# organic papers

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## Key indicators

Single-crystal X-ray study
$T$ = 295 K
Mean $\sigma$(C–C) = 0.004 Å
Disorder in main residue
$R$ factor = 0.043
$wR$ factor = 0.116
Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

# Tetrachlorvinphos

The crystal structure of 2-chloro-1-(2,4,5-trichlorophenyl)-vinyl dimethyl phosphate (also known as Tetrachlorvinphos, Stirofos, and Gardona®), $C_{10}H_9Cl_4O_4P$, contains two molecules per asymmetric unit. In one of the molecules, three O atoms of the phosphate group are disordered. Increased precision is presented compared to a previously reported structure.

## Comment

As part of an ongoing study of organophosphorus (OP) pesticides (Baker & Baughman, 1995; Baughman & Allen, 1995; Baughman, 1997; Baughman & Paulos, 2005, and references therein), the structure of the insectide Tetrachlorvinphos, (I), was redetermined. Since Rohrbaugh & Jacobson (1978) reported the structure of (I) with an $R$-factor of 0.123, a re-determination seemed appropriate to make more precise geometric parameters available for studies that model this pesticide's mode of action in inhibiting the enzyme acetylcholinesterase (AChE).



(I)
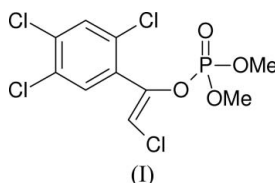
The s.u's for the lattice constants and geometric parameters in this report are approximately one-third those of the Rohrbaugh & Jacobson study. Disorder is still noted for three phosphate O atoms in one molecule (molecule $A$ in Fig. 1). The Cl1 atoms in both molecules ($A$ and $B$) present in the asymmetric unit are *trans* to the phenyl groups (*i.e.*, the $\beta$ form), in agreement with the previously reported structure.

The distances presented in Table 2 suggest that the disorder of the O atoms in molecule $A$ may be due to inter- and intramolecular interactions with Cl atoms. These $\delta(-)\cdots\delta(-)$ interactions may not only cause, but also limit the amount of motion. It is unclear why no concomitant disorder of the C9$A$ and C10$A$ methyl groups was noted. No significantly short intermolecular distance that would restrict the methyl groups was observed. As nearly the same number of contacts with methyl groups (at near van der Waals distances) for $A$ and $B$ molecules was noted, it would appear that the disorder is not particularly packing-induced. Apart from the disorder, there are only subtle differences in most distance and angle values (Table 1) between molecules $A$ and $B$. The most notable exceptions are the torsion angles in $A$ involving the split O atoms, where large spreads are noted. As Rohrbaugh &
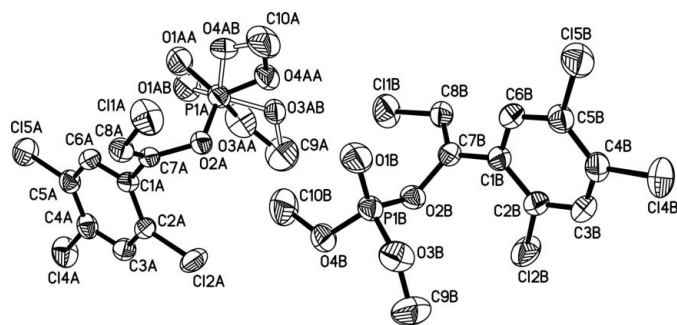
**Figure 1**
The asymmetric unit of (I), showing the labeling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level. Atoms labeled with the suffixes A and B correspond to molecules A and B, respectively. Both components of the disordered O atoms are shown. H atoms have been omitted for clarity.

Jacobson (1978) suggested, the non-disordered molecule (B in this case) is more suited for comparison studies.

As the $\delta(-)$ anionic and $\delta(-)$ esteratic site-separation distance in insect AChE is 5.0–5.5 Å (Hollingworth *et al.*, 1967) or 4.5–5.9 Å (O'Brien, 1963), knowing the corresponding $\delta(+) \cdots \delta(+)$ distances in an OP insecticide is important. The distances in Table 1 suggest that the most likely candidate is the $P1 \cdots H3$ distance. Although atoms H3 and H6 in each molecule are undoubtedly $\delta(+)$, only weak intermolecular interactions involving these atoms and Cl's are observed in the crystal structure (Table 2).

## Experimental

Crystals of the title compound were grown by slow evaporation of an ethanol solution.

### Crystal data

| | |
|---|---|
| $C_{10}H_9Cl_4O_4P$ | $V = 1448.88\,(19)$ Å$^3$ |
| $M_r = 365.96$ | $Z = 4$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.678$ Mg m$^{-3}$ |
| $a = 6.9371\,(5)$ Å | Mo $K\alpha$ radiation |
| $b = 14.0202\,(11)$ Å | $\mu = 0.93$ mm$^{-1}$ |
| $c = 15.1206\,(12)$ Å | $T = 295\,(2)$ K |
| $\alpha = 98.986\,(5)°$ | Block cut from larger crystal, |
| $\beta = 93.986\,(6)°$ | colorless |
| $\gamma = 90.256\,(6)°$ | $0.58 \times 0.53 \times 0.32$ mm |

### Data collection

| | |
|---|---|
| Bruker P4 diffractometer | 4239 reflections with $I > 2\sigma(I)$ |
| $\theta/2\theta$ scans | $R_{int} = 0.032$ |
| Absorption correction: integration | $\theta_{max} = 25.0°$ |
| (*XSHELL*; Bruker, 1999) | 3 standard reflections |
| $T_{min} = 0.58$, $T_{max} = 0.74$ | every 100 reflections |
| 6417 measured reflections | intensity decay: 3.9% |
| 5061 independent reflections | |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0427P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | $+ 1.5005P]$ |
| $wR(F^2) = 0.116$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.12$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 5061 reflections | $\Delta\rho_{max} = 0.41$ e Å$^{-3}$ |
| 372 parameters | $\Delta\rho_{min} = -0.32$ e Å$^{-3}$ |
| H-atom parameters constrained | Extinction correction: *SHELXL97* |
| | Extinction coefficient: 0.0019 (6) |

**Table 1**
Selected geometric parameters (Å,°).

| Molecule A | | Molecule B | |
|---|---|---|---|
| Cl1A—C8A | 1.720 (3) | Cl1B—C8B | 1.714 (3) |
| Cl2A—C2A | 1.736 (3) | Cl2B—C2B | 1.730 (3) |
| Cl4A—C4A | 1.726 (3) | Cl4B—C4B | 1.726 (3) |
| Cl5A—C5A | 1.730 (3) | Cl5B—C5B | 1.736 (3) |
| P1A—O1AA | 1.436 (5) | P1B—O1B | 1.449 (3) |
| P1A—O1AB | 1.467 (7) | | |
| P1A—O2A | 1.601 (2) | P1B—O2B | 1.598 (2) |
| P1A—O3AA | 1.530 (5) | P1B—O3B | 1.545 (3) |
| P1A—O3AB | 1.574 (5) | | |
| P1A—O4AA | 1.553 (4) | P1B—O4B | 1.560 (2) |
| P1A—O4AB | 1.528 (6) | | |
| O2A—C7A | 1.395 (4) | O2B—C7B | 1.392 (4) |
| P1A⋯H3A | 5.83 | P1B⋯H3B | 5.65 |
| P1A⋯H6A | 3.89 | P1B⋯H6B | 4.07 |
| P1A⋯ring center | 4.38 | P1B⋯ring center | 4.35 |
| | | | |
| O1AA—P1A—O2A | 113.8 (2) | O1B P1B O2B | 113.74 (14) |
| O1AB—P1A—O2A | 114.6 (3) | | |
| O1AA—P1A—O3AA | 113.0 (4) | O1B P1B O3B | 112.87 (17) |
| O1AB—P1A—O3AB | 116.3 (4) | | |
| O1AA—P1A—O4AA | 118.8 (3) | O1B P1B O4B | 118.41 (15) |
| O1AB—P1A—O4AB | 112.8 (4) | | |
| O2A—P1A—O3AA | 105.4 (2) | O2B P1B O3B | 105.98 (14) |
| O2A—P1A—O3AB | 101.2 (2) | | |
| O2A—P1A—O4AA | 100.38 (18) | O2B P1B O4B | 100.97 (13) |
| O2A—P1A—O4AB | 106.4 (3) | | |
| O3AA—P1A—O4AA | 104.0 (2) | O3B P1B O4B | 103.36 (14) |
| O3AB—P1A—O4AB | 104.3 (3) | | |
| | | | |
| O1AA—P1A—O2A—C7A | 21.1 (4) | O1B—P1B—O2B—C7B | 25.0 (3) |
| O1AB—P1A—O2A—C7A | −28.9 (5) | | |
| O3AA—P1A—O2A—C7A | −103.2 (3) | O3B—P1B—O2B—C7B | −99.6 (2) |
| O3AB—P1A—O2A—C7A | −154.9 (3) | | |
| O4AA—P1A—O2A—C7A | 149.0 (3) | O4B—P1B—O2B—C7B | 152.9 (2) |
| O4AB—P1A—O2A—C7A | 96.4 (3) | | |
| P1A—O2A—C7A—C1A | 72.9 (3) | P1B—O2B—C7B—C1B | 73.5 (3) |
| C2A—C1A—C7A—O2A | 64.1 (4) | C2B—C1B—C7B—O2B | 56.9 (4) |
| C2A—C1A—C7A—C8A | −112.9 (4) | C2B—C1B—C7B—C8B | −120.8 (4) |
| C1A—C7A—C8A—Cl1A | −178.7 (2) | C1B—C7B—C8B—Cl1B | −177.7 (3) |

**Table 2**
Close chlorine⋯oxygen and H⋯Cl Interactions (Å, °).

| Interaction | Distance |
|---|---|
| O1AA⋯Cl4B$^i$ | 3.274 (6) |
| O1AB⋯Cl4B$^i$ | 3.151 (7) |
| O3AA⋯Cl5B$^{ii}$ | 3.510 (5) |
| O3AB⋯Cl1B | 3.367 (6) |
| O4AA⋯Cl1B | 3.270 (4) |
| O4AB⋯Cl1B$^{iii}$ | 3.378 (7) |
| O1B⋯Cl4A$^{iv}$ | 3.463 (3) |
| O3B⋯Cl4A$^{iv}$ | 3.100 (3) |

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| C3A—H3A⋯Cl5A$^v$ | 0.93 | 3.09 | 3.959 (4) | 157 |
| C6A—H6A⋯Cl2A$^{vi}$ | 0.93 | 3.09 | 3.957 (3) | 156 |
| C3B—H3B⋯Cl5B$^v$ | 0.93 | 3.03 | 3.916 (4) | 160 |
| C6B—H6B⋯Cl2B$^{vi}$ | 0.93 | 2.99 | 3.882 (3) | 160 |

Symmetry codes: (i) $x - 1, y, 1 + z$; (ii) $x, y, 1 + z$; (iii) $1 - x, -y, 1 - z$; (iv) $x, y, z - 1$; (v) $1 + x, y, z$; (vi) $x - 1, y, z$.

The structure initially refined to an $R$ value of 0.076, but atoms O1A, O3A, and O4A showed unusually elongated displacement ellipsoids. The split-atom refinement for these three atoms led to a significant decrease in the $R$ factor to 0.043. Unlike the previous determination, the occupancies of the two trios of O atoms were

refined to 0.594 (5) and 0.406 (5). Although a number of H atoms were observed in a difference map, all H atoms were placed in calculated positions and refined as riding. Bond lengths were constrained to 0.93 Å for aromatic and vinyl C—H and 0.96 Å for methyl C—H, and $U_{iso}$(H) were fixed at $1.5U_{eq}$(parent) for methyl H atoms and $1.2U_{eq}$(parent) for all other H atoms. In the final stages of refinement, four very small or negative $F_o$ values were deemed to be in severe disagreement with their $F$c values and were eliminated from the final refinement.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXTL/PC* and *SHELXL97*.

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