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Mesogenic Biphenyl Derivatives with Azo and Ester Central Linkage

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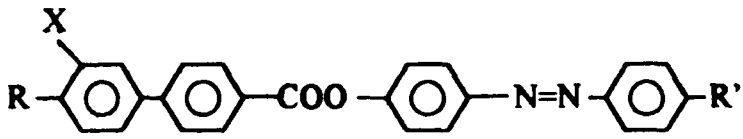
Biphenyl nucleus comprises one of the most interesting research areas in the study of relations between chemical constitution and mesomorphic properties. Few biphenyl derivatives with azo and ester central linkage having following general formula have been synthesized and their mesomorphic properties were evaluated.



Where R=-H, $-OCH_3$; R'=$-CH_3$, $-OCH_3$, $-OC_2H_5$, $-OC_4H_9$; X=-H, -Br. All the synthesized compounds were characterized by elemental analysis and spectroscopic methods.

Keywords: Nematic; Biphenyl Derivatives

INTRODUCTION

A vast number of liquid crystals showing nematic or other mesophases are obtained using benzene, biphenyl or terphenyl units as core systems. Gray et. al.[1-3] reported few mesogenic homologous series comprising of biphenyl moiety. Goodby [4] carried out systematic study of the variation in transition temperature with phase type for the 4-halogenophenyl 4'-n-octyloxybiphenyl -4-carboxylates. This particular family or materials have smectic A phases that exist over very long temperature ranges. Smectic B phases are found to occur but they are all monotropic. Goodbye [4] also carried out comparative study of some phenylbiphenyl carboxylates where a methyl substituent has been

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positioned in the phenyl ring and noted that the methyl substituted systems tend to exhibit more disordered phases but at lower temperatures, then their unsubstituted analogues. Systematic comparable study for the alkyl 4-n-octyloxy biphenyl-4-carboxylates where the alkyl chain either carries a methyl substituent at the first position or does not [5] indicated that the clearing points are substantially reduced, conversely the melting points are not reduced as much. Ouchi et. al.[6] synthesized series of compounds where the branching chain is increased in length until it matches the length of the terminal aliphatic chain. Goodby [7] reported tow closely related biphenyl derivatives that only differ in the structure of the linking group : one is an ester whereas the other is thioester. Sadashiva and Subba Rao [8] and Sadashiva [9] also reported esters containing a biphenyl moiety. Interest in the biphenyl unit is increasing considerably and recent work on non-chiral [10-14], chiral [15-21], dimesogens [22-25], trimesogens [26,27] and high [28-30] molecular mass liquid crystal materials incorporating biphenyl has shown very attractive properties for some of these structures. Recently we [31] have reported two mesogenic homologous series with biphenyl nucleus countaining less studied central linkage like amide and α-methylazine. In continuation of our work on biphenyl nucleus, in the present study few compounds containing the biphenyl moiety have been synthesized and their mesomorphic properties are evaluated.

EXPERIMENTAL

Paracetamol, n-butylbromide, anhydrous potassium carbonate, sodium nitrite, p-toluidine, p-phenitidene, phenol, biphenyl, 4-hydroxybihenyl, acetyl chloride, anhydrous aluminium chloride, liquid bromine, dimethyl sulfate and sodium acetate were used as received. Solvents were dried and distilled prior to use. Microanalysis of the compounds was performed on a Coleman carbon-hydrogen analyzer. IR spectra were recorded on a Shimadzu IR-408. NMR spectra were measured on a Perkin-Elmer R-32 spectrometer. Liquid crystalline properties were investigated on a Leitz Labolux 12 POL microscope

provided with a heating stage. DSC was performed on a Mettler TA-4000 system by adopting a heating rate of 10 ^{0}C /min.

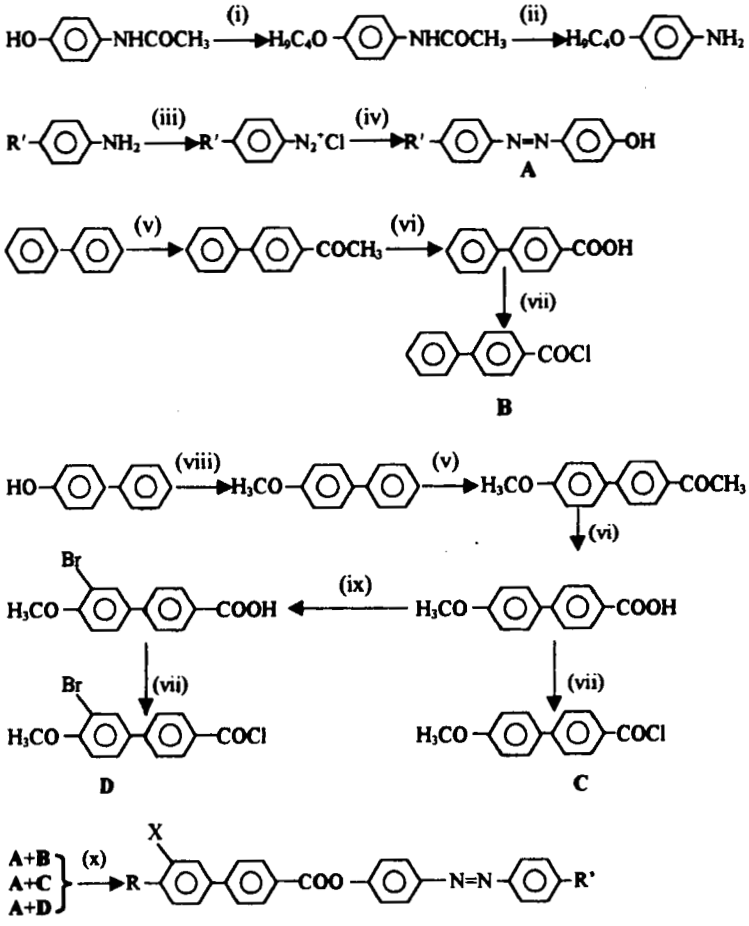
Synthetic route for the preparation of all the present compounds is shown in the scheme 1. 4-n-Butoxy aniline was prepared by known method [32] as it gives over all better yields. All the dyes having general structural formula **A** were synthesized by the convenient method [33] of diazotization of respective 4-substituted aniline and coupling it with phenol. Diphenyl-4-carboxylic acid, 4'-methoxydiphenyl-4-carboxylic acid [1] and 3'-bromo-4'-methoxy-diphenyl-4-carboxylic acid [3] were synthesized following the method described in the literature. Their acid chlorides (**B, C** and **D**) were prepared in the usual way from the appropriate acid and thionly chloride.

The eleven compounds listed below were prepared following the general procedure.

1. 4(4-phenyl) benzoate-4'-methylazobenzene.
2. 4(4-phenyl) benzoate-4'-methoxyazobenzene.
3. 4(4-phenyl) benzoate-4'-ethoxyazobenzene.
4. 4(4-phenyl) benzoate-4'-n-butyloxyazobenzene.
5. 4(4-methoxyphenyl) benzoate-4'-methylazobenzene.
6. 4(4-methoxyphenyl) benzoate-4'-methoxyazobenzene.
7. 4(4-methoxphenyl) benzoate-4'-ethoxyazobenzene.
8. 4(4-methoxyphenyl) benzoate-4'-n-butyloxyazobenzene.
9. 4(3-bromo-4-methoxyphenyl) benzoate-4'-methoxyazobenzene.
10. 4(3-bromo-4-methoxyphenyl) benzoate-4'-ethoxyazobenzene.
11. 4(3-bromo-4-methoxyphenyl) benzoate-4'-n-butyloxyazobenzene.

General procedure for the synthesis of compounds 1 to 11

Appropriate dye **A** (10 mmol) was dissolved in dry pyridine (15 ml) and added slowly into acid chloride **B, C** or **D** (10 mmol) in dry pyridine (15 ml) below 15 ^{0}C. The mixture was then heated on water bath for an hour and was allowed to stand overnight at room temperature. It was acidified with cold 1: 1 aqueous hydrochloric acid. The solid was separated, dried and triturated by stirring 30



1 R=-H, R'=-CH_3, X=-H
2 R=-H, R'=-OCH_3 X=-H
3 R=-H R'=-OC_2H_5, X=-H
4 R=-H R'=-OC_4H_9 X=-H
5 R=-OCH_3 R'=-CH_3 X=-H
6 R=-OCH_3 R'=-OCH_3 X=-H
7 R=-OCH_3 R'=-OC_2H_5 X=-H
8 R=-OCH_3 R'=-OC_4H_9 X=-H
9 R=-OCH_3 R'=-OCH_3 X=-Br
10 R=-OCH_3 R'=-OC_2H_5 X=-Br
11 R=-OCH_3 R'=-OC_4H_9 X=-Br

Scheme 1 Reagents and conditions: (i) C_4H_9Br, Anhyd. K_2CO_3, dry acetone, reflux (ii) HCl, 100 ^{0}C, NaOH (iii) HCl, $NaNO_2$, 0-5 ^{0}C (iv) Phenol in NaOH, HCl, 0-5 ^{0}C (v) Anhyd. $AlCl_3$, CH_3COCl, CS_2 (vi) NaOH, Br_2 (vii) $SOCl_2$ (viii) $(CH_3)_2SO_4$, NaOH (ix) Sodiumacetate, acetic acid, Br_2, 100 ^{0}C, reflux (x) Pyridine, HCl.

min. with 10% aqueous sodium hydroxide and washed with water. The insoluble product was thus separated from the reactants. Finally all the products crystallized from dimethylformamide till constant transition temperatures were obtained. The elemental analysis (Table I) of all the compounds was found to be satisfactory.

TABLE-I Elemental data

Compound	Found(%)			Formula	Required(%)		
No.	C	H	N		C	H	N
1.	79.42	5.23	7.32	$C_{26}H_{20}N_2O_2$	79.59	5.10	7.14
2.	76.56	4.83	6.94	$C_{26}H_{20}N_2O_3$	76.47	4.90	6.86
3.	76.72	5.40	6.58	$C_{27}H_{22}N_2O_3$	76.78	5.21	6.64
4.	77.51	5.48	6.20	$C_{29}H_{26}N_2O_3$	77.33	5.78	6.22
5.	76.66	5.28	6.49	$C_{27}H_{22}N_2O_3$	76.78	5.21	6.64
6.	73.82	4.86	6.44	$C_{27}H_{22}N_2O_4$	73.97	5.02	6.39
7.	74.55	5.16	6.38	$C_{28}H_{24}N_2O_4$	74.34	5.31	6.19
8.	74.68	5.78	5.89	$C_{30}H_{28}N_2O_4$	75.00	5.83	5.83
9.	62.60	4.25	5.38	$C_{27}H_{21}N_2O_4Br$	62.67	4.06	5.42
10.	63.43	4.52	5.10	$C_{28}H_{23}N_2O_4Br$	63.28	4.33	5.27
11.	64.58	4.73	5.22	$C_{30}H_{27}N_2O_4Br$	64.40	4.83	5.01

IR and ^1H NMR spectral data of few compounds are given below.

IR (KBr) spectra : (ν_{max}, Cm^{-1})

Compound 1: 3040, 1720 (-COO-),1600, 1500, 1455,840.

Compound 5: 3030, 1730 (-COO-),1600, 1510, 1455, 1210 and 1040(-O-), 835.

Compound 6: 3030, 1725 (-COO-),1600, 1500, 1450, 1200 and 1045(-O-), 835.

Compound 11: 3035,1730(-COO-),1600, 1500, 1450, 1220 and 1050(-O-), 840, 600(-Br).

^1H NMR spectra (Solvent $CDCl_3$, Standard TMS, 200 MHz)

Compound 1 : δ 2.30(s, 3H, $-CH_3$), 7.05(d, 2H), 7.20(d, 2H), 7.30-7.50(m, 7H), 7.60 (d, 2H), 7.74 (d, 2H), 8.05 (d, 2H).

Compound 5 : δ 2.30(s, 3H, $-CH_3$), 3.80(s, 3H, $-OCH_3$), 6.85(d, 2H), 7.1(d, 2H), 7.24 (d, 2H), 7.32-7.55(m, 4H), 7.65(d, 2H), 7.83(d, 2H), 8.10(d, 2H).

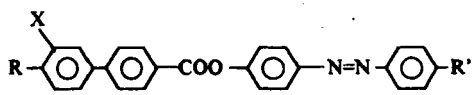
Compound 6 : δ 3.85(s, 6H, 2 x $-OCH_3$), 6.85-7.05(m, 4H), 7.20(d, 2H), 7.35-7.55 (m, 4H), 7.70(d, 2H) 7.85(d, 2H), 8.25(d, 2H).

Compound 11 : δ 0.90(t, 3H, $-CH_3$), 1.40-1.95(m, 4H, 2 x $-CH_2-$), 3.80(s, 3H, $-OCH_3$) 4.3(t, 2H, $-OCH_2-$), 6.85-7.00(m, 3H), 7.25(d, 2H), 7.31(dd, 1H), 7.40-7.55(m, 3H), 7.70(d, 2H), 7.88(m, 2H), 8.30(d, 2H).

RESULTS AND DISCUSSION

The transition temperatures of the new synthesized compounds 1-11 are summarized in the table II.

TABLE II : Transition temperatures (^{0}C) for compounds 1-11.



Compound No	R	R'	X	Transition temperatures (^{0}C) N	I
1	-H	$-CH_3$	-H	154	262
2	-H	$-OCH_3$	-H	173	273
3	-H	$-OC_2H_5$	-H	171	287
4	-H	$-OC_4H_9$	-H	159	276
5	$-OCH_3$	$-CH_3$	-H	157	298
6	$-OCH_3$	$-OCH_3$	-H	189	334
7	$-OCH_3$	$-OC_2H_5$	-H	184	347
8	$-OCH_3$	$-OC_4H_9$	-H	169	338
9	$-OCH_3$	$-OCH_3$	-Br	223	308
10	$-OCH_3$	$-OC_2H_5$	-Br	197	328
11	$-OCH_3$	$-OC_4H_9$	-Br	176	316

DSC data of few of these compounds are given in table III. All the synthesized compounds exhibit enantiotropic nematic mesophase with very high thermal stability. This may be due to the greater length of the molecules because of the

presence of ester and azomethine central linkages along with four phenyl rings in the core.

TABLE III : DSC data of few present biphenyl derivatives.

Sr. No.	Compound No	Transition State	Peak Temperatures	ΔH J/G	ΔS J/g.^{0}k
1	1	K-N	153.4	34.32	0.0805
		N-I	260.8	0.984	0.0018
2	2	K-N	174.2	38.86	0.0869
		N-I	273.5	0.873	0.0016
3	5	K-N	155.9	32.54	0.0757
		N-I	297.3	0.935	0.0016
4	11	K-N	176.3	41.38	0.0921
		N-I	314.6	1.052	0.0018

Compound 1 exhibits an N-I transition temperature higher by 32 ^{0}C and compound 2 by 43 ^{0}C than the structurally related compound bearing no terminal substituent [34]. This suggests that the presence of terminal group promote the nematic thermal stability. The comparison of the two compounds 1 and 2, i.e. methyl versus methoxy reveals that methoxy substitution favours the thermal stabilization favors the thermal stabilization of nematic phase. This is possibly due to the oxygen atom adjacent to the phenyl ring undergoing an electronic interaction with it, which in turn stabilizes the mesophase. This is further confirmed by the comparison of the compounds 5 and 6, where the compound 6 with $-OCH_3$ terminal group has higher nematic thermal stability by 36 ^{0}c than the compound 5 with $-CH_3$ terminal group.

It is observed that the lower n-alkoxy derivatives viz. methoxy, ethoxy and n-butyloxy members (compounds 2-4, 6-8 and 9-11) exhibit odd-even effect in their N-I transition temperature as explained by Gray [35]; the nematic mesophase range being least for the compound having $-OCH_3$ group at the terminal position and the same being maximum when the $-OCH_3$ group is replaced by $-OC_2H_5$ group.

The average nematic thermal stabilities of the compounds 9, 10 and 11 are lower than those of the compounds 6, 7 and 8 respectively. Compared with the molecules of compounds 6-8, molecules of compounds 9-11 have increased breadth due to the lateral bromo group on the biphenyl nucleus at 3'-position.

Gray [35] has explained that the increase in the breadth of the molecules reduces the mesophase thermal stabilities, which is the case.

The average nematic thermal stability of the present biphenyl derivatives 6-8 is 339.66 °C whereas that of their phenyl [36] analogues is 298.33 °C. This is understandable, as the molecules of the biphenyl derivative is longer due to second aromatic ring, which, as a result of polarisability, increases the intermolecular cohesive forces. Hence the average nematic thermal stability of the present biphenyl derivatives 6-8 is greater by 41.33 °C then their phenyl analogues.

On the basis of above discussion the terminal group efficiency order, which has been compiled for nematic phase is:

$$Ph > -OC_2H_5 > n\text{-}OC_4H_9 > -OCH_3 > -Br > -CH_3 > -H$$

It agrees well with the nematic group efficiency order obtained by Gray [35] for pure mesogenic systems and also recently obtained by Dave and Menon [37] for pyridine system instead of biphenyl nucleus of the present system.

CONCLUSION

Eleven new mesogenic biphenyl derivatives have been synthesized. Compounds having terminal group at both the ends of the molecules exhibited nematic mesophases with higher thermal stability compared to those of the compounds having terminal group at only one end of the molecule. Incorporation of lateral bromo substituent in the system depressed the mesophase thermal stability. The mesophase thermal stability of the present biphenyl derivatives is found to be higher than those of their benzene analogues.

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