Preparation and Photochemistry of Homologous Chiral Nitrones, New Chiral Sc Liquid Crystals

Mortimer M. Labes and John H. MacMillan

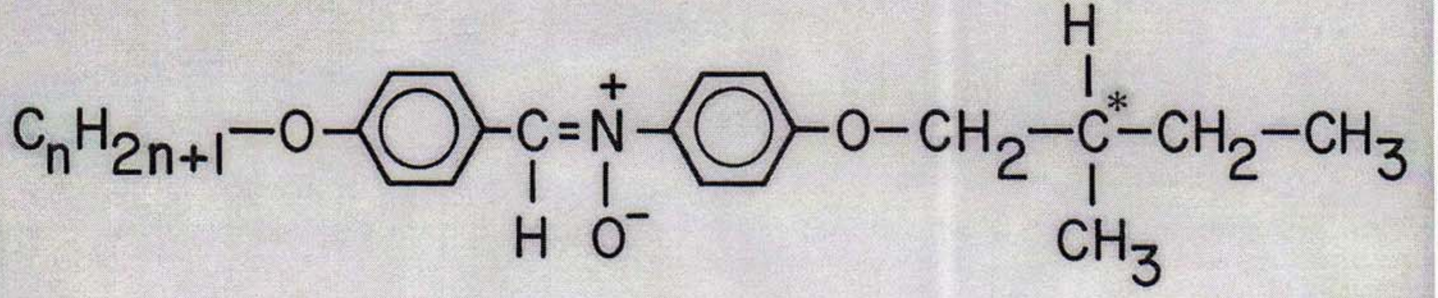
Department of Chemistry, Temple University, Philadelphia, Pa 19122

Abstract:

A series of Chiral N-(p-2methoxybutoxyphenyl)-alpha-(p-n-alkoxyphenyl) nitrones, 5a-h, was prepared and examined for mesogenic properties. The methyl derivative 5a showed only a transient cholesteric texture on rapid supercooling, while the ethyl homolog 5b was a monotropic cholesteric. Propyl and butyl homologs 1c-d were non mesogenic while pentyl derivative 5e 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.

We report the synthesis, mesogenic properties, and photochemical isomerization of a series of chiral nitrones 5a-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), 1. Hydroxylamine intermediates 4a-h were not isolated, but reacted in situ with the appropriate p-alkoxy substituted benzaldehyde, resulting in quantitative precipitation of 5a-h. Recrystallization from cyclohexane gave white crystalline solids, whose IR,NMR and UV spectra were similar to those previously described[1-4] for non chiral mesogenic nitrones. All gave satisfactory

NEW CHIRAL S_C MESOPHASES



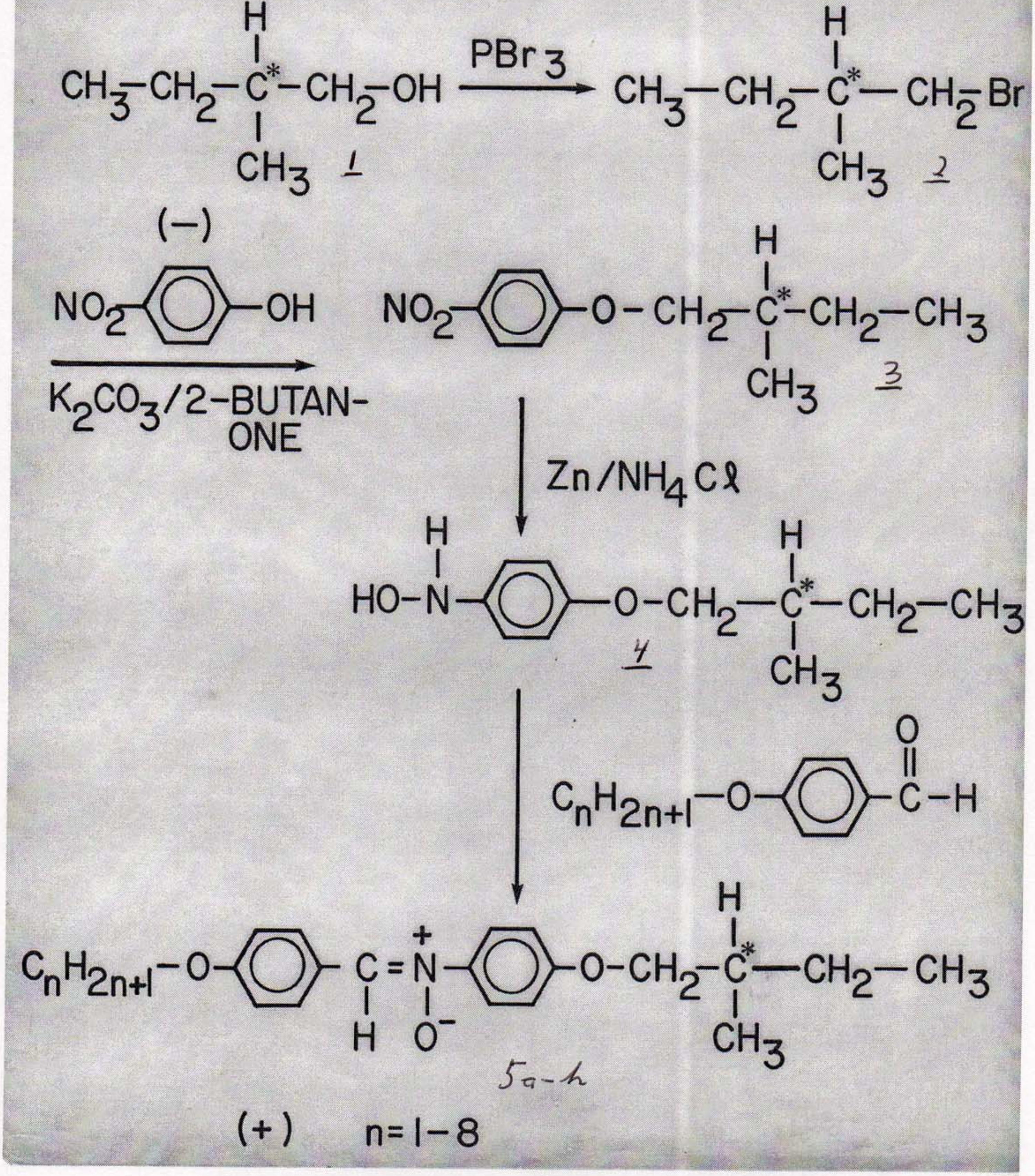
n=5−8

(1) POLYGONAL TEXTURES

(2) HIGH VISCOSITIES

(3) HIGH MESOPHASE—
ISOTROPIC TRANSITION
ENTHALPIES

CHIRAL NITRONES SYNTHESIS

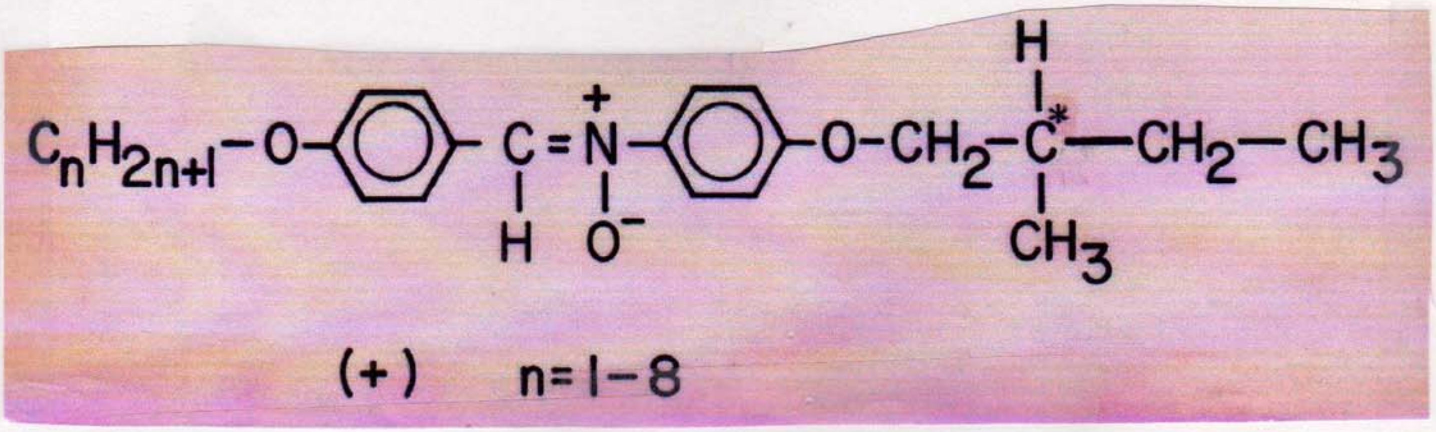


combustion analyses (see table 1). The optical purity of 5a-h was determined to be ~80% by NMR analyses employing the chiral shift reagent $Eu(TFC)_3$. 5a-h were examined for mesogenic behaviour by both polarized optical microscopy and differential scan calorimetry. The results are summarized in table 1 and figures 1-3. 5a showed a transient cholesteric texture with "peacock" colors only on extremely rapid supercooling to ~ 55°C. The phase change was not detectable via DSC. 5b showed monotropic behaviour, also exhibiting "peacock" colors. The oily streak texture and low isotropic transition enthalpy (0.29kcal/mol) indicated a cholesteric mesophase. 5c and d were non mesogenic while the n-pentyl derivative 5e showed a monotropic Sc mesoophase with well developed striated fan shaped or Schlieren textures. The higher homologs 5f-h showed enantiotropic behaviour with textures identical to 5e. The mesophases of 5e-h were classified as chiral Sc due to their high viscosity, high isotropic transition enthalpies(~1.4kcal/mol) and failure to exhibit grandjean texture when placed in wedged cells with SiO coated glass[5]. Texturally the phases were identical to published pictures of the chiral Sc mesophase[6]. Careful cooling of the mesophases failed to show further transitions to Sb, Sg or Se phases prior to crystallization. Thus 5f-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. Yhis conjecture was verified with a 1:1 wt% mixtureof 5a and 5f, which posseses 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.

TABLE 1

TRANSITION TEMPERATURES, ENTHALPIES AND COMBUSTION ANALYSES FOR THE (+)-N-[P-(2METHYL BUTOXY) PHENYL]-ALPHA-(p-N-ALKOXYPHENYL) NITRONES 5a-h



					ANALYSES					
				ENTHALPY	CALC			FOUND		
COMPOUND	n	TRANSITION TYPE	TRANSITION T °C	CHANGE KCAL/MOL	C	H	N	C	H	N
5a	1	K-I	95.3	7.08	72.82	7.4	4.47	73.01	7.45	4.51
5b	2	K-I	111.6	5.33	73.36	7.7	4.28	73.23	7.89	4.31
		Ch-I	94*	0.29						
5c	3	K-I	106	4.49	73.87	7.97	4.10	73.75	7.89	4.32
5d	4	K-I	111.5	4.15	74.33	8.22	3.94	74.21	8.34	3.95
5e	5	K-I	103	4.19	74.76	8.46	3.79	74.87	8.60	3.78
		Sc-I	100*	1.44						
5f	6	K-Sc	96.5	5.83	75.16	8.67	3.65	75.06	8.76	3.64
		Sc-I	106	1.33						
5g	7	K-Sc	100	5.81	75.53	8.87	3.52	75.48	8.88	3.52
		Sc-I	107.5	1.41						
5h	8	K-Sc	101.5	5.60	75.87	9.06	3.40	76.05	9.25	3.42
		Sc-I	109	1.28						

* = Monotropic Transition

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 elsewhere[7] . The branched 2-methylbutoxy group has the expected deleterious effect on chiral nematic stability. Thus 5a is a non-mesogen while the nitrone described by Young[2] with n=1 and a n-pentyloxy group in the p' position is an enantiotropic nematic with clearing points some 25°C higher than 5a. All of Young's mesogenic nitrones show higher clearing points and wider mesogenic ranges than 5a-h.

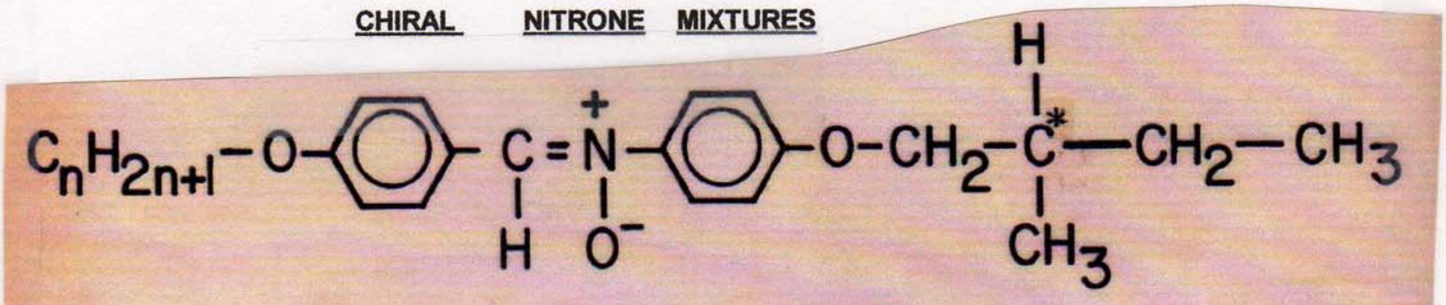
The qualitative thermal and photochemical stability of 5a-h were investigated. Thermally the materials slowly developed yellow colors while held for ~1-2 hours in the mesogenic range (~105 °C), with concurrent slight decreases (~1 °C) in the isotropic points. At lower temperatures as in various mixtures of 5a-h (see Table 2), the thermal degradation was negligible. Photo chemically the materials slowly degrade in fluorescent light (see Figure 4), with rapid degradation under a mercury lamp. The UV spectra (Figure 4) showed the characteristic[3] 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 1.[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.

TABLE 11

CHIRAL NITRONE MIXTURES



(+) n=1–8

TRANSITION TEMPERATURES °C

n	WT % s	K-Sc	Sc-Ch	Ch-I	Sc-I
1,5	EQUAL	76	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	–

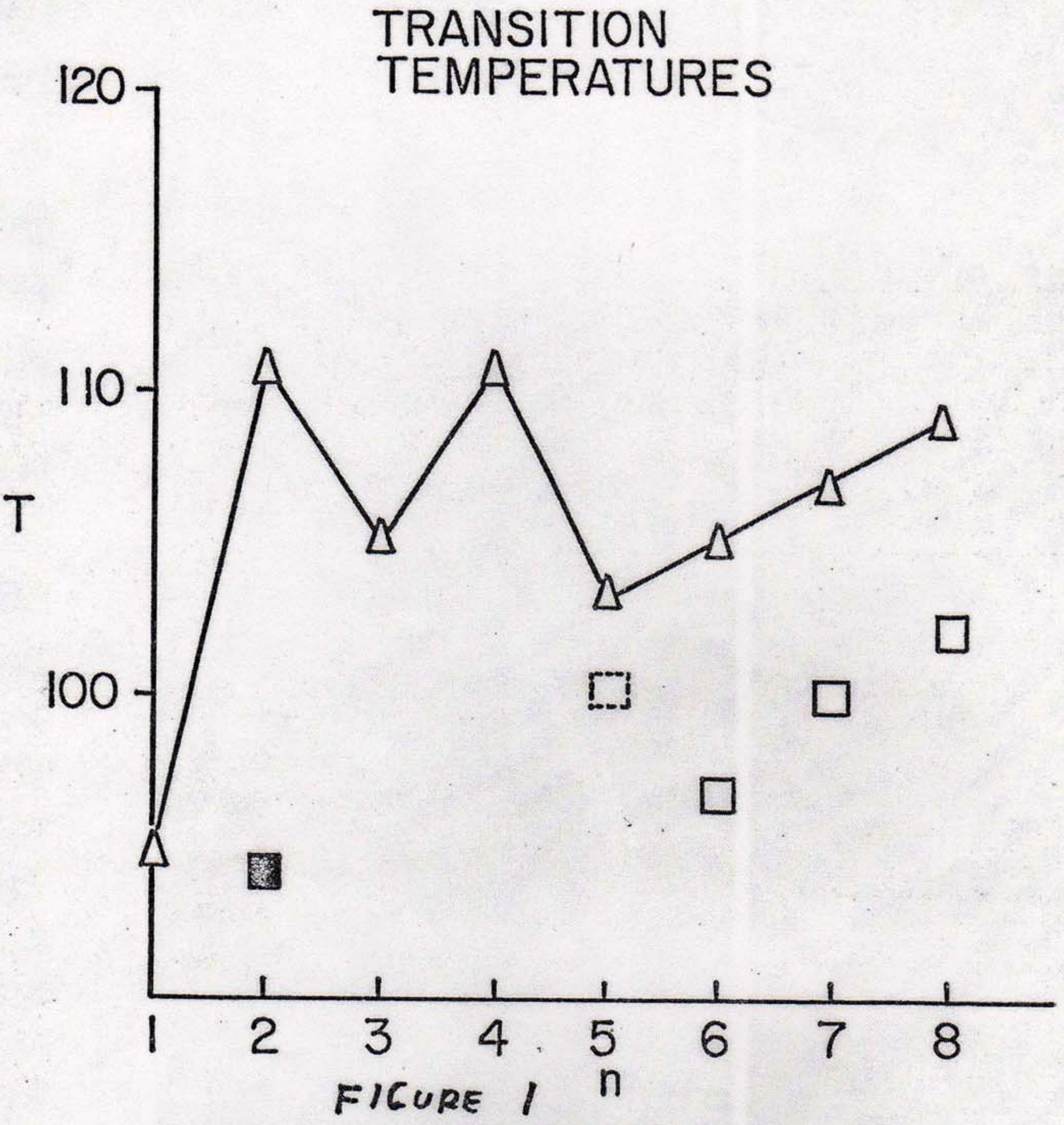


FIGURE 1

△ ISOTROPIC POINT

☐ K—S_C

■ Ch—I (MONOTROPIC)

⬚ S_C—I (MONOTROPIC)

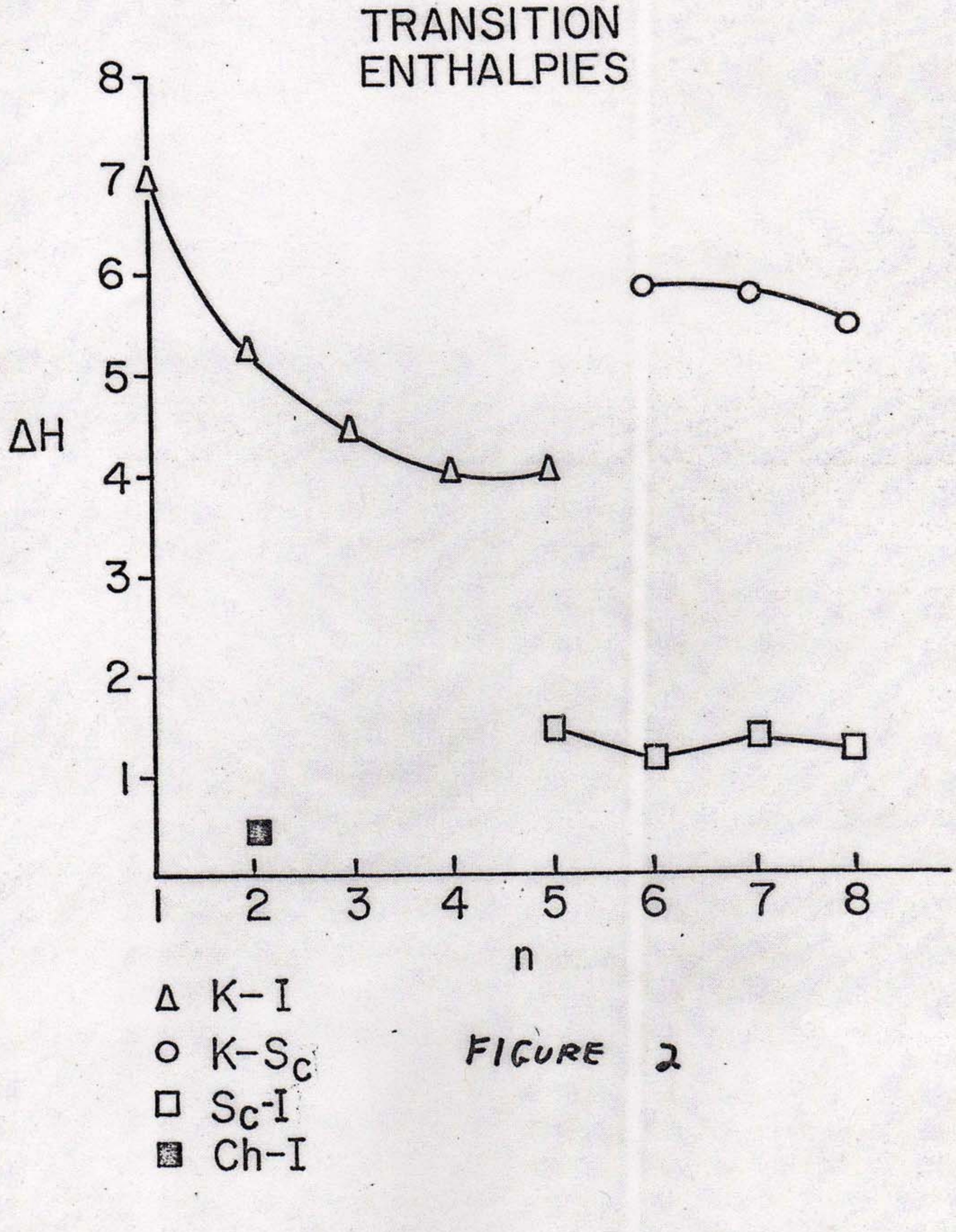

TRANSITION ENTHALPIES
ΔH
8
7
6
5
4
3
2
1
n
1
2
3
4
5
6
7
8
△ K–I
○ K–S_c
□ S_c-I
▨ Ch–I

FIGURE 2

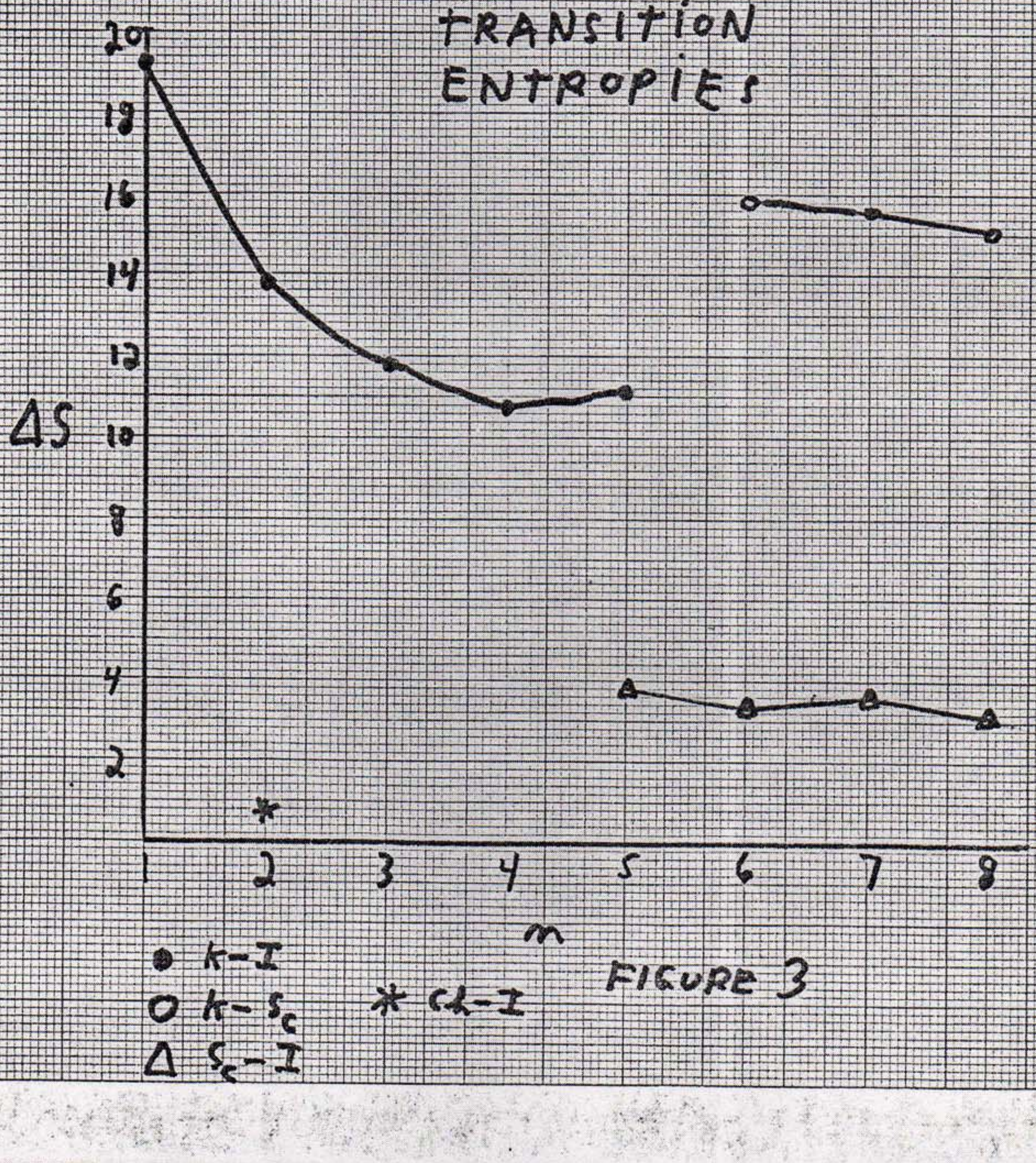
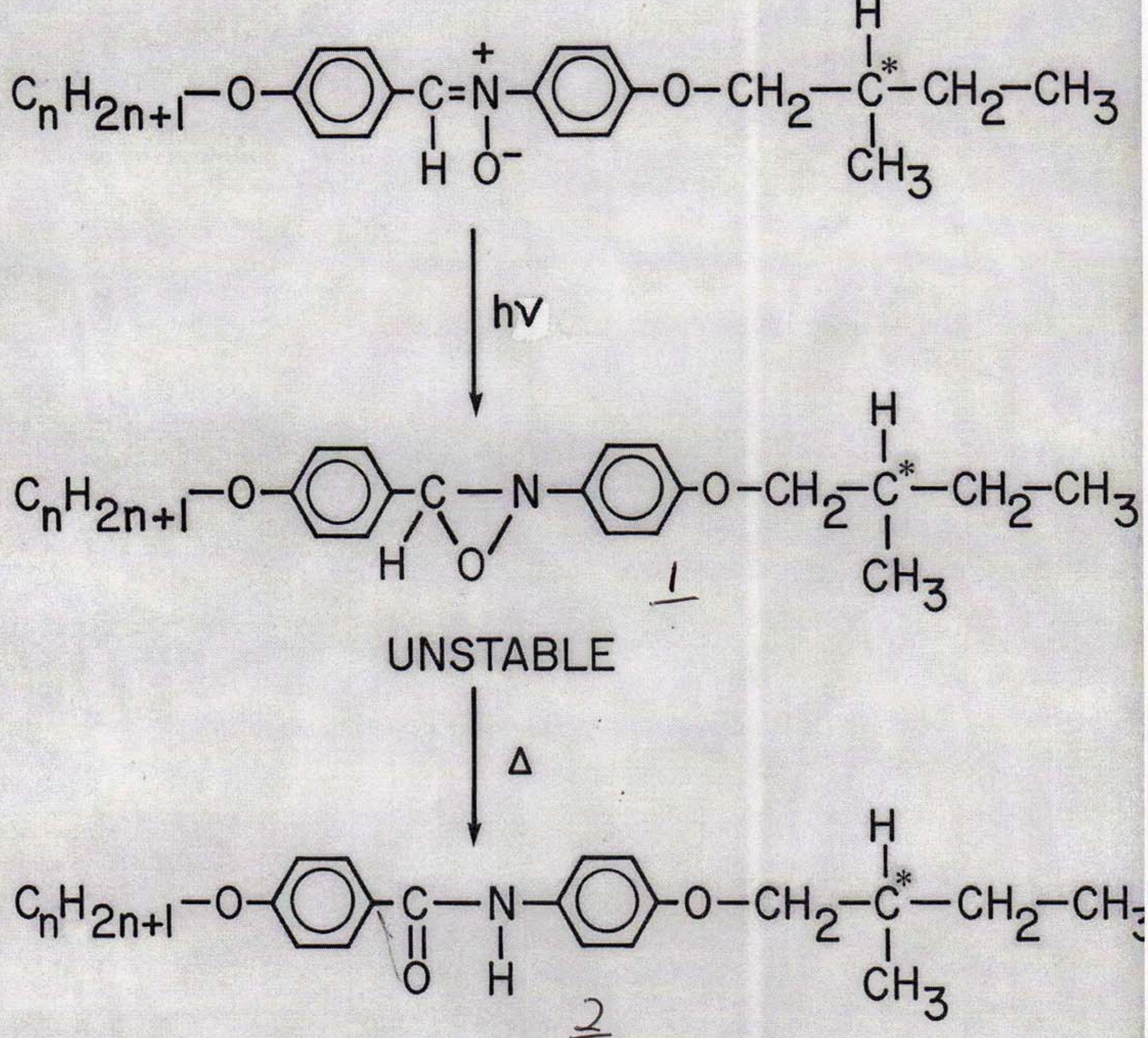

TRANSITION ENTROPIES
ΔS
20
18
16
14
12
10
8
6
4
2
1
2
3
4
5
6
7
8
m
● K-I
○ K-S_c
Δ S_c-I
* Ch-I

FIGURE 3

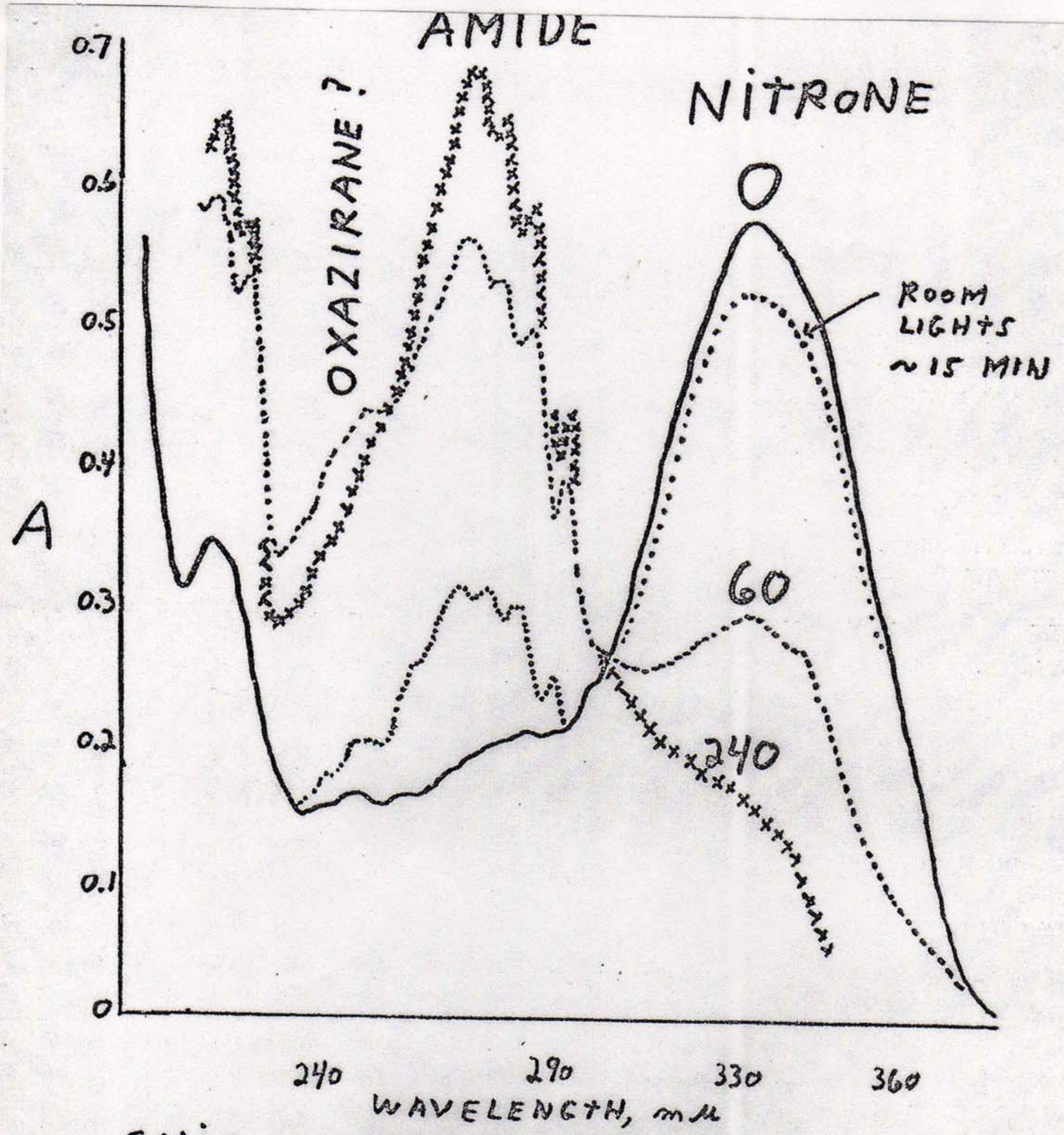
FIGURE 4

PHOTOCHEMISTRY OF CHIRAL NITRONES



n=1-8

NON-MESOMORPHIC



CHIRAL NITRONE (n=1)

c = 2×10^{-5} (cycloHEXANE)

IRRADIATION TIMES (H_2 LAMP) IN SECONDS

FIGURE 5

Due to the strong dipole associated with the nitrone moiety, these materials may prove useful for studies of pyroelectric behavior[8].

Acknowledgements

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References

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

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 Cystals", 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).