Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Calorimetric Investigation of 4-n-Butyryl-4′-n-Alkanoyloxyazobenzenes

Mario Braghetti [a] , Enzo Fanelli [a] & Giovanni Poeti [a]
[a] Dipartimento di Scienze Chimiche, dell'Università di Camerino, Via S. Agostino 1, 62032, Camerino, (Italy)
Version of record first published: 21 Mar 2007.

To cite this article: Mario Braghetti , Enzo Fanelli & Giovanni Poeti (1983): Calorimetric Investigation of 4-n-Butyryl-4′-n-Alkanoyloxyazobenzenes, Molecular Crystals and Liquid Crystals, 92:7, 209-216

To link to this article: http://dx.doi.org/10.1080/01406568308084061

Mol. Cryst. Liq. Cryst. Vol. 92 (Letters), pp. 209-216
0140-6566/83/9207-0209$18.50/0

Printed in the United States of America

CALORIMETRIC INVESTIGATION OF 4-n-BUTYRYL-4'-n-ALKANOYLOXYAZOBENZENES

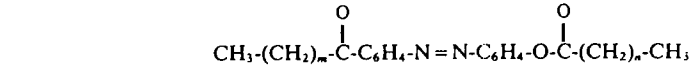
MARIO BRAGHETTI, ENZO FANELLI, GIOVANNI POETI
Dipartimento di Scienze Chimiche dell'Università di Camerino, Via S. Agostino 1, 62032 Camerino (Italy)

(Received for Publication October 3, 1983)

ABSTRACT: *By means of a differential scanning calorimeter the different members of the 4-n-butyryl-4'-n-alkanoyloxyazobenzene series were investigated. Calorimetric data are presented and enthalpy and entropy trends are discussed and correlated with other series.*

INTRODUCTION

In a previous paper[1] we reported on the synthesis and mesomorphic properties of a new homologous series of esters of the type:



having $m = 2$ and $0 \leq n \leq 16$.

We pointed out smectic and/or nematic phases for all members. In this paper we give plots of their transition energies and entropies vs the number of $-CH_2$ group in the terminal alkyl chain. A comparison has been made with the homologous series having $m = 0$[2] and $m = 1$[3].

CALORIMETRIC MEASUREMENTS

They have been performed using a differential scanning calorimeter Perkin-Elmer DSC-2C. Calibration, taken into account the range of

temperatures, has been centred on Indium metal samples (purty 5N). Four samples minimum of each compound have been analysed with a rate ≤ 2.5 °C/min.

Table 1 shows the results obtained. The values relative to monotropic transitions and the separation of I-N transition for the members $n = 1$ and $n = 4$ were determined in the course of cooling.

Because of the meaningless differences (± 0.5 °C) among the values of each temperature obtained by DSC-2C and a Mettler type FP 52 mycrofurnace, the values given in table 1 are the same as the ones previosly shown[1].

DISCUSSION

In fig. 1 we show the variation of the heat of transition between the solid phase and the smectic A phase closely related[3] to the disorganization of the terminal aliphatic chains. The same figure shows also the values

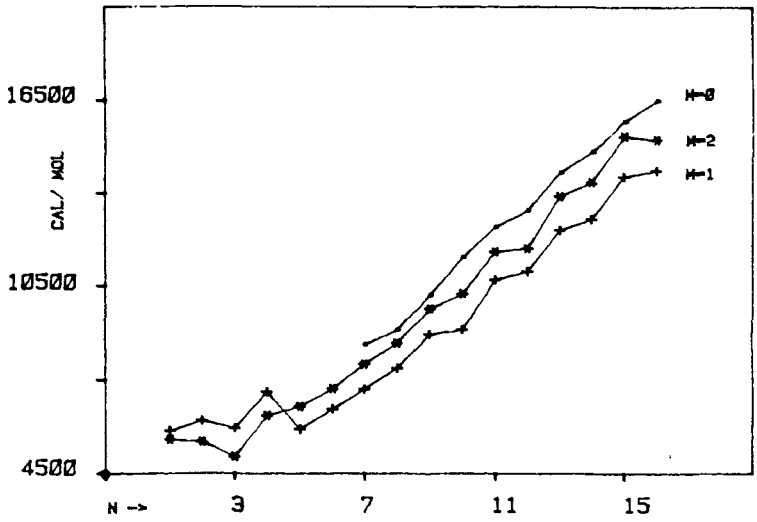


Fig. 1: Transition enthalpies K-S_A versus chain length n for the homologous series $m = 0, 1, 2$.

relative to the series m = 0 and m = 1. For the compounds of three series for which no direct K-S_A transition has been found, the enthalpy values were obtained by addition or difference of the values of other transitions. For example, for the homologs m = 2 n = 1 and m = 2 n = 3, the enthalpy value results from (K-N) - (N-S_A) and from (K-S_1) + (S_1-S_A) respectively.

Fig. 1 already shows the similar behaviour of the three series and, the existence of a critical length of the terminal alkyl chain beyond which the enthalpy increase is regular. At last from fig. 1 we deduce, for the series m = 2, a contribution to the heat of transition of about 0.8 Kcal for each methylene group. This value is equal to that of the series m = 1, inferior to that of the series m = 0 (0.9 Kcal) and close to that found in other homologous series of liquid crystals[3,4].

Fig. 2 shows the enthalpies relative to the transition from the smectic A phase into isotropic phase as a function of n. In the absence of direct

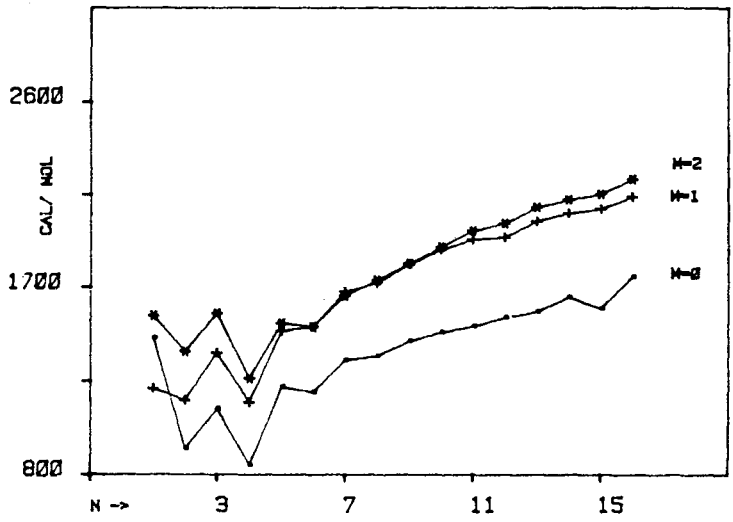


Fig. 2: Transition enthalpies S_A-I versus chain length n for the homologous series m = 0, 1, 2.

transition S_A-I we have taken into consideration the same criteria as for the K-S_A transitions.

Also in this case, the three series have a similar thermodynamic behaviour. The critical length of the chain is observed close to the member with n = 5. Moreover we have pointed out that the contribution of each methylene group decreases when n increases. This fact, as well as the sequence m = 0-1-2, is related to the disorganization which, during S-I transition, takes place in the rigid central parts of molecules.

Fig. 3 shows the total entropy ($\sum_i \frac{\Delta H_i}{T_i}$) for those compounds whose evaluation was possible.

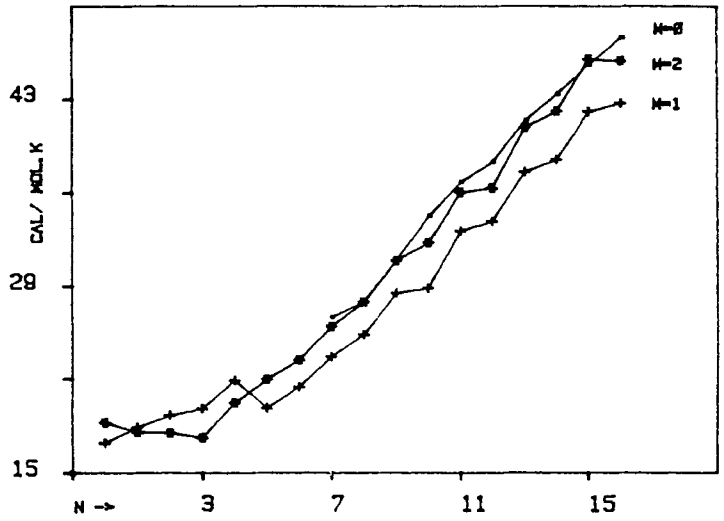


Fig. 3: Total entropy K-I $\left(\sum_i \frac{\Delta H_i}{T_i}\right)$ versus chain length n for the homologous series m = 0, 1, 2.

The particular thermodynamic behaviour of the first members of each series restrict the comparaison to those with n > 6.

In the case of the series m = 2, the least square slope of the straight line obtained by interpolation of the points of the curve K-I is 2.28 cal. mol^{-1}. K^{-1}, an intermediate value between that of the series m = 0 (2.40 cal. mol^{-1}. K^{-1}) and that of the series m = 1 (2.20 cal. mol^{-1}. K^{-1}).

All these values are not far from those obtained by Bondi[5] (2.38 cal. mol^{-1}. K^{-1}) for the normal alkyl compounds with orthorombic crystal structure.

Fig. 4 shows the ratio $\Delta S_{S_A \rightarrow I}/\Delta S_{K-I}$ as a function of n for each member of the series m = 2. We point out the heavy discontinuity of entropic contribution of $\Delta S_{S_A \rightarrow I}$ transition with respect to ΔS_{K-I}, total entropy, for the first members of the series and the tendency of the total entropy to be equal to that of the smectic A phase.

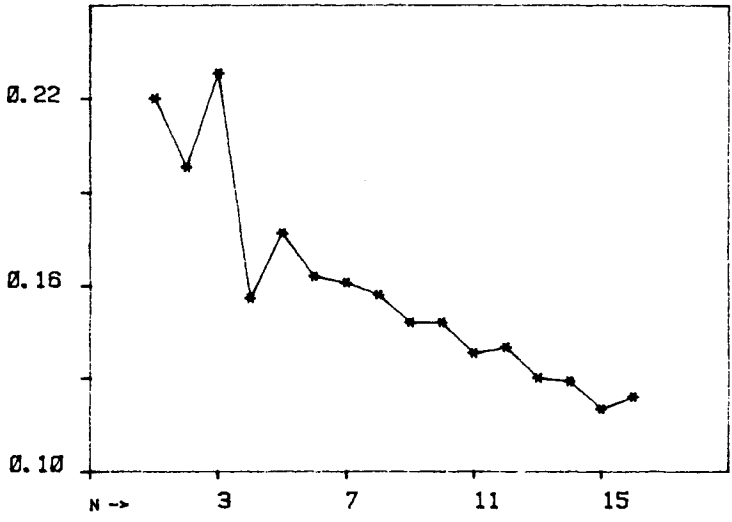


Fig. 4: ΔS (S_A-I)/ΔS (K-I) ratio versus chain length n for the series m = 2.

Table 1: Measured transition temperatures, enthalpies and derived entropies for 4-n-Butyryl-4'-n-alkanoyloxyazobenzenes. (* = monotropic phase)

n	Transition	Temperature (°K)	Enthalpy (cal. mol^{-1})	Entropy (cal. mol.$^{-1}$ K^{-1})
0	K I	398.0	7451 ± 7	18.72
	I N*	390.5	82 ± 4	0.21
1	K N	397.0	7151 ± 37	
	N I	398.0		
	I N	398.0	98 ± 4	0.25
	N S_A^*	393.5	1465 ± 8	3.72
2	K_1 S_A	383.0	5518 ± 8	14.41
	S_A N	392.5	1267 ± 11	3.23
	N I	396.5	126 ± 9	0.32
	S_A S_1^*	379.5	1504 ± 22	3.96
	S_1^* S_2^*	372.5	990 ± 94	2.66
3	K S_1	363.0	2277 ± 23	6.27
	S_1 S_A	377.0	2758 ± 18	7.32
	S_A I	392.5	1574 ± 5	4.01
4	K S_A	373.0	6365 ± 40	17.06
	I N	392.5	159 ± 9	0.40
	N S_A	391.5	1106 ± 19	2.82
	S_A S_1^*	367.0	1444 ± 5	3.93
5	K_1 S_A	368.0	6656 ± 42	18.09
	S_A I	392.5	1526 ± 15	3.89
	S_A S_1^*	361.5	1176 ± 11	3.25
	S_1^* S_2^*	353.0	2055 ± 37	5.82
6	K S_A	368.5	7217 ± 29	19.58
	S_A I	395.0	1510 ± 12	3.82
	S_A S_1^*	357.0	986 ± 14	2.76

TABLE 1 (continued)

7	K S_A	367.5	7998 ± 56	21.76
	S_A I	396.0	1660 ± 14	4.19
	S_A S_I^*	356.5	828 ± 11	2.32
8	K S_A	369.5	8659 ± 42	23.44
	S_A I	397.0	1735 ± 24	4.37
9	K S_A	371.0	9772 ± 32	26.34
	S_A I	397.0	1817 ± 14	4.58
10	K S_A	372.0	10246 ± 60	27.54
	S_A I	397	1894 ± 14	4.77
11	K S_A	373.5	11605 ± 31	31.07
	S_A I	396.0	1972 ± 16	4.98
12	K S_A	374.5	11716 ± 49	31.28
	S_A I	395.0	2008 ± 8	5.08
13	K S_A	376.5	13392 ± 50	35.57
	S_A I	394.0	2088 ± 16	5.30
14	K S_A	377.5	13850 ± 87	36.69
	S_A I	393.0	2126 ± 28	5.41
15	K S_A	379.5	15358 ± 43	40.47
	S_A I	391.5	2154 ± 17	5.50
16	K S_A	379.5	15241 ± 98	40.16
	S_A I	390.5	2225 ± 41	5.70

REFERENCES

1. F. Fanelli, G. Poeti, M. Braghetti, G. Torquati - *Mol. Cryst. Liq. Cryst.* **87**, 77-95 (1982).
2. E. Fanelli, G. Poeti, M. Braghetti - *Mol. Cryst. Liq. Cryst.* **64**, 199-204 (1981).
3. E. Fanelli, G. Poeti, M. Braghetti - *Mol. Cryst. Liq. Cryst.* **92**, 127-134 (1983).
4. P. Seurin, D. Guillon, A. Skoulios - *Mol. Cryst. Liq. Cryst.* **65**, 85 (1981).
5. A. Bondi - *Chem. Rev.* **67**, 565 (1967).