$-x$, $1 - y$, $1 - z$. This short contact at one point in the ring may be responsible for the non-symmetrical thermal motion of the ring.

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References

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV, 73–74. Birmingham: Kynoch Press.

McMillan, J. A., Curtin, D. Y. & Paul, I. C. (1978). *Acta Cryst.* B**34**, 2878–2882.

Puckett, S. A. (1975). *Recent Studies in Solid State Organic Chemistry*, PhD Thesis. Univ. of Illinois, Urbana, Illinois.

Puckett, S. A., Greensley, M. K., Paul, I. C. & Curtin, D. Y. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 847–859.

Puckett, S. A., Paul, I. C. & Curtin, D. Y. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 1873–1881.

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(±)-2-(3,5-Dichlorophenoxy)propanoic Acid*

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Abstract. $C_9H_8Cl_2O_3$, triclinic, $P\bar{1}$, $a = 9\cdot615$ (4), $b = 8\cdot503$ (3), $c = 7\cdot505$ (3) Å, $\alpha = 114\cdot36$ (3), $\beta = 106\cdot62$ (3), $\gamma = 97\cdot37$ (3)°, $M_r = 235\cdot1$, $Z = 2$, $D_x = 1\cdot52$ g cm^{-3}, μ(Mo $K\alpha$) = 6·09 cm^{-1}; $R = 0\cdot065$, 1168 reflections. The molecules form synplanar hydrogen-bonded cyclic dimers. The molecular conformation is very similar to that observed in (±)-2-(2,4,5-trichlorophenoxy)propanoic acid (2,4,5-TP) with the dihedral angle between the planes of the benzene ring and the carboxylic acid group being 87·0° (2,4,5-TP = 77·8°). The distance between the carboxylic acid O atom and C(2) of the aromatic ring (3·68 Å) is short compared with those in other members of the phenoxyalkanoic acid series.

Introduction. The title compound (3,5-DP) is a member of the series of commercially important synthetic auxin herbicides which include 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) and Fenoprop [(±)-2-(2,4,5-trichlorophenoxy)propanoic acid (2,4,5-TP)], the structures of which have been described (Smith, Kennard, White & Hodgson, 1977). Some herbicidally inactive members of the series of chloro-substituted phenoxyacetic acids are the 2,4,6-trichloro (2,4,6-T) and 3,5-dichloro (3,5-D) analogues. The structure of 2,4,6-T has been determined (Smith, Kennard & White, 1977) but the growing of suitable crystals of 3,5-D has so far proved impossible. Since activity in the propanoic acid series usually parallels the acetic acid series with respect to ring chlorine substitution, the structure of 3,5-DP was investigated. The compound was prepared by the interaction of ethyl 2-bromopropanoate with sodium 3,5-dichlorophenoxide (Synerholm & Zimmerman, 1945). White crystals were grown from a mixture of toluene and chloroform. 1168 reflections with $|F_o| > 2\cdot5|\sigma(F_o)|$ were considered observed out of 1800 collected from a crystal (0·5 × 0·35 × 0·15 mm) mounted on a Syntex $P\bar{1}$ four-circle diffractometer ($2\theta_{\max} = 50°$) using graphite-monochromated Mo $K\alpha$ radiation. No absorption corrections were made [μ(Mo $K\alpha$) = 6·09 cm^{-1}].

The structure was solved by multisolution $\sum_2$ sign expansion (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic temperature factors on all

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* Herbicides. VI. Part V: Smith, Kennard, White & Hodgson (1977).

non-hydrogen atoms reduced R from 0·31 to 0·07. The H positions were located in a difference-Fourier synthesis and included in the calculations but their positional parameters were not refined. Their thermal parameters were also fixed at the same value as the adjacent bonded atom. No extinction effects were observed. The final R $(= \sum |F_o - F_c| / \sum F_o)$ was 0·065 and R_w $[= (\sum w|F_o - F_c|^2 / \sum w|F_o|^2)^{1/2}]$ was 0·074. The value of w in the weighting scheme was $1 \cdot 00/(\sigma^2 F + 0 \cdot 001094 F^2)$. A final difference synthesis revealed no features higher than 0·27 e Å^{-3}. Positional and H atom thermal parameters are given in Table 1.* Bond lengths and angles are in Fig. 1.

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

	x	y	z	U (Å^2)
Cl(3)	6731 (2)	2268 (2)	7119 (3)	
Cl(5)	6693 (2)	9101 (2)	11421 (3)	
O(7)	2186 (4)	4626 (5)	5053 (6)	
O(10)	475 (5)	2259 (6)	5747 (7)	
O(11)	681 (5)	−10 (6)	3072 (7)	
C(1)	3633 (7)	4843 (8)	6337 (9)	
C(2)	4336 (6)	3485 (8)	6034 (9)	
C(3)	5781 (7)	3919 (8)	7440 (10)	
C(4)	6564 (7)	5650 (8)	9151 (10)	
C(5)	5782 (7)	6927 (8)	9316 (10)	
C(6)	4343 (7)	6592 (8)	7978 (9)	
C(8)	1330 (7)	2864 (8)	3346 (9)	
C(9)	804 (6)	1651 (8)	4163 (10)	
C(12)	−71 (7)	3129 (9)	1993 (10)	
H(2)	3912	2205	4694	43
H(4)	7671	6018	10402	43
H(6)	3795	7562	8096	36
H(8)	1939	2294	2304	38
H(11)	328	−892	3705	43
H(121)	−664	3750	2856	59
H(122)	161	3806	1487	59
H(123)	−647	2171	966	59

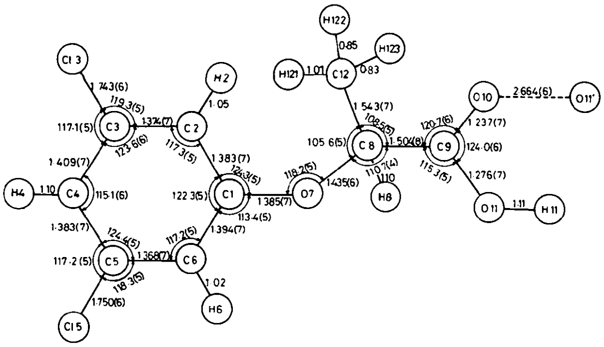

Fig. 1. Bond lengths (Å) and angles (°) in 3,5-DP.

Discussion. The molecules of 3,5-DP form synplanar hydrogen-bonded cyclic dimers [O—H···O, 2·664 (6) Å]. The angle between the normals to the plane of the benzene ring and the carboxylic acid group is 87·0° and is very similar to that reported in the case of 2,4,5-TP (77·8°) (Smith, Kennard, White & Hodgson, 1977). The quasi-racemic compound containing (+)-3-bromophenoxypropanoic acid and (−)-3-methoxyphenoxypropanoic acid molecules (Karle & Karle, 1966) also has similar angles (85·5°) for its conformers. This constancy is in contrast to the range observed for the phenoxyacetic acid series where dihedral angles vary from 4·2 (2,4,5-T) to 85·2° (2,4-D).

The plane containing the carboxylic acid group is synclinal (IUPAC, 1970) with respect to the plane of the benzene ring on the basis of the torsion angle (−73·1°) about the bond O(7)—C(8). Comparative torsion angles and dihedral angles for a series of synthetic auxins listed previously (Smith, Kennard, White & Hodgson, 1977) are 2,4-D (−75·2, 85·2°), 2,5-D (−73·9, 81·2°), 2,4,5-T (−174·6, 4·2°), 2,4,6-T (−152·3, 32·0°), 2,4,5-TP (−80·0, 77·8°).

In 2-chlorophenoxyacetic acid (Chandrasekhar & Pattabhi, 1977), the two independent molecules in the asymmetric unit have dihedral angles of 6·6 and 7·0° and torsion angles of −173·6 and 173·3° while the natural plant-growth hormone 3-indolylacetic acid (IAA) (Karle, Britts & Gum, 1964) has values of 62·9 and −85·6° respectively for the equivalent angles. The quasi-racemate (Karle & Karle, 1966) has angles of 85·5° (dihedral) and ±76·5° (torsion).

The distance between O(11) of the carboxylic acid and C(2) of the aromatic ring (3·678 Å) is comparatively short compared with the distances found for other members of the phenoxyalkanoic acid series, with the exception of the 3-bromo and 3-methoxy analogues (Karle & Karle, 1966), where similar distances were found (3·733, 3·774 Å). The decrease is significant and is considered to be the result of the absence of substituent groups in either of the *ortho* positions in the ring. The two O atoms of the carboxylic acid group are also symmetrical with respect to C(2) [O(10)···C(2), 3·644 Å]. Irrespective of conformational orientations, however, the distance between the hydroxyl [O(11)] and the carbonyl [O(10)] O atoms and the ether O atom [O(7)] is relatively constant with the oxoacetic acid group planar. The distance range for O(10)···O(7) over six members of the series is 2·501–2·756 Å (mean 2·672 Å) while the O(11)···O(7) range is 3·509–3·573 Å (mean 3·540 Å). This is comparable with the equivalent distances O(10)···C(7) (2·824 Å) and O(11)···C(7) (3·559 Å) found for the analogous α,β-saturated acid, 2-(p-chlorophenyl)propanoic acid (Glusker, Zacharias & Carrell, 1975).

It is considered (Leiserowitz, 1976) that in similar α,β-saturated carboxylic acids, this preferred orien-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33572 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

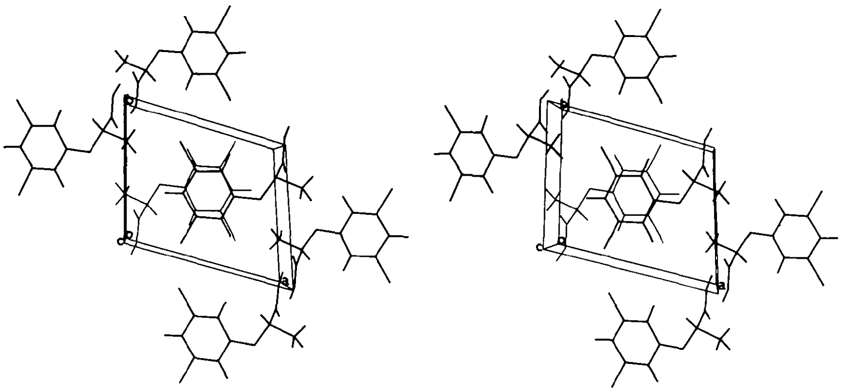

Fig. 2. Stereoview perpendicular to the *ab* plane.

tation, resulting in the synplanar conformation, was determined by the non-bonded interactions between H atoms on the β-C and the carbonyl O. The C—O(carbonyl) and C—O(hydroxyl) distances [1·237 (6) and 1·276 (7) Å respectively] are significantly different from the mean values of 1·21 and 1·31 Å (Leiserowitz, 1976) for dimeric carboxylic acids. The only other member of the phenoxy series to exhibit a similar effect is 2,4,6-T [1·235 (5) and 1·262 (5) Å] (Smith, Kennard & White, 1977) which is also symmetrically substituted and is herbicidally inactive. This phenomenon suggests partial orientational disorder of the carboxyl group as a result of the intermolecular environment of the carboxyl dimer.

The molecules pack in the cell with the planes of the benzene rings lying approximately parallel to the *ab* plane and separated by *c*/2, giving pseudo *C* centering (Fig. 2). However, the 3,5-chlorine substituents do not superimpose, this effect being less pronounced than is observed in 2,5-D where exact superimposition occurs.

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References

Chandrasekhar, K. & Pattabhi, V. (1977). *Acta Cryst.* B33, 1257–1260.
Glusker, J. P., Zacharias, D. E. & Carrell, H. L. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 68–74.
IUPAC (1970). *J. Org. Chem.* **35**, 2861.
Karle, I. L., Britts, K. & Gum, P. (1964). *Acta Cryst.* **17**, 496–499.
Karle, I. L. & Karle, J. (1966). *J. Am. Chem. Soc.* **88**, 24–27.
Leiserowitz, L. (1976). *Acta Cryst.* B32, 775–802.
Sheldrick, G. M. (1976). *SHELX*-76. A program for crystal structure determination. Univ. of Cambridge.
Smith, G., Kennard, C. H. L. & White, A. H. (1977). *Cryst. Struct. Commun.* **6**, 49–52.
Smith, G., Kennard, C. H. L., White, A. H. & Hodgson, P. G. (1977). *Acta Cryst.* B33, 2922–2924.
Synerholm, M. E. & Zimmerman, P. W. (1945). *Contrib. Boyce Thompson Inst.* **14**, 91–103.

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[3-Benzyl-5-(4-nitrophenyl)-2-phenyl-1,3-thiazolio]-4-oxide

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Abstract. $C_{22}H_{16}N_2O_3S$, orthorhombic, *Pbca*, $a = 14{\cdot}77$ (2), $b = 7{\cdot}94$ (1), $c = 32{\cdot}76$ (2) Å, $Z = 8$, $D_c = 1{\cdot}34$ g cm^{-3}, μ(Mo $K\alpha$) = $1{\cdot}96$ cm^{-1}. The structure was refined to an R value of 0·11 for 592 independent reflexions. The mesoionic character of the molecule is established.