Absolute Configuration of the Potent Insecticide α-Cyano-3-phenoxybenzyl *cis*-2,2-Dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate by *X*-Ray Crystal Structure Analysis

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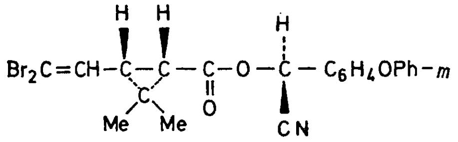
Summary *X*-Ray structure determination on the highly insecticidal isomer of the title compound shows it to be (*S*) about the benzylic α-carbon atom.

The molecule of the cyclopropanecarboxylate (I) has three asymmetric centres. The configuration about the cyclopropane ring can be deduced chemically and has been shown[1] to be *cis*-(1*R*,3*R*). Of the two isomers derived from the benzylic α-carbon asymmetric centre, one is crystalline and an insecticide considerably more active than any other compound available at present.[1]

The absolute configuration of this isomer (designated NRDC 161) has been suggested by a fairly indirect argument[1] but in view of its properties, it needs to be known with certainty for meaningful structure–activity analysis[2] to be carried out. The results of *X*-ray diffraction studies on NRDC 161 are now presented. Although the structure of the 6-bromo-2,4-dinitrophenylhydrazone derivative of (*S*) bioallethrin has been determined by *X*-ray diffraction methods,[3] the present work is the first determination of the structure of an actual pyrethroid insecticide to be reported.

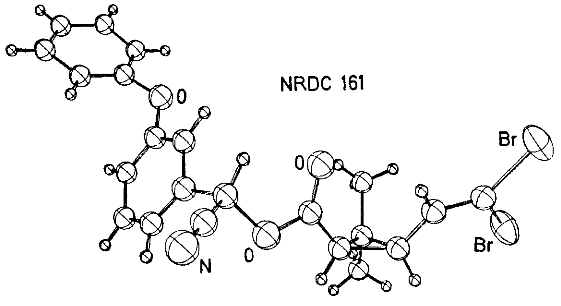
Crystals of $C_{22}H_{19}Br_2NO_3$ are orthorhombic colourless needles, $a = 12{\cdot}32$, $b = 27{\cdot}17$, $c = 6{\cdot}29$ Å, space group $P2_12_12_1$, $Z = 4$. Intensity data were collected using Mo-K_α radiation on a 4-circle diffractometer, and both the hkl and $hk\bar{l}$ octants were collected. 616 of the hkl reflections were



(I)

classed as observed and were used to solve the structure initially. A Patterson synthesis located the bromine atoms, and the rest of the atoms (including hydrogens) were located by successive Fourier maps and least squares refinements. The bromine atoms were allowed to refine with anisotropic thermal parameters; the hydrogen atoms were not refined.

At this stage the absolute configuration was sought by carrying out two structure factor calculations of all the *hkl* and $hk\bar{l}$ reflections classed as observed. The isomer used so far gave $R = 8{\cdot}30\%$ for 1083 planes, whereas that obtained by reversing the signs of all three co-ordinates of each atom gave $R = 7{\cdot}43\%$. This second isomer also showed the correct configuration about the cyclopropane ring so confirming the results of the anomalous dispersion effects. The correct isomer was refined using the 616 observed *hkl* reflections to $R = 7{\cdot}02\%$ and the resulting structure is shown in the Figure.



FIGURE

This work confirms the chemical methods[1] in assigning the configuration (*S*) at the benzylic α-carbon atom, and shows several conformational features which may prove of interest in structure–activity analysis.

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