

- Enraf-Nonius (1983). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- IBERS, J. A. & SNYDER, R. G. (1962). *Acta Cryst.* **15**, 923–930.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KNUPP, G., FRAHM, A. W., KIRFEL, A., FRÖHLICH, T. & WILL, G. (1985). *Acta Cryst.* **C41**, 468–470.
- KOORTS, J. & CAIRA, M. (1985). *Acta Cryst.* **C41**, 552–554.
- MCKAY, I. D. & PAYNE, N. C. (1985a). In preparation.
- MCKAY, I. D. & PAYNE, N. C. (1985b). In preparation.
- MCKAY, I. D. & PAYNE, N. C. (1986). *Acta Cryst.* **C42**, 304–306.
- MASON, R. & SCOLLARY, G. R. (1978). *Aust. J. Chem.* **31**, 781–789.
- SOWRIRAJAN, S., ARAVAMUDAN, G., SESHASAYEE, M. & ROUT, G. C. (1985). *Acta Cryst.* **C41**, 576–579.
- STEPHAN, D. W. (1980). *Studies in Asymmetric Synthesis*. PhD Thesis, Univ. of Western Ontario.
- STEPHAN, D. W. & PAYNE, N. C. (1982). *Inorg. Chem.* **21**, 182–188.
- TAKENAKA, A., SASADA, Y., YAMAMOTO, K. & TSUJI, J. (1977). *Bull. Chem. Soc. Jpn.*, **50**, 3177–3181.

Acta Cryst. (1986). **C42**, 310–312

(±)-2-(3-Chlorophenoxy)propionic Acid

BY THOMAS C. W. MAK

Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong

GRAHAM SMITH

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

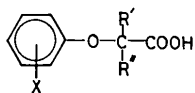
AND COLIN H. L. KENNARD*

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

(Received 3 May 1985; accepted 20 September 1985)

Abstract. C₉H₉ClO₃, m.p. 386 K, *M_r* = 200.62, monoclinic, *C*2/*c*, *a* = 31.731 (8), *b* = 5.056 (1), *c* = 11.534 (2) Å, β = 90.47 (2)°, *V* = 1850.3 (5) Å³, *Z* = 8, *D_x* = 1.439 Mg m⁻³, *F*(000) = 832, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 0.39 mm⁻¹, *T* = 293 K, *R* = 0.032 for 940 unique observed reflections. The molecules form centrosymmetric cyclic hydrogen-bonded dimers [O...O 2.669 (4) Å] similar to the majority of the phenoxyalkanoic acids. The oxo-propionic acid side chain is synclinally related to the benzene ring.

Introduction. The title compound (3-CPPA) is a member of the phenoxyalkanoic acid series which includes a number of herbicidally active ring-substituted acetic and 2-propionic acid analogues. Activity in the phenoxypropionic acids parallels the phenoxyacetic acids, requiring substituents such as Cl or methyl groups in the 2 and 4 positions of the benzene ring. 3-CPPA is inactive (Synerholm & Zimmerman, 1945), and provides another example of a *meta*-substituted acid.



X = Cl, Me
R' = H
R'' = H, Me

Others previously determined are racemic 2-(3,5-dichlorophenoxy)propionic acid (Smith, Kennard & White, 1978) and the quasi-racemic (+)-2-(3-bromophenoxy)propionic acid/(-)-2-(3-methoxyphenoxy)propionic acid (Karle & Karle, 1966). In the first example, as in most phenoxyalkanoic acids, the molecules form centrosymmetric hydrogen-bonded cyclic dimers whereas in the quasi-racemate, the cyclic dimers are located about a pseudo centre of symmetry. The only known example of a phenoxy acid having other than a dimer motif is (2-carbamoylphenoxy)-acetic acid which forms one-dimensional polymer chains, hydrogen bonded through the carboxylic acid groups. The structure of 3-CPPA was determined to complete the series of mono chloro substituted 2-phenoxypropionic acids, which include (±)-2-(2-chlorophenoxy)propionic acid (2-CPPA) (Smith, Kennard & White, 1981) and (±)-2-(4-chlorophenoxy)propionic acid (4-CPPA) (Kennard, Smith & White, 1982).

Experimental. Colourless prismatic crystals. A section (0.24 × 0.20 × 0.12 mm) cleaved from a crystal prism was used to collect intensity data on a Nicolet R3m diffractometer. 24 non-axial reflections (28 < 2θ < 30°) used for lattice-parameter determinations. Systematic absences [*hkl* (*h* + *k* = 2*n* + 1); *h0l* (*l* = 2*n* + 1)] indicated either *C*2/*c* or *Cc*. Successful refinement achieved in *C*2/*c*. No absorption or extinction correc-

* To whom correspondence should be addressed.

tions applied. Range of data h (0 to 31), k (0 to 3), l (−10 to +10); $(\sin\theta/\lambda)_{\max} = 0.54 \text{ \AA}^{-1}$. Three standards were used (12,0,0; 020; 006), and did not vary significantly over the period of data collection. 1213 reflections were measured, of which 940 with $I > 2.5\sigma(I)$ were unique (71 unobserved) and used in structure refinement. Data processed using the profile-fitting procedure of Diamond (1969). Structure solved using the multiresolution Σ_2 sign expansion direct methods of *SHELX76* (Sheldrick, 1976). Blocked least-squares refinement (F^2 s) with anisotropic thermal parameters on all non-hydrogens (H atoms isotropic) gave $R = 0.032$ and $wR = 0.034$ with $w = 1.9/[\sigma^2(F_o) + 0.0003F_o^2]$. All H atoms located from a difference Fourier synthesis and their positional and thermal parameters refined. Max., av. Δ/σ in final cycle 0.6, 0.3. Max. peak in final difference Fourier map was 0.20 e \AA^{-3} above a background of 0.13 e \AA^{-3} . The computer programs used for collecting and processing data were *SHELXTL* (Sheldrick, 1981), and *SHELX76* (Sheldrick, 1976), for structure determination, with the scattering factors for C, H and Cl included in the program. These were run on Nova and IBM 3083 computers respectively. Molecular geometry was determined using *APPLECRYST83* (Kennard, 1983).

Table 1. Atomic parameters ($\times 10^4$) with estimated standard deviations in parentheses [and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$), defined as $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$]

	x	y	z	U_{eq}
C(1)	3638 (1)	−1074 (7)	1317 (3)	37 (2)
C(2)	3370 (1)	−2906 (7)	1801 (3)	37 (2)
C(3)	3080 (1)	−4177 (6)	1099 (3)	37 (2)
Cl(3)	2744 (1)	−6501 (2)	1712 (1)	52 (1)
C(4)	3047 (1)	−3628 (8)	−71 (3)	48 (2)
C(5)	3317 (1)	−1784 (8)	−538 (3)	51 (2)
C(6)	3619 (1)	−513 (7)	138 (3)	45 (2)
O(7)	3919 (1)	82 (4)	2085 (1)	42 (1)
C(8)	4181 (1)	2184 (6)	1688 (2)	40 (2)
C(81)	4372 (1)	3448 (7)	2763 (3)	55 (2)
C(9)	4534 (1)	1128 (6)	923 (2)	38 (2)
O(10)	4675 (1)	−1126 (5)	1054 (2)	59 (2)
O(11)	4673 (1)	2805 (4)	194 (2)	60 (2)

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

C(1)–C(2)	1.378 (4)	C(5)–C(6)	1.388 (5)
C(1)–C(6)	1.390 (4)	O(7)–C(8)	1.428 (4)
C(1)–O(7)	1.380 (4)	C(81)–C(8)	1.517 (4)
C(2)–C(3)	1.381 (4)	C(8)–C(9)	1.528 (4)
Cl(3)–C(3)	1.740 (3)	C(9)–O(10)	1.233 (4)
C(3)–C(4)	1.381 (4)	C(9)–O(11)	1.275 (4)
C(4)–C(5)	1.379 (5)		
C(6)–C(1)–C(2)	120.8 (3)	C(5)–C(6)–C(1)	118.7 (3)
O(7)–C(1)–C(2)	114.9 (3)	C(8)–O(7)–C(1)	119.0 (2)
O(7)–C(1)–C(6)	124.3 (3)	C(81)–C(8)–O(7)	106.3 (2)
C(3)–C(2)–C(1)	119.0 (3)	C(9)–C(8)–O(7)	110.9 (2)
Cl(3)–C(3)–C(2)	118.9 (2)	C(9)–C(8)–C(81)	109.2 (2)
C(4)–C(3)–C(2)	121.7 (3)	O(11)–C(9)–C(8)	114.1 (3)
C(4)–C(3)–Cl(3)	119.4 (2)	O(10)–C(9)–C(8)	121.3 (3)
C(5)–C(4)–C(3)	118.4 (3)	O(11)–C(9)–O(10)	124.6 (3)
C(6)–C(5)–C(4)	121.5 (3)		

Discussion. Table 1 lists the atomic parameters while bond distances and angles are given in Table 2.*

The molecules of 3-CPPA (Fig. 1) adopt a conformation with the propionic acid side chain synclinally related to the phenoxy residue [torsion angle C(1)–O(7)–C(8)–C(9) $-74.5 (3)^\circ$] which is similar to other *meta*-substituted 2-phenoxypropionic acids (Table 3) and also to all known 2-phenoxypropionic acids, irrespective of the position and nature of the ring substituent. This conformation has been described as predictable among such acids (Kennard *et al.*, 1982) and contrasts with the preferred planarity of the acetic acid analogues. Other distance and angular parameters are also closely comparable to other series members, including the synplanar placement of the 'carbonyl' oxygen [O(10)] of the carboxyl group [torsion angle O(7)–C(8)–C(9)–O(10) $-28.6 (5)^\circ$], with an O(7)–O(10) interactive distance of $2.754 (4) \text{ \AA}$.

* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42503 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

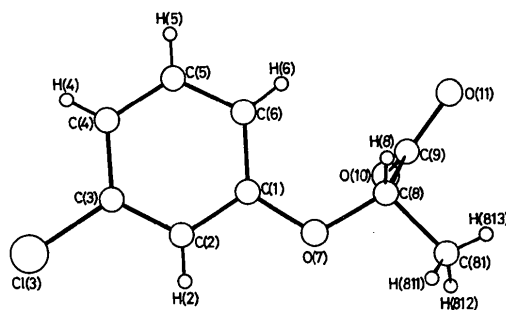


Fig. 1. Molecular conformation and atom-naming scheme for (\pm)-2-(3-chlorophenoxy)propionic acid.

Table 3. Comparative structural features for the *meta*-substituted 2-phenoxypropionic acids

	3-CPPA (this work)	3-BrPPA, 3-MeOPPA (Karle & Karle, 1966)	3,5-DPPA (Smith, Kennard & White, 1978)	
Distances				
O–H...O	2.669 (4)	2.60 (4)	2.62 (4)	2.664 (6)
O(7)–O(10)	2.754 (4)	2.76 (4)	2.76 (4)	2.745 (6)
Dihedral angles ($^\circ$)				
Benzene plane to carboxylic acid group	87.3 (5)	85.5 (6)	85.5 (6)	87.0 (5)
Torsion angles ($^\circ$)				
C(2)–C(1)–O(7)–C(8)	−174.0 (2)	+171.8 (6)	−172.0 (6)	−178.2 (5)
C(1)–O(7)–C(8)–C(9)	−74.5 (2)	+76.5 (6)	−76.5 (6)	+73.1 (5)
O(7)–C(8)–C(9)–O(10)	−28.6 (2)	+27.4 (6)	−25.7 (6)	+33.4 (5)

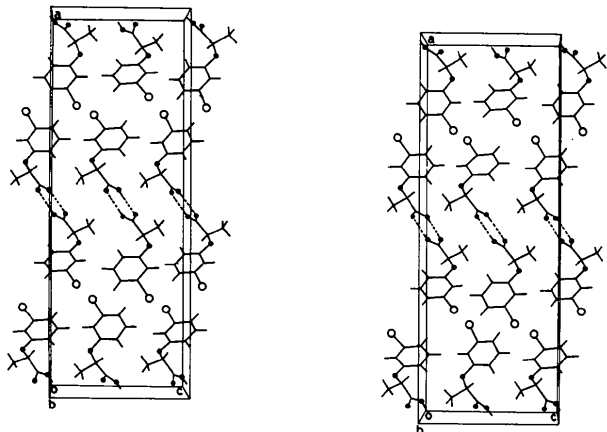


Fig. 2. Stereoview perpendicular to *ac*.

The packing of the molecules of 3-CPPA in the unit (Fig. 2) involves the usual centrosymmetric hydrogen-bonded cyclic dimers [O...O 2.669 (4) Å], while outside these units there are no significant intermolecular associations.

Acta Cryst. (1986). C42, 312–314

Structure du Tétraphényl-2,2',6,6' Bisélénapyranylidène-4:4'*

PAR A. LECLAIRE

Laboratoire de Cristallographie, Chimie et Physique des Solides, UA 251, ISMRA-Université,
14032 Caen CEDEX, France

ET C. REGNAULT DU MOTTIER ET G. LE COUSTOMER

Laboratoire des Composés Thioorganiques, UA 480, Université de Caen, 14032 Caen CEDEX, France

(Reçu le 8 janvier 1985, accepté le 17 septembre 1985)

Abstract. C₃₄H₂₄Se₂, *M_r* = 590.5, monoclinic, *C*2/*c*, *a* = 28.93 (3), *b* = 5.5330 (9), *c* = 17.934 (2) Å, β = 118.91 (9)°, *V* = 2513 (1) Å³, *Z* = 4, *D_x* = 1.561 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 3.19 mm⁻¹, *F*(000) = 1184, *T* = 294 K. *R* = 0.049 for 1255 observed reflections. The centrosymmetric molecules are approximately planar. The length of the C(3)–C(3') bond between the two selenapyranylidene rings is 1.418 Å and the average bond lengths in the ring are 1.884 Å for Se–C, 1.330 Å for C=C and 1.443 Å for C(3)–C. The molecules are packed in columns parallel to *b*, leading to a herring-bone stacking in the *bc* plane.

* Tétraphényl-3,3',5,5' diséléna-4,4' bicyclohexadiène-2,5 ylidène-1:1'.

The authors thank the Chinese University of Hong Kong for data collection, the Insecticides Department, Rothamsted Experimental Station, Harpenden, England, for the compound, and the University of Queensland for the use of computing facilities.

References

- DIAMOND, R. (1969). *Acta Cryst.* A25, 43–55.
 KARLE, I. L. & KARLE, J. (1966). *J. Am. Chem. Soc.* 88, 24–27.
 KENNARD, C. H. L. (1983). *APPLECRYST83*. A set of crystallographic programs for an Apple. Univ. of Queensland, Australia.
 KENNARD, C. H. L., SMITH, G. & WHITE, A. H. (1982). *Acta Cryst.* B38, 868–875.
 SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1981). *SHELXTL User Manual*, revision 3. Nicolet XRD Corporation, Cupertino, California.
 SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1978). *Acta Cryst.* B34, 2885–2887.
 SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1981). *Acta Cryst.* B37, 275–277.
 SYNERHOLM, M. E. & ZIMMERMAN, P. W. (1945). *Contrib. Boyce Thompson Inst.* 14, 91–103.

Introduction. Les bisélénapyranylidènes-4:4' offrent un intérêt dans le domaine des conducteurs organiques unidimensionnels. En effet, ils peuvent jouer le rôle de donneurs d'électron π dans les complexes organiques, lorsqu'associés à certains accepteurs tels que le tétracyano-7,7,8,8 *p*-quinodiméthane (TCNQ), ils sont oxydés et forment un cation radical possédant un sextet aromatique. De plus, lorsqu'ils sont substitués par des phényles porteurs en *para* de longues chaînes *n*-alkylées, ils présentent des états mésomorphes.

Ainsi, le tétraphényl-2,2',6,6' bisélénapyranylidène-4:4' a donné avec le TCNQ et la dichloro-2,3 dicyano-5,6 benzoquinone-1,4 (DDQ) des complexes à transfert de charge et avec l'iode des sels dont les propriétés électriques et optiques ont été étudiées (Es-Seddiki, Le Coustumer, Mollier & Devaud, 1982;