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Synthesis, Spectral Study and Antimicrobial Screening of Poly(4,4'-Cyclohexylidene-R,R'-Diphenylene Diphosphate)

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ABSTRACT

Polyphosphate of 1,1-bis(R,R'-4-hydroxyphenyl)cyclohexane (R,R'=H,$CH_3$and Cl) are synthesized by refluxing bisphenol-c derivative with phosphorous oxytrichloride in pyridiene at 95°C for 4hr and then at 240°C for 6hr. Polyphosphate have been ascertained by IR and NMR spectral data. Polyphosphate are also Characterized by their antibacterial and antifungal activities. The activity is interpreted in light of bisphenol Structure and the nature of substituent(s).

Key words: Bisphenol, Polyphosphate, IR, NMR, Antimicrobial screening.

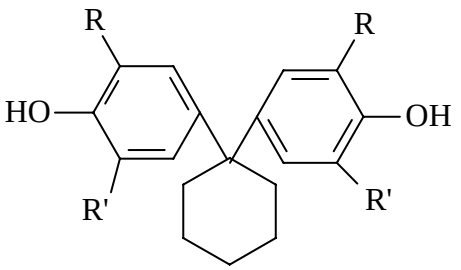
INTRODUCTION

Bisphenols and their derivatives are effective fungicides, antibacterial, coccicidal, antifertility agent, disinfectants, agricultural fungicides[1,2] etc. Phosphate of bisphenols are useful as insecticides as well as miticides[3]. The wide scale use of bisphenolic bioactive agent has brought many advantages particularly to the agricultural industries which involve delivery systems in which the agrochemical is chemically bound to a polymeric system. Good and resistant plastic materials have been obtained from bisphenols and phosphorous oxychloride. Organo-phosphorous ester resins find their use as additive in gasoline and plastic materials as well as plasticizers and fire retardant[4].

EXPERIMENTAL

Section-1 synthesis of bisphenol derivatives

Cyclohexanone (0.05mole) was condensed with Phenol or O-Cresol (0.1mole) in

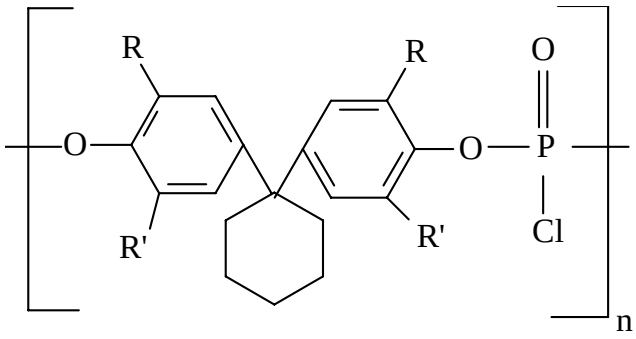


BC: R=R'=H
ClBC: R=R'=Cl
MeBC: R= CH_3 and R'=H
ClMeBC: R=CH_3 and R'=Cl

the presence of mixture of hydrochloric acid and acetic acid (2:1v/v) at 55-60°C for 3h[5]. Bisphenols (0.056mole) were chlorinated by $SOCl_2$ (10ml) in CCl_4 (90ml) using Na_2S (0.005mole) as a catalyst at 55°C for 3hr and 70°C for 1h[6].

Section-2 synthesis of polyphosphate

Polyphosphates of bisphenol-C derivatives are synthesized by refluxing 0.01 mole of corresponding bisphenol-C derivatives with a 0.01 mole(1ml) $POCl_3$ and 25ml Pyridine at 95°C for 4h and then at 240°C for 6h. The phosphate were isolated from cold water, washed well with water, dried at room temperature and repeatedly recrystallized from DMF-Water system.



PHO-1 : R=R'=H PHO-2 : R= CH_3 and R'=H

PHO-3 : R=R'=Cl PHO-4 : R=CH_3 and R'=Cl

Antimicrobial screening of polyphosphate

In order to grow different micrograms, the nutrient agarmedia was prepared according to reported method and antimicrobial screening was measured by cup-plate method[7,8]. The zones of inhibition for standard drugs and compounds under investigation against different microbes are reported in Table-4.

RESULTS AND DISCUSSION

Physical data of polyphosphate are reported in Table-1

The IR spectra (KBr pellets) of polyphosphate PHO-1 to PHO-4 were scanned on a Shimadzu (FTIR-8400) over the frequency range 4000-400 cm^{-1} and shown in Fig-1. The characteristic adsorption frequencies are reported in Table-2.

The NMR spectra of polyphosphate PHO-1 to PHO-4 were scanned on a Bruker FT NMR (300MHz) spectrometer by using a mixture of $CDCl_3$-DMSO-d_6 as a solvent and TMS as an internal standard. NMR spectra are shown in Fig-2. Different types of protons, multiplicity and chemical shifts are reported in Table-3.

It is clear from antimicrobial screening of polyphosphate that PHO-1 to PHO-4 possess comparable activity with amoxicillin, ampicillin and erythromycin against *E.coli* but PHO-1 possesses

Table 1: Physical data on polyphosphate

Polyphosphate	Z	R	R'	Yield%	m.p.°C
PHO-1	Cyclohexyl	H	H	82	169
PHO-2	Cyclohexyl	CH_3	H	78	144
PHO-3	Cyclohexyl	Cl	Cl	81	110
PHO-4	Cyclohexyl	CH_3	Cl	75	75

moderate activity as compared to ciprofloxacin against the same microbe.

PHO-1, PHO-3 are active as amoxicillin and ampicillin against *B.mega* but PHO-2, PHO-4 are moderately active with ampicillin against *P. vulgaris*. PHO-1, PHO-4 possess comparable activity with erythromycin against *S. aureus*. PHO-2 and PHO-4 are moderately active with erythromycin against *A*. *niger*. In conclusion the compounds under investigation possess moderate to superior activity against selected microbes.

Table 2: The characteristic IR(KBr) absorption frequiences of PHO-1 to PHO-4

Type	Group Vibration mode	Observed IR frequiences cm^{-1}				Expected IR Frequience cm^{-1}
		PHO-1	PHO-2	PHO-3	PHO-4	
ArOH	O-H (str)	3587.4	3275	3435	3375.2	3580-3230
	O-H (def)	1365.5	1390	1365.5	1350.1	1410-1310
	C-O (Str)	1180.4	1240.1	1238.2	1203.5	1230-1140
Aromatic	C-H (str)	3016.5	3031	3016.5	3031.9	3080-3030
	C=C (str) 1,4 sub	1612.4	1608.5	1612.4	1608.5	1606 ± 6
		1510.2	1500.5	1593.1		1579 ± 6
						1520-1480
	C=C (str) 1,2,4sub	1512.8	1452.3	1510.2	1450.4	1510 ± 8
						1456 ± 8
	C-H (i.p. def) 1,4 sub	1238	1118.6	1180.4	1120.6	1258 ± 11
						1175 ± 6
						1117 ± 7
	C-H (i.p. def) 1,2,4 sub	1180.4	1082	1012.6	1168.8	1175-1125
						1070-1000
	C-H (o.o.p. def) 1,4 sub	817.8	813.9	819.7	812	817 ± 15
	C-H (o.o.p. def) 1,2,4 sub	893	856.3	894.9	856.3	900-860
		817.8	813.9			860-800
Alkane	C-H (str) y as	2933.5	2931.6	2935.5	2931.6	2975-2950(CH_3)
						2940-2915(CH_2)
	C-H (str) y s	2858.3	2856.4	2858.3	2856.4	2880-2860(CH3)
						2870-2845(CH2)
	$-CH_3$ δs		1390		1356.1	1385-1370
	$-CH_2$ δas	1446.5	1452.3	1448.4	1450.4	1480-1440
Phosphrous	P=O (str)	1238.2	1203.5	1238.2	1238.2	1350-1150
		1180.4		1180.4		
	P-O (str)	1103.2	1118.6	1103.2	1120.6	1240-900
		1012.6	1082	1012.6	1080.1	
	P-Cl	500	503.4	526.5	499.5	500
	-P=O	930	923.8	930	923.8	950
Halogen	C-Cl(str)			729	678.9	800-600
				640.3	750.3	

Table 3: The chemical shifts of polyphosphates

Polyphosphate	Chemical shift	Types of
	δ ppm	proton(s)
PHO-1	8.708	Ar-OH(s)
	7.061-7.013	Ar-H(m)
	6.708-6.660	Ar-H(m)
	2.16	α -CH_2-(s)
	1.473	β+γ -CH_2-(s)
PHO-2	8.54	Ar-OH(s)
	7.162-6.911	Ar-H(m)
	2.225-2.107	α -CH_2 - + -CH_3(d)
	1.468	β+γ -CH_2-(s)
PHO-3	8.753	Ar-OH(s)
	7.045-7.017	Ar-H(d)
	6.695-6.648	Ar-H(m)
	2.156	α -CH_2-(s)
	1.471	β+γ -CH_2-(s)
PHO-4	8.595	Ar-OH(s)
	7.339	Ar-H(s)
	6.938-6.827	Ar-H(m)
	2.112	α -CH_2 - + -CH_3(d)
	1.472	β+γ -CH_2-(s)

Table 4: The zone of inhibition for polyphosphate and standard drugs

Compound	Zone of inhibition (mm)				
	Antibacterial				Antifungal
	E.coli	***B.mega***	***P.vulgaris***	***S.aureus***	***A.niger***
Amoxycillin	16	20	24	25	20
Ampicillin	16	22	21	29	15
Ciprofloxacin	30	30	28	26	21
Erythromycin	17	25	23	17	19
DMF	9	9	9	9	9
PHO-1	23	20	15	19	13
PHO-2	17	15	11	14	16
PHO-3	19	20	10	16	12
PHO-4	16	15	10	17	15

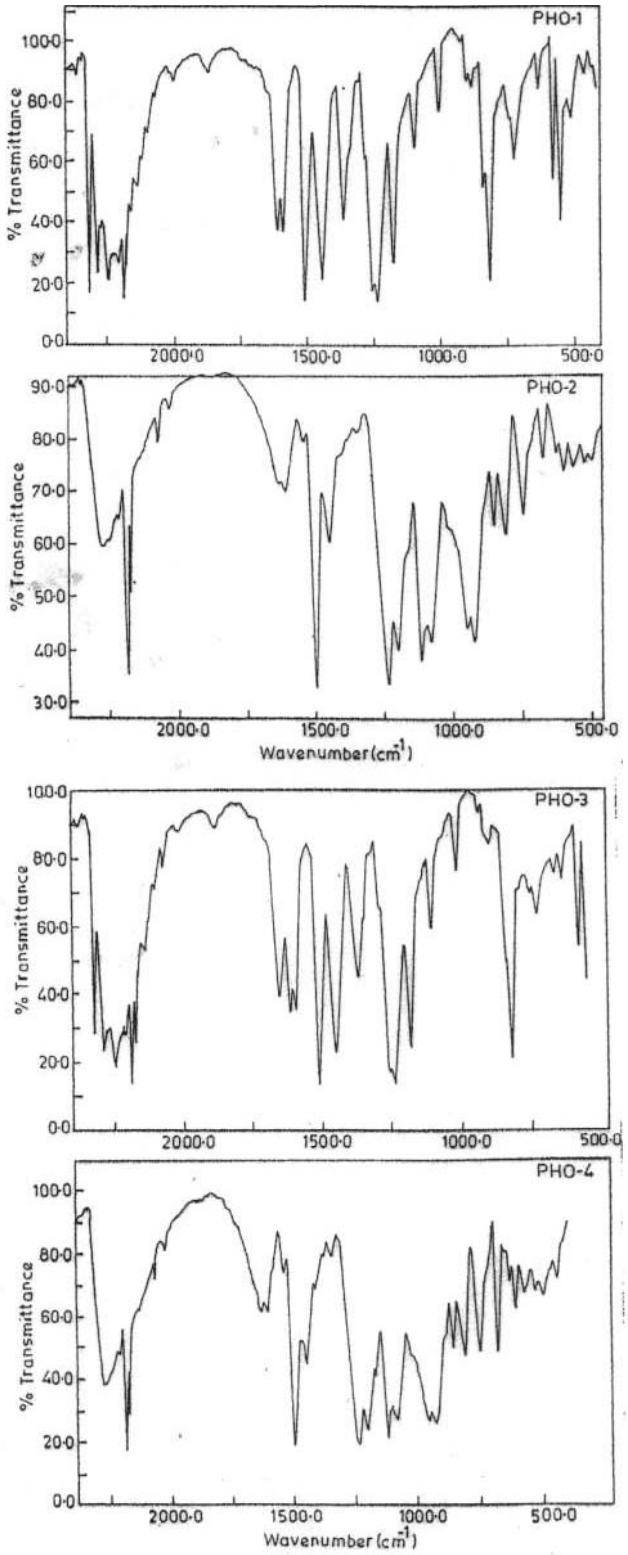


Fig. 1: The IR Spectrum of PHO-1 to PHO-4

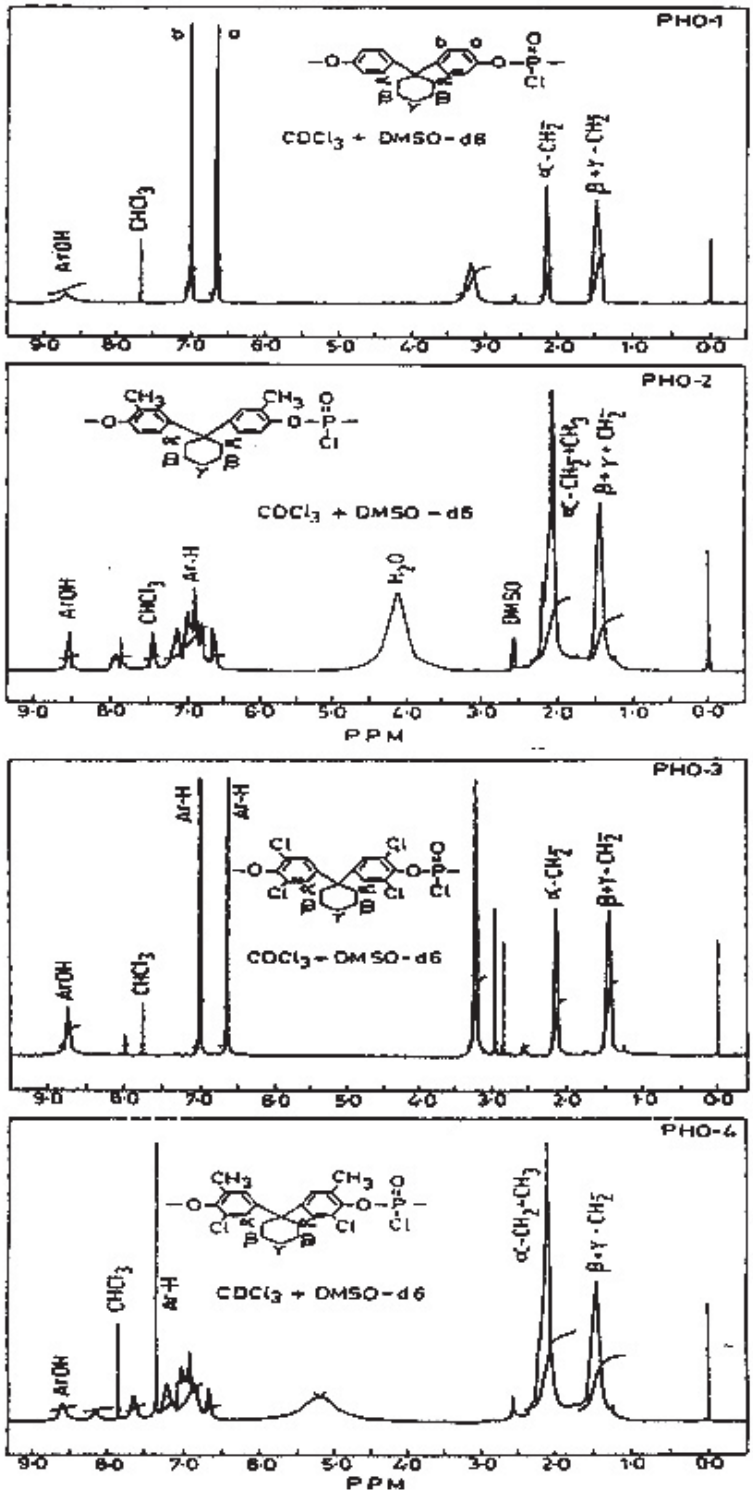


Fig. 2: The NMR Spectrum of PHO-1 to PHO-4

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