Table 4. *Intermolecular distances*

Predominant–predominant

	Symmetry position	
H(2)···H(10)	$x-1, y-1, z$	2·48 Å
H(1)···H(9)	$y, x-1, -z$	2·65
H(1)···H(5)	$\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{4}+z$	2·64
C(4)···H(6)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$	2·87
C(5)···H(6)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	2·91
C(6)···H(5)	$1+y, x, -z$	2·90

Predominant–alternate

	Symmetry position	
H(3)···H(10)	$x-1, y-1, z$	2·46 Å
H(7)···H(9)	$y, x, -1-z$	2·49
H(8)···H(1)	$\frac{1}{2}-y, \frac{1}{2}+x, z-1$	2·60
H(4)···H(5)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$	2·52
C(4)···H(3)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	2·83
C(5)···H(3)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	2·84
C(6)···H(7)	$1+y, x, -z$	2·68
C(6)···H(3)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	3·01
C(*p*)···C(4)	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{4}-z$	3·61
C(*p*)···C(5)	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{4}-z$	3·52
C(*p*)···C(6)	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{4}-z$	3·75

from 180° than the other [166·7 for C(3)–C(4)–C(5) compared to 174·8° for C(2)–C(3)–C(4)]. This is surprising in that by moving C(3) further from the twofold axis these two angles would become more similar and C(1)–C(2)–C(3) would increase towards 109·5°, the tetrahedral angle. We have no explanation for this feature of the structure.

Table 4 shows important intermolecular contacts, with those dependent on the conformation grouped together. The alternate–alternate distances are not reported as there are no unusually short distances, other than those between alternate positions and positions unchanged by the conformation, *i.e.* not involved in the disorder. These positions are reported for the predominant–predominant case. An examination of these contacts shows only one disruptive feature associated with the disorder: the C(6)–H(7) contact of 2·68 Å which is considerably less than the van der Waals contact sum of 2·90 Å. This is presumably the major contributor to the preference for a C(*p*)–C(*p*′) bond approximately perpendicular to the fourfold screw axis.

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Insecticides. I. The Crystal Structure and Absolute Configuration of (−)-1-(*o*-Chlorophenyl)-1-(*p*-chlorophenyl)-2,2,2-trichloroethane, (−)-*o*,*p*′-DDT

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(−)-1-(*o*-Chlorophenyl)-1-(*p*-chlorophenyl)-2,2,2-trichloroethane or (−)-*o*,*p*′-DDT, $C_{14}H_9Cl_5$, is orthorhombic, $P2_12_12_1$, $a = 11{\cdot}419$ (2), $b = 17{\cdot}635$ (3), $c = 7{\cdot}501$ (1) Å, $Z = 4$, $\rho_o = 1{\cdot}53$, $\rho_c = 1{\cdot}54$ g cm^{-3}. The structure was solved by direct methods and refined to $R = 5{\cdot}6\%$ for 942 counter reflexions. The more oestrogenically active (−) isomer is shown to be the *R* form.

Introduction

The crystal structure of racemic (±)-*o*,*p*′-DDT was reported by Delacy & Kennard (1972); it crystallizes in the triclinic class with two independent molecules per asymmetric unit and the molecular structures of these two independent molecules are very similar, suggesting a dominance of intramolecular forces. Recently McBlain & Wolfe (1975) and McBlain, Currie & Wolfe (1976) have reported a method of resolving the isomers.

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McBlain, Lewin & Wolfe (1976) have shown that the (−) isomer is a far more potent oestrogen than the (+) isomer. On the basis of similarities in shapes of the *R* form (Cahn, Ingold & Prelog, 1956) and the natural oestrogen (+)-17*β*-oestradiol, McBlain (1976) tentatively suggested that (−)-*o,p*-DDT is the *R* form. The crystal structure of (−)-*o,p'*-DDT was undertaken to confirm this assignment.

Experimental

Large crystals of the compound were kindly supplied by Drs McBlain and Wolfe. After preliminary photographic work a fresh crystal was ground to an approximate sphere of radius 0·043 mm and mounted in a random orientation on a Picker-FACS1 diffractometer. 12 reflexions were carefully centred in 2θ (Cu $K\alpha_1$ radiation, no monochromator) and cell constants, as in the abstract, obtained. Two equivalent octants of data within the range $0 \leq 2\theta \leq 127°$ were collected in the coupled $\omega/2\theta$ scan mode (Cu $K\alpha$ radiation, graphite 002 monochromator). The two octants of data were merged and reduced to $|F|$ and σF (Doedens & Ibers, 1967); of the 1432 independent reflexions 942 satisfied the criterion $I \geq 3\sigma I$ and were used in subsequent calculations. No absorption correction was applied (μr, Cu $K\alpha$ radiation = 0·37).

Solution and refinement

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The structure was initially refined without anomalous dispersion corrections and with anisotropic temperature factors for the Cl and iso-

Table 1. *Bond distances* (Å) *and their standard deviations*

Cl(1)–C(1)	1·773 (9)	C(4)–C(5)	1·38 (1)
Cl(2)–C(1)	1·780 (9)	C(6)–C(5)	1·37 (1)
Cl(3)–C(1)	1·792 (9)	C(6)–C(7)	1·34 (1)
Cl(4)–C(4)	1·740 (9)	C(8)–C(7)	1·40 (1)
Cl(5)–C(12)	1·730 (9)	C(10)–C(9)	1·40 (1)
C(1)–C(2)	1·52 (1)	C(14)–C(9)	1·40 (1)
C(3)–C(2)	1·52 (1)	C(10)–C(11)	1·38 (1)
C(9)–C(2)	1·52 (1)	C(12)–C(11)	1·38 (1)
C(4)–C(3)	1·38 (1)	C(12)–C(13)	1·39 (1)
C(8)–C(3)	1·41 (1)	C(14)–C(13)	1·36 (1)

Table 2. *Bond angles* (°), *all standard deviations* ~ 0·75°

Cl(1)–C(1)–Cl(2)	106·5	Cl(4)–C(4)–C(3)	119·9	C(10)–C(9)–C(14)	118·0
Cl(1)–C(1)–Cl(3)	106·9	C(2)–C(3)–C(4)	120·1	C(9)–C(14)–C(13)	120·8
Cl(2)–C(1)–Cl(3)	108·2	C(2)–C(3)–C(8)	123·9	C(14)–C(13)–C(12)	120·4
Cl(1)–C(1)–C(2)	109·2	C(4)–C(3)–C(8)	115·9	C(13)–C(12)–C(11)	119·8
Cl(2)–C(1)–C(2)	114·2	C(3)–C(8)–C(7)	120·3	C(12)–C(11)–C(10)	119·7
Cl(3)–C(1)–C(2)	110·9	C(8)–C(7)–C(6)	120·8	C(11)–C(10)–C(9)	121·1
C(9)–C(2)–C(3)	112·3	C(7)–C(6)–C(5)	121·0	Cl(5)–C(12)–C(11)	120·8
C(9)–C(2)–C(1)	113·5	C(6)–C(5)–C(4)	118·2	C(2)–C(9)–C(10)	122·1
C(3)–C(2)–C(1)	116·3	C(5)–C(4)–C(3)	123·7	C(2)–C(9)–C(14)	119·8
Cl(4)–C(4)–C(5)	116·4	Cl(5)–C(12)–C(13)	119·4		

Table 3. *Atomic coordinates* (× 10^4; *for* H × 10^3) *and thermal parameters* (× 10^3) *with their standard deviations*

Anisotropic *U*'s are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$; isotropic *U*'s are in the form $\exp[-2\pi^2U(1/d^2_{hkl})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	−265 (2)	−3005 (2)	2611 (4)	60 (2)	91 (2)	57 (2)	35 (1)	5 (1)	−1 (2)
Cl(2)	1724 (3)	−2867 (1)	4874 (3)	93 (2)	69 (2)	36 (1)	7 (2)	−11 (1)	−12 (1)
Cl(3)	338 (2)	−1544 (2)	4004 (4)	71 (2)	75 (2)	57 (2)	−3 (1)	7 (1)	12 (1)
Cl(4)	1949 (2)	−1347 (1)	−1916 (3)	59 (1)	68 (2)	39 (1)	−7 (1)	0 (1)	−10 (1)
Cl(5)	3820 (3)	−5069 (1)	−1707 (4)	86 (2)	56 (2)	107 (2)	−14 (1)	−7 (2)	21 (2)

	x	y	z	U		x	y	z	U
C(1)	936 (8)	−2408 (5)	3130 (10)	48 (3)	C(13)	2131 (1)	−4006 (6)	−1370 (10)	54 (3)
C(2)	1655 (8)	−2257 (5)	1460 (10)	41 (2)	C(14)	1647 (8)	−3367 (5)	−660 (10)	45 (2)
C(3)	2505 (8)	−1593 (5)	1550 (10)	40 (2)	H(2)	122	−209	86	63
C(4)	2688 (7)	−1147 (5)	60 (10)	40 (2)	H(5)	385	−24	−97	63
C(5)	3467 (8)	−548 (5)	10 (10)	50 (3)	H(6)	472	3	152	63
C(6)	4100 (9)	−391 (6)	1510 (10)	63 (3)	H(7)	444	−68	409	63
C(7)	3967 (9)	−805 (6)	3000 (10)	64 (3)	H(8)	309	−174	413	63
C(8)	3187 (9)	−1415 (6)	3050 (10)	56 (3)	H(10)	370	−292	218	63
C(9)	2217 (7)	−2964 (5)	690 (10)	36 (2)	H(11)	459	−409	99	63
C(10)	3311 (8)	−3223 (5)	1250 (10)	46 (2)	H(13)	174	−432	−232	63
C(11)	3794 (8)	−3875 (5)	560 (10)	48 (2)	H(14)	88	−317	−110	63
C(12)	3221 (9)	−4259 (5)	−780 (10)	51 (2)					

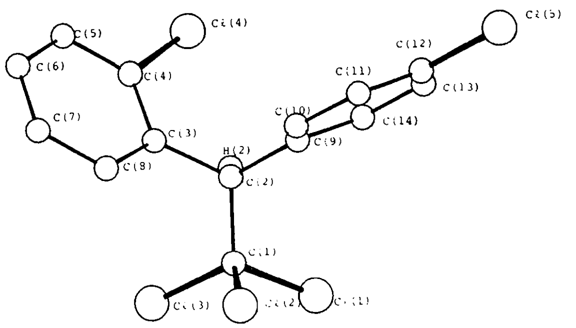

Fig. 1. A schematic view of the (–)-*o,p'*-DDT molecule seen from the side remote from the hydrogen attached to the asymmetric carbon atom and showing the molecule to be the *R* form.

tropic factors for the C atoms. Scattering factors for neutral atoms were taken from Cromer & Mann (1968). When refinement ceased, the H atoms were placed at the calculated positions with C–H = 1·0 Å. Anomalous dispersion corrections were then applied and both enantiomorphs refined to their limit for the heavy atoms; H atom parameters were used only in structure factor calculations. The *R* form refined to unweighted and weighted *R* values of 5·6 and 5·8% respectively; the equivalent values for the *S* form were 6·4 and 6·6%. The assignment of the *R* form to (–)-*o,p'*-DDT can therefore be justified by Hamilton's (1965) test.

Discussion

A schematic view of the molecule seen from the side remote from the H attached to the asymmetric C atom is given in Fig. 1. All bond distances and angles are as expected and are given in Tables 1 and 2 respectively. Atomic parameters are given in Table 3.* Given normal geometry for molecules of the study compound all gross differences in molecular structure must result from rotations of the functional groups about bonds to the asymmetric C atom. The molecular structure of (–)-*o,p'*-DDT is available in three different crystallographic environments, one from this work and two from Delacy & Kennard (1972). Comparison of these three molecular structures shows a remarkable constancy of the angular orientation of the functional groups. These orientations may conveniently be expressed as follows. (i) Angle *A*, the angle between the plane defined by the C atoms of the *p*-chlorophenyl group and that defined by the three Cl atoms of the trichloro group. (2) Angle *B*, the angle between the plane defined by the C atoms of the *o*-chlorophenyl group and that defined by the three Cl atoms of the trichloro group. (3) Angle *C*, the angle H(2)–C(2)–Cl(2) as seen in projection down C(2)–C(1). Angles *A*, *B* and *C* are given in degrees for each of the three molecules in Table 4.

The similarity of these angles in all three molecules indicates a dominance of intramolecular forces and suggests that free molecules of (–)-*o,p'*-DDT will show a similar shape to those in Table 4. The similarity in shape and size of the *R* form of *o,p*-DDT, shown by this work to be the correct form of the (–) isomer as proposed by McBlain (1976), and that of (+)-17*β*-oestradiol might well indicate that the difference in oestrogenic potency of the (+) and (–) forms results from the inability of one enantiomeric form to meet the steric requirements of an inherently dissymmetric enzyme or receptor site (Ariens & Simonis, 1964) rather than the differences in chemical properties of the diastereomers formed by the coupling of the enantiomers with the active sites as noted by Alworth (1972).

Table 4. *Values for angles A, B and C for three different molecular environments* (°)

	A	*B*	*C*
This work	24·2	56·0	3·1
Delacy & Kennard (1)	24·9	56·4	7·2
Delacy & Kennard (2)	25·2	66·1	11·1

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32217 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.