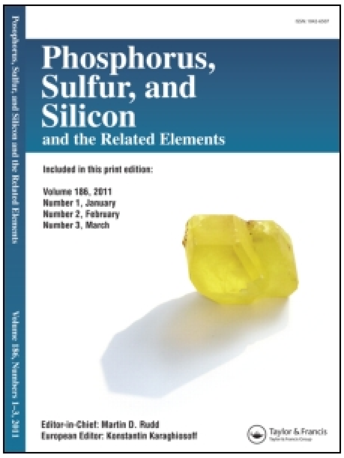

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CRYSTAL AND MOLECULAR STRUCTURE OF TWO INSECTICIDES: AMIDO-O,S-DIMETHYLTHIOPHOSPHATE AND N-ACETAMIDO-O,S-DIMETHYLTHIOPHOSPHATE

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CRYSTAL AND MOLECULAR STRUCTURE OF TWO INSECTICIDES: AMIDO-O,S-DIMETHYLTHIOPHOSPHATE AND N-ACETAMIDO-O,S-DIMETHYLTHIOPHOSPHATE

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The crystal and molecular structure of title compounds have been determined by means of X-ray analysis. The amido-O,S-dimethylthiophosphate (**1**) crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions $a = 5.374(3)$, $b = 9.220(4)$, $c = 13.847(5)$ Å and $\beta = 101.08(5)°$ at the −100°C. The N-acetamido-O,S-dimethylthiophosphate (**2**) crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 11.547(3)$, $b = 8.545(2)$, $c = 8.954(5)$ Å and $\beta = 93.03(4)°$. The structures were solved by direct methods and refined by least-squares to $R = 0.0493(1)$ and $0.0482(2)$. The coordination around P of the molecules (**1**) and (**2**) is distorted tetrahedrally. Molecules have nearly planar moieties HCSP=O and HNPOC (**1**), HCSP=O and HCC(O)NHPOC (**2**) with trans-orientation HCSP, CSP=O and NPOC groups. The angle between these planes is 85.3° (**1**) and 90.3° (**2**). There are intermolecular P=O . . . H—N hydrogen bonds in the crystal structures (**1**) and (**2**).

Key words: Amidothiophosphates; insecticides; crystal structure.

INTRODUCTION

Compounds of phosphorus are one of the most important and widely used classes of the modern pesticides. Many derivatives of the phosphorous, thiophosphorous, phosphoric, thio- and dithiophosphoric, phosphonic and thiophosphonic acids possess pesticidal properties and have been successfully used in agriculture.[1] The amido-O,S-dimethylthiophosphate (methamidophos[2]) and N-acetamido-O,S-dimethylthiophosphate (acephate)[3,4] insecticides are derivatives of thiophosphoric acid. Molecular and crystal structures of the amidothiophosphates are of a definite interest (for example, for understanding structure-activity relations), having been however insufficiently studied. In this paper we report results of the X-ray crystal structure analysis of the methamidophos and acephate.

RESULTS AND DISCUSSION

The molecular structures of amido-O,S-dimethylthiophosphate (**1**) and N-acetamido-O,S-dimethylthiophosphate (**2**) are shown in Figure 1 with the atom num-

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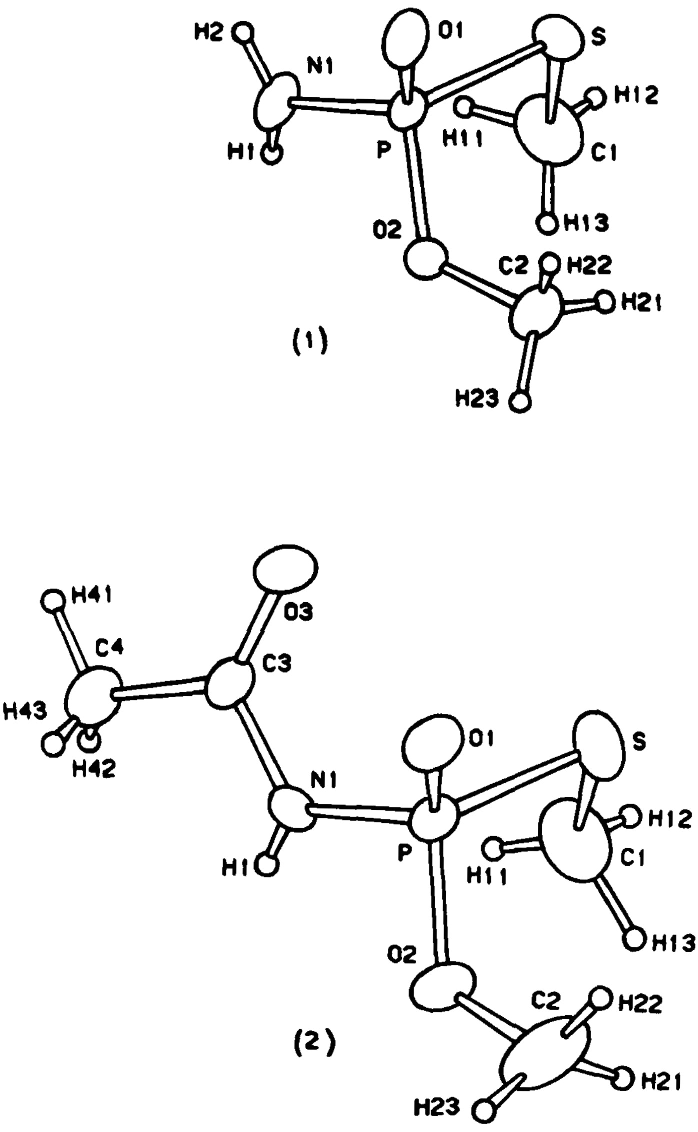


FIGURE 1 ORTEPII[12] drawings of (1) and (2). Non-H atoms are displayed as principal ellipses at 30% probability level, H atoms as small spheres of arbitrary size.

bering. Final atomic coordinates and equivalent isotropic thermal factors of (**1**) and (**2**) are given in Tables I and II, respectively. Bond lengths and bond angles are listed in Tables III and IV.

The coordination of the P atom in the molecules (**1**) and (**2**) is distorted tetrahedrally: the O1=P—O2, O1=P—N1, S—P—N1 angles are increased and the O1—P—S, O2—P—N1, S—P—O2 angles are decreased from the ideal value 109.5°. The P—N bond length of the molecule (**1**) is sufficiently shorted (1.609(2) Å) although it is known, that in the molecules of amidophosphates the corresponding bond lengths range from 1.61 to 1.71 Å.[5] The P—N bond length of molecule (**2**)

TABLE I

Positional parameters (X10^4, X10^3 for H atoms) with estimated standard deviations in parentheses and equivalent isotropic temperature factors (Å^2) for non-H atoms of the molecule (**1**)

	X	Y	Z	B
S	5139(2)	6476.2(8)	5828.4(6)	3.31(2)
P	5307(1)	8576.9(7)	6332.6(5)	2.32(1)
O1	7618(4)	9196(2)	6082(2)	3.61(4)
O2	5211(5)	8501(2)	7455(2)	3.47(4)
N1	2809(4)	9528(3)	5935(2)	3.75(5)
C1	2272(7)	5866(5)	6177(4)	5.97(9)
C2	7082(10)	7691(4)	8124(3)	6.0(1)
H1	140(6)	925(4)	615(2)	3.8(7)
H2	281(7)	988(4)	540(3)	6(1)
H11	99(14)	656(6)	582(5)	11(2)
H12	202(10)	515(6)	592(3)	8(1)
H13	237(7)	604(4)	689(3)	4.7(8)
H21	710(9)	680(5)	807(4)	7(1)
H22	867(8)	792(4)	795(3)	6.0(9)
H23	674	792	875	7

TABLE II

Positional parameters (X10^4, X10^3 for H atoms) with e.s.d'.s in parentheses and equivalent isotropic temperature factors (Å^2) for non-H atoms of the molecule (**2**)

		Y	Z	B
S	2106(1)	6000(2)	2590(1)	5.18(3)
P	3127(1)	4060(1)	2818(1)	3.02(2)
O1	3450(3)	3849(4)	4407(3)	4.01(7)
O2	4167(3)	4247(4)	1754(3)	4.31(7)
O3	1032(3)	2362(4)	3488(3)	4.71(7)
N1	2498(3)	2565(4)	1959(4)	2.86(7)
C1	1730(6)	5971(7)	607(6)	7.0(2)
C2	5101(5)	5331(8)	2153(7)	8.4(2)
C3	1532(3)	1837(5)	2432(5)	3.08(8)
C4	1152(4)	412(6)	1585(6)	4.6(1)
H1	268(2)	234(3)	137(3)	0.3(6)
H11	155(6)	511(10)	16(10)	14(3)
H12	137(4)	662(6)	49(5)	6(1)
H13	245(6)	667(9)	18(7)	11(2)
H21	484(6)	629(9)	146(9)	13(2)
H22	508(7)	586(10)	299(8)	13(2)
H23	593(7)	458(11)	241(9)	15(3)
H41	47(3)	-8(5)	202(4)	3.3(9)
H42	93(5)	47(8)	61(7)	9(2)
H43	169(5)	-7(8)	160(7)	10(2)

and P=O, P—O, P—S, C—S and C—O bond lengths of molecules (**1**) and (**2**) are normal.[5,6]

In the acetamide fragment of the molecules (**2**) C3=O3 and C3—C4 bond lengths are decreased, but N1—C3 are increased in comparison to the corresponding bond lengths in the acetamides of the α- and β-modifications for which C=O 1.286(6),[7]

TABLE III

Bond distance (Å) and angles (°) of molecule (1) with e.s.d'.s in parentheses

S—P	2.055(1)	N1—H2	0.80(4)
S—C1	1.792(4)	C1—H11	1.00(6)
P—O1	1.467(2)	C1—H12	0.75(5)
P—O2	1.566(2)	C1—H13	1.00(4)
P—N1	1.609(2)	C2—H21	0.83(4)
O2—C2	1.439(4)	C2—H22	0.96(4)
N1—H1	0.90(3)	C2—H23	0.95
P—S—C1	100.9(2)		
S—P—O1	105.69(9)	S—C1—H12	104(4)
S—P—O2	106.70(6)	S—C1—H13	109(2)
S—P—N1	114.7(1)	H11—C1—H12	106(5)
O1—P—O2	116.2(1)	H11—C1—H13	107(4)
O1—P—N1	113.3(1)	H12—C1—H13	126(5)
O2—P—N1	100.3(1)	O2—C2—H21	119(3)
P—O2—C2	120.7(2)	O2—C2—H22	106(3)
P—N1—H1	116(2)	O2—C2—H23	104
P—N1—H2	113(2)	H21—C2—H22	100(4)
H1—N1—H2	124(2)	H21—C2—H23	108(3)
S—C1—H11	102(4)	H22—C2—H23	121

TABLE IV

Bond distances (Å) and angles (°) of (2) with e.s.d'.s in parentheses

S—P	2.038(2)	C1—H12	0.70(6)
S—C1	1.805(7)	C1—H13	1.11(8)
P—O1	1.463(3)	C2—H21	1.06(9)
P—O2	1.580(3)	C2—H22	0.87(9)
P—N1	1.641(4)	C2—H23	1.17(10)
O2—C2	1.452(6)	C3—C4	1.488(6)
O3—C3	1.219(4)	C4—H41	0.99(4)
N1—C3	1.365(5)	C4—H42	0.89(7)
N1—H1	0.61(3)	C4—H43	0.75(7)
C1—H11	0.86(9)		
P—S—C1	101.3(3)	H12—C1—H13	89(6)
S—P—O1	108.3(1)	O2—C2—H21	100(5)
S—P—O2	108.2(1)	O2—C2—H22	119(6)
S—P—N1	110.3(1)	O2—C2—H23	107(5)
O1—P—O2	115.9(2)	H21—C2—H22	95(7)
O1—P—N1	116.4(2)	H21—C2—H23	138(7)
O2—P—N1	97.3(2)	H22—C2—H23	100(7)
P—O2—C2	119.6(4)	O3—C3—N1	120.1(4)
P—N1—C3	123.9(3)	O3—C3—C4	123.9(4)
P—N1—H1	119(3)	N1—C3—C4	116.0(4)
C3—N1—H1	117(3)	C3—C4—H41	111(2)
S—C1—H11	121(7)	C3—C4—H42	120(5)
S—C1—H12	104(5)	C3—C4—H43	103(6)
S—C1—H13	101(3)	H41—C4—H42	102(5)
H11—C1—H12	119(8)	H41—C4—H43	116(6)
H11—C1—H13	118(7)	H42—C4—H43	104(7)

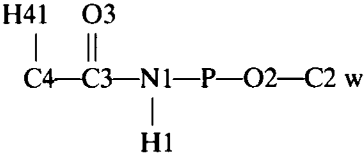
1.250, 1.271[8] Å, C—C 1.530(5),[7] 1.492, 1.519[8] Å, C—N 1.338(7),[7] 1.351, 1.317[8] Å was observed. However, it should be noted that the C3=O3 bond length is close to that of C=O (1.192(5) and 1.210(8) Å) in aldehydes and ketones,[6] and the N1—C3 bond length is less than that of N—C in β-lactams in the fragments

TABLE V

Torsional angles (°) of molecules (**1**) and (**2**)

	Molecule (1)		
C1—S—P—O1	-179.9	S—P—N1—H1	67.1
C1—S—P—O2	55.7	S—P—N1—H2	-84.2
C1—S—P—N1	-54.4	O1—P—N1—H1	-171.5
P—S—C1—H11	59.1	O1—P—N1—H2	37.3
P—S—C1—H12	169.5	O2—P—N1—H1	-46.9
P—S—C1—H13	-54.3	O2—P—N1—H2	161.9
S—P—O2—C2	57.9	P—O2—C2—H21	-67.6
O1—P—O2—C2	-59.7	P—O2—C2—H22	43.9
N1—P—O2—C2	177.8	P—O2—C2—H23	172.4
	Molecule (2)		
C1—S—P—O1	-176.2	O1—P—N1—C3	54.1
C1—S—P—O2	57.4	O1—P—N1—H1	-130.2
C1—S—P—N1	-47.9	O2—P—N1—C3	177.8
P—S—C1—H11	42.1	O2—P—N1—H1	-6.5
P—S—C1—H12	178.9	P—O2—C2—H21	-100.1
P—S—C1—H13	-89.9	P—O2—C2—H22	0.7
S—P—O2—C2	73.9	P—O2—C2—H23	112.8
O1—P—O2—C2	-47.9	P—N1—C3—O3	5.6
S—P—N1—C3	-69.7	P—N1—C3—C4	-174.6
S—P—N1—H1	106.0	H—N1—C3—O3	-170.2
		H1—N1—C3—C4	9.6

C*—NH—C=O (1.388(19) Å).[6] The N atom has a planar-trigonal hybridization and the P—N1—C3 angle is somewhat exceeding 120°.

Both molecules have nearly planar moieties. In the (**1**) it is H12—C1—S—P=O1 and H2—N1—P—O2—C2 and in the (**2**) it is H12—C1—S—P=O1 and  $\overset{\text{H41}}{\overset{|}{\text{C4}}}\text{—}\overset{\text{O3}}{\overset{\|}{\text{C3}}}\text{—}\underset{\text{H1}}{\underset{|}{\text{N1}}}\text{—P—O2—C2}$ with the largest deviation being 0.22(4) Å (for H2 of (**1**)) and 0.163(7) Å (for C2 of (**2**)). The conformation of these moieties is perfectly described by torsion angles given in Table V. So the H12—C1—S—P and C1—S—P=O1 groups of (**1**) and (**2**) have a trans-orientation and the H1—N1—P—O2 group of (**1**) has a cis- and of (**2**) a gauche-orientation. Conformation of N1—P—O2—C2 group is trans in both molecules. The angle between the title planes is 85.3° (1) and 90.3° (2).

There are intermolecular P=O . . . H—N hydrogen bonds in the crystal structures of (**1**) and (**2**). For the P=O1 . . . H1—N1 $[x + 1, y, z]$ and P=O1 . . . H2—N1 $[1 - x, 2 - y, 1 - z]$ hydrogen bonds of the crystal structure (**1**) the corresponding interatomic distances and angles are equal to: O1 . . . N1 = 2.852(3) and 2.999(3), O1 . . . H1 = 2.02(3), O1 . . . H2 = 2.20(4) Å, O1 . . . H1—N1 = 153(3)°, O1 . . . H2—N1 = 174(4)°. Thus the O1 atom of molecule (**1**) participates in two hydrogen bonds. By the O1 . . . H1—N1 hydrogen bonds the molecules form centrosymmetric dimers and by the O1 . . . H2—N1 hydrogen bonds they are connected into infinite chains along the *a* crystallographic axis (Figure 2).

For the P=O1 . . . H1—N1 $[x, \frac{1}{2} - y, \frac{1}{2} + z]$ hydrogen bond of the crystal

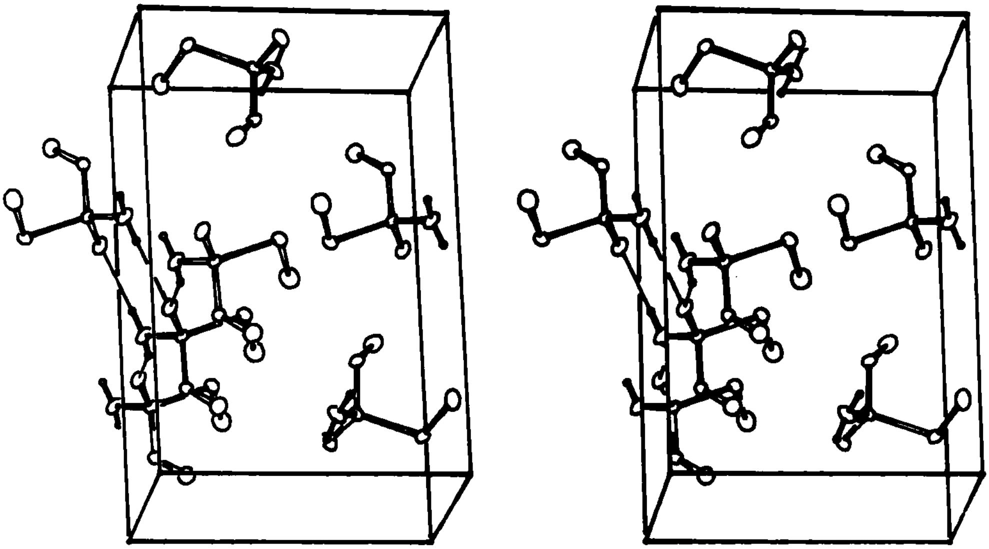


FIGURE 2 A stereoscopic view showing the crystal packing of (**1**), viewed upwards the *a* axis with the *b* axis horizontal and the *c* axis vertical. Fine lines denote hydrogen bonds.

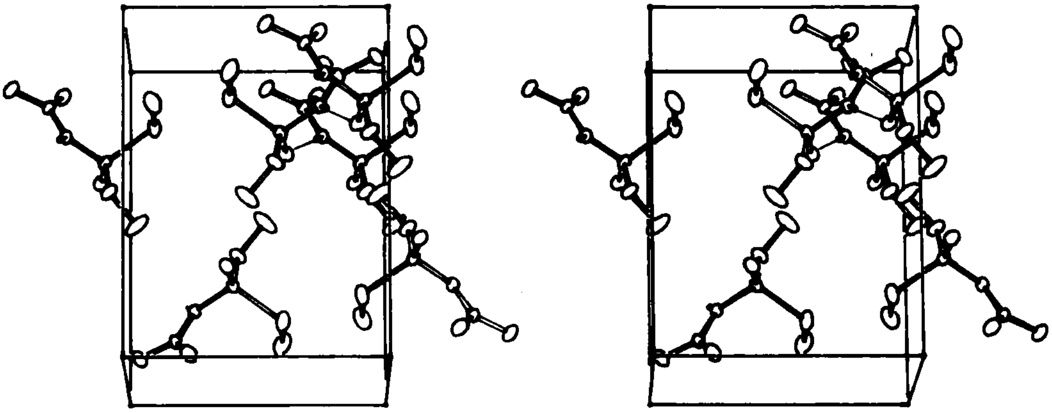


FIGURE 3 A stereoscopic view showing the crystal packing of (**2**), viewed down the *c* axis with the *b* axis horizontal and the *a* axis vertical. Fine lines denote hydrogen bonds.

structure (**2**) the corresponding interatomic distances and angles are equal to: O1 . . . N1 = 2.856(4), O1 . . . H1 = 2.25(3) Å, O1 . . . H1—N1 = 170(4)°. This intermolecular hydrogen bonding connects the molecules along the *c* axis (Figure 3).

EXPERIMENTAL

Crystal data for (**1**). – $C_2H_8NO_2PS$, $M = 141.13$, monoclinic, $P2_1/n$, $a = 5.374(3)$, $b = 9.220(4)$, $c = 13.847$ (5) Å; $\beta = 101.08(5)°$, $V = 673(1)$ Å^3, $Z = 4$, $D_{calc} = 1.392$ g·cm^{-3}, μ (MoK$_\alpha$) = 6.078 cm^{-1}.

Crystal data for (**2**). – $C_4H_{10}NO_3PS$, $M = 183.17$, monoclinic, $P2_1/c$, $a = 11.547(4)$, $b = 8.545(2)$, $c = 8.954(5)$ Å; $\beta = 93.03(4)°$, $V = 882(1)$ Å,^{3} $Z = 4$, $D_{calc} = 1.379$ g·cm^{-3}, μ (MoK_α) = 4.879 cm^{-1}.

Data Collection, Structure Solution and Refinement. Intensity data collections were carried out on an automated four-circle single-crystal Enraf-Nonius CAD4 diffractometer (graphite monochromated MoK_α radiation, $\lambda = 0.71073$ Å) at −100°C for (**1**) and at room temperature for (**2**). Together 1617 (1) and 2262 (2) reflections in the hkl and $\bar{h}$kl octants were measured from crystals of dimensions 0.64 x 0.50 x 0.50 mm (1) and 0.90 x 0.10 x 0.15 mm (2) using an ω/θ-scan technique ($2\theta_{max} \leq 55°$); 1077(1) and 962(2) reflections were considered significant ($I \geq 5\delta(I)$ for (**1**) and $I \geq 3\delta(I)$ for (**2**)). The intensities of three standard reflections, monitored every 3600 seconds of X-ray exposure, showed a maximum variation of 2.2% (**1**) and 0.5% (**2**). The data were corrected for Lorentz and polarization factors, but not for absorption or extinction. Structures solved by direct methods using MULTAN 11/82[9] and refined by full-matrix least squares based upon F with weights $\omega = 4F_0^2[\delta^2(I) + (p \cdot F_0^2)^2]^{-1}$ ($p = 0.075(1)$ and $0.06(2)$). Scattering factors and anomalous-dispersion correction were taken from International Tables for X-ray Crystallography.[10,11] Hydrogens were located by difference-Fourier syntheses. All atomic positional parameters except that of H23 atom of (**1**) were refined. Non-H atoms were refined anisotropically; H-atoms isotropically. Final $R = 0.049$, $R_w = 0.066$ (**1**) and $R = 0.048$, $R_w = 0.062$ (**2**), $S = 1.63$ (**1**) and 1.40 (**2**) for 92 (**1**) and 131 (**2**) variables. Largest parameter shift is 0.01 (**1**) and 0.03 (**2**) in the final cycle.

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