Insecticides. Part 7.[1] Crystal Structures of 1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (DDE) and 1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (DDD)

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The crystal structure of DDE has been determined from three-dimensional diffractometer data: $Z = 8$. in the monoclinic space group $P2_1/c$. with $a = 921.9(1)$. $b = 3\,549.6(5)$. $c = 943.8(1)$ pm. $\beta = 114.70(1)°$. The structure was refined by full-matrix least-squares to R 0.049. The inactivity of DDE could be due to its low conformational angles or to the effect of the double bond on the planarity of part of the molecule. The structure of the related compound, DDD, was also determined by direct methods. $Z = 8$. in the monoclinic cell, space group $C2/c$. $a = 2\,011.4(2)$. $b = 769.2(1)$. $c = 1\,908.6(3)$ pm. $\beta = 105.42(1)°$. The structure was similarly refined to R 0.068. It is active and has similar conformational angles to those found in DDT.

BECAUSE of the enormous use of DDT [1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane] and the stability of its primary degradation product DDE [1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene], DDT and its degradation products have been found as residues throughout the world. It has been reported [2] that in 'the housefly, a dominant gene on chromosome II controls the production of an enzyme DDT'ase which functions to dehydrochlorinate DDT to the non-insecticidal DDE.' It is also possible for DDT to undergo reductive dechlorination to form DDD [1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane]. The object of our structure determinations is to provide additional stereochemical information for the general investigation on a mode of action theory for DDT-type insecticides.

DISCUSSION

The 'butterfly' configuration DDT [3] is repeated in DDD (Figure 1). These two structures are very similar, the two Cl–C distances in the two *p*-chlorophenyl groups being 170(1.5) and 175(1.5) in DDT, compared with those listed for DDD (Table 1), and in the halogenomethyl

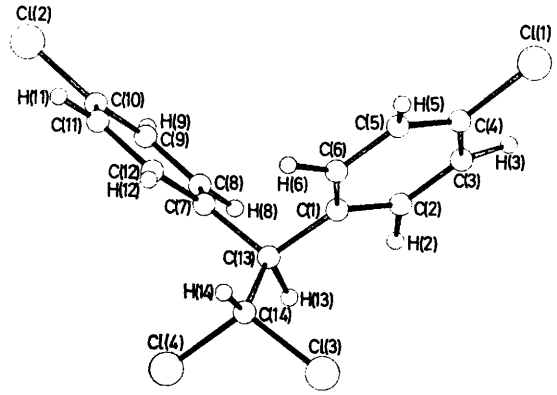

FIGURE 1 General view of DDD, showing the atom labelling system

group 174(1.5), 178(1.5), and 181(1.5) pm. The conformation angles between the plane of C(1), C(13), C(7) and the two phenyl rings are 84.2 and 47.4° (DDT), and 85.4 and 73.6° (DDD), and between phenyl rings 64.9 (DDT) and 75.4° (DDD). The DDD results compare very well with those for an active insecticide 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)cyclopropane [4] at 81.4, 79.6, and 69.1° for one molecule, and 82.2, 79.5, and 66.1° for the other. Figure 2 is a packing diagram.

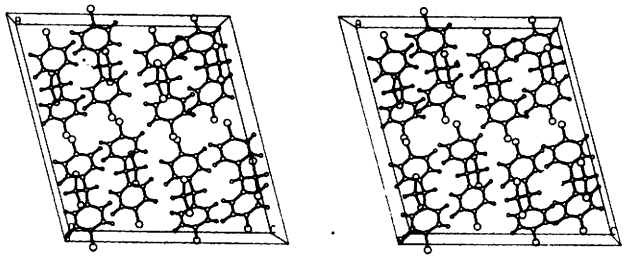

FIGURE 2 Stereoview of the packing of DDD in the unit cell, viewed perpendicular to *ac*

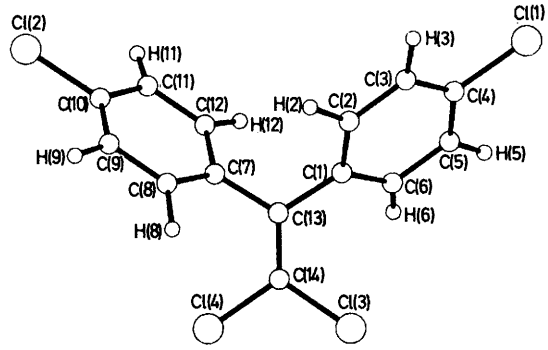

FIGURE 3 General view of DDE, showing the atom labelling system

It is difficult to find fully comparable reported toxicity data. However one such data set is relevant in this case, although it is only approximate. The 'Handbook of Toxicology' [5] refers to the lowest concentration in which certain compounds were found toxic to *anopheles quadrimaculatus* 4th instar. The relevant results were: *p,p'*-DDT 0.002 5, DDD 0.002 5, and DDE 1.0 p.p.m. In this same text, there are other references to the low toxicity of DDE. The ethylene group in DDE (Figure 3)

[1] Part 6, G. Smith, C. H. L. Kennard, and A. H. White, *Austral. J. Chem.*, 1976, **29**, 743.
[2] R. L. Metcalf, *J. Agric. Food. Chem.*, 1973, **21**, 511.
[3] T. P. DeLacy and C. H. L. Kennard, *J.C.S. Perkin II*, 1972, 2148.
[4] T. P. DeLacy and C. H. L. Kennard, *J.C.S. Perkin II*, 1972, 2141.
[5] W. O. Negherbon, 'Handbook of Toxicology,' vol. III, 'Insecticides, A Compendium,' Saunders, Philadelphia, 1959, p. 114.

TABLE 1

Molecular geometry of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDD)

(*a*) Bond distances (pm)

Cl(1)–C(4)	172.7(11)	Cl(2)–C(10)	173.7(12)
Cl(3)–C(14)	179.0(11)	Cl(4)–C(14)	179.1(11)
C(1)–C(2)	136.7(14)	C(7)–C(8)	138(2)
C(1)–C(6)	138(2)	C(7)–C(12)	139.8(14)
C(1)–C(13)	153(2)	C(7)–C(13)	153.4(15)
C(2)–C(3)	137(2)	C(8)–C(9)	136(2)
C(2)–H(2)	101(8)	C(8)–H(8)	96(6)
C(3)–C(4)	137(2)	C(9)–C(10)	139(2)
C(3)–H(3)	116(7)	C(9)–H(9)	86(7)
C(4)–C(5)	137.2(15)	C(10)–C(11)	136(2)
C(5)–C(6)	140(2)	C(11)–C(12)	137(2)
C(5)–H(5)	92(8)	C(11)–H(11)	94(7)
C(6)–H(6)	106(6)	C(12)–H(12)	90(7)
C(13)–H(13)	113(7)	C(14)–H(14)	98(7)
C(13)–C(14)	150.4(13)		

(*b*) Bond angles (°)

C(2)–C(1)–C(6)	118.2(9)	C(8)–C(7)–C(12)	118.6(9)
C(2)–C(1)–C(13)	120.3(9)	C(8)–C(7)–C(13)	118.4(8)
C(6)–C(1)–C(13)	121.5(8)	C(12)–C(7)–C(13)	122.9(9)
C(1)–C(2)–C(3)	122.1(9)	C(7)–C(8)–C(9)	121.3(8)
C(1)–C(2)–H(2)	109(4)	C(7)–C(8)–H(8)	119(5)
C(3)–C(2)–H(2)	129(4)	C(9)–C(8)–H(8)	120(5)
C(2)–C(3)–C(4)	119.1(8)	C(8)–C(9)–C(10)	118.4(11)
C(2)–C(3)–H(3)	122(4)	C(8)–C(9)–H(9)	115(5)
C(4)–C(3)–H(3)	118(4)	C(10)–C(9)–H(9)	126(5)
Cl(1)–C(4)–C(3)	120.6(7)	Cl(2)–C(10)–C(9)	116.7(10)
Cl(1)–C(4)–C(5)	118.6(8)	Cl(2)–C(10)–C(11)	120.9(8)
C(3)–C(4)–C(5)	120.9(9)	C(9)–C(10)–C(11)	122.4(10)
C(4)–C(5)–C(6)	118.9(9)	C(10)–C(11)–C(12)	118.2(8)
C(4)–C(5)–H(5)	118(5)	C(10)–C(11)–H(11)	111(15)
C(6)–C(5)–H(5)	123(5)	C(12)–C(11)–H(11)	131(15)
C(1)–C(6)–C(5)	120.9(8)	C(7)–C(12)–C(11)	121.2(9)
C(1)–C(6)–H(6)	125(4)	C(7)–C(12)–H(12)	127(5)
C(5)–C(6)–H(6)	113(4)	C(11)–C(12)–H(12)	112(5)
C(1)–C(13)–C(14)	111.5(8)	C(7)–C(13)–C(14)	113.5(8)
C(1)–C(13)–H(13)	108(4)	C(7)–C(13)–H(13)	115(4)
C(1)–C(13)–C(7)	109.3(8)	C(14)–C(13)–H(13)	100(4)
Cl(3)–C(14)–C(13)	110.0(6)	Cl(4)–C(14)–C(13)	110.8(7)
Cl(3)–C(14)–H(14)	107(5)	Cl(4)–C(14)–H(14)	101(5)
Cl(3)–C(14)–Cl(4)	108.6(5)	C(13)–C(14)–H(14)	119(5)

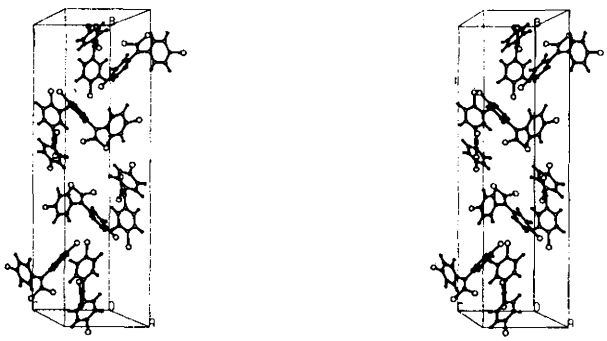

FIGURE 4 Stereoview of the packing of DDE in the unit cell, viewed perpendicular to *bc*

appears to shorten the chlorine–carbon distances on the terminal carbon atom (Table 2). This has been reported in other compounds.[6] Because of the double bond, the C(1)–C(13)–C(7) angle is close to 120°. Consequently the overall stereochemistry is vastly changed with the conformational angles between the plane of C(1), C(13), C(7) with both phenyl rings at 55.1°, and between phenyl groups at 82.1°. This compound could be inactive owing to low conformational angles or to the effect of the double bond on the planarity of part of the molecule. The packing scheme is drawn in Figure 4.

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

TABLE 2

Molecular geometry of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (DDE)

	Molecule (1)		Molecule (2)
(*a*) Bond distances (pm)			
Cl(1)–C(4)	175.3(8)	Cl(1)–C(4)	175.5(8)
Cl(2)–C(10)	176.0(7)	Cl(2)–C(10)	175.5(7)
Cl(3)–C(14)	173.9(6)	Cl(3)–C(14)	172.9(6)
Cl(4)–C(14)	174.1(8)	Cl(4)–C(14)	174.3(7)
C(1)–C(2)	139.3(9)	C(1)–C(2)	140.0(12)
C(1)–C(6)	138.6(10)	C(1)–C(6)	138.2(9)
C(1)–C(13)	149.2(11)	C(1)–C(13)	147.1(10)
C(2)–C(3)	139.8(11)	C(2)–C(3)	136.3(11)
C(2)–H(2)	106(4)	C(2)–H(2)	104(3)
C(3)–C(4)	137.4(11)	C(3)–C(4)	139.0(9)
C(3)–H(3)	108(4)	C(3)–H(3)	101(5)
C(4)–C(5)	137.2(10)	C(4)–C(5)	138.8(12)
C(5)–C(6)	140.3(11)	C(5)–C(6)	138.7(11)
C(5)–H(5)	104(4)	C(5)–H(5)	98(4)
C(6)–H(6)	89(4)	C(6)–H(6)	101(5)
C(7)–C(8)	138.6(12)	C(7)–C(8)	139.9(8)
C(7)–C(12)	139.2(10)	C(7)–C(12)	140.1(8)
C(7)–C(13)	148.7(9)	C(7)–C(13)	149.1(9)
C(8)–C(9)	139.6(10)	C(8)–C(9)	137.8(11)
C(8)–H(8)	114(4)	C(8)–H(8)	99(3)
C(9)–C(10)	135.7(11)	C(9)–C(10)	136.5(9)
C(9)–H(9)	93(5)	C(9)–H(9)	122(3)
C(10)–C(11)	137.2(13)	C(10)–C(11)	137.5(9)
C(11)–C(12)	138.5(10)	C(11)–C(12)	137.9(10)
C(11)–H(11)	99(4)	C(11)–H(11)	103(3)
C(12)–H(12)	98(5)	C(12)–H(12)	110(3)
C(13)–C(14)	132.0(10)	C(13)–C(14)	132.2(11)
(*b*) Bond angles (°)			
C(2)–C(1)–C(6)	118.8(6)	C(2)–C(1)–C(6)	119.2(6)
C(2)–C(1)–C(13)	118.5(6)	C(2)–C(1)–C(13)	119.0(5)
C(6)–C(1)–C(13)	122.7(6)	C(6)–C(1)–C(13)	121.7(6)
C(1)–C(2)–C(3)	121.3(6)	C(1)–C(2)–C(3)	121.4(6)
C(1)–C(2)–H(2)	123(3)	C(1)–C(2)–H(2)	120(3)
C(3)–C(2)–H(2)	116(3)	C(3)–C(2)–H(2)	119(3)
C(2)–C(3)–C(4)	117.6(6)	C(2)–C(3)–C(4)	118.5(7)
C(2)–C(3)–H(3)	124(3)	C(2)–C(3)–H(3)	127(2)
C(4)–C(3)–H(3)	118(3)	C(4)–C(3)–H(3)	114(2)
Cl(1)–C(4)–C(3)	118.6(5)	Cl(1)–C(4)–C(3)	118.6(6)
Cl(1)–C(4)–C(5)	118.1(5)	Cl(1)–C(4)–C(5)	119.8(5)
C(3)–C(4)–C(5)	123.4(6)	C(3)–C(4)–C(5)	121.6(6)
C(4)–C(5)–C(6)	118.0(6)	C(4)–C(5)–C(6)	118.7(6)
C(4)–C(5)–H(5)	127(3)	C(4)–C(5)–H(5)	112(3)
C(6)–C(5)–H(5)	115(3)	C(6)–C(5)–H(5)	129(3)
C(1)–C(6)–C(5)	120.9(6)	C(1)–C(6)–C(5)	120.5(6)
C(1)–C(6)–H(6)	129(3)	C(1)–C(6)–H(6)	127(2)
C(5)–C(6)–H(6)	110(3)	C(5)–C(6)–H(6)	112(2)
C(8)–C(7)–C(12)	119.7(6)	C(8)–C(7)–C(12)	118.0(5)
C(8)–C(7)–C(13)	121.1(6)	C(8)–C(7)–C(13)	122.5(5)
C(12)–C(7)–C(13)	119.1(6)	C(12)–C(7)–C(13)	119.4(5)
C(7)–C(8)–C(9)	119.4(6)	C(7)–C(8)–C(9)	121.9(5)
C(7)–C(8)–H(8)	118(2)	C(7)–C(8)–H(8)	113(2)
C(9)–C(8)–H(8)	122(2)	C(9)–C(8)–H(8)	125(2)
C(8)–C(9)–C(10)	119.2(7)	C(8)–C(9)–C(10)	117.5(5)
C(8)–C(9)–H(9)	117(2)	C(8)–C(9)–H(9)	122(2)
C(10)–C(9)–H(9)	123(2)	C(10)–C(9)–H(9)	121(2)
Cl(2)–C(10)–C(9)	119.5(6)	Cl(2)–C(10)–C(9)	119.7(5)
Cl(2)–C(10)–C(11)	117.5(5)	Cl(2)–C(10)–C(11)	116.9(4)
C(9)–C(10)–C(11)	122.9(6)	C(9)–C(10)–C(11)	123.4(6)
C(10)–C(11)–C(12)	117.9(6)	C(10)–C(11)–C(12)	118.6(5)
C(10)–C(11)–H(11)	119(3)	C(10)–C(11)–H(11)	122(2)
C(12)–C(11)–H(11)	123(3)	C(12)–C(11)–H(11)	118(2)
C(7)–C(12)–C(11)	120.7(7)	C(7)–C(12)–C(11)	120.6(5)
C(7)–C(12)–H(12)	117(2)	C(7)–C(12)–H(12)	112(2)
C(11)–C(12)–H(12)	123(2)	C(11)–C(12)–H(12)	127(2)
C(1)–C(13)–C(7)	116.6(6)	C(1)–C(13)–C(7)	117.7(6)
C(1)–C(13)–C(14)	121.1(6)	C(1)–C(13)–C(14)	123.1(6)
C(7)–C(13)–C(14)	122.3(6)	C(7)–C(13)–C(14)	119.1(6)
Cl(3)–C(14)–Cl(4)	110.7(3)	Cl(3)–C(14)–Cl(4)	109.9(3)
Cl(3)–C(14)–C(13)	125.5(5)	Cl(3)–C(14)–C(13)	126.1(5)
Cl(4)–C(14)–C(13)	123.8(5)	Cl(4)–C(14)–C(13)	124.0(5)

EXPERIMENTAL

(*a*) DDE : 1,1-*Dichloro*-2,2-*bis*-(p-*chlorophenyl*)*ethylene*.—*Crystal data*. $C_{14}H_8Cl_4$, $M = 318.1$. Monoclinic, $a = 921.9(1)$, $b = 3\,549.6(5)$; $c = 943.8(1)$ pm, $\beta = 114.70(1)°$, $U = 2.8059(11)$ nm^3, $D_m = 1.51(2)$ (by flotation), $Z = 8$, $D_c = 1.505$ g cm^{-3}, $F(000) = 1\,280$. Mo-K_α radiation, $\lambda = 71.07$ pm (graphite monochromator; μ(Mo-K_α) = 8.2 cm^{-1}. Space group, $P2_1/c$ (C_{2h}^5, No. 14).

TABLE 3

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

Atom	*x/a*	*y/b*	*z/c*
(*a*) Molecule (1)			
Cl(1)	−1 892(2)	3 547.9(5)	7 686(2)
Cl(2)	2 332(3)	2 587.9(5)	250(2)
Cl(3)	4 198(2)	4 383.2(5)	6 796(2)
Cl(4)	5 131(2)	4 149.6(5)	4 393(2)
C(1)	1 712(8)	3 734(2)	5 674(7)
C(2)	1 588(8)	3 385(2)	6 289(7)
C(3)	477(9)	3 323(2)	6 916(7)
C(4)	−495(8)	3 618(2)	6 898(7)
C(5)	−422(8)	3 967(2)	6 306(7)
C(6)	715(8)	4 024(2)	5 701(7)
C(7)	2 775(9)	3 485(2)	3 774(8)
C(8)	4 104(8)	3 275(2)	3 944(7)
C(9)	3 955(8)	2 992(2)	2 861(9)
C(10)	2 521(11)	2 937(2)	1 640(8)
C(11)	1 170(9)	3 132(2)	1 462(7)
C(12)	1 312(8)	3 413(2)	2 532(9)
C(13)	2 861(8)	3 775(2)	4 945(8)
C(14)	3 888(8)	4 057(2)	5 322(7)
H(2) *	222(5)	314(1)	619(4)
H(3)	31(5)	305(1)	738(4)
H(5)	−112(4)	419(1)	627(4)
H(6)	62(4)	425(1)	530(4)
H(8)	531(5)	337(1)	485(4)
H(9)	489(5)	288(1)	292(4)
H(11)	17(5)	308(1)	52(4)
H(12)	41(5)	357(1)	245(4)
(*b*) Molecule (2)			
Cl(1)	11 707(2)	5 060.4(5)	2 958(2)
Cl(2)	7 469(2)	2 430.4(5)	1 244(2)
Cl(3)	3 813(2)	4 654.7(5)	377(2)
Cl(4)	2 827(2)	3 890.1(5)	177(2)
C(1)	7 300(8)	4 335(2)	1 472(7)
C(2)	8 446(9)	4 271(2)	887(7)
C(3)	9 764(8)	4 494(2)	1 305(8)
C(4)	9 978(8)	4 783(2)	2 369(8)
C(5)	8 854(9)	4 858(2)	2 954(7)
C(6)	7 523(8)	4 627(2)	2 512(7)
C(7)	6 262(7)	3 664(2)	1 052(8)
C(8)	5 644(7)	3 442(2)	−296(7)
C(9)	5 992(8)	3 063(2)	−268(8)
C(10)	6 997(9)	2 912(2)	1 128(10)
C(11)	7 662(7)	3 116(2)	2 488(8)
C(12)	7 289(7)	3 493(2)	2 450(7)
C(13)	5 935(8)	4 076(2)	1 031(6)
C(14)	4 449(8)	4 191(2)	599(6)
H(2) *	826(4)	406(1)	6(4)
H(3)	1 062(4)	447(1)	92(4)
H(5)	924(4)	504(1)	378(4)
H(6)	688(5)	468(1)	313(4)
H(8)	494(5)	358(1)	−123(4)
H(9)	540(5)	286(1)	−144(4)
H(11)	822(4)	298(1)	356(4)
H(12)	775(4)	369(1)	343(4)

* B 4.4 Å^2 for all H atoms.

Crystals were obtained from chloroform–acetone. Intensity data were collected from one crystal by use of the Monash University's Philips PW 1100 four-circle X-ray diffractometer. The Philips data-collection system was used, 1 751 reflections having $F > 2.5\sigma(F)$ being considered observed out of 2 607 collected. No correction was applied for absorption.

(*b*) DDD : 1,1-*Dichloro*-2,2-*bis*-(p-*chlorophenyl*)*ethane*.—*Crystal data*. $C_{14}H_{10}Cl_4$, $M = 320.1$. Monoclinic, $a = 2\,011.4(3)$, $b = 769.2(1)$, $c = 1\,908.6(3)$, $\beta = 105.42(1)$, $U = 2.8466(11)$ nm^3, $D_m = 1.49(1)$ (by flotation), $Z = 8$, $D_c = 1.493$ g cm^{-3}, $F(000) = 1\,296$. Mo-K_α radiation. μ(Mo-K_α) = 8.0 cm^{-1}. Space group $C2/c$ (C_{2h}^6, No. 15).

Crystals were obtained from chloroform–acetone. Intensity data were collected from one crystal by use of the University of Canterbury's PDP 8 controlled Hilger and Watts four-circle X-ray diffractometer. The Hilger and Watts data collection scheme was used, 877 reflections having $F > 2.5\sigma(F)$ being considered observed out of 1 333 collected. No correction was applied for absorption.

Structure Determination.—Both structures were determined by symbolic addition with the FAME–MAGIC–LINK–SYMPL set of programs [7] with all non-hydrogen atoms being located from E maps. Full-matrix least-squares refinement reduced the residual R from an initial value of 0.19 to 0.049 for DDE, and from 0.28 to 0.068 for DDD. Difference-Fourier syntheses indicated the positions of the hydrogen atoms which were assigned isotropic temperature factors obtained from a Wilson plot. Final difference-Fourier syntheses revealed no unexplained electron density. Also plots of I_c/I_o *vs.* F_c gave no indication of any extinction effects.

Atomic parameters for both compounds are listed in Tables 3 and 4. Thermal parameters and observed and calculated structure amplitudes are available in Supplementary Publication No. SUP 21872 (13 pp., 1 microfiche).*

TABLE 4

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

Atom	*x/a*	*y/b*	*z/c*
Cl(1)	4 502(2)	8 403(4)	1 464(2)
Cl(2)	−327(2)	8 509(4)	1 149(2)
Cl(3)	2 766(2)	970(4)	1 075(2)
Cl(4)	1 289(2)	929(4)	920(2)
C(1)	2 717(5)	4 867(12)	1 429(7)
C(2)	3 205(6)	5 217(13)	2 063(6)
C(3)	3 755(5)	6 297(14)	2 088(6)
C(4)	3 825(5)	7 018(12)	1 457(7)
C(5)	3 358(6)	6 670(20)	804(6)
C(6)	2 798(5)	5 590(20)	797(6)
C(7)	1 452(5)	4 889(12)	1 328(7)
C(8)	1 282(6)	5 501(14)	1 938(5)
C(9)	737(7)	6 590(20)	1 882(7)
C(10)	364(5)	7 122(13)	1 193(9)
C(11)	510(6)	6 540(20)	575(6)
C(12)	1 057(6)	5 430(20)	645(5)
C(13)	2 093(6)	3 733(12)	1 433(5)
C(14)	2 004(5)	2 282(12)	887(5)
H(2) *	311(4)	448(10)	247(4)
H(3)	410(4)	683(10)	263(4)
H(5)	346(4)	705(10)	39(4)
H(6)	243(4)	555(10)	29(4)
H(8)	155(4)	512(10)	241(4)
H(9)	67(4)	693(10)	229(4)
H(11)	19(4)	698(10)	16(4)
H(12)	111(4)	510(10)	21(4)
H(13)	223(4)	296(10)	195(4)
H(14)	188(4)	257(10)	37(4)

* B 4.8 Å^2 for all H atoms.

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

[7] R. Dewar and A. Stone, FAME–MAGIC–LINK–SYMPL (symbolic addition) set of programmes, modified by K. G. Shields for CYBER 76, 1973.

Scattering factors for chlorine and carbon were taken from ref. 8 and for hydrogen from ref. 9. No correction was applied for anomalous dispersion.

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[8] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968, p. 202.

[9] R. F. Stewart, E. R. Davidson. and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.