

the cyclohexene ring are caused by the same effect. The distortions observed in the P atom tetrahedron are typical for a phosphoryl compound, *i.e.* O=P—C valency angles increase to 112–113° while C—P—C angles decrease to 106–107°. The cyclohexene ring adopts a C(3)-sofa conformation flattened at the C(11) end. The asymmetry parameters (Duax & Norton, 1975) are:  $\Delta C_s^3 = 6.3$  (4),  $\Delta C_2^{2,3} = 25.0$  (4),  $\Delta C_s^{1,2} = 52.5$  (4) and  $\bar{\varphi} = 30.2$  (4)°.

Newman projections about the C(1)—C(2) and C(2)—P bonds are shown in Fig. 2.

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## (±)-2-(2-Chlorophenoxy)propionic Acid

BY GRAHAM SMITH

*Department of Chemistry, Queensland Institute of Technology, Brisbane 4000, Australia*

COLIN H. L. KENNARD

*Department of Chemistry, University of Queensland, Brisbane 4067, Australia*

AND ALLAN H. WHITE

*Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Australia*

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**Abstract.** C<sub>9</sub>H<sub>9</sub>ClO<sub>3</sub>, *M<sub>r</sub>* = 200.6, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 7.400 (2), *b* = 7.913 (4), *c* = 16.495 (5) Å, β = 93.16 (2)°, *D<sub>c</sub>* = 1.38 Mg m<sup>-3</sup>, *Z* = 4, *F*(000) = 416, μ(Mo *K*α) = 0.37 mm<sup>-1</sup>. The structure was solved by direct methods and refined to a final *R* = 0.041 for 1007 observed reflexions. The molecules form centrosymmetric hydrogen-bonded cyclic dimers (O...O, 2.626 Å) and adopt the synclinal conformation found for all known phenoxypropionic acids.

**Introduction.** The title compound was first prepared by Synerholm & Zimmerman (1945), who found its useful herbicidal properties to be similar to those of the acetic

acid homologue. Although the crystal structures of a number of 2-phenoxypropionic acid analogues are now known, including the parent acid, 2-phenoxypropionic acid (Kennard, Smith & White, 1980), 2-(3,5-dichlorophenoxy)propionic acid (Smith, Kennard & White, 1978), 2-(2,4,5-trichlorophenoxy)propionic acid (Smith, Kennard, White & Hodgson, 1977) and 2-(4-chloro-2-methylphenoxy)propionic acid (Smith, Kennard, White & Hodgson, 1980), the structure of the title compound was determined as a check on the predictions of Smith *et al.* (1980) regarding preferred conformations in the propionic acids. In the case of 2-chlorophenoxyacetic acid (Chandrasekhar & Pat-

tabhi, 1977), the presence of the 2-chloro ring substituent appears to produce an anomalous effect in inducing the rare *syn-anti* conformation.

Colourless prisms of the compound, prepared by the method of Synerholm & Zimmerman (1945), were grown from a mixture of toluene and chloroform. 1007 reflections with  $|I| > 2.5\sigma|I|$  were considered observed out of 1265 collected from one crystal ( $0.25 \times 0.40 \times 0.15$  mm) mounted about the prism ( $b$ ) axis on a Syntex  $P2_1$  four-circle diffractometer ( $2\theta_{\max} = 50^\circ$ ; monochromatic Mo  $K\alpha$  radiation). No correction was

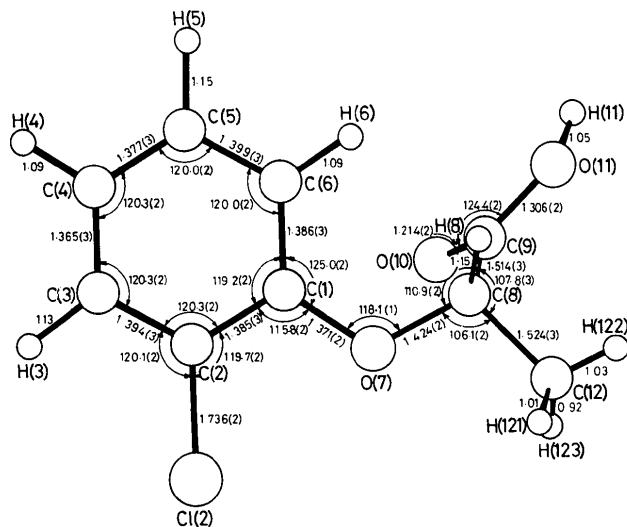


Fig. 1. Bond lengths (Å) and angles ( $^\circ$ ) in 2-(2-chlorophenoxy)propionic acid.

Table 1. Atomic coordinates ( $\times 10^4$ ) with estimated standard deviations in parentheses ( $B_{\text{eq}}$  are  $\times 10^3 \text{ \AA}^2$ )

$$B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	x	y	z	$B_{\text{eq}}$
Cl(2)	-2370 (1)	2314 (1)	6475 (1)	68
C(1)	958 (4)	1459 (4)	6011 (2)	36
C(2)	-226 (4)	1444 (4)	6633 (2)	42
C(3)	293 (6)	720 (5)	7380 (2)	54
C(4)	1970 (6)	15 (5)	7505 (2)	62
C(5)	3166 (5)	26 (5)	6895 (2)	51
C(6)	2657 (4)	741 (4)	6141 (2)	42
O(7)	321 (2)	2199 (2)	5300 (1)	39
C(8)	1495 (4)	2273 (4)	4645 (2)	36
C(9)	3094 (4)	3420 (4)	4852 (2)	35
O(10)	3083 (3)	4507 (3)	5371 (1)	48
O(11)	4441 (3)	3142 (3)	4390 (1)	50
C(12)	395 (4)	3059 (4)	3934 (2)	46
H(3)	-799	740	7832	
H(4)	2409	-647	8062	
H(5)	4572	-584	6958	
H(6)	3586	653	5652	
H(8)	1988	952	4466	
H(11)	5526	3949	4551	
H(121)	-728	2348	3822	
H(122)	26	4279	4076	
H(123)	1098	3089	3490	

made for absorption. The structure was solved by direct methods using the multiresolution  $\Sigma_2$  sign-expansion procedure of *SHELX* (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms reduced  $R$  ( $=\sum ||F_o| - |F_c|| / \sum |F_o|$ ) to 0.041 and  $R_w$  ( $[(\sum w||F_o| - |F_c||)^2 / \sum |F_o|^2]^{1/2}$ ) to 0.047. The weighting scheme used was  $w = 1.00 / (\sigma^2 F + 2.36 \times 10^{-4} F^2)$ . H atom positions were located in a difference Fourier synthesis and included in the refinement at fixed positions with isotropic  $U$  values set invariant at  $0.05 \text{ \AA}^2$ . Four intense low-angle reflections (012, 020,  $\bar{1}05$ , 113) were considered to be seriously affected by extinction and were removed before the final cycle of refinement. The maximum residual background peak in a final difference Fourier synthesis was  $0.05 \text{ e \AA}^{-3}$ . Final positional parameters are listed in Table 1,\* while bond distances and angles and the atom-numbering scheme are shown in Fig. 1

**Discussion.** The molecules of 2-(2-chlorophenoxy)propionic acid form centrosymmetric hydrogen-bonded cyclic dimers [ $\text{O}-\text{H} \cdots \text{O}$ ,  $2.626(2) \text{ \AA}$ ] (Fig. 2) and adopt the synclinal [*syn-syn*(carbonyl)] conformation (Leiserowitz, 1976) (Fig. 1) found for all known phenoxypropionic acids having no additional methyl substituent on the  $\alpha$  carbon. Those with an  $\alpha$ -methyl group, *i.e.* the phenoxyisobutyric acids, invariably have the *syn-anti* conformation, *e.g.* 2-methyl-2-phenoxypropionic acid and 2-(4-chlorophenoxy)-2-methylpropionic acid (Kennard, Smith & White, 1980), 2-(4-dibenzofuranyloxy)-2-methylpropionic acid (Wagner & Malmros, 1979a) and 2-methyl-2-[2-(phenoxy)phenoxy]propionic acid (Wagner & Malmros, 1979b). The oxypropionic acid side chain adopts the conformation with the  $\alpha$ -methyl group lying close to the plane of the benzene ring, with the plane of the carboxylic acid group making an angle of  $76.7^\circ$  with the plane of the benzene ring. Torsion angles associated with the  $\text{C}(1)-\text{O}(7)$ ,  $\text{O}(7)-\text{C}(8)$  and  $\text{C}(8)-\text{C}(9)$  vectors [ $\text{C}(2)-\text{C}(1)-\text{O}(7)-\text{C}(8)$ ,  $\text{C}(1)-\text{O}(7)-\text{C}(8)-\text{C}(9)$  and  $\text{O}(7)-\text{C}(8)-\text{C}(9)-\text{O}(11)$ ] are  $+179.0(2)$ ,  $-66.3(2)$  and  $+161.0(2)^\circ$  respectively. Bond distances and angles agree with those of other members of the series, including the phenoxyacetic acids; this includes the usual distortion of the *exo*- $\text{C}(1)$  bond angles [ $125.0(2)$ ,  $115.8(2)^\circ$ ]. There is no evidence of disorder within the carboxylic acid dimer unit, the  $\text{C}=\text{O}$  and  $\text{C}-\text{O}(\text{H})$  distances [ $1.214(2)$  and  $1.306(2) \text{ \AA}$  respectively] and  $\text{C}-\text{C}=\text{O}$  and  $\text{C}-\text{C}-\text{OH}$  angles [ $123.2(2)$  and  $112.3(2)^\circ$  respectively] being typical of

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35593 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

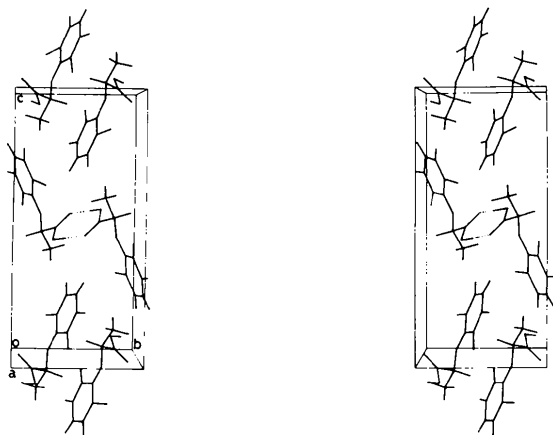


Fig. 2. Stereoview perpendicular to the *bc* plane.

non-disordered carboxylic acid groups (Leiserowitz, 1976).

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Structure of (Z)-9,10-Dihydro-4H-benzocyclohepta[7,6-b]thiophen-4-ylideneacetic Acid

BY E. GUTIÉRREZ-PUEBLA AND A. MONGE

Departamento de Química Inorgánica, Facultad de Químicas, Universidad Complutense, Madrid-3, Spain and Instituto de Química Inorgánica 'Elhuyar', CSIC, Serrano 113, Madrid-6, Spain

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**Abstract.** C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>S, *M<sub>r</sub>* = 256, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 14.089 (4), *b* = 5.9123 (6), *c* = 16.9075 (6) Å, β = 112.65 (1)°, *U* = 1299.7 (6) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.31 Mg m<sup>-3</sup>. Final *R* = 0.036 for 1751 observed reflexions. The COOH group is *cis* with respect to the thiophene ring.

**Introduction.** A clear, colourless, prismatic crystal prepared by Arribas & Vega (1980) was mounted on a four-circle CAD-4 diffractometer. The intensities of 2819 reflexions within 2 < θ < 27° were collected at 295 K with monochromatic Mo Kα radiation and an ω/2θ scan technique. Two reflexions were monitored periodically and showed no crystal decomposition. The intensities were corrected for Lorentz and polarization effects and 1751 of them were considered as observed,

*I* > 2σ(*I*). Absorption effects (μ = 0.228 mm<sup>-1</sup>) were not corrected.

Scattering factors for neutral atoms and anomalous-dispersion corrections for S were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The best *E* map revealed all the non-hydrogen atoms. After

Table 1. Coefficients for the weighting scheme

	<i>a</i>	<i>b</i>
<i>F<sub>o</sub></i>   < 6.9	1.40	-0.16
6.9 <   <i>F<sub>o</sub></i>   < 13.8	0.43	0.00
13.8 <   <i>F<sub>o</sub></i>	0.14	0.02