

(±)-2-(4-Chloro-2-methylphenoxy)propionic Acid (Mecoprop)

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Abstract. $C_{10}H_{11}ClO_3$, $M_r = 214.6$, monoclinic, $P2_1/c$, $a = 4.395$ (3), $b = 6.813$ (5), $c = 36.75$ (2) Å, $\beta = 106.01$ (5)°, $V = 1057.7$ Å³, $Z = 4$, $D_x = 1.35$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 3.04$ mm⁻¹, $R = 0.058$ for 914 observed reflections. The molecules of Mecoprop form synplanar hydrogen-bonded cyclic dimers with an O...O distance of 2.660 Å. The molecule is not planar but adopts a synclinal conformation with a torsion angle of +85.5° between the plane of the benzene ring and that of the carboxylic acid group about the ether- α -carbon bond. The magnitude of this angle appears to be a common feature among those phenoxyalkanoic acids having at least one substituent methyl group on the α -carbon of the acetic acid residue. The presence of the 2-methyl group in the ring has little effect upon the conformation of the side chain. The results are similar to those found for the unsubstituted 2-phenoxypropionic acid.

Introduction. Mecoprop is the name accepted by the IOS (International Organization for Standardization) and BSI (British Standards Institution) for racemic 2-(4-chloro-2-methylphenoxy)propionic acid, previously known as 2-[(4-chloro-*o*-tolyl)oxy]propionic acid. Alternative names for the commercial product are Mecopar, Mecopex, Mecotox, MCPP and CMPP. The auxin properties of this compound became known in 1953 (Fawcett, Osborne, Wain & Walker, 1953) while its usefulness as a translocatable postemergence herbicide was reported by Lush & Leafe (1956). Although the name Mecoprop in general usage refers to the racemic form, herbicidal activity is possessed by only the (+)-enantiomer. The structure of this compound is the first of a herbicidally active ring-methyl-substituted phenoxyalkanoic acid. Other important commercial

compounds are MCPA (4-chloro-2-methylphenoxyacetic acid) and MCPB [4-(chloro-2-methylphenoxy)butyric acid]. Structural information is now available for a number of other active and inactive phenoxyalkanoic acids (Smith & Kennard, 1979; Smith, Kennard & White, 1980*a,b*).

Colourless prismatic crystals (m.p. 363 K) were obtained by repeated recrystallization of technical Mecoprop from a mixture of toluene and acetone. Three-dimensional X-ray data were obtained from one crystal (0.05 × 0.25 × 0.30 mm) mounted about the prism a axis on a Syntex P1 four-circle diffractometer at the University of Western Australia. Monochromatic Cu $K\alpha$ radiation was used. 914 unique reflections with $I > 2.5\sigma(I)$ were considered observed of 1275 collected in a sphere up to 2θ 100°. No

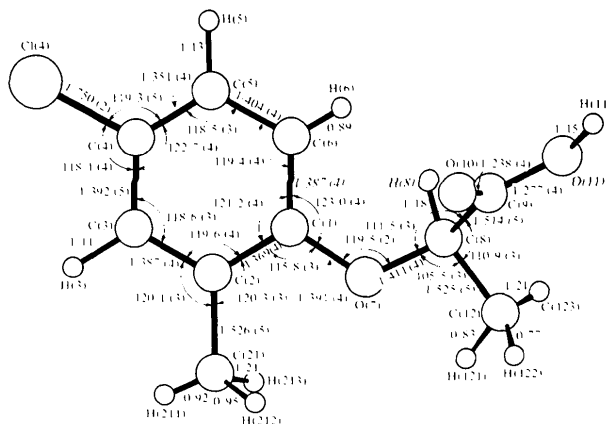


Fig. 1. Molecular conformation and numbering scheme used for Mecoprop in a view perpendicular to the plane of the benzene ring.

Table 1. Atomic positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
Cl(4)	-6235 (4)	7525 (2)	2238 (1)
O(7)	-12021 (8)	13069 (5)	1022 (1)
O(10)	-14817 (9)	10642 (6)	446 (1)
O(11)	-11974 (9)	11822 (6)	83 (1)
C(1)	-10644 (11)	11684 (7)	1296 (1)
C(2)	-11014 (11)	12008 (7)	1649 (1)
C(3)	-9692 (12)	10708 (8)	1940 (1)
C(4)	-7966 (12)	9120 (8)	1865 (1)
C(5)	-7540 (13)	8790 (8)	1520 (1)
C(6)	-8918 (12)	10095 (8)	1225 (1)
C(8)	-11014 (12)	13202 (7)	690 (1)
C(9)	-12765 (14)	11760 (8)	392 (1)
C(12)	-11700 (16)	15310 (9)	552 (2)
C(21)	-12830 (14)	13803 (8)	1724 (1)
H(3)	-10137	10940	2220
H(5)	-6068	7624	1429
H(6)	-8656	9929	996
H(8)	-8377	12656	763
H(11)	-13721	10757	-113
H(121)	-13590	15479	543
H(122)	-10550	15400	428
H(123)	-10675	16464	808
H(211)	-13750	13532	1916
H(212)	-12038	14895	1618
H(213)	-15473	13863	1511

correction was made for absorption. The structure was solved by the multiresolution Σ_2 sign expansion procedure of *SHELX* (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms reduced R ($= \sum |F_o - |F_c|| / \sum F_o$) to 0.058 and R_w [$(= \sum w|F_o - |F_c||^2 / \sum w|F_o|^2)^{1/2}$] to 0.068. The value of w used in the weighting scheme was $1.00 / (\sigma^2 F + 0.0004 F^2)$. H positions were located in a difference-Fourier synthesis and were included in the calculation at fixed positions with U also fixed at 0.05 \AA^2 . Four very intense low-angle reflections (110, 011, $\bar{1}02$, 100) were considered to be badly affected by extinction and were removed before the last cycle of refinement. A final difference electron density synthesis revealed no features greater than 0.12 e \AA^{-3} .

Positional parameters are given in Table 1.* Interatomic distances (\AA) and angles ($^\circ$) are given in Fig. 1.

Discussion. The molecules of Mecoprop form the usual centrosymmetric hydrogen-bonded cyclic dimers [$\text{O} \cdots \text{O}$, $2.660(4) \text{ \AA}$] with the *syn-syn* conformational motif (Fig. 2). The angle between the normals to

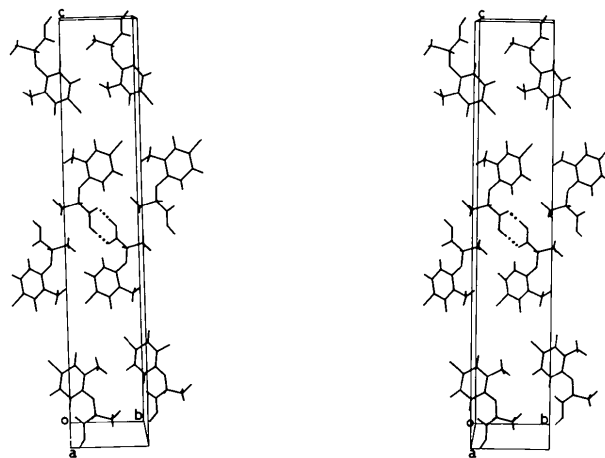


Fig. 2. Stereoview of the packing perpendicular to the bc plane.

the planes of the benzene ring and the carboxylic acid group is 78.6° , which is similar to those found for the equivalent angle in seven other phenoxypropionic acids for which structural data are available (Smith & Kennard, 1979; Smith *et al.*, 1980*a,b*). Furthermore, the torsion angle $\text{C}(1)-\text{O}(7)-\text{C}(8)-\text{C}(9)$ is $+85.5^\circ$ (synclinal) which compares with a mean of $+73.9^\circ$ (range $+61.6$ to $+80.0^\circ$) for the same series of acids. Synclinal examples also occur among the phenoxyacetic acid analogues, *e.g.* 2,4- and 2,5-dichlorophenoxyacetic acids (2,4-D and 2,5-D) (Smith & Kennard, 1979), but the majority are antiperiplanar with torsion angles close to 180° [2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (Smith & Kennard, 1979); phenoxyacetic acid (Smith *et al.*, 1980*a*); 2-chlorophenoxyacetic acid (Chandrasekhar & Pat-tabhi, 1977); 4-ethylphenoxyacetic acid (Gałdecki & Kozłowska, 1979)]. Only one example with an intermediate angle (2,4,6-T; 152.3°) is known (Smith & Kennard, 1979), but this is obviously due to the presence of Cl substituents in both *ortho* positions of the ring. It is now reasonable to predict that the preferred conformation in the solid among the 2-(phenoxy)propionic acids without both 2- and 6-ring substitution, is one with the carboxylic acid group synclinally related to the benzene ring and the α -methyl group [C(12)] lying close to the plane which contains the benzene ring. In the present structure, C(12) lies 1.27 \AA below the plane. This is the approximate conformation predicted for the free molecules of phenoxyisobutyric acids on the basis of multiple-regression analysis (Zeelen, 1976). However, NMR studies have suggested that the anti conformer, with the benzene ring and carboxylic acid group coplanar, is favoured in 2-methyl-2-phenylpropionic acid, which is analogous to the phenoxypropionic acids (Spassov & Stefanova, 1979).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35008 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The presence of the 2-methyl group appears to have little effect on the minor conformational differences among the series except that the acid groups adopt a position *trans* to the substituent methyl group of the ring. Distortion of the *exo*-C(1) angles, a feature of the majority of the phenoxy acid structures, is also observed (115.8, 123.0°). The angles about the carboxylic acid group are likewise distorted, C(8)–C(9)–O(10) [122.3 (3)°], C(8)–C(9)–O(11) [114.4 (3)°] and O(10)–C(9)–O(11) [123.5 (3)°].

Partial disorder in the cyclic carboxylic acid dimer unit is also evident, appearing as a contraction in the difference between the C–O(carbonyl) and C–O(hydroxyl) bond distances (1.238 and 1.277 Å). A similar degree of disorder is found for the symmetrically substituted 2-(3,5-dichlorophenoxy)propionic acid (3,5-DP) (1.237, 1.276 Å) and 2,4,6-trichlorophenoxyacetic acid (2,4,6-T) (1.234, 1.262 Å) (Smith & Kennard, 1979). The only example of complete disorder is phenoxyacetic acid where both bonds are equal and the acid proton is delocalized. In considering the packing environment of the dimer unit (Fig. 2) there appears to be no good reason for the disorder phenomenon. The closest intermolecular contact to either O(10) or O(11) (outside the dimer unit) is 3.163 Å [O(10)···O(11)] although there is an intramolecular contact between O(11) and C(12) (2.91 Å).

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References

- CHANDRASEKHAR, K. & PATTABHI, V. (1977). *Acta Cryst.* **B33**, 1257–1261.
 FAWCETT, C. H., OSBORNE, D. J., WAIN, R. L. & WALKER, R. D. (1953). *J. Appl. Biol.* **40**, 231–243.
 GALDECKI, Z. & KOZLOWSKA, K. (1979). *Acta Cryst.* **A34**, S116.
 LUSH, G. B. & LEAFE, E. L. (1956). *Proc. 3rd Br. Weed Control Conf.* pp. 625–633.
 SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SMITH, G. & KENNARD, C. H. L. (1979). *J. Agric. Food Chem.* **27**, 779–786.
 SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1980a). *Acta Cryst.* **B36**. To be published.
 SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1980b). *Acta Cryst.* **B36**. To be published.
 SPASSOV, S. L. & STEFANOVA, R. (1979). *J. Mol. Struct.* **53**, 219–224.
 ZEELEN, F. J. (1976). *Quantitative Structure–Activity Relationships*, edited by M. TICHY, pp. 161–164. Basel: Springer-Verlag.

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Methyl 3 β -Acetoxy-17 α -methyl-18-nor-5 α -androstane-17 β -carboxylate*

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Abstract. C₂₃H₃₆O₄, *M_r* = 376.5, triclinic, *P*1, *a* = 7.813 (2), *b* = 11.360 (2), *c* = 6.860 (2) Å, α = 101.44 (3), β = 112.11 (3), γ = 71.99 (3)°, *V* = 534.12 Å³, *Z* = 1, *D_m* = 1.167 (floatation in KI solution at 294 K), *D_x* = 1.171 Mg m⁻³, μ (Cu *K* α) = 0.586 mm⁻¹; *R* = 0.042 and *R_w* = 0.040 for 1753 observed reflexions. The 17 angular methyl group adopts an α -axial orientation as predicted by studies on Favorsky

rearrangement of 17-halogenated 20-keto steroids devoid of the 18-methyl group.

Introduction. A unifying explanation of the complex results in Favorsky rearrangements of α -halogenated acetylcycloalkanes was advanced by Engel, Roy, Capitaine, Bilodeau, McPherson-Foucar & Lachance (1970). Their basic assumptions concerning the multiplicity of mechanisms and the influence of the 18-methyl group on the stereochemical course of the

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