

## Synthesis, Fungitoxicity and QSAR Study of Some New Phosphorothionates

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**ABSTRACT.** Twenty O,O-diaryl O-2-chloroethyl phosphorothionates, having different phenyl substitutions, were synthesized and characterized by physico-chemical techniques. The compounds were evaluated for their fungicidal activity against two phytopathogenic fungi viz., *Rhizoctonia solani* and *Sclerotium rolfsii*. The most active compounds were O,O-di (pentachlorophenyl) O-2-chloroethyl phosphorothionate (ED<sub>50</sub> 419 ppm) and O,O-di (2-methylphenyl) O-2-chloroethyl phosphorothionate (ED<sub>50</sub> 426 ppm) against *R. solani* and *S. rolfsii*, respectively. The quantitative structure-activity relationship (QSAR) was analyzed using *in-vitro* fungitoxicity data and various physico-chemical parameters for hydrophobic, electronic and steric properties of the phenyl ring by multiple regression analysis. The QSAR model for the fungicidal activity of O,O-diaryl O-2-chloroethyl phosphorothionates against *R. solani* revealed that the presence of electron donating groups in the benzene ring and a high value of  $\pi$ , hydrophobic parameter irrespective of being negative or positive will impart high fungicidal activity to the compounds. The shape of the para-substituents as determined by high and low value of STERIMOL length [ $\Sigma L(p)$ ] and width [ $\Sigma B_1(p)$ ] parameters, respectively, and also low value of hydrophobic parameter  $R_{11}$  are favourable for fungicidal activity of compounds in this series against *S. rolfsii*.

### INTRODUCTION

Among the synthetic pesticides, organophosphates are the most widely used group to control crop pests. The antifungal activity of organophosphorus compounds was discovered when Erwin *et al.* (1958) reported the fungicidal activity of phorate against *Rhizoctonia solani* in cotton seeds. Phosphorothiolate type of compounds are the first in the organophosphorus group that were commercialized as fungicides (Eto; 1977), and mostly anti rice blast agents (*Pyricularia oryzae*). The first such compound was Kitazin (S-benzyl O,O-diethyl phosphorothiolate) introduced in 1965 by Kumai Chemical Co., Japan, which was subsequently replaced by Kitazin P, a more active isopropyl analogue, in 1967. Although several phosphorothionates, (parathion, chlorpyrifos, quinalphos, etc.) are well known as insecticides, only very few reports are available on fungicidal phosphorothionates. Sasaki *et al.* (1984) were the first to report the synthesis and fungicidal activity of O,O-dialkyl O-aryl phosphorothionates, which resulted in the development of tolclofos-methyl [O,O-dimethyl O-(2,6-dichloro-4-methylphenyl) phosphorothionate] as a practical fungicide to control soil borne diseases caused by *Rhizoctonia solani*. Gupta and Roy (1993) reported the fungicidal activity of a series of O,O-diaryl O-methyl phosphorothionates of which O,O-di-(2,4,6-trichlorophenyl) O-methyl phosphorothionate was found to be the most active compound against *S. rolfsii*. Further testing showed that it has an excellent activity against *R. solani* (Gupta, 2000). Fungitoxicity of various phosphorothionates are also reported elsewhere (Gupta and Roy, 1995; Patra and Gupta,

1999). These recent findings of the excellent fungitoxicity of phosphorothionates particularly against *R. solani* and *S. rolfsii* led the present study to explore further to obtain new potent fungicides.

## MATERIALS AND METHODS

### General

All the reagents and solvents required in the present investigation were purified by distillation (for liquids) or recrystallization (for solids). Thin layer chromatography (TLC) was performed on 250  $\mu\text{m}$  thick silica gel-G (30% gypsum as binder) plates, activated at 110°C for 1 h using hexane and benzene (1:1 v/v) as developing solvent and iodine vapour as visualizing agent. Compounds were purified by column chromatography using glass column packed with silica gel preactivated at 120°C. Melting point of solid compounds was determined by using sulphuric acid bath and were uncorrected. The infra-red (IR) spectra were recorded in a Nicolet Fourier Transform Infra-red spectrophotometer (Model Impact-400, Nicolet Analytical Instrument Corp., Madison, WI, USA). The liquid samples were analysed as thin film and solid samples as KBr pellets. The absorption bands in IR spectra were expressed in terms of frequency *i.e.*,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ . The proton magnetic resonance (PMR) spectra were recorded on a Varian EM 360 L, 60 MHz instrument in carbon tetrachloride using tetramethylsilane as an internal standard. The chemical shifts ( $\delta$ ) were expressed in ppm and coupling constant (J) in Hz.

In the present research programme, twenty O,O-diaryl O-2-chloroethyl phosphorothionates were synthesized, as represented by the general structural formula 6 (Fig. 1). The compounds were prepared by the reaction of thiophosphoryl trichloride (formula 2) with ethylene chlorohydrin (formula 3) in presence of pyridine to obtain O-2-chloroethyl phosphorodichloridothioate (formula 4), which in turn reacted with various substituted phenols (formula 5) to obtain the desired phosphorothionates as illustrated in the following scheme of synthesis.

### Synthesis

Thiophosphoryl trichloride (formula 2) was prepared by reaction of phosphorus trichloride (formula 1) (206 g, 1.5 mol) with crystallized sulphur (48 g, 1.5 mol) in presence of catalytic quantity of anhydrous aluminium chloride (4 g, 0.03 mol). The optimum molar ratio for best yield of thiophosphoryl trichloride is 1 phosphorus trichloride : 1 sulphur : 0.02 aluminium chloride. The product was then distilled and thiophosphoryl trichloride was collected at 118-120°C (yield 230 g, 90%). O-2-Chloroethyl phosphorodichloridothioate (formula 4) was prepared by reacting thiophosphoryl trichloride (102 g, 0.6 mol) with ethylene chlorohydrin (formula 3) (40.25 g, 0.5 mol) in a three necked round bottom flask fitted with a mechanical stirrer and a thermometer. To the content of the flask, pyridine (39.5 g, 0.5 mol) was added dropwise with continuous stirring, maintaining temperature at 25-30°C. After addition of pyridine the mixture was stirred for additional 30 min and extracted in dichloromethane. The fraction boiled at 84-88°C/10 mm was collected after removal of solvent, with a yield of 80%. The structure was confirmed by PMR and IR spectroscopy.

PMR  $\delta_{\text{TMS}}^{\text{CDCl}_4}$  ppm: 3.8 [2H, t, J= 6-7 Hz, Cl-CH<sub>2</sub>-CH<sub>2</sub>-O-P], 4.6 [2H, m, Cl-CH<sub>2</sub>-CH<sub>2</sub>-O-P]

IR  $\nu_{\text{max}}^{\text{neat}}$  cm<sup>-1</sup>: 1074.7 and 946.3 (C-O str P-O-C aliphatic); 730.0 and 854.1 (P=S str) and 663.3 (C-Cl str aliphatic).

O,O-diaryl O-2-chloroethyl phosphorothionates (formula 6) were prepared by condensation of O-2-chloroethyl phosphorodichloridothioate (formula 4) (1.2 mol) in dry benzene with different substituted phenols (formula 5) (2 mol) in presence of triethylamine (2 mol) as acid scavenger. The reaction mixture was stirred for 3-4 h after addition of the acid chloride at room temperature. The completion of the reaction was monitored by TLC. After filtering out the triethylamine hydrochloride, the product isolated from the filtrate was further purified by recrystallization if it was solid or by column chromatography using silica gel in case of liquid. The purity of each compound was checked by TLC and also by melting point in case solid and structure was confirmed by PMR and IR spectroscopy.

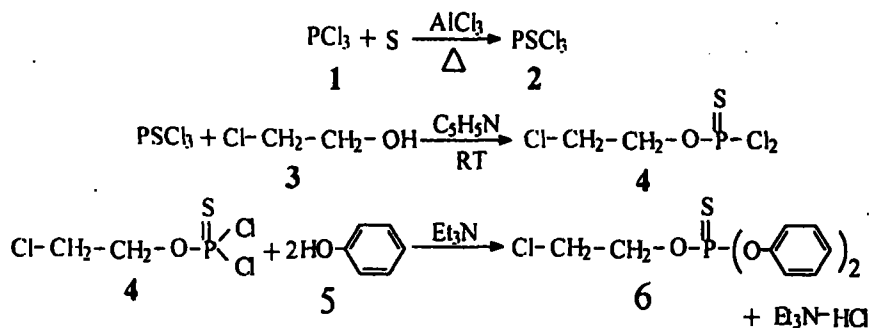


Fig. 1. Scheme of synthesis of O,O-diaryl O-2-chloroethyl phosphorothionates.

### Fungitoxicity testing

Fungicidal activity of the synthesized compounds was carried out by poison food technique, using potato dextrose agar (PDA) medium (Nene and Thapliyal, 1997) against two fungi viz., *Rhizoctonia solani* and *Sclerotium rolfsii*. Cultures of the fungi were collected from the division of Plant Pathology, IARI, New Delhi and maintained by subculturing prior to testing at 25°C. Media was prepared by conventional method and inoculated by test fungi in media taken in 9 cm diameter petriplates containing test concentrations (up to 1000 ppm) of the compounds in a laminar flow. After the full growth in control in a BOD incubator, the ED<sub>50</sub> (effect dose required for 50% inhibition of the mycellial growth) values were calculated in a personal computer, calculating the percent inhibition (I) and corrected percent inhibition (I<sub>c</sub>) by using the following formulae:

$$\%I = \frac{C-T}{C} \times 100 \quad \%I_c = \frac{\%I - CF}{100 - C} \times 100 \quad CF = \frac{9-C}{C} \times 100$$

Where, C = Growth in control (cm), T = Growth in treatment (cm), CF = Correction factor.

### Quantitative structure activity relationship (QSAR) analysis

The QSAR was studied using experimentally determined  $pED_{50}$  values and different physico-chemical parameters representing hydrophobic, electronic and steric properties of the prepared compounds. The dependent variable  $pED_{50}$  was calculated by taking negative logarithm of molar  $ED_{50}$  values for each compound. The  $R_M$  and  $\pi$  values were used as measure of hydrophobicity, where  $\pi$  values were taken from the literature (Hansch and Leo, 1979) and  $R_M$  values were determined by reverse phase TLC (by coating the normal silica gel TLC plates with paraffin) using the following formula after calculating  $R_f$  (retention factor)  $\therefore RM = \log[1/R_f - 1]$ .

The Hammett constants  $\sigma_p$  and  $\sigma_m$  were taken from the literature (Hansch and Leo, 1979) and for *ortho* substituents  $\sigma_p$  along with  $F$ , the Swain Lupton constant for "proximity polar effect" suggested by Fujita and Nishioka (1976) were used as electronic parameters. Steric parameters used in QSAR study were, Taft steric parameter ( $E_s$ ), molar refractivity (MR) and Verloop STERIMOL parameters ( $L$ ,  $B_1$ ,  $B_4$ ), taken from literature (Hansch and Leo, 1979). For the value of physico-chemical parameters for each compound, the additive nature of all the substituent constants was presumed, the  $\pi$ ,  $\sigma$  and  $F$  values for multisubstituents *i.e.*, for di-, tri- and penta- substituted compounds were obtained by adding the value of all ring substituents corresponding to their positions (Gupta *et al.*, 1988). The values of the steric parameters were used as summation for each position (*ortho*, *meta*, *para*), which was considered separately for each three positions *e.g.*  $B_1(o)$ ,  $B_1(m)$  and  $B_1(p)$  corresponding to *ortho*, *meta* and *para* positions, respectively. Also the values of various parameters were considered only for one phenyl ring, since substitution pattern on both the rings is the same in all the compounds.

The structure activity correlation were analysed by the multiple regression analysis technique using experimental  $pED_{50}$  values for the fungicidal activity as dependent variable and the physico-chemical parameters for the hydrophobic, electronic, and steric properties of each member of the series as independent variables. The multiple regression analysis was carried out using the statistical software package MICROSTAT.

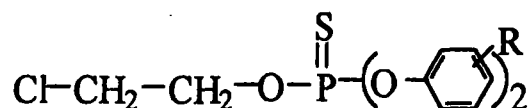
### RESULTS AND DISCUSSION

In the present study, twenty O,O-diaryl O-2-chloroethyl phosphorothionates were synthesized. The compounds synthesized along with their physical data are given in Table 1. The synthesized compounds were characterized on the basis of IR and PMR spectra. The IR spectra of O,O-diaryl O-2-chloroethyl phosphorothionates showed characteristic peaks for P=S stretching vibrations, C-O stretching vibrations of P-O-C aromatic and P-O-C aliphatic bonds (Table 2).

The most characteristic feature of the PMR spectra of O,O-diaryl O-2-chloroethyl phosphorothionates is the presence of a multiplet at around  $\delta$  4.5 corresponding to the  $\alpha$  protons ( $CH_2$ ). This is due to the presence of vicinal phosphorus atom ( $^{31}P$  is present in nature in 100% abundance has a spin of  $1/2$ , Hendricson *et al.*, 1964). The  $\beta$  protons give a triplet due to coupling with  $\alpha$  protons. It was also observed that the chemical shift value of  $\beta$  protons is much higher than normal  $CH_3$ . The lower field peak of  $\beta$  protons is due to

the presence of chlorine, which is highly electronegative. The chemical shift values of  $\alpha$ ,  $\beta$ , aromatic and phenyl substituent protons are listed in Table 3.

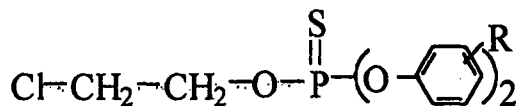
**Table 1.** O,O-diaryl O-2-chloroethyl phosphorothionates synthesized and their physical data.



Compound No.	R	Molecular formula	Yield obtained		Physical state	Melting point (°C)
			(g)	(%)		
1	H	C <sub>14</sub> H <sub>14</sub> O <sub>3</sub> PSCl	5.98	72.9	Liquid*	-
2	2-CH <sub>3</sub>	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> PSCl	6.50	72.8	Liquid*	-
3	3-CH <sub>3</sub>	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> PSCl	6.52	73.0	Liquid*	-
4	4-CH <sub>3</sub>	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> PSCl	6.55	73.3	Liquid*	-
5	2-Cl	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub> PSCl <sub>3</sub>	6.23	62.9	Solid	48-50
6	4-Cl	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub> PSCl <sub>3</sub>	5.98	60.4	Solid	51-53
7	4-NO <sub>2</sub>	C <sub>14</sub> H <sub>12</sub> O <sub>7</sub> PSClN <sub>2</sub>	5.96	56.7	Solid	93-95
8	2-OCH <sub>3</sub>	C <sub>16</sub> H <sub>18</sub> O <sub>5</sub> PSCl	7.21	74.3	Liquid*	-
9	4-C(CH <sub>3</sub> ) <sub>3</sub>	C <sub>22</sub> H <sub>30</sub> O <sub>3</sub> PSCl	8.15	74.3	Liquid*	-
10	2,4-Cl <sub>2</sub>	C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> PSCl <sub>5</sub>	6.98	59.6	Solid	82-84
11	4-Cl,3-CH <sub>3</sub>	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> PSCl <sub>3</sub>	6.85	64.7	Liquid*	-
12	2,3-(CH <sub>3</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>22</sub> O <sub>3</sub> PSCl	7.08	73.6	Liquid*	-
13	2,4-(CH <sub>3</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>22</sub> O <sub>3</sub> PSCl	7.12	74.0	Liquid*	-
14	2,5-(CH <sub>3</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>22</sub> O <sub>3</sub> PSCl	7.06	73.4	Liquid*	-
15	2,6-(CH <sub>3</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>22</sub> O <sub>3</sub> PSCl	7.04	73.2	Liquid*	-
16	3,5-(CH <sub>3</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>22</sub> O <sub>3</sub> PSCl	7.07	73.5	Liquid*	-
17	2,3,5-(CH <sub>3</sub> ) <sub>3</sub>	C <sub>20</sub> H <sub>24</sub> O <sub>3</sub> PSCl	6.62	64.5	Liquid*	-
18	2,4,5-Cl <sub>3</sub>	C <sub>14</sub> H <sub>8</sub> O <sub>3</sub> PSCl <sub>7</sub>	8.45	63.1	Solid	96-98
19	2,4,6-Cl <sub>3</sub>	C <sub>14</sub> H <sub>8</sub> O <sub>3</sub> PSCl <sub>7</sub>	8.62	64.3	Solid	78-80
20	Cl <sub>5</sub>	C <sub>14</sub> H <sub>4</sub> O <sub>3</sub> PSCl <sub>11</sub>	9.85	58.6	Solid	152-154

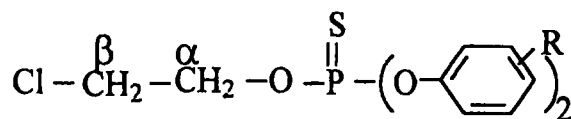
\* = Column purified.

Table 2. IR spectra of O,O-diaryl O-2-chloroethyl phosphorothionates.



Compound No.	R	P-O-C(ali.)	P-O-C(aro.)	P=S
1	H	1027.9, 939.7	1188.8	762.5, 849.3
2	2-CH <sub>3</sub>	1023.8, 950.7	1222.4	762.9, 857.1
3	3-CH <sub>3</sub>	1016.5, 961.6	1235.8	781.7, 869.5
4	4-CH <sub>3</sub>	1016.5, 959.4	1196.3	792.7, 827.8
5	2-Cl	1032.4, 943.1	1213.3	752.8, 804.8
6	4-Cl	1034.0, 959.4	1202.9	775.1, 834.4
7	4-NO <sub>2</sub>	1038.4, 929.4	1201.9	745.8, 855.1
8	2-OCH <sub>3</sub>	1029.6, 959.4	1194.4	753.2, 805.9
9	4-C(CH <sub>3</sub> ) <sub>3</sub>	1027.4, 947.1	1076.5	797.5, 840.1
10	2,4-Cl <sub>2</sub>	1055.3, 946.5	1214.1	746.7, 830.6
11	4-Cl,3-CH <sub>3</sub>	1083.7, 970.4	1226.3	732.7, 815.0
12	2,3-(CH <sub>3</sub> ) <sub>2</sub>	1023.4, 955.0	1224.5	762.0, 818.3
13	2,4-(CH <sub>3</sub> ) <sub>2</sub>	1027.4, 966.0	1196.3	792.7, 814.6
14	2,5-(CH <sub>3</sub> ) <sub>2</sub>	1027.4, 962.9	1241.2	792.8, 812.1
15	2,6-(CH <sub>3</sub> ) <sub>2</sub>	1026.9, 968.6	1228.8	779.5, 809.7
16	3,5-(CH <sub>3</sub> ) <sub>2</sub>	1024.7, 966.0	1191.0	790.7, 818.1
17	2,3,5-(CH <sub>3</sub> ) <sub>3</sub>	1066.5, 972.8	1193.8	790.4, 859.8
18	2,4,5-Cl <sub>3</sub>	1030.5, 964.5	1234.5	733.5, 871.0
19	2,4,6-Cl <sub>3</sub>	1045.0, 939.7	1232.7	801.5, 834.4
20	Cl <sub>3</sub>	1031.8, 939.7	1249.0	715.9, 808.0

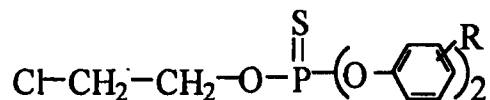
Table 3. PMR spectra of O,O-diaryl O-2-chloroethyl phosphorothionates.



Compound No.	R	CH <sub>2</sub> (β)	CH <sub>2</sub> (α)	Aromatic protons	Others
1	H	3.70	4.55	7.5	-
2	2-CH <sub>3</sub>	3.75	4.50	7.2	2.42
3	3-CH <sub>3</sub>	3.80	4.55	7.3	2.40
4	4-CH <sub>3</sub>	3.70	4.45	7.4	2.40
5	2-Cl	3.75	4.55	7.4	-
6	4-Cl	3.65	4.40	7.2	-
7	4-NO <sub>2</sub>	3.80	4.55	7.4, 8.4	-
8	2-OCH <sub>3</sub>	3.90	4.64	7.3	3.98
9	4-C(CH <sub>3</sub> ) <sub>3</sub>	3.75	4.52	7.4	1.40
10	2,4-Cl <sub>2</sub>	3.85	4.60	7.5	-
11	4-Cl,3-CH <sub>3</sub>	3.65	4.35	7.2	2.35
12	2,3-(CH <sub>3</sub> ) <sub>2</sub>	3.86	4.58	7.2	2.58
13	2,4-(CH <sub>3</sub> ) <sub>2</sub>	3.80	4.60	7.2	2.35
14	2,5-(CH <sub>3</sub> ) <sub>2</sub>	3.70	4.43	7.1	2.20
15	2,6-(CH <sub>3</sub> ) <sub>2</sub>	3.80	4.53	7.1	2.45
16	3,5-(CH <sub>3</sub> ) <sub>2</sub>	3.75	4.53	6.9	2.35
17	2,3,5-(CH <sub>3</sub> ) <sub>3</sub>	3.73	4.45	6.9, 7.2	2.23
18	2,4,5-Cl <sub>3</sub>	3.85	4.65	7.7	-
19	2,4,6-Cl <sub>3</sub>	3.64	4.54	7.5	-
20	Cl <sub>5</sub>	3.70	4.65	-	-

The fungitoxicity data of O,O-diaryl O-2-chloroethyl phosphorothionates against *R. solani* (Table 4) reveal that the fungitoxicity of the phosphorothionates is not totally

Table 4. Fungicidal activity of O,O-diaryl O-2-chloroethyl phosphorothionates against *Rhizoctonia solani* and *Sclerotium rolfsii*.



Compound No.	R	ED <sub>50</sub> (ppm)	
		<i>R. solani</i>	<i>S. rolfsii</i>
1	H	2236	2672
2	2-CH <sub>3</sub>	3606	426
3	3-CH <sub>3</sub>	712	1262
4	4-CH <sub>3</sub>	443	810
5	2-Cl	5122	3733
6	4-Cl	4157	1319
7	4-NO <sub>2</sub>	1392	2799
8	2-OCH <sub>3</sub>	1299	2627
9	4-C(CH <sub>3</sub> ) <sub>3</sub>	748	5495
10	2,4-Cl <sub>2</sub>	2512	890
11	4-Cl,3-CH <sub>3</sub>	2097	5411
12	2,3-(CH <sub>3</sub> ) <sub>2</sub>	1132	794
13	2,4-(CH <sub>3</sub> ) <sub>2</sub>	1266	2501
14	2,5-(CH <sub>3</sub> ) <sub>2</sub>	1395	766
15	2,6-(CH <sub>3</sub> ) <sub>2</sub>	1783	6307
16	3,5-(CH <sub>3</sub> ) <sub>2</sub>	2311	1201
17	2,3,5-(CH <sub>3</sub> ) <sub>3</sub>	794	1457
18	2,4,5-Cl <sub>3</sub>	2888	1010
19	2,4,6-Cl <sub>3</sub>	452	1281
20	Cl <sub>5</sub>	419	2091

dependent on the electronic nature of different substituents in the phenyl ring. Among monosubstituted compounds, the electron donating groups viz., -CH<sub>3</sub>, -C(CH<sub>3</sub>)<sub>3</sub>, -OCH<sub>3</sub> and also the most electron withdrawing, NO<sub>2</sub> group showed better activity than the unsubstituted compound. The trend in activity among the chloro-substituted compounds was Cl<sub>5</sub> > 2,4,6-Cl<sub>3</sub> > 2,4-Cl<sub>2</sub> > 4-Cl > 2-Cl. O,O-Di-(pentachlorophenyl) O-2-chloroethyl phosphorothionate (No. 20) exhibited the highest activity (ED<sub>50</sub> 419 ppm) against *Rhizoctonia solani*. The study against *Sclerotium rolfsii* revealed that among the monosubstituted compounds, the methyl analogues were better in terms of fungitoxicity than the unsubstituted as well as compounds having other substituents such as Cl, NO<sub>2</sub>, OCH<sub>3</sub>, t-butyl. However, no systematic order of activity was observed among the monosubstituted compounds (Table 4). The trend in fungicidal activity among the chlorosubstituted compounds was Cl<sub>5</sub> < Cl<sub>3</sub> < Cl<sub>2</sub> > Cl. The O,O-di-(2-methylphenyl)



O-2-chloroethyl phosphorothionate exhibited the highest activity against *Sclerotium rolfsii* (ED<sub>50</sub> 426 ppm) in this series.

To identify exactly the structural features favourable for fungitoxicity, QSAR have been analyzed by means of multiple regression analysis using measured pED<sub>50</sub> values of O,O-diaryl O-2-chloroethyl phosphorothionates against *R. solani* and *S. rolfsii* as dependent variable and different physicochemical parameters for hydrophobic, electronic and steric properties of each member of the series as independent variables. A correlation matrix of the parameters appeared in the regression equations is given in Table 5.

Table 5. Correlation matrix for the parameters used in the regression equations.

	$\Sigma\sigma$	$\Sigma L(p)$	$\Sigma B_4(p)$	$R_M$	$(\Sigma\pi)^2$
$\Sigma\sigma$	1.000				
$\Sigma L(p)$	0.587	1.000			
$\Sigma B_4(p)$	0.372	0.915	1.000		
$R_M$	0.368	-0.275	-0.103	1.000	
$(\Sigma\pi)^2$	0.372	0.459	0.289	-0.312	1.000

The following statistically best models were obtained:

*R. solani*

$$pED_{50} = 2.058 + 0.155 (\Sigma\pi)^2 - 0.548 \Sigma\sigma$$

$(\pm 0.032)$                        $(\pm 0.205)$

$$n = 15, s = 0.112, r = 0.952, r^2 = 0.907, F_{2,12} = 58.38$$

*S. rolfsii*

$$pED_{50} = 1.940 + 0.254 \Sigma L(p) - 0.504 \Sigma B_4(p) - 1.709 R_M$$

$(\pm 0.224)$                        $(\pm 0.264)$                        $(\pm 0.717)$

$$n = 15, s = 0.102, r = 0.937, r^2 = 0.879, F_{3,11} = 26.59$$

where, n = number of compounds included in correlation, s = standard error of estimate, r = correlation coefficient,  $F_{v_1, v_2}$  = F ratio of correlation where  $v_1 = m$ ,  $v_2 = n - m - 1$ , m = number of independent variables used in correlation. The figures in the parentheses are the 95% confidence interval for the respective constants.

The QSAR model for *R. solani* and terms included in it are highly significant. This accounts for 95.2% variation in fungitoxicity. The model revealed that the fungicidal

activity of O,O-diaryl O-2-chloroethyl phosphorothionates against *R. solani* is favoured by the presence of electron donating groups in the benzene ring and also a high value of  $\pi$ , hydrophobic parameter, whether negative or positive. The best fit regression equation obtained for fungicidal activity of the phosphorothionates in this series against *S. rolfssii* is also highly significant and explains 87.9% variation in fungicidal activity in terms of STERIMOL parameters  $L$  and  $B_4$  for the para phenyl substituents and the hydrophobicity of the compounds *i.e.*, by  $R_M$ . Further the shape of the para phenyl substituents *i.e.*, the high value for length parameter  $[\Sigma L(p)]$  and low value of width parameter  $[\Sigma B_4(p)]$  and low value of hydrophobic parameter  $R_M$ , are favourable for the fungicidal activity of the compounds against *S. rolfssii*.

## CONCLUSIONS

The study revealed that the most active compounds against *Rhizoctonia solani* and *Sclerotium rolfssii* are O,O-di-(pentachlorophenyl) O-2-chloroethyl phosphorothionate ( $ED_{50}$  419 ppm) and O,O-di-(2-methylphenyl) O-2-chloroethyl phosphorothionate ( $ED_{50}$  426 ppm), respectively. The structure activity relationship study indicated that the fungitoxicity is not totally dependent on the electronic nature of the phenyl substituents and possesses no order of activity. The QSAR study however, has clearly revealed the different structural requirement for fungitoxicity against *R. solani* and *S. rolfssii* of the O,O-diaryl O-2-chloroethyl phosphorothionates.

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