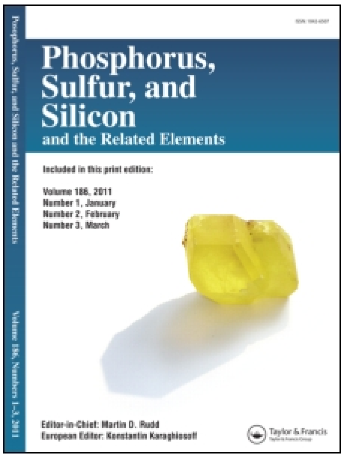

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Synthesis and Insecticidal Activity of Novel Dithiophosphonates

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Synthesis and Insecticidal Activity of Novel Dithiophosphonates

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A new series of dithiophosphonates has been synthesized using cycloiminium halides of pyridine, thiazole, and benzothiazole as starting material, dichlorophenylphosphine as phosphorylating agent, and 2-propanethiol as nucleophilic substituent. These compounds were tested for their insecticidal activity against a polyphagous insect plutella xylostella and found to exhibit potent pesticidal activity.

Keywords Dichlorophenylphosphine; dithiophosphonates; insecticidal activity; phosphorylation

INTRODUCTION

Dithiophosphonates have been found to have diverse applications in a number of technological areas such as antioxidants, additives in oil and in the petroleum industry,[1] agricultural pesticides,[2] metal ore extraction reagents,[3] and as ligands in metal chemistry.[4] Metal phosphonate chemistry has flourished due to potential use of these complexes in electrochemistry, catalysis, material science, and photophysics.[5] The literature on dithiophosphonate chemistry is not as comprehensive as in the case of their analogues—i.e., dithiophosphinates and dithiophosphates—although application of dithiophosphonates in industry and agriculture are highly valued.[6]

Viewing the importance of these precursor thiophosphonate derivatives, we report a novel synthetic strategy based upon our previous research work,[7–11] using cycloiminium salts of N-heterocycles as starting material, and we synthesized and characterized nine dithiophosphonate compounds incorporating pyridine, thiazole, and benzothiazole

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heterocyclic nuclei. These compounds have proven to be potential agriculture chemicals and valuable ligands for metal chemistry.

RESULT AND DISCUSSION

N-alkyl-2-aminopyridin/thiazole/benzothiazoles (**1a–i**) were reacted with haloalkanes (**2**) in THF and generated the corresponding N-alkyl-2-aminopyridinium/thiazolium/benzothiazolium halides (**3a–i**). These quaternary salts then were subjected to phosphorylation with dichlorophenylphosphine (1 equivalent) in the presence of a weak base triethylamine (2 equivalents) using a methylene chloride and toluene mixture (40 mL + 20 mL) as a solvent at 0–5°C. Iminochlorophenylphosphines (**4a–i**) that were first formed were converted to compounds **5a–i** after addition of sulfur (1/8 equivalent), which was further converted to N-alkyl-2-cycloiminylidenamido(s-isopropylthiol)phenylthiophosphonates (**6a–i**) on addition of propane-2-thiol (1 equivalent; Scheme 1).

All the synthesized products were white to yellow crystalline solids, having sharp melting points, and were characterized by ^{1}H, ^{31}P, and ^{13}C NMR techniques. All physical and spectral data are reported in Table I and insecticidal data are included in Table II.

Characterization

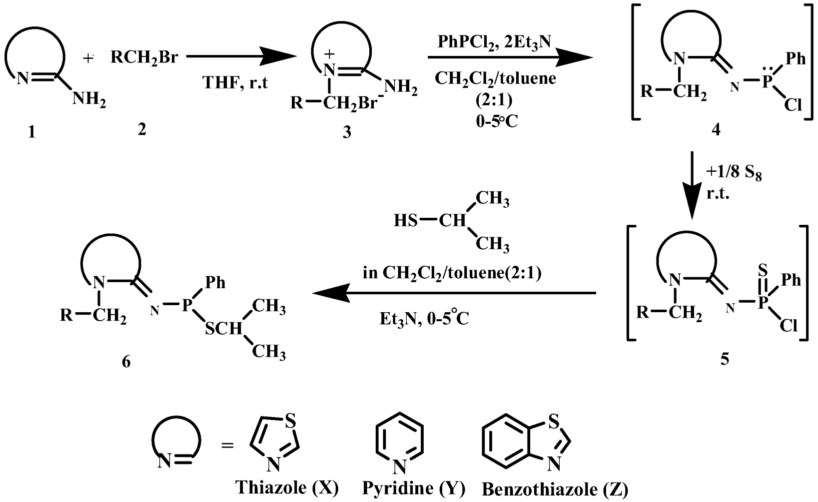
^{31}P NMR

The reaction course was monitored through ^{31}P NMR spectroscopy. This monitoring showed that the ^{31}P signal of the reagent $PhPCl_2$ at 161.00 δ ppm first changed to tricoordinated halophosphines (**4**) at 106.00–128.00 δ ppm, which, on addition of sulfur and the thiol, were converted to tetracoordinated dithiophosphonates (**6**) with signals at 50.20–70.10 δ ppm. These values were in accordance with tetracoordinated pentavalent phosphorus.[12] Pure solids **6a–i** have shown signal in the range 47.40–69.50 δ ppm (Table I).

^{1}H NMR

The CH_3 protons of $SCH(CH_3)_2$ moiety appeared as an unresolved multiplet because both the CH_3 groups attached to the SCH group were nonequivalent due to the nearby chiral phosphorus. Each of these methyl groups showed merged multiplets in the range 1.02–1.52 δ ppm.

The SCH proton appeared as a septet between 2.80–3.62 δ ppm due to three-bond coupling with nonequivalent methyl protons of $SCH(CH_3)_2$ moiety and three-bond coupling with phosphorus.



1– 6	a	b	c	d	e	f	g	h	i
R	$COOCH_2Ph$	$COOCH_2CH_3$	$COOCH_2CH_3$	$COOCH_2CH_3$	$COOCH_3$	$COOCH_3$	$COOCH_3$	C_6H_5	C_6H_5
Ring	X	Y	X	Z	Y	X	Z	Y	X

SCHEME 1

TABLE I Physical and Spectral Data of the Compounds 6a–i

Compd.	Mol. formula (mol. wt.)	Yield (%)	mp (°C)	Elemental analysis Calcd % (Found %)			^{31}P NMR	^{1}H NMR δ (ppm) J(Hz)	^{13}C NMR δ (ppm)
				C	H	N			
6a	$C_{21}H_{23}N_2PS_3O_2$ (462.6)	68	78	54.52 (54.50)	5.01 (4.98)	6.06 (6.01)	52.3	1.16–1.36 (m, 6H, $SCHCH_3$); 3.13 (sept, 1H, $^3J_{HH}$ =6.61, SCH);4.65 (s, 2H, OCH_2); 5.09 (d, H_a,NCH_2); 5.12 (s, H_b,NCH_2); 6.48 (d, 1H, $^3J_{HH}$ = 4.74, H-5); 6.65 (d, 1H, $^3J_{HH}$ = 6.9, H-4); 7.17 (m, 5H, Arom)	25.2 ($SCHCH_3$); 42.3 (SCH); 47.8 (NCH_2); 67.3 (OCH_2); 104.4 (C-5);125.5 (C-4); Ci = 131.9, Co = 129.9, Cm = 127.7, Cp = 127.8 (C_6H_5); 164.7 (C-2); 167.4 (C=O)
6b	$C_{18}H_{23}N_2PS_2O_2$ (394.5)	48	62	54.80 (54.75)	5.88 (5.85)	7.10 (6.98)	47.4	1.05–1.34 (m, 9H, OCH_2CH_3, $SCHCH_3$); 3.11 (sept, 1H, SCH); 3.44 (q, 2H,$^3J_{HH}$ = 7.1, OCH_2); 4.89 (d, H_a, NCH_2); 4.92 (d, H_b,NCH_2); 7.15 (d, 1H, $^3J_{HH}$ = 8.0, H-7); 7.19 (dd, 1H, $^3J_{HH}$ = 6.7, H-5); 7.25 (d, 1H, $^3J_{HH}$ = 8.0, H-3); 7.36 (dd, 1H, $^3J_{HH}$ = 8.1, H-4); 7.6 (d, 1H, $^3J_{HH}$ = 8.1, H-6); 7.2–7.6 (m, 5H, Arom)	25.0 ($SCHCH_3$); 38.0 (OCH_2CH_3); 40.3 (SCH); 55.5 (OCH_2); 112.3 (NCH_2); 114.9 (C-5); 127.9 (C-3); 129.7 (C-4); 131.9 (C-6); 134.6 (C-2); 166.8 (C=O); Ci = 132.0, Co = 128.8, Cm = 129.4, Cp = 127.6 (C_6H_5)

6c	$C_{16}H_{21}N_2PS_3O_2$ (400.5)	55	80	47.98 (47.96)	5.28 (5.25)	6.99 (6.94)	52.5	1.09–1.38 (m, 9H, OCH_2CH_3, $SCHCH_3$); 3.17–3.20 (sept, 1H, SCH); 4.03–4.08 (q, 2H, $^3J_{HH}$ = 7.4, OCH_2); 4.36 (d, H_a, NCH_2); 4.56 (d, H_b,NCH_2); 6.20 (d, 1H, $^3J_{HH}$ = 6.4, H-5); 6.6 (d, 1H, $^3J_{HH}$ = 7.0, H-4); 7.19–7.94 (m, 5H, Arom)	14.0 ($SCHCH_3$); 25.0 (OCH_2CH_3); 30.9 (SCH); 47.7 (NCH_2); 61.7 (OCH_2); 104.2 (C-5); 125.3 (C-4); Ci = 130.2, Co = 127.5, Cm = 128.9, Cp = 126.9 (C_6H_5); 130.5 (C-2); 167.6 (C=O)
6d	$C_{20}H_{23}N_2PS_3O_2$ (450.6)	65	126	53.31 (53.29)	5.14 (5.11)	6.22 (6.20)	69.5	1.14–1.26 (m, 9H, OCH_2CH_3, $SCHCH_3$); 3.46–3.49 (sept, 1H, SCH); 4.19–4.27 (q, 2H, $^3J_{HH}$ = 7.1, OCH_2); 4.89 (d, H_a, NCH_2); 4.92 (d, H_b,NCH_2); 7.41 (d, 1H, $^3J_{HH}$ = 7.9, H-7); .44–7.56 (m, 2H, H-5, H-6); 7.6 (d, 1H, $^3J_{HH}$ = 7.6, H-4); 7.5–8.2 (m, 5H, Arom)	14.1 ($SCHCH_3$); 31.0 (OCH_2CH_3), 45.6 (SCH); 62.2 (OCH_2); 72.3 (NCH_2); 110.9 (C-7); 122.9 (C-4); 124.4 (C-6); 127.1 (C-5); 132.2 (C-8); 136.6 (C-9); 139.3 (C-2); Ci = 131.9, Co = 126.5, Cm = 127.3, Cp = 126.5 (C_6H_5); 166.44 (C=O)
6e	$C_{17}H_{21}N_2PS_2O_2$ (380.4)	67	99	53.67 (53.65)	5.56 (5.53)	7.36 (7.33)	55.8	1.02–1.38 (m, 6H, $SCHCH_3$); 3.27 (sept, 1H, $^3J_{HH}$ = 6.9, SCH);3.5 (s, 2H, OCH_2);4.2(d,H_a,NCH_2); 4.5(d, H_b,NCH_2); 7.22 (dd, 1H, $^3J_{HH}$ = 7.1, H-5); 7.31 (d, 1H, $^3J_{HH}$ = 8.0, H-3); 7.86 (dd, 1H, $^3J_{HH}$ = 8.4, H-4); 7.97 (d, 1H, $^3J_{HH}$ = 8.4, H-6); 7.2–7.9 (m, 5H,Arom)	25.3 ($SCHCH_3$); 40.6 (SCH); 54.0 (OCH_2); 109.8 (NCH_2); Ci = 132.3, Co = 127.1, Cm = 127.7, Cp = 127.4 (C_6H_5); 115.5 (C-5); 128.4 (C-3); 130.3 (C-4); 130.8 (C-6); 156.1 (C-2); 166.7 (C=O)
6f	$C_{15}H_{19}N_2PS_3O_2$ (386.5)	71	82	46.61 (46.30)	4.95 (4.91)	7.25 (7.20)	52.6	1.18–1.44 (m, 6H, $SCHCH_3$); 3.62 (sept, 1H, $^3J_{HH}$ = 7.51, SCH); 4.6 (s,2H,OCH_2); 4.64 (d,H_a,NCH_2); 4.68 (d, H_b,NCH_2); 6.28 (d, 1H, H-5); 6.76 (d, 1H, H-4); 7.26–7.90 (m, 5H, Arom)	18.5 ($SCHCH_3$); 25.0 (SCH); 47.6 (NCH_2); 52.5 (OCH_2); 104.3 (C-5); 125.3 (C-4); Ci = 130.2, Co = 126.5, Cm = 125.3, Cp = 127.9 (C_6H_5); 131.2 (C-2); 168.1 (C=O)

(Continued on next page)

TABLE I Physical and Spectral Data of the Compounds 6a–i (*Continued*)

Compd.	Mol. formula (mol. wt.)	Yield (%)	mp (°C)	Elemental analysis Calcd % (Found %)			^{31}P NMR	^{1}H NMR δ (ppm) J(Hz)	^{13}C NMR δ (ppm)
				C	H	N			
6g	$C_{19}H_{21}N_2PS_3O_2$ (436.6)	58	140	52.27 (52.10)	4.85 (4.81)	6.42 (6.40)	69.3	1.16–1.27 (m, 6H,SCHCH_3); 3.45–3.56 (sept, 1H,SCH); 4.23 (s, 2H, OCH_2); 4.90 (d, H_a,NCH_2); 4.94 (d, H_b,NCH_2); 7.31 (d, 1H, $^3J_{HH} = 7.6$, H-7); 7.38–7.47 (m, 2H, H-5, H-6); 7.48 (d, 1H, H-4); 7.4–8.2 (m, 5H, Arom)	14.0 (SCHCH_3); 30.4 (SCH); 47.5 (NCH_2); 60.1 (OCH_2); 109.3 (C-7); 121.2 (C-4); 124.2 (C-6); 127.2 (C-5); Ci = 130.9, Co = 127.5, Cm = 126.3, Cp = 127.9 (C_6H_5); 131.1 (C-8); 135.5 (C-9); 139.1 (C-2); 166.38 (C=O)
6h	$C_{21}H_{23}N_2PS_2$ (398.5)	63	108	63.29 (63.11)	5.82 (5.00)	7.03 (7.01)	52.1	1.10–1.36 (m, 6H, SCHCH_3); 3.42 (sept, 1H, $^3J_{HH} = 6.9$, SCH); 5.19 (d,H_a,NCH_2); 5.24 (d, H_b,NCH_2); 6.6 (dd, 1H, $^3J_{HH} = 6.75$, H-5); 7.23 (d, 1H, $^3J_{HH} = 7.8$,H-3); 7.35 (dd, 1H,$^3J_{HH} = 7.6$, H-4); 7.53 (d, 1H, $^3J_{HH} = 7.8$, H-6); 7.30–7.90 (m,10H,Arom)	
6i	$C_{19}H_{21}N_2PS_3$ (404.6)	49	96	56.41 (56.39)	5.23 (5.20)	6.92 (6.90)	53.6	1.21–1.52 (m, 6H, SCHCH_3); 2.8–3.4 (sept, 1H, $^3J_{HH} = 6.9$, SCH); 5.46 (d,H_a,NCH_2); 5.72 (d, H_b,NCH_2); 6.46 (d, 1H, H-5); 6.83 (d, 1H, H-4); 7.2–8.1 (m, 10H, Arom)	11.2 (SCHCH_3); 25.0 (SCH); 42.3 (NCH_2); 107.4 (C-5); 128.2 (C-4); Ci = 131.7, Co = 127.4, Cm = 127.9, Cp = 128.7 (C_6H_5); 167.5 (C-2)

TABLE II Percentage Mortality of *Plutella xylostella* Pest after 1, 3, 5, 7, and 10 Days Treatment by Food Dipping Method

		Percentage mortality									
		1 Day		3 Day		5 Day		7 Day		10 Day	
S. No.	Treatment	a	b	a	b	a	b	a	b	a	B
6a	N-benzylethanoate-2-thiazolinylidenamido (S-isopropylthiol) phenylthiophosphonate	40 (39.04)	35 (36.12)	65 (54.16)	60 (50.81)	90 (74.14)	80 (63.60)	95 (80.78)	90 (74.14)	100 (90)	100 (90)
6c	N-(ethoxy-2-oxoethyl)-2-thiazolinylidenamido (S-isopropylthiol) phenylthiophosphonate	30 (32.88)	20 (26.48)	55 (47.91)	50 (45.01)	75 (60.86)	70 (57.45)	85 (67.50)	80 (63.60)	98.75 (86.77)	96.25 (82.16)
6f	N-(methoxy-2-oxoethyl)-2-thiazolinylidenamido (S-isopropylthiol) phenylthiophosphonate	25 (29.48)	15 (19.84)	50 (45.01)	45 (42.12)	70 (57.45)	65 (54.16)	85 (67.50)	75 (60.86)	96.25 (82.16)	91.25 (72.95)
6i	N-benzyl-2-thiazolinylidenamido (S-isopropylthiol) phenylthiophosphonate	10 (18.14)	5 (11.07)	40 (39.04)	30 (32.88)	65 (54.16)	60 (50.81)	80 (63.60)	70 (57.45)	95 (80.78)	90 (74.14)
	Endosulfan	30 (32.88)	30 (32.88)	57.5 (49.47)	50 (45.01)	75 (60.86)	60 (50.81)	95 (80.78)	90 (74.14)	98.75 (86.77)	96.25 (82.16)
	Control	0.00 (0.00)		0.00 (0.00)		0.00 (0.00)		0.00 (0.00)		0.00 (0.00)	

a = 0.05% concentration; b = 0.025% concentration.
Figures in parentheses are the angular transformed values.

Two geminal NCH_2 protons of **6a–i** appeared as two separate doublets showing a diastereotopic nature due to a nearby stereogenic phosphorus in their characteristic region between 4.50–4.90 δ ppm and 4.72–5.73 δ ppm.

In **6a**, two protons of $OCH_2C_6H_5$ gave a singlet at 4.65 δ ppm, and in **6b–d** two protons of OCH_2CH_3 gave a quartet between 3.44–4.27 δ ppm due to three-bond coupling with adjacent methyl protons. Three protons of OCH_2CH_3 were absorbed in the range 1.05–1.38 δ ppm and were merged with other methyl protons of the $SCH(CH_3)_2$ moiety. In **6e–g**, OCH_3 protons gave a singlet between 3.50–4.60 δ ppm.

All the heterocyclic protons appeared in the aromatic region with expected multiplicities together with the aromatic protons of phenyl group of $OCH_2C_6H_5$, $NCH_2C_6H_5$ (**6h**, **i**), and PC_6H_5.

^{13}C NMR

As expected in the ^{13}C NMR, $SCHCH_3$ carbon gave a singlet in the most upfield region between 11.1–25.3 δ ppm, whereas SCH carbon gave a singlet between 25.0–45.6 δ ppm. NCH_2 carbon in **6a–i** gave a singlet between 42.3–109.8 δ ppm. OCH_2 carbon in **6a–d** appeared between 55.4–67.2 δ ppm, whereas OCH_3 carbons of **6e–g** appeared between 52.5–60.1 δ ppm as a singlet. Similarly, CH_3 carbon of OCH_2CH_3 in **6b–d** gave a singlet between 25.0–38.0 δ ppm.

C-2 carbon of heterocyclic ring absorbed at the most downfield region between 130.5–167.5 δ ppm with minimum intensity due to its quaternary nature.

All the aromatic carbons were found in their expected range.

EXPERIMENTAL

All the synthetic procedures were carried out in an inert atmosphere of nitrogen, and due to the highly hygroscopic nature of the synthesized products, inert nitrogen was used to store them. All glassware used was washed with alkali followed by dilute acid, water, and acetone and dried in an electric oven for 4–6 h at high temperature until just before use. Standard syringe techniques were used for the addition of chemicals. All solvents and reagents were used after drying. Fine chemicals like 2-aminopyridine, 2-aminobenzothiazole, 2-aminothiazole, and 2-propanethiol were procured from Aldrich and Merck and used as received. Elemental analyses were carried out on Heraeus Carlo Erba 1108 analyzer. ^{31}P NMR spectrum were recorded on Jeol AL 300 at 121.50 MHz (Obset 156 KHz) using 85% H_3PO_4 as an external standard. ^{1}H NMR spectra were recorded in $CDCl_3$ on Jeol AL300 at 300.4

MHz (Obset 130 KHz) using TMS as internal reference. Their melting points were determined by a standard capillary method on Electric Tempo Instrument and are uncorrected.

General Procedure for the Synthesis of N-Substituted-2-ylidenamido(S-isopropylthiol)(phenyl)thiophosphonate (6a–i)

N-alkyl-2-pyridinium/thiazolium/benzothiazolium halides (**3**) were synthesized using reported procedures. These halides were characterized by reported melting point and NMR spectral data.[7–11]

To a suspension of N-alkyl-2-pyridinium/thiazolium/benzothiazolium halides (13.7 mmol) in a methylene chloride (40 mL/toluene 20 mL) (2:1) mixture, triethylamine (27.4 mmol) and dichlorophenylphosphine (13.7 mmol) were added at ambient temperature. After 3–4 h stirring, powdered sulfur 1/8 S_8 (13.7 mmol) was added to the reaction mixture at room temperature. After 24 h of stirring, 2-propanethiol (13.7 mmol) in methylene chloride/toluene mixture (40 + 20 mL) was added drop-wise in the presence of triethylamine (13.7 mmol) at 0–5°C. The stirring was continued for the next 50–55 h. After that, the solvent was removed *in vacuo*, and the residue was extracted with diethylether and kept in a refrigerator, whereupon a white- to yellow-colored solid separated out, which was filtered, dried, and recrystallized.

Bioactivity

Four synthesized dithiophosphonates (**6a**, **c**, **f**, **i**) having a chiral phosphorus were screened for their insecticidal activity against a polyphagous insect *Plutella xylostella*, quite prevalent in the vegetable crops of northern India, and results are presented in Table II and Figure 1. In our previous publication,[9] we studied the activity of trithiophosphates on the same insect and found that those molecules exhibited substantial insecticidal activity. To study the structure-activity relationship here we have selected four dithiophosphonate derivatives where the heterocyclic ring was same; i.e., thiazole ring. The phosphorus moiety was also the same; the only variation was in the N-alkyl substituted group. This study has suggested that an increase in the bulkiness of N-alkyl substituent enhanced the bioactivity as evidenced from the experimental details of the study (Table II, Figure 1). Compound **6a** at concentrations 0.05% and 0.025% showed the best insecticidal activity, which was found to be superior to that of a standard

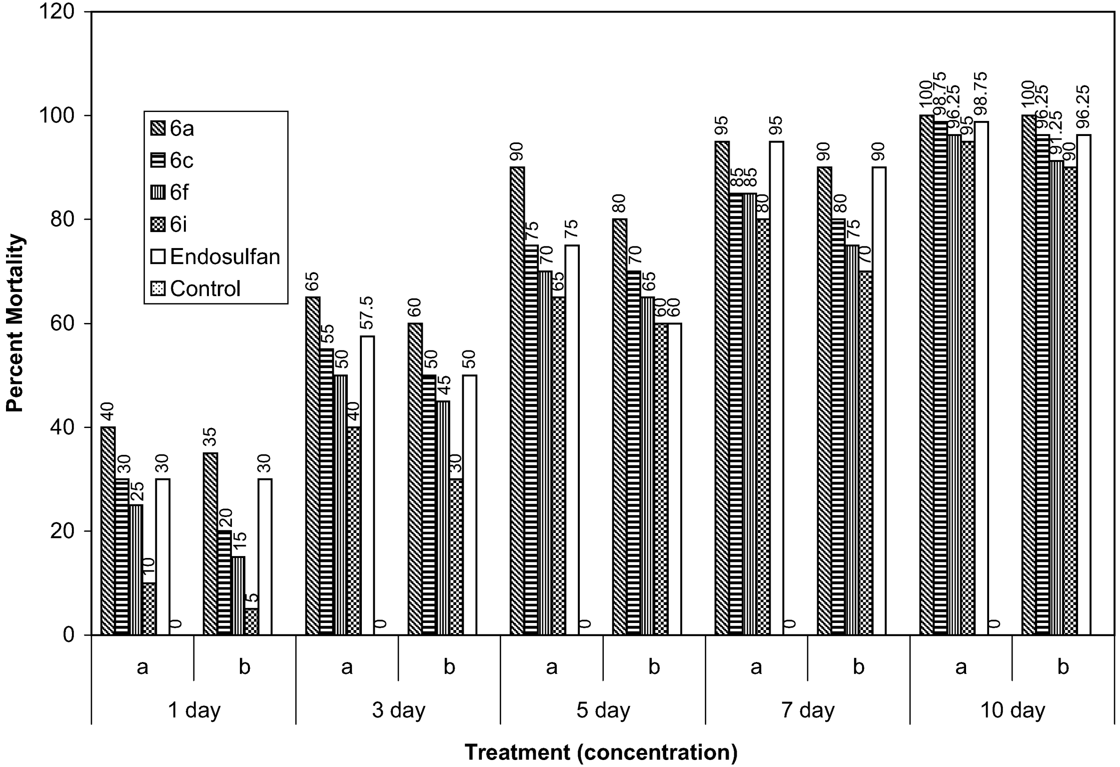


FIGURE 1 Percentage mortality of *Plutella xylostella* pest after 1, 3, 5, 7, and 10 days.

insecticide endosulfan. Derivative **6a** incorporated a bulky benzylethanoate moiety at ring nitrogen, thus confirming the potentiality of this derivative as insecticidal compound. The bulky nature of insecticide hindered the activity of the enzyme acetyl cholinesterase and thus impaired the activity of the insect nervous system.[13]

CONCLUSION

Nine novel dithiophosphonates that can have potential metal ligand properties and pesticidal activities have been synthesized and their insecticidal activity was screened on a polyphagous insect *Plutella xylostella*. Compounds exhibited potent activity in comparison to a standard insecticide endosulfan. In our further research work we will use these compounds as metal ligands to generate different metal complexes.

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