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Liquid Crystalline Compounds Bearing Pyridine Ring: 3-(4-Alkoxyphenylazoxy)-6-alkoxypyridines

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3-(4-Alkoxyphenylazo)-6-alkoxypyridines (6) with n-alkoxyl (C_1-C_6) groups were synthesized by the coupling reaction of phenol with 6-alkoxy-3-pyridine diazonium chloride prepared from 2-chloro-5-nitropyridine via 2-alkoxy-5-nitro and 2-alkoxy-5-aminopyridines and subsequent etherification with n-alkyl iodides. Mild oxidation of 6 with hydrogen peroxide in acetic acid provided 3-[(4-alkoxyphenyl)-NON-azoxy]-6-alkoxy-pyridines (7) containing nearly equimolar amounts of ONN (8) and NNO (8′) isomers. Centrifugal liquid chromatography satisfactorily separated these two isomers.

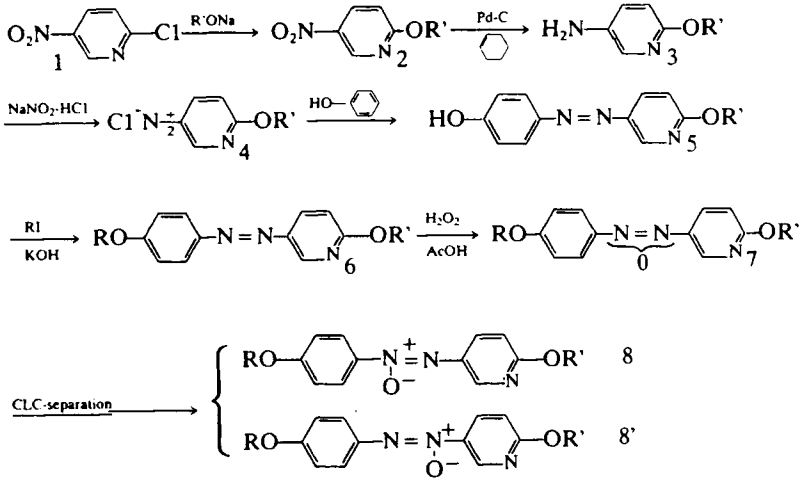
Mesomorphic behaviors of 8 and 8′ are characteristic in that the pyridine ring exerts polar effects and 8 are more balanced in polarity than 8′. Compounds 7 possess rather lower mesomorphic ranges than 8 and 8′. Some of compounds 6 indicate mesomorphic ranges but generally azo compounds are inferior to azoxy ones.

1. INTRODUCTION

Relatively few studies have been reported on liquid crystalline compounds bearing pyridine ring as a principal constituent. Thus, a couple of studies on the liquid crystalline Schiff bases containing pyridine ring are seen in the literature.[1,2]

These pyridine Schiff bases showed lower transition temperatures than the corresponding benzene compounds. We have prepared a series of 3-(4-alkoxyphenylazoxy)-6-alkoxypyridines to determine if replacing the benzene with a pyridine one in the alkoxy series would have a similar effect on the mesomorphic properties.

The following synthetic sequence was adopted.



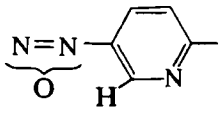
where R = n–CH_3, n–C_2H_5, n–C_6H_{13} and R′ = n–CH_3, n–C_3H_7, n–C_4H_9, n–C_6H_{13}.

Mesomorphic behaviors of azoxy compounds 7 and their separation products 8 and 8′ as well as their precursors, azo compounds 6, were investigated.

2. RESULTS AND DISCUSSION

2-Alkoxy-5-nitropyridines (2) were prepared in a conventional manner by replacing the activated chlorine atom of 2-chloro-5-nitropyridine (1) with alkoxide ions. The yield became progressively lower with higher alkyl (R′) groups (99, 83, 55, and 49% for CH_3, C_3H_7, C_4H_4, and C_6H_{13}), reflecting lower reactivities of long chain alkoxide ions. Reductions of the nitro to the amino groups to afford 2-alkoxy-5-aminopyridines (3) in the presence of Pd-C proceeded quantitatively. Diazotizations of 3 followed by coupling with phenol in a conventional manner provided azo compounds 5 in reasonable yields (43–90%). Etherifications of the phenolic hydroxyl group of 5 via their phenoxide ions with RI in DMF at room temperature for 48 hr provided crude 3-(p-alkoxyphenylazo)-6-alkoxypyridines (6), which were purified by silica gel column chromatography using choloroform or chloroform—carbon tetrachloride (3 : 7 v/v) as eluting solvents and subsequent recrystallizations from ethanol-water to afford yellow-orange crystals which showed only one spot by TLC. Oxidative conversion of 6 to their azoxy derivatives 7 with hydrogen peroxide in

acetic acid was carried out under much milder conditions than those for the conventional azoxybenzenes. Thus, oxidation at 60–65°C for a couple of hours sufficiently decolorized azo compounds 6 to afford light yellow products. Recrystallizations from ethanol-water provided the azoxy compounds (7), which gave acceptable elemental analyses. Mass spectra indicated that only one oxygen atom was incorporated into the products and ^{1}H-NMR signals for the α–proton atom of the pyridine ring were shifted downfield (δ = 8.7–8.8 → 8.9–9.2) in the product from this, thereby excluding the possibility of the formation of the pyridine N-oxide which should cause an upfield shift.[3]



Proton signals at δ = 7.7–8.0, characteristic of the azo compound 6 were also absent in the NMR of the product. Oxidations at higher temperatures or for longer times appear to destroy the azoxy structure once formed. This high susceptibility of 6 to oxidation may be due to the presence of the RO and R′O groups at the conjugate positions to the azo group, thereby increasing the electron density of the latter by electron donations. Since azoxy compounds 7 included two isomers (8 and 8′) by TLC, silica gel centrifugal liquid chromatography (CLC) was used to separate these isomer mixtures using ether-hexane (1 : 5 v /v) as the eluting solvent. Identification of the azoxy compounds thus separated were satisfactorily made by ^{1}H-NMR. Thus, the α-proton signals of the pyridine ring for 8 should be located a little upfield from those for 8′ due to the electron donation from the azoxy oxygen through conjugation: δ (α-H) for 8 and 8′ are 9.0–9.1 and 9.1–9.2, respectively. The electron donation causes a shielding effect and therefore an upfield shift.

In Tables 1, 2, and 3 are summarized the mesomorphic ranges of 7, 8, 8′, and their precursors 6, together with the values of molar absorptivity (ε) in ethanol at absorption maxima.

It is recognized from Tables 1 and 2 that azoxy compounds 7–1, 7–4, 8–1, 8′–1, 8–4, 8′–4, and 8′–7 with R = Me either do not show liquid crystal behaviors at all or show only narrow nematic ranges, whereas 7–2 and 8′–2 with R′ = Me show distinct nematic phases even with a short OR (R = C_2H_5). This fact may indicate that the effect of the pyridine ring located at one side of the azoxy group on the nematic structure formation is greater than that of the benzene ring at the other side. The appearance of a smectic phase

TABLE 1.

Mesomorphic range of azoxy compound (7)

No.	R	R′	Mesomorphic range [a] °C	[b] ε EtOH x10⁴ 1.cm.⁻¹ mol.⁻¹
1.	CH_3	CH_3	C73N76I	2.20(351)
2.	C_2H_5	CH_3	C88N102I	2.44(352)
3.	C_6H_{13}	CH_3	C78N99I	2.78(354)
4.	CH_3	C_3H_7	C68I	2.64(352)
5.	C_2H_5	C_3H_7	C89N101I	2.63(354)
6.	C_6H_{13}	C_3H_7	C92N98I	2.58(352)
7.	CH_3	C_6H_{13}	C66N84I	2.76(354)
8.	C_2H_5	C_6H_{13}	C69N104I	2.74(354)
9.	C_6H_{13}	C_6H_{13}	C97N100I	2.90(352)
10.	C_2H_5	C_4H_9	C84N108I	—

[a]C, cyrstal; N, nematic; I, isotropic.
[b]Figures in parentheses indicate absorption maxima in nm.

TABLE 2.

Mesomorphic ranges of azoxy compounds (8 and 8′) [a]

No.	R	R′	RO—⟨⟩—X—⟨N⟩—OR′ X = —N⁺(O⁻)=N— (8)		X = —N=N⁺(O⁻)— (8′)	
			Range	εEtOH	Range	εEtOH
1.	CH_3	CH_3	C105I	2.44(345)	C92I	2.52(356)
2.	C_2H_5	CH_3	C103N106I	2.59(347)	C106N112I	2.76(358)
3.	C_6H_{13}	CH_3	C74S88N98I	2.56(347)	C51N96I	2.56(358)
4.	CH_3	C_3H_7	C88I	2.55(348)	C77N79I	2.56(358)
5.	C_2H_5	C_3H_7	C96N102I	2.27(348)	C96N102I	2.72(358)
6.	C_6H_{13}	C_3H_7	C78N106I	2.61(348)	C58N87I	2.31(358)
7.	CH_3	C_6H_{13}	C66N82I	2.63(347)	C83I	2.64(358)
8.	C_2H_5	C_6H_{13}	C69N107I	2.61(348)	C88N103I	2.64(358)
9.	C_6H_{13}	C_6H_{13}	C96N105I	2.65(348)	C70N91I	2.40(358)
10.	C_2H_5	C_4H_9	C103N112I	1.86(348)	C89N105I	2.30(358)

[a]S,smectic. C, N, I, and figures represent the same terms as in Table I.

in 8–3 may indicate the polar effects of the pyridine ring in combination with the ONN-azoxy group.

Figure 1 indicates that some of the azoxy isomers 8′ have lower CN temperatures than 8, denoting that the polar effects of the NNO-azoxy group and the pyridine ring are less balanced for 8′. It is also recognized from this figure that compounds with pyridine ring (8 and 8′) possess rather lower mesomorphic temperature ranges, especially NI-temperatures, as compared with those for the benzene ring analogs

TABLE 3.

Mesomorphic range of azo compound (6) [a]

No.	R	R'	Mesomorphic range °C	ϵEtOH x10⁴ 1.cm.⁻¹ mol.⁻¹
1.	CH_3	CH_3	C95I	2.36(352)
2.	C_2H_5	CH_3	C91N93I	2.67(353)
3.	C_6H_{13}	CH_3	C94I	2.30(354)
4.	CH_3	C_3H_7	C69I	2.71(354)
5.	C_2H_5	C_3H_7	C95N99I	2.68(354)
6.	C_6H_{13}	C_3H_7	C81N86I	2.84(355)
7.	CH_3	C_6H_{13}	C65I	3.20(355)
8.	C_2H_5	C_6H_{13}	C82N92I	2.82(354)
9.	C_6H_{13}	C_6H_{13}	C91I	2.88(354)
10.	C_2H_5	C_4H_9	C85N98I	2.53(355)

[a]All terms are the same as in Table 1.

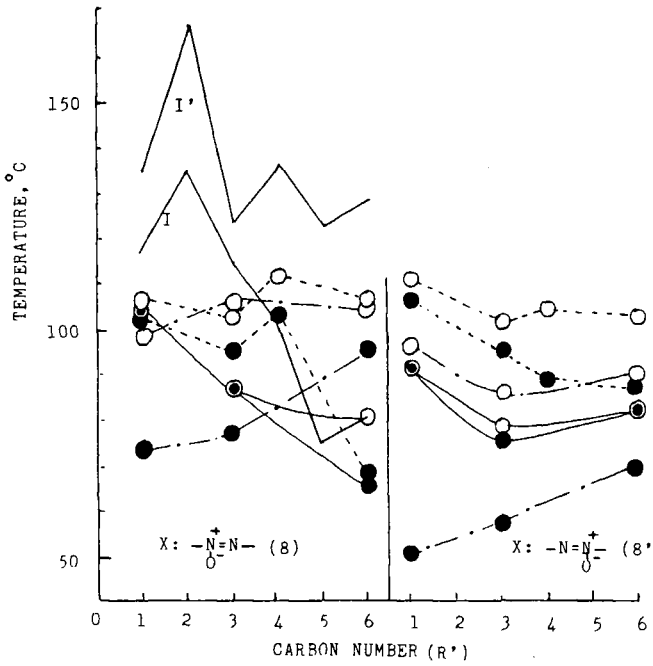


FIGURE 1 Relationships between mesomorphic temperature ranges and alkyl chain lengths for compounds 8 and 8' (RO—⟨⟩—X—⟨N⟩—OR'). ○ Upper temperature; ● Lower temperature. — R = CH_3; ---- R = C_2H_5; — · — R = C_6H_{13}. I and I' are data for R'O—⟨⟩—N=N—⟨⟩—OR', O⁻.

(I and I'), presumably due to the less balanced lateral interactions in the former.

Compounds 7, nearly equimolar mixtures of 8 and 8' by ^{1}H-NMR, indicate rather lower CN temperatures than those for either of 8 and 8' as expected (Tables 1 and 2).

The mesomorphic behaviors of the precursor azo compounds (6) are poor and half of the 6 investigated indicate no mesomorphic ranges, as known in Table 3.

Absorption maxima and their molar absorptivities (ϵ) in ethanol do not change appreciably with conversion of 6 to 7, as recognized from Tables 1 and 3. However, absorbances in the range of 400–500 nm, i.e. visible region, for 6 result in remarkable decreases by this conversion, thereby bringing about decolorations. It is also recognized that the absorption maxima for 8 are about 10 nm blue-shifted than those for 8'.

In conclusion, introduction of a 2,5-disubstituted pyridine in place of the conventional benzene ring in the azoxy compounds of the present study appears to give rise to polar effects on molecules due to the unshared electron pair present on the pyridine nitrogen as well as the polarity of pyridine itself.

3. EXPERIMENTAL

IR, ^{1}H-NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6 spectrometer, respectively, under standard conditions. Elemental analyses were carried out with a Perkin-Elmer 250 instrument. Mesomorphic ranges were determined by means of either a Yamato MP-21 melting point apparatus or an optical microscope, both equipped with crossed polarizers. Centrifugal Liquid Chromatography (CLC) were carried out with a Hitachi CLC-5 instrument.

2-Alkoxy-5-nitropyridines (2)

Sodium metal (1.15 g. 50 mmol) was reacted with n-alkyl alcohol (30 ml) by the application of heat. To the resulting solution was added a solution of 2-chloro-5-nitropyridine (4.8 g, 30 mmol) in the same alcohol (40 ml), and the mixture heated at 70°C for 24 hr. The reaction mixture was poured into ice water to isolate either crystals (R' = CH_3, C_3H_7) or an oil (C_4H_9, C_6H_{13}) which solidified upon cooling with the addition of hexane. Recrystallizations of crude products from ethanol-water provided slightly colored needles (2).

	R′ = CH_3	C_3H_7	C_4H_9	C_6H_{13}
Mp,°C	110–111	88–89	75–76	93–95
Yield, %	99	83	55	49

IR($CHCl_3$) 1340 (NO_2) cm.$^{-1}$ NMR($CDCl_3$) δ 6.9(d, 1 H), 8.4(q, 1 H), 9.2(d, 1 H) pyridine for all; 4.1(s, 3 H, OMe) for R′ = CH_3; 0.9–2.0(alkyl) and 4.4(t, 2 H, CH_2O) except for R′ = CH_3.

2-Alkoxy-5-aminopyridines (3)

A mixture of a solution of 2 (10 mmol) and cyclohexene (5 ml) in ethanol (70 ml) and 5% Pd-C (Japan Engelhard Ind., 1 g) was refluxed for 2 hr with stirring. The reaction mixture was filtered and the filtrate was concentrated on a rotary evaporator to afford an oily product 3 almost quantitatively. IR($CHCl_3$) 3430, 3370(NH_2) cm.$^{-1}$ NMR ($CDCl_3$) δ 3.3–3.6(b, 2 H, NH_2); 6.5–6.6(d, 1 H), 6.9–7.0(q, 1 H), 7.5–7.7(d, 1 H) pyridine for all; 3.8(s, 3 H, OMe) for R′ = CH_3; 0.7–2.0(alkyl), 4.2–4.3(t, 2 H, CH_2O) except for R′ = CH_3.

3-(p-Hydroxyphenylazo)-6-alkoxypyridines (5)

To an ice-cold solution of 3 (10 mmol) in a mixture of 12N-hydrochloric acid (4.5 ml) and water (10 ml) was added dropwise a solution of sodium nitrite (0.7 g, 10 mmol) in water (10 ml), followed by stirring in an ice bath for 10 min. A solution of phenol (0.94 g, 10 mmol) and sodium hydroxide (1.0 g, 25 mmol) in water (20 ml) was added dropwise at 0–5°C with stirring. Stirring was continued further for about one hour, then the reaction mixture was neutralized with solid sodium hydrogen carbonate, and the resulting precipitate removed by filtration. Recrystallizations from chloroform-hexane provided yellow crystals 5, which showed one spot by TLC(Et_2O/Hexane = 3/7).

R′	Yield,%	Mp,°C	C,% *	H,%*	N,% *	Mass (M^+)
CH_3	87	158–159	62.81(62.88)	4.70(4.80)	18.11(18.34)	229
C_3H_7	62	134–136	65.28(65.36)	5.80(5.84)	16.01(16.34)	257
C_4H_9	90	132–134	66.48(66.42)	6.24(6.27)	15.50(15.50)	271
C_6H_{13}	43	117–118	67.94(68.23)	7.17(7.02)	14.19(14.05)	299

*Figures in parentheses indicate Calcd values.

IR($CHCl_3$) 3700–3000(OH) cm.$^{-1}$, NMR($CDCl_3$ + DMSO-d_6) δ 6.5–8.5(m, ArH), 8.7(d, 1 H, ), 9.5–10(b, 1 H, OH) for all; 4.0(s, 3 H, OMe) for R′ = CH_3; 0.8–2.0(alkyl), 4.3–4.5(t, 2 H, CH_2O) except for R′ = CH_3.

3-(p-Alkoxyphenylazo)-6-alkoxypyridines (6)

A solution of 5 (10 mmol) in methanol (20 ml) containing potassium hydroxide (0.8 g, 12 mmol) was evaporated to dryness and the residue dissolved in anhydrous DMF (20 ml). n-Alkyl iodide (12 mmol) was added dropwise to the resulting solution and the mixture stirred at 20°C for 48 hr with exclusion of moisture. The reaction mixture was made basic with 1N-sodium hydroxide solution, followed by extraction with chloroform. The organic layer was washed with aqueous sodium hydroxide, then with water, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator to afford the crude product. This material was purified by silica gel column chromatography (Wakogel C-300) using $CHCl_3$-CCl_4 (3 : 7 v/v) as the eluting solvent. All of the yellow to orange needles thus obtained showed one spot by TLC (Et_2O/Hexane = 3/7 v/v).

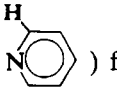
	Yield,%	C,%	H,%	N,%	Mass(M^+)
6–1	37	64.15(64.20)	5.40(5.35)	17.15(17.28)	243
6–2	78	65.30(65.37)	5.85(5.84)	16.31(16.34)	257
6–3	58	69.45(69.61)	7.33(7.35)	13.18(13.42)	313
6–4	54	66.18(66.42)	6.21(6.27)	15.32(15.50)	271
6–5	65	67.15(67.37)	6.64(6.67)	14.59(14.74)	285
6–6	55	70.25(70.38)	7.95(7.92)	12.18(12.32)	341
6–7	77	69.11(69.01)	7.33(7.35)	13.37(13.42)	313
6–8	55	69.85(69.72)	7.71(7.65)	12.80(12.84)	327
6–9	81	71.86(72.06)	8.72(8.62)	10.92(10.97)	383
6–10	68	68.36(68.23)	6.96(7.02)	14.00(14.05)	299

IR($CHCl_3$) 3000–2800(alkyl), 1600(aromatic cm.$^{-1}$ NMR($CDCl_3$) δ 6.7–8.2(m, 6 H, ArH), 8.7–8.8(d, 1 H, ) for all; 3.9(s, 3 H, MeO) for 6–1, 6–4, 6–7; 4.0–4.1(s, 3 H, MeO) for 6–1, 6–2, 6–3; 0.8–2.0(alkyl), 3.9–4.5(m, 2 H, OCH_2) except for 6–1.

3-[(4-Alkoxyphenyl)-NON-azoxy]-6-alkoxypyridines (7)

Hydrogen peroxide (30%, 17 ml) was added to a solution of 6 (5 mmol) in glacial acetic acid (100 ml). The resulting orange solution was kept at 65°C for 1.5 hr to effect decoloration. The light yellow reaction mixture was poured onto ice to effect crystallization. Recrystallizations of the crude product from ethanol-water provided yellow needles indicating two spots almost identical in area by TLC(Et_2O/Hexane = 1/5).

Yield,%		C,%	H,%	N,%	Mass (M^+)
7–1	67	60.87(60.94)	5.25(5.02)	16.23(16.22)	259
7–2	68	61.28(61.34)	5.51(5.49)	15.35(15.38)	273
7–3	69	65.75(65.65)	7.03(6.99)	12.78(12.77)	329
7–4	58	62.55(62.72)	6.30(6.27)	14.58(14.67)	287
7–5	37	63.56(63.79)	6.42(6.31)	13.74(13.95)	301
7–6	58	67.21(67.23)	7.61(7.56)	11.70(11.76)	357
7–7	29	65.32(65.65)	6.85(6.99)	12.41(12.77)	329
7–8	65	66.28(66.47)	7.42(7.29)	12.20(12.24)	343
7–9	29	69.02(69.17)	8.26(8.23)	10.54(10.53)	399
7–10	50	65.09(64.76)	6.75(6.67)	13.27(13.33)	315

IR($CHCl_3$) 3000–2800(alkyl), 1600(aromatic) $cm.^{-1}$ NMR($CDCl_3$) δ 6.7–7.3, 8.1–8.8(m, 6 H, ArH), 8.9–9.2(q, 1 H, ) for all; 3.8–3.9(s, 3 H, MeO) for 6–1, 6–4, 6–7; 4.0(s, 3 H, MeO) for 6–1, 6–2, 6–3; 0.8–2.0(alkyl), 3.9–4.5(m, OCH_2) except for 6–1.

3-[(4-Alkoxyphenyl)-ONN-azoxy]-6-alkoxypyridines (8) and 3-[(4-Alkoxyphenyl)-NNO-azoxy]-6-alkoxypyridines (8′)

Centrifugal liquid chromatography (CLC) using silica gel (Fujigel Co., KT2061) as adsorbent and ether-hexane (1 : 5 v/v) as the eluting solvent was applied to 7. Compound 8′ was first eluted at 300–400 rpm, then the rotation was raised to 500–600 rpm to elute 8. All of 8 and 8′ in the form of light yellow crystals provided a single spot by TLC(Et_2O/Hexane = 1/5).

Elemental analyses and determinations of M^+ in mass spectra provided satisfactory results. NMR($CDCl_3$) δ 6.7–8.8(m, 6 H, ArH) for all; 3.9(s, 3 H, MeO) for 8–1, 8′–1, 8–4, 8′–4, 8–7, 8′–7; 4.0–4.1(s,

3 H, MeO) for 8-1, 8′-1, 8-2, 8′-2, 8-3, 8′-3; 9.0-9.1(d, 1 H, ) for 8–1 — 8–10; 9.1–9.2(d, 1 H, ) for 8′–1 — 8′–10; 0.9–2.0(alkyl) 3.9–4.5(m, OCH_2) except for 8–1, 8′–1.

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