

The central ring is in a boat conformation as shown in Fig. 2 and also by the torsion angles (Table 2) and the puckering parameters (Cremer & Pople, 1975) $q_2 = 0.489$ (3), $q_3 = -0.083$ (3), $Q = 0.496$ (3) Å, $\varphi_2 = 116.9$ (3) and $\theta = 99.7$ (3)°. In the ideal boat conformation, these parameters are $q_2 = Q$, $q_3 = 0$ Å, $\varphi_2 = 120$ and $\theta = 90$ °. The tricyclic ring is folded along the line S(5)···N(10). The folding angle of 149.1 (1)° in (III) has a value comparable to those of 155.2 and 157.1° found in the two independent molecules of 10-(4-methoxyphenyl)pyrido[3,2-*b*][1,4]benzothiazine, (IV) (de Meester, Chu, Jovanovic & Biehl, 1985), and those of 150.7 (5) and 162.6 (5)° observed in the two independent molecules of (II) (Klein *et al.*, 1985), but is considerably larger than those found in (I) (120.8 and 124.4° for the two independent molecules). The smaller folding angles in (I) are apparently due to the different orientation of the 10-phenyl substituent with respect to the tricyclic ring system.

The 10-phenyl substituent is in an equatorial position with respect to the central ring as shown in Fig. 2. The orientation of the phenyl ring relative to the plane formed by the three atoms S(5), N(10) and C(1') (bisecting the tricyclic ring) is given by the angle of 19.1 (9)° between these two planes, a value similar to those found in many 10-phenyl-substituted phenothiazines (where these two planes are approximately parallel). However, the values of 80.5 and 79.3° were found in the two independent molecules of (I) where the 4-nitrophenyl group is approximately perpendicular to the plane bisecting the tricyclic ring. The perpendicular conformation in (I) indicates that there is an electronic interaction between the two ring systems since the 4-nitrophenyl is an electron-withdrawing substituent as evidenced by the short N(10)—C(1') distance. The electronic interaction between the two ring systems cannot take place when the 10-aryl is an electron-

releasing substituent as in (IV) or is an electron-neutral substituent as in (II). In the case of the title compound, (III), the 4-nitrophenyl is an electron-withdrawing substituent; however, the electronic interaction cannot take place when there is also an electron-withdrawing group in the tricyclic ring system [the replacement of CH in (I) by N in (III)]. The conformation of the 4-nitrophenyl substituent in (III) has been studied by ¹³C NMR spectroscopy. The conformation deduced in solution agrees with that observed in the solid state.

The packing of the molecules of (III) in the cell is shown in Fig. 3. There is no intermolecular distance shorter than the van der Waals separations. The shortest intermolecular contact is C(3)···O(41') of 3.374 (4) Å.

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Structural Chirality of the Insecticide (–)-2,2-Dichloro-1-(4-ethoxyphenyl)-1-cyclopropanecarboxylic Acid

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Abstract. C₁₂H₁₂Cl₂O₃, $M_r = 275.131$, orthorhombic, $P2_12_12_1$, $a = 6.594$ (1), $b = 8.167$ (2), $c = 23.443$ (4) Å, $V = 1262$ (2) Å³, $Z = 4$, $D_m = 1.443$, $D_x = 1.448$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu =$

44.3 cm⁻¹, $F(000) = 568$, room temperature. Final $R = 0.039$ for all 2452 intensities. There are no unusual bond lengths or angles in the molecule. The configuration of the biologically active isomer is *S*. The

motif adopted by the carboxylic groups results in infinite chains of moderate-strength hydrogen bonds parallel to the *x* axis of the unit cell and around the twofold screw axis; O...O 2.67 Å, O—H...O 153°.

Introduction. The X-ray structure analysis of the title compound reported here was undertaken as part of an extensive investigation into biologically active substances which combine structural features common to both DDT and pyrethroid insecticides (Holan, O'Keefe, Virgona & Walser, 1978). The title compound is the more biologically active isomer of the two possible forms and the primary objective of the present study was to establish its absolute configuration.

Experimental. Crystal: clear acicular crystals {m.p. 444 K, $[\alpha]_D^{20.0^\circ} = -99.6^\circ$ (chloroform, 10 g dm⁻³)} crystallized from petroleum ether were provided by Mr G. Holan of the Division of Applied Organic Chemistry, CSIRO. A specimen with volume 0.0223 mm³ and approximate dimensions (100) (face), 0.281 (distance from an arbitrary point in mm); (100), 0.281; (012), 0.081; (012), 0.081; (012), 0.106; (011), 0.106 used in data collection following photographic assessment with precession camera. Density measured by flotation in a bromo/chlorobenzene mixture.

Space group: orthorhombic, *P*2₁2₁2₁ from systematic absences $h00 \neq 2n$, $0k0 \neq 2n$, $00l \neq 2n$.

Data collection: Enraf-Nonius CAD-4 diffractometer; lattice parameters from 25 general reflections ($\theta = 9-60^\circ$); 2452 intensity measurements collected at room temperature as $hkl/\bar{h}\bar{k}\bar{l}$ pairs using $\omega-2\theta$ scans; three reference reflections (1,2,17, 252, 626) checked following every 100 intensity measurements and displayed no significant deterioration; θ range 0.5–75°, $h = 0-8$, $k = 0-10$, $l = 0-29$.

Data reduction: absorption corrections applied (max./min. transmission factors 0.557/0.273) to Friedel pairs prior to sorting, averaging zonal reflections, and applying Lp factors. Weights assigned during final refinement cycle according to the formula $w = 0.1986/[\sigma(F)^2 + 0.00890F^2]$, where $\sigma = (\text{measured intensity} + 8 \text{ MBC})^{1/2}$ and MBC is the mean background count measured at the end of scan ranges. The net intensity from which *F*'s are derived is the measured intensity less 4 MBC.

Structure solution and refinement: Cl atoms from a vector map, other atoms from difference electron-density synthesis; full-matrix weighted least squares against *F* varying all atom coordinates and anisotropic/isotropic temperature factors for non-H/H atoms but with thermal parameters of methyl H's constrained to be equal; $R = 0.039$, $wR = 0.048$; ratio of max. least-squares shift to e.s.d. in final refinement cycle < 0.6. Computer program suite *SHELX76* (Sheldrick, 1976) supplemented with in-house programs. Atomic scattering factors from *SHELX76*.

Table 1. Atomic coordinates and $B_{eq} [= \frac{1}{3}\sum U_{ii} (\text{non-H atoms}) \text{ or } U_{iso} (\text{H atoms})]$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/U_{iso}(\text{\AA}^2)$
Cl(1)	0.2285 (1)	0.2053 (1)	0.3975 (1)	0.0652
Cl(2)	0.2082 (1)	0.3637 (1)	0.5084 (1)	0.0632
C(1)	0.0675 (3)	0.5212 (3)	0.4093 (1)	0.0383
C(2)	0.2034 (4)	0.3895 (3)	0.4342 (1)	0.0464
C(3)	0.2967 (4)	0.5397 (4)	0.4099 (1)	0.0500
C(4)	-0.0451 (4)	0.6222 (3)	0.4525 (1)	0.0410
C(1')	-0.0423 (3)	0.4924 (2)	0.3541 (1)	0.0355
C(2')	-0.2088 (4)	0.3874 (2)	0.3508 (1)	0.0403
C(3')	-0.3172 (4)	0.3705 (3)	0.3004 (1)	0.0395
C(4')	-0.2617 (4)	0.4585 (2)	0.2525 (1)	0.0403
C(5')	-0.0937 (4)	0.5614 (3)	0.2552 (1)	0.0482
C(6')	0.0126 (4)	0.5777 (3)	0.3052 (1)	0.0471
C(7')	-0.5514 (5)	0.3695 (3)	0.1990 (1)	0.0528
C(8')	-0.6423 (7)	0.4059 (4)	0.1414 (1)	0.0725
O(1)	0.0255 (3)	0.7362 (3)	0.4777 (1)	0.0702
O(2)	-0.2318 (3)	0.5738 (3)	0.4597 (1)	0.0553
O(4')	-0.3601 (3)	0.4531 (3)	0.2017 (1)	0.0552
H(2)	-0.288 (5)	0.632 (4)	0.490 (1)	0.059 (8)
H(3A)	0.365 (6)	0.526 (5)	0.370 (1)	0.061 (8)
H(3B)	0.342 (5)	0.622 (4)	0.434 (1)	0.047 (7)
H(2')	-0.254 (5)	0.321 (4)	0.387 (1)	0.047 (7)
H(3')	-0.405 (6)	0.318 (5)	0.299 (1)	0.056 (10)
H(5')	-0.056 (6)	0.636 (5)	0.221 (1)	0.064 (9)
H(6')	0.132 (6)	0.645 (5)	0.304 (1)	0.062 (9)
H(7'A)	-0.511 (6)	0.249 (5)	0.203 (1)	0.062 (9)
H(7'B)	-0.619 (6)	0.413 (4)	0.229 (1)	0.062 (9)
H(8'A)	-0.805 (8)	0.357 (6)	0.145 (2)	0.099 (9)
H(8'B)	-0.563 (7)	0.357 (6)	0.109 (2)	0.099 (9)
H(8'C)	-0.674 (7)	0.520 (6)	0.136 (2)	0.099 (9)

The absolute configuration was determined originally (Poppleton, 1984) by refining the anomalous-dispersion term of the Cl atom in a least-squares refinement with the full data set. This gave $f'' = +0.71$ which agrees with the literature value of 0.702 (*International Tables for X-ray Crystallography*, 1974). The assignment of the present refinement was checked by calculating the *Z* score for each reflection, where $Z_i = 2*[F(H)_i - F(\bar{H})_i]/[\sigma F(H) + \sigma F(\bar{H})]$ and *i* = observed or calculated. For the 100 most-sensitive reflections ($Z_i > 0.5$) there were no contrary indications of relative sign. This unequivocally confirms the validity of the assigned *S* configuration.

Discussion. Final positional and isotropic thermal parameters are given in Table 1† and selected distances and angles in Table 2. The conformation of the molecule in the crystal and the atom-numbering sequence are depicted in Fig. 1.

The mean observed length of the C—C bond of the aromatic ring is 1.386 (11) Å which is to be compared with the expected figure of 1.395 (3) Å (Kennard *et al.*, 1972).

† A list of structure factors and tables of anisotropic temperature factors for the non-H atoms, bond lengths and angles involving H, and *Z* scores for selected reflections have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42754 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond angles of the benzene ring exhibit considerable variation although they are consistent with distortions expected for 1,4-substitution: by equating the cyclopropane moiety to a CH=CNR group and the ethoxy to a methoxy the predicted angles calculated by the method of Domenicano & Murray-Rust (1979) may be compared with those observed; position 1 [C(1')] 117.7 (obs. 117.8), *ortho*- 121.5 (120.0, 121.5), *meta*- 119.8 (120.2, 120.3), *para*- 119.7° (119.2°).

The geometry of the cyclopropane ring is consistent with other reported structures. The mean C—C bond length of 1.508 Å agrees with the expected value of 1.510 (2) Å. Also the pattern of substituent-induced asymmetry in the cyclopropane ring bonds is in reasonable agreement with the conclusions of a statistical analysis of some 299 cyclopropane structures (Allen, 1980).

Table 2. Bond lengths (Å) and angles (°)

C(1)—C(2)	1.518 (1)	C(1')—C(2')	1.395 (1)
—C(3)	1.519 (2)	—C(6')	1.389 (1)
—C(4)	1.503 (1)	C(2')—C(3')	1.388 (1)
—C(1')	1.500 (1)	C(3')—C(4')	1.382 (1)
C(2)—C(1)	1.741 (1)	C(4')—C(5')	1.392 (1)
—Cl(2)	1.751 (1)	—O(4')	1.357 (1)
—C(3)	1.486 (2)	C(5')—C(6')	1.371 (1)
C(4)—O(1)	1.198 (1)	C(7')—C(8')	1.506 (2)
—O(2)	1.304 (1)	—O(4')	1.435 (1)

Central atom	Contiguous atoms	Central atom	Contiguous atoms	
Benzene ring		Cyclopropane ring		
C(1')	C(6') C(2')	C(1)	C(2) C(3) 58.6 (0.1)	
	C(1) C(2')		C(2) C(4) 114.8 (0.1)	
	C(1) C(6')		C(2) C(1')	120.4 (0.1)
C(2')	C(1') C(3')		C(3) C(4)	115.5 (0.1)
C(3')	C(4') C(2')		C(3) C(1')	120.3 (0.1)
C(4')	C(5') C(3')		C(1') C(4)	115.4 (0.1)
	C(5') O(4')	C(2)	Cl(1) Cl(2) 112.7 (0.1)	
	O(4') C(3')		Cl(1) C(1)	118.5 (0.1)
C(5')	C(6') C(4')		Cl(1) C(3)	118.9 (0.1)
C(6')	C(1') C(5')		Cl(2) C(1)	118.6 (0.1)
			Cl(2) C(3)	118.2 (0.1)
Carboxylic group			C(1) C(3)	60.7 (0.1)
C(4)	C(1) O(2)	C(3)	C(1) C(2)	60.7 (0.1)
	C(1) O(1)			
	O(1) O(2)			
		Ethoxy group		
		C(7')	O(4') C(8')	107.2 (0.1)
		O(4')	C(4') C(7')	118.3 (0.1)

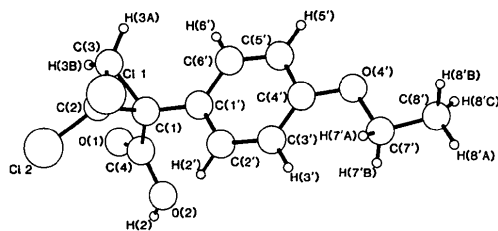


Fig. 1. Atom numbering and molecular conformation. Drawn by PLUTO78 (Motherwell, 1978).

Thus, in reference to the work of Allen (1980), the torsion angle O(1)C(4)C(1)X of 49.1°, where X represents the midpoint of the C(2)C(3) bond, suggests the carbonyl group is sufficiently far from the bisected position to assume negligible carbonyl/ring interaction; secondly, the influence of the *gem*-dichloro increases the C(1)C(3) bond length by 0.025 Å and decreases both C(1)C(2) and C(2)C(3) by 0.012 Å; finally, the phenyl group is close to the bisecting position with torsion angle XC(1)C(1')C(2') of 107.6°, and this decreases the length of the C(2)C(3) bond by 0.018 Å and concomitantly increases C(1)C(2) and C(1)C(3) each by 0.009 Å. On the assumption that for multiple substituents the individual contributions are additive, one finds C(1)C(2) 1.518 (obs.), 1.505 (calc.), C(1)C(3) 1.519, 1.542, C(2)C(3) 1.486, 1.478 Å.

The ethoxy group lies in the plane of the benzene ring and the *exo*-ring angles exhibit the same, well known distortion displayed by the *O*-methyl group; the angle C(3')C(4')O(4') is substantially greater than the angle C(5')C(4')O(4') (Anderson, Kollman & Houk, 1979; Karle, Flippin-Anderson, Chiang & Lowrey, 1984).

The carboxylic group is in the synplanar conformation and the catemer motif (Berkovitch-Yellin & Leiserowitz, 1982) which is adopted results in infinite chains of hydrogen bonds of moderate strength parallel to the *x* axis of the unit cell and around the twofold screw axis; O...O 2.67, OH...O 1.80 Å, O—H...O angle 153°.

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