# Further Details on the Crystal and Molecular Structure of the Organophosphorus Insecticide Chlorpyrifos Methyl

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Chlorpyrifos methyl crystallizes with two different conformations present in the unit cell. Indirect evidence and a series of CNDO/2 calculations are presented to point to one of the structures as being more probably encountered in the "free" state.

The crystal and molecular structure of the organophosphorus insecticide chlorpyrifos methyl (I) [Dowco 214, *O,O*-dimethyl *O*-(3,5,6-trichloro-2-pyridyl) thiophosphate] was recently determined in this laboratory and is

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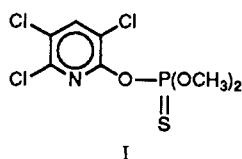
in agreement with the work of Beckman and Jacobson (1979) in which two molecules are present in the asymmetric unit. During the present work, additional details of the structures were investigated. As it is somewhat unusual to have two fluxional molecules (which implies slightly different ΔH_f°'s) in an asymmetric unit, it would seem that one molecule is more stable than the other and is therefore the more probable in vivo structure.

To aid in the visualization of the two different geometries, an ORTEP drawing (Johnson, 1971) is given in Figure 1, which, along with any unreferenced distances and angles given here, are from the present work. As the fractional coordinates in both works are essentially the same, they are not given in this paper. The only differences in the former and present works are that the R factors are 0.078 and 0.052, respectively, and the labeling of O2/O3 and C6/C7 has been switched.

The most apparent structural differences in A and B can be seen in Figure 1 as corresponding to the values of the torsional angles about the C1–O1 and P–O2 bonds. With use of the convention of Klyne and Prelog (1960), the C2–C1–O1–P angles in A and B are –164.4 (2) and –144.3 (3)°, respectively; S–P–O2–C6 = 178.0 (2) and –23.3 (4)°. The O1–P–O3–C7 torsional angles in both molecules are essentially identical [–78.6 (8)° for A;–73.0 (3)° for B]. So, the most striking difference is the way in which C6 is directed. Deviations of the corresponding angles in A and B are likely due to intramolecular and/ or intermolecular interactions, which will be shown to primarily affect A.

In chlorpyrifos (Baughman et al., 1978) the value of the C2–C1–O1–P angle is 145.9°, which is quite close to the *magnitude* of the corresponding angle in B (144.3°). In the oxygen analogue to chlorpyrifos methyl, fospirate (Baughman and Jacobson, 1977), the angle is 168.4°. Though this value is comparable to that in chlorpyrifos and chlorpyrifos methyl, the difference may likely be a consequence of the presence of the smaller doubly bonded oxygen. The C1–O1–P–S angle in chlorpyrifos (52.2°) is but slightly closer to that in A (51.4 (3)°) than B (47.1 (3)°) though the S⋯N and O2⋯N distances in chlorpyri-

fos (3.616 and 3.159 Å, respectively) are closer to the same separations in B (3.506 (4) and 3.222 (5) Å). The S⋯N and O2⋯N distances in B not only are longer than the sums of the van der Waals radii (3.15 and 2.9 Å; Pauling, 1960) but are longer than or comparable to the corresponding distances in A (3.390 (3) and 3.181 (4) Å). This would seem to favor B as the lower energy moiety, as less repulsive strain would be present around the nitrogen in B.

For the most part, packing in the chlorpyrifos methyl crystal is van der Waals in nature, and a few of these interactions are likely responsible for the slightly different geometries of molecules A and B. The closest contact within the asymmetric unit shown in Figure 1 is Cl1 in B with O2 in A. The interatomic distance is 3.574 (3) Å, which is substantially greater than the sum of the van der Waals radii, 3.20 Å . However, distances from the Cl2 in B to atoms in molecule A in a neighboring unit cell (translated by –1 in *z* from Figure 1) indicate contacts that are close enough to probably cause molecular distortion(s) of A. The following B–A distances (Å), with van der Waals radii sums (Pauling, 1960) given in parentheses, are the most important in this regard: Cl2⋯O3, 3.045 (3), (3.20); Cl2⋯C6(methyl), 3.675 (5), (3.8); Cl2⋯C7(methyl), 3.638 (5), (3.8). That is, a Cl2 in a B molecule seems to be distorting portions of the thiophosphate group in each A. As no contacts close enough to cause distortion of the thiophosphate group of B are noted, the geometry is more likely to be closer to that of an isolated molecule.

A more definitive indication of the preferred geometry would be a comparison of the ΔH_f° values for A and B. However, as separate experimental determinations of ΔH_f° for A and B are not possible, a series of theoretical quantum mechanical calculations may help to resolve the problem of which of the isolated species is the preferred conformation in the crystal. As ab initio calculations are not particularly suited to this size of a problem, separate CNDO/2 calculations (Pople and Beveridge, 1970) were performed on A and B. Since the information from a CNDO calculation is most useful when similar molecules are compared, the present problem should be not only well suited but also resolvable.

Charge density information from the calculations shows similarities to the charge densities calculated for chlorpyrifos (Baughman et al., 1978). The computed E_{tot} values for A and B, respectively, are –511.5704 and –511.6956 MJ/mol, a difference of 125 kJ/mol ($\approx$30 kcal/ mol), indicating that B is the more stable of the two fixed conformations. This conclusion would also be in accordance with the known preference of dipoles, for example the methoxy group, to point in opposite directions,
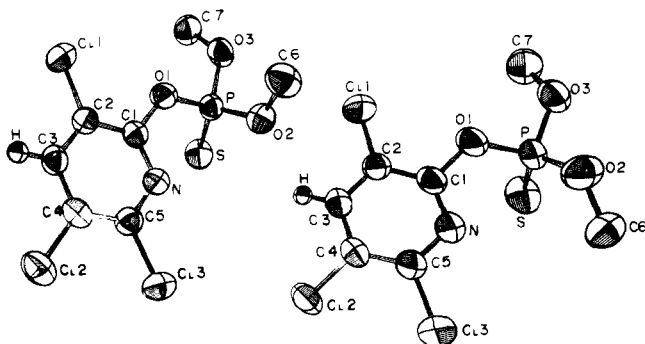
1506 *J. Agric. Food Chem.*, Vol. 37, No. 6, 1989

Baughman

Figure 1. Two symmetry-independent chlorpyrifos methyl molecules showing 50% probability ellipsoids; 30% for hydrogens: A, left; B, right.
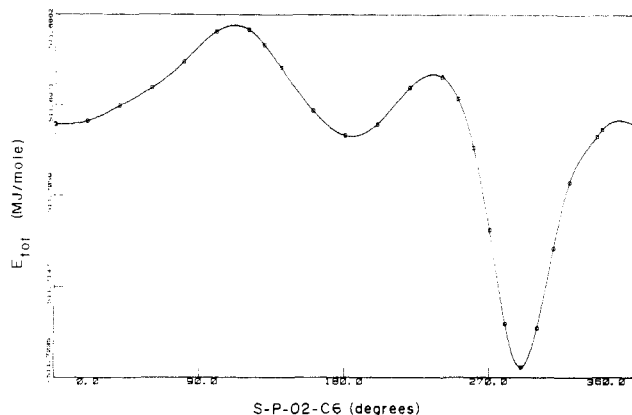

S-P-O2-C6 (degrees)

Figure 2. Dependence of the total molecular energy (E_{tot}) as a function of the S-P-O2-C6 angle calculated by the CNDO/2 method.

S-P-O2-C6 (degrees)

Figure 3. Dipole moment of the chlorpyrifos molecule as a function of the S-P-O2-C6 angle.

Cl-O1-P-S (degrees)

Figure 4. Dependence of the total molecular energy (E_{tot}) as a function of the C1-O1-P-S angle calculated by the CNDO/2 method.

C2-Cl-O1-P (degrees)

Figure 5. Dependence of the total molecular energy (E_{tot}) as a function of the C2-C1-O1-P angle calculated by the CNDO/2 method.

analogous to the "anomeric effect" (Ternay, 1976).

Since the structures of A and B differ most dramatically in the way C6 is positioned, the variation of the total molecular energy as a continuous function of the C6-methyl group position should give additional insight as to the favored geometry not only in the crystal but possibly in vivo. Using the atomic coordinates for all atoms in B as the "basis" molecular geometry and then rotating *only* the C6-methyl group about the P-O2 bond, the total molecular energies for a number of S-P-O2-C6 angles were calculated by the CNDO/2 method.

The results of this "slice" of the molecular energy surface are given in Figure 2, which illustrates that *two* local minima exist. These minima imply the presence of two preferred positions of the C6 in chlorpyrifos methyl. The deepest minimum ($\approx$25 kJ/mol) at $\approx$290° (-70°) roughly corresponds to the -23° torsional angle in B. The smaller minimum ($\approx$8 kJ/mol) near 180° corresponds very closely to the 178° angle in A. It is interesting to note in Figure 3 that the dipole moment of the *molecule* (μ) maximizes roughly at the same angle (290°) as the deepest energy minimum in Figure 2. Exact matching of the observed torsional angles and those predicted from Figure 2 should not necessarily be expected for three reasons: (1) *Only* the C6 position has been allowed to change in this calculation. (2) Approximations are used in the CNDO/2 method. (3) van der Waals interactions exist in the crystal, though *individual* contributions would be weak since no distances less than van der Waals contacts were noted between the thiophosphate group in B and any other atoms in the crystal. Nevertheless, any *trend* should be valid. It would be reasonable to consider that the contact of C12 in B noted earlier pushes the C6 in A into the higher energy local minimum.
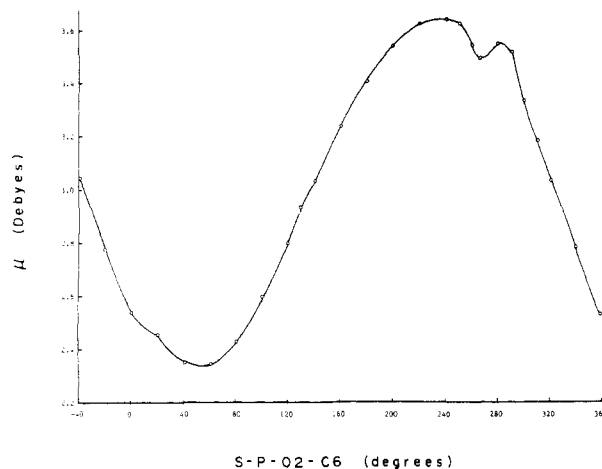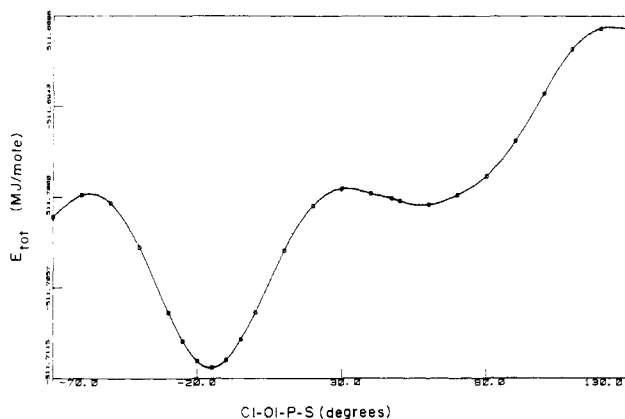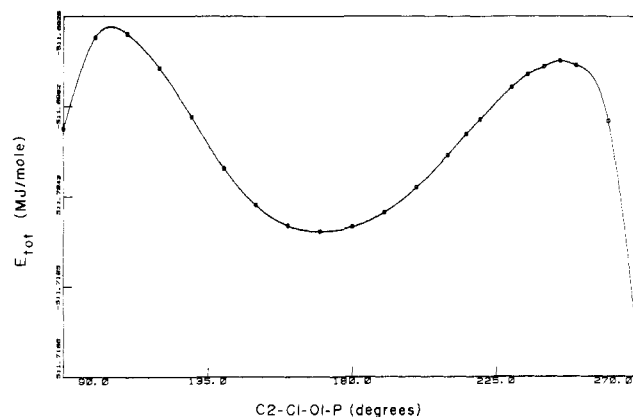
Similar CNDO/2 calculations were also performed for E_{tot} vs C1-O1-P-S (Figure 4) and E_{tot} vs C2-C1-O1-P (Figure 5). The observed C1-O1-P-S angles of 51.4 (3)° for A and 47.1 (3)° for B both lie in the shallow ($\approx$0.8 kJ/mol) local minimum. As room temperature provides $\approx$2.5 kJ/mol, both angles could change to $\approx$-15°. As noted earlier, the observed C2-C1-O1-P angles for A and B are -164.4 (2)° and -144.3 (3)°, respectively. Both fall well within the energy minimum in Figure 5. One could infer that C2-C1-O1-P angles of 180 ± 40° are likely to

be encountered not only as seen in the crystal but also in "free" (gaseous) and in vivo situations.

All of the evidence presented points to the structure of B as being the better one to use for theoretical arguments when discussing isolated molecules.

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Methyl Bromide Residues in Fumigated Mangos

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Mangos (*Mangifera indica* Linn) were fumigated in temperature-controlled chambers with methyl bromide (MB) at 16, 48, 56, and 64 g/m³. Gas chromatographic analysis for MB residues in the peel and flesh showed that residue concentrations were above 20 mg/kg at 0.17 h after fumigation at the highest doses. One hour after fumigation, residue levels were below 15 mg/kg. Analyses of the peel and flesh at 0.17, 1, 2, 5, 24, and 48 h after fumigation indicated that the MB residue levels followed an exponential regression, decreasing rapidly during the first hour followed by gradual decline.

The mango (*Mangifera indica* Linn, one of several subtropical fruits that is a host of the Mexican fruit fly, *Anaestrepha ludens* (Loew), requires an acceptable fumigation program prior to being imported into the United States (USDA—APHIS, 1976). The ban by the Environmental Protection Agency (EPA) on the use of the fumigant ethylene dibromide (EDB) for controlling this citrus pest (*Fed. Regist.* 1984) has necessitated finding a suitable substitute to provide quarantine security. Studies in 1979 suggested that methyl bromide (MB) could be a possible substitute for EDB (Benschoter, 1979). Reports by Benschoter et al. (1984) and Williamson et al. (1986) concluded that MB could be used successfully to fumigate grapefruit against the pests *A. suspensa* Loew and *A. ludens*.

In 1981, a rapid sensitive headspace analysis method for determining residues of MB by gas chromatography in fumigated grapefruit was developed (King et al., 1981), but no information was found in King et al. (1981) or in a full literature search on residues of MB in mangos.

This study was initiated (1) to assess the validity of the citrus method for residue analysis on and in the mango and (2) to determine residues of MB in the mango following fumigation with different doses of MB.

MATERIALS AND METHODS

Fruit. Mango variables used in this investigation were Haden, Tommy Atkins, and Kent. All were imported from Mexico.

Fumigation. Each dosage of MB, replicated five times (one fruit/replicate), was separately applied for 2 h at 16, 48, 56, and 64 g/m³, respectively, in a 0.71-m³ chamber, designed and constructed as described by Williamson et al. (1986). Commercially available MB in pressurized 4.54-kg tanks was passed through a chilled 2.0 m × 6.4 mm (i.d.) coiled copper tubing. A calculated amount of the liquified MB was allowed to flow into a graduated volumetric glass chamber. The MB in the glass chamber was then allowed to vent rapidly into the fumigation chamber. The temperature of the chamber was kept at 20 ± 2 °C. A halide detector was used to monitor the MB in the chamber. At 2 h after fumigation, the chamber was evacuated to the atmosphere for 5 min by an exhaust blower prior to removing the treated fruit. The fruit were then placed in a fume hood with a 24.4 m/min face velocity. At various time intervals after evacuation of the chamber fruit were removed from the fume hood and samples taken for MB residue analysis.

Headspace Analysis. At 0.17, 1, 2, 5, 24, and 48 h after fumigation at the desired dose, a 50-g peel or pulp sample and 100 mL of distilled water were blended in a 500-mL Eberbach blender container for 3 min at low speed. The container was a standard Waring glass with a modified Teflon-lined screw cap