Crystal and Molecular Structure of Organophosphorus Insecticides. 14. Iodofenphos

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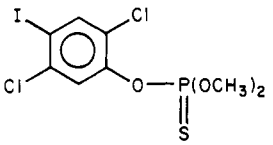
The crystal and molecular structure of iodofenphos [jodfenphos, *O,O*-dimethyl *O*-(2,5-dichloro-4-iodophenyl) phosphorothioate, $(H_3CO)_2P(S)OC_6H_2Cl_2I$, monoclinic, $P2_1/c$, a = 11.999 (3) Å, b = 8.263 (2) Å, c = 14.032 (4) Å, β = 98.89 (4)°, Z = 4, Mo Kα radiation] has been determined by three-dimensional X-ray analysis. The structure was solved by Patterson, Fourier, and full-matrix least-squares techniques to a final R = 0.052 for 1479 observed reflections. The phosphorus to hydrogen distances are 3.13 and 5.59 Å. Comparisons with other similarly halogen-substituted organophosphates show variations in the bond lengths about the phenoxy oxygen and the no. 4 carbon. The presence of an inversion center in the unit cell implies the existence of a racemic mixture in the crystal.

The crystal and molecular structure of iodofensphos was



undertaken as part of an ongoing study of the structures of organophosphate (OP) insecticides (Baughman and Jacobson, 1975, 1976, 1978). By investigating any subtle differences in the geometries of very similar OP's, one should obtain better insight into any structure–activity relationships. The structures of iodofenphos, ronnel (Baughman and Jacobson, 1975), and bromophos (Baughman and Jacobson, 1976) differ in their structural formulas by having an I, Cl, or Br in the 4 position.

EXPERIMENTAL SECTION

Crystal Data. From a 99.5% pure sample of the title compound a rectangular prismatic crystal with approximate dimensions 0.10 × 0.29 × 0.26 mm was chosen and mounted on a glass fiber by using Elmer's Glue-All. Subsequent experimental work was essentially as previously described (Baughman and Jacobson, 1975).

The lattice constants were obtained from a least-squares refinement based on the precise ±2θ (24° < |2θ| < 33°) measurements of 17 strong, independent reflections. at 27 °C by use of graphite-monochromated Mo Kα radiation (λ = 0.71002 Å) a = 11.999 (3) Å, b = 8.263 (2) Å, c = 14.032 (4) Å, and β = 98.89 (4)°.

Collection and Reduction of X-ray Intensity Data. The data were collected at 27 °C with graphite-monochromated Mo Kα radiation on an automated four-circle diffractometer designed and built in the Ames Laboratory and previously described by Rohrbaugh and Jacobson (1974). (This unit utilized a Datex circle.) All data within a 2θ sphere of 45° in the hkl, $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$, and $h\bar{k}\bar{l}$ octants were measured by using an ω step scan technique.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 75 reflections. These standard reflections were not observed to vary significantly throughout the entire period of data collection (~4 days). A total of 4681 reflections were recorded in this manner. Examination of the data revealed the following systematic absences: 0k0, when k is odd and $h0l$ when l is odd, uniquely identifying the space group as $P2_1/c$.

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The intensity data were corrected for Lorentz and polarization effects, and, since μ = 29.9 cm^{-1}, an absorption correction was applied. The estimated variance was calculated by

$$\sigma_I^2 = [C_T + 2C_B^2 + (0.03C_T)^2 + (0.03C_B)^2 + (0.03C_N)^2]/A^2$$

where C_T, C_B, and C_N represent the total, background, and net counts, respectively, A is the transmission factor, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calcualted by the finite difference method (Lawton and Jacobson, 1968). Equivalent data were averaged and the 1479 reflections with $|F_o| > 3\sigma(F_o)$ were retained for use in subsequent calculations.

Solutions and Refinement. The location of the iodine atom was obtained from a sharpened Patterson map (Powell and Jacobson, 1980). The remaining atoms were located by successive structure factor (Lapp and Jacobson, 1979) and electron density map calculations (Powell and Jacobson, 1980). The atomic positions were subsequently refined by a block-diagonalized least-squares procedure (Lapp and Jacobson, 1979), minimizing the function $\sum[\omega(|F_o| - |F_c|)^2]$, where $\omega = 1/\sigma_F^2$. This yielded a conventional discrepancy factor of $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.154 by using isotropic thermal parameters for all atoms. The scattering factors used were those of Hanson et al. (1960), modified for the real and imaginary parts of anomalous dispersion (Templeton, 1962). The scattering factors for hydrogen were those of Stewart et al. (1965).

As an electron density difference map did not reveal either the hydrogen positions or any electron density greater than approximately 0.5 e, the hydrogen positions were assigned as follows: ring hydrogens at 0.95 Å and methyl hydrogens in tetrahedral positions at 1.07 Å from the respective carbons. With the hydrogen positions fixed, subsequent anisotropic full-matrix least-squares refinement converged at R = 0.052. Since this refinement yielded slightly different nonhydrogen atom positions, new hydrogen positions were recalculated. Further refinement cycles did not significantly alter any atomic positions and R did not change.

The final positional parameters are listed in Table I. Standard deviations were calculated from the inverse matrix of the final least-squares cycle. Bond lengths and angles are listed in Tables II and III, respectively (Busing et al., 1964). A listing of the observed and calculated structure factor amplitudes are provided as supplementary material (see paragraph at end of paper regarding supplementary material).

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Table I. Final Fractional Unit Cell Positional Parameters for Iodofenphos

atom	x	y	z
I	0.63104 (6)[a]	0.50205 (9)	0.28658 (5)
Cl1	0.1859 (2)	0.6359 (4)	0.3514 (2)
Cl2	0.6052 (2)	0.1863 (3)	0.4416 (2)
S	0.1267 (3)	0.1007 (5)	0.3154 (2)
P	0.1259 (2)	0.1807 (3)	0.4423 (2)
O1	0.2013 (6)	0.3430 (8)	0.4687 (5)
O2	0.0122 (5)	0.238 (1)	0.4698 (5)
O3	0.1716 (7)	0.056 (1)	0.5221 (6)
C1	0.2976 (8)	0.374 (1)	0.4323 (7)
C2	0.3028 (8)	0.508 (1)	0.3739 (8)
C3	0.3983 (9)	0.544 (1)	0.3358 (8)
C4	0.4915 (8)	0.447 (1)	0.3532 (7)
C5	0.4887 (8)	0.309 (1)	0.4133 (7)
C6	0.3914 (8)	0.274 (1)	0.4526 (7)
C7	−0.065 (1)	0.344 (2)	0.4100 (9)
C8	0.173 (1)	0.094 (2)	0.6239 (9)
H1	0.3990	0.6377	0.2967
H2	0.3895	0.1826	0.4932

[a] Estimated standard deviations are given in parentheses for the least significant figures. Since the hydrogens were not refined, no standard deviations are given. ESD's in later tables include the errors in the lattice constants.

Table II. Selected Interatomic Distances (Angstroms)

C1-C2	1.39 (1)	C4-I	2.09 (1)
C2-C3	1.37 (2)	C5-Cl2	1.72 (1)
C3-C4	1.37 (1)	P-S	1.901 (4)
C4-C5	1.42 (1)	P-O1	1.628 (7)
C5-C6	1.40 (1)	P-O2	1.548 (7)
C6-C1	1.39 (1)	P-O3	1.561 (8)
C1-O1	1.36 (1)	O2-C7	1.44 (1)
C2-Cl1	1.74 (1)	O3-C8	1.46 (1)

Table III. Selected Interatomic Angles (Degrees)

	Angles		
C1-C2-C3	121.4 (9)	Cl2-C5-C4	121.1 (8)
C2-C3-C4	121 (1)	Cl2-C5-C6	118.9 (8)
C3-C4-C5	118.7 (9)	C1-O1-P	123.0 (6)
C4-C5-C6	120.0 (9)	O1-P-S	114.6 (3)
C5-C6-C1	119.7 (9)	O1-P-O2	99.9 (4)
C6-C1-C2	119.2 (9)	O1-P-O3	105.2 (4)
O1-C1-C2	119.4 (9)	S-P-O2	118.2 (3)
O1-C1-C6	121.4 (9)	S-P-O3	112.9 (4)
Cl1-C2-C1	118.9 (8)	O2-P-O3	104.4 (5)
Cl1-C2-C3	119.7 (8)	P-O2-C7	123.3 (7)
I-C4-C3	119.0 (8)	P-O3-C8	120.5 (9)
I-C4-C5	122.2 (7)		
	Torsional Angles[a]		
C2-C1-O1-P	116.9 (8)	O1-P-O3-C8	56.9 (9)
C6-C1-O1-P	−63 (1)	O1-P-O2-C7	77.6 (9)
C1-O1-P-S	−32.7 (8)	C8-O3-P-O2	−48 (1)
S-P-O3-C8	−177.4 (9)	O3-P-O2-C7	−173.8 (9)
S-P-O2-C7	−47 (1)		

[a] Signs per Klyne and Prelog (1960).

DESCRIPTION OF STRUCTURE AND DISCUSSION

The nonhydrogen atoms constituting the phenoxy group are essentially planar as the absolute values of the maximum, minimum, and average deviations from a least-squares plane are 0.057, 0.000, and 0.025 Å, respectively [see also Figure 1 (Johnson, 1971)].

As previously noted (Baughman and Jacobson, 1978), certain P···δ+ distances may give some insight into the toxicity/activity of OP's. Although the quantum mechanical calculations are essentially not available for larger molecules containing a heavy atom, it is likely that H1, H2, C3, C4, and C5 are all δ+ as they are in ronnel and ronnel oxon (Baughman and Jacobson, 1978). The partial charge densities from a CNDO/2 calculation (Pople and Beveridge, 1970) for H1, H2, C3, C4, and C5 in *ronnel* are respectively 0.065, 0.043, 0.129, 0.057, and 0.033. One would expect these atoms to have similar δ+ charges in iodofenphos. The P···H1, P···H2, P···C3, P···C4, and P···C5 distances are as follows: 5.589 (3), 3.133 (3), 4.84 (1), 5.23 (1), and 4.56 (1) Å.

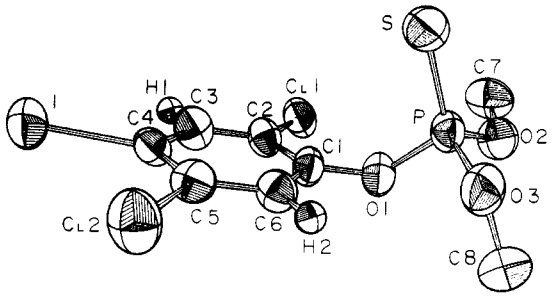

Figure 1. The iodofenphos molecule showing 50% probability ellipsoids, 30% for the hydrogens.

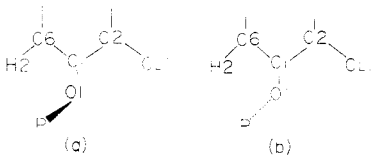

Figure 2. Partial views of the enantiomers of iodofenphos. View a corresponds to the molecule whose coordinates are in Table I; view b corresponds to the molecule related by the crystallographic center of inversion.

Iodofenphos shows a number of similarities and contrasts with ronnel and bromophos. The methoxy groups in ronnel exhibit a much larger thermal vibration than either iodofenphos or bromophos. In iodofenphos and bromophos the methyl groups are pointed in opposite directions; in ronnel both are pointed toward the sulfur side of the thiophosphate group. The magnitudes of the C6–C1–O1–P angles in ronnel, bromophos, and iodofenphos are 69.4, 78.4, and 63°, respectively. No trend is evident. In fact, the difference may not even be significant.

Some of the interatomic distances in the phenoxy group are noteworthy. Although the C–Cl distances in ronnel, bromophos, and iodofenphos are essentially the same ($\leq 3\sigma$), carbon–carbon distances in the ring *do* seem to be affected by changing the substituent at the 4 position. In ronnel the C3–C4 and C4–C5 distances are the same whereas the C4–C5 distance is significantly ($>3\sigma$) longer in bromophos and iodofenphos (Table II). These distances are about the carbon atom which is bonded to the halogen which makes the three structural formulas different. The C1–O1 and O1–P distances in ronnel, bromophos, and iodofenphos, respectively, also show a trend as follows: C1–O1, 1.400 (6), 1.391 (9), and 1.36 (1); O1–P, 1.592 (4), 1.607 (6), and 1.628 (7). The simultaneous shortening of the C1–O1 bond and the lengthening of the O1–P bond very likely affect phosphorylation (Clark et al., 1964) of acetylchlolinesterase.

Iodofenphos and ronnel separately crystallize in a centrosymmetric space group; bromophos does not. This implies that iodofenphos and ronnel exist in the crystal as a racemic mixture; the presence of *R* and *S* molecules leads to the crystallographic center of symmetry. Consequently, the iodofenphos molecule which is related via the center of inversion (=mirror + rotation of 180°) to the molecule in Table I has torsional angles which are the negative of those in Table III. Specifically, half of the molecules have the thiophosphate group "above" the ring (Figure 2a) and the other half "below" (Figure 2b). Perhaps one of the iodofenphos or ronnel configurations is biologically more active with regard to either AChE inhibition or oxon

formation and could be isolated for future investigations.

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Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

LITERATURE CITED

Baughman, R. G.; Jacobson, R. A. *J. Agric. Food Chem.* **1975**, *23* (4), 811.
Baughman, R. G.; Jacobson, R. A. *J. Agric. Food Chem.* **1976**, *24* (5), 1036.
Baughman, R. G.; Jacobson, R. A. *J. Agric. Food Chem.* **1978**, *26* (2), 403.
Busing, W. R.; Martin, K. O.; Levy, H. A. "OR FFE, A Fortran Crystallographic Function and Error Program"; U.S. Atomic Energy Commission, Oak Ridge National Laboratory: Oak Ridge, TN, 1964; Report ORNL-TM-306.
Clark, V. M.; Hutchinson, D. W.; Kirby, A. I.; Warren, S. G. *Angew. Chem.* **1964**, *76*, 704.
Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1960**, *17*, 1040.
Johnson, C. K. "OR TEP-II: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations"; U.S. Atomic Energy Commission, Oak Ridge National Laboratory: Oak Ridge, TN, 1971; Report ORNL-3794 (Second Revision with Supplemental Instructions).
Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 521.
Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program"; Ames Laboratory, DOE, Iowa State University: Ames, IA, 1979.
Lawton, S. L.; Jacobson, R. A. *Inorg. Chem.* **1968**, *7*, 2124.
Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.
Powell, D. R.; Jacobson, R. A. "FOUR: A Generalized Fourier Program"; Ames Laboratory, DOE, Iowa State University: Ames, IA, 1980.
Rohrbaugh, W. J.; Jacobson, R. A. *Inorg. Chem.* **1974**, *13* (11), 2535.
Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
Templeton, D. H. In "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1962; Vol. III, Table 3.3.2c, pp 215–216.

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Fate and Impact of Wood Preservatives in a Terrestrial Microcosm

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The transport and effects of ^{14}C-labeled wood preservatives [creosote with labeled phenanthrene or acenaphthene, pentachlorophenol, and bis(tri-*n*-butyltin) oxide] impregnated in wood posts were examined in a terrestrial microcosm chamber (TMC-II) in comparison to a reference compound, the insecticide dieldrin. The TMC-II contained a Willamette Valley topsoil, ryegrass, invertebrates, and a gravid gray-tailed vole (*Microtus canicaudus*). Approximately 2.5 months after introduction of the posts, 95% of the chemicals remained in the posts. Of the material released into the ecosystem, most remained in the upper soil layer immediately surrounding the posts. Concentrations in plants ranged from 0.7 ppm for dieldrin to 8.8 ppm for phenanthrene. Residue accumulation by the invertebrates was highly variable. Of the chemicals tested, creosote accumulated in the vole to the greatest extent (e.g., whole body concentrations of 7.2 and 37.0 ppm for phenanthrene and acenaphthene, respectively). Only dieldrin exhibited any acute toxic effects (e.g., cricket survival).

The preservation of wood from fungal and insect attack is a major function of pest control. Chemical preservatives can extend the useful life of wood by decades, thereby reducing the demand on wood production. Although wood is a renewable resource, the limitations on resource renewal make it necessary to protect our timber supply. However, there are problems associated with each of the wood preservatives. Creosote is a potential carcinogen included in a Rebuttable Presumption Against Reregistration (*Fed. Regist.*, 1978). Practically nothing is known about the fate of creosote in the environment resulting from treated telephone poles, bridge structures, railroad ties, and other wooden materials. Aquatic studies on pentachlorophenol indicate there may be environmental damage caused by the parent material and congeners in the technical product. Bis(tri-*n*-butyltin) oxide, which is not registered as a wood preservative in the United States, is used as such mostly in Europe on above-ground structures. It is quite toxic to fish, but little is known of its terrestrial fate and effects. Chlordane and heptachlor (cyclodiene insecticides) have been banned except for structural uses, but even this limited usage is under dispute.

Wood preservation represents the extreme of controlled release of a chemical. Barring deterioration by pests, accident, or storm, a wood structure is expected to have utility for decades. Wood preservative agents act as toxicants, feeding inhibitors, or growth inhibitors for boring animals (i.e., termites, carpenter ants, woodpeckers and wood-rotting fungi). Chemical release is not desirable in this type of application. Adverse effects can be anticipated from exposure to these chemicals if they are released into the environment. However, the characteristically slow release rate of wood preservatives makes the evaluation of that release rate and potential impacts extremely difficult. The terrestrial microcosm chamber (TMC) is a

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