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Symmetrically Substituted Ethylenes: Structures of (I) 1,1-Dichloro-2,2-bis(*p*-methoxyphenyl)ethylene, $C_{16}H_{14}Cl_2O_2$, and (II) 1,1-Bis(*p*-ethoxyphenyl)ethylene, $C_{18}H_{20}O_2$

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Abstract. (I): $M_r = 309·19$, monoclinic, $C2/c$, $a = 18·290\,(4)$, $b = 7·964\,(1)$, $c = 11·103\,(2)$ Å, $\beta = 115·76\,(2)°$, $V = 1456·6\,(5)$ Å^3, $Z = 4$, $D_m = 1·392$, $D_x = 1·410$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·4451$ mm^{-1}, $F(000) = 640$, $T = 297$ K, final $R = 0·042$ for 1290 observed reflections. (II): $M_r = 268·36$, orthorhombic, $Pbcn$, $a = 7·714\,(13)$, $b = 6·656\,(15)$, $c = 29·682\,(4)$ Å, $V = 1524\,(4)$ Å^3, $Z = 4$, $D_m = 1·18$, $D_x = 1·17$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·5971$ mm^{-1}, $F(000) = 576$, $T = 297$ K, final $R = 0·044$ for 867 observed reflections. Both structures retain their diad symmetry in the lattice and are held together by van der Waals forces. In (I) the C—Cl distance is 1·728 (2) Å. The C—C ethylene distance is 1·326 (4) and 1·342 (3) Å in (I) and (II) respectively. The twist about the ethylene bond is 9·7 (1)° for (I) and 0·9 (7)° for (II).

Introduction. The crystal structure analysis of the two symmetrically substituted ethylenes (I) and (II) was undertaken to study their stereochemistry, the effects of substitution on the ethylenic bond and the twist about this bond.

Compound (I) is a structural analogue of 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE) (Shields, Kennard & Robinson, 1977), a primary degradation product of DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethanol] (Delacy & Kennard, 1972*a*). The stereochemistries of the present compounds are compared with those of a number of DDT-type insecticides.

Experimental. (I): needles from alcohol, crystal 0·25 × 0·18 × 0·18 mm, graphite-monochromatized Mo $K\alpha$, 2102 unique reflections ($0 \le h \le 24$, $0 \le k \le 11$, $-15 \le l \le 15$, $2 \le \theta \le 32°$), 1290 with $I \ge 3\sigma(I)$, intensity variation <2%, Patterson heavy-atom method, $R = 0·042$, $R_w = 0·053$, $w = 1/\sigma^2(|F_o|)$, $S = 1·35$, $(\Delta/\sigma)_{max} < 0·01$, peak heights from $-0·23$ to $0·28$ e Å^{-3} in final ΔF synthesis.

(II): plates from cyclohexane, crystal 0·45 × 0·20 × 0·12 mm, graphite-monochromatized Cu $K\alpha$, 1383 unique reflections ($0 \le h \le 33$, $0 \le k \le 8$, $0 \le l \le 7$, $2 \le \theta \le 60°$), 867 with $I \ge 3\sigma(I)$, intensity variation <2%, direct methods (*MULTAN*78: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), $R = 0·044$, $R_w = 0·055$, $w = 1/\sigma^2(|F_o|)$, $S = 1·62$, $(\Delta/\sigma)_{max} < 0·05$, peak heights from $-0·21$ to $0·26$ e Å^{-3} in final ΔF synthesis.

For both (I) and (II) symmetry information was derived from oscillation and Weissenberg photographs [systematic absences: (I) hkl: $h + k$ odd, $h0l$: l odd; (II) $0kl$: k odd, $h0l$: l odd, $hk0$: $h + k$ odd]; density by flotation in benzene–bromoform mixture; intensity data collected on Enraf–Nonius CAD-4 diffractometer; 3 orientation-control reflections monitored every 50 reflections and 3 intensity-control reflections monitored every hour of X-ray exposure; data corrected for variation in intensity and for Lp; no correction for absorption; accurate cell parameters from 25 selected reflections [(I): $13 \le \theta \le 16°$, (II): $18 \le \theta \le 22°$]; both structures refined by full-matrix anisotropic least squares based on F (*ORFLS*: Busing, Martin & Levy, 1962); H (from ΔF syntheses) isotropic; scattering factors for non-H atoms from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections for all non-H atoms from *International Tables for X-ray Crystallography* (1974).

Discussion. A common feature of the two crystal structures is that in both cases the molecular diad axes coincide with crystallographic diad axes.

The positional coordinates of the atoms constituting the asymmetric units together with their isotropic temperature factors are listed in Table 1.* Bond distances, bond angles and some selected torsion angles involving the non-hydrogen atoms are given in Table 2. The numbering schemes of the molecules (I) and (II) are shown in Fig. 1.

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* Lists of structure factors, anisotropic thermal parameters, distances and angles involving H atoms and least-squares-planes' data for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39791 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and thermal parameters* (Å^2) *with e.s.d.'s in parentheses for* (I) *and* (II)

Equivalent isotropic temperature factors, B_{eq} (Hamilton, 1959), are given for non-H atoms and isotropic temperature factors, B, for H atoms.

	x	y	z	B_{eq}/B
Compound (I)				
Cl	0·43855 (4)	0·09098 (8)	0·11650 (6)	4·9
O	0·73124 (8)	0·7394 (2)	0·6900 (1)	4·1
C(1)	0·5000	0·2150 (4)	0·2500	3·2
C(2)	0·5000	0·3815 (4)	0·2500	2·9
C(3)	0·5637 (1)	0·4787 (3)	0·3612 (2)	2·8
C(4)	0·5414 (1)	0·6113 (3)	0·4208 (2)	3·1
C(5)	0·5991 (1)	0·6960 (3)	0·5294 (2)	3·3
C(6)	0·6800 (1)	0·6514 (3)	0·5801 (2)	3·1
C(7)	0·7039 (1)	0·5262 (3)	0·5181 (2)	3·5
C(8)	0·6456 (1)	0·4414 (3)	0·4097 (2)	3·3
C(9)	0·8142 (1)	0·6877 (3)	0·7541 (2)	4·8
H(4)	0·487 (1)	0·638 (2)	0·393 (2)	2·7 (4)
H(5)	0·583 (1)	0·778 (3)	0·568 (2)	4·0 (5)
H(7)	0·756 (1)	0·498 (3)	0·547 (2)	3·4 (4)
H(8)	0·662 (1)	0·364 (2)	0·371 (2)	3·2 (4)
H(91)	0·837 (1)	0·752 (3)	0·825 (2)	5·8 (7)
H(92)	0·839 (1)	0·070 (3)	0·693 (3)	5·8 (6)
H(93)	0·816 (1)	0·567 (3)	0·782 (2)	5·4 (6)
Compound (II)				
O	−0·0049 (2)	0·0059 (2)	0·41713 (4)	6·5
C(1)	0·0000	0·6154 (4)	0·2500	6·5
C(2)	0·0000	0·4138 (3)	0·2500	4·8
C(3)	−0·0053 (2)	0·3013 (2)	0·29321 (6)	4·6
C(4)	0·0886 (2)	0·1245 (3)	0·29874 (5)	4·7
C(5)	0·0943 (2)	0·0233 (2)	0·33950 (5)	4·8
C(6)	0·0019 (2)	0·0967 (3)	0·37582 (6)	5·0
C(7)	−0·0941 (2)	0·2726 (3)	0·37095 (6)	5·6
C(8)	−0·0966 (2)	0·3706 (3)	0·33049 (6)	5·4
C(9)	0·0818 (3)	−0·1833 (3)	0·42217 (7)	7·4
C(10)	0·0401 (5)	−0·2634 (5)	0·46735 (9)	11·4
H(1)	0·002 (2)	0·692 (3)	0·2194 (5)	7·8 (5)
H(4)	0·152 (2)	0·071 (2)	0·2729 (5)	5·4 (4)
H(5)	0·163 (2)	−0·098 (2)	0·3425 (5)	4·7 (3)
H(7)	−0·161 (2)	0·319 (3)	0·3972 (6)	6·8 (4)
H(8)	−0·160 (2)	0·480 (2)	0·3268 (5)	5·2 (4)
H(91)	0·039 (3)	−0·264 (4)	0·3965 (7)	9·5 (6)
H(92)	0·214 (3)	−0·154 (3)	0·4190 (5)	8·9 (5)
H(101)	−0·092 (4)	−0·280 (5)	0·4641 (11)	17·6 (11)
H(102)	0·063 (4)	−0·182 (5)	0·4927 (10)	15·7 (10)
H(103)	0·101 (4)	−0·395 (5)	0·4723 (8)	13·5 (8)

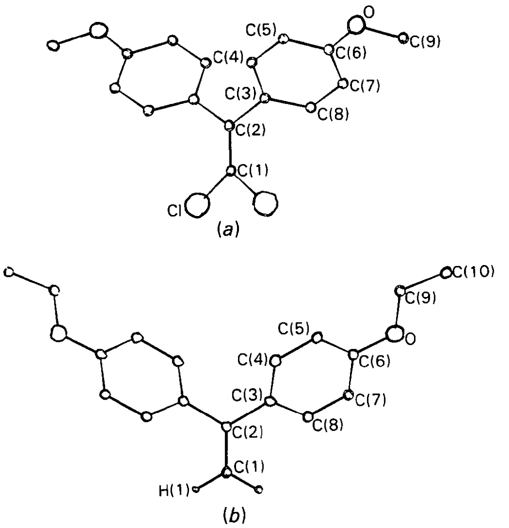


Fig. 1. Perspective views of (*a*) 1,1-dichloro-2,2-bis(*p*-methoxyphenyl)ethylene and (*b*) 1,1-bis(*p*-ethoxyphenyl)ethylene showing the numbering schemes. Atoms related by diad axes have been indicated by primes in the text.

Table 2. *Bond lengths* (Å) *and angles* (°), *and some selected torsion angles* (°)

	(I)	(II)
Cl—C(1)	1·728 (2)	
C(1)—C(2)	1·326 (4)	1·342 (3)
C(2)—C(3)	1·494 (3)	1·486 (2)
C(3)—C(4)	1·398 (3)	1·392 (2)
C(4)—C(5)	1·384 (3)	1·385 (2)
C(5)—C(6)	1·382 (2)	1·382 (2)
C(6)—O	1·365 (2)	1·368 (2)
O—C(9)	1·428 (2)	1·433 (3)
C(6)—C(7)	1·386 (3)	1·393 (3)
C(7)—C(8)	1·388 (3)	1·367 (3)
C(8)—C(3)	1·386 (2)	1·390 (2)
C(9)—C(10)		1·479 (4)
C(1)—H(1)		1·04 (2)
Cl—C(1)—C(2)	124·8 (2)	
Cl'—C(1)—Cl	110·3 (2)	
C(1)—C(2)—C(3)	121·2 (2)	120·3 (1)
C(3)—C(2)—C(3')	117·5 (2)	119·5 (1)
C(2)—C(3)—C(4)	120·0 (2)	120·9 (1)
C(2)—C(3)—C(8)	122·2 (2)	122·3 (1)
C(4)—C(3)—C(8)	117·8 (2)	116·8 (1)
C(3)—C(4)—C(5)	120·8 (2)	122·1 (2)
C(4)—C(5)—C(6)	120·4 (2)	119·5 (1)
C(5)—C(6)—C(7)	119·7 (2)	119·4 (2)
C(5)—C(6)—O	115·5 (2)	124·3 (2)
C(7)—C(6)—O	124·8 (2)	116·4 (2)
C(6)—C(7)—C(8)	119·4 (2)	120·0 (2)
C(7)—C(8)—C(3)	121·7 (2)	122·3 (2)
C(6)—O—C(9)	117·7 (2)	117·6 (1)
O—C(9)—C(10)		108·1 (2)
H(1)—C(1)—H(1')		121·4 (13)
C(9)—O—C(6)—C(5)	174·1 (2)	−3·6 (2)
C(9)—O—C(6)—C(7)	−6·7 (3)	175·4 (2)
C(10)—C(9)—O—C(6)		−173·5 (2)

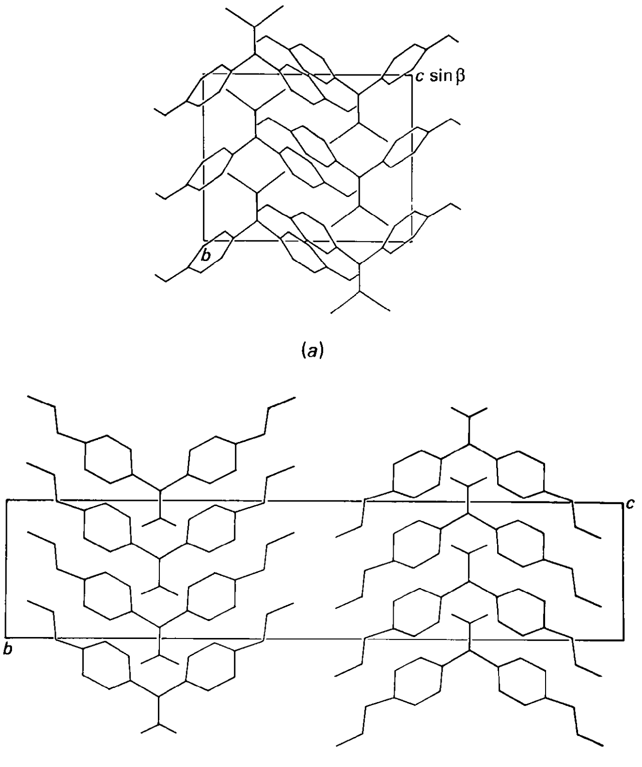
The C—C bond distances in the aromatic rings of the two compounds agree with each other and with other similar structures (Shields *et al.*, 1977; Delacy & Kennard, 1972*a*,*b*; Norrestam, Hovmöller, Palm, Göthe & Wachtmeister, 1977). The C—Cl distance in (I) is shortened as observed in the structure of DDE (Shields *et al.*, 1977). Similar shortening has also been observed in the *cis* and *trans* isomers of tetrachlorostilbene (Norrestam *et al.*, 1977). This shortening is due to the conjugation of an unshared pair of electrons on the Cl with the double bond (Pauling, 1960).

The C—C ethylene bond distances in the present structures [1·326 (4) in (I) and 1·342 (3) Å in (II)] are slightly longer than the reported value of 1·314 (6) Å in unsubstituted ethylene (van Nes & Vos, 1977). In the case of polarized ethylenes an appreciable lengthening of this bond has been reported (Adhikesavalu & Venkatesan, 1981, 1982, 1983; Hazell & Mukhopadhyay, 1980). The H(1)—C(1)—H(1') angle [121 (1)°] in compound (II) is larger than in unsubstituted ethylene [116·8 (7)°] (van Nes & Vos, 1977). The narrowing of the Cl—C(1)—Cl' angle in compound (I) may be attributed to lone-pair–bond-pair interaction. An angular dissymmetry, as observed in the case of anisoles (Domiano, Nardelli, Balsamo, Macchia & Macchia, 1979), has been observed in the exocyclic angles at C(6) in both compounds.

The twists about the ethylenic bonds, as measured by the angles between the planes through Cl, C(1), Cl' and C(3), C(2), C(3') in (I) and H(1), C(1), H(1') and C(3), C(2), C(3′) in (II), are 9·7 (1) and 0·9 (7)°, respectively. This twist angle in DDE, computed from the published data of Shields *et al.* (1977), is found to be 6·3 (4)° in molecule (1) and 4·2 (3)° in molecule (2). For polarized ethylenes, however, the twist angles are 38·3 (4), 20·2 (3) and 31·5 (6)°, and 21·7 and 29·3° (Adhikesavalu & Venkatesan, 1981, 1982, 1983).

Table 3. *Conformational angles* (°)

	φ_1	φ_2	δ
1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)-ethane (DDT) (Delacy & Kennard, 1972*a*)	84·3 (8)	47·2 (10)	64·3 (4)
1,1-Dichloro-2,2-bis(*p*-chlorophenyl)-ethylene (DDE) (Shields *et al.*, 1977)	Molecule (1) 51·4 (4) Molecule (2) 78·7 (4)	 54·5 (5) 45·4 (4)	 81·6 (2) 80·2 (2)
1,1-Dichloro-2,2-bis(*p*-chlorophenyl)-ethane (DDD) (Shields *et al.*, 1977)	85·4 (8)	74·3 (8)	75·5 (3)
1,1-Dichloro-2,2-bis(*p*-chlorophenyl)-cyclopropane (Delacy & Kennard, 1972*b*)	Molecule (1) 81·4 (6) Molecule (2) 82·2 (7)	 79·9 (7) 79·5 (7)	 69·1 (3) 66·2 (3)
Compound (I)	47·8 (1)		82·9 (1)
Compound (II)	36·4 (1)		115·0 (1)



(*a*)

(*b*)

Fig. 2. Molecular packing of (*a*) 1,1-dichloro-2,2-bis(*p*-methoxyphenyl)ethylene and (*b*) 1,1-bis(*p*-ethoxyphenyl)ethylene.

The 'butterfly' configuration of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) (Delacy & Kennard, 1972*a*) has been observed in both compounds. In molecule (I) the phenyl ring and the ethylene group deviate significantly [$\sum(\Delta/\sigma)^2 = 303{\cdot}4$ and 15047, respectively] from planarity; the conformation of the ring is approximately 'boat' with a pseudo mirror along C(3)···C(6). The conformational angles, as defined by Shields *et al.* (1977), for compounds (I) and (II) together with those of a number of DDT-type insecticides, as calculated from the published coordinates, are listed in Table 3, where φ_1 and φ_2 are the dihedral angles between the planes of C(2), C(3), C(3′) and the first and second phenyl ring, respectively, and δ is the dihedral angle between the two phenyl rings.

Projection views of the two crystal structures are shown in Fig. 2. The structures are stabilized by van der Waals forces with no significant intermolecular short contacts.

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