# Herbicides. Part I. Crystal Structure of 2,4-D (2,4-Dichlorophenoxyacetic Acid)

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The crystal structure of 2,4-D has been determined by the symbolic addition procedure from 1 635 reflections collected by diffractometer. Crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions: $a = 913.1(2)$, $b = 782.7(2)$, $c = 725.2(2)$ pm, $\alpha = 111.39(3)°$, $\beta = 105.79(3)°$, and $\gamma = 90.87(3)°$. The structure was refined by least-squares to $R$ 0·046. The two molecules are hydrogen bonded [263.2(6) pm] through their carboxylic acid groups to form a dimer about a centre of symmetry at $\frac{1}{2},0,\frac{1}{2}$.

THE programme of investigation into the crystal structures of agriculturally important chemicals[1] has now been extended to include herbicides. The synthesis of 2,4-dichlorophenoxyacetic acid (2,4-D) was first carried out in 1917 [2] and a modification involving the condensation of 2,4-dichlorophenol with chloroacetic acid was published in 1941.[3]

The herbicidal properties of 2,4-D were reported in 1945.[4]

## DISCUSSION

The stereochemistry of 2,4-D is indicated in Figure 1. Uncorrected Cl–C distances are significantly longer [174.1(4) pm] when compared to those from a recent structure determination of hexachlorobenzene [5] [171.5(2) pm] (Table 1). Other similar Cl–C distances are found in 2-chloro-5-nitrobenzoic acid [6] (175), *o*-chlorobenzoic acid [7] (174), and potassium hydrogen bis-*p*-chlorobenzoate [8] (174 pm). This is in conformity with a previous observation [9] that the Cl–C bond lengths for bonds on aromatic rings are significantly shorter (mean 170.9 pm) when the bonds are mutually *ortho*, than when they are more widely separated, or in isolation (mean 173.7 pm).

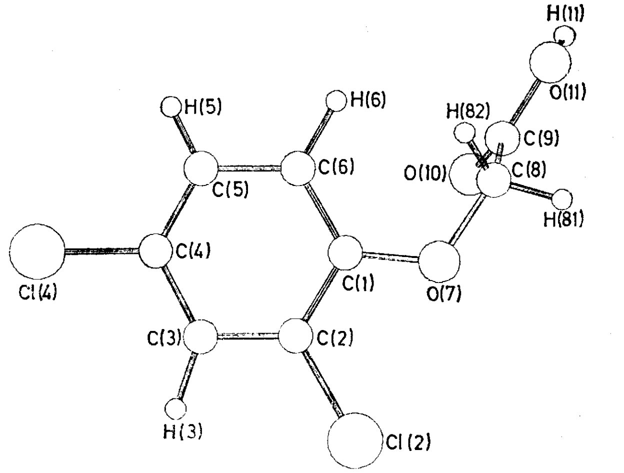

FIGURE 1 The structure of 2,4-dichlorophenoxyacetic acid, drawn perpendicular to the plane of the benzene ring

TABLE 1

Interatomic distances (pm) and angles (°), with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*a*) Distances | | | |
| Cl(2)–C(2) | 174.1(4) | C(6)–H(6) | 112(3) |
| Cl(4)–C(4) | 174.1(4) | C(8)–H(81) | 106(3) |
| | | C(8)–H(82) | 109(3) |
| C(1)–C(2) | 139.0(6) | O(11)–H(11) | 103(3) |
| C(2)–C(3) | 138.4(6) | O(11)–H(11) · · · O(10) | 263.2(6) |
| C(3)–C(4) | 139.5(6) | | |
| C(4)–C(5) | 136.4(7) | C(1)–O(7) | 136.5(5) |
| C(5)–C(6) | 141.3(7) | O(7)–C(8) | 142.3(5) |
| C(6)–C(1) | 139.7(7) | C(8)–C(9) | 152.0(6) |
| | | C(9)–O(10) | 121.7(6) |
| C(3)–H(3) | 103(3) | C(9)–O(11) | 130.4(5) |
| C(5)–H(5) | 100(3) | | |
| (*b*) Angles | | | |
| C(6)–C(1)–C(2) | 119.1(2) | Cl(2)–C(2)–C(3) | 118.8(2) |
| C(1)–C(2)–C(3) | 122.2(2) | Cl(4)–C(4)–C(3) | 117.6(2) |
| C(2)–C(3)–C(4) | 117.3(2) | Cl(4)–C(4)–C(5) | 119.6(2) |
| C(3)–C(4)–C(5) | 122.7(2) | C(2)–C(1)–O(7) | 116.2(3) |
| C(4)–C(5)–C(6) | 119.1(2) | C(6)–C(1)–O(7) | 124.7(3) |
| C(5)–C(6)–C(1) | 119.6(2) | C(1)–O(7)–C(8) | 118.8(4) |
| | | O(7)–C(8)–C(9) | 111.1(3) |
| C(9)–O(11)–H(11) | 111.5(2) | | |
| C(9)–O(10) · · · H(11) | 123.1(2) | C(8)–C(9)–O(10) | 123.2(3) |
| | | C(8)–C(9)–O(11) | 112.2(2) |
| Cl(2)–C(2)–C(1) | 118.9(2) | | |

The two molecules of 2,4-D are hydrogen bonded [O · · · H–O 263.2(6) pm] through their carboxylic acid groups to form a dimer about a centre of symmetry at $\frac{1}{2},0,\frac{1}{2}$. The hydrogen-bond distance is comparable to that in other cyclic dimers.[10-14]

The planar carboxylic acid group subtends an angle of 85.23° with the plane of the benzene ring. Packing of the dimeric molecules is indicated in Figure 2, which

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[1] G. Smith, C. H. L. Kennard, and A. H. White, *J.C.S. Perkin II*, 1976, 614.

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shows that the benzene rings do not stack upon each other, and consequently there is no interaction between overlapping π-electron systems. Atom Cl(2) is 5.3 pm out of a plane (σ 0.7 pm) defined by the benzene ring. The distance between the benzene ring C-6 position (δ +) and the carboxylato-oxygen of the acid is 420 pm, *vs.* 550 pm postulated[15] in a suggestion for a structural basis of auxin activity.

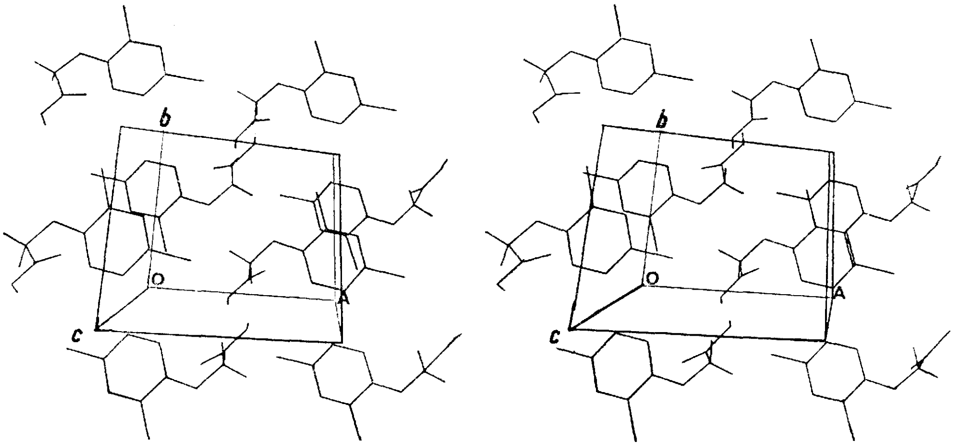

FIGURE 2 Stereoscopic view of the packing viewed perpendicular to *ab*. For clarity, no aromatic hydrogens are included

## EXPERIMENTAL

*Crystal Data.*—$C_8H_6Cl_2O_3$, $M = 221.1$. Triclinic $a = 913.1(2)$, $b = 782.7(2)$, $c = 725.2(2)$ pm, $\alpha = 111.39(3)°$, $\beta = 105.79(3)°$, $\gamma = 90.87(3)°$, $U = 0.4606$ nm$^3$, $D_m = 1.60$ (by flotation), $Z = 2$, $D_c = 1.59$ g cm$^{-3}$, $F(000) = 224$, Mo-$K_\alpha$ radiation, $\lambda = 71.07$ pm (graphite monochromator); $\mu$(Mo-$K_\alpha$) = 6.79 cm$^{-1}$. Space group, $P\bar{1}$ ($C_i^1$, No. 2). Commercial 2,4-D was recrystallised from benzene; m.p. 411 K. Intensity data were collected from one crystal (0.20 × 0.20 × 0.32 mm) by use of a Nova 1200 controlled Syntex $P\bar{1}$ four-circle *X*-ray diffractometer, with the Syntex data collection scheme. Of 1 635 reflections collected up to $2\theta$ 50°, 1 422 having $I > 2.5\sigma(I)$ were considered observed. No absorption correction was applied.

*Structure Determination.*—The structure was determined by symbolic addition on 250 reflections by use of the FAME, MAGIC, LINK, and SYMPL set of programs.[16] All non-hydrogen atoms were located from an *E* map. Full-matrix least-squares refinement reduced *R* from an initial value of 0.360 to 0.061. A difference-Fourier synthesis revealed the positions of the hydrogen atoms. Further refinement reduced *R* to 0.046 and the weighted residual $R^1$ $\{= \Sigma[w| |F_o| - |F_c| |^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ to 0.043. A plot of $I_c/I_o$ *vs.* $I_o$ indicated that 20 low-angle reflections were seriously affected by extinction, and these were removed in the final refinement. A final difference-Fourier synthesis did not reveal any unexplainable electron density.

Atomic parameters are listed in Table 2. Observed and calculated structure factor amplitudes and thermal parameters are listed in Supplementary Publication No. SUP 21642 (7 pp., 1 microfiche).* Scattering factors for chlorine and carbon were from ref. 17, and for hydrogen from ref. 18. No correction was applied for anomalous dispersion effect.

TABLE 2

Atomic parameters (× $10^4$; H atom parameters × $10^3$), with estimated standard deviations in parentheses

| Atom | *x*/*a* | *y*/*b* | *z*/*c* | *B*/Å$^2$ |
|---|---|---|---|---|
| Cl(2) | 8 812.9(1.7) | 7 548.9(1.8) | 7 370.9(2.2) | |
| Cl(4) | 13 216.2(1.7) | 3 321.4(2.5) | 8 843.4(2.7) | |
| O(7) | 6 745(3) | 4 238(3) | 5 845(4) | |
| O(10) | 6 138(3) | 1 842(4) | 1 839(4) | |
| O(11) | 4 296(3) | 130(4) | 2 117(4) | |
| C(1) | 8 219(4) | 3 901(5) | 6 510(5) | |
| C(2) | 9 351(4) | 5 401(5) | 7 274(6) | |
| C(3) | 10 892(5) | 5 253(6) | 7 997(6) | |
| C(4) | 11 280(4) | 3 521(6) | 7 937(6) | |
| C(5) | 10 210(5) | 2 015(6) | 7 241(6) | |
| C(6) | 8 645(5) | 2 189(5) | 6 485(6) | |
| C(8) | 5 533(5) | 2 763(6) | 5 075(6) | |
| C(9) | 5 369(4) | 1 526(5) | 2 847(6) | |
| H(5) | 1 054(3) | 83(4) | 731(4) | 3.7 |
| H(6) | 777(3) | 95(4) | 590(4) | 4.0 |
| H(7) | 1 161(3) | 644(4) | 841(4) | 3.6 |
| H(81) | 577(3) | 185(4) | 592(4) | 4.0 |
| H(82) | 449(3) | 333(4) | 506(4) | 4.0 |
| H(11) | 408(3) | −58(4) | 55(4) | 4.3 |

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

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