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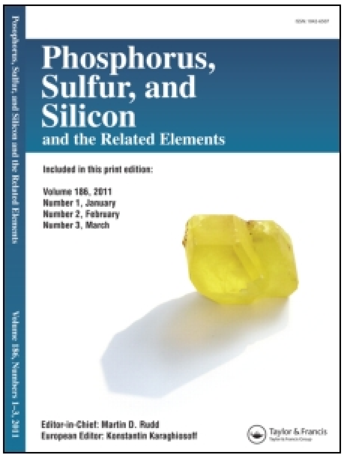

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SPECTROSCOPIC STUDY ON THE ELECTRON DELOCALIZATION WITHIN THE PHOSPHAZO RING

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To cite this Article Abd-ellah, I. M. , Al-shaibi, Y. , Ba-issa, A. A. and El-hammadi, M. S.(1998) 'SPECTROSCOPIC STUDY ON THE ELECTRON DELOCALIZATION WITHIN THE PHOSPHAZO RING', Phosphorus, Sulfur, and Silicon and the Related Elements, 139: 1, 29 — 43

To link to this Article: DOI: 10.1080/10426509808035675

URL: http://dx.doi.org/10.1080/10426509808035675

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Phosphorus, Sulfur and Silicon, 1998, Vol. 139, pp. 29-43
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SPECTROSCOPIC STUDY ON THE ELECTRON DELOCALIZATION WITHIN THE PHOSPHAZO RING

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(Received 2 December, 1996; In final form 14 March, 1997)

Interaction of hexachlorocyclodiphosph(V)azanes (1) with some aminocompounds such as aniline,o-aminophenol,p-toluidine,p-anisidine,p-chloroaniline,2-aminothiazol in acetonitrile furnished geminal aminocylcodiphosph(V)azanes of type (II_{a-x}). Reaction of these products with sulfur (solid) led to the formation of the disulfo-derivatives of type(III_{a-g}). The structure of the isolated substances was proposed on the basis of microanalytical data, infrared, ^{1}H n.m.r., and mass spectra. Ultraviolet studies on the electron delocalization within the four-membered ring of the dimeric structure were also discussed.

Keywords: cyclodephosphazane; disulfo derivatives; Nmr; UV; mass spectra

Although the synthesis of geminal and non-geminal aminocyclodiphosphazanes has been repoited$^{(1-2)}$ little is known about the affecting of the electron delocalization within the four membered ring by inductive and mesomeric effects.

EXPERIMENTAL

Microanalytical analyses were carried out by the microanalytical laboratory, Cairo University. Infrared spectra were recorded on a PYE-Unicam SP3-300 spectrophotometer (KBr technique). Ultraviolet spectra were recorded on shimadzu Uv.vis recording spectrophotometer. ^{1}H n.m.r. spectra were measured on a Varian EM-360L, 200 Mhz spectrophotometer,

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and mass spectra were measured out using a Finnigan MAT 1125 mass spectrometer by the direct inlet system.

STARTING MATERIALS

The preparation and purification of hexachlorocyclodiphosphazanes (I_{a-e}) has been reported $^{(2-4)}$ All the amino compounds used were B.D.H reagent grade products.

SYNTHESIS OF AMINOCYCLODIPHOSPH(V)AZANE DERIVATIVES (II_{A-X}) GENERAL PROCEDURE

The solid amino compound (0.01 mole) was added in small portions to a well stirred solution of the hexachlorocyclodiphosph(V)azane (I_{a-e}) (0.005 mole) in 100 ml acetonitrile during ½ hour. After the addition was complete, the reaction mixture was heated under reflux for two hours with continuous stirring. After the completion of the reaction (HCl gas ceased to evolve) the reaction mixture was filtered while hot and the solid obtained was washed several times with acetonitrile, diethylether and dried in vacuo to give the corresponding aminocyclodiphosph(V)azane derivatives (II_{a}-x), the data obtained are listed in table (I).

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PREPARATION OF DISULFUO-DIAMINOCYCLODIPHOSPH(V) AZANE DERIVATIVES OF TYPE (III_{a-g})

The solid amino compound (0.01) mole was added in small portions to a will stirred cold solution of the hexachlorocyclodiphosph(V)azane (I_{a-e}) (0.005 mole) in 100 ml acetonitrile during half hour. After the addition was completed the reaction mixture was heated under reflux for two hours with continous stirring. After the completion of the reaction (HCl gas ceased to evolve), then (0.32 g) of sulfur (solid) was added and the reaction mixture was heated under reflux for one hour with continous stirring.

The reaction mixture was filtered while hot at the pump. Then washed several times with acetonitrile then dry diethylether, disulfuoaminocyclodiphosph(V)azane (III_{a-g}) was obtained as solid crystals, (see table II).

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TABLE I Equimolar amounts and analytical data for amino cyclodipliosph(V)azane derivatives ($II_{a\text{-}x}$)

No. of Compd.	*Reactants*		*m.p.c°*	*colour*	*Empirical formula*	*Elements analysis Calc./Found*				
	cyclodiphosphazane	*Amino compound*				*%C*	*%H*	*%N*	*%P*	*%S*
II_a	I_a (2.29g, 0.005 mole)	aniline (0.93g,0.01 mole)	250d	white	$C_{24}H_{22}N_4P_3Cl_4$	50.50 50.60	3.50 3.90	9.82 9.50	10.87 10.20	- -
II_b	Ia (2.29g, 0.005mole)	p-toluidin (1.07g, 0.01mole)	153–155	pale cream	$C_{26}H_{26}N_4P_2Cl_4$	- -	- -	- -	10.36 11.18	- -
II_c	Ia (2.29g, 0.005mole)	p-anisidine (1.23g;0.01mole)	136–138	pale gray	$C_{26}H_{26}N_4P_2Cl_4O_2$	- -	- -	8.88 8.60	9.84 10.33	- -
II_d	I_a (2.29g, 0.005mole)	p-chloroaniline (1.28g;0.01mole)	178–180	white	$C_{24}H_{20}N_4P_2Cl_6$	45.00 44.80	- -	8.76 8.60	9.70 9.10	- -
II_e	Ia (2.29g, 0.005mole)	2-aminothaiazol (1.02g;0.01mole)	184	buff	$C_{18}H_{16}N_6P_2Cl_4S_2$	36.98 37.10	2.73 3.05	14.38 14.00	10.61 9.84	10.95 10.60
II_f	la (2.29g, 0.005 mole)	p-aminobenzoic acid (1.37g;0.01mole)	304 d	pale yellow	$C_{26}H_{22}N_4P_2Cl_4O_4$	47.41 48.20	3.34 3.45	8.51 8.80	9.42 8.84	- -
II_g	I_b (2.43g;0.005 mole)	aniline (0.93g;0.01mole)	184–186	white	$C_{26}H_{26}N_4P_2Cl_4$	- -	- -	9.36 9.50	10.36 11.21	- -
II_h	I_b (2.43g;0.005mole)	p-toluidine (1.07g;0.01mole)	158–160	pale yellow	$C_{28}H_{30}H_4P_2Cl_4$	- -	- -	8.94 8.60	9.90 9.20	- -
II_i	I_b (2.43g ;0.005 mole)	p-chloroaniline (1.28g;0.01mole)	193–195 d	cream	$C_{26}H_{24}N_4P_2Cl_6$	46.77 46.90	3.59 3.80	8.39 8.40	9.30 9.70	- -
II_j	I_b (2.43g;0.005 mole)	2-aminothaiazol (1.02g;0.01mole)	160 d	buff	$C_{20}H_{20}N_6P_2Cl_4S_2$	39.21 39.00	3.27 3.50	13.72 13.50	10.13 11.02	10.45 10.70
II_k	I_c (2.58g;0.005 mole)	aniline (0.93g;0.01mole)	156	white	$C_{26}H_{26}N_4P_2Cl_4O_2$	49.52 49.30	4.12 4.40	8.88 8.60	9.84 9.93	- -

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No. of Compd.	*Reactants*		*m.p.c°*	*colour*	*Empirical formula*	*Elements analysis Calc./Found*				
	cyclodiphosphazane	*Amino compound*				*%C*	*%H*	*%N*	*%P*	*%S*
II_l	I_c (2.58g;0.005mole)	p-toluidine (1.07g;0.01mole)	146–148	white	$C_{28}H_{30}N_4P_2Cl_4O_2$	- -	- -	8.51 8.50	9.42 8.80	- -
II_m	I_c (2.58g;0.005mole)	p-anisidine (1.23g;0.01mole)	172	gray	$C_{20}H_{30}N_4P_2Cl_4O_4$	48.69	4.34	8.11	8.98	-
II_n	I_c (2.58g;0.005mole)	2-aminophenol (1.09g;0.01mole)	146	white	$C_{26}H_{26}N_4P_2Cl_4O_4$	-	-	8.45	9.36	-
II_o	I_d (2.63g;0.005 mole)	aniline (0.93g;0.01mole)	160–162	white	$C_{24}H_{20}N_4P_2Cl_6$	-	-	8.76	9.70	-
II_s	I_d (2.63g ;0.005 mole)	2-aminophenol (1.09g;0.01mole)	150 d	cream	$C_{24}H_{20}N_4P_2Cl_6O_2$	-	-	8.34	9.24	-
II_t	I_c (2.45g ;0.005 mole)	p-toluidine (1.07g;0.01mole)	178–180 d	yellow	$C_{26}H_{26}N_4P_2Cl_4O_2$	49.52	4.12	8.88	9.84	-
II_u	I_c (2.45g;0.005 mole)	p-chloroaniline (1.28g;0.01mole)	138–140	pink	$C_{24}H_{30}N_4P_2Cl_6O_2$	-	-	8.34	9.24	-
II_v	I_c (2.45g;0.005 mole)	2-aminophenol (1.09g;0.01mole)	310 d	white	$C_{24}H_{22}N_4P_2Cl_4O_4$	45.42	3.47	8.36	9.78	-
II_w	I_c (2.45g ;0.005 mole)	2-aminobenzoic acid (1.37g;0.01mole)	198–200	pale yellow	$C_{26}H_{22}N_4P_2Cl_4O_6$,	45.21	3.18	8.11	9.00	-
II_x	I_c (2.45g;0.005 mole)	2-aminothiazol (1.02g;0.01mole)	138–140 d	buff	$C_{18}H_{16}N_6P_2Cl_4O_2S_2$	35.06	2.60	13.63	10.06	10.39

(d) means decomposed.

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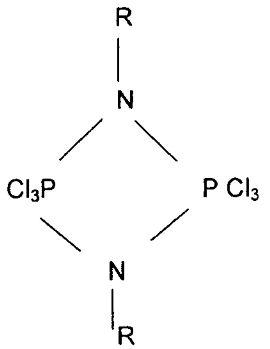
TABLE II Equimolar amount, and analytical data for the reaction of products 2,4-diamino cyclodiphosphazane dimer (II) with 0.32 g sulfur

No. Of Compd.	Reactants		m.pc°	Colour	Empirical formula	Element analysis Calc./Found		
	Cyclodiphosphazane(I)	Amino Compound				%N	%P	%S
III_a	I_a (2.29g ; 0.005 mole)	aniline (0.93g ; 0.01 mole)	120–122	pale yellow	$C_{24}H_{22}N_4P_2S_2$	- -	12.60 11.90	13.00 12.90
III_b	I_d (2.63g ; 0.005 mole)	aniline (0.93g ; 0.01 mole)	160-162	greenish yellow	$C_{24}H_{20}N_4P_2S_2O_2$	9.98 9.70	11.05 11.60	11.40 11.60
III_c	I_d (2.63g ; 0.005 mole)	p – chloroaniline (1.28g ; 0.01 mole)	230	pale yellow	$C_{24}H_{18}N_4P_2Cl_4S_2$	8.88 8.90	9.84 9.16	- -
III_d	I_c (2.58g ; 0.005 mole)	p – toluidine (1.07g ; 0.01 mole)	154	greenish yellow	$C_{28}H_{30}N_4P_2S_2O_2$	9.65 9.30	10.68 10.32	11.03 10.90
III_e	I_c (2.58g ; 0.005 mole)	aniline (0.93g ; 0.01 mole)	154	greenish yellow	$C_{26}H_{26}N_4P_2S_2O_2$	10.14 9.90	11.23 10.41	- -
III_f	I_c (2.58g ; 0.005 mole)	p-chloroaniline (1.28g ; 0.01 mole)	184–186	greenish yellow	$C_{26}H_{24}N_4P_2Cl_2S_2O_2$	9.01 8.90	9.98 9.31	10.30 10.3010 .30
III_g	I_d (2.63g ; 0.005 mole)	2-aminothiazol (1.02g ; 0.01 mole)	142–144 d	pale brown	$C_{18}H_{14}N_6P_2Cl_2S_4$	14.60 14.20	10.78 10.30	22.26 22.00

(d) means decomposed.

Results and discussion

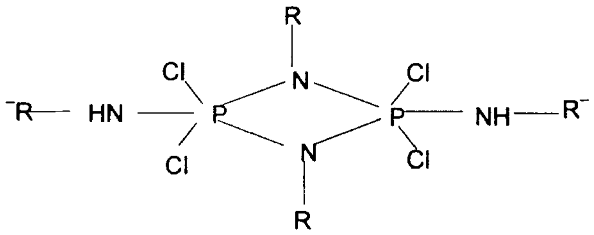
In the present work, different hexachlorocyclodiphosphazanes of type ($I_{a\text{-}e}$) have been prepared essentially by the method described in the literature$^{(2–4)}$



($I_{a\text{-}f}$)

I_a; R = C_6H_5
I_a; R= C_6H_5
I_b; R = $C_6H_4 - CH_3$- p
I_c; R = $C_6H_4 - OCH_3$ – p
I_d; R = C_6H_4 – Cl – p
I_e; R = C_6H_4 – OH – o

The direct reaction between halophosphazanes (I) and amino aromatic compounds in acetonitrile led to the formation of geminal amino cyclodiphosphazane derivatives of type ($II_{a\text{-}x}$).



($II_{a\text{-}x}$)

No. Of Compd.	*R*	*R'*
II_a	C_6H_5	C_6H_5
II_b	C_6H_5	$C_6H_4 - CH_3$ – p

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No. Of Compd.	*R*	R^{-}
II_c	C_6H_5	$C_6H_5 - OCF_H - p$
II_d	C_6H_5	$C_6H_4 - Cl - p$
II_e	C_6H_5	$C_3H_2NS - \alpha$
II_f	C_6H_5	$C_6H_4 - COOH - p$
II_g	$C_6H_4 - CH_3$- p	C_6H_5
II_h	$C_6H_4 - CH_3 - p$	$C_6H_4 - CH_3 - p$
II_i	$C_6H_4 - CH_3 - p$	$C_6H_4 - Cl - p$
II_j	$C_6H_4 - CH_3 - p$	$C_3H_2NS - \alpha$
II_k	$C_6H_4 - OCH_3 - p$	C_6H_5
II_l	$C_6H_4 - OCH_3 - p$	C_6H_4 - CH3 - p
II_m	$C_6H_4 - OCH_3 - p$	$C_6H_4 - OCH_3 - p$
II_n	$C_6H_4 - OCH_3 - p$	$C_6H_4 - OH - o$
II_o	$C_6H_4 - Cl - p$	C_6H_5
II_p	$C_6H_4 - Cl - p$	$C_6H_4 - CH_3 - p$
II_q	$C_6H_4 - Cl - p$	$C_6H_4 - OCH_3 - p$
II_r	$C_6H_4 - Cl - p$	$C_6H_4 - Cl - p$
II_s	$C_6H_4 - Cl - p$	$C_6H_4 - OH - o$
II_t	$C_6H_4 - OH - o$	$C_6H_4 - CH_3 - p$
II_u	$C_6H_4 - OH - o$	$C_6H_4 - Cl - p$
II_v	$C_6H_4 - OH - o$	$C_6H_4 - OH - o$
II_w	$C_6H_4 - OH - o$	$C_6H_4 - COOH - o$
II_x	$C_6H_4 - OH - o$	$C_3H_2NS - \alpha$

The structure of these compounds has been substantiated on the basis of the following points :

i. Elemental analysis are in good agreement with the proposed structures (see table I)

ii. The infrared spectra of these compounds showed the characteristic absorption bands, which are summarized in table (III)

iii. ^1H n.m.r. spectra of the isolated compounds (I-II) showed the aromatic proton signal at delta $\delta = 7.4$ ppm and a signal characteristic for $-CH_3$protons and $-OCH_3$ protons at $\delta = 2.1$ ppm and 3.8 ppm respectively, the characteristic proton signals are listed in table (IV).

iv. Mass spectrometric measurements shed light on the structure of these products, thus the spectra showed the mole peaks for many compounds which are given in table (V), also most of the expected fragments were observed in the spectra.

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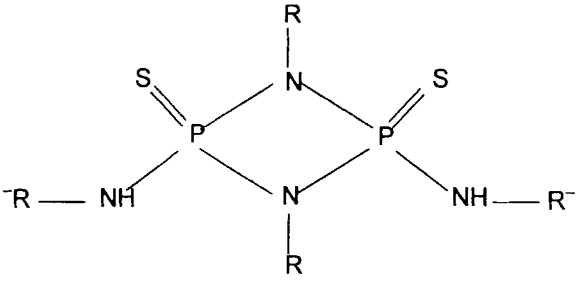
Further confirmation of the structural assignment of these products was gleaned from the preparation of sulfur derivative. Thus the interaction of hexachlorocyclodiphosphazane (I) and aminocompounds in the presence of sulfur solid in acetonitrile led to the formation of a well defined material which gave analytical data suggesting structure (III_{a-g}).



(III_{a-g}

No. of Compound	*R*	*R^-*
III_a	C_6H_5	C_6H_5
III_b	$C_6H_4 - Cl - p$	C_6H_5
III_c	$C_6H_4 - Cl - p$	$C_6H_4 - Cl - p$
III_d	$C_6H_4 - OCH_3 - p$	$C_6H_4 - CH_3 - p$
III_e	$C_6H_4 - OCH_3\ p$	C_6H_5
III_f	$C_6H_4 - OCH_3 - p$	$C_6H_4\text{-}Cl - p$
III_g	$C_6H_4 - Cl - p$	$C_3H_2NS - \alpha$

The Assignment of the products (III_{a-g}) was based on elemental analysis which are in good agreement with the proposed structures (III_{a-g}) (See table II).

TABLE III Infrared of Compounds (II_{a-x})

	Strentching Frequencies in Cm^{-1}					
No. of Comp.d	*ν N-H*	*ν P-N-H*	*ν OH*	*ν P-N*	*ν disub. Ar. ring*	*ν P-Cl*
II_a	3360(w)	2560(w)	-	1175(w)		465(s)
II_b	3050(br)	2600(br)	-	1140(w)	850 (s)	500(w)
II_c	3000(br)	2560(br)	-	1160(w)	845(v.s)	500(s)

Strertching Frequencies in Cm^{-1}						
No. of Comp.d	*v N-H*	*v P-N-H*	*v OH*	*v P-N*	*v disub. Ar. ring*	*v P-Cl*
II$_d$	3300(br)	2660(v.w)	-	1180(w)	850(s)	500(w)
II$_e$	3400(br)	2750(br)	-	1180(w)	845(m)	490(br)
II$_f$	3340(w)	2600(br)	-	1190(w)	860(s)	450(br)
II$_g$	3020(br)	2600(w)	-	1170(v.w)	860(s)	470(w)
II$_h$	3000(br)	2600(w)	-	1190(m)	850(s)	470(m)
II$_i$	3000(br)	2590(w)	-	1175(w)	860(s)	470(w)
II$_j$	3000(br)	2550(br)	-	1150(w)	860(m)	475(w)
II$_k$	3000(br)	2600(v.w)	-	1170(w)	810(m)	450(br)
II$_l$	3360(br)	2600(br)	-	1170(w)	815(s)	460(br)
II$_m$	3000(br)	2600(w)	-	1160(m)	810(s)	460(br)
II$_n$	3000(br)	2570(br)	1370(m)	1160(w)	820(s)	460(w)
II$_o$	3000(br)	2600(m)	-	1170(w)	870(s)	470(br)
II$_p$	3350(br)	2740(br)	-	1150(m)	830(s)	510(w)
II$_q$	3000(br)	2600(br)	-	1160(s)	860(v.s)	480(br)
II$_r$	3350(v.w)	2750(m)	-	1170(s)	820(v.s)	480(s)
II$_s$	3350(br)	2600(br)	1360(m)	1200(s)	830(s)	480(s)
II$_t$	3200(br)	2600(m)	1360(s)	1175(v.w)	845(m)	480(m)
II$_u$	3050(br)	2610(br)	1360(s)	1180(w)	820(s)	480(w)
II$_v$	3280(s)	2610(w)	1365(v.s)	1165(v.s)	840(m)	470(s)
II$_W$	3200(br)	2760(br)	1350(s)	1160(m)	845(m)	460(br)
II$_x$	3100(br)	2600(br)	1340(m)	1160(m)	830(br)	450(m)

(v.w) means very weak. (m) means moderate. (v.s) means very strong. (w) means weak. (s) means strong. (br) means broud

TABLE IV ^{1}Hn.m.r. data for compounds (I-II)

Chemical Shifts δ in ppm					
No. of compd.	*CH$_3$*	*OCH$_3$*	*Aromatic*	*NH*	*OH*
I$_a$	-	-	6.90	-	-
I$_b$	2.2	-	7.15	-	-
I$_c$	-	3.7	7.10	-	-
I$_d$	-	-	7.36	-	-
I$_f$	-	-	7.30	-	-

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	Chemical Shifts δ in ppm				
No. of compd.	*CH_3*	*OCH_3*	*Aromatic*	*NH*	*OH*
II_a	-	-	7.30	5.2	-
II_b	2.2	-	7.35	6.8	-
II_c	-	3.7	7.10	6.8	-
II_d	-	-	7.17	6.8	-
II_e	-	-	7.10	8.0	-
II_i	2.3	-	7.10	6.6	-
II_o	-	-	7.36	4.8	-
II_x	-	-	7.00	5.4	9.5

TABLE V Mass Spectra For Compounds (I-II)

No.of compound	*Mole peak*		
	Calc.	*Found*	*Abundance %*
Ia	457	457	0.05
II_a	570	569	0.10
II_b	598	597.5	0.03
II_c	630	630	0.01
II_d	639	637.9	0.23
II_e	584	588.5	0.04
II_i	667	667	0.03
II_t	630	630.5	0.01
II_v	634	633.9	3.09
II_x	616	616	0.02

TABLE VI Infrared data for compound (III_{a-g})

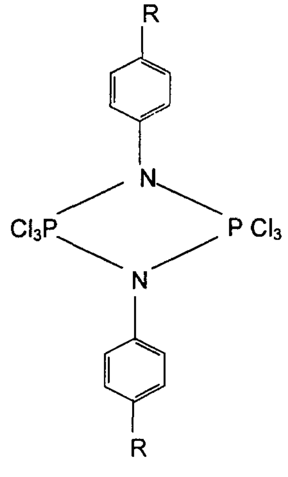
	Stretching Frequencies in Cm^{-1}				
No of Compd	*ν N-H*	*ν P-N-H*	*ν P-N*	*ν disub. Ar. ring*	*ν P = S*
III_a	3350(v.w)	2500(br)	1180(w)		670(s)
III_b	3000(br)	2680(v.w)	1170(w)	860 (m)	630(m)
III_c	3300(br)	2690(w)	1170(w)	850(w)	660(m)
III_d	3100(br)	2740(br)	1190(s)	820(v.s)	660(s)
III_e	3300	2710(br)	1160(w)	840(w)	640(m)
III_f	3000(br)	2800(br)	1170(m)	820(s)	620(w)
III_g	3300(br)	2740(br)	1150(w)	810(w)	660(m)

(v.w) means very weak. (m) means moderate. (v.s) means very strong. (w) means weak. (s) means strong. (br) means broad.

The infrared spectra for these products (III_{a-g}) showed the characteristic νNH stretching vibrations at $\lambda = 3400–3100\ cm^{-1}$, νP-N-H stretching mode at $2700–2500\ cm^{-1}$, and νP = S stretching mode at $\lambda = 620–670\ cm^{-1}$ the data are listed in table (VI). The mass spectra for compounds of type (III_{a-g}) showed the expected fragments.

Ultraviolet spectra

The fact that the expected band between 270–290 nm$^{(5)}$, characteristic for electron delocalization within the four-membered ring of the dimeric structure, was observed in the spectra for compounds of type(I-III)suggests the presence of the phosphazo four-membered ring. The ultraviolet spectrum for compound (I_a), show an absorption peak at λ max =283.9 nm (extinction coefficient=379.8), this band was shifted to lower wave lenght and high intensity of peak upon placement of groups having (+ I and + M effects) such as-CH_3(I_b), -OCH_3 (I_c) in the para and/or-OH(I_e) in the ortho position of the chromophoric system. (phenyl group) attached to nitrogen atom of the phosphazo ring while upon placement of -Cl atom (I_d), the band was shifted to a longer wale lenght with an increase in the intensity of the band (Fig. 1) and Table(VII).



(I_{a-e})

I_a; R=-H
I_b; R-CH_3-p
I_c; R=-OCH_3-p
I_d; R=-Cl-p
I_e; R=-OH-o

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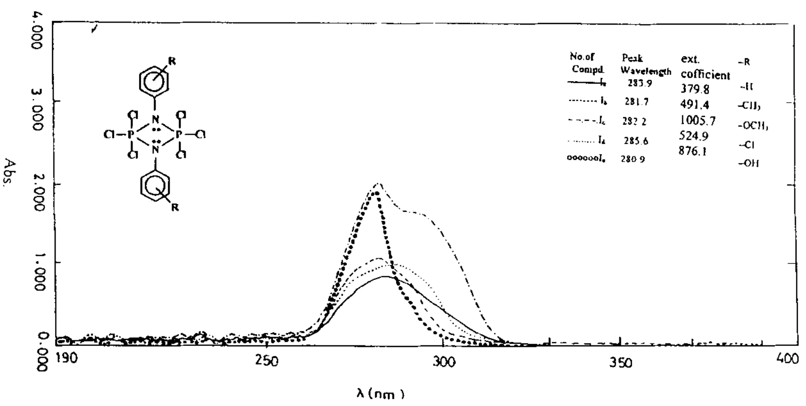

FIGURE 1 Ultraviolet Spectra for Compounds(I_{a-e}) in ethanol

TABLE VII Ultraviolet spectral data for compounds (I- III)

No. of compound	*λ max in nm*	*ext.coeff*
Ia	283.9	379.8
I_b	281.7	491.4
I_c	282.2	1005.7
Id	285.6	524.9
I_e	280.9	876.1
II_a	275.5	502.7
II_b	277.8	653.0
II_c	280.2	895.9
II_d	281.8	1528.5
II_e	300.0	1868.8
III_a	283.1	933.3
III_b	286.3	1348.9
III_c	289.5	1848.9
III_d	287.9	1614.2
III_e	290.0	1835.3
III_f	283.6	1656.8
III_g	300.7	1936.8

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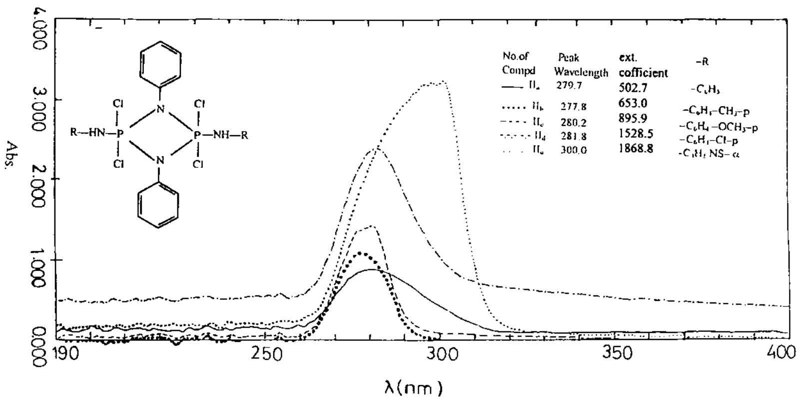

FIGURE 2 Ultraviolet Spectra for Compounds(II_{a-e}) in ethanol

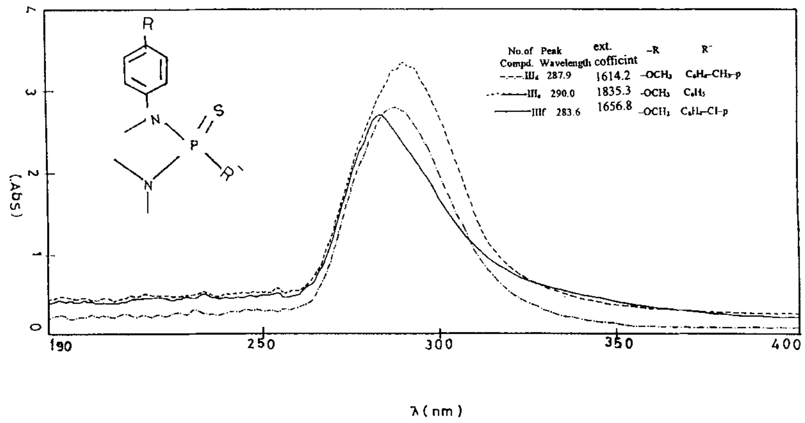

FIGURE 3 U.v spectra for Compounds ($III_{d,e,f}$)

On placement of chlorine atom on phosphorus by electron with drawing groups (-I effects), (+M effects)(II_d) or chromophoric groups containing conjugated system such as thiazol ring (II_e) show an absorption peak at λ = 281.8nm (extinction coefficient 1528.5) and at λ = 300.0 nm (extinction coefficient 1839.8) respectively, while the replacement of the chlorine atom on phosphorus by groups with donating electrons (+I or +M) such as tolyl or anisidyl groups (II_b and II_c) stabilize the resonance within the four-membered ring (Fig. 2)

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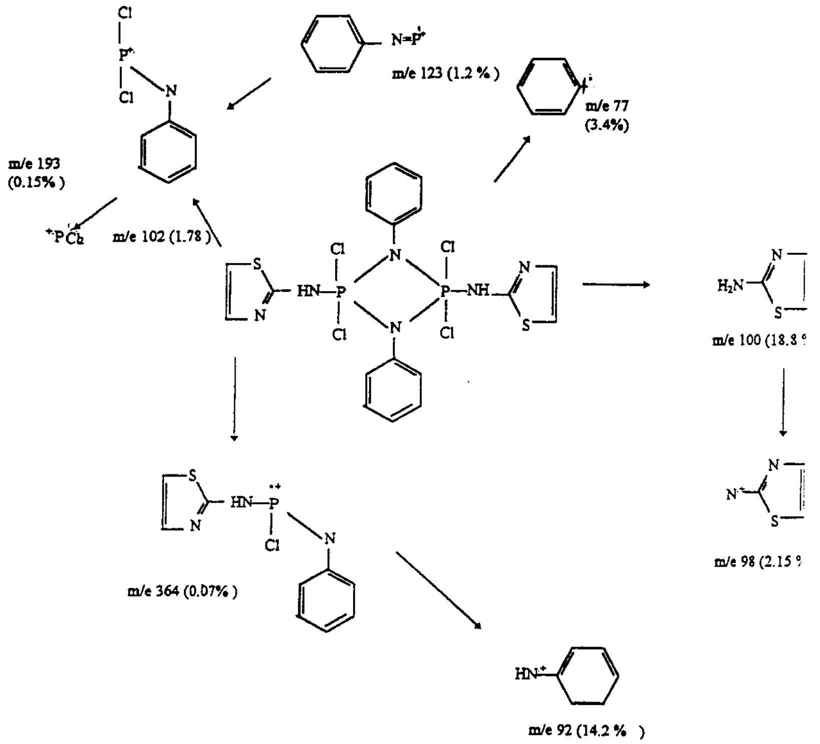

SCHEME 1 fragmentation pathway for compound (IIe)

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Replacement of of the dichloro atoms on phosphorous in compounds of type (II) by a sulfur atom led to an increase in the intensity of the absorption peak, and the band was shifted to longer wave length may be due to the differences in electronegativity between phosphorous and sulfur, ($III_{d,e,f}$) Fig (3) the data are listed in table (VII). We concluded by the electron delocalization within the phosphazoring are much affected by groups having electron attracting or electron donating character attached to phosphorus atom, because such groups are in plane with phosphorus and nitrogen atoms of phosphazo-ring. Fig.(4).

References

[1] Abd-Ellah, I.M; Ibmhh% E.H.M; and El-Khazandar, AN; J. *Phosph. and sulfur*, **31**,13 (1987), *Phosph. and sulfur*, **33**, 109 (1987).

[2] Abd-Ellah, I.M; Ibrahim, E.H.M; and El-Khazandar, A.N; J. Sci. Ind. Res., 31(6),395 (1988).

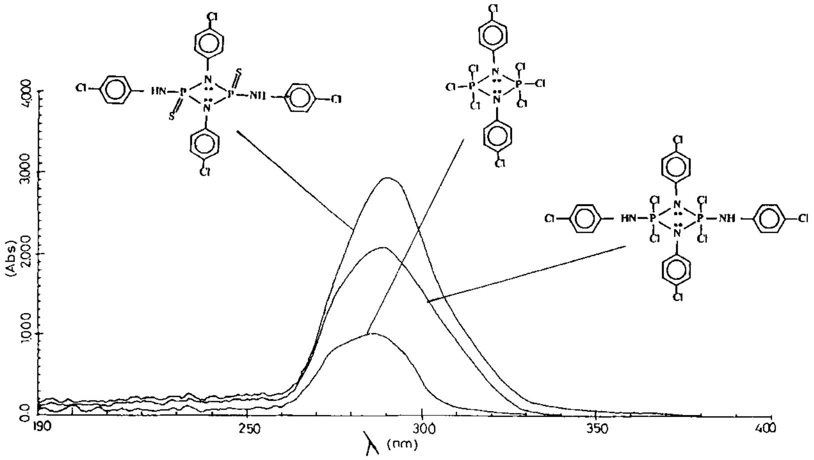

FIGURE 4 Ultraviolet Spectra for Compounds(I_d, II_r, III_c in ethanol

[3] Chapman, A.C.,Padddock, N.L. and Searle, H.T., J. Chem. Soc., 1825 (1961).
[4] Kirsanov, A.V., Zhmurova, I.N. andObsch. Khim., Zh. 32,2576 (1963).
[5] Abd-Ellah, I.M; Ibrahim, E.H.M; and El-Khazandar, A.N; J. Phosph. and sulfur, vol.29, 239(1987)

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