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Synthesis, Biological and Thermal Properties of Schiff Bases of Bisphenol-C

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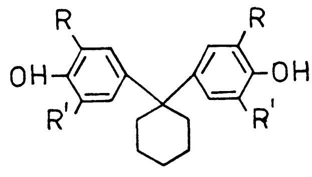
Schiff bases based on bisphenol-C were synthesized by reacting substituted benzaldehyde (o-NO_2, p-NO_2 and p-OCH_3) and amino bisphenol-C in DMF. The structures are supported by UV, IR and NMR spectral data. The schiff bases showed promising antibacterial and antifungal activities against *E. coli* and *A. awamori* and moderate activities against *B. mega.* BSB-3 has excellent thermal stability (662°C) while MSB-2 has least thermal stability (188°C) and the rest have comparatively good thermal stability.

INTRODUCTION

Bisphenols and their derivatives find their extensive applications in various fields[1–8]. The literature survey on Schiff bases based on cardo bisphenols revealed that no work has been reported so far, which prompted us to investigate synthesis and characterization of Schiff bases of structure-I:



(I)

BSB-1 R = R′ = —N═CH-o-NO_2Ar
BSB-2 R = R′ = —N═CH-p-OCH_3Ar
BSB-3 R = R′ = —N═CH-p-ClAr
BSB-4 R = R′ = —N═CH—Ar

MSB-1 R = CH_3, R′ = —N═CH-o-NO_2Ar
MSB-2 R = CH_3, R′ = —N═CH-p-OCH_3Ar
MSB-3 R = CH_3, R′ = —N═CH-p-ClAr
MSB-4 R = CH_3, R′ = —N═CH—Ar

EXPERIMENTAL

All the chemicals and solvents used were purified according to literature processes. Precoated silica gel plates were used for analytical TLC. M.Ps. were determined in open capillaries and are uncorrected.

1,1′-Bis(4-hydroxyphenyl)cyclohexane (BC) and 1,1′-bis(3-methyl-4-hydroxyphenyl)cyclohexane (MeBC) were synthesized according to our earlier work[9, 10]. BC and MeBC (0.1 mol) in 100 mL CH_3COOH were nitrated using HNO_3 and H_2SO_4 (2 : 1 v/v) nitrating mixture (100 mL) at 70°C for 3 h. Nitro BC and MeBC were reduced using tin metal (0.01 mol) and concentrated hydrochloric acid (7.5 mL) at reflux temperature for 2 h. The residual tin was separated and solution was made alkaline with concentrated ammonia. The separated product was filtered, washed well with water and dried at 50°C. The amino BC and MeBC were purified repeatedly from methanol-water system.

Schiff bases were synthesized by reacting substituted benzaldehyde (*o*-NO_2, *p*-nitro and *p*-OCH_3) (0.04/02 mol) with amino BC and MeBC (0.01 mol) in DMF (15 mL) at reflux temperature for 8 h. The product was isolated from chilled water, filtered, washed well with distilled water and dried at 50°C. Schiff bases were repeatedly recrystallized from DMSO-MeOH-H_2O system. The purity of Schiff bases was ehecked by TLC using benzene : acetone (4.5 : 5.5 v/v).

Antibacterial and antifungal activities were tested by cup-plate method[11] against different microbes at 37°C using DMF as a solvent. The sample concentration was 50 μg.

RESULTS AND DISCUSSION

Physical and spectral data of schiff bases are reported in Table-1. IR spectra displayed characteristic bands (cm^{-1}) at 3423–3391 ν(—OH), 1683–1597 ν(N=CH), 1530–1527 ν_{as}ν(—NO_2), 1349 ν_s, 1252–1251 ν(ArOCH_3), 640–607 ν(ArCl) besides normal modes of the alicyclic and aromatic groups.

TABLE-1
THE PHYSICAL AND SPECTRAL DATA OF SCHIFF BASES

Compound	m.p. (°C) (% yield)	λ_{max} nm	δ ppm
BSB-1	296 (70)	252.0 200.0	1.25 (s, β + γ—CH_2—), 2.1 (s, α—CH_2—), 8.44–7.12 (m, Ar—H)
BSB-2	308 (66)	252.2 (200.0)	1.45 (s, β + γ—CH_2), 2.11 (s, α—CH_2—), 4.34–4.30 (d, —OCH_3), 7.47–6.90 (m, Ar—H), 7.65–7.55 (m, Ar—H), 8.15–8.06 (m, Ar—H) and 8.44 (s, Ar—OH)
BSB-3	262 (67)	281.0 200.0	1.24 (s, β + γ—CH_2—), 1.44 (s, α—CH_2—), 6.8–6.61 (m, Ar—H), 7.15–7.02 (m, Ar—H), 7.26–7.18 (m, Ar—H), 7.45–7.30 (m, Ar—H), 8.21–8.1 (m, Ar—H) and 8.39 (s, Ar—OH)
BSB-4	292 (63)	286.4 200.0	1.25 (s, β + γ—CH_2—), 1.78 (s, α—CH_2—), 7.42–7.1 (m, Ar—H) and 8.42 (s, Ar—OH)
MSB-1	— (72)	214.4	0.94–0.83 (t, β + γ—CH_2), 1.26 (s, —CH_2— + Ar—CH_3), 7.97–7.0 (m, Ar—H) and 8.4 (s, Ar—OH)
MSB-2	294 (65)	293.6 281.0 200.0	1.25 (s, β + γ—CH_2—), 2.15 (s, α—CH_2— + Ar—CH_3), 4.35–4.23 (d, —OCH_3), 7.99–7.07 (m, Ar—OH) and 8.39 (s, Ar—OH)
MSB-3	163 (69)	416.0 293.6 281.0 200.0	1.25 (s, β + γ—CH_2—), 1.60 (s, α—CH_2— + Ar—CH_3), 6.86–6.83 (d, Ar—H) and 7.29–7.26 (d, Ar—H)
MSB-4	— (66)	416.0 293.6 281.0 200.0	1.26 (s, β + γ—CH_2—), 2.77 (s, α—CH_2— + Ar—CH_3), 7.76–6.90 (m, Ar—H) and 8.45 (s, Ar—OH)

Antibacterial and Antifungal Activities: All compounds were screened against different strains of gram positive and gram negative bacteria such as *E. coli, B. subtillis, B. mega* and *A. awamori.* The zones of inhibition of the standard drugs and schiff bases are reported in Table-2. It is evident from Table-2 that Schiff bases possess promising antibacterial and antifungal activities against *E. coli* and *A. awamori* and moderate activities against *B. mega.*

TABLE-2
ANTIBACTERIAL AND ANTIFUNGAL ACTIVITIES OF SCHIFF BASES

Sample	Zone of inhibiton, mm			
	E. coli	*B. subtillis*	*B. mega*	*A. awamori*
Griseofulvin	—	—	—	18
Chloramphenicol	29	20	26	—
Norfloxacin	21	16	15	—
Ampicillin	14	25	26	—
DMF	12	11	12	12
BSB-1	20	16	17	16
BSB-2	18	13	19	18
BSB-3	20	17	20	19
BSB-4	20	18	19	17
MSB-1	25	22	19	19
MSB-2	24	18	20	18
MSB-3	21	17	14	19
MSB-4	22	19	20	17

Thermal Analysis: Several so called exact methods have been proposed for estimation of kinetic parameters. All these methods involve two important assumptions that thermal and diffusion barriers are negligible and Arrhenius equation is valid. DSC and TGA data on schiff bases are reported in Table-3. From Table-3, it is observed that BSB-2, BSB-4, MSB-4 involved a single-step decomposition whereas BSB-1, BSB-3, MSB-1, MSB-2, MSB-3 involve two-step decomposition. BSB-3 has excellent thermal stability while MSB-2 is less thermally stable than others. The maximum degradation temperature is observed at about 280–292°C except BSB-4 and MSB-4 (325–340°C).

The energy of activation (E_a) for Schiff bases was determined according to single heating rate method of Horowitz-Metzger method[12]. The least squared values of E_a and of frequency factor (A) along with correlation coefficient (γ) for Schiff bases are reported in Table-3.

In conclusion Schiff bases possess promising biological activities and good thermal stability except MSB-2.

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TABLE-3
DSC AND TGA DATA OF SCHIFF BASES

Compd.	DSC							TGA			
	Transition	Transition temp (°C)	ΔH $J g^{-1}$	IDT (°C)	Decomposition range, (°C)	% Wt.loss	% Residual wt.	T_{max} (°C)	E_a $kJ mol^{-1}$	A min^{-1}	γ
BSB-1	Exo	259.7	276.8	245	245–315	16	—	—	410.9	1.67×10^{39}	0.9882
				638	638–750	18	40	274	208.206	—	—
BSB-2	—	173.5	3.3	235	235–263	40	55 (up to 675)	272.4	208.2	8.37×10^{10}	0.9979
BSB-3	Endo	329.3	636.2	662	662–740	8	75	—	—	—	—
BSB-4	Exo •	81.8	431.2	268	268–380	62	23 (up to 725)	340	532.1	3.03×10^{45}	0.9721
MSB-1	Exo	299.7	366.4	238	238–320	25	23	280	496.4	1.83×10^{36}	0.9756
					425–510	12	46–50	443.6			
MSB-2	Endo	480.0	—	188	188–375	42	38	—	—	—	—
					375–500	13	(up to700)				
MSB-3	—	328.6	—	—	—	—	79 (up to 650)	—	—	—	—
MSB-4	Exo	328.4	—	238	238–393	55	35	325	499.0	2.07×10^{41}	0.9985
							(400–800)	367	471.5	6.72×10^{40}	0.9792

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