

Structure of (η -Bicyclo[2.2.1]hepta-2,5-diene)chloro($\{(R)$ -1-[o -(dicyclohexylphosphino)phenyl]ethyl}dimethylammonium)rhodium(I) Perchlorate

By I. D. MCKAY AND N. C. PAYNE*

Chemistry Department, University of Western Ontario, London, Ontario, Canada N6A 5B7

(Received 2 July 1985; accepted 26 November 1985)

Abstract. $[\text{Rh}(\text{C}_{22}\text{H}_{37}\text{NP})\text{Cl}(\text{C}_7\text{H}_8)]\text{ClO}_4$, $M_r = 676.47$, orthorhombic, $P2_12_12_1$, $a = 15.288$ (2), $b = 18.440$ (3), $c = 10.966$ (2) Å, $V = 3091$ (1) Å³, $Z = 4$, $D_m = 1.460$ (1), $D_x = 1.455$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.801$ mm⁻¹, $F(000) = 1408$, $T = 293$ K. Refinement of 343 variables by full-matrix least-squares techniques on F converged at agreement factors $R = 0.0398$ and $wR = 0.0533$ using 3271 observations with $F > 2\sigma(F)$. The geometry about the Rh atom is tetrahedrally distorted square planar (the diene viewed as a bidentate ligand) with Rh–Cl(2) and Rh–P distances of 2.390 (2) and 2.315 (1) Å, respectively. The absolute configuration of the ligand was determined by the Bijvoet method to be R .

Introduction. As part of our investigations into the asymmetric, homogeneous hydrosilation of prochiral ketones using chiral Rh–aminophosphine species as catalysts, we are exploring possible methods of tailoring the catalysts to improve optical selectivity. Two catalysts prepared using the ligand (R)- o -[(C₆H₅)₂E]–C₆H₄CHCH₃N(CH₃)₂, $E = \text{P}$, R -amphos, and $E = \text{As}$, R -amars, gave similar chemical yields but markedly different optical yields (Stephan & Payne, 1982). ¹H and ³¹P NMR studies have been used to probe the cause of this difference in optical selectivity (Stephan, 1980). The size and spatial arrangement of the phosphine or arsine substituents is thought to provide an asymmetric environment which induces preferential coordination of one face of the substrate, thus effecting optical discrimination. It was concluded that, since the substrate ketone molecule can coordinate in a position either *cis* or *trans* to the phosphine group in these molecules, the catalyst system which favoured *cis* coordination produced the greater optical yields. Several solid-state studies have been made of the coordination geometry of such complexes; the structures of three chiral complexes of Rh containing a norbornadiene ligand, nbd, and either an aminoarsine (Stephan & Payne, 1982) or an aminophosphine ligand (McKay & Payne, 1985*a,b*) have been reported, and the structure of a chiral dichloropalladium amino-phosphine complex was determined by Takenaka, Sasada, Yamamoto & Tsuji (1977).

By replacing the phenyl substituents with cyclohexyl groups we hoped to improve the catalyst efficiency. In the course of this work the title complex, $[\text{RhCl}\{(\text{R})\text{-}o\text{-}[(\text{cyclo-C}_6\text{H}_{11})_2\text{P}]\text{C}_6\text{H}_4\text{CHCH}_3\text{N}(\text{CH}_3)_2\}\text{-}(\text{C}_7\text{H}_8)]\text{ClO}_4$, $[\text{RhCl}(\text{R}\text{-dicyphosH})(\text{nbd})]\text{ClO}_4$, was prepared by adding 98.7 mg of R -dicyphos.HCl (McKay & Payne, 1985*b*) to a solution of 100 mg of $[\text{Rh}(\text{nbd})_2]\text{ClO}_4$ in 4 ml of dry CH₂Cl₂, maintained under an Ar atmosphere. After being stirred for 10 min the solution was filtered through a 20 mm column of Florosil and a roughly equal volume of hexanes was added. The mixture was left to stand at room temperature, and produced suitable, orange pyramidal crystals.

Experimental. Elemental analysis: found: C 50.29, H 6.25, N 2.10; calculated: C 51.49, H 6.71, N 2.07%.

Photographic analysis suggested space group $P2_12_12_1$, systematic absences h odd for $h00$, k odd for $0k0$, l odd for $00l$. Eleven crystal faces, $\{100\}$, $\{101\}$, $(1\bar{1}0)$, $(\bar{1}\bar{1}0)$, $(\bar{1}10)$, (010) , and (011) , approximate dimensions $0.62 \times 0.23 \times 0.09$ mm, $V = 1.26 \times 10^{-2}$ mm³. Density by flotation in a mixture of 1,2-dibromoethane and hexane. Enraf–Nonius CAD-4F diffractometer, Mo radiation, monochromatized by graphite. Cell parameters at 293 K from 24 reflections with $30 < 2\theta < 36^\circ$. Average width at base of ω scans 0.32° . 3944 observations ($0 \leq h \leq 19$, $0 \leq k \leq 24$, $0 \leq l \leq 14$), over 5 d by θ - 2θ scan, max. $2\theta = 55^\circ$; max. $(\sin\theta)/\lambda = 0.650$ Å⁻¹. Dispersion-corrected scans of width 1.20° using variable scan rates; maximum time per datum 75 s. Background measurements recorded at 25% extensions of scan (Enraf–Nonius, 1983). Standard reflections 600, 040, and 002 recorded every 10 000 s of X-ray exposure time, average decay 0.2%, no correction applied. Data reduction, structure solution and refinement performed using Enraf–Nonius *Structure Determination Package* running on a DEC PDP 11/23+ computer (Enraf–Nonius, 1983). Background, monochromator polarization, Lorentz, and polarization corrections applied, standard deviations assigned based on counting statistics, $p = 0.08$ (Busing & Levy, 1957). Gaussian absorption correction, transmission factors from 0.810 to 0.955. Solution by Patterson and Fourier methods, refinement by full-

* To whom correspondence should be addressed.

matrix least-squares techniques minimizing $\sum w(|F_o| - |F_c|)^2$; $w = 4F_o^2/\sigma^2(F_o^2)$. Scattering factors for neutral atoms and real and imaginary components of anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Absolute configuration, *R*, based on ligand synthesis (McKay & Payne, 1985*b*) and confirmed by Bijvoet analysis. All 45 H atoms located and included in idealized positions (sp^2 hybridization, C—H 0.90 Å; sp^3 hybridization, C—H 0.95, N—H 0.92 Å). Convergence [343 variables and 3271 unique observations with $F > 2\sigma(F)$] at $R = 0.0398$ and $wR = 0.0533$, $S = 1.07$; max. $(\Delta/\sigma) < 0.01$; final maximum $\Delta\rho$ 0.77 (9) e Å⁻³ (at -0.1445, -0.2148, 0.0547) at a distance of 0.76 Å from the Rh atom, no chemical significance. Statistical analysis of *R* and wR in terms of data-collection order, F_o , $\lambda^{-1} \sin\theta$, and classes of indices showed no unusual trends, indicating a satisfactory weighting scheme and no significant secondary extinction. Final positional parameters with e.s.d.'s and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 1.*

Confirmation of absolute configuration. The absolute configuration of the molecule was determined by the Bijvoet absorption-edge technique using Cu *K*α radiation ($\lambda = 1.5418$ Å), and a second crystal. Friedel pairs were measured for a selection of structure factors calculated from the final model and its enantiomorph for which $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$ differed by more than 25%. The results have been deposited and without exception indicate that the assignment of absolute configuration based upon the ligand synthesis was correct.

Discussion. A stereoview (Johnson, 1965) of the cation showing the atom-numbering scheme is given in Fig. 1, with atoms drawn as 50% probability thermal ellipsoids. Selected intramolecular distances and angles are given in Table 2. The unit cell contains discrete cations and anions with a shortest Rh...Cl(1) distance of 5.509 (2) Å. The shortest Rh...Rh and Cl(1)...Cl(1) distances are 7.810 (1) and 8.102 (3) Å, respectively. The shortest non-bonded cation-anion distances are O(2)...H2C(23)($-\frac{1}{2} - x, -y, -\frac{1}{2} + z$) of 2.689 and O(1)...H3C(18)($-\frac{1}{2} + x, -\frac{1}{2} - y, -z$) of 2.692 Å. Between cations the shortest distances are H2C(25)...H1C(35)($\frac{1}{2} - x, -y, -\frac{1}{2} + z$) at 2.201 and H1C(19)...H1C(25)($-\frac{1}{2} + x, -\frac{1}{2} - y, -z$) at 2.337 Å. The perchlorate anions are disordered, as evidenced by

* Lists of anisotropic thermal parameters, H-atom parameters, additional bond distances and angles, root-mean-square amplitudes of vibration, selected torsional angles, mean-plane calculations, Friedel pairs and structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42482 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cl—O distances ranging from 1.309 (10) to 1.412 (8) Å and angles ranging from 105.9 (1.2) to 115.3 (8)°. Several models using rigid groups with the Cl atom either included in the group or treated separately with an anisotropic thermal parameter were evaluated in an attempt to describe the disordered perchlorate anion. None of these models were able to account for the observed electron density as well as the slightly distorted model with anisotropic thermal parameters (some of which are large and physically unreasonable) reported herein.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$; for Rh, Cl and P $\times 10^4$) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Rh	-967.6 (3)	-2254.3 (2)	611.5 (4)	339.0 (7)
Cl(1)	-5549 (1)	-1949 (1)	-5807 (2)	623 (5)
Cl(2)	-2320 (1)	-1686 (1)	78 (2)	593 (4)
P	-242.0 (8)	-1169.6 (7)	944 (1)	301 (3)
O(1)	-6243 (5)	-2313 (4)	-6398 (7)	112 (2)
O(2)	-5465 (5)	-1243 (4)	-6172 (9)	132 (3)
O(3)	-4780 (6)	-2255 (5)	-5920 (20)	280 (10)
O(4)	-5732 (9)	-1964 (9)	-4642 (8)	302 (6)
N	-2430 (3)	-1513 (3)	2847 (5)	47 (1)
C(1)	-225 (5)	-3512 (4)	-311 (7)	63 (2)
C(2)	154 (4)	-2923 (3)	510 (7)	47 (1)
C(3)	-237 (5)	-3003 (3)	1630 (6)	51 (2)
C(4)	-861 (5)	-3661 (4)	1493 (7)	61 (2)
C(5)	-1558 (5)	-3341 (3)	652 (8)	66 (2)
C(6)	-1153 (5)	-3252 (4)	-447 (6)	60 (2)
C(7)	-335 (6)	-4134 (3)	613 (8)	67 (2)
C(11)	-840 (3)	-387 (3)	1589 (5)	33 (1)
C(12)	-705 (4)	300 (3)	1085 (5)	41 (1)
C(13)	-1142 (4)	915 (3)	1477 (6)	47 (2)
C(14)	-1727 (5)	852 (3)	2425 (7)	57 (2)
C(15)	-1857 (5)	184 (4)	2967 (6)	53 (2)
C(16)	-1436 (4)	-439 (3)	2574 (5)	39 (1)
C(17)	-1590 (4)	-1154 (3)	3252 (5)	42 (1)
C(18)	-1558 (5)	-1054 (5)	4635 (6)	67 (2)
C(19)	-2518 (6)	-2258 (4)	3358 (8)	79 (2)
C(20)	-3252 (4)	-1083 (5)	3019 (9)	75 (2)
C(21)	102 (3)	-852 (3)	-579 (5)	35 (1)
C(22)	-660 (4)	-720 (3)	-1455 (5)	46 (2)
C(23)	-333 (6)	-377 (4)	-2627 (6)	63 (2)
C(24)	358 (6)	-853 (4)	-3228 (6)	70 (2)
C(25)	1091 (5)	-1016 (4)	-2368 (7)	68 (2)
C(26)	770 (4)	-1362 (3)	-1191 (6)	45 (1)
C(31)	796 (3)	-1201 (3)	1815 (5)	39 (1)
C(32)	651 (4)	-1366 (4)	3191 (6)	56 (2)
C(33)	1539 (5)	-1455 (5)	3825 (8)	82 (2)
C(34)	2116 (5)	-808 (5)	3702 (9)	95 (3)
C(35)	2242 (6)	-617 (5)	2360 (10)	103 (3)
C(36)	1370 (5)	-528 (4)	1678 (8)	70 (2)

* Defined as $(1/6\pi^2)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

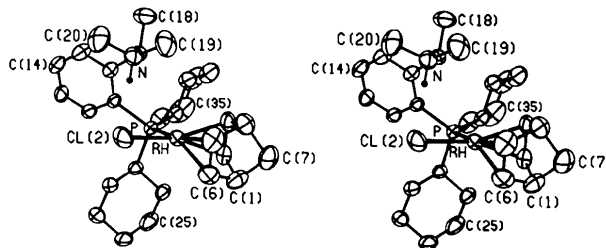


Fig. 1. A stereoview of the cation.

The geometry about the Rh atom is square planar with a tetrahedral distortion, if the diene is considered a bidentate ligand. The midpoints of the alkene bonds, *M23* and *M56*, are displaced -0.109 and 0.333 Å out of the plane formed by the Rh, Cl(2) and P atoms, and there is a dihedral angle between the Rh—Cl(2)—P and Rh—*M23*—*M56* planes of 11.3° . The phenylene ring in the aminophosphine ligand is planar within experimental error. A summary of the least-squares planes has been deposited.

A search of the Cambridge Structural Database (1984) indicated that there are several complexes with similar structural units which have been characterized by structure analyses. The Rh—Cl(2) distance of $2.390(2)$ Å is the same as the mean Rh—Cl distance $2.39(1)$ Å in $[\text{Rh}(\text{cyclo-C}_6\text{H}_{12})\text{Cl}]_2$ (Ibers & Snyder, 1962) and that of $2.398(5)$ Å in $[\text{RhCl}\{[(t\text{-C}_4\text{H}_9)_2\text{P}(\text{CH}_2)_2\text{CH}]_2\}]$ (Mason & Scollary, 1978). The Rh—P

distance of $2.315(1)$ Å is somewhat longer than that of $2.279(1)$ Å in $[\text{Rh}\{(R)\text{-}o\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]\text{C}_6\text{H}_4\text{CHCH}_3\text{N}(\text{CH}_3)_2\}(\text{C}_7\text{H}_8)]\text{ClO}_4$, (I) (McKay & Payne, 1985a) and the mean value of $2.271(1)$ Å in $[\text{Rh}(\eta\text{-C}_8\text{H}_{12})\{(\text{2S},\text{3S})\text{-}[(\text{C}_6\text{H}_5)_2\text{PCHCH}_3]_2\}]\text{ClO}_4\cdot\text{C}_4\text{H}_8\text{O}$, (II) (Ball & Payne, 1977). The P—C(11) bond of $1.848(5)$ Å is longer than the mean P—C sp^2 distance of $1.826(3)$ Å in (I), and that of $1.817(5)$ Å in $[\text{Ni}\{(R)\text{-}o\text{-}[(\text{cyclo-C}_6\text{H}_{11})_2\text{P}]\text{C}_6\text{H}_4\text{CHCH}_3\text{N}(\text{CH}_3)_2\}(\text{NCS})_2]$, (III) (McKay & Payne, 1986). The average P—C sp^3 distance, $1.850(4)$ Å, compares favourably with the average P—C sp^3 value of $1.847(4)$ Å in (III). For the phenylene ring in the aminophosphine ligand, C—C distances range from $1.376(10)$ to $1.418(8)$ Å with an average of $1.392(4)$ Å and C—C—C angles range from $117.2(5)$ to $123.3(6)^\circ$. In (III), which contains the non-protonated dicyphos ligand, the average phenyl C—C distance is $1.389(5)$ Å and C—C—C angles range from $117.7(6)$ to $121.2(6)^\circ$. Other values are in close agreement with the corresponding values in (III) except for the C(16)—C(17) distance of $1.531(8)$ Å which is longer than that of $1.499(8)$ Å for this bond in (III). Both cyclohexyl rings have chair conformations with an average C—C distance of $1.528(3)$ Å and angles at C ranging from $109.1(5)$ to $114.5(5)^\circ$.

The norbornadiene ligand is coordinated to the Rh atom in an unsymmetrical fashion with Rh—C distances *trans* to the P ligand being longer than their counterparts *trans* to Cl(2). The alkene bond lengths are C(2)—C(3) $1.375(10)$ and C(5)—C(6) $1.365(11)$ Å with the longer bond *trans* to Cl(2). This type of unsymmetric coordination has also been observed in (I). Average C sp^3 —C sp^3 and C sp^3 —C sp^2 distances within the diene are $1.533(8)$ and $1.529(5)$ Å, respectively.

The protonated amino group is involved in a strong hydrogen bond with Cl(2) with distances N—HN 0.92 and HN...Cl(2) $2.142(2)$ Å, and an angle N—H...Cl(2) of 174.5° . Other reported distances for N—H...Cl hydrogen bonds are H...Cl 2.27 , 2.40 and 2.25 Å (Knupp, Frahm, Kirfel, Fröhlich & Will, 1985), 2.14 , 2.28 , 2.31 and 2.47 Å (Sowrirajan, Aravamudan, Seshasayee & Rout, 1985), and 2.03 and 2.15 Å (Koorts & Cairns, 1985).

We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work in the form of operating and equipment grants, and IDM gratefully acknowledges the award of an NSERC Scholarship.

References

- BALL, R. G. & PAYNE, N. C. (1977). *Inorg. Chem.* **16**, 1187–1191.
 BUSING, W. R. & LEVY, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.
 Cambridge Structural Database (1984). Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.

Table 2. *Intramolecular bond distances (Å) and angles (°)*

Numbers in parentheses are estimated standard deviations in the least significant digits.

Rh—Cl(2)	2.390 (2)	N—C(20)	1.497 (9)	C(16)—C(17)	1.531 (8)
Rh—P	2.315 (1)	C(1)—C(2)	1.525 (10)	C(17)—C(18)	1.529 (9)
Rh—C(2)	2.114 (6)	C(1)—C(6)	1.504 (11)	C(21)—C(22)	1.529 (8)
Rh—C(3)	2.097 (6)	C(1)—C(7)	1.539 (11)	C(21)—C(26)	1.542 (8)
Rh—C(5)	2.198 (6)	C(2)—C(3)	1.375 (10)	C(22)—C(23)	1.517 (9)
Rh—C(6)	2.194 (7)	C(3)—C(4)	1.549 (9)	C(23)—C(24)	1.521 (11)
Cl(1)—O(1)	1.412 (8)	C(4)—C(5)	1.528 (11)	C(24)—C(25)	1.495 (11)
Cl(1)—O(2)	1.368 (7)	C(4)—C(7)	1.527 (11)	C(25)—C(26)	1.522 (10)
Cl(1)—O(3)	1.310 (10)	C(5)—C(6)	1.365 (11)	C(31)—C(32)	1.556 (9)
Cl(1)—O(4)	1.309 (10)	C(11)—C(12)	1.397 (8)	C(31)—C(36)	1.527 (9)
P—C(11)	1.848 (5)	C(11)—C(16)	1.418 (8)	C(32)—C(33)	1.534 (10)
P—C(21)	1.846 (6)	C(12)—C(13)	1.384 (8)	C(33)—C(34)	1.489 (13)
P—C(31)	1.853 (5)	C(13)—C(14)	1.376 (10)	C(34)—C(35)	1.529 (14)
N—C(17)	1.511 (8)	C(14)—C(15)	1.382 (9)	C(35)—C(36)	1.537 (12)
N—C(19)	1.490 (10)	C(15)—C(16)	1.384 (9)		
Cl(2)—Rh—P	94.25 (6)	C(3)—C(4)—C(7)	100.6 (6)		
Cl(2)—Rh—C(2)	160.7 (2)	C(5)—C(4)—C(7)	101.8 (6)		
Cl(2)—Rh—C(3)	151.5 (2)	C(4)—C(5)—C(6)	105.2 (6)		
Cl(2)—Rh—C(5)	92.8 (2)	C(1)—C(6)—C(5)	107.6 (6)		
Cl(2)—Rh—C(6)	97.3 (2)	C(1)—C(7)—C(4)	92.8 (5)		
P—Rh—C(2)	97.1 (2)	P—C(11)—C(12)	118.9 (4)		
P—Rh—C(3)	103.3 (2)	P—C(11)—C(16)	123.9 (4)		
P—Rh—C(5)	168.7 (2)	C(12)—C(11)—C(16)	117.2 (5)		
P—Rh—C(6)	150.4 (2)	C(11)—C(12)—C(13)	123.3 (6)		
C(2)—Rh—C(3)	38.1 (3)	C(12)—C(13)—C(14)	118.6 (6)		
C(2)—Rh—C(6)	65.7 (3)	C(13)—C(14)—C(15)	119.6 (6)		
C(3)—Rh—C(5)	66.9 (3)	C(14)—C(15)—C(16)	122.5 (6)		
C(5)—Rh—C(6)	36.2 (3)	C(11)—C(16)—C(15)	118.7 (5)		
O(1)—Cl(1)—O(2)	112.9 (5)	C(11)—C(16)—C(17)	121.8 (5)		
O(1)—Cl(1)—O(3)	115.3 (8)	C(15)—C(16)—C(17)	119.4 (5)		
O(1)—Cl(1)—O(4)	106.2 (7)	N—C(17)—C(16)	111.3 (5)		
O(2)—Cl(1)—O(3)	107.3 (6)	N—C(17)—C(18)	111.8 (5)		
O(2)—Cl(1)—O(4)	109.0 (8)	C(16)—C(17)—C(18)	111.9 (5)		
O(3)—Cl(1)—O(4)	106.0 (1)	P—C(21)—C(22)	113.8 (4)		
Rh—P—C(11)	119.8 (2)	P—C(21)—C(26)	112.9 (4)		
Rh—P—C(21)	105.5 (2)	C(22)—C(21)—C(26)	109.1 (5)		
Rh—P—C(31)	117.7 (2)	C(21)—C(22)—C(23)	110.4 (6)		
C(11)—P—C(21)	103.9 (2)	C(22)—C(23)—C(24)	110.9 (6)		
C(11)—P—C(31)	104.5 (2)	C(23)—C(24)—C(25)	111.2 (6)		
C(21)—P—C(31)	103.5 (3)	C(24)—C(25)—C(26)	112.2 (6)		
C(17)—N—C(19)	111.7 (5)	C(21)—C(26)—C(25)	109.2 (5)		
C(17)—N—C(20)	116.4 (5)	P—C(31)—C(32)	112.6 (4)		
C(19)—N—C(20)	111.4 (6)	P—C(31)—C(36)	114.5 (5)		
C(2)—C(1)—C(6)	101.0 (6)	C(32)—C(31)—C(36)	109.6 (6)		
C(2)—C(1)—C(7)	100.5 (6)	C(31)—C(32)—C(33)	109.6 (5)		
C(6)—C(1)—C(7)	101.5 (6)	C(32)—C(33)—C(34)	113.4 (7)		
C(1)—C(2)—C(3)	106.7 (5)	C(33)—C(34)—C(35)	110.3 (8)		
C(2)—C(3)—C(4)	105.3 (5)	C(34)—C(35)—C(36)	112.5 (7)		
C(3)—C(4)—C(5)	100.7 (5)	C(31)—C(36)—C(35)	111.3 (7)		

- 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

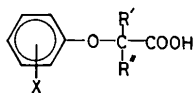
AND COLIN H. L. KENNARD*

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.