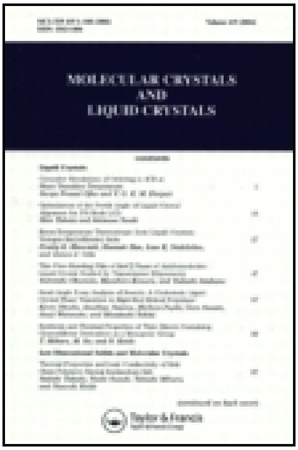

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Low Melting Liquid Crysalline Heterocyclc Anils(1)

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Low Melting Liquid Crystalline Heterocyclic Anils(1)

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Abstract—A homologous series of 3-N-(4′-alkoxybenzilideneamino)-6-*n*-alkylpyridines has been synthesized and compared to the carbocyclic analogs. The pyridine anils exhibit low melting points and generally nematic behavior with much lower thermal nematic stability. The lateral attractive effect of a permanent dipole was exhibited without concomitant interference from the steric interactions which usually accompany an added dipole. The effect of heteroatomic ring position was assessed by comparison to the synthetic 2-N-(4′-alkoxybenzilideneamino)-5-*n*-alkylpyridine isomers. The role of symmetry in the heterocyclic materials and the influence of an additional permanent dipole was investigated. A simple, rapid, high yield synthesis was developed for making the required intermediate disubstituted pyridines.

1. Introduction

There have been a variety of Schiff bases reported to exhibit liquid crystallinity but only a few of these systems contained heterocyclic moieties. These systems include unsubstituted pyridine biphenyl anils,(2) 2,5-diphenylpyrimidines(3) and pyridazines(4) and some few derivatives of benzoxazole and benzthiazole.(5) None of these exhibits a liquid crystalline phase at or below room temperature. This paper describes the preparation of a new series of heterocyclic anils exhibiting low temperature mesomorphic behavior.

It has been suggested(6) that the occurrence of a mesomorphic state depends upon a variety of parameters: the geometry and conformation, the lateral to terminal attractive force ratio, the length-to-breadth ratio and the influence of the number, presence and position of permanent dipoles. Previous studies on the effect of dipole–dipole interactions have had to isolate the counter-effect of increased molecular breadth.(7) The pyridine anils have lower symmetry than the corresponding benzene analogs. They also possess an additional permanent dipole that affects the magnitude and direction of the total molecular moment while affording a lateral dipole without increased molecular breadth.

Thus, a study of heterocyclic analogs of the well known MBBA family of Schiff bases was undertaken to help sort the variety of parameters required for mesomorphic behavior mentioned above. It was also hoped that new single component homogeneous nematic liquid crystals would be attained that would be useful as electrooptic display materials.

The syntheses of many of the 18 Schiff bases prepared from 3-amino-6-alkylpyridines (3A6AP) and 4-alkoxybenzaldehydes were accomplished with the aid of a simple, high yield procedure for making the intermediate 3,6-disubstituted pyridines.

2. Experimental

Transition temperatures were determined with an AO-20 series polarizing microscope equipped with a Mettler heating/cooling stage. In some cases optical observations were checked with a Dupont 900 DTA which was calibrated to indicate transition temperatures to within ± 1 °C. The 2- and 3-aminopyridines,(8) 2-amino-5-methylpyridine,(9) the 4-alkoxybenzaldehydes(11) and the 2-chloro-5-nitropyridine(10) were available commercially.

3-AMINO-6-*n*-ALKYLPYRIDINES

Sodium (metallic balls, 3.5 g) was made into a sand under xylene, cooled to room temperature and diethyl-*n*-alkyl malonate (0.15 mol) was added with stirring and heating (40–50°) until the sodium was completely dissolved (0.5–2 hrs). 2-chloro-5-nitropyridine (0.15 mol, 23.8 g) was added, the mixture refluxed (4 hrs) and the xylene distilled from the reaction flask. The flask was cooled to room temperature and water (200 cc) added followed by exhaustive ether extractions.† The ether layer was dried ($MgSO_4$), concentrated and distilled giving 2-(diethyl-*n*-alkylmalonyl)-5-nitropyridines (50–60%) as viscous dark orange oils: bp ranges were ≃150–210°/0.1 mm;

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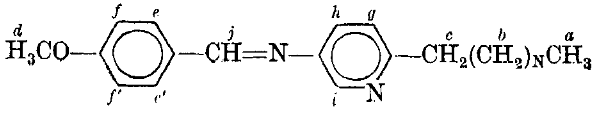
† Layer separation was difficult to detect and required filtration through Johns–Manville Celite.

nmr spectra were consistent with the expected 2,5-disubstituted pyridines. The above adducts were added to 50% sulfuric acid (110 cc) and heated (105–110°) until carbon dioxide evolution ceased (2–3 hrs) then cooled, neutralized with aqueous sodium hydroxide and exhaustively extracted with ether. The ethereal extracts were dried ($MgSO_4$), concentrated and distilled giving (75–85%) yellow liquids: bp $\simeq 100°/0.1$ mm; ir and nmr agreed well with a 2-alkyl-5-nitropyridine structure. The reduction was carried out in 3–4 g quantities utilizing a Paar apparatus with PtO_2 (25–30 mg) in absolute methanol (80 cc). The usual workup and distillation afforded colorless liquids which darkened upon standing: boiling points were similar to the nitro precursors; ir (neat) 3 and 3.1 μ ($-NH_2$).

SCHIFF BASES

Equimolar quantities of *p*-anisaldehyde or *p*-ethoxybenzaldehyde and 3-amino-6-alkyl or 2-amino-5-alkylpyridines were dissolved in toluene and refluxed; water was collected by azeotropic distillation (1–2 hrs). The toluene was removed and residues were vacuum distilled giving (95%) light yellow liquids: boiling points ranged from 180–230°/0.05–0.1 mm. Materials that solidified on standing or chilling were recrystallized several times from hexane or hexane/ethanol until sharp and reproducible transition temperatures were obtained: ir (neat) 1600–1610 cm^{-1} (CH=U); nmr ($CDCl_3$, TMS internal standard) δ 0.85–0.98 (*m*, *a*, 3H), 1.12–2.0 (*m*, *b*), 3.87 (*s*, *d*, 3H), 2.8 (*t*, *c*, 2H), 7.87 (*d*, *e*, 2H), 7.05 (*m*, *f*, 2H), 7.13 (*m* overlapped with *f*, *g*, 1H), 7.45 (doublet of doublets, *h*, 1H) and 8.42 ppm (*s* broad), *i* and *j*, 2H). The ethoxy compounds showed the characteristic ethyl splitting and the spectra were considerably simplified with $Eu(fod)_3$ to confirm the assignments; glc indicated purities $\geqslant 99.5\%$; mass spectral analysis gave the expected parent peaks.

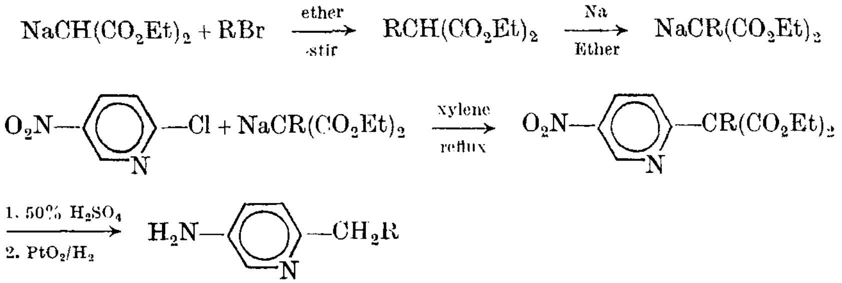
In nmr descriptions, first letter *m* = multiplet, *t* = triplet, *d* = doublet, *s* = singlet; second letter identifies the proton.



3. Results and Discussion

At the beginning of this study an attempt was made to investigate mesomorphicity as a function of the position of the heteroatom relative to the central linkage. Syntheses of heterocyclic homologous series of liquid crystals have been limited, at least in part, by the often tedious synthesis of the heterocyclic precursors. The present study required the synthesis of 2-amino-5-substituted- and 3-amino-6-substituted pyridines.

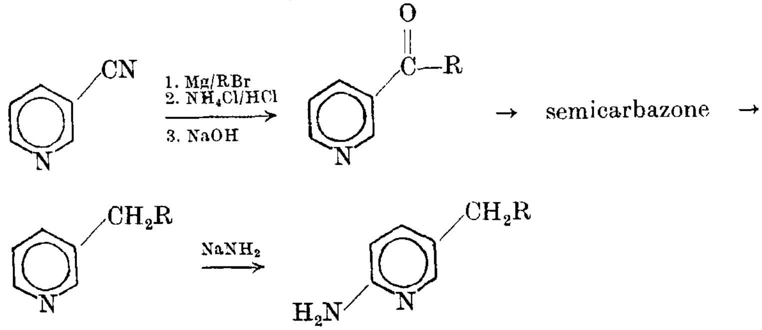
The 3-amino-6-substituted pyridines were synthesized according to the sequence depicted in the following scheme:



The method of Gruber(12) was unsuccessfully attempted, obtaining only sublimed starting material (2-chloro-5-nitropyridine). A simple, more rapid procedure was developed which allowed much of the synthesis to be carried out in one flask utilizing the reaction sequence above. Moreover, the yields were generally higher than those reported by Gruber† and eliminated the need to isolate and carefully dry the intermediate sodium diethylalkylmalonates.

Two routes to the 2,5-disubstituted pyridines were considered(13,14)

(A)



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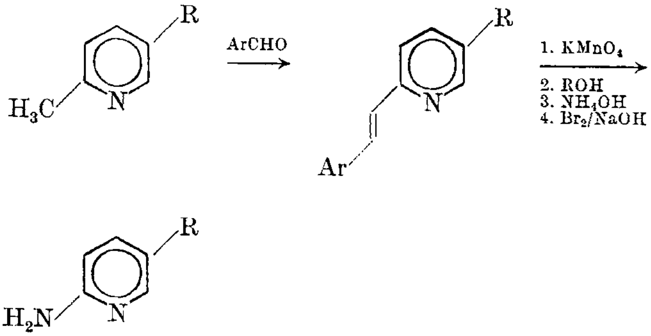
† Typically 37% reported by Gruber as compared to 50% in this study.

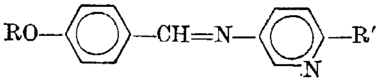
(B)

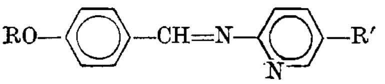


Both schemes reportedly result in overall yields of less than 3% while requiring several tedious steps. One of these (B), has the advantage of obtaining intermediate stilbazoles.⁽¹⁵⁾ It became evident that syntheses of the 2-amino-5-alkyl- or alkoxypyridines would be much more difficult than for the 3,6-disubstituted isomers. Therefore, before proceeding with the synthesis of a homologous series of 2-amino-5-substituted pyridines, data were obtained from a comparison of the anils derived from commercially available 2-amino-5-substituted pyridines and *p*-alkoxybenzaldehydes.

Table 1 lists some melting points for 2- and 3-N-(4′-alkoxybenzilideneamino)-5- and 6-substituted pyridines. Although the melting point was decreased 25° when R′=H (anil 1 vs. anil 4) it increased when R=ethyl (2 vs. 5) or R′=methyl (3 vs. 6). Young, Haller and Williams reported a 59° decrease in melting point by

TABLE 1

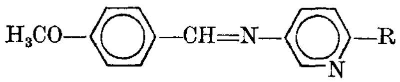




No.	*R*	*R′*	m.p.	No.	*R*	*R′*	m.p.
1	CH_3	H	55–57.5°†	4	CH_3	H	29–30
2	C_2H_5	H	56–57	5	C_2H_5	H	73–75
3	CH_3	CH_3	53–55	6	CH_3	CH_3	62–64
				7	n-C_8H_{17}	CH_3	67–68 ($n \rightarrow i$ 64)

† Ref. 24.

Table 2



No.	m.p. (°C)	$S \to n$ (°C)	$n \to i$ (°C)	R
8	55–57.5[9]			H
9	53–55			CH_3
10	12–14			C_2H_5
11	57–58.5		9.3	n-C_3H_7
12	40–41		6.4	n-C_4H_9
13	27–29		26.5	n-C_5H_{11}
14	12–13.3		11.6	n-C_6H_{13}
15	39–40		38.2	n-C_7H_{15}
16	29–29.5[a]	33	38	n-C_8H_{17}
17	39.4	40.1[b]	46.6[c]	n-$C_{10}H_{21}$

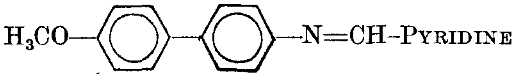
n = nematic; S = smectic; i = isotropic

(*a*) DTA didn't show any transition until 33° preceded by a shoulder; also the $n \to i$ transition was observed at 38°. The first transition may have been missed because the program had to be started at 26°.

(*b*) $Sm_{II} \to Sm_I$.

(*c*) $S_{II} \to i$; DTA indicated a transition at 39.1° and $S \to i$ at 46.1°.

shifting the position of the ring heteroatom from *meta-* to *ortho-* with respect to the central linkage in the following:[†]



The irregularity of these initial results and the tediousness of the 2-amino-5-substituted pyridine synthesis dissuaded any further effort of studying ring heteroatom position–central linkage relationships.

The remainder of the investigation concentrated on the hope of achieving low temperature liquid crystals by exploiting the properties associated with the dipole moment and asymmetry of the heterocyclic pyridine moiety in the 3-N-(4′-alkoxybenzilideneamino-6-alkylpyridines.

The transition points of the anils derived from 3A6AP and *p*-anisaldehyde are shown in Table 2 and those derived from 3A6AP and

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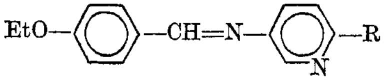
[†] It should be noted that a direct comparison between Young's work and this study is difficult since a biphenyl moiety is used and the central linkage is reversed. The effect of the direction of anil linkage on transition temperatures has already been determined.(16)

p-ethoxybenzaldehyde are presented in Table 3. In both series an alternation of mesomorphic–isotropic transition temperatures is found as the number of carbon atoms in the alkyl chain of the pyridine ring is increased. In general (except for compounds **11** and **12**) the heterocyclic compounds exhibited lower melting points than the corresponding carbocyclic analogs (Fig. 1). The results also show consistently lower clearing points for all comparable cases (Fig. 2); the thermal nematic stabilities are lowered an average of about 40° for the pyridine anils.

TABLE 3



No.	m.p. (°C)	$Sm_{II}\rightarrow Sm_{I}$ (°C)	$S_1\rightarrow n$ (°C)	$n\rightarrow i$ (°C)	R
18	56–57				H
19	55–57				CH_3
20	27–28[a]	39[b]	49–50	57.6[c]	n-C_4H_9
21	52		58	69[c]	n-C_5H_{11}
22	35–36		61.7–62	65.4	n-C_6H_{13}

(*a*) After recrystallization on the microscope slide, the compound melted 24.5–25.5°.

(*b*) DTA showed a fairly strong transition at 39°, a weaker one at 52° and $n\rightarrow i$ at 57.5°. The first transition may have been missed because the analysis was started only a few degrees below the first expected transition (23°), see Ref. 22.

(*c*) This was a homoeotropic nematic phase; compound 13 exhibited a reversible homogeneous to homeotropic nematic change at 54.5 °C.

The differences in transition temperatures between the benzene and pyridine anils are dependent upon at least two factors. One is the presence of an additional permanent dipole in the pyridine anils. The second factor is the difference in symmetry. The presence of dipole moments should tend to increase the melting points while the lower degree of symmetry should tend to decrease the melting points.(6) The generally lower melting points of the heterocyclic compounds could thus be explained by assuming that the symmetry is the dominant factor. It is noted, however, that compounds **11** and **12** with 3 and 4 carbon atoms in a wing group have higher melting

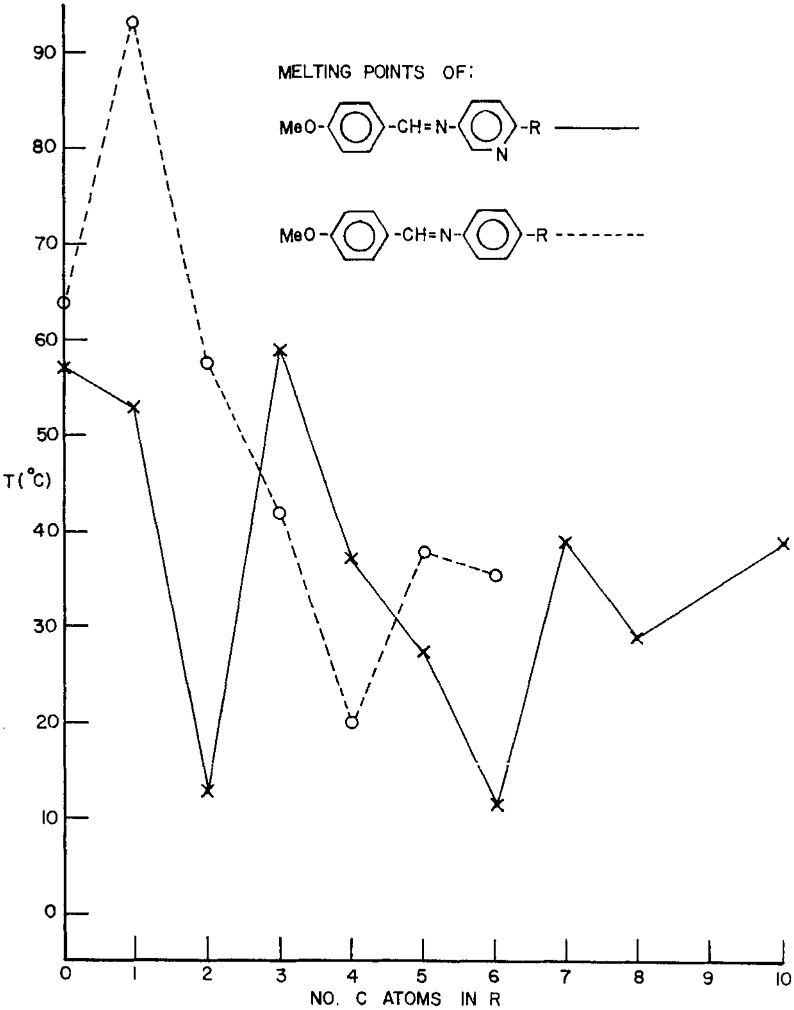

MELTING POINTS OF:
MeO-⟨⟩-CH=N-⟨⟩-R ———
N
MeO-⟨⟩-CH=N-⟨⟩-R - - - - - -
T(°C)
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
NO. C ATOMS IN R

Figure 1

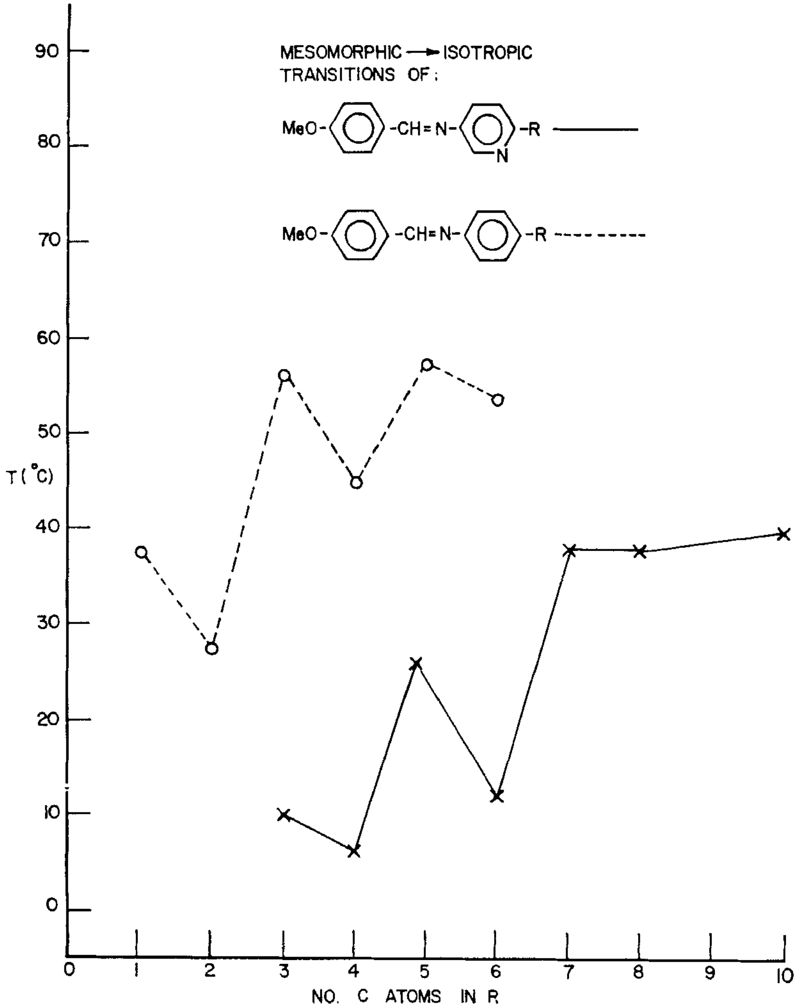

MESOMORPHIC → ISOTROPIC
TRANSITIONS OF:
MeO-⟨⟩-CH=N-⟨N⟩-R ———
MeO-⟨⟩-CH=N-⟨⟩-R - - - - -
T (°C)
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
NO. C ATOMS IN R

Figure 2

points. This is somewhat surprising in view of earlier work on benzene anils(5,17) where the lowest melting member of an homologous series contained four carbon atoms in a wing group.

It is more difficult to account for the consistently lower clearing points of the pyridine anils. In a recent paper by Young et. al.(18) permanent dipoles are assessed as playing relatively unimportant roles in the intermolecular attractions responsible for mesomorphic alignment. Even more recently van der Veen *et al.*(6) account for the higher clearing points of *p,p*′-dialkylazoxybenzenes, relative to the azo analogs, by the *presence* of a permanent dipole moment. Both groups, however, seem to suggest the importance of symmetry and/or conformation on the intermolecular forces of the mesomorphic as well as the solid state. The reduced symmetry of the heterocyclic anils could be a factor in lowering the thermal nematic stability. However, the role of an additional permanent dipole with its attendant alteration of molecular polarizability and lateral to terminal force ratio cannot be ignored.

The additional permanent dipole in the pyridine anils, without an attendant increase in molecular breadth, might also be expected to increase the lateral to terminal attractive force ratio to the exclusion of a nematic phase. Indeed, other work on dialkoxy substituted pyridine anils indicated almost entirely smectic behaviour.(19) The subtle interplay of the forces controlling the mesomorphic state is clearly indicated by the fact that this study produced predominantly low temperature nematic liquid crystals with compound **12** clearing at 6.4 °C.

The 3-N-(4′-methoxybenzilideneamino)-6-*n*-alkylpyridines showed dynamic scattering with rise times similar to the carbocyclic analogs while decay times were a factor of 2 to 3 slower in a typical test cell.(20) Mixtures of these anils with the carbocyclic analogs afforded very low temperature nematic phases. This aspect of the study is continuing.

4. Conclusion

Relatively low temperature nematic liquid crystals were obtained with the heterocyclic Schiff bases of 4-alkoxybenzaldehydes and 3-amino-6-*n*-alkylpyridines. Although most of the nematic phases were monotropic, enantiotropic nematics were obtained with several compounds. Pure smectic behavior was noted only for the decyl analog although the lateral heteroatom might have been expected to exert more influence toward smectic behavior. A room temperature smectic liquid crystal, reported earlier, occurred with 3-N-(4′-ethoxybenziledeneamino)-6-*n*-butylpyridine (EBBP).(21,22) The heterocyclic anils generally melted lower than the carbocyclic analogs and all the corresponding mesomorphic–isotropic transitions were lower. The lower melting points most probably result from the lower symmetry of the pyridine anils; the lower clearing points from a combination of the lower symmetry and the presence of an additional dipole with its alteration of the molecular polarizability.

Acknowledgements

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stilbazole cleared at 61°C. Thus, the thermal nematic stability of the stilbene was lowered to about the same degree as the corresponding anil series (presumably due to the presence of the heteroatom).

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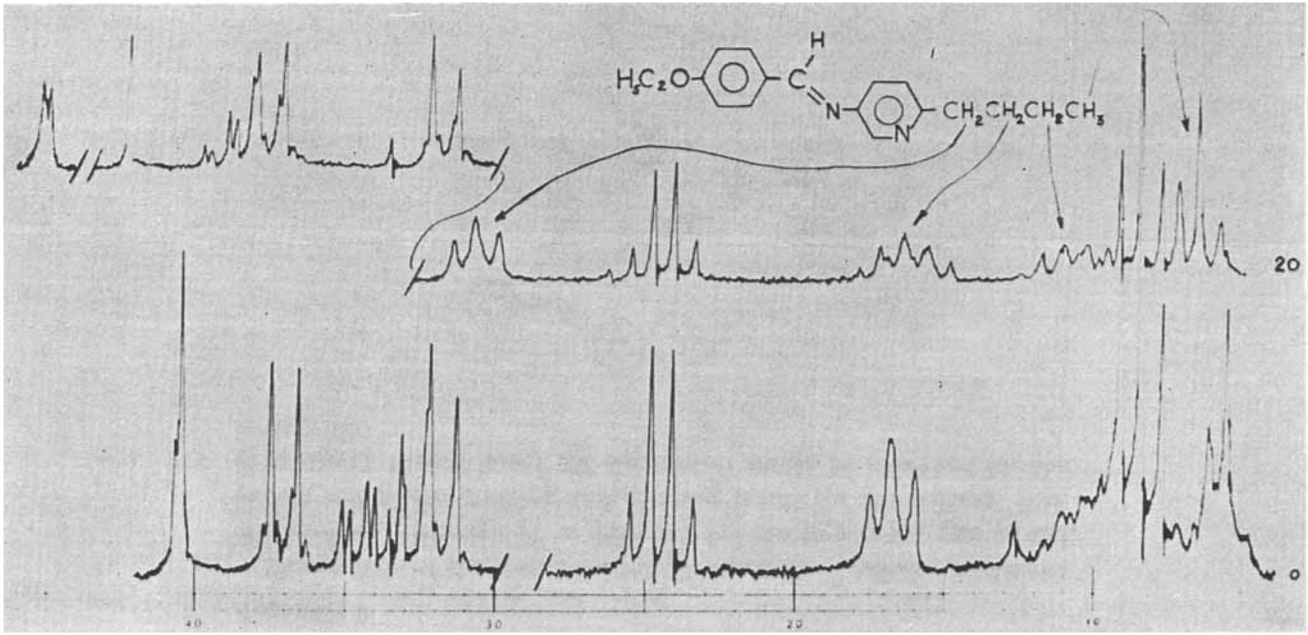
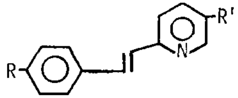
Appendix 1

Clarification of the nmr spectrum of neat EBBP (lower trace) with $Eu(fod)_3$ (upper trace). The overlapping 2-proton of pyridine and benzilidene are resolved. Thus, it is seen that Europium is tying up the more basic pyridine nitrogen which also results in a resolution of each methylene unit in the alkyl chain.

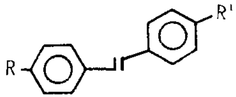


Appendix 2

Comparison of the transition temperatures for a stilbene and some stilbazoles. Although R′ is different for the two cases, one would expect still higher melting and clearing points for the stilbene with R′=ethyl; thus a larger ΔT depression would be observed for the stilbazole.



R	R'	m.p.	n→i
H	Et	57	—
MeO	Et	70	61



R	R'	m.p.	n→i
MeO	Bu	118	121

Appendix 3

Differential thermal analysis of 3-N-(4′-ethoxybenzilideneamino)-6-*n*-alkylpyridine (EBBP). The crystal to mesomorphic transition may have been missed because the program had to be started at ambient temperature which was only a couple of degrees below the expected transition.