distances are found.

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Structure du Bis(*p*-chlorophényl)-1,3 Bis(triméthyl-2,4,6 phényl)-2,4 Diaza-1,3 Diphosphétidine

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Abstract. $C_{30}H_{30}Cl_2N_2P_2$, $M_r = 551.4$, monoclinic, $P2_1/a$, $a = 11.947$ (2), $b = 14.067$ (2), $c = 8.557$ (4) Å, $\beta = 98.08$ (1)°, $V = 1423.8$ (4) Å^3, $Z = 2$, $D_x = 1.28$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 3.3$ mm^{-1}, $F(000) = 576$, $T = 295$ K, $R = 0.051$ for 1697 observed independent reflections. The molecule is centrosymmetric.

Introduction. La connaissance des structures des molécules organophosphorées est particulièrement utile dans la mesure où elle permet de lever l'ambiguïté qui peut parfois exister en ce qui concerne les liaisons du phosphore avec les atomes voisins. Nous avons donc entrepris ce travail dans le but d'analyser l'agencement d'une structure cyclique à quatre chaînons, dans laquelle l'atome de phosphore est tricoordiné. Cette molécule a été sommairement décrite dans un travail précédent (Dubourg, 1990).

Partie expérimentale. Cristal 0,2 × 0,2 × 0,3 mm. Diffractomètre utilisé: Syntex $P2_1$, balayage ω–2θ, spectre recueilli à température ambiante. Radiation utilisée: Cu $K\alpha$ ($\lambda = 1{,}54178$ Å) avec monochromateur graphite. Maille déterminée à partir du centrage de 15 reflexions avec $10 < 2\theta < 25°$. Pas de correction d'absorption. La réflexion 110 contrôlée toutes les 50 mesures était stable. $2\theta_{\max} = 114°$, 1915 réflexions indépendantes mesurées, 1697 utilisées [$I > 2{,}5\sigma(I)$]. Echelle des indices: $h = -12/12$, $k = 0/14$, $l = 0/9$.

La structure a été résolue par les méthodes directes de *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). La molécule étant située sur un centre de symmétrie, seule une moitié de celle ci a eté révélée. Les paramètres des atomes ont été affinés en matrices complètes par la méthode des moindres carrés, utilisant *F*, de *SHELX*76 (Sheldrick, 1976). Les coefficients des facteurs de diffusion sont tirés de *International Tables for X-ray Crystallography* (1974, Tome IV). Les hydrogènes ont été placés en positions théoriques.

Aprés le dernier affinement anisotrope, nous avions les critères suivants: $R = 0{,}051$, $wR = 0{,}065$ avec le schéma de pondération: $w = 1/[\sigma^2(F) + 0{,}00279F^2]$, $(\Delta/\sigma)_{\max} < 0{,}6$, $S = 1{,}6$. Densités electroniques résiduelles aprés la dernière synthèse de Fourier-différence: $-0{,}3 < \Delta\rho < 0{,}4$ e Å^{-3}.

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