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Mesogenic Semicarbazones and Amino Oxadiazoles-I

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Number of semicarbazones of 4(4′-*n*-alkoxybenzoyloxy) benzaldehydes are synthesized. They are cyclized to respective amino-oxadiazoles. Both the series of compounds exhibit mesomorphism. However, the decomposition is a major problem for semicarbazones. Compounds of both the series are characterized by elemental analysis, UV, IR spectra and NMR spectra.

Keywords: mesogenic, semicarbazones, aminooxadiazoles

INTRODUCTION

Heterocyclic compounds exhibiting mesomorphic properties[1–11] are relatively less studied. Mesogenic compounds with the amino group are rare. The effect of the heterocyclic moiety and the amino group on mesomorphism would be quite interesting to investigate. With this in view, it was proposed to synthesize amino oxadiazoles and to study their mesogenic properties.

EXPERIMENTAL

The route adopted for the synthesis of amino oxadiazoles, is shown in Figure 1.

Microanalysis of compounds were performed on Coleman instruments. UV spectra were recorded on Specord UV VIS. IR spectra were recorded on Shimadzu IR 408.90 MHz NMR spectra were recorded on Perkin Elmer R-32 instrument. Mesogenic properties were investigated by using Leitz-Lobolux Polarizing microscope provide with a heating stage.

The new compounds were synthesized by the following steps. The methods described in the literature were used to synthesize, 4-(4′-*n*-alkoxybenzoyloxy)benzaldehydes.[12]

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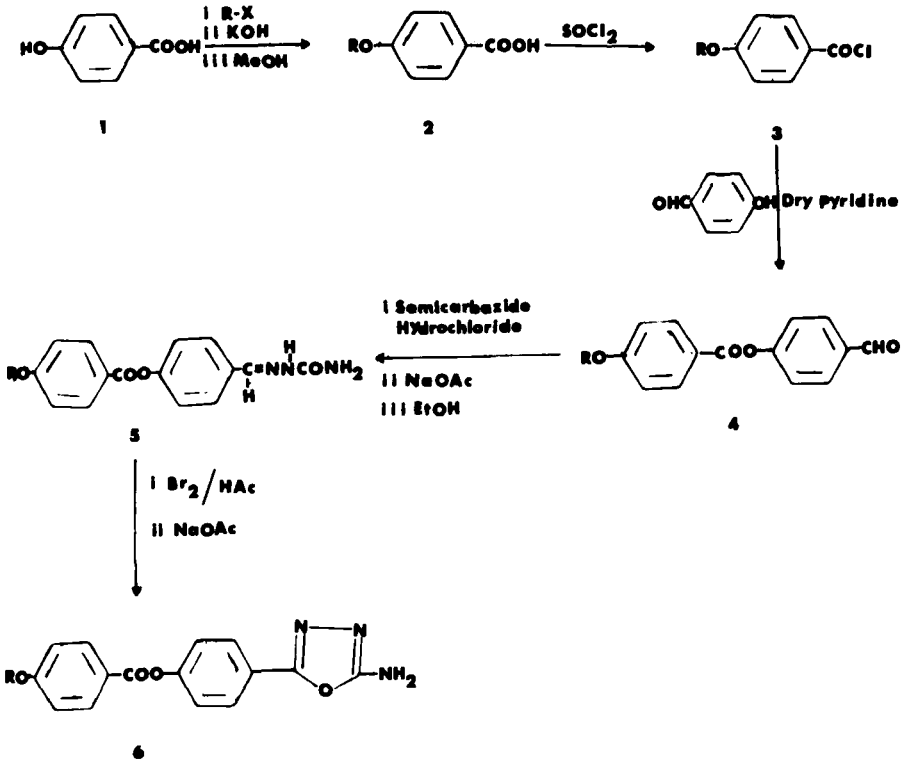


FIGURE 1

I. *Synthesis of 4(4'-*n*-alkoxybenzoyloxy)benzaldehyde semicarbazones*[13]: In a 100 ml round bottom flask, 1 g of respective 4(4'-*n*-alkoxybenzoyloxy)benzaldehyde was dissolved in 10 ml ethanol, then 1 g. of semicarbazide hydrochloride and 1.5 g. of fused sodium acetate were added to alcoholic solution. The solution was refluxed, with constant stirring, for about 40 minutes. After the reaction period the material was allowed to cool to room temperature and then it was poured in water. The solid separated was filtered and recrystallized from glacial acetic acid.

Spectral aspect of the semicarbazones

UV (MeOH): λ max 270 nm.
IR (KBr): ν 3500–3300 (—NH_2), 3150 (—CONH—), 1730 (—COO—), 1665 (—$CONH_2$) cm^{-1}.

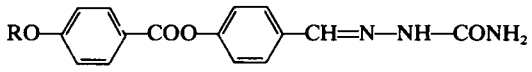
NMR (90 MHz, DMSO - d^6) of the compound No. 1 in the Table I, δ 8.00 (*d*, J = 9 Hz, 2H, aromatic H), 7.80 (*s*, 1H, azo-methane H), 7.70 (*d*, J = 9 Hz, 2H, aromatic H), 7.25 (*d*, J = 9 Hz, 2H, aromatic H) 6.4 (brs, 2H, NH_2), 3.80 (*s*, 3H, —OCH_3), 1.90 (*s*, 1H, NH).

II. Synthesis of 2-amino-5[4'-(4''-n-*alkoxybenzoyloxy) phenyl*]-*1,3,4-oxadiazoles*[14]: Bromine (0.6 ml) in acetic acid (5 ml) was added to a stirred slurry of 4(4'-*n*-alkoxybenzoyloxy)benzaldehyde semicarbazone (2 g) and anhydrous sodium acetate (4 g) in acetic acid (5 ml) contained in a 150 ml flat bottom flask.

TABLE I

Melting Points

4(4′-*n*-alkoxybenzoyloxy)benzaldehyde semicarbazones



Compound No.	*n*-alkyl group R	Melting point °C
1[a]	Methyl	235.0 (*d*)
2	Ethyl	242.0 (*d*)
3	Propyl	258.0 (*d*)
4	Butyl	244.0 (*d*)
5	Pentyl	228.0 (*d*)
6	Hexyl	257.0 (*d*)

[a]Indicate compound identified by NMR.

Due to exothermic reaction, the mixture became warm and rapidly became colorless. This mixture was poured in water, solid which separated was filtered and dried. All the amino oxadiazoles were recrystallized from the mixture of alcohol and glacial acetic acid.

Spectral aspect of the amino oxadiazoles

UV (MeOH): λ max 285 nm
IR (KBr): ν 3350–3100 (—NH_2), 1730 (—COO—), 1040 (—C—O—) cm^{-1}.

NMR (90 MHz, DMSO-d^6) of the compound No. 1 in Table II. δ 8.0 (*d*, J = 9 Hz, 2H, aromatic H), 7.80 (*d*, J = 9 Hz, 2H, aromatic H), 7.45 (*d*, J = 9 Hz, 2H, aromatic H), 7.15 (*s*, 2H, NH_2), 7.05 (*d*, J = 9 Hz, 2H, aromatic H), 3.85 (*s*, 3H, —OCH_3).

The synthesized compounds of both the series mentioned above gave satisfactory elemental analysis.

The melting point of semicarbazones and transition temperatures of amino oxadiazoles are recorded in Tables I and II respectively.

Semicarbazones

Semicarbazones on heating exhibit biphasic region and decomposition tendencies as the temperature increases. The biphasic region (crystalline + nematic) turns into homogenous nematic phase at higher temperature but decomposition and the final transformation of semicarbazone to the product is being studied in detail, the results will be published later on.

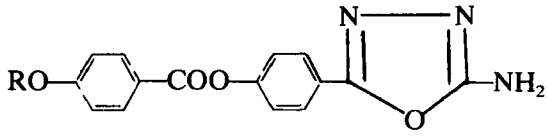
Amino oxadiazoles

Liquid crystals with heterocyclic moiety are known.[1–11] However low molecular mesogens with oxadiazoles ring with free amino group are being reported for the first time. A survey of the literature indicates that mesogenic compounds having

TABLE II

Transition Temperature

2-amino-5[4′-(4″-*n*-alkoxybenzoyl)phenyl]1,3,4-oxadiazoles



SERIES II

Compound	*n*-alkyl group	Transition Temperature °C: Nematic[a]	Transition Temperature °C: Isotropic liquid
1[ab]	Methyl	(208.0)	269.0
2	Ethyl	(194.0)	251.0
3	Propyl	(206.0)	282.0
4	Butyl	(186.0)	290.0
5	Pentyl	(171.0)	270.0
6	Hexyl	(179.0)	259.0

[a]Values in parentheses indicate monotropy
[b]indicate compound identified by N.M.R.

free phenolic hydroxy group and/or amino groups are rare. Vora *et al.*[16] for the first time reported mesogenic homologous series with terminal and lateral phenolic group. Schroeder and Schroeder[17] have reported a few mesogenic compounds with terminal hydroxy and amino group.

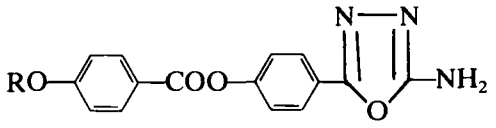
Gray[15] has explained the rarity of mesomorphism in such compounds by taking into consideration, the intermolecular hydrogen bonding, which raise the melting points above the mesomorphic isotropic liquid transition temperatures and may encourage a nonlinear structural arrangement that is incompatible with mesophase formation.

However, recent studies have indicated that compounds with terminal phenolic, alkylamino and a few compounds with free amino group exhibit mesomorphism.

The free amino group raises the melting point of series II high enough hence none of the derivatives synthesized exhibit enantiotropic phases. However, on cooling methoxy to hexyloxy derivatives exhibit monotropic nematic phase. This indicates that even though molecules of series II have terminal amino groups, they exhibit mesomorphism. This can be attributed to the ester central linkage and three aromatic nuclei present in the molecules of series II.

The geometry of molecules of series II are compared with those of series A,[17] as two alkoxy derivative of series II and series A have same chain length.

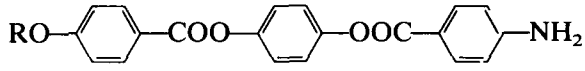
The difference between molecules of series A and series II is in the central linkage and terminal phenyl ring. Series A is highly mesogenic compared to series II. Again this mesogenic behavior of series A compared to series II can be attributed to flexible ester group and terminal phenyl group. It is known that intermolecular hydrogen bonding will increase the rigidity, in such a situation presence of a flexible



SERIES II

Sr. No.	*n*-alkyl group, R	Solid–Nematic[a]	Nematic–Isotropic
1	CH_3	(208.0)	269.0
2	C_6H_{13}	(179.0)	259.0

[a]Values in parentheses indicate monotropy.



SERIES A

Sr. No.	*n*-alkyl group R	Solid–Nematic	Nematic–Isotropic
1	CH_3	212.5	277.5
2	C_6H_{13}	191.0	207.0

central linkage would help to overcome strong attractive forces. Moreover in the molecule of series II, the heterocyclic ring due to the presence of lone pair of electrons on two nitrogen atoms will enhance lateral cohesive forces due to high polarizability of the molecules. This will raise the melting point of the system.

The study has provided a new class of compounds and helped to understand the role of free amino group for the mesogenic behavior.

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