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Novel Liquid Crystalline Materials: Synthesis and preliminary characterization of new 4,4′-disubstituted diphenyldiacetylene, tolane and stilbene derivatives

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Novel Liquid Crystalline Materials

Synthesis and preliminary characterization of new 4,4'-disubstituted diphenyldiacetylene, tolane and stilbene derivatives

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The synthesis and mesomorphic properties of several new series of liquid crystalline materials are described. These include two novel diacetylenic structures, 4,4'-di-*n*-acyloxydiphenyldiacetylene and the unsymmetrical 4-*n*-alkoxy,4'-cyanodiphenyldiacetylene, and the analogous 4-*n*-alkoxy,4'-cyanotolanes and stilbenes. A discussion of the effect of structure on transition temperatures is included.

INTRODUCTION

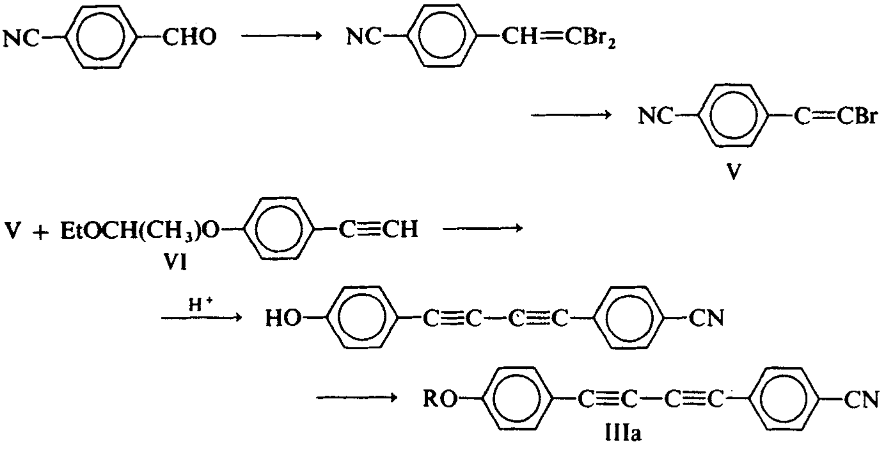
The mesomorphic behavior of rigid rod-like organic molecules has been of great interest for application to various information display technologies. In particular, the 4,4'-disubstituted biphenyl materials I, (e.g., 4-*n*-alkyl, 4'-cyano)[1] are considered important examples because of their desirable physical and thermal properties. By analogy the structurally similar tolane II and diphenyldiacetylene III materials were also of interest.

In an earlier report[2] we described the first examples of liquid crystalline materials possessing a diacetylenic nucleus IIIc and IIId. We have now extended this observation to two additional classes of diacetylenes, the 4,4'-di-*n*-acyloxydiphenyldiacetylenes IIIb, and the 4-*n*-alkoxy,4'-cyanodiphenyldiacetylenes IIIa. In addition, we have prepared the previously unknown 4-*n*-alkoxy,4'-cyanotolanes IIa from the appropriate trans-stilbenes IVa, and found both of these series to be mesomorphic. The synthesis of these materials and a preliminary report of the observed liquid crystalline properties are described in this report.

SYNTHESIS

The symmetrical 4,4'-di-*n*-acyloxydiphenyldiacetylenes IIIb were prepared by esterification of the previously reported 4,4'-dihydroxydiphenyldiacetylene[2] using conventional techniques. The 4-*n*-alkoxy,4'-cyanotolanes IIa were prepared via the corresponding trans-stilbenes IVa by the procedure reported previously for the preparation of the 4-*n*-alkyl,4'-cyanotolanes and stilbenes.[3]

The synthesis of the 4-*n*-alkoxy,4'-cyanodiphenyldiacetylenes IIIa is given in Scheme 1. The standard procedure for the synthesis of unsymmetrical diacetylenes, such as IIIa, is the Cadiot–Chodkiewicz coupling of terminal acetylenes with 1-bromoacetylenes.[4] This procedure was employed for the present synthesis. The compound 4-cyanobenzaldehyde was converted into the β,β-dibromostyryl derivative by reaction with carbon tetrabromide and triphenylphosphine in the presence of zinc dust.[5] This material could be converted in high yield into the bromoacetylide V by reaction with one equivalent to potassium *t*-butoxide in refluxing toluene. Compound V was coupled to the previously reported acetal derivative of 4-hydroxyphenylacetylene VI under standard Cadiot–Chodkiewicz conditions.[4] Deprotection of the resulting diacetylene with dilute acid followed by base catalyzed alkylation gave the desired alkoxycyano derivatives IIIa.



SCHEME 1 Synthesis of 4-*n*-alkoxy,4'-cyanodiphenyldiacetylenes IIIa.

The thermal properties as determined by optical microscopy and analytical characterization data obtained for the diphenyldiacetylenes are given in Table I, and for the tolanes and stilbenes in Table II.

TABLE 1

Transition temperatures (°C) and analytical data for the diphenyldiacetylene derivatives IIIa and IIIb

Entry no.		x	y	$C_1 \rightarrow C_2$	$C_2 \rightarrow N$	$N \rightarrow IL$	Combustion analysis					
							Calculated			Found		
							C	H	N	C	H	N
IIIb	1	n-$C_4H_9CO_2$-	n-$C_4H_9CO_2$-	106.4	132.5	160.2	77.59	6.51		77.12	6.41	
	2	n-$C_7H_{15}CO_2$-	n-$C_7H_{15}CO_2$-	82.3	129.3	136.5	78.98	7.87		78.94	8.02	
	3	n-$C_8H_{17}CO_2$-	n-$C_8H_{17}CO_2$		127.4	(126.6)	78.34	8.23		78.88	8.16	
	4	n-$C_{10}H_{21}CO_2$-	n-$C_{10}H_{21}CO_2$-	68.4	88.4	125.1	79.96	8.83		79.67	8.75	
IIIa	1	n-C_4H_9O-	-CN		190.2	193.9	84.25	5.72		83.31	5.61	
	2	n-$C_7H_{15}O$-	-CN		160.6	165.6	84.42	6.78	4.10	84.39	6.87	4.21
	3	n-$C_9H_{19}O$-	-CN		153.8	158.9	84.51	7.36		83.69	7.14	

TABLE II

Transition temperatures (°C) and analytical data for the 4′-*n*-alkoxy,4′-cyano tolanes IIa and stilbenes IVa

					Combustion analysis					
					Calculated			Found		
Entry no.	R	$C_1 \rightarrow C_2$	$C_2 \rightarrow N$	$N \rightarrow IL$	C	H	N	C	H	N
IIa 1	n-C_4H_9-	73.2	85.3	105.9	82.9	6.18	5.09	82.46	6.29	4.93
2	n-C_5H_{11}-	46	85	94.8	83.04	6.57	4.84	83.25	6.60	4.82
3	n-C_6H_{13}-		74.6	96.3	83.1	6.93	4.62	83.01	7.27	4.64
IVa 1	n-C_4H_9-		115	139	82.3	6.86	5.05	82.19	7.02	5.03
2	n-C_5H_{11}-	86	96.7	128.9	82.47	7.21	4.81	82.50	6.99	4.74
3	n-C_6H_{13}-		89 (76.8)	131.9	82.60	7.54	4.59	82.1	7.48	4.58

DISCUSSION

Several interesting generalizations can be drawn from the thermal data indicated in Tables I and II. All of the materials synthesized in the present study displayed a nematic liquid crystalline phase. Smectic behavior was not observed in any of these compounds. An interesting comparison of the data is revealed in Figure 1 where the transition temperatures are plotted as a function of chain length for the 4-*n*-alkoxy,4′-cyanodiphenyldiacetylenes, -tolanes and -stilbenes as well as the previously reported data for the analogous biphenyl compounds.[6] For the series biphenyl, tolane and diphenyldiacetylene in which only minor perturbation of the shape and electronic properties of the molecule are expected, one observes a dramatic dependence of transition temperature on molecular length. Interestingly, the increase observed from biphenyl to tolane (~2.6 Å increase in molecular length) is much smaller than that seen for the tolane to diacetylene comparison (~2.6 Å increase). A similar dependence is observed for the mesophase range. The alkoxycyanobiphenyls and tolanes display a mesophase range of approximately 15 to 20°C. Whereas, the corresponding diphenyldiacetylenes IIIa possess a much smaller nematic range (3 to 5°C). It appears that for the cyanoalkoxy diphenyldiacetylenes the crystallinity has increased to the point of virtually eliminating the mesophase. This effect is not as dramatic for the less polar symmetrical diacetylenes IIIb–d.[2]

Comparison of the data for the trans-stilbenes IVa and tolanes IIa (Table II) indicates lower nematic to isotropic transition temperatures for the linear tolanes which is consistent with the data reported for the 4-*n*-alkyl,4′-cyano series.[3]

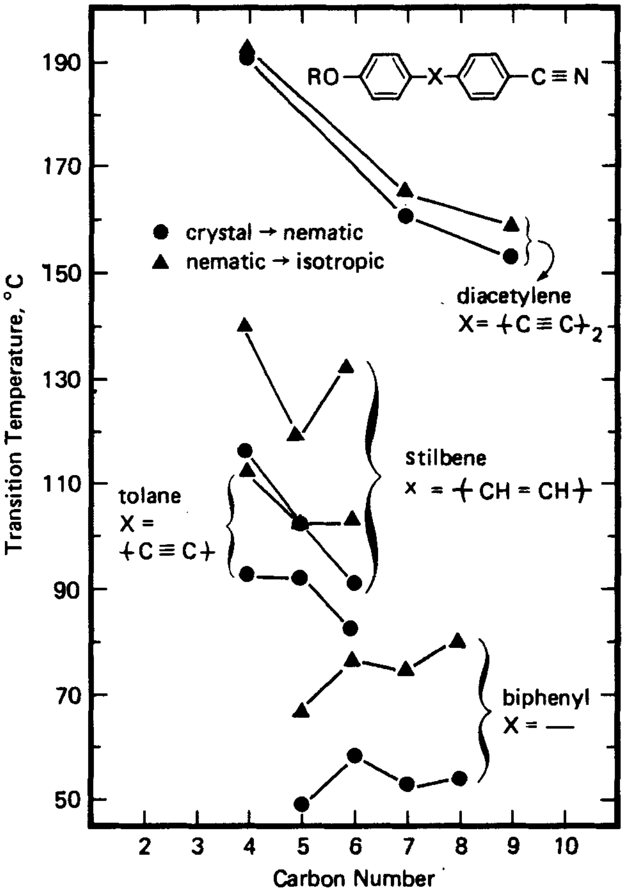


FIGURE 1 Transition temperatures (circles, C → N; triangles, N → IL) as a function of chain length for 4-*n*-alkoxy,4′-cyanodiphenyldiacetylenes, -tolanes, -stilbenes and -biphenyls.[6]

Finally, the 4-*n*-alkoxy,4′-cyanostilbenes and -diphenyldiacetylenes and to a lesser extent the tolanes were observed to undergo light induced reactions in the mesophase. For the stilbene materials this is presumably an isomerization reaction. For the diacetylenes this may be due to an ordered phase polymerization as has been reported previously for solid phases of materials of this type.[8]

EXPERIMENTAL

The microscopy data were obtained with polarized light using a Mettler FP52 hot stage.

The synthesis of 4,4'-dihydroxydiphenyldiacetylene V via 4-(1-ethoxyethoxy)-phenylacetylene has been described in detail previously.[2] The 4-*n*-alkoxy,4'-cyanostilbenes and tolanes were prepared by the methods reported previously for the alkyl analogs.[3]

4-*n*-Alkoxy,4'-Cyanodiphenyldiacetylenes IIIa

A suspension of CBr_4 (33.1 g, 0.1 mole), Zn powder (6.5 g, 0.1 mole) and triphenylphosphine (26.2 g, 0.1 mole) in CH_2Cl_2 (340 ml) was stirred at room temperature for 48 hours. To the purple suspension was added 4-cyano-benzaldehyde (6.5 g, 0.05 mole) and the reaction stirred an additional 1.5 hours. Filtration and evaporation of the filtrate gave the crude dibromoolefin which was purified by chromatography on silica gel (hexane/ethyl acetate, 3 : 1) yielding 6.5 g of product (mp 85–86°C). The 4'-cyano,β,β-dibromostyrene (5.74 g, 0.02 mole) and potassium *t*-butoxide (2.24 g, 0.02 mole) in toluene (75 ml) were heated at reflux for four hours. The reaction was cooled to room temperature, filtered and the filtrate cooled to −78°C. The product VI precipitates out as yellow crystals (2.8 g; mp 142–143°C; $C{\equiv}N$, 2229 cm^{-1}; $C{-}Br$, 2195 cm^{-1}). The bromoacetylide VI (3.2 g, 15 mole) was stirred in ethanol (50 ml) and added portionwise to a stirred solution containing $NH_2OH \cdot HCl$ (747 mg), *n*-butylamine (14.9 ml), cuprous chloride (10 mg) and 4-(1-ethoxyethoxy)-phenylacetylene (2.6 g, 15 mole) in ethanol (50 ml). After 1.5 hours the product was removed by filtration (1.8 g; $C{\equiv}N$, 2230 cm^{-1}; $C{\equiv}C{-}C{\equiv}C{-}$, 2215 cm^{-1}). Hydrolysis of the acetal group was accomplished by treatment with 200 ml of 20% HCl in ether (500 ml) for two hours. Filtration, phase separation and evaporation of the organic layer gave the desired 4-cyano,4'-hydroxydiphenyldiacetylene as a white solid (0.54 g, mp 125–127°C). Alkylation with the appropriate alkyl halide in refluxing cyclohexanone containing excess K_2CO_3 gave the compounds IIIa shown in Table I.

References

1. (a) F. J. Kahn, *Appl. Phys. Lett.*, **22**, 111 (1973); (b) W. E. L. Haas and J. E. Adams, *Appl. Phys. Lett.*, **25**, 535 (1974).
2. Grant, B., *Mol. Cryst. Liq. Cryst.*, *in press*.
3. R. J. Cox and N. J. Clecak, *Mol. Cryst. Liq. Cryst.*, **37**, 241, 263 (1976).
4. G. Eglinton and W. McCrae in *Advances in Organic Chemistry*, Vol. 4, (R. A. Raphael, E. C. Taylor, and H. Wynberg, Eds.), Interscience Pub., New York, 1963.
5. E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).
6. Gray, G. W. *et al.*, in *Proceeding of the Symposium of Ordered Fluids and Liquid Crystals* (R. S. Porter and J. F. Johnson, Eds.), Interscience, New York, 1974, p. 617.
7. R. J. Cox, R. C. Gaskill, J. F. Johnson, and N. J. Clecak, *Thermochemica Acta* **18**, 37 (1977); **21**, 369 (1977).
8. G. Wegner, *Makromol. Chem.*, **154**, 35 (1972).