

Fig. 4. Conformation de la géogénine dans la structure $P4_1$ (cristallisation dans le mélange chloroforme-tétrachlorure de carbone). Plan de projection: C(1)–C(2)–C(6).

12,100 (8), $c = 15,290$ (8) Å. Un essai de résolution de cette structure a mis en évidence, dans le cristal, en plus de la molécule de géogénine, la présence de molécules des deux solvants, en positions désordonnées. Ceci n'a pas permis un affinement précis de la structure; mais un modèle approché de la molécule de géogénine est représenté sur la Fig. 4 [plan de projection C(1)–C(2)–C(6)]. La comparaison des Figs. 3 et 4 montre que, dans les deux cas, la molécule de géogénine a la même conformation; les deux molécules sont inverses optiques l'une de l'autre. La variation du champ cristallin induite par le changement de structure n'entraînant pas de modification de cette conformation, elle a donc une grande probabilité d'exister

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Structure of *rel*-(αR), (1*R*,*trans*)- α -Cyano-3-phenoxybenzyl 3-(2,2-Dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, Non-Insecticidal Components of Cypermethrin

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Abstract. $C_{22}H_{19}Cl_2NO_3$, $M_r = 416.3$, triclinic, $P\bar{1}$, $a = 9.632$ (4), $b = 10.365$ (3), $c = 12.855$ (3) Å, $\alpha = 85.39$ (3), $\beta = 109.72$ (3), $\gamma = 116.96$ (3)°, $U = 1072.8$ Å³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $Z = 2$, $D_m = 1.27$, $D_c = 1.29$ Mg m⁻³, $\mu = 0.322$ mm⁻¹, $F(000) = 432$. The structure was solved by direct methods from observations collected on a four-circle diffractometer. Full-matrix refinement gave a conventional R factor of

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en solution et de jouer un rôle lors de l'activité biologique de la molécule.

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0.073 for 2724 reflections classed as observed. The conformation is different from those found in similar molecules, especially around the two benzene rings.

Introduction. Cypermethrin (NRDC 149, Elliott, 1976) is a mixture of eight isomers formed by combinations of configurations about the three asymmetric carbon atoms [C(3), C(7) and C(11), Fig. 1]. Its insecticidal

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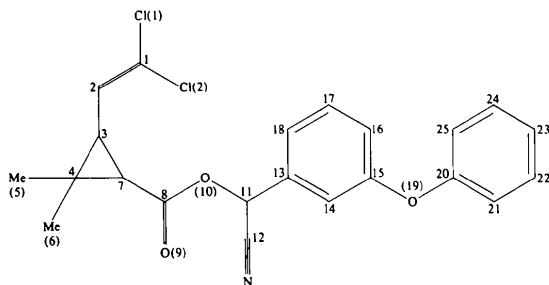


Fig. 1. Numbering scheme for the non-H atoms. The benzyl α -carbon atom is C(11), and the atoms 1, 2, 3 of the cyclopropyl ring are C(7), C(4) and C(3) respectively.

activity is mainly due to the presence of two isomers, (αS)(1*R*,*trans*) and (αS)(1*R*,*cis*). The latter isomer corresponds to the dibromo analogue, deltamethrin (NRDC 161), the most potent commercial insecticide of any class.

Crystallization from solutions of cypermethrin in hexane deposits colourless crystals (m.p. 342–343 K), which have been shown by NMR and bioassay to contain the less insecticidal pair of enantiomers (αR)(1*R*,*trans*) and (αS)(1*S*,*trans*) (Elliott, Janes, Pulman & Soderlund, 1978). Crystallization of this racemic pair contrasts with the spontaneous resolution shown by a racemic solution of NRDC 157 and its optical antipode, which deposits crystals which consist either of the 1*R* isomer, NRDC 157, or of the 1*S* isomer. In view of the paucity of crystal structure data on the pyrethroids (Owen, 1975, 1976), an X-ray diffraction study was carried out on these crystals.

A crystal of dimensions 0.20 × 0.30 × 0.43 mm was mounted on an Enraf–Nonius CAD-4 automatic diffractometer. The orientation matrix and cell dimensions were refined from the positions of 18 reflections. Intensities were collected for all planes with $h \geq 0$ up to a maximum 2θ of 50°. Two standard reflections (062, 335) were measured after every 100 normal reflections. The intensities of these standards fell over the whole data collection by 7% and the data were corrected for this during processing. A total of 3772 unique reflections were obtained, of which 2724 had $I \geq 2\sigma(I)$ and were classed as observed. An analysis of the E distribution indicated the structure was centrosymmetric, and the space group was therefore $P\bar{1}$, confirmed by the successful refinement of the structure. The structure was solved by multiresolution direct methods (Sheldrick, 1976). The numbering scheme is shown in Fig. 1, with the H atoms numbered according to the C atom to which they are bonded. The H atoms were included in positions calculated from the geometry of the rest of the molecule except for H(3), H(7) and the methyl H atoms. The common C–H distance for these eight H atoms was refined to a value of 0.98 (2) Å, and the H...H distances in the methyl groups restrained to

be 1.633 times the C–H distance. The positions of these H atoms were otherwise freely refined. The methyl H atoms were given a common isotropic temperature factor, refined value $U = 0.157$ (11) Å², and the other H atoms treated in a similar way, to give $U = 0.082$ (4) Å². Full-matrix refinement with anisotropic temperature factors for the non-H atoms gave $R = 0.073$ and $R' = 0.074$. The final atomic parameters are given in Table 1. Scattering factors were calculated using an analytical approximation (*International Tables for X-ray Crystallography*, 1974). The weights

Table 1. Fractional coordinates ($\times 10^4$, $\times 10^3$ for H) and U_{eq} values ($\times 10^3$) with e.s.d.'s in parentheses

$$U_{eq} = \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i, \mathbf{a}_j) \text{ for the anisotropic atoms.}$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Cl(1)	3582 (2)	10825 (1)	9773 (1)	75 (1)
Cl(2)	5865 (2)	13808 (1)	9889 (1)	99 (1)
C(1)	4794 (6)	12121 (5)	9143 (3)	56 (2)
C(2)	4979 (6)	11958 (5)	8212 (4)	68 (3)
C(3)	4093 (6)	10623 (5)	7495 (4)	64 (3)
C(4)	3943 (7)	10555 (6)	6297 (4)	69 (3)
C(5)	4863 (10)	11908 (7)	5801 (5)	106 (6)
C(6)	2289 (8)	9498 (8)	5519 (5)	111 (5)
C(7)	5038 (5)	9974 (5)	7130 (3)	54 (2)
C(8)	4501 (5)	8423 (5)	7224 (3)	48 (2)
O(9)	3220 (4)	7498 (4)	7274 (3)	66 (2)
O(10)	5758 (3)	8118 (3)	7249 (2)	46 (1)
C(11)	5515 (5)	6655 (4)	7467 (3)	46 (2)
C(12)	4290 (6)	5638 (5)	6479 (4)	56 (2)
N	3359 (6)	4848 (5)	5740 (4)	89 (3)
C(13)	7202 (5)	6715 (4)	7778 (3)	45 (2)
C(14)	8220 (5)	7117 (4)	8874 (3)	46 (2)
C(15)	9836 (5)	7319 (4)	9172 (4)	54 (2)
C(16)	10431 (6)	7124 (4)	8396 (5)	66 (3)
C(17)	9398 (7)	6704 (5)	7322 (5)	74 (3)
C(18)	7774 (6)	6489 (5)	6993 (4)	61 (3)
O(19)	10958 (4)	7745 (4)	10229 (3)	78 (2)
C(20)	10361 (5)	7725 (5)	11082 (4)	60 (2)
C(21)	9783 (7)	6491 (5)	11577 (5)	81 (3)
C(22)	9262 (8)	6465 (7)	12451 (5)	100 (4)
C(23)	9322 (7)	7706 (8)	12812 (4)	95 (4)
C(24)	9928 (7)	8949 (7)	12318 (5)	87 (3)
C(25)	10453 (6)	8967 (5)	11448 (4)	71 (3)
H(2)	578	1281	798	
H(3)	329 (5)	988 (4)	781 (4)	
H(5) <i>a</i>	505 (7)	1162 (6)	517 (3)	
H(5) <i>b</i>	599 (4)	1256 (6)	634 (4)	
H(5) <i>c</i>	425 (6)	1246 (6)	558 (4)	
H(6) <i>a</i>	258 (7)	929 (6)	491 (4)	
H(6) <i>b</i>	171 (7)	859 (4)	582 (5)	
H(6) <i>c</i>	161 (7)	1000 (6)	528 (5)	
H(7)	621 (3)	1064 (4)	731 (4)	
H(11)	507	630	807	
H(14)	781	726	943	
H(16)	1158	728	861	
H(17)	981	655	677	
H(18)	705	618	622	
H(21)	974	561	1131	
H(22)	885	557	1282	
H(23)	893	769	1342	
H(24)	999	984	1259	
H(25)	1089	987	1109	

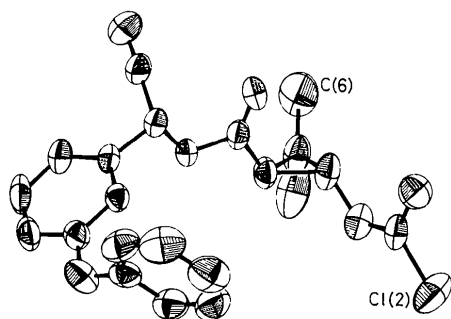


Fig. 2. The conformation of the (αR), (1*R*,*trans*) isomer in the crystal. The 50% thermal ellipsoids are shown.

used were those derived from the counting statistics. The final difference map showed one peak of height $1.2 \text{ e } \text{\AA}^{-3}$ near Cl(2), and all the rest were $\leq 0.5 \text{ e } \text{\AA}^{-3}$. The atom Cl(2) has very anisotropic thermal motion (Fig. 2), so the presence of this peak indicates possible

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

E.s.d.'s for bond angles are $\sim 0.4^\circ$.

Cl(1)—C(1)	1.692 (5)	C(4)—C(3)—C(7)	60.0
Cl(2)—C(1)	1.735 (4)	C(3)—C(4)—C(5)	120.1
C(1)—C(2)	1.302 (6)	C(3)—C(4)—C(6)	116.0
C(2)—C(3)	1.448 (6)	C(5)—C(4)—C(6)	115.1
C(3)—C(4)	1.503 (6)	C(3)—C(4)—C(7)	61.4
C(3)—C(7)	1.548 (6)	C(5)—C(4)—C(7)	114.8
C(4)—C(5)	1.507 (8)	C(6)—C(4)—C(7)	119.1
C(4)—C(6)	1.502 (8)	C(3)—C(7)—C(4)	58.5
C(4)—C(7)	1.527 (6)	C(3)—C(7)—C(8)	116.2
C(7)—C(8)	1.457 (6)	C(4)—C(7)—C(8)	122.0
C(8)—O(9)	1.191 (5)	C(7)—C(8)—O(9)	129.7
C(8)—O(10)	1.374 (4)	C(7)—C(8)—O(10)	108.8
O(10)—C(11)	1.444 (4)	O(9)—C(8)—O(10)	121.6
C(11)—C(12)	1.481 (6)	C(8)—O(10)—C(11)	116.4
C(11)—C(13)	1.510 (5)	O(10)—C(11)—C(12)	110.2
C(12)—N	1.124 (5)	O(10)—C(11)—C(13)	105.8
C(13)—C(14)	1.383 (5)	C(12)—C(11)—C(13)	112.8
C(13)—C(18)	1.380 (5)	C(11)—C(12)—N	178.9
C(14)—C(15)	1.388 (6)	C(11)—C(13)—C(14)	117.4
C(15)—C(16)	1.374 (6)	C(11)—C(13)—C(18)	121.9
C(15)—O(19)	1.371 (5)	C(14)—C(13)—C(18)	120.5
C(16)—C(17)	1.365 (7)	C(13)—C(14)—C(15)	119.2
C(17)—C(18)	1.389 (6)	C(14)—C(15)—C(16)	121.0
O(19)—C(20)	1.396 (6)	C(14)—C(15)—O(19)	124.0
C(20)—C(21)	1.346 (6)	C(16)—C(15)—O(19)	115.0
C(20)—C(25)	1.361 (6)	C(15)—C(16)—C(17)	118.9
C(21)—C(22)	1.371 (8)	C(16)—C(17)—C(18)	121.7
C(22)—C(23)	1.372 (8)	C(13)—C(18)—C(17)	118.7
C(23)—C(24)	1.357 (8)	C(15)—O(19)—C(20)	117.6
C(24)—C(25)	1.370 (7)	O(19)—C(20)—C(21)	119.3
		O(19)—C(20)—C(25)	119.9
Cl(1)—C(1)—Cl(2)	112.4	C(21)—C(20)—C(25)	120.7
Cl(1)—C(1)—C(2)	127.2	C(20)—C(21)—C(22)	120.3
Cl(2)—C(1)—C(2)	120.4	C(21)—C(22)—C(23)	119.4
C(1)—C(2)—C(3)	125.2	C(22)—C(23)—C(24)	119.8
C(2)—C(3)—C(4)	123.8	C(23)—C(24)—C(25)	120.4
C(2)—C(3)—C(7)	120.8	C(20)—C(25)—C(24)	119.4

site disorder for this atom, though this was not investigated further.*

Discussion. Bond lengths and angles and estimated standard deviations are given in Table 2, torsion angles in Table 3 and mean planes in Table 4. The Cl(1)—C(1) distance at $1.692 (5) \text{ \AA}$ is significantly shorter than the Cl(2)—C(1) bond, $1.735 (4) \text{ \AA}$. The expected value is $1.72 (1) \text{ \AA}$ (*International Tables for X-ray Crystallography*, 1962). The possible statistical disorder of the vinyl group may explain these distances; the final

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35923 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Torsion angles ($^\circ$)

E.s.d.'s are $\sim 0.6^\circ$.

C(1)—C(2)—C(3)—C(4)	161.4
C(1)—C(2)—C(3)—C(7)	-126.1
C(3)—C(7)—C(8)—O(9)	20.8
C(4)—C(7)—C(8)—O(9)	-46.9
O(9)—C(8)—O(10)—C(11)	-6.9
C(8)—O(10)—C(11)—C(13)	-164.1
O(10)—C(11)—C(13)—C(14)	85.2
C(14)—C(15)—O(19)—C(20)	11.7
C(15)—O(19)—C(20)—C(25)	-96.7

Table 4. Deviations (\AA) of atoms from mean planes (atoms in *italics* were excluded from the calculations of the planes)

Plane A: dichlorovinyl group					
Cl(1)	0.003 (2)	Cl(2)	-0.014 (3)	C(1)	0.005 (4)
C(2)	0.027 (5)	C(3)	-0.021 (6)	C(4)	-0.394 (8)
C(7)	1.060 (7)				
Plane B: ester group					
C(7)	0.000 (4)	C(8)	0.000 (3)	O(9)	0.000 (3)
O(10)	0.000 (3)	C(3)	0.492 (7)	C(4)	-0.947 (7)
C(11)	0.153 (6)	C(13)	0.518 (8)		
Plane C: benzyl benzene ring					
C(13)	0.008 (4)	C(14)	-0.004 (4)	C(15)	-0.004 (4)
C(16)	0.007 (4)	C(17)	-0.003 (5)	C(18)	-0.005 (4)
C(11)	0.150 (6)	O(19)	0.011 (6)	C(20)	-0.224 (8)
Plane D: phenoxy benzene ring					
C(20)	0.007 (5)	C(21)	0.001 (6)	C(22)	0.006 (7)
C(23)	-0.008 (7)	C(24)	0.003 (7)	C(25)	0.004 (6)
O(19)	0.053 (7)	C(15)	-1.131 (10)		
Angles between planes ($^\circ$)					
Plane A/Plane B	62.8 (1)	Plane B/Plane C	96.2 (2)		
Plane A/Plane C	113.3 (1)	Plane B/Plane D	49.7 (2)		
Plane A/Plane D	28.2 (3)	Plane C/Plane D	88.6 (2)		

difference map showed low peaks ($\sim 0.5 \text{ e } \text{Å}^{-3}$) close to Cl(1), as well as the higher peak near Cl(2) noted in the experimental section. This indicates some freedom of rotation about the C(2)–C(3) bond.

The C–C bond lengths in the cyclopropane ring follow the trend noted for attached electron-acceptor groups (Allen, 1980). The bond between the carbon atoms to which such groups are attached [C(3)–C(7)] is longer [1.548 (6) Å] than the other two [1.503 (6) and 1.527 (6) Å]. The latter are not as equal as would have been expected by more strict adherence to the additivity rule.

Other bond lengths and angles are similar to those found in other pyrethroids (Owen, 1976, and references therein).

The torsion angles and mean planes, however, show how flexible these molecules are. Thus the plane of the dichlorovinyl group does not bisect C(4)–C(7), though the torsion about C(2)–C(3) is not as extreme as that found in deltamethrin itself (Owen, 1975). The ester group also deviates slightly from the bisecting position, to a greater extent than found in other pyrethroids. The torsions around the other bonds about which free rotation may be expected are completely different from those in similar molecules, and bring the terminal benzene ring round towards the dichlorovinyl group, rather than towards the dimethyl group as found in NRDC 157 (Owen, 1976).

There are no close intermolecular contacts of note, so the conformation is not determined by strong interactions between the molecules, such as stacking of benzene rings, *etc.* Left- and right-handed forms of the molecule, (αS), (1*S*,*trans*) and (αR), (1*R*,*trans*), are present in equal numbers, giving the racemic crystals.

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(±)-2-(4-Chlorophenoxy)-2-phenylpropionic Acid

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Abstract. C₁₅H₁₃ClO₃, m.p. 379–381 K, $M_r = 276.7$, monoclinic, $P2_1/c$, $a = 15.328$ (8), $b = 6.079$ (5), $c = 16.398$ (7) Å, $\beta = 113.79$ (3)°, $Z = 4$, $D_x = 1.314$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.278$ mm⁻¹, $R = 0.086$, 918 observed reflexions. The molecules, which form hydrogen-bonded cyclic dimers [O...O, 2.638 (9) Å], adopt a conformation with the phenoxy and benzene rings

nearly coplanar. The carboxylic acid group has the *syn-anti* conformational motif relative to the phenoxy residue, common to all known phenoxyalkanoic acids having tertiary substitution about the α -carbon.

Introduction. The title compound is an experimental anti-hypolipidaemic compound from the Merck Com-