

(±)-2-(2,4,5-Trichlorophenoxy)propanoic acid*

BY GRAHAM SMITH

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

COLIN H. L. KENNARD

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

ALLAN H. WHITE

Department of Physical and Inorganic Chemistry, University of Western Australia, Perth, Australia 6009

AND PETER G. HODGSON

Department of Chemistry, University of Papua New Guinea, Port Moresby, New Guinea

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Abstract. $C_9H_7Cl_3O_3$, triclinic, $P1$, $a = 11.060(3)$, $b = 7.263(2)$, $c = 7.255(2)$ Å, $\alpha = 101.18(3)$, $\beta = 104.51(3)$, $\gamma = 99.12(3)^\circ$, $M_r = 269.5$, $Z = 2$, $D_x = 1.66$ g cm $^{-3}$, $\mu(\text{Mo } K\alpha) = 8.3$ cm $^{-1}$. $R = 0.045$, 1379 observed reflexions. The molecules are hydrogen bonded [O—H...O, 2.645(3) Å] through their synplanar carboxylic acid groups to form cyclic dimers about a centre of symmetry in the cell. The dihedral angle between the normals to the planes of the benzene ring and the carboxylic acid group is 77.8°.

Introduction. The herbicidal properties of the title compound were reported by Synerholm & Zimmerman (1945). Its commercial names are Fenoprop, Silvex, 2,4,5-TP, Kurosol and Kuron (Spencer, 1973). Colourless prismatic crystals were grown from a mixture of acetone and chloroform. 1379 reflexions with $|F_o| > 2.5\sigma(F_o)$ were considered observed out of 1902 collected from one crystal (0.3 × 0.2 × 0.2 mm) mounted on a Syntex P1 four-circle diffractometer ($2\theta_{\text{max}} = 54.6^\circ$; Mo $K\alpha$ radiation, graphite monochromator). No correction was made for absorption ($\mu_{\text{Mo } K\alpha} = 8.27$ cm $^{-1}$).

The structure was solved by multiresolution Σ_2 sign expansion (Sheldrick, 1976). All non-hydrogen atoms were refined anisotropically by full-matrix least squares. The H atoms were located in a difference Fourier electron density synthesis and included in the refinement, but their coordinates and isotropic thermal parameters were fixed and were given the same value as that of the isotropic parameter of the atom they were attached to. Eight low-angle intense reflexions (021; 100; 113; 110; 210; 211; 012; 112) were found to be seriously affected by extinction and were removed

before the final cycle of refinement. The final R [$= \Sigma ||F_o| - |F_c|| / \Sigma F_o$] was 0.045 and R_w [$= (\Sigma w||F_o| - |F_c||^2 / \Sigma w|F_o|^2)^{1/2}$] = 0.047. The weighting scheme used was $w = 2.12 / [\sigma^2(F) + 0.0004F^2]$. A final difference synthesis revealed no features higher than 0.095 e Å $^{-3}$. Positional and H isotropic thermal parameters are given in Table 1.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32705 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic positional parameters ($\times 10^4$) and H thermal parameters ($\times 10^3$) with estimated standard deviations in parentheses

	x	y	z	U (Å 2)
Cl(2)	7503 (1)	4105 (2)	8757 (1)	
Cl(4)	11367 (1)	2811 (2)	5837 (2)	
Cl(5)	9397 (1)	1174 (2)	1592 (2)	
O(7)	5903 (2)	2582 (4)	4809 (3)	
O(10)	5657 (2)	4905 (3)	2257 (4)	
O(11)	4412 (3)	2464 (4)	-194 (4)	
C(1)	7154 (3)	2580 (5)	4894 (5)	
C(2)	8034 (3)	3273 (5)	6762 (5)	
C(3)	9312 (3)	3316 (5)	7031 (5)	
C(4)	9744 (3)	2692 (5)	5448 (6)	
C(5)	8886 (4)	1989 (5)	3599 (5)	
C(6)	7590 (3)	1913 (5)	3326 (5)	
C(8)	4951 (4)	1862 (5)	2931 (5)	
C(9)	5067 (4)	3247 (5)	1646 (5)	
C(12)	3680 (4)	1752 (6)	3383 (6)	
H(3)	10011	3895	8469	33
H(6)	6956	1420	1986	40
H(8)	5022	550	2237	32
H(11)	4506	3526	-907	57
H(121)	3468	680	3990	35
H(122)	3663	3257	4158	35
H(123)	3064	1306	2323	35

* Herbicides. V. Part III: Smith, Whitnall & Kennard (1976). Part IV: Smith, Kennard & White (1977).

Discussion. The molecules are hydrogen bonded [O—H...O, 2.645 (3) Å] through a centre of symmetry in the cell. These groups adopt the usual synplanar conformation for cyclic dimers (Leiserowitz, 1976). The angle between the normals to the plane of the benzene ring and the carboxylic acid group is 77.8° and is markedly different from that found in another herbicide, 2,4,5-trichlorophenoxyacetic acid (4.15°).

The plane containing the carboxylic acid group is synclinal (IUPAC, 1970) with respect to the benzene plane on the basis of the torsion angle (80.0°) about the bond O(7)—C(8).

Bond distances and angles are given in Fig. 1 and a comparison with other similar structures is tabulated in

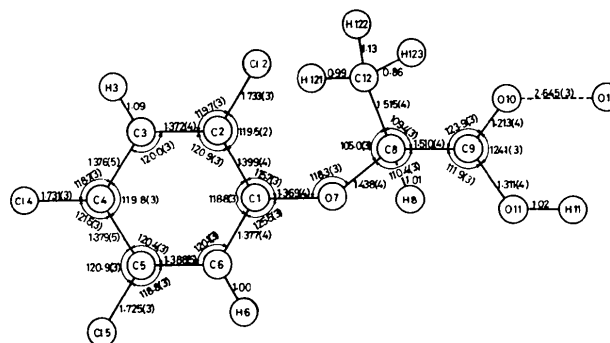


Fig. 1. Bond lengths (Å) and angles (°) in (±)-2-(2,4,5-trichlorophenoxy)propanoic acid.

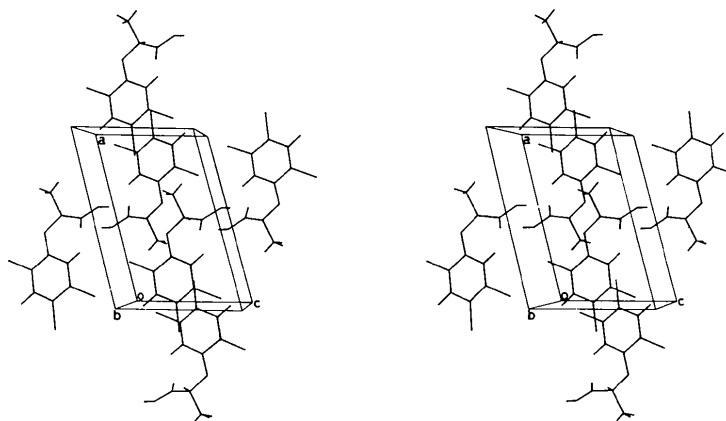


Fig. 2. Stereoview perpendicular to the ac plane.

Table 2. Comparative distances (Å) and angles (°) for a series of auxins and related compounds

	2,4-D ^a	2,5-D ^b	2,4,5-T ^c	2,4,6-T ^d	IAA ^e	This work
C—Cl	174.1, 174.1	174.6, 175.3	172.6, 173.1 173.0	173.4, 172.6 173.0	—	173.3, 173.1 172.5
O—H...O	[174.1 (4)]	[175.0 (5)]	[173.0 (6)]	[173.0 (4)]	266.5	[173.0 (3)]
O(7)—C(1)—C(6)	124.7 (3)	125.1 (2)	124.0 (4)	118.5 (4)	—	125.5 (3)
O(7)—C(1)—C(2)	116.2 (3)	117.8 (2)	116.1 (3)	122.9 (4)	—	115.7 (3)
Dihedral angle (ring to carboxylic acid group)	85.2	81.2	4.2	32.0	62.9	77.8

(a) 2,4-D: 2,4-dichlorophenoxyacetic acid (Smith, Kennard & White, 1976a). (b) 2,5-D: 2,5-dichlorophenoxyacetic acid (Smith, Whitnall & Kennard, 1976). (c) 2,4,5-T: 2,4,5-trichlorophenoxyacetic acid (Smith, Kennard & White, 1976b). (d) 2,4,6-T: 2,4,6-trichlorophenoxyacetic acid (Smith, Kennard & White, 1977). (e) IAA: 3-indolylacetic acid (Karl, Britts & Gum, 1964).

Table 2. The angles O(7)—C(1)—C(2) and O(7)—C(1)—C(6) in all cases are significantly different from 120°. A packing diagram has been drawn in Fig. 2.

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Guanidinium Trichromate

BY A. STĘPIEŃ AND M. J. GRABOWSKI

Department of Crystallography, Institute of Chemistry, University of Łódź, 91-416 Łódź, Nowotki 18, Poland

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Abstract. $(\text{CN}_3\text{H}_6)_2\text{Cr}_3\text{O}_{10}$, monoclinic, space group $C2/c$, with $a = 13.303$ (4), $b = 7.791$ (2), $c = 14.667$ (4) Å, $\beta = 107.08$ (3)°, $V = 1510.75$ Å³, $Z = 4$, $D_m = 1.998$, $D_x = 2.00$ g cm⁻³. 618 independent non-zero reflexions were estimated by photographic methods; systematic absences: hkl , $h + k = 2n + 1$, $h0l$, $l = 2n + 1$. The structure was solved by the Patterson method and refined by full-matrix least squares; the final R is 0.135. The trichromate ion consists of three nearly tetrahedral CrO_4 groups joined through shared O atoms. The value of the Cr—O—Cr angle is 132.7°. The mean (uncorrected) Cr—O bond distances are 1.75 Å and 1.65 Å for bridge and terminal bonds respectively. The ions are linked by N—H...O hydrogen bonds.

Introduction. Cr, like S, P, As and some other elements, exhibits a tendency to form polyions. Of these, the following are structurally well known: chromates and dichromates of alkaline metals (Martin & Durif, 1964; McGinety, 1972; Carter & Margulis, 1972; Panagiotopoulos & Brown, 1970, 1972a,b, 1973; Brandon & Brown, 1968; Panagiotopoulos, 1972; Löfgren, 1971; Löfgren & Waltersson, 1971), ammonium (Stephens & Cruickshank, 1970; Byström & Wilhelmi, 1951) and guanidinium (Cygler, Grabowski, Stępień & Wajsman, 1976; Wajsman, Cygler, Grabowski & Stępień, 1976).

The trichromate ion has been studied once by X-ray diffraction so far – in rubidium trichromate (Löfgren, 1974). It seemed interesting to determine the structure of the trichromate ion joined to cations not only through ionic bonds, but also hydrogen bonds. On the other hand, crystals of guanidinium chromate,

dichromate and trichromate display great differences in mechanical properties. The guanidinium chromate crystals possess cleavage planes and undergo plastic deformation very easily. The crystals of guanidinium dichromate are hard and those of guanidinium trichromate are brittle but possess no cleavage planes and are not plastic. To elucidate the problem of the structure dependence of the above mentioned properties, the crystal structure investigations of the chromate (Cygler, Grabowski, Stępień & Wajsman, 1976) and the dichromate (Wajsman, Cygler, Grabowski & Stępień, 1976) were undertaken. The present paper is a continuation of an earlier investigation of the guanidinium trichromate crystal structure (Stępień, 1973).

Crystals chosen for X-ray analysis were ground into a cylindrical shape ($\mu r = 1.5$). The accurate cell constants were obtained by least-squares methods from Weissenberg photographs. The diffraction data were collected from the integrated Weissenberg photographs taken with $\text{Cu } K\alpha$ radiation. The intensities were corrected for Lp and absorption factors for a cylinder (*International Tables for X-ray Crystallography*, 1962).

The structure was determined by the heavy-atom method, with a three-dimensional Patterson synthesis. From the analysis of this function two Cr atoms were located, one of which must have been in a special position on the twofold axis. Five O atoms were also located. The positions of the remaining non-hydrogen atoms were located with the electron density function. The structure was refined by the full-matrix least-squares method, taking into account the Cruickshank weighting scheme, $w^{-1} = A + BF_o + CF_o^2$, with A , B ,