Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Mesomorphic Properties of the 4, 4′-Di(n) Alkoxybenzalazines

S. C. Bennur [a b], J. D. Gault [a], T. Kroin [a], G. R. Ouriques [a] & T. R. Taylor [a]

[a] Departamento de Fisica, Universidade Federal de Santa Catarina, 88000, Florianópolis, SC, Brasil

[b] Department of Chemistry, Karnatak University, Dharwad, India

Version of record first published: 19 Dec 2006.

To cite this article: S. C. Bennur , J. D. Gault , T. Kroin , G. R. Ouriques & T. R. Taylor (1988): Mesomorphic Properties of the 4, 4′-Di(n) Alkoxybenzalazines, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 154:1, 267-275

To link to this article: http://dx.doi.org/10.1080/00268948808078736

Mol. Cryst. Liq. Cryst., 1988, Vol. 154, pp. 267–275
Photocopying permitted by license only

Printed in the United States of America

Mesomorphic Properties of the 4,4′-Di(*n*) Alkoxybenzalazines

S. C. BENNUR,† J. D. GAULT, T. KROIN, G. R. OURIQUES and T. R. TAYLOR‡

Departamento de Física, Universidade Federal de Santa Catarina, 88000 Florianópolis, SC, Brasil

(*Received July 1, 1987*)

We have reinvestigated the mesomorphic properties of the 4,4′-Di(*n*) alkoxybenzalazines, first reported by Shaw and Brown.[1] Thirteen members of the series were prepared with the number (*n*) of carbon atoms varying from 1 to 16. A Nematic phase was always observed except for $n \geq 13$; a monotropic smectic phase was observed for $n = 5, 6$ and another smectic phase for $n \geq 10$. The compounds were examined with a polarizing microscope and heats of transition determined using a DSC-2 calorimeter. Our results differ from those of Shaw and Brown as they did not observe the monotropic smectic phase for $n = 5, 6$. They also cite a smectic phase for $n = 7, 8, 9, 10$ whereas we observe a smectic phase only for $n \geq 10$ ($n = 9$, was not synthesized by us). The temperature given by Shaw and Brown for the crystal–smectic transitions for $n = 7, 8, 9, 10$ we identify as the temperatures of crystal–crystal transitions. Of these only $n = 10$ has a smectic phase and the transition temperature is considerably higher than that given by Shaw and Brown.

1. INTRODUCTION

We have reinvestigated the mesomorphic phases of the 4,4′-Di(*n*) alkoxybenzalazines reported by Shaw and Brown[1] in 1959. The reason for the reinvestigation is that in the synthesis of some other compounds the expected reaction did not occur and the end product was the 4,4′-Di(*n*) alkoxybenzalazines. Examination of these compounds gave results different from those of Shaw and Brown and we decided

†Permanent address: Department of Chemistry, Karnatak University, Dharwad, India.
‡To whom correspondence should be addressed.

to undertake a more complete investigation of the 4,4′-Di(n) alkoxybenzalazines.

2. EXPERIMENTAL PROCEDURES

2.1.1. Alkoxybenzaldehydes. 4-Methoxybenzaldehyde and 4-ethoxybenzaldehyde were obtained from commercial sources. 4-n-propyloxybenzaldehyde (b.p. 91–92°C/2 mm Hg), 4-n-butyloxybenzaldehyde (b.p. 111–111°C/2 mm Hg), 4-n-pentoxybenzaldehyde (b.p. 114–115°C/2 mm Hg), 4-n-hexyloxybenzaldehyde,† p. 4-n-heptyloxybenzaldehyde (b.p. 136–137°C/2 mm Hg), 4-n-octyloxybenzaldehyde (b.p. 152–153°C/2 mm Hg), 4-n-decyloxybenzaldehyde,† 4-n-undecyloxybenzaldehyde,† 4-n-dodecyloxybenzaldehyde, 4-n-tridecyloxybenzaldehyde† and 4-n-hexadecyloxybenzaldehyde were prepared from 4-hydroxybenzaldehyde and the corresponding alkyl bromide by the method of Gray and Jones.[2] The yields were 60–80%.

2.1.2. 4-4′-Di(n) alkyloxybenzalazines. All the 4-4′-Di(n) alkyloxybenzalazines were prepared from the corresponding 4-n-alkyloxybenzaldehyde (freshly destilled) and hydrazine hydrate by the method described in the literature[1] and recrystallized from an alcohol-acetic acid mixture until the transitions temperatures were reproducible. The CHN analysis data are given in Table I.

2.2. Microscopic observation

The compounds were examined with a Leitz-Ortholux polarizing microscope using a Mettler FP-5 hot stage. The transition temperatures determined optically agreed to within ±1.0°C of those determined with the DSC-2 and the temperatures reported in the tables are those determined with the DSC. The monotropic smectic phase of $n = 5$ and 6 shows a mosaic texture and the smectic phase for $n \geq 10$ shows a schlierien texture and thus we suppose these phases to be different. This conclusion is supported by the fact that the transition heats of the smectic–nematic transition for $n = 5$ and 6 are approximately five times those of the smectic–nematic transition for $n = 10$, 11 and 12 and by the x-ray results we report in the next section.

†These compounds were used without purification.

TABLE I

CHN Analysis of 4,4′-Di(*n*) alkoxybenzalazines

R	Mol. Formula	Analysis % Calculated C	H	N	Found. C	H	N
—OCH_3	$C_{16}H_{16}N_2O_2$	71.64	5.97	10.44	71.39	6.02	10.53
—OC_2H_5	$C_{18}H_{20}N_2O_2$	72.97	6.75	9.45	73.01	6.52	9.71
—OC_3H_7	$C_{20}H_{24}N_2O_2$	74.04	7.46	8.64	73.93	7.19	8.83
—OC_4H_9	$C_{22}H_{28}N_2O_2$	74.96	8.01	7.95	75.01	7.92	7.59
—OC_5H_{11}	$C_{24}H_{32}N_2O_2$	75.75	8.48	7.37	75.86	8.59	7.08
—OC_6H_{13}	$C_{26}H_{36}N_2O_2$	76.43	8.88	6.86	76.39	8.88	6.63
—OC_7H_{15}	$C_{28}H_{40}N_2O_2$	77.02	9.24	6.42	77.41	9.54	6.81
—OC_8H_{17}	$C_{30}H_{44}N_2O_2$	77.54	9.54	6.03	77.50	9.75	5.89
—$OC_{10}H_{21}$	$C_{34}H_{52}N_2O_2$	78.40	10.07	5.38	78.31	10.37	5.08
—$OC_{11}H_{23}$	$C_{36}H_{56}N_2O_2$	78.83	10.21	5.10	78.73	10.64	5.16
—$OC_{12}H_{25}$	$C_{38}H_{60}N_2O_2$	79.16	10.41	4.86	79.13	10.20	4.91
—$OC_{13}H_{27}$	$C_{40}H_{64}N_2O_2$	79.47	10.59	4.63	79.50	10.39	4.71
—$OC_{16}H_{33}$	$C_{46}H_{74}N_2O_2$	80.46	10.78	4.08	80.39	10.91	4.46

2.3. X-ray diffraction

The compounds $n = 5$ and $n = 11$ were studied by X-ray diffraction using a temperature controlled furnace with 0.7 mm Lindemann glass capillaries and a flat plate camera. Bragg's Law was used to calculate the interplanar distances d in the smectic phases and also to calculate a "characteristic" distance in the nematic phase.

The compound $n = 5$ shows a typical crystalline powder pattern at room temperature and at 120°C on first heating. At temperatures between 123°C and 152°C the diffraction pattern is typical of a partially aligned nematic phase; one outer diffuse peak corresponding to a distance 5.7 ± 0.2 Å and the absence of an inner peak (to be explained later). In the monotropic smectic phase of $n = 5$ there are various sharp reflections at large angles (2θ between 16 and 20 degrees) and two sharp reflections of the first and second order corresponding to $d = 49.0 \pm 2.0$ Å; all reflections in the smectic phase are independent of temperature to within experimental error. The calculated length of the molecule is $l = 26.1$ Å and therefore $d = 49$ Å indicates smectic layers formed of two molecules and the presence of high angle reflections is characteristic of a highly ordered smectic phase. The microscopic texture is mosaic and no homeotropic mosaic blocks were detected. This together with the X-ray results indicates that the phase is highly ordered with a double layer structure and that the molecules are inclined at a relatively small angle with

respect to the layer normal. The absence of a small angle peak in the nematic phase probably indicates that even in the nematic phase there is association between molecules such that the characteristic molecular length is greater than about 51 Å (the approximate resolution limit of the X-ray setup was 51 Å).

The compound $n = 11$ at room temperature and at 110°C on first heating shows a typical crystalline powder pattern with many sharp rings. Between 128.0°C and 130.0°C the pattern is that of a disordered nematic phase with a diffuse outer ring corresponding to a distance of 4.7 ± 0.2 Å and a sharper inner ring corresponding to 38.4 ± 2.0 Å. In the smectic phase, there is a diffuse outer ring corresponding to 4.7 ± 0.2 Å and a sharp inner ring with $d = 34.4 \pm 2.0$ Å, independent of temperature within experimental error. The calculated length of the $n = 11$ molecule is $l = 42.9$ Å; therefore the molecule would be tilted at an angle of approximately 35° with respect to the layer normal. The X-ray and optical data indicate that this smectic phase should probably be classified as smectic C.

2.4. Thermal analysis

Thermal studies were done using a Perkin-Elmer DSC-2 with nitrogen as a purge gas. The temperature scale on the calorimeter was calibrated at a scanning rate of 10°C/min using indium, tin and lead standards furnished by the manufacturer. The standards were checked at other scanning rates and the corrections for these were established. A scanning rate of 2.5°/min was used in the determination of the heats of transition except when slower rates were necessary to resolve two transitions with a small temperature separation. The transition temperature was taken as the intersection of a straight line drawn through the part of the peak with the greatest slope and a base-line determined by the straight line joining the calorimeter trace before and after the peak. Samples were placed in aluminium pans supplied by Perkin-Elmer with hermetically scaled pans being used only for the first members of the series which showed a considerable tendency to sublime.

Heats of transition were determined by planimetry of the area between the calorimeter trace of the peak and the baseline. Repeated runs on the same sample show a reproducibility of ±0.2°C in temperature and ±2% in the transition heats, when these were of the order of 30 cal/g. The nematic-isotropic transition (~1.3 cal/g) had a reproducibility of only ±5% due in part to the difficulty in determining the correct base-line. The method used, as described above,

resulted in peaks which were over a range of 8°C and with as much as 40% of their area at temperatures below the line determining the transition temperature. This method may include contributions from the specific heat or other effects, but we were unable to find another method which gave consistent results. The transition heats of the first melting were consistently one percent higher than on successive meltings; the peak height was also slightly less after the first melt.

Taking into account all of these factors, we believe our temperatures are reliable to ±1°C and the heats of transition (ΔH) to ±3%, except for the nematic–isotropic transition where the errors are greater for the reasons discussed above.

The measured transition temperatures and heats of transition are given in Table II. From Figure 1 it can be seen that the first four members of the series (n = 1–4) and n = 7, 8 show only a nematic phase. A monotropic smectic phase was observed for the compounds with n = 5 and 6. Compounds with n = 10, 11 and 12 show a smectic as well as a nematic phase while those with n = 13 and 16 show only a smectic phase.

An odd–even effect is observed in the nematic–isotropic (N–I) transitions with the even members of the series having consistently higher transition temperatures than the odd. The melting temperatures do not show this odd–even effect except for the first two members of the series. The melting temperatures of those compounds which have a smectic phase seem to be consistently lower than those that do not. This is observed for n = 5 and 6 and the transition is crystal–nematic (C–N), and with $n \geq 10$ when the transition is crystal–smectic (C–S). The sum of the S–N and the N–I transition enthalpies for the compounds with n = 10, 11 and 12 fall on the same curve as the S–I enthalpies for those with n = 13 and n = 16.

3. DISCUSSION

Shaw and Brown[1] reported the transition temperatures for the first ten members of the series 4,4′-Di(n) alkoxybenzalazines and within our experimental error the temperatures for the nematic–isotropic transition are the same as our results; also for n = 1 to 6 the temperatures of the crystal–nematic transition agree with our results (with the exception, in both transitions of n = 3 where our temperatures are 10° higher). For n = 5 and 6, we observed a monotropic smectic phase not reported by Shaw and Brown. For n = 7, 8, 9 and 10, Shaw report a crystal–smectic transition at temperatures less than

TABLE II

Temperatures and enthalpies of transition for the series 4,4′-Di(n) alkoxybenzalazines

		Crystal–Nematic (C–N)				Smectic–Nematic (S–N)				Nematic–Isotropic (N–I)			
			ΔH cal	ΔH kcal	ΔS cal		ΔH cal	ΔH kcal	ΔS cal		ΔH cal	ΔH kcal	ΔS cal
n	R	T(°C)	gr	mol	mol°K	T(°C)	gr	mol	mol°K	T(°C)	gr	mol	mol°K
1	O CH_3	169.4	34.4	9.23	20.86	—	—	—	—	182.9	1.27	0.341	0.747
2	O CH_2CH_3	173.0	35.0	10.37	23.25	—	—	—	—	199.3	2.15	0.637	1.35
3	O $(CH_2)_2CH_3$	158.4	24.6	7.98	18.50	—	—	—	—	164.7	1.16	0.376	0.859
4	O $(CH_2)_3CH_3$	145.9	19.4	6.84	16.23	—	—	—	—	168.9	1.44	0.508	1.15
5	O $(CH_2)_4CH_3$	129.0	30.5	11.61	28.89	122.4	14.4	5.48	13.86	152.0	1.15	0.438	1.03
6	O $(CH_2)_5CH_3$	126.3	33.6	13.73	34.38	124.2	17.1	6.97	17.59	151.4	1.29	0.527	1.24
7	O $(CH_2)_6CH_3$	131.6	19.8	8.64	21.37	—	—	—	—	142.5	1.20	0.524	1.26
8	O $(CH_2)_7CH_3$	130.4	18.7	8.69	21.54	—	—	—	—	141.9	1.40	0.650	1.57
		Crystal–Smectic (C–S)											
10	O $(CH_2)_9CH_3$	122.7	14.7	7.66	19.35	124.6	1.62	0.84	2.12	135.2	1.58	0.823	2.02
11	O $(CH_2)_{10}CH_3$	120.4	14.2	7.79	19.81	126.1	2.25	1.23	3.09	131.3	1.47	0.807	2.00
12	O $(CH_2)_{11}CH_3$	120.1	15.0	8.65	22.01	127.6	2.78	1.60	4.00	129.6	1.76	1.01	2.52
										Smectic–Isotropic (S–I)			
13	O $(CH_2)_{12}CH_3$	118.3	14.3	8.65	22.11	—	—	—	—	126.5	4.96	3.00	7.51
16	O $(CH_2)_{15}CH_3$	117.5	15.3	10.54	27.00	—	—	—	—	122.7	5.41	3.73	9.42

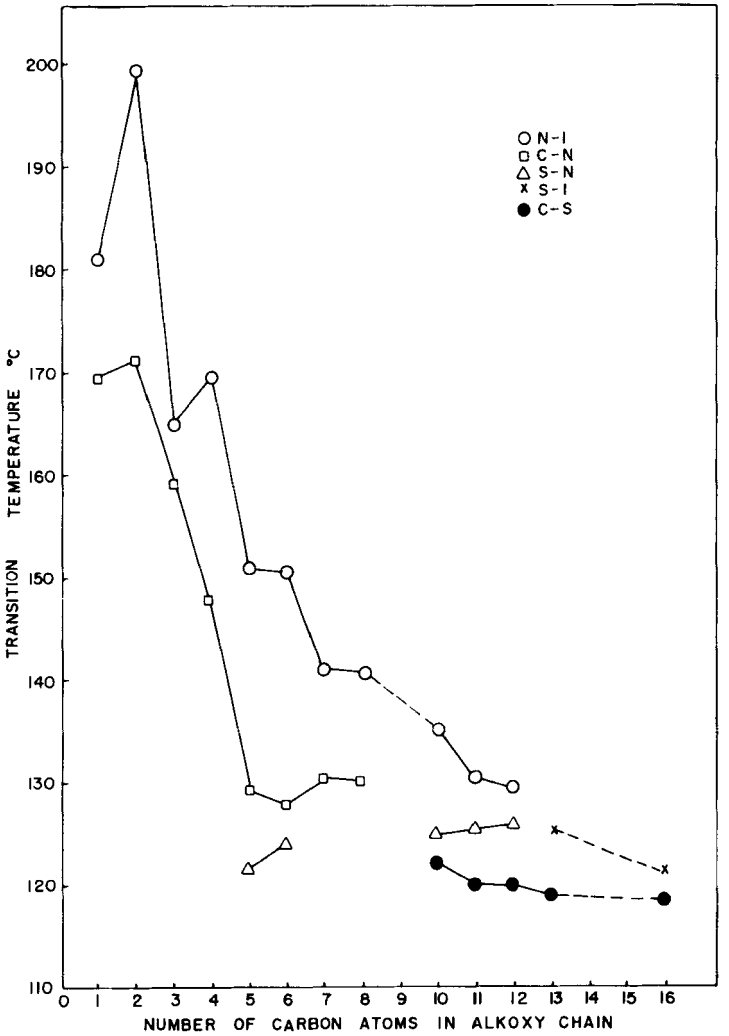

FIGURE 1 Transition temperatures for the series 4,4'-Di(*n*) alkoxybenzalazines.

100°C. We could not reproduce these results and believe that crystal–crystal transitions were mistaken for crystal–smectic transitions. Using the DSC or the polarizing microscope these compounds all show crystal–crystal transitions at approximately the temperatures given by Shaw and Brown. We observed no crystal–smectic transition for $n = 7$, 8 and with $n = 10$ a crystal–smectic transition at 122.7°C.

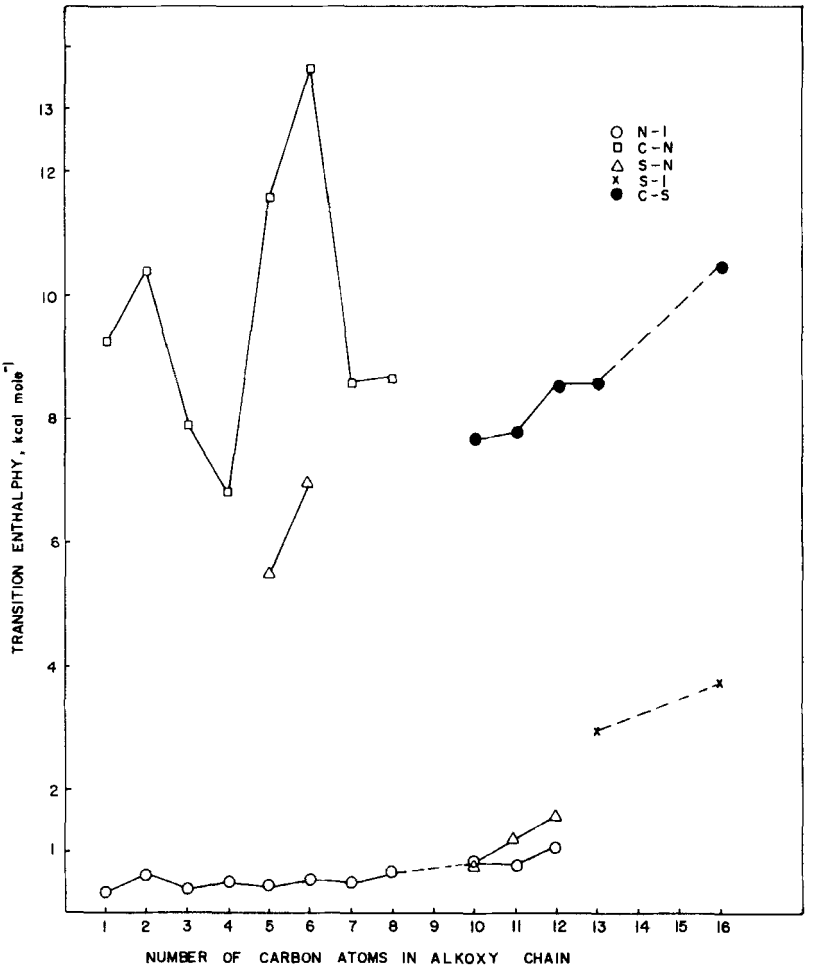

FIGURE 2 Enthalpies of transition for the series 4,4′-Di(n) alkoxybenzalazines.

The compounds with $n = 11$ and 12 have both a smectic and nematic phase and $n = 13$ and 16 only a smectic phase.

It is interesting to note that the smectic phases for $n = 5$ and 6 and $n \geq 10$ are different types of smectic phases. Microscopically the textures are completely different and ΔH of the smectic–nematic transition is the order of 15 kcal/mol for $n = 5$ and 6 whereas it is order of 3 kcal/mol for $n \geq 10$. X-Ray diffraction and textures indicate that the smectic phase of compounds with $n \geq 10$ should probably be classified as a smectic C and that the smectic phase for $n = 5$ and 6 is a highly ordered type with a double layer structure.

Acknowledgments

This work was partially supported by grants from FINEP, CNPq and CAPES.

References

1. W. G. Shaw and G. H. Brown, *J. Chem. Soc.*, **81**, 2532 (1959).
2. G. W. Gray and B. J. Jones, *J. Chem. Soc.*, 1467 (1954).