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Mesomorphic properties of a new homologous series: 2-(4'-N-alkoxy benzoyloxy)-naphthyl-1-azo-4''-nitro benzenes

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ABSTRACT

New homologous series with -COO- and -N=N- as central group have been synthesized by the treatment of 4-n-alkoxy benzoyl chloride with 2-Hydroxy - naphthyl – 1 – azo – 4' – nitro benzene. All the homologues of the series are enantiotropically nematogenic without exhibition of smectic mesophase. The texture of nematic mesophase is of threaded type. Well known odd-even effect is clearly observed in the nematic isotropic transition curve. Thermal stabilities and liquid crystalline properties are compared with other structurally identical homologous series. Transition temperatures are observed through hot stage polarizing microscope. Analytical data support the structure of molecules.

Key words: azomesogens, Liquid crystal, Smectic, nematic.

INTRODUCTION

A vast number of mesogenic compounds exhibiting nematic or other mesophases are reported [1-3] containing naphthalene unit as a part of core system. Gray and Jones[4] investigated liquid crystalline properties of different alkoxy naphthoic acids. Increasing demand of liquid crystalline materials in various fields of applications has inspired to plan for synthesis of liquid crystalline material.

MATERIALS AND METHODS

Homologues of the titled homologous series were synthesized by usual established methods.[5-7] Analytical data of purified samples of the compounds confirms the structure of the homologues. The melting points and transition temperatures were determined by Leitz Laborlux polarizing microscope provided with heating stage. Analytical data and transition temperatures are recorded in table 1 (A) and table 1(B) and table 2 respectively.

RESULTS AND DISCUSSION

Homologous series 2-(4'-n-alkoxy benzoyloxy)-napthyl-1-azo- 4''-nitro benzenes is entirely mesomorphic in character. All the members of the series display mesomorphism in enantiotropic manner with enough range of liquid crystallinity. All the homologues display mesomorphism of nematic type without exhibition of smectic mesophase. Transition temperatures of the homologues are plotted versus the number of carbon atoms in n- alkyl chain of left n-alkoxy terminal as given in figure 1. Smooth curves are drawn through like or related points. The solid-mesomorphic transition curve follows a zig-zag path of rising and falling nature. The nematic –isotropic transition curve exhibits falling tendency as the series is ascended except at the seventh to tenth member of the series in which nematic-isotropic transition curve abnormally behaves otherwise nematic isotropic transition curve behaves in a normal manner. Well known odd-even effect is observed in the nematic-isotropic transition curve with alternation of transition temperatures and merges into each other at the nineth homologue. The texture of nematic mesophase is threaded type as clearly judged from the field of view of hot stage polarizing microscope while observing the samples. The mesomorphic-isotropic transitions are between 130.0 ^{0}c and 190.0 ^{0}c with mesomorphic range varying from 29.0 ^{0}c at the fourteenth member to a maximum of 93.0 ^{0}c at the tenth member of the series. Thus, the present homologues series is considered as middle ordered melting type with wide range of liquid crystallinity.

Display of nematic mesophase without exhibition of any smectic character is attributed to the only statistically parallel orientations of molecules with maintainance of two dimensional arrays of molecules in the floating condition. Formation of sliding layered arrangement of molecules does not occur in crystal structure which resulted in absence of smectic mesophase for all the homologue. Terminal $–NO_2$ is highly polar group which contributes to the stronger intermolecular end to end attractions. Thus all the members of the series are enantiotropic nematic in character. $–NO_2$ group is generally nematogenic and present homologous series is also entirely nematogenic. Thus present investigation supports earlier views of Gray[9]. Solid-nematic transition curve rises and falls in zigzag manner. However rise and fall does not take place from homologue to homologue in regular manner due to presence of highly polar $–NO_2$ end group. Emergence of odd-even effect in nematic-isotropic transition curve is observed due to presence of methylene units linked through oxygen atom as alkoxy group. This effect diminishes and disappears from tenth homologue and onwards because longer n-alkyl chain bends and coils as series is ascended. Thus, presence of odd or even number of methylene units does not contribute to odd-even effect beyond tenth homologue as series is ascended.

The present homologues series (1) is compared with structurally similar other homologous series (A);[8] for molecular characteristics and thermal stabilities which are shown in Table 3 (Figure 2).

The above homologous series (1) and (A) under discussion have the basic length due to one naphthyl ring and two phenyl rings linked through central linking units –COO- and –N=N-, left n-alkoxy group and right terminal $–NO_2$ functional group at para position which are the constant unchanging features. Hence, display of mesomorphic properties due to the molecular forces arising on account of these remains the same. The homologous series (1) and (A) differ only at middle part of the molecules. Middle part of the molecules is changing with respect to position of –N=N- unit with naphthyl ring. i.e. naphthyl ring is attached with –COO- unit at ortho position with respect to –N=N- bridge for series (1) while naphthyl ring is attached with –COO- unit at para position with respect to –N=N- bridge for series (A). Thus, positionally

substitution of central bridges linked with naphthyl ring is different for series (1) and (A). Hence, the variation in mesomorphic characteristics has direct relation with substitution of central bridges with naphthyl unit at different positions.

As naphthyl is positioned at ortho position with –COO- unit with respect to -N=N- bridge for series (1), it does not increase the length of molecule but it broadens the molecule. Hence, the length to breadth ratio is diminished for series (1) as compared to series (A).

Broadening of molecules increases intermolecular distance and hence it lowers the intermolecular forces of attractions on one hand while broadening of molecule increases polarizability of molecules and hence results in increase of intermolecular forces of attractions. Thus two opposing forces play on broadening a molecule. However the net effective resultant forces of intermolecular attractions are capable to resist thermal vibrations and maintain only statistically parallel orientations of molecules in floating condition displaying only nematogenic character without exhibition of any smectic character even in the monotropic condition. Net resultant intermolecular forces of attractions out of two opposing effects in case of series (1) (i.e. due to broadening of molecule) is less as compared to series (A); in which molecules are relatively more linear lath like than the molecules of series (1). Thus forces of attractions are weakening due to broadening a molecule. Thus in case of series (1) as compared to series (A) melting and transition temperatures of titled homologous series (1) are relatively lower than series (A). This is also reflected in relative thermal stability of series (1) and (A).

Therefore, nematic-isotropic thermal stability for series (1) is lower than series (A), or on other hand series (A) being longer and linear or rod-like decreases intermolecular distance increasing intermolecular of attractions as compared to series (1) results into higher nematic-isotropic thermal stability.

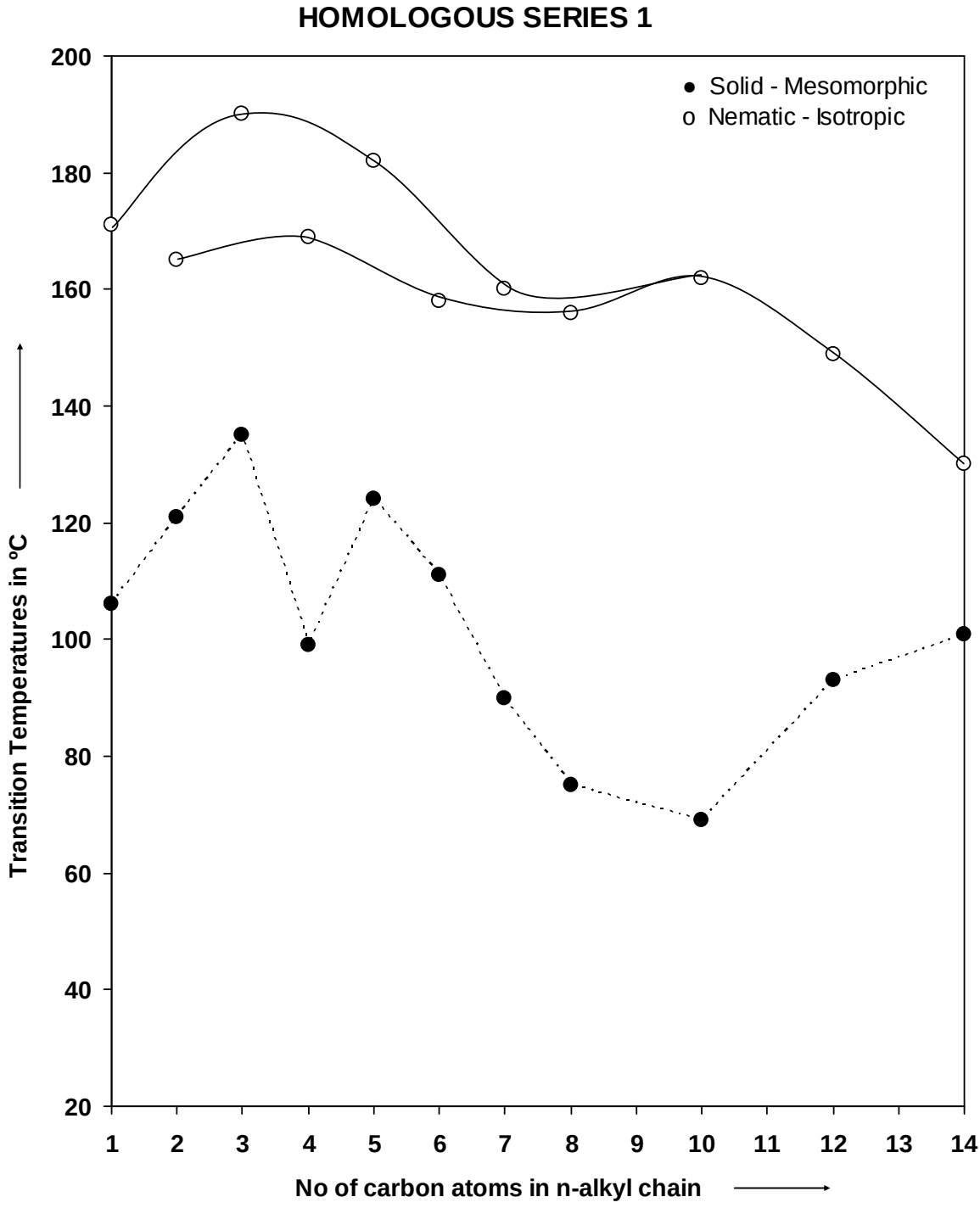
Thus, nematic group efficiency order with respect to type of linking central bridges i.e. middle part positional substitution is as under on the basis of average thermal stability.

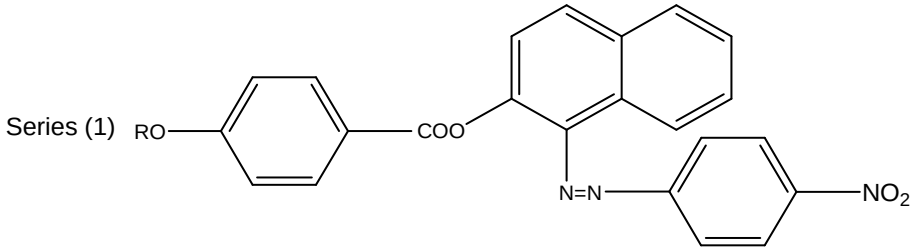
Nematic group efficiency order:	Napthyl ring (para substitution) Series (A)	>	Napthyl ring (ortho substitution) Series (1)

Table-1(A): Spectral data Elemental analysis for 2-(4'-n-alkoxy benzoyloxy)-napthyl-1-azo- 4''-nitro benzenes

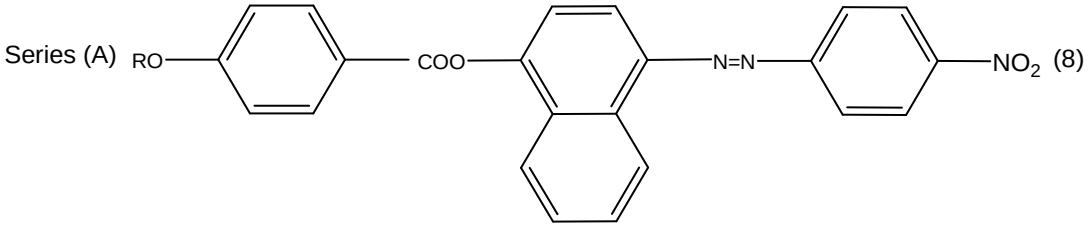
Sr.No.	R = n-alkyl Chain	% of Nitrogen	
		Calculated	Observed
1	Methyl	9.80	9.53
2	Ethyl	9.50	9.64
3	Propyl	9.23	9.36
4	Butyl	8.95	8.86
5	Pentyl	8.69	8.58
6	Hexyl	8.45	8.39
7	Heptyl	8.21	8.19
8	Octyl	8.00	7.88
9	Decyl	7.59	7.46
10	Dodecyl	7.22	7.19
11	Tetradecyl	6.89	6.69

Fig 1. 2-(4'-n-alkoxy benzoyloxy)-napthyl-1-azo-4"-nitro benzenes.





2-(4'-n-alkoxy benzoyloxy)-naphthyl-1-azo 4''-nitro benzenes



4-(4'-n-alkoxy benzoyloxy) naphthyl azo-4''-nitro benzenes

FIGURE 2

Table 1(B) Spectral Data

Homologue	IR Spectra (cm $^{-1}$)
Octyl	1419,2852,2919 cm $^{-1}$ → Alkyl group
	1310,1559 cm $^{-1}$ → Ar-NO_2
	1169 cm $^{-1}$ → C-N str due to -N=N-
	1063,1684,1733 cm $^{-1}$ → -COO- group
	845 cm $^{-1}$ → para substituted benzene
	771 cm $^{-1}$ → ortho substituted benzene
	IR confirms the above structure.
Homologue	IR Spectra (cm $^{-1}$)
dodecyl	2920,2848,1419,1457 cm $^{-1}$ → Alkyl group
	1340,1559 cm $^{-1}$ → Ar-NO_2
	1163 cm $^{-1}$ → C-N str due to -N=N-
	1058,1201,1683,1733 cm $^{-1}$ → -COO- group
	838 cm $^{-1}$ → para substituted benzene
	748 cm $^{-1}$ → ortho substituted benzene
	IR confirms the above structure.

Table 1(B) Spectral Data

Homologue	NMR Spectra in $CDCl_3$, δ ppm.
Propyl	1.03 (t, 3H, –CH_3)
	1.25 (m, 2H, -CH_2)
	3.93 (t, 2H, -OCH_2)
	6.8-9.02 (m, 14 H, Ar-H)
Homologue	NMR Spectra δ ppm
hexyl	0.89 (t, 3H –CH_3)
	1.35 (m, 8H, -CH_2)
	4.02 (t, 2H -OCH_2)
	6.93-8.13 (m,14H, Ar-H)

Table 2 Transition Temperatures for 2-(4'-n-alkoxy benzoyloxy) -napthyl-1-azo-4''-nitro benzenes

No of carbon atoms in n-alkyl chain	Transition Temperatures in °C		
	Smectic	Nematic	sotropic
1	-	106.0	171.0
2	-	121.0	165.0
3	-	135.0	190.0
4	-	99.0	169.0
5	-	124.0	182.0
6	-	111.0	158.0
7	-	90.0	160.0
8	-	75.0	156.0
10	-	69.0	162.0
12	-	93.0	149.0
14	-	101.0	130.0

Table 3 Average Thermal Stabilities in ^{0}C

Series	Series (1)	Series (A)
Nematic-Isotropic or Isotropic -Nematic	162.90	193.41
Commencement of Nematic phase	C_1	C_1

CONCLUSION

Present investigation supports Gray's[9] view, that broadening of a molecule reduces average thermal stability for nematic and smectic mesophases. Moreover homologous series with Naphthyl ring are nematogenic.

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