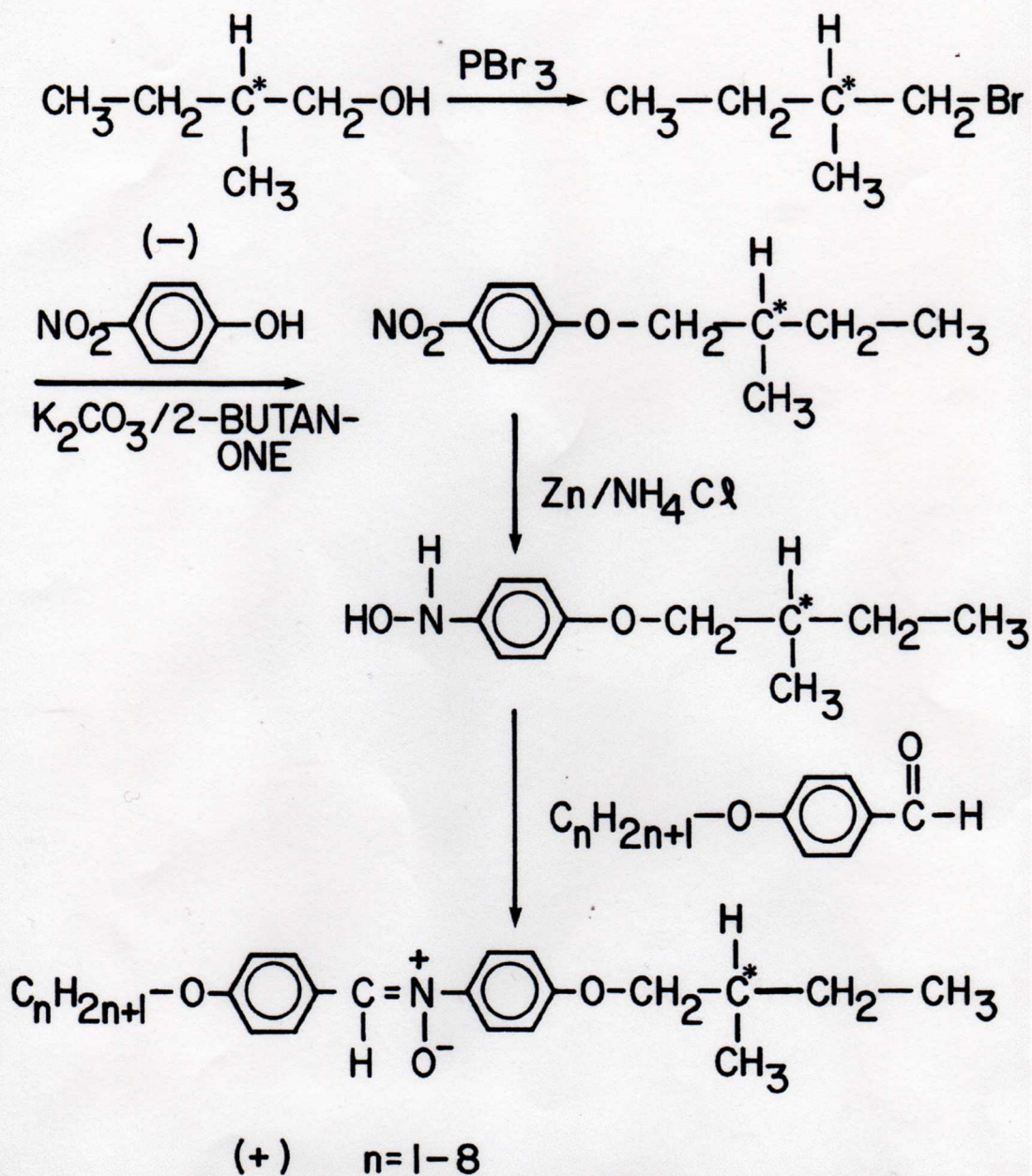


Preparation and Photochemistry of Homologous Chiral Nitrones, Chiral Sc Liquid Crystals; Chiral N-(p-2-methoxybutoxyphenyl)- α -(p-n-alkoxyphenyl) nitrones, Mortimer M. Labes and John H. MacMillan, Department of Chemistry, Temple University, Philadelphia, Pa 19122

CHIRAL NITRONES SYNTHESIS



(-) 2-Methyl-1-butanol
Phosphorous Tribromide
p-Nitro Phenol
Potassium Carbonate
2-Butanone
Zinc Moss
Ammonium Chloride
p-(n-Alkoxy) Benzaldehydes

Procedure

A series of chiral N-(p-2methoxybutoxyphenyl)- α -(p-n-alkoxyphenyl) nitrones, a-h, was prepared and examined for mesogenic properties. The methyl derivative a showed only a transient cholesteric texture on rapid supercooling, while the ethyl homolog b was a monotropic cholesteric. Propyl and butyl homologs c-d were non mesogenic while pentyl derivative e showed a monotropic chiral Sc mesophase. The higher members of the series were enantiotropic, exhibiting only chiral Sc mesophases. The materials exhibited both thermal and photochemical instability, however, suitable eutectization resulted in lower temperature chiral Sc and cholesteric phases with adequate stability under long wavelength (> 400 nm) illumination.

Author's Comments

We report the synthesis, mesogenic properties, and photochemical isomerization of a series of chiral nitrones a-h. These compounds were prepared with minor modifications by the procedure of Young,^{1,2} from 83% optically pure l-amyl alcohol (2-methyl-1-butanol). The hydroxylamine intermediates were not isolated, but reacted in situ with the appropriate p-alkoxy substituted benzaldehyde, resulting in quantitative precipitation of a-h. Recrystallization from cyclohexane gave white crystalline solids, whose IR, NMR and UV spectra were similar to those previously described¹⁻⁴ for non chiral mesogenic nitrones. All gave satisfactory combustion analyses (see table 1). The optical purity of a-h was determined to be ~80% by NMR

analyses employing the chiral shift reagent $\text{Eu}(\text{TFC})_3$. Compounds a-h were examined for mesogenic behaviour by both polarized optical

microscopy and differential scan calorimetry. The results are summarized in table 1 and figures 1-3. Compound a showed a transient cholesteric texture with "peacock" colors only on extremely rapid supercooling to $\sim 55^\circ\text{C}$. The phase change was not detectable via DSC. Compound b showed monotropic behaviour, also exhibiting "peacock" colors. The oily streak texture and low isotropic transition enthalpy (0.29kcal/mol) indicated a cholesteric mesophase. Compounds c and d were non mesogenic while the n-pentyl derivative e showed a monotropic Sc mesophase with well developed striated fan shaped or Schlieren textures. The higher homologs f-h showed enantiotropic behaviour with textures identical to 5e. The mesophases of e-h were classified as chiral Sc due to their high viscosity, high isotropic transition enthalpies ($\sim 1.4\text{kcal/mol}$) and failure to exhibit grandjean texture when placed in wedged cells with SiO coated glass⁵. Texturally the phases were identical to published pictures of the chiral Sc mesophase⁶. Careful cooling of the mesophases failed to show further transitions to Sb, Sg or Se phases prior to crystallization. Thus f-h constitute materials with pure chiral Sc phases, there also being no evidence for higher temperature Sa or cholesteric phases.

The chiral Sc phases showed no visible reflection, probably due to the pitch band being in the ultraviolet. This conjecture was verified with a 1:1 wt% mixture of a and f, which possesses both a chiral Sc and a cholesteric phase (see Table 2). The cholesteric phase showed blue reflection and on cooling to the Sc phase, only a blue-colorless change was observed, that is, the reflection band was further blue shifted.

Figure 1 shows odd-even effects in the isotropic points for $n=1-4$, with a merger point at $n=5$. This behaviour is typical for homologous mesogenic substances and has been discussed elsewhere⁷. The branched 2-methylbutoxy group has the

ChemSpider SyntheticPage 527 Page 5 of 13

expected deleterious effect on chiral nematic stability. Thus **a** is a non-mesogen while the nitrone described by Young² with $n=1$ and a *n*-pentyloxy group in the *p'* position is an enantiotropic nematic with clearing points some 25°C higher than for **a**. All of Young's mesogenic nitrones show higher clearing points and wider mesogenic ranges than **a-h**.

The qualitative thermal and photochemical stability of **a-h** were next investigated. Thermally, the materials slowly developed yellow colors while held for ~1-2 hours in the mesogenic range (~105 °C), with concurrent slight decreases (~1 °C) in the isotropic points. At lower temperatures as in various mixtures of **a-h** (see Table 2), the thermal degradation was negligible. Photochemically the materials slowly degrade in fluorescent light (see Figure 5), with rapid degradation under a mercury lamp. The UV spectra (Figure 5) showed the characteristic³ decrease in the 330nm chromophore, with concurrent growth of bands at ~280nm. The 280nm chromophore is attributed to the amides **2** resulting from the thermal isomerization of an intermediate oxazirane.^{3,4} In two cases the crystalline photoproducts were identified as amides by the characteristic infrared absorbances at 3350 and 1660cm⁻¹. The photoproducts were non-mesogenic.

Conclusions

We have prepared a series of chiral nitrones whose higher homologs possess enantiotropic chiral Sc mesophases. These materials are pure chiral Sc mesophases. Although these materials exhibit both thermal and photochemical instability, eutectic mixtures under long wavelength, > 400nm irradiation are reasonably stable. Due to the strong dipole associated with the nitrone moiety, these materials may prove useful for studies of pyroelectric behavior⁸.

Acknowledgements

This work was supported by the National Science Foundation under grant number DMR-07811. We thank Dr. Hosull Lee for assistance with the chiral shift reagent NMR studies.

TABLE 1

TRANSITION TEMPERATURES, ENTHALPIES AND COMBUSTION ANALYSES FOR THE
 (+)-N-[p-(2METHYL BUTOXY) PHENYL]- α -(p-N-ALKOXYPHENYL) NITRONES, a-h

COMPOUND	n	TRANSITION TYPE	TRANSITION T °C	ENTHALPY CHANGE Kcal/Mol	C	ANALYSES				
						CALC H	N	C	FOUND H	N
a	1	K-I	95.3	7.08	72.82	7.4	4.47	73.01	7.45	4.51
b	2	K-I	111.6	5.33	73.36	7.7	4.28	73.23	7.89	4.31
		Ch-I	94*	0.29						
c	3	K-I	106	4.49	73.87	7.97	4.1	73.75	7.89	4.32
d	4	K-I	111.5	4.15	74.33	8.22	3.94	74.21	8.34	3.95
e	5	K-I	103	4.19	74.76	8.46	3.79	74.87	8.6	3.78
		Sc-I	100*	1.44						
f	6	K-Sc	96.5	5.83	75.16	8.67	3.65	75.06	8.76	3.64
		Sc-I	106	1.33						
g	7	K-Sc	100	5.81	75.53	8.87	3.52	75.48	8.88	3.52
		Sc-I	107.5	1.41						
h	8	K-Sc	101.5	5.6	75.87	9.06	3.4	76.05	9.25	3.42
		Sc-I	109	1.28						

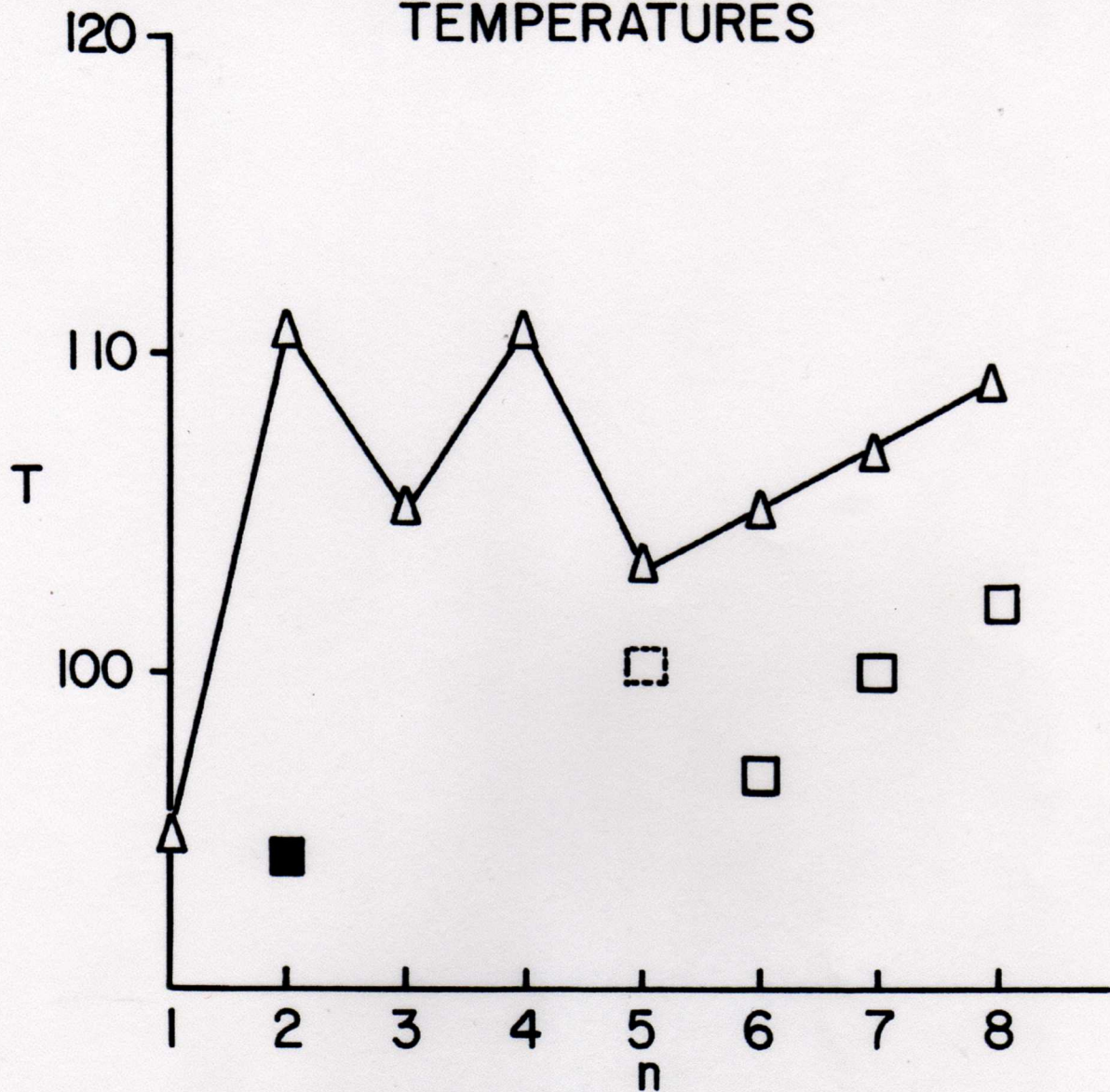
* = Monotropic Transition

TABLE 11

n	WT % s	<u>CHIRAL</u>	<u>NITRONE</u>	<u>MIXTURES</u>	
		TRANSITION °C	TEMPERATURES	Ch-I	Sc-I
1,5	EQUAL	K-Sc 76	Sc-Ch 78	79.5	-
1,6	EQUAL	52.8	67	82	-
2,6	EQUAL	65	93	98.1	-
1,2,6	EQUAL	53.5	74	89.5	-
1,6,7	EQUAL	49	78	88.5	-
5,6,7,8	EQUAL	82	-	-	104
1 through 8	EQUAL	60	91.5	93	-

Figure-1
Phase Transition
Temperatures
for
Chiral N-(p-2-
methoxybutoxyphenyl)- α -
(p-n-alkoxyphenyl)
nitrones

TRANSITION TEMPERATURES



Δ ISOTROPIC POINT

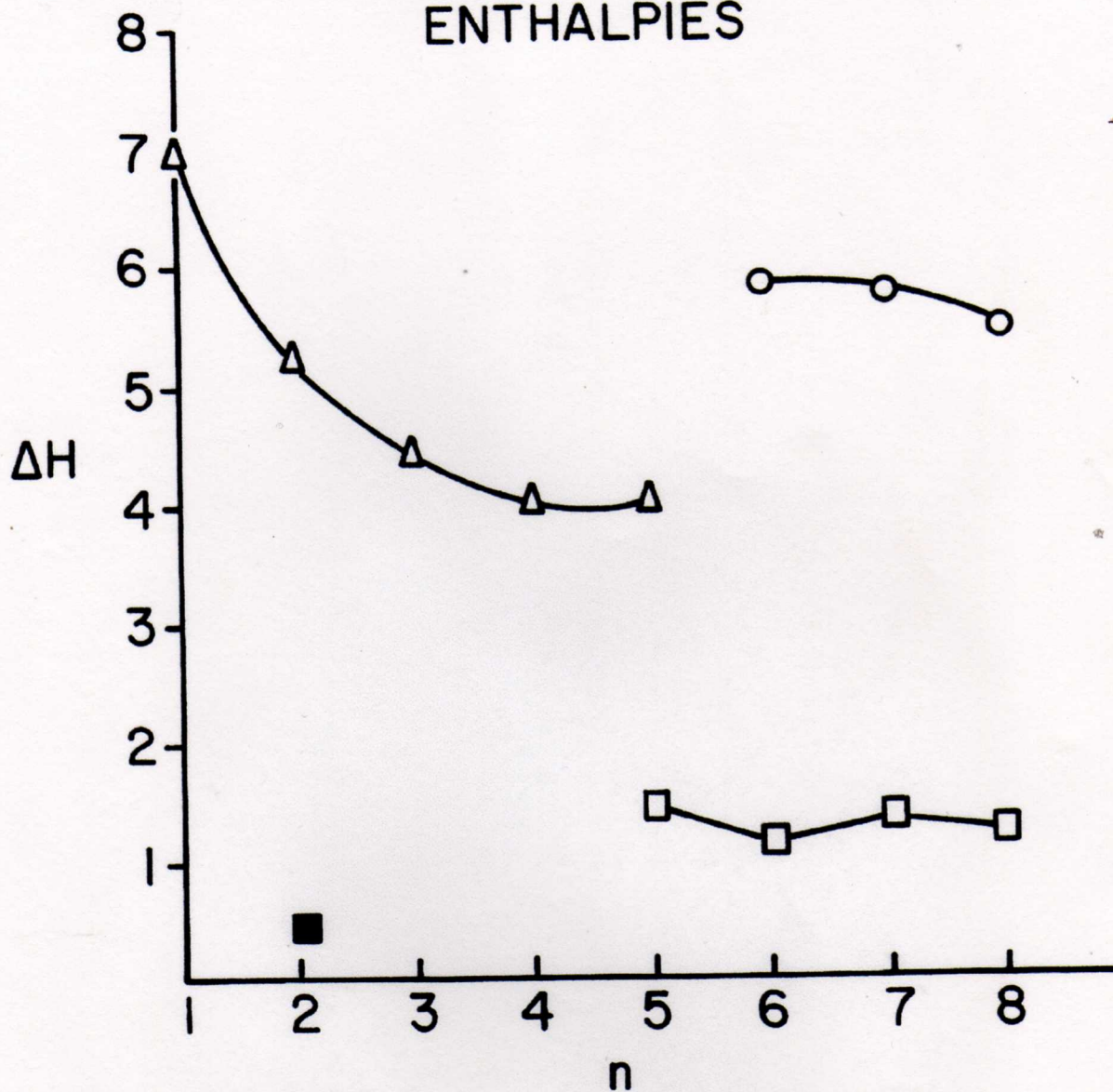
□ K- S_C

■ Ch-I (MONOTROPIC)

□ S_C -I (MONOTROPIC)

Figure-11
Transition
Enthalpies
for
Chiral N-(p-2-
methoxybutoxyphenyl)- α -
(p-n-alkoxyphenyl)
nitrones

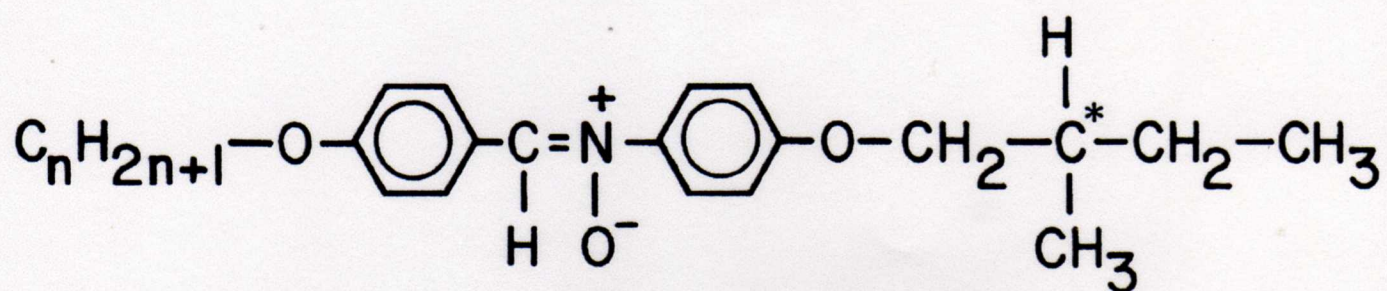
TRANSITION ENTHALPIES



- Δ K-I
- \circ K-Sc
- \square Sc-I
- \blacksquare Ch-I

Figure-111
Chiral Sc
Mesophases
for
Chiral N-(p-2-
methoxybutoxyphenyl)- α -
(p-n-alkoxyphenyl)
nitrones

NEW
CHIRAL S_C
MESOPHASES

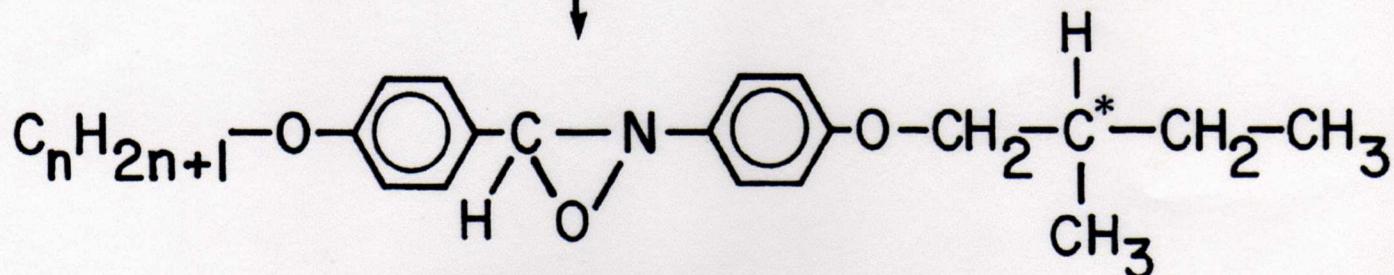
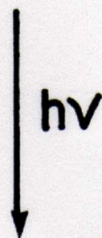
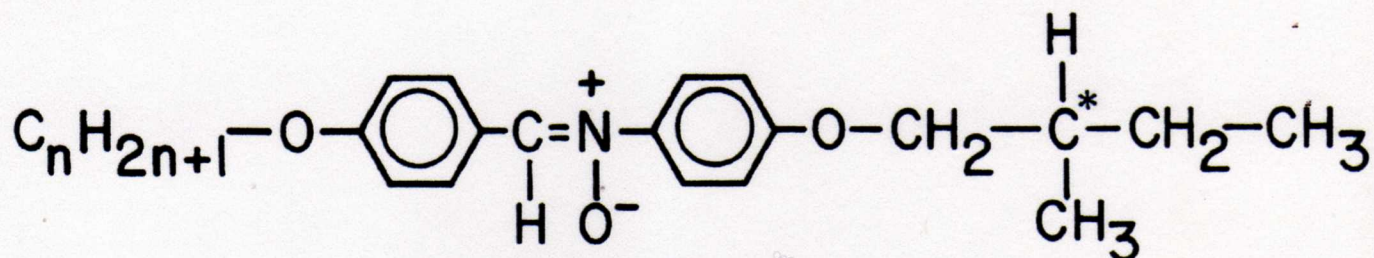


$$n=5-8$$

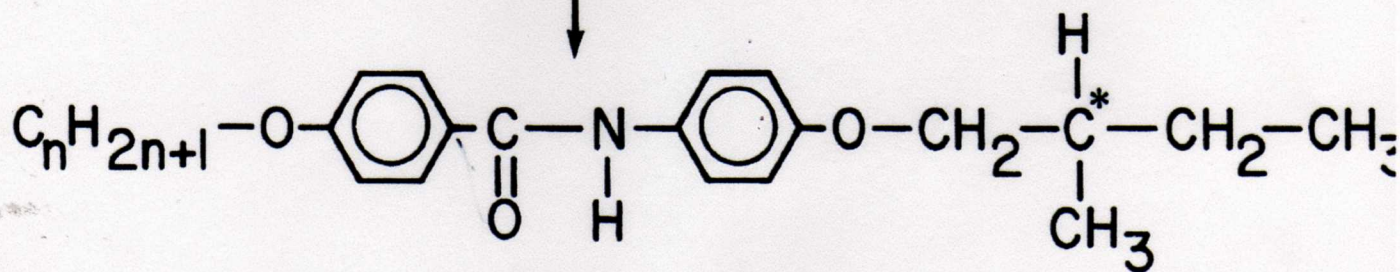
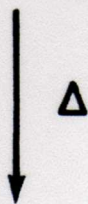
- (1) POLYGONAL TEXTURES
- (2) HIGH VISCOSITIES
- (3) HIGH MESOPHASE —
ISOTROPIC TRANSITION
ENTHALPIES

Figure-4
Photochemistry
of
Chiral N-(p-2-
methoxybutoxyphenyl)- α -
(p-n-alkoxyphenyl)
nitrones

PHOTOCHEMISTRY
OF
CHIRAL NITRONES



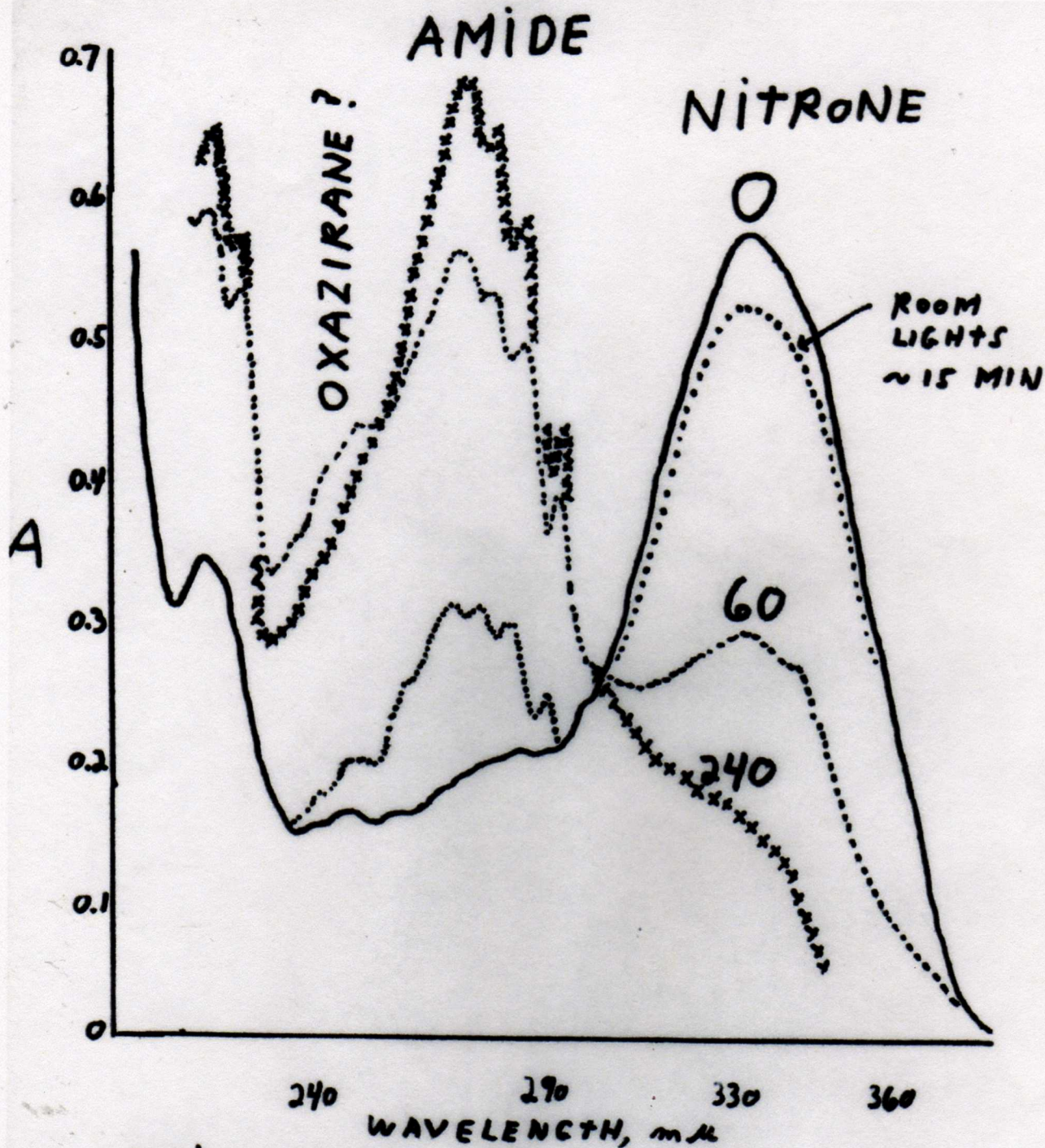
UNSTABLE



$n=1-8$

NON-MESOMORPHIC

Figure-5
Ultraviolet Spectra
of
Irradiated
Chiral N-(p-2-
methoxybutoxyphenyl)- α -
(p-n-alkoxyphenyl)
nitrones



CHIRAL NITRONE ($n=1$)

$c = 2 \times 10^{-5}$ (CYCLOHEXANE)

IRRADIATION TIMES (H_2 LAMP) IN SECONDS

Lead Reference

1) W.R. Young, *Mol Cryst. Liq Cryst.*, **10**, 237 (1970).

Other References

2) W.R. Young, I. Haller and A. Aviram, *Mol Cryst. Liq Cryst.*, **13**, 357 (1971).

3) K. Shinzawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1205 (1964).

4) K. Koyano, H. Suzuki, Y. Mori and I. Tanaka, *Bull Chem. Soc Japan*, **43**, 3582 (1970).

5) G.W. Gray and P.A. Windsor, "Liquid Crystals and Plastic Crystals", Ellis Horwood LTD, Chichester, 1974, Vol 1, p41.

6) D. Demus, L. Richter, "Textures of Liquid Crystals", Verlag Chemie, Weinheim, New York, 1978, Plates 162, 164.

7) G.W. Gray, *Molecular Structure and the Properties of Liquid Crystals*", Academic Press, Inc., New York, 1962.

8) L.J. Yu, H. Lee, C.S. Bak and M.M. Labes, *Phys. Rev. Lett.*, **36**, 388 (1976).