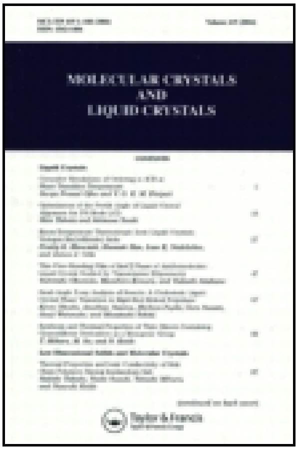

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Diacetylenic Liquid Crystals: A Systematic Investigation of the Homologous Series of 4, 4^1 -Dialkanoyloxydiphenyldiacetylenes

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DIACETYLENIC LIQUID CRYSTALS: A SYSTEMATIC INVESTIGATION OF THE HOMOLOGOUS SERIES OF 4,4'-DIALKANOYLOXYDIPHENYLDIACETYLENES

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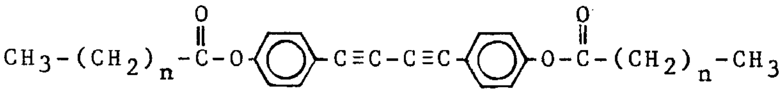
The homologous series of 4,4'-dialkanoyloxydiphenyldiacetylenes



with n ranging from zero to ten have been prepared. Optical microscopy, differential scanning calorimetry and X-ray diffraction have been used to study the mesomorphic behavior of these compounds. All homologs with n=1-7 are liquid crystals having nematic phases. In addition to nematic phases, these esters have extensive solid-state polymorphism. The transition enthalpies and entropies have also been calculated.

1. INTRODUCTION

The 1,4-disubstituted diacetylenes have been used in solid (crystalline) state polymerizations[1].

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Structural similarity of diphenyldiacetylene to the well known tolane[2,3,4] liquid crystals has drawn the attention of investigators. The linear rod-like structure of diphenyldiacetylenes meets the requirement for liquid crystallinity. Para-substitution and the introduction of a dipole should further increase the likelihood of liquid crystallinity of the diacetylenic compounds. Recently, a systematic investigation of thermal properties of a homologous series ot p,p'-di-n-alkyl-diphenyl and p,p'-di-n-alkoxydiphenyldiacetylenes was reported[5,6]. Para-substituted esters of aliphatic straight chain acids with 3,6,7 and 9 methylene units were described as having only crystal-crystal and crystal-nematic transitions[4]. The study was based exclusively on thermal microscopy and no calorimetric data were provided. In this paper, we are describing a more complete study of this system by means of hot-stage microscopy, differential scanning calorimetry and X-ray diffraction.

2. EXPERIMENTAL

The intermediate diol, 4,4-dihydroxydiphenyldiacetylene was prepared from p-hydroxybenzaldehyde by the method reported in the literature[5,7,8]. Acid chlorides were obtained by using acids or anhydrides and oxalyl chloride or thionyl chloride. Esterification was performed by treating acid chlorides and diols in absolute ether solution by using pyridine as proton acceptor.

Great care has been taken in the purification of intermediates and final compounds. Silica column chromatography was used to purify the diol and the diesters. Standard characterization of each compound included proton NMR, elemental analysis and IR.

The transition characteristics and textures of the diesters were studied by using a Leitz Ortholux polarizing microscope equipped with a hot stage and a Mettler FP-52 temperature programmer. The thermal properties were investigated by means of a Perkin-Elmer 2C differential scanning calorimeter equipped with a cooler under nitrogen atmosphere with a heating rate of 20°C/min.

X-ray studies on the samples were performed with a Rigaku wide angle diffractometer (SG 7B) as well as with a low angle Warhus camera. CuK_α radiation was used.

3. RESULTS AND DISCUSSION

The DSC scans of 4,4'-dialkanoyloxydiphenyldiacetylene diesters exhibit a complicated pattern of transitions (Table I). A typical DSC thermogram for a compound with a pronounced solid-state polymorphism (n=4) is given in Fig. 1. This compound also displays a nematic region.

A thermogram for a higher homolog (n=8) is given in Fig. 2. One may notice the disappearance of the nematic phase. Well reproducible thermograms were obtained after a full heating and cooling cycle.

TABLE I. Thermal properties of a homologous series of 4,4'-dialkanoyloxydiphenyldiacetylenes (derived from DSC measurements).

n	Transition*	Transition Temperature* °K(°C)	Transition Heat* ΔH, KJ/mole	Transition Entropy*, ΔS J/mole°K
0	K_I-K_{II}	449(176)**	7.11	15.86**
	K_{II}-K_{III}	488(215)**	40.2	62.38**
1	K_I-K_{II}	351(78)	0.586	1.674
	K_{II}-K_{III}	359(86)	7.53	20.96
	K_{III}-N	430(157)	19.4	45.35
	N-I	470(197)	1.38	2.929
2	K_I-K_{II}	319(46)	10.4	32.51
	K_{II}-K_{III}	368(95)	1.51	4.100
	K_{III}-K_{IV}	400(127)	0.0125	0.2929
	K_{IV}-K_V	408(135)		
	K_V-N	416(143)	20.1	48.28
	N-I	453(180)	1.25	2.761
3	K_I-K_{II}	272(-1)	1.24	4.309
	K_{II}-K_{III}	290(17)		
	K_{III}-N	405(132)	24.7	61.04
	N-I	434(161)	2.30	3.390
4	K_I-K_{II}	343(70)	19.0	55.40
	K_{II}-K_{III}	396(123)	1.46	3.682
	K_{III}-N	407(134)	26.3	64.64
	N-I	430(157)	1.71	3.975
5	K_I-K_{II}	305(32)	18.9	60.67
	K_{II}-K_{III}	318(45)		
	K_{III}-N	402(129)	25.5	63.47
	N-I	411(138)	1.17	2.845
6	K_I-K_{II}	359(86)	35.4	98.70
	K_{II}-N	406(133)	34.0	83.76
	N-I	412(139)	2.18	5.272
7	K_I-K_{II}	326(53)	19.5	59.79
	K_{II}-N	400(127)	33.5	83.76
	N-I	401(128)***	1.46	3.640
8	K_I-K_{II}	308(95)	44.9	122.1
	K_{II}-I	403(130)	42.2	104.6
9	K_I-K_{II}	339(66)	18.1	53.54
	K_{II}-K_{III}	359(86)	7.59	21.14
	K_{III}-I	399(126)	36.2	90.85
10	K_I-K_{II}	374(101)	50.2	134.1
	K_{II}-I	401(128)	44.0	109.7

* Second (and subsequent) heatings. Heating rate 20°C/min.

** First heating (gradual decomposition observed on cycling).

*** Heating rate 3°C/min.

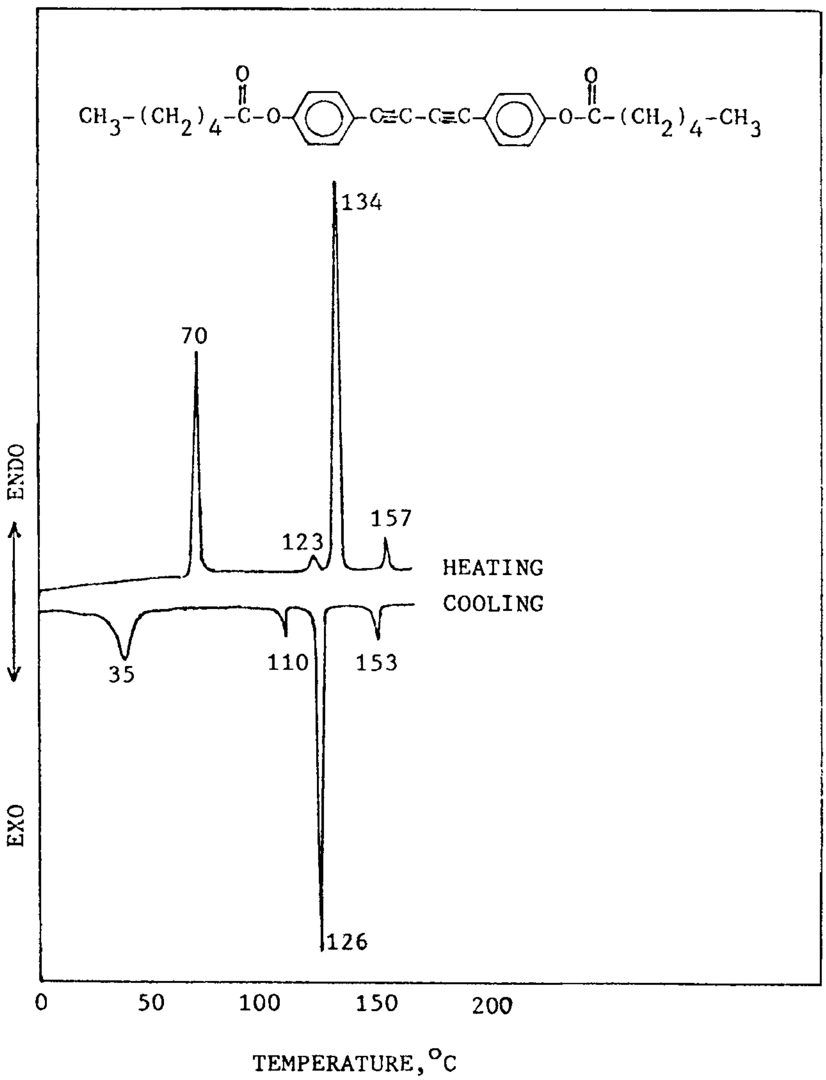

FIGURE 1 DSC scan of 4,4'-hexanoyloxydiphenyldiacetylene (heating and cooling rate 20°C/min).

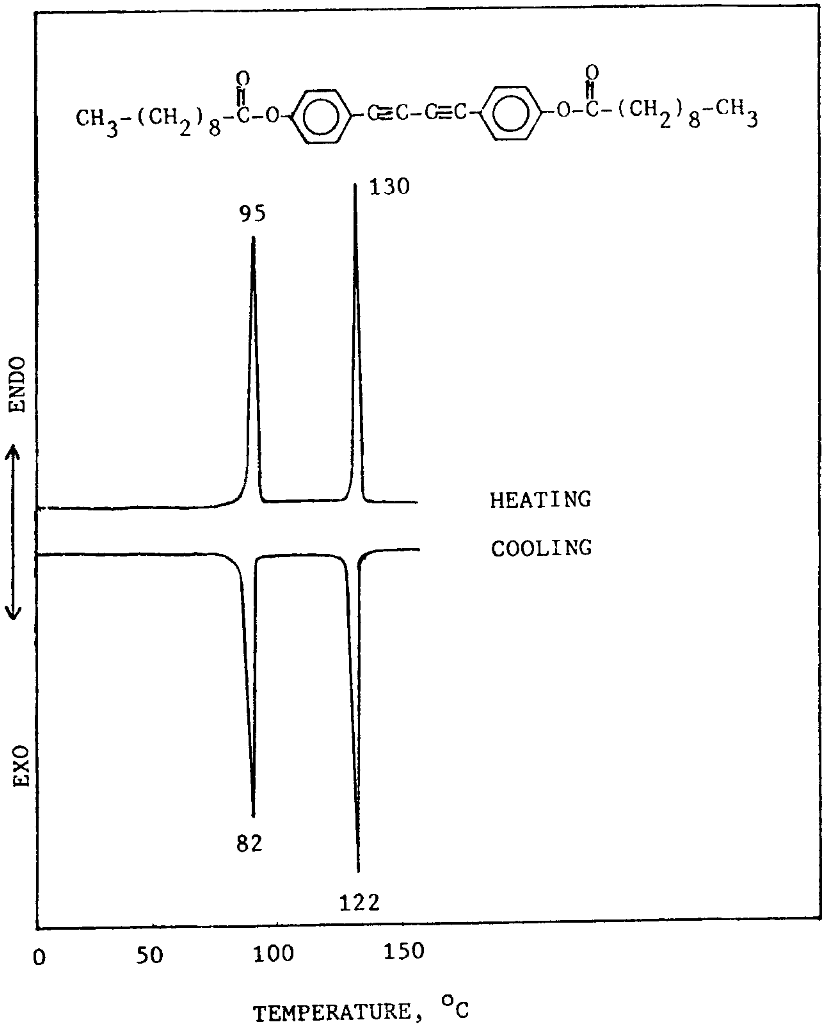

FIGURE 2 DSC scan of 4,4'-decanoyloxydiphenyldiacetylene (heating and cooling rate 20° C).

Under the microscope, a "Schlieren" texture was apparent for the nematic phases (Fig. 3). X-ray photographs show a halo in the nematic region. No evidence was found for smectic phases. X-ray diffraction confirmed the highly crystalline structure of compounds below the nematic region. This is apparent in Table II, which gives X-ray spacings at different temperatures for two diesters (n=4 and n=8). The solubility of the compounds remained unchanged in spite of slight yellowish color after X-ray exposure. The ^{13}C NMR spectra and DSC thermograms of samples subjected to the X-rays have not shown any changes when com-

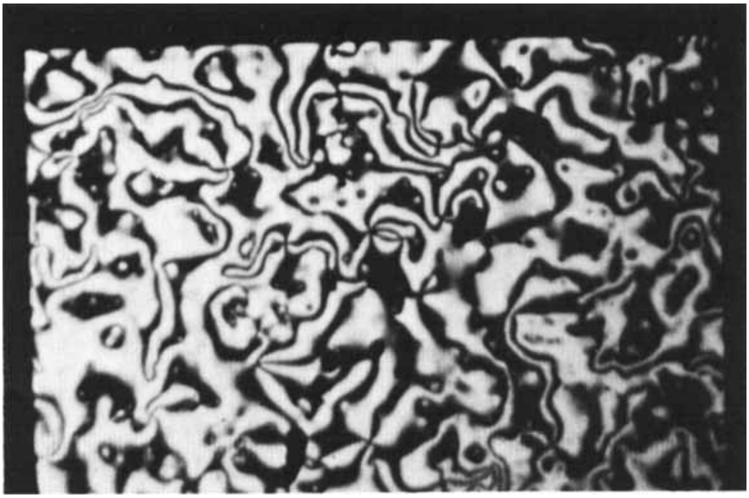

FIGURE 3 Photomicrograph of 4,4'-dipentanoyl oxydiphenyldiacetylene at 134.2°C in the nematic phase (mag. x 200).

TABLE II. Spacings in Å from X-ray diffraction at different temperatures for two representative 4,4'-dialkanoyloxydiphenyldiacetylenes.

n=4

Room Temperature	105°C
2.28(s), 2.36(w)	2.56(s), 2.72(s)
2.45(s), 2.52(w)	2.78(w), 3.14(w)
2.61(w), 2.81(s)	3.35(w), 3.67(s)
3.31(s), 5.31(w)	5.73(s), 6.00(w)
6.15(w), 7.13(w)	10.28(s)
7.52(s)	

127°C	153°C
2.36(s), 2.61(m)	2.76 Halo
2.81(s), 3.09(w)	
3.39(s), 3.91(m)	
5.31(m)	

n=8

Room Temperature	115°C
2.29(s), 2.37(w)	2.46(s), 2.63(s)
2.57(w), 2.69(w)	2.68(s), 2.80(s)
2.81(s), 3.21(s)	2.97(w), 3.28(w)
3.42(w), 4.80(m)	3.90(w), 4.25(m)
4.96(w), 6.31(w)	4.90(w), 5.49(m)
9.35(m), 9.48(w)	8.02(m)

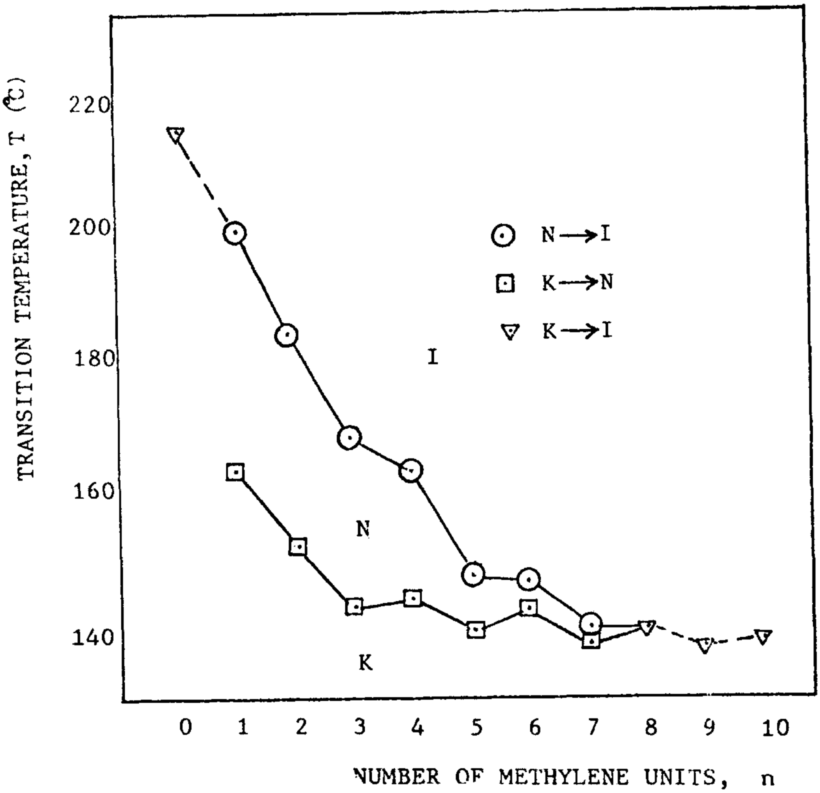

FIGURE 4 The N→I and K→N transition temperatures of the homologous series of 4,4'-dialkanoyloxydiphenyldiacetylenes

pared to the spectra of the fresh samples.

The absence of smectic phases is surprising since, for nematic homologs with n>8, a smectic mesophase could be expected. It has been reported[6] that the less polar dialkyl derivatives of the diphenyl diacetylenes display only nematic phases up to n=7.[6] The dialkoxyl derivatives also have not shown any smectic phases (for n<13).

In the case of the diacetylenic diesters, the presence of a more polar carbonyl group in the chain enhances the melting point (of crystals) and consequently decreases the likelihood of a smectic phase.

The reason for the reported non-nematogenic behavior of the tolane diesters[9] could be the lower axial ratio of the mesogen (5.8 to 4.7). The solid-nematic and the nematic-isotropic liquid transition temperatures decrease with increasing length of the alkyl chain (Fig. 4). Table I sum-

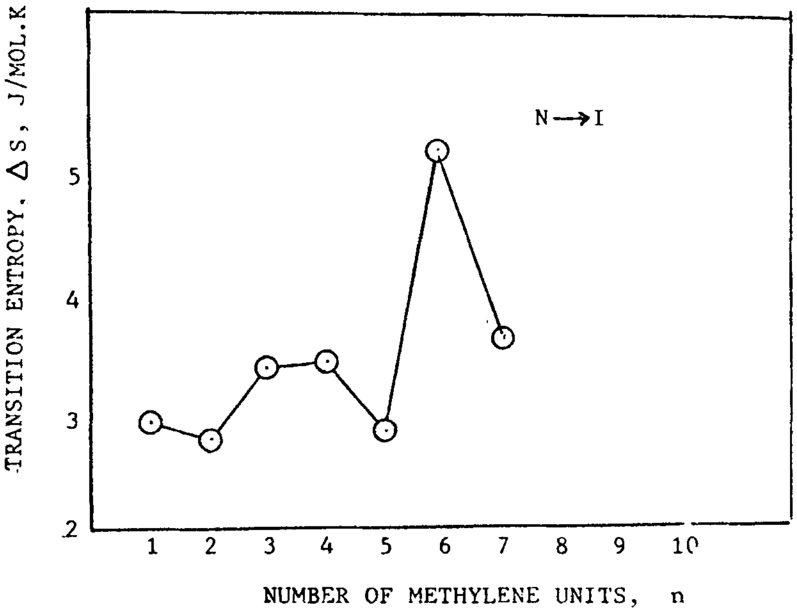

FIGURE 5 The N→I transition entropies of a homologous series of 4,4'-dialkanoyloxydiphenyldiacetylenes

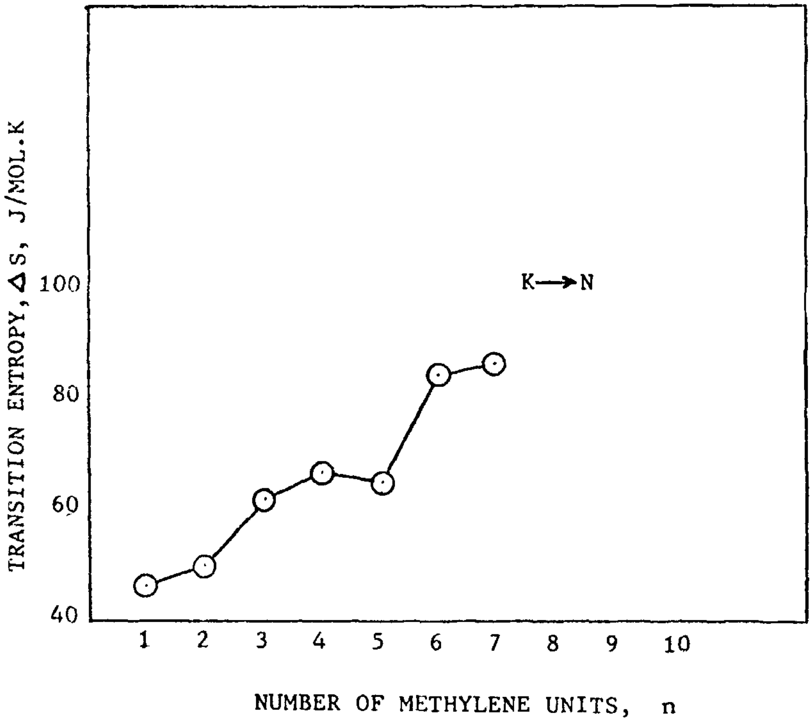

FIGURE 6 The K→N transition entropies of 4,4'-dialkanoyloxydiphenyldiacetylenes

marizes the corresponding transition temperatures and calorimetric values. For n larger than 4, an odd-even effect is observed for both transitions (Figs. 4,5). Fig. 6 gives the transition entropies of crystal-nematic transitions. No characteristic pattern other than gradually increasing entropy is seen. Fig. 7 gives the sum of the entropies for all crystal to nematic (for n=1-7) and crystal to isotropic (for n=8-10) transitions. We can see here a sustained odd-even effect throughout the whole range of n, reflecting the

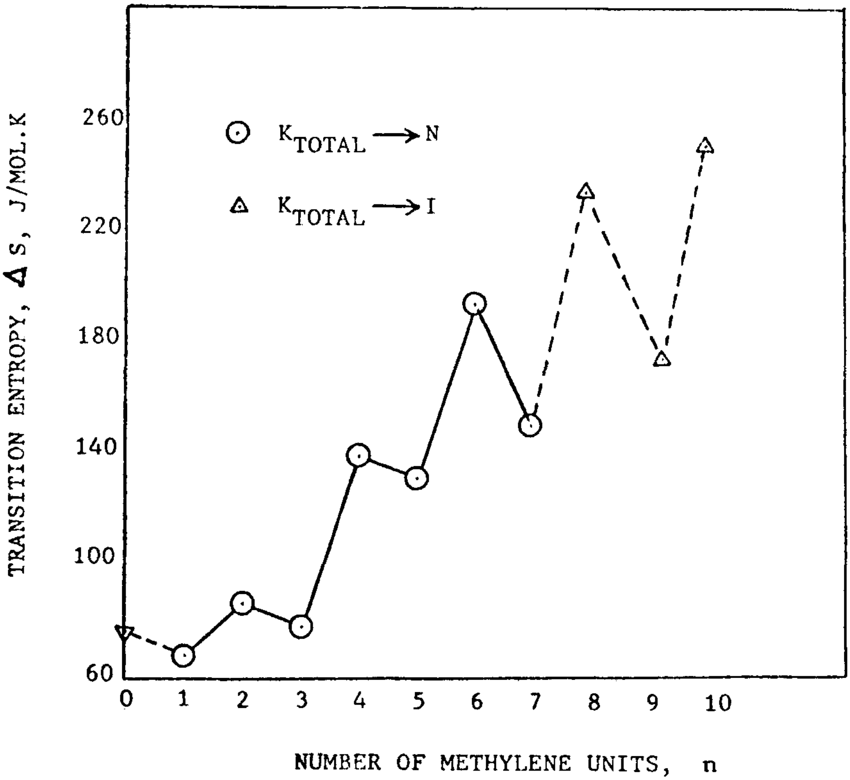

FIGURE 7 The total K→N transition entropies of a homologous series of 4,4'-dialkanoyloxydiphenyldiacetylenes

periodic odd-even differences in molecular interactions of 4,4'-dialkanoyloxvdiphenyldiacetylenes in the crystal lattice.

The nematic range narrows with the increasing length of the alkyl chain and the mesophase disappears for n=8. For n=7 an enantiotropic nematic phase was observed for a heating rate of 3° C/min. This is at variance with the data in ref. 4, which reports a monotropic nematic phase

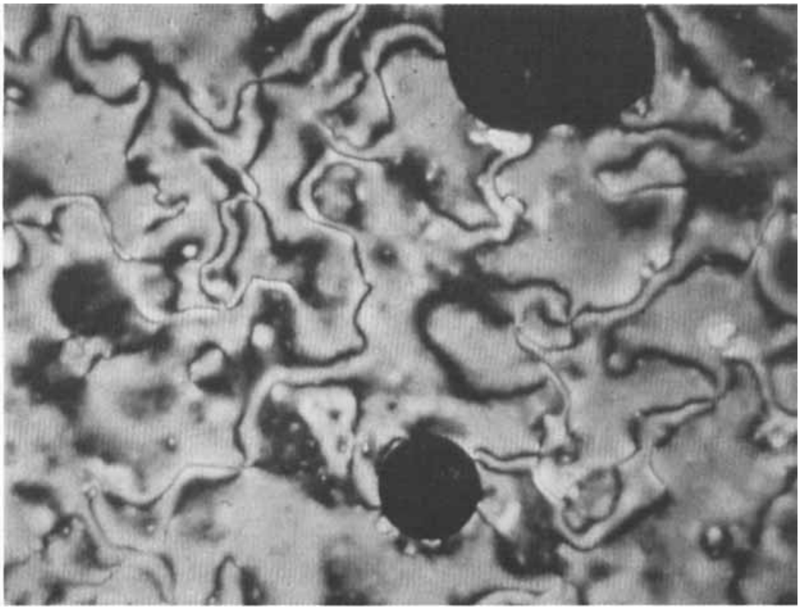

FIGURE 8 Photomicrograph of 4,4'-dinonanoyloxydiphenyldiacetylene at 127.5°C (at the N→I transition; mag. x 200).

for the same compound. Fig. 8 shows the texture of the enantiotropic phase for n=7. We have not found any mesophase for n=8,9 and 10, at variance with the reported nematic phase for n=9. This is also confirmed by the value of the corresponding transition entropy, much too high for a N→I transition.

4. CONCLUSIONS

We have prepared and characterized the homologous series of 4,4'-dialkanoyloxydiphenyldiacetylenes. Nematic phases were detected in all compounds for $1 \leqslant n \leqslant 7$. A progressive narrowing of the nematic phase takes place and the nematic phase disappears for n≥8. No smectic phases were detected. The crystalline state of the series is characterized by a strong polymorphism shown by DSC and X-ray scattering. A sustained odd-even effect characterizes the transition temperatures, enthalpies and entropies of the series. Contrary to previous reports[4], a narrow enantiotropic nematic phase was detected for n=7, but no nematic phase was detected for n=9.

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REFERENCES

1. G. Wegner, Die Makromol. Chem., 154, 35 (1972).
2. J. Malthete et al., Mol. Cryst. Liq. Cryst., 23, 233 (1973).
3. R.J. Cox and N.J. Clecak, Mol. Cryst. Liq. Cryst., 37, 241 (1976).
4. B. Grant, N.J. Clecak and R.J. Cox, Mol. Cryst. Liq. Cryst., 51, 209 (1979).
5. B. Grant, Mol. Cryst. Liq. Cryst., 48, 175 (1978).
6. E.M. Barrall, II, B. Grant, A.R. Gregges, in Liquid Crystals and Ordered Fluids, Vol.3, edited by J.F. Johnson and R.S. Porter (Plenum Press, New York, 1979), p. 19.
7. E.J. Corey and P.L. Fuchs, Tetrahedron (Letters), 3769 (1972).
8. U. Fritzshe and S. Hunig, Tetrahedron (Letters), 4831 (1972).
9. J.C. Dubois, A. Zann, and A. Couttet, Mol. Cryst. Liq. Cryst., 27, 187 (1974).