position of the *N*-propyl groups present in the molecule (Figure 1a), and the two azobenzenes III and IV were analogous to the azoxybenzenes I and II, respectively (Figure 1a). Photolysis of trifluralin in benzene solution yielded azobenzenes and azoxybenzenes in sufficient quantities to be a reasonably convenient route to their synthesis. Another compound, isolated in fairly large yield, was VII (Figure 1a). These compounds represented the major photolysis products out of some 30–40 compounds that were demonstrated by thin-layer chromatography.

Because of the large number of azo and azoxy compounds which have been shown to produce significant biological effects (Miyadera, 1975), the evaluation of the biological activity of these compounds is of some significance. Several azo and azoxy compounds such as 4-dimethylaminoazobenzene (DAB) are known to be carcinogenic. Although the mechanism of carcinogenicity of these compounds is not well understood, it is known that the biological activity is dependent upon the pattern of ring substitution; for instance, the 2-methyl derivative of DAB is noncarcinogenic (Chaveau et al., 1977). Quantities of three products I, II, and III were sufficient for mutagenesis testing by the method of Ames et al. (1975). None of the three compounds tested exhibited significant toxicity at concentrations from 0.001 to 1.0 mg/plate.

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Crystal and Molecular Structures of Organophosphorus Insecticides. 13. *S*-Isopropyl *O*-Methyl *O*-(3,5,6-Trichloro-2-pyridyl) Phosphoramidothioate and Dimethoate

Rick L. Lapp and Robert A. Jacobson*

The crystal and molecular structures of *S*-isopropyl *O*-methyl *O*-(3,5,6-trichloro-2-pyridyl) phosphoramidothioate, $C_9H_{12}N_2O_2PSCl_3$, and dimethoate [*O,O*-dimethyl *S*-(*N*-methylcarbamoyl)methyl phosphorodithioate], $C_5H_{12}NO_3PS_2$, have been determined by three-dimensional X-ray analysis. The former compound crystallizes in the triclinic space group $P\bar{1}$ with a = 10.319 (5) Å, b = 10.730 (6) Å, c = 8.44 (4) Å, α = 99.01 (2)°, β = 114.02 (1)°, and γ = 62.64 (1)° with Z = 2, and the latter compound crystallizes in the monoclinic space group $P2_1$ with a = 6.574 (2) Å, b = 9.354 (2) Å, c = 9.885 (2) Å, and β = 107.4 (2)° with two molecules per unit cell. The structures were refined by a full-matrix, least-squares procedure to final residual indices of R = 0.058 and 0.068, respectively, using reflections with $F_o > 3\sigma(F_o)$. Atomic charge densities were calculated via CNDO/2 methods in order that positive charge center separations as well as geometric factors could be compared between these insecticides, acetylcholinesterase, and previous insecticides studied in this series.

In order to understand acetylchlolinesterase (AChE) inhibition by organophosphorus (OP) insecticides, it is desirable to know the three-dimensional structure of the active sites of this enzyme. Although the complexity of AChE makes direct elucidation of the structure difficult, accurate structural information on a large number of smaller molecules which interact strongly with the active sites of AChE should allow inferences to be made about the topography of the AChE molecule. A series of such structural studies has been carried out in this laboratory (Baughman and Jacobson, 1975, 1976, 1977, 1978a,b;

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Baughman et al., 1978; Gifkins and Jacobson, 1976; Rohrbaugh and Jacobson, 1976, 1977, 1978; Beckman and Jacobson, 1979) via single-crystal X-ray diffraction techniques. The purpose of this work is to build up a body of information about structurally similar molecules in order to find correlations between the toxicity/activity of an insecticide and its structure and electronic features. As has been discussed, the effectiveness of an insecticide is affected by gross topological features, relative charge densities on the sites binding to the enzyme, and esteratic–anionic site separations. Such information should aid in the construction of more specific insecticides conforming to the most favorable configuration to interact with the target AChE molecule.

Ronnel, bromophos, ronnel oxon, and crufomate (the first, second, fourth, and sixth references, respectively, above) are all phenoxy OP's. The study of heteronuclear ring systems such as fospirate, chlorpyrifos, and Dowco 214 (the third, fifth and eleventh references above) was begun in order to note any conformational similarities and/or dissimilarities resulting from the replacement of one or more ring carbon atoms with nitrogen. Continuing with the latter series, we carried out a crystal structure analysis of isopropyl O-methyl O-(3,5,6-trichloro-2-pyridyl) phosphoroamidothioate, hereafter referred to as IPAT, an amido homologue of Dowco 214. Although this compound was never commercially produced, it has been shown to have good insecticidal properties (Osborne, 1979).

Dimethoate is a highly species specific insecticide with a toxicity ratio (LD_{50} mouse/LD_{50} housefly) of 280 and an oral LD_{50} for rats of over 600 mg/kg. It might also be expected to show several structural similarities to azinphos-methyl ($LD_{50} = 16$ mg/kg) and amidithion ($LD_{50} = 600$ mg/kg, the eighth and ninth references, respectively, above). For these reasons, a crystal of dimethoate (dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate) was also selected for three-dimensional analysis.

EXPERIMENTAL SECTION

Crystal Data. A rectangular prismatic crystal of IPAT with approximate dimensions $0.40 \times 0.44 \times 0.30$ mm was selected and mounted on the end of a glass fiber with Elmer's Glue-All and subsequently attached to a standard goniometer head. From three preliminary ω-oscillation photographs taken on an automated four-circle X-ray diffractometer at various χ and ϕ settings, 10 independent reflections were selected and their coordinates were input to an automatic indexing algorithm (Jacobson, 1976). The resulting reduced cell and reduced cell scalars indicated triclinic symmetry, and observed layer line spacings were within experimental error of those predicted for this cell.

A rectangular prismatic crystal of dimethoate with approximate dimensions $0.15 \times 0.21 \times 0.25$ mm was selected and mounted inside a 0.30-mm thin-walled Lindeman glass capillary. The coordinates of seven independent reflections were input to the indexing algorithm, again using three ω-oscillation photographs. The resulting reduced cell and reduced cell scalars indicated monoclinic symmetry, and observed layer line spacings were within experimental error of those predicted for this cell.

The lattice constants for each cell were refined by least-squares methods based on precise $\pm 2\theta$ measurements of 15 strong independent reflections, using Mo K_α radiation, $\lambda = 0.70954$ Å, at 25 °C, yielding $a = 10.319$ (5) Å, $b = 10.730$ (6) Å, $c = 8.449$ (4) Å, $\alpha = 99.01$ (2)°, $\beta = 114.02$ (1)° and $\gamma = 62.64$ (1)° for IPAT, and $a = 6.574$ (2) Å, $b = 9.354$ (2) Å, $c = 9.885$ (2) Å, and $\beta = 107.42$ (2)° for dimethoate. For IPAT $d_c = 1.53$ g cm^{-3} with $Z = 2$, and for dimethoate $d_c = 1.31$ g cm^{-3} with $Z = 2$.

Collection and Reduction of X-ray Intensity Data. Data were collected at room temperature on an automated four-circle diffractometer designed and built in this laboratory (Rohrbaugh and Jacobson, 1974). The diffractometer is interfaced to a PDP-15 computer in a time-sharing mode and is equipped with a scintillation counter. Graphite-monochromated Mo K_α radiation was used for data collection.

As a general check on electronic and crystal stability, the intensities of six standard reflections for IPAT and three standard reflections for dimethoate were remeasured every 75 reflections. These standard reflections were not observed to vary throughout the entire data collection period.

The data were collected by an ω-scan technique. For IPAT all data (2812 reflections) within a 2θ sphere of 50° were measured in the hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ octants, and for dimethoate all data (953 reflections) within a 2θ sphere of 45° were measured in the hkl and $hk\bar{l}$ octants.

The intensity data were corrected for Lorentz–polarization effects. However, since $\mu = 8.33$ cm^{-1} for IPAT and $\mu = 5.59$ cm^{-1} for dimethoate, the minimum and maximum transmission factors differed by less than 5% and no absorption corrections were made. The estimated variance in each intensity was calculated by

$$\sigma_I^2 = C_T + k_t C_B + (0.03 C_T)^2 + (0.03 C_B)^2$$

where C_T, k_t, and C_B represent the total count, a counting time factor, and the background count, respectively; the factor 0.03 represents an estimate of nonstatistical errors. The estimated standard deviations in the structure factors were calculated by the finite difference method (Lawton and Jacobson, 1968). Equivalent zone data were averaged and 2173 reflections for IPAT and 737 reflections for dimethoate for which $F_o > 3\sigma(F_o)$ were retained for structural refinement.

SOLUTION AND REFINEMENT

a. IPAT. A statistical test of the IPAT data (Howells et al., 1950) indicated centric symmetry and the space group $P\bar{1}$ was assumed. The structure was determined by using a direct method program written in this laboratory, utilizing a symbolic addition approach (Karle and Karle, 1966). Fourteen nonhydrogen atoms were located on the resulting E map, using 300 reflections with $|E| > 1.5$. The positions of the remaining nonhydrogen atoms were determined by successive structure factor (Busing et al., 1962) and electron-density map calculations (Hubbard et al., 1971). These atomic positions were subsequently refined by a full-matrix, least-squares procedure (Busing et al., 1962), minimizing the function $\sum \omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma_F^2$. This refinement yielded a conventional residual index of $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.074$. At this stage all 18 nonhydrogen atoms had been refined, using anisotropic thermal parameters. 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 factor for hydrogen was that of Stewart et al. (1965).

The aromatic hydrogen position was calculated at 0.95 Å from the corresponding carbon atom (C3), and hydrogens were placed 1.0 Å from N2 and C6, assuming tetrahedral geometry. For each methyl group a ring of six hydrogen positions lying in a plane perpendicular to the A–Me bond was calculated such that the C–H distances were 1.0 Å. Each methyl hydrogen was assigned half-occupancy, and all isotropic hydrogen temperature factors were set equal to 4.5 Å^2.

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Table I. Final Atomic Positional Parameters for IPAT^a

atom	x	y	z
Cl1	0.6195 (2)	0.3810 (1)	−0.2675 (2)
Cl2	0.7011 (2)	0.7296 (1)	0.2577 (2)
Cl3	0.8302 (2)	0.4756 (1)	0.5173 (2)
S	0.6139 (1)	0.1145 (1)	0.2451 (1)
P	0.7517 (1)	0.0589 (1)	0.1217 (1)
O1	0.7342 (4)	0.1831 (3)	0.0144 (4)
O2	0.9345 (3)	0.0006 (3)	0.2328 (4)
N1	0.7783 (4)	0.3298 (3)	0.2421 (5)
N2	0.7265 (4)	−0.0530 (3)	−0.0250 (4)
C1	0.7311 (5)	0.3103 (4)	0.0751 (6)
C2	0.6772 (5)	0.4134 (4)	−0.0493 (6)
C3	0.6687 (5)	0.5441 (4)	0.0069 (6)
C4	0.7155 (5)	0.5659 (4)	0.1843 (7)
C5	0.7720 (5)	0.4553 (4)	0.2977 (6)
C6	0.8211 (6)	−0.1188 (6)	−0.1340 (6)
C7	0.8732 (7)	−0.2758 (6)	−0.1354 (8)
C8	0.7276 (8)	−0.0503 (8)	−0.3167 (7)
C9	0.0137 (6)	−0.1259 (5)	0.3419 (7)

^{a} In this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures.

Table II. Bond Distances (Å) for IPAT

P–S	1.923 (2)	C1–C2	1.400 (7)
P–O1	1.629 (4)	C2–C3	1.383 (6)
P–O2	1.577 (3)	C3–C4	1.393 (7)
P–N2	1.614 (3)	C4–C5	1.390 (7)
O2–C9	1.456 (6)	C5–N1	1.336 (6)
N2–C6	1.481 (7)	N1–C1	1.309 (6)
C6–C7	1.514 (9)	C2–Cl1	1.723 (5)
C6–C8	1.531 (7)	C4–Cl2	1.728 (5)
O1–C1	1.371 (6)	C5–Cl3	1.714 (5)

Subsequent anisotropic least-squares refinement without varying the hydrogen parameters converged to R = 0.058. Since the nonhydrogen atom parameters shifted slightly, all of the hydrogen positions were recalculated. Further refinement cycles did not significantly alter any atomic parameters and the residual index did not change.

b. Dimethoate. Examination of the dimethoate data revealed systematic absences for 0k0 when k = 2n + 1 and a statistical test (Howells et al., 1950) indicated acentric symmetry; hence the space group was determined to be $P2_1$.

The position of one sulfur atom was obtained by analysis of a sharpened three-dimensional Patterson function. The remaining atoms were found by successive structure factor (Busing et al., 1962) and electron-density map calculations (Hubbard et al., 1971). These atomic positions were subsequently refined by the same methods used for IPAT until the residual index R was 0.069. The hydrogen positions were then calculated as before with bond lengths of 1.0 Å. The isotropic hydrogen temperature factors were set equal to 4.0 Å^2. Further refinement cycles without varying the hydrogen parameters did not significantly alter any atomic parameters and the residual index converged to R = 0.068.

The final positional parameters for IPAT and dimethoate are listed in Tables I and V, respectively. Standard deviations were calculated from the inverse matrix of the final least-squares cycle. Bond lengths and angles for IPAT are listed in Tables II and III, respectively, and those for dimethoate are listed in Table VI (Busing et al., 1964). Torsional angles for IPAT are given in Table IV.

DESCRIPTION OF STRUCTURE AND DISCUSSION

a. IPAT. The pyridoxyl group in IPAT, shown in Figure 1 (Johnson, 1971), is essentially planar. The greatest deviation from the least-squares plane defined by

Table III. Bond Angles (deg) for IPAT

S–P–O1	116.4 (1)	C3–C4–C5	119.0 (4)
S–P–O2	117.4 (1)	C4–C5–N1	122.2 (4)
S–P–N2	113.2 (2)	C5–N1–C1	118.7 (4)
O1–P–O2	97.6 (2)	Cl1–C2–C1	121.5 (3)
O1–P–N2	102.9 (2)	Cl1–C2–C3	120.2 (4)
O2–P–N2	107.4 (2)	Cl2–C4–C3	119.3 (4)
P–O2–C9	119.0 (4)	Cl2–C4–C5	121.7 (4)
P–N2–C6	124.9 (4)	Cl3–C5–C4	121.3 (3)
P–O1–C1	126.8 (3)	Cl3–C5–N1	116.4 (4)
O1–C1–C2	116.7 (4)	N2–C6–C7	109.7 (6)
O1–C1–N1	119.9 (4)	N2–C6–C8	110.4 (4)
C1–C2–C3	118.3 (4)	C7–C6–C8	112.4 (5)
C2–C3–C4	118.3 (4)	N1–C1–C2	123.4 (4)

Table IV. Torsional Angles (deg) for IPAT

P–O1–C1–C2	−164.9	S–P–O2–C9	61.2
P–O1–C1–N1	15.6	S–P–N2–C6	−177.0
C1–O1–P–S	49.1	O1–P–O2–C9	−173.7
C1–O1–P–N2	173.5	O1–P–N2–C6	56.4
C1–O1–P–O2	−76.6		

Table V. Final Atomic Positional Parameters for Dimethoate

atom	x	y	z
S1	0.3636 (7)	0.1397 (0)	0.1037 (5)
S2	−0.0399 (4)	0.2210 (7)	0.2089 (3)
P	0.2804 (5)	0.2508 (7)	0.2384 (3)
O1	0.402 (1)	0.229 (1)	0.3996 (7)
O2	0.232 (1)	0.419 (1)	0.2406 (9)
O3	−0.041 (2)	0.145 (1)	0.510 (1)
N	0.065 (2)	0.366 (1)	0.593 (1)
C1	0.444 (2)	0.085 (2)	0.458 (2)
C2	0.250 (3)	0.504 (2)	0.114 (2)
C3	−0.087 (2)	0.339 (1)	0.344 (1)
C4	−0.015 (2)	0.273 (1)	0.491 (1)
C5	0.133 (3)	0.321 (2)	0.743 (2)
H	0.0837	0.4685	0.5678
C3H1	0.017	0.423	0.350
C3H2	0.767	0.380	0.333
C1H1	0.3082	0.0442	0.4704
C1H2	0.5558	0.0871	0.5508
C1H3	0.4898	0.0223	0.3901
C2H1	0.3129	0.6027	0.1344
C2H2	0.0919	0.5106	0.0847
C2H3	0.2983	0.4594	0.0376
C5H1	0.0047	0.3109	0.7770
C5H2	0.2329	0.3923	0.8024
C5H3	0.2067	0.2254	0.7516

Table VI. Bond Distances (Å) and Angles (deg) for Dimethoate

Distances			
P–S1	1.894 (6)	S2–C3	1.83 (1)
P–S2	2.056 (4)	C3–C4	1.52 (1)
P–O1	1.568 (7)	C4–O3	1.23 (1)
P–O2	1.597 (6)	C4–N	1.32 (1)
O1–C1	1.46 (2)	N–C5	1.48 (1)
O2–C2	1.44 (2)		

Angles			
S1–P–O1	118.4 (3)	P–O2–C2	121.4 (4)
S1–P–O2	117.6 (4)	P–S2–C3	101.8 (2)
S1–P–S2	108.9 (3)	S2–C3–C4	112.4 (2)
O1–P–O2	94.6 (4)	C3–C4–O3	122 (1)
O1–P–S2	108.4 (2)	C3–C4–N	114 (1)
O2–P–S2	107.7 (3)	C4–N–C5	121 (1)
P–O1–C1	120.1 (4)	O3–C4–N	125 (1)

the six-membered ring, the three attached chlorines and O1 is 0.042 Å, in good agreement with the results from previous pyridoxy OP structure determinations. The crystal packing may be regarded as primarily van der Waals in nature as all intermolecular distances are larger than or on the order of the sum of the van der Waals radii. Consequently, the molecular configuration is not likely to be a result of crystal packing.
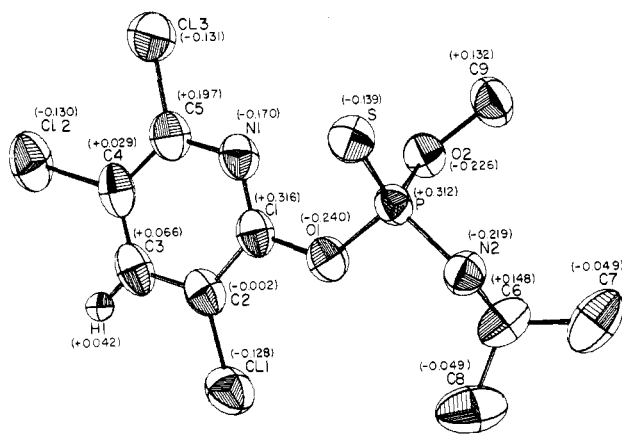
Figure 1. View of IPAT with partial charge densities obtained from CNDO/2 molecular orbital calculations. The thermal ellipsoids are drawn at the 50% probability level.

Figure 2. View of the dimethoate molecule with methyl and ethyl hydrogens omitted. Charge densities are from CNDO/2 calculations and ellipsoids are at 50% probability level.

As has been found in previous studies of OP insecticides, the O1–C1 distance is significantly shorter than the O2–C9 distance, while the P–O1 bond is longer than the P–O2 bond. This is consistent with overlap of a p_z orbital on O1 with the ring system leading to a weakening of the P–O1 bond, an effect which should enhance phosphorylation (Clark et al., 1964). In addition, the P–O1 bond in IPAT is longer than in any other OP studied thus far; this is apparently a result of replacing an oxygen with nitrogen in the phosphate group. IPAT, like the other pyridoxy OP insecticides chlorpyrifos, fospirate, and Dowco 214, has a C1–O1 bond length significantly shorter than the corresponding bond in the phenoxy insecticides; this appears to be a result of the replacement of a ring carbon by the more electronegative nitrogen. The geometry about the phosphorus atom is distorted tetrahedral such that the S=P–X (X = O or N) angles are all greater than the tetrahedral angle of 109.47°, while the O–P–O and O–P–N angles are all less than 109°.

The internal ring angles are all identical with their counterparts in the other pyridoxy insecticides. Those angles with nitrogen as a terminal atom are greater than 120°, while the other angles are all less than 120°. The angle between the normal to the ring and the P=S vector is 33.4°, which is in the range of 20–40° observed with most of the OP's studied.

The phosphorus and Cl1 atoms lie on opposite sides of a plane perpendicular to the ring and containing the O1–C1 bond. The position of the phosphorus is apparently influenced by several intramolecular interactions. The N1–S and N1–O2 distances are 3.45 and 3.14 Å, respectively, while the sums of the respective van der Waals radii are 3.35 and 2.9 Å (Pauling, 1960), and the Cl1–C8 distance of 4.2 Å is 0.4 Å greater than the sum of their van der Waals radii. The absence of a substituent on N1 allows the phosphate group to avoid Cl1. Due to the π character of the O1–C1 bond, suggested above, one would expect the phosphorus atom to lie in the plane of the aromatic group and indeed it is only 0.4 Å away from the least-squares plane defined by the ring and the four atoms attached to it. The resulting N1–C1–O1–P torsional angle (cf. Table IV) of 15.6° is in the range of 10–30° observed for the other pyridoxy OP's; the corresponding angle in the phenoxy OP's is in the range 50–80°.

In considering autotoxicosis through inhibition of AChE by organophosphorus insecticides, it is useful to recall that the nitrogen to carbonyl carbon distance in acetylcholine is estimated at 4.7 Å (Chothia and Pauling, 1969) when the molecule is in a proper configuration to react with
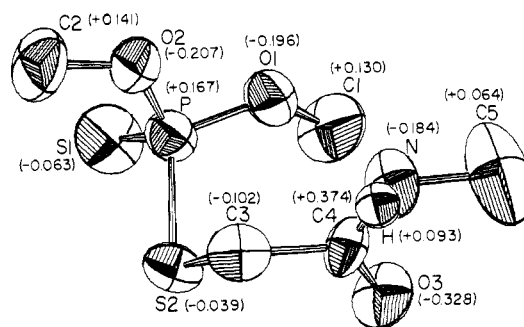
bovine erythrocyte AChE. The distance between anionic and esteratic sites of fly head AChE, however, may be as much as 1 Å longer than in the mammalian enzyme (Hollingworth et al., 1967). O'Brien (1963) has reported a range of 4.5–5.9 Å for the insect AChE. A comparison of intramolecular distances with these values should give some insight into the toxicity/activity of any insecticide. In addition to appropriate site separations, the two atoms involved must both have a net δ(+) charge to be in agreement with the AChE model of Krupka (1964).

CNDO/2 molecular orbital calculations (Pople and Beveridge, 1970) were carried out to compute approximate values for the charge density distribution in IPAT; the results are shown in Figure 1. Examination of this figure shows that there are four possible positive sites that could be involved in enzyme binding. They are C3, C4, C5, and H1, and the corresponding distances from the phosphorus are, respectively, 5.06, 5.24, 4.35, and 5.89 Å. It is interesting to note that these distances are all greater than the corresponding distances in the other pyridoxy OP's. With a charge of only 0.029e, C4 is probably not a major contributor to inhibition. C3 and H1 lie within the range of distances appropriate for insect AChE and are slightly longer than the mammalian distance. The C5 distance is too short for insect AChE but could be an important factor in reactions with mammalian AChE.

An examination of intramolecular interactions indicates that rotation about the P–O1 and O1–C1 bonds could occur in vivo. Rotation about the P–O1 bond would have no effect on the positive charge center separations but rotation about the O1–C1 bond to a P–O1–C1–N1 torsional angle of about 90°, similar to the solid state configuration of the phenoxy OP's, would decrease the P–C3 distance, for example, by about 0.25 Å, bringing it into a range suitable for interaction with mammalian AChE. Such a rotation would change the position of the phosphorus relative to other ring substituents and this could be an important factor.

b. Dimethoate. A drawing of the dimethoate molecule is provided in Figure 2. As was found for all previously studied organophosphorus insecticides, the geometry around the phosphorus atom in dimethoate can be described as a distorted tetrahedron and within experimental error is identical with that found in amidithion. The angles including the doubly bonded sulfur and the methoxy oxygens are about 9° greater than the tetrahedral angle, while the O1–P–O2 angle is 94.7°.

The results of a CNDO/2 molecular orbital calculation (Pople and Beveridge, 1970) are also shown in Figure 2. The notable centers of positive charge in dimethoate are on atoms C4, H (connected to the nitrogen) and C5 which are respectively 3.60, 4.35, and 5.40 Å from the phosphorus. The relatively small charge on C5 makes it an unlikely site

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for binding. The P–C4 distance is significantly shorter and the P–H distance longer than the corresponding distances in amidithion (3.91 and 4.24 Å, respectively). By contrast, the primary positive center separation distance in azinphos-methyl is 4.83 Å. The site separation for dimethoate would appear to be too short for efficient binding to the enzyme. On the basis of solid state configurations, one would expect the toxicity of dimethoate in mammalian systems to be similar to that of amidithion and much less than that of azinphos-methyl. A comparison of acute oral LD_{50}'s for rats confirms this trend: over 600 mg/kg for dimethoate, 600–660 for amidithion and 15 for azinphos-methyl (Eto, 1974). However, this distance argument would suggest that dimethoate would be significantly less effective in insect systems unless enzyme interactions with C5 are greater than we have assumed. It is generally accepted that the oxidized phosphate form is responsible for enzyme inhibition. Such oxidation, however, would most likely enhance the charge on the phosphorus and cause only minor perturbations on the rest of the molecular configuration.

An examination of intramolecular interactions indicates that the in vivo configuration could be quite different from the solid state configuration. By allowing free rotation about the S2–C3 bond the positive center separations could be increased to approximately 4.5 Å for P–C4 and 5.4 Å for P–H. In dimethoate, as in amidithion, delocalization effects cause the C3, C4, O3, N, and C5 atoms to be nearly coplanar, the greatest deviation from the least-squares plane defined by these five atoms being 0.02 Å. However, in the solid state configuration the angle between the normal to this plane and the P=S bond is 50.47°. For most of the OP's studied thus far, this angle is in the range of 20–40° and intramolecular interactions tend to restrict this angle to a narrow range even in solution. If the angle between the P=S bond and the planar moiety of the molecule is an important topographical factor in the binding of the insecticide to the enzyme, then some rotation to modify this angle and at the same time increase the positive site separations may be expected. Hence, for dimethoate, the most favorable configuration for interaction with the enzyme is most likely not the same as the solid state configuration.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes and the final nonhydrogen thermal parameters (11 pages). Ordering information is given on any current masthead page.

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