Insecticides. Part 8.[1] Crystal Structures of 1,1-Bis-(*p*-chlorophenyl)-acetic acid (DDA) and 4,4'-Dichlorobenzophenone (DBP)

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The crystal structure of DDA has been determined by direct methods from three-dimensional diffractometer data. $Z = 4$ in the monoclinic unit cell, space group $P2_1/c$, $a = 1\,411.3(2)$, $b = 612.3(1)$, $c = 1\,600.5(2)$ pm, $\beta = 111.51(1)°$. The structure was refined by least squares to R 0.079 for 1 600 observed reflections. DDA is non-active but has conformational angles similar to those of DDT. It forms a dimer, with its centre at a centre of symmetry, and a hydrogen bond of 200 pm. The structure of 4,4'-dichlorobenzophenone (DBP) was determined by the same methods. $Z = 4$ in the monoclinic cell, space group $C2/c$, $a = 2\,516.1(11)$, $b = 612.8(3)$, $c = 758.6(3)$ pm, $\beta = 102.05(3)°$. The molecule has a space-group implied two-fold axis. It is non-active and has small conformational angles like those of DDE.

BOTH DDA [1,1-bis-(*p*-chlorophenyl)acetic acid] and DBP [4,4'-dichlorobenzophenone] are degradative products of DDT found in the environment.

In a two-dimensional structure determination of DBP[2] the *b*-axis projection was solved by trial-and-error, and the *a*-axis projection by the Patterson–Fourier method. The cell used was body centred, space group $I2/a$, $a = 7.66(1)$, $b = 611(1)$, $c = 2\,468(3)$ pm, $\beta = 95.33°$, $Z = 4$. Because it is intended to compare the structural parameters for a number of DDT-like insecticides, it was decided to redetermine the structure of DBP, and to complete this survey of DDT-breakdown products with the structure of DDA.

DISCUSSION

The 'Handbook of Toxicology'[3] gives the lowest concentration in which certain DDT-related compounds were found toxic to *anopheles quadrimaculatus* 4th instar. They were DDT 0.002 5, DDA 10, and DBP 10 p.p.m. No other toxicity data were available for DDA; in this text other data confirmed the low toxicity of DBP. Although these results are only approximate, they give some comparison with those for DDT.

Neither of these structures has a trichloroethane group or any other of *ca.* 600—630 pm diameter in projection, which Holan suggests as an essential requirement for activity.[4]

DBP, like DDE,[1] has small conformational angles: plane C(15),C(13),C(7) with both phenyl rings 27.9°, and between phenyl rings 50.7°. DDA has angles very similar to those of DDT:[5] plane C(1),C(13),C(7) with phenyl rings 85.6 and 49.6° (DDA), 84.2 and 47.4° (DDT), and between phenyl rings 75.5 (DDA) and 64.9° (DDT). However, both the nature of the carboxylic group and the dimerisation might be responsible for the reduction in activity of the compound. The dimer has its centre at a centre of symmetry, with a hydrogen bond of 200 pm between the carboxy-oxygen O(4) and H(O3), and a distance between the alcoholic O(3) · · · O'(3) of 272 pm.

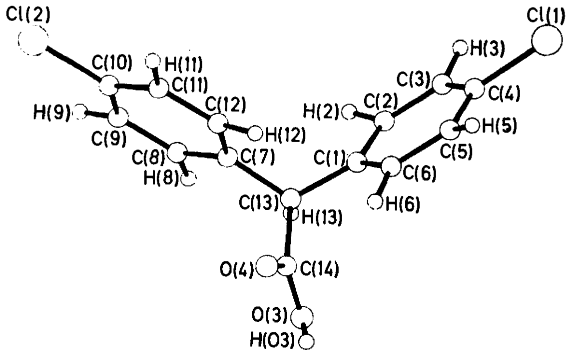

FIGURE 1 General view of DDA

Most interatomic distances and angles are similar to others found in this series of investigations,[6] with the notable exception of the Cl–C distances in the two *p*-chlorophenyl groups in DBP. They are very much longer [179.2(5) pm] compared with those in DDT [170(1.5) and 175(1.5) pm] and others reported here and in the previous paper.[1]

Figures 1—4 show molecular arrangements and

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[6] K.G. Shields and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 1374.

packing diagrams for both compounds. Interatomic distances and angles are listed in Tables 1 and 2.

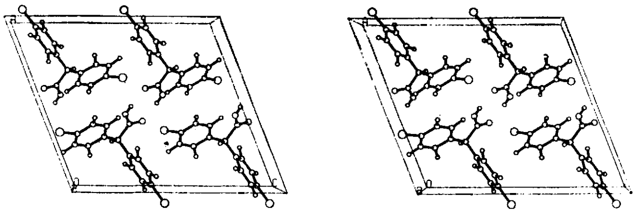

FIGURE 2 Stereoview of the packing of DDA in the unit cell, viewed perpendicular to *b*

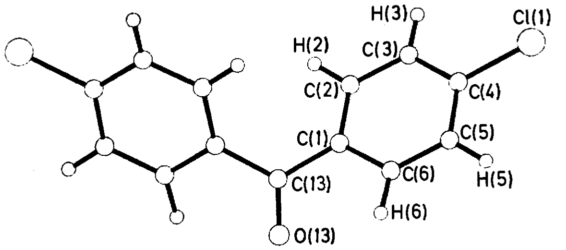

FIGURE 3 General view of DBP

EXPERIMENTAL

(*a*) DDA: 1,1-*Bis*-(p-*chlorophenyl*)*acetic Acid*.—Crystals were obtained from ethanol–chloroform–water.

Crystal data.—$C_{14}H_{10}Cl_2O_2$, $M = 281.2$, $a = 1\,411.3(2)$, $b = 612.3(1)$, $c = 1\,600.5(2)$ pm, $\beta = 111.51(1)°$, $U = 1.2867(5)$ nm^3, $D_m = 1.45(2)$ (by flotation), $Z = 4$, $D_c = 1.451$ g cm^{-3}, $F(000) = 576$. Space group $P2_1/c$ (C^5_{2h}, No. 14). Mo-K_α radiation, $\lambda = 71.07$ pm; μ(Mo-K_α) = 5.0 cm^{-1}. Graphite monochromator.

Intensity measurements were carried out on a single crystal *ca.* 0.25 mm in three orthogonal directions, mounted about a general axis on the Monash University's Philips PW 1100 automatic diffractometer. Cell dimensions were obtained from a least-squares refinement using twenty-five intense reflections ($5° < \theta < 10.5°$) from all parts of the diffracting sphere. Data were collected with the diffractometer set in the θ—ω scanning mode. Intensities were corrected for Lorentz and polarization factors, including polarization by the monochromator, but not for absorption. 1 600 intensities out of a total 2 921 collected had $F > 2.5\sigma$.

(*b*) DBP: 4,4′-*Dichlorobenzophenone*.—*Crystal data*. $C_{13}H_8Cl_3O$, $M = 251.1$. Monoclinic, $a = 2\,516.1(11)$, $b = 612.8(3)$, $c = 758.6(3)$ pm, $\beta = 102.05(3)°$, $U = 1.144(2)$ nm^3, $D_m = 1.45(2)$ (by flotation), $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 512$. Space group C_2/c (C^6_{2h}, No. 15); Mo-K_α radiation; μ(Mo-K_α) = 5.4 cm^{-1}. Graphite crystal monochromator.

Counter data, from crystals mounted about two different axes, were used to obtain accurate unit-cell dimensions. Intensity data were collected up to 2θ 55° about two axes using two different crystals. Data for the layers ($h0$—$5l$) and ($hk0$—9) were collected on the University of Sydney's Supper equi-inclination diffractometer. Intensities were measured by the ω scan method at a rate of 2.5° min^{-1} with a counter aperture of 2.5°. The operating procedure has

TABLE 1

Molecular geometry of 1,1-bis-(*p*-chlorophenyl)acetic acid (DDA)

(*a*) Bond distances (pm)

Cl(1)–C(4)	174.4(6)	Cl(2)–C(10)	173.6(8)
O(3)–C(14)	125.0(7)	O(4)–C(14)	126.4(6)
C(1)–C(2)	139.9(6)	C(7)–C(8)	138.7(8)
C(1)–C(6)	138.5(8)	C(7)–C(12)	140.0(8)
C(1)–C(13)	151.3(7)	C(7)–C(13)	151.1(9)
C(2)–C(3)	138.1(9)	C(8)–C(9)	137.0(11)
C(2)–H(2)	96	C(8)–H(8)	106
C(3)–C(4)	136.2(9)	C(9)–C(10)	138.4(10)
C(3)–H(3)	105	C(9)–H(9)	98
C(4)–C(5)	137.5(7)	C(10)–C(11)	137.6(10)
C(5)–C(6)	138.6(8)	C(11)–C(12)	137.5(10)
C(5)–H(5)	104	C(11)–H(11)	113
C(6)–H(6)	108	C(12)–H(12)	108
C(13)–C(14)	153.6(7)	C(13)–H(13)	105
H(O3)–O(3)	79		

(*b*) Bond angles (°)

C(2)–C(1)–C(6)	117.9(4)	C(8)–C(7)–C(12)	117.7(5)
C(2)–C(1)–C(13)	117.9(4)	C(8)–C(7)–C(13)	120.3(5)
C(6)–C(1)–C(13)	124.2(4)	C(12)–C(7)–C(13)	121.9(5)
C(1)–C(2)–C(3)	120.6(5)	C(7)–C(8)–C(9)	122.0(5)
C(1)–C(2)–H(2)	108	C(7)–C(8)–H(8)	114
C(3)–C(2)–H(2)	127	C(9)–C(8)–H(8)	124
C(2)–C(3)–C(4)	120.2(5)	C(8)–C(9)–C(10)	119.0(6)
C(2)–C(3)–H(3)	123	C(8)–C(9)–H(9)	127
C(4)–C(3)–H(3)	117	C(10)–C(9)–H(9)	114
Cl(1)–C(4)–C(3)	119.8(3)	Cl(2)–C(10)–C(9)	118.9(5)
Cl(1)–C(4)–C(5)	119.6(4)	Cl(2)–C(10)–C(11)	120.5(5)
C(3)–C(4)–C(5)	120.6(5)	C(9)–C(10)–C(11)	120.6(6)
C(4)–C(5)–C(6)	119.5(5)	C(10)–C(11)–C(12)	119.9(5)
C(4)–C(5)–H(5)	117	C(10)–C(11)–H(11)	121
C(6)–C(5)–H(5)	123	C(12)–C(11)–H(11)	119
C(1)–C(6)–C(5)	121.2(4)	C(7)–C(12)–C(11)	120.7(5)
C(1)–C(6)–H(6)	120	C(7)–C(12)–H(12)	115
C(5)–C(6)–H(6)	118	C(11)–C(12)–H(12)	124
C(1)–C(13)–C(14)	111.9(4)	C(7)–C(13)–C(14)	110.0(4)
C(1)–C(13)–H(13)	108	C(7)–C(13)–H(13)	109
C(1)–C(13)–C(7)	114.4(4)	C(14)–C(13)–H(13)	103
O(3)–C(14)–C(13)	117.2(4)	O(4)–C(14)–C(13)	118.5(4)
O(3)–C(14)–O(4)	124.3(4)	C(14)–O(3)–H(O3)	97

TABLE 2

Molecular geometry of 4,4′-dichlorobenzophenone (DBP)

(*a*) Bond distances (pm)

Cl(1)–C(4)	179.2(5)	C(3)–H(3)	96(6)
C(1)–C(2)	139.8(7)	C(4)–C(5)	138.9(8)
C(1)–C(6)	137.0(7)	C(5)–C(6)	142.8(7)
C(1)–C(13)	153.5(6)	C(5)–H(5)	96(6)
C(2)–C(3)	142.1(7)	C(6)–H(6)	104(6)
C(2)–H(2)	94(6)	C(13)–O(13)	122.0(9)
C(3)–C(4)	134.0(7)		

(*b*) Bond angles (°)

C(2)–C(1)–C(6)	114.4(4)	Cl(1)–C(4)–C(5)	124.1(4)
C(2)–C(1)–C(13)	126.6(4)	C(3)–C(4)–C(5)	116.9(4)
C(6)–C(1)–C(13)	118.8(4)	C(4)–C(5)–C(6)	123.1(4)
C(1)–C(2)–C(3)	124.8(4)	C(4)–C(5)–H(5)	117(3)
C(1)–C(2)–H(2)	115(3)	C(6)–C(5)–H(5)	120(3)
C(3)–C(2)–H(2)	120(3)	C(1)–C(6)–C(5)	120.8(4)
C(2)–C(3)–C(4)	120.0(4)	C(1)–C(6)–H(6)	112(3)
C(2)–C(3)–H(3)	126(3)	C(5)–C(6)–H(6)	127(3)
C(4)–C(3)–H(3)	113(3)	C(1)–C(13)–O(13)	119.2(3)
Cl(1)–C(4)–C(3)	119.0(4)	C(1)–C(13)–C(1)	121.5(4)

FIGURE 4 Stereoview of the packing of DBP in the unit cell, viewed perpendicular to *b*

been already described.[7,8] The two data sets corrected for Lorentz-polarization effects were scaled together. 726 of the 1 040 independent reflections were considered observed $[F > 2.5\sigma(F)]$.

TABLE 3

Fractional co-ordinates ($\times$ 10^4, H $\times$ 10^3) for DDA

Atom	x/a	y/b	z/c
Cl(1)	3 451(2)	2 867(3)	560(1)
Cl(2)	−701(2)	−2 359(4)	4 134(2)
O(3)	4 420(3)	−5 927(7)	3 929(3)
O(4)	4 035(3)	−3 048(6)	4 589(2)
C(1)	3 121(4)	−2 235(9)	2 480(3)
C(2)	2 598(5)	−2 428(11)	1 553(4)
C(3)	2 709(5)	−866(11)	972(4)
C(4)	3 338(5)	874(9)	1 297(3)
C(5)	3 879(5)	1 086(10)	2 203(4)
C(6)	3 767(5)	−468(9)	2 789(3)
C(7)	2 008(4)	−3 487(8)	3 328(3)
C(8)	1 288(5)	−5 104(9)	3 235(4)
C(9)	461(5)	−4 772(11)	3 474(5)
C(10)	342(4)	−2 766(11)	3 822(4)
C(11)	1 036(5)	−1 116(10)	3 916(4)
C(12)	1 856(4)	−1 458(9)	3 663(4)
C(13)	2 924(4)	−3 941(9)	3 081(3)
C(14)	3 867(4)	−4 337(8)	3 933(3)
H(2) *	204	−339	145
H(3)	225	−84	29
H(5)	426	255	242
H(6)	425	−34	349
H(8)	144	−659	296
H(9)	−8	−582	343
H(11)	94	54	418
H(12)	248	−33	381
H(13)	282	−546	275
H(O3)	490	−556	435

* B 4.5 Å^2 for all H atoms.

Structure Determination.—Both structures were solved using the symbolic-addition direct method.[9] The E map revealed the location of all non-hydrogen atoms. Full-matrix least-squares refinement reduced the initial R from 0.30 to 0.091 for DDA and from 0.39 to 0.088 for DBP. Difference electron-density syntheses showed the positions of all the hydrogen atoms in both cases. Further refinement and the use of modified weighting schemes reduced R to 0.079 (DDA) and 0.075 (DBP). Final-difference Fourier syntheses in both cases revealed no prominent unexplained features. Atomic co-ordinates are listed in Tables 3 and 4. Thermal parameters and observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 21873 (12 pp., 1 microfiche).* Scattering factors for chlorine, oxygen, and carbon were from ref. 10 and for hydrogen from ref. 11. No correction was applied for anomalous dispersion effects.

TABLE 4

Fractional co-ordinates for DBP ($\times$ 10^4, H atoms $\times$ 10^3)

Atom	x/a	y/b	z/c
Cl(1)	2 883.1(5)	170(3)	3 641(2)
C(1)	4 483(2)	3 611(7)	6 587(6)
C(2)	4 457(2)	1 561(8)	5 763(7)
C(3)	3 971(2)	536(8)	4 850(7)
C(4)	3 491(2)	1 537(10)	4 743(7)
C(5)	3 501(2)	3 579(10)	5 545(7)
C(6)	3 991(2)	4 625(8)	6 436(7)
C(13)	5 000	4 834(12)	7 500
O(13)	5 000	6 825(9)	7 500
H(2) *	479(2)	80(9)	594(8)
H(3)	394(2)	−88(10)	430(8)
H(5)	316(2)	435(9)	536(8)
H(6)	403(2)	611(10)	713(8)

* B 3.8 Å^2 for all H atoms.

We thank W. J. Roulston, Division of Entomology of C.S.I.R.O., for the crystals, Dr. B. M. Gatehouse, Monash University, and Professor H. C. Freeman, University of Sydney, for making their diffractometers available for data collection, Dr. B. Miskin for collecting the data for DDA, and the Australian Research Grants Committee and the University of Queensland for financial support. K. G. S. was supported by a Commonwealth Postgraduate Scholarship.

[6/890 *Received*, 10*th May*, 1976]

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

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