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(2-Chlorophenoxy)acetic Acid

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Abstract. $C_8H_7ClO_3$, M_r = 186·6, triclinic, $P\bar{1}$, a = 7·606 (2), b = 22·211 (5), c = 5·337 (1) Å, α = 89·56 (2), β = 114·20 (1), γ = 93·11 (1)°, V = 821·1 Å^3, D_x = 1·509 Mg m^{-3}, Z = 4, μ(Mo $K\alpha$) = 0·43 mm^{-1}; R = 0·055 for 1034 observed reflections. The molecules form almost planar centrosymmetric hydrogen-bonded cyclic dimers [O···O, 2·628 (10), 2·651 (10) Å] similar to those found in the majority of the phenoxyacetic acid structures. Both molecules in the asymmetric unit have identical conformations and pack in the triclinic cell with pseudo $2_1/c$ space-group symmetry.

Introduction. The title compound (2-CPA) is a herbicidally active member of the phenoxyalkanoic acid series, the crystal structure of which has previously been reported (Chandrasekhar & Pattabhi, 1977). However, certain features of this structure were considered anomalous in the light of the structural information which is now available on 19 phenoxy acids (Kennard, Smith & White, 1981). In particular, the two molecules in the cyclic dimer units found were not symmetry-related in the non-centrosymmetric space group $P2_1$ and did not have the usual inversion symmetry characteristic of the acids of this series. Furthermore, the short OH···O hydrogen-bond lengths between the carboxylic acid groups in the dimers (2·45, 2·47 Å) appeared untenable for normal aromatic carboxylic acids (mean 2·645 Å, 25 examples) (Smith & Kennard, 1979) and phenoxyalkanoic acids (mean 2·644 Å, 19 examples) (Kennard, Smith & White, 1981). The structure of 2-CPA was determined to resolve these anomalies so that a systematic correlation study of this group of compounds might be completed.

Colourless diamond-shaped plates or prisms (m.p. 417–419 K), prepared by the general method of Synerholm & Zimmerman (1945), were obtained from benzene. Preliminary X-ray examination indicated a cell and space group similar to that reported by Chandrasekhar & Pattabhi (1977) [a = 7·602 (6), b = 22·164 (17), c = 5·328 (4) Å, β = 114·26 (3)°, Z = 4, space group $P2_1$]. However, cell parameters obtained by least-squares refinement and intensity data collected from a single crystal (0·40 × 0·25 × 0·10 mm) [epoxy-coated to prevent surface deterioration; mounted about the a (prism) axis on a Hilger & Watts four-circle diffractometer] indicated a triclinic crystal class. The apparent systematic absences ($0k0$, k = odd, absent; $h0l$, l = odd, weak or unobserved) were the result of molecular pseudosymmetry, which was confirmed in the structure determination. 1742 reflections were collected up to 44° 2θ (Zr-filtered Mo $K\alpha$ radiation, λ = 0·7107 Å), of which 1034 with $I > 2·5\sigma(I)$ were considered observed and were used in the structure solution and refinement. No corrections were made for absorption [μ(Mo $K\alpha$) = 0·43 mm^{-1}]. A Buerger reduction (Azaroff & Buerger, 1958) failed to give a reduced or higher-symmetry cell. Intensity statistics (mean $|E^2 - 1|$ = 0·82) were not indicative of a non-centrosymmetric cell and the structure was solved by the automatic Σ_2 sign-expansion direct-methods 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 0·055 and R_w[= $(\sum w|F_o - |F_c||^2/\sum w|F_o|^2)^{1/2}$] to 0·052. The value of w used in the weighting scheme was 1·88/($\sigma^2 F_o$ + 0·0004F_o^2). All H positions were located in a difference Fourier synthesis and included in the refinement at fixed positions with their isotropic U's set invariant at 0·05 Å^2. Six intense reflections (100, $\bar{1}30$, $0\bar{9}1$, 121, $\bar{1}31$, $\bar{1}\bar{3}1$) were considered to be affected by extinction and were removed before the last refinement cycle. A final difference Fourier synthesis revealed no features larger than 0·09 e Å^{-3}.

Scattering factors used were those of Cromer & Mann (1968) (non-hydrogen) while those for H were the Stewart, Davidson & Simpson (1965) values. Final positional parameters are listed in Table 1* while

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36020 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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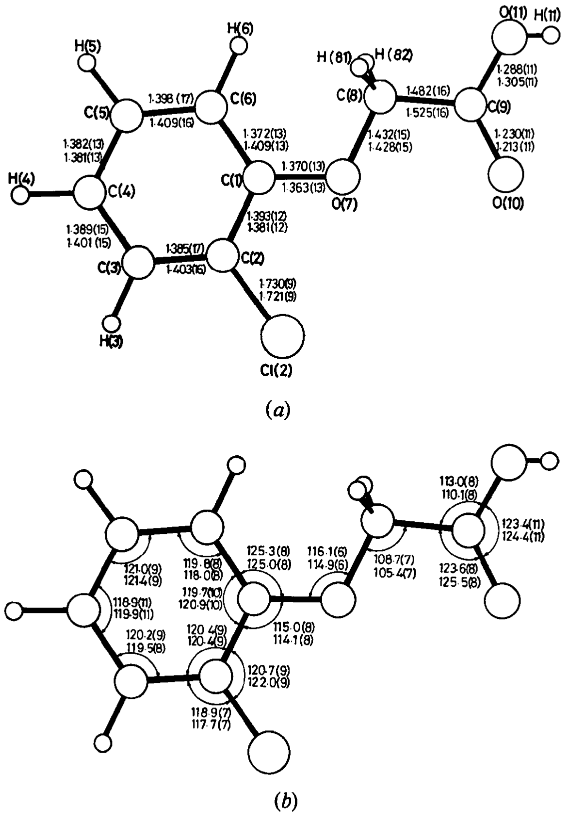
Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$) *with estimated standard deviations in parentheses*

U_{eq} is defined as $(U_{11}\,U_{22}\,U_{33})^{1/3}$.

	Molecule *A*				Molecule *B*			
	x	*y*	*z*	U_{eq} (Å²)	*x*	*y*	*z*	U_{eq} (Å²)
Cl(2)	−655 (3)	8268 (1)	558 (6)	65 (2)	−96 (3)	6704 (1)	−4246 (5)	61 (2)
C(1)	2874 (13)	8784 (4)	3785 (17)	35 (6)	3288 (13)	6216 (4)	−1046 (17)	41 (7)
C(2)	1812 (12)	8389 (4)	1610 (20)	45 (6)	2339 (12)	6610 (4)	−3116 (20)	46 (6)
C(3)	2723 (15)	8076 (5)	291 (20)	51 (7)	3343 (14)	6940 (4)	−4416 (19)	55 (7)
C(4)	4711 (14)	8149 (5)	1145 (20)	58 (7)	5340 (15)	6893 (4)	−3493 (20)	56 (7)
C(5)	5753 (14)	8542 (5)	3304 (20)	52 (7)	6286 (13)	6504 (4)	−1397 (21)	57 (7)
C(6)	4836 (12)	8861 (4)	4629 (19)	42 (7)	5290 (12)	6156 (4)	−121 (17)	45 (7)
O(7)	1809 (8)	9075 (3)	4890 (13)	50 (4)	2132 (8)	5918 (3)	2 (12)	51 (4)
C(8)	2865 (12)	9488 (4)	7113 (18)	65 (6)	3090 (11)	5508 (4)	2144 (17)	43 (6)
C(9)	1519 (14)	9718 (4)	8202 (19)	40 (6)	1593 (14)	5292 (4)	3216 (19)	39 (7)
O(10)	−199 (8)	9551 (3)	7335 (12)	48 (4)	−57 (8)	5444 (3)	2351 (11)	47 (4)
O(11)	2345 (8)	10100 (3)	10202 (14)	55 (5)	2336 (8)	4912 (3)	5202 (13)	59 (4)
H(3)	1917	7834	−1589		2611	7318	−5668	
H(4)	5408	7836	212		6039	7130	−4960	
H(5)	7277	8549	4150		8193	6518	−477	
H(6)	5806	9089	6595		6050	5834	1563	
H(81)	3681	9813	6568		4207	5715	3756	
H(82)	4318	9397	8446		3905	5048	1866	
H(11)	1214	10208	11154		1293	4727	5729	



(*a*)

(*b*)

Fig. 1. (*a*) Bond distances (Å) and atom-numbering scheme for 2-CPA. The upper and lower values are for the two independent molecules (*A* and *B*) in the asymmetric unit. (*b*) Bond angles (°) for 2-CPA.

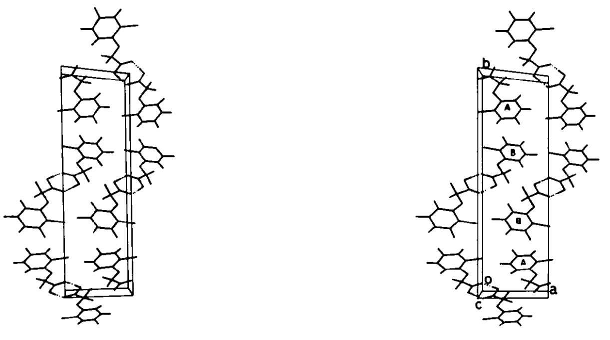


Fig. 2. Stereoview of the packing of 2-CPA in the cell viewed down **c**.

interatomic distances and angles are given in Fig. 1. A stereoview of the packing is shown in Fig. 2.

Discussion. Both molecules of 2-CPA (*A* and *B*) in the asymmetric unit form the usual centrosymmetric hydrogen-bonded cyclic organic acid dimers [O···O, 2·628 (10) (*A*); 2·651 (10) Å (*B*)] with their inversion-related pair. The gross molecular conformation of the oxoacetic acid side chain in both molecules is synplanar–synplanar (carbonyl) (Fig. 1*a*), which is the preferred conformation among the phenoxyacetic analogues (Kennard *et al.*, 1981). The torsion angles about bonds in the side chain [C(2)–C(1)–O(7)–C(8); C(1)–O(7)–C(8)–C(9); O(7)–C(8)–C(9)–O(11)] are −179·4(8), +179·9 (8); −175·1 (8), −173·2 (8); −179·3 (9), −179·9 (8)° for (*A*) and (*B*) respectively.

This results in intramolecular O(ether)—O(carbonyl) interactive distances of 2·643 (10) (*A*) and 2·637 (10) Å (*B*) compared with 2·51 and 2·50 Å found in the previous determination of 2-CPA (Chandrasekhar & Pattabhi, 1977). The range and mean for this distance over 19 phenoxyalkanoic acids, irrespective of their conformation, is 2·605 Å [(2,4,5-trichlorophenoxy)acetic acid] to 2·775 Å [2-(4-chlorophenoxy)propionic acid]; mean 2·711 Å (Kennard *et al.*, 1981). Bond distances and angles for both molecules *A* and *B* are essentially the same and are similar to those found in the previous determination and in all other members of the series. This includes the usual distortion of the *exo*-C(1) bond angles [*A*, 125·3 (8), 115·0 (8); *B*, 125·0 (8), 114·1 (8)°]. The structure is comparable to that of (±)-2-(2-chlorophenoxy)propionic acid (Smith, Kennard & White, 1981) in that there is no evidence of orientational disorder in the carboxylic acid dimer unit, the C=O and C—O(H) distances being 1·230 (11), 1·213 (11); 1·288 (11), 1·305 (11) Å respectively, and the C—C=O and C—C—OH angles 123·6 (8), 125·5 (8); 113·0 (8), 110·1 (8)°. In 2-CPA the angle between the benzene plane and the plane of the carboxylic acid group in the same molecule is 5·6 (8) and 8·2 (8)° for *A* and *B* respectively.

Packing of molecules *A* and *B* in the triclinic cell gives a pseudo $2_1/c$ relationship (x,y,z; $x, \frac{1}{2}-y, \frac{1}{2}+z$) and results in an absence of observed reflections of the $0k0$ set for k = odd and a paucity of observed reflections of the $h0l$ set for l = odd (for l = 1, 3, 5, number of observed reflections = 11, 5, 0 respectively; maximum $|F_o| = 23·0$ for $\bar{6}03$). The reason for this subtle deviation from perfect $P2_1/c$ space symmetry is not understood since all other examples, even of lower molecular symmetry, pack with only one molecular asymmetric unit in either triclinic or monoclinic cells.

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Structure of 1,4-Diacetyl-2,5-dimethoxybenzene

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Abstract. $C_{12}H_{14}O_4$, monoclinic, $P2_1/n$, $a = 9·618$ (3), $b = 14·097$ (4), $c = 4·118$ (1) Å, $\beta = 98·6$ (1)°, $Z = 2$, $D_m = 1·33$, $D_x = 1·337$ Mg m^{-3}. The structure was solved by direct methods and refined by least squares to a final $R = 0·053$ for 785 observed reflections. The molecules are centrosymmetric and are linked by van der Waals forces only.

Introduction. It has been reported (Madeja-Kotkowska, 1974) that 2,5-diacetylhydroquinone (I) can be very easily reduced to 3,6-dihydro-2,5-diacetylhydroquinone (II). The reduction of its methoxy derivative 1,4-diacetyl-2,5-dimethoxybenzene (III) in the same experimental conditions does not give any stable dihydro derivative. Short communications about structures (I) and (II) have been published previously (Wajsman, Grabowski, Stępień & Cygler, 1978*a*,*b*). The crystal-structure investigation of (III) was undertaken to elucidate the above statement concerning chemical reactivity and compare the molecular structures of these compounds.

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