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Diacetylenic Liquid Crystalline Diesters

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Diesters of 10,12-docosadiyne-1, 22-dioic acid with 4-hydroxy-4'methoxybiphenyl (I), 4-hydroxy-4'-methoxyazoxybenzene (II), and 4-hydroxy-4'-methoxy(2,2'-dimethyl) azoxybenzene have been prepared.

The diester I displayed high sensitivity to light and u.v. irradiation while it was not mesomorphic.

In contrast, diesters II and III were nematic while displaying considerably less radiation sensitivity. A suggested reason for this difference in behavior is the difference in the molecular packing of the corresponding crystal.

The difference in the mesomorphic behavior between II and III is explained in terms of mesogen broadening and distortion of the mesogen molecule of III by the methyl substituents.

Keywords: diacetylenic diesters, synthesis of, liquid crystalline order

INTRODUCTION

Diacetylenic compounds with various substituent groups have been since 1970 objects of intensive activity.[1,2] Attention has been given in particular to solid-state polymerization and solid-state properties of diacetylenics. Synthesis of stable liquid crystalline diacetylenic systems could open the possibility of various applications of such compounds including in the field of non-linear optics.[3]

We have previously reported on liquid crystalline properties of monomeric diesters with flexible-rigid-flexible sequence of moieties such as *p,p'*-alkanoic acid ester of diphenyldiacetylene.[4] The diacet-

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ylenic group was a part of the rigid unit. These diesters display a nematic mesophase for $n = 1-7$ (n, number of methylene units) and are stable in the solid-state to heat and radiation.

In this work, we describe the synthesis and properties of some diacetylenic diesters in which the acetylenic unit is in the center of the flexible moiety of the diester (rigid-flexible-rigid-flexible-rigid sequence of moieties). In such diesters the mesomorphic properties are enhanced by the the presence of two terminal rigid mesogenic groups and one central rigid diacetylenic group separated by two flexible sequences of methylene groups (flexible spacers).

EXPERIMENTAL

All reagents were purchased from Aldrich Chemical Company. 10,12-docosadiyne-1, 22-dioic acid has been prepared from 10-undecenoic acid.[5,6]

The preparation is schematically illustrated below:

$$CH_2{=}CH{-}(CH_2)_8{-}COOH$$

$$\xrightarrow[0°C]{Br_2} CH_2(Br){-}CH(Br){-}(CH_2)_8{-}COOH \xrightarrow[-HBr]{NaNH_2}$$

$$HC{\equiv}C{-}(CH_2)_8{-}COOH$$

$$\xrightarrow[O_2]{CuCl} HOOC{-}(CH_2)_8{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8{-}COOH$$

The acid was recrystallized from ethanol. Elemental Analysis: Calculated: C=72.89, H=9.45; Found: C=73.27, H=9.50. M.P.=111-112°C.

The ^{13}C and ^{1}H NMR spectra were consistent with the structure. (^{13}C NMR diacetylene = 77.95, 65.33 ppm.)

Since the diacetylenic diacid is very sensitive to light, it was kept under dark during storage and treatment with oxalyl chloride.

The acid chloride of 10,12-docosadiyne-1, 22-dioic acid was obtained by stirring the diacid with excess oxalyl chloride for four hours. The excess oxalyl chloride was then removed at room temperature

under vacuum and the mixture stirred for four more hours under vacuum to remove the last traces of oxalyl chloride.

4-Hydroxy-4′-methoxybiphenyl was obtained by treating 4,4′-dihydroxybiphenyl with dimethylsulfate. The product was purified by column chromatography and characterized by IR and NMR.

4-Hydroxy-4′-methoxyazoxybenzene and 4-hydroxy-4′-methoxy (2,2′-dimethyl)-azoxybenzene were prepared from 4-methoxyaniline and 4-methoxy-2-methylaniline.[7]

Diesters were prepared according to the procedure below: 0.003 moles acid chloride was chilled with a dry-ice acetone mixture. 0.006 moles of diol in 25 ml. of dry, freshly distilled 1,2-dichloroethane and 2.5 ml. of pyridine mixture was added over the acid chloride. The flask was closed with a ground glass stopper and wrapped with parafilm to exclude the moisture. The mixture was stirred overnight. The contents of the flask were poured into an ice-water mixture in a separating funnel. After shaking, the organic layer was precipitated in methanol. The product was filtered and purified by column chromatography. The purity was checked by thin layer chromatography.

Standard characterization of the diacetylenic diesters included ^{1}H and ^{13}C NMR, IR and elemental analysis (Table I).

The transition characteristics and the 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 (heating rate of 20°C/min). X-ray diffractograms of the diesters were obtained with a Laue camera mounted on a Norelco generator using Ni-filtered CuK alpha radiation (1.54 A°) with a sample to film distance of 5 cm (WAXS) and 17 cm (SAXS).

Ultraviolet irradiation was carried out by placing the sample between quartz plates using a medium pressure Hg lamp (Hanovia #40767 type SH) at a distance of 20 cm for an hour.

RESULTS AND DISCUSSION

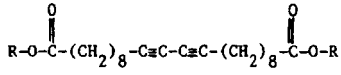
Table II gives the transition temperatures and isotropization enthalpies of the prepared diacetylenic diesters.

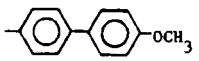
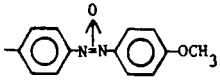
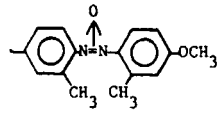
All diesters have been found highly crystalline at room temperature (Table III).

The compound I did not show any mesophase. The DSC ther-

TABLE I

Elemental analysis of the diacetylenic diesters



Compound	R	Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
I		79.30	7.49	--	79.10	7.45	--
II		70.74	6.68	6.87	70.54	6.88	7.00
III		71.70	7.17	6.43	71.60	7.10	6.50

mogram gave only one peak on heating and cooling. The absence of mesophase on heating and cooling was also confirmed by microscopy. The compound I develops beautiful spherulites on cooling from the melt.

The diester I is light sensitive. It polymerizes in the solid-state in daylight (it changes color from colorless to blue). The change of color occurs also under ultraviolet irradiation, but it is deeper (deep blue). Upon extraction of unreacted monomer with chloroform, the diester undergoes an irreversible blue to red color change. The red polymer is insoluble in all common solvents. The u.v. irradiated sample was found completely insoluble.

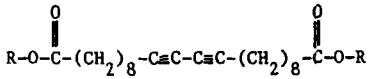
Partially and completely polymerized samples were thermochromic (reversible change of the color from blue-to-red on heating and back to blue on cooling). The phenomenon of thermochromism observed also in other polyacetylenics was explained by changes in the backbone conformation induced by heating.[8]

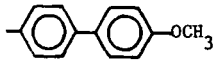
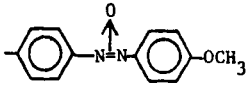
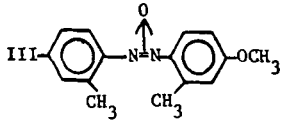
The diester I was in contrast to its behaviour on irradiation, rather unresponsive to heating: kept at 120°C for 24 hours under nitrogen, it did not show any change in its thermal characteristics and texture observed under microscope.

The diacetylenic diester II has an enanthiotropic nematic mesophase. The DSC thermogram displayed two peaks on heating and

TABLE II

Phase transitions of the diacetylenic diesters



Compound	R	Transition Temp.*°C Heating	Cooling	ΔH* Kcal/mole Heating	Cooling
I		C138I	I126C	20.42	19.72
II		C131N	N119C	17.55	17.14
		N148I	I143N	1.59	1.48
III		$C_161C_275C_390I$**			
		g13N48I	I41N	1.97	2.02

* Second heating and cooling (20°C/min. heating and cooling rate)

** First heating

C - Crystal, I - Isotropic, N - Nematic

TABLE III

X-ray spacings of diacetylenic diesters at room temperature

Diester	d Spacings in A°
I	3.5±0.05(w), 3.7±0.05(w), 3.9±0.05(s) 4.3±0.05(s), 4.6±0.05(m), 6.7±0.05(w) 8.0±0.05(w), 13.3±0.05(m), 20.6±0.5(m) 40.0±0.5(s)
II	3.6±0.05(s), 4.1±0.05(m), 4.9±0.05(s) 5.3±0.05(m), 7.0±0.05(w), 8.0±0.05(w) 23.4±0.5(w)
III	3.5±0.05(s), 3.8±0.05(s), 4.3±0.05(m) 4.7±0.05(w), 5.0±0.05(s), 5.4±0.05(w) 5.9±0.05(s), 6.8±0.05(m), 7.7±0.05(m) 8.9±0.05(w), 11.7±0.05(m)

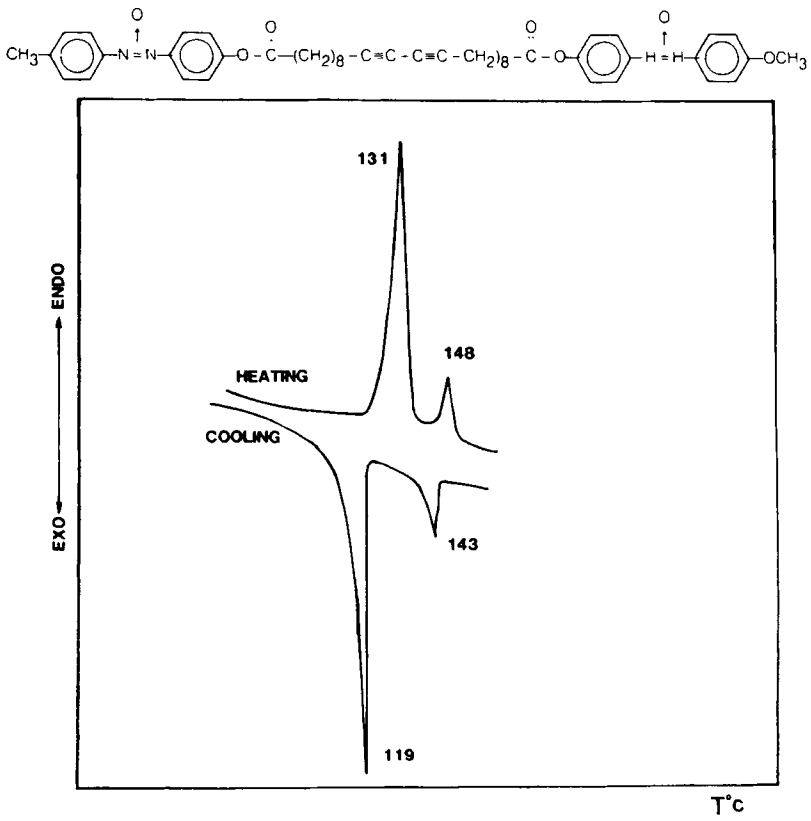


FIGURE 1 DSC scan of diester II (heating and cooling rate 20°C/min.).

cooling (Figure 1, Table II). A nematic phase was observed under the microscope below the isotropization peak (Figure 2a). An easy shear induced alignment of disclinations by cover slip displacement was obtained (Figure 2b).

This diester did not show any noticeable color change in day-light. After ultraviolet radiation only slight color intensification (pale yellow to yellow) was observed.

The diacetylenic diester III displayed a monotropic nematic mesophase. The first heating cycle gave multiple peaks (DSC). Those were identified as multiple melting peaks by microscopy (Table II, Figure 3a). The second and further heating and cooling cycles gave only one peak which was identified by microscopy as an N↙↗I transition (Figure 3b,d). The sample kept 24 hours at room temper-

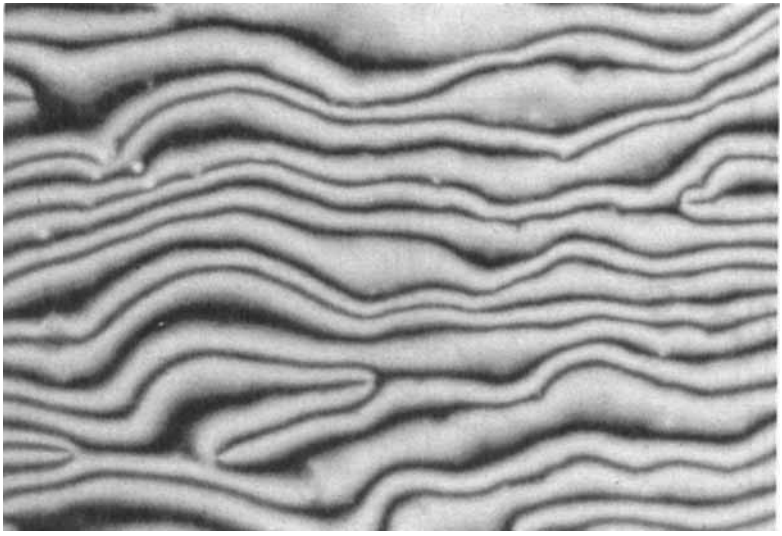


FIGURE 2a Photomicrograph of compound II at 137.5°C in the nematic phase (mag. × 320).
See Color Plate I.

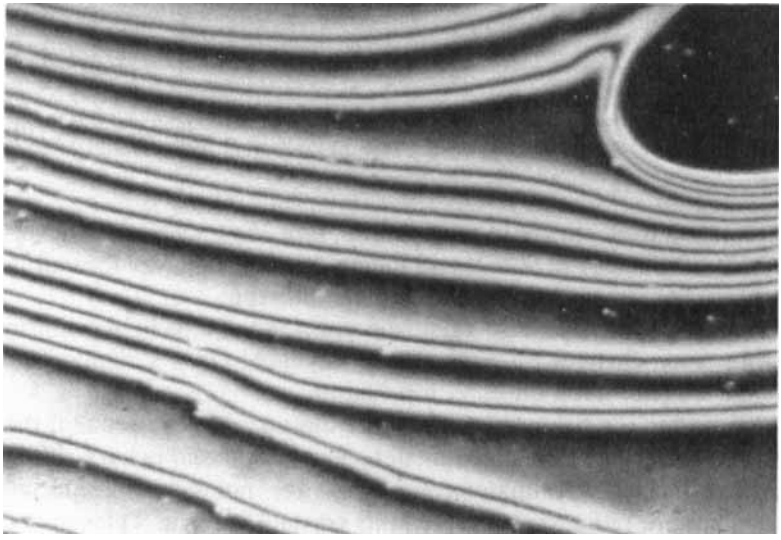
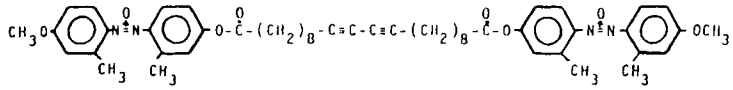


FIGURE 2b Photomicrograph of compound II at 137.5°C in the nematic phase (mag. × 320), shear aligned.
See Color Plate II.



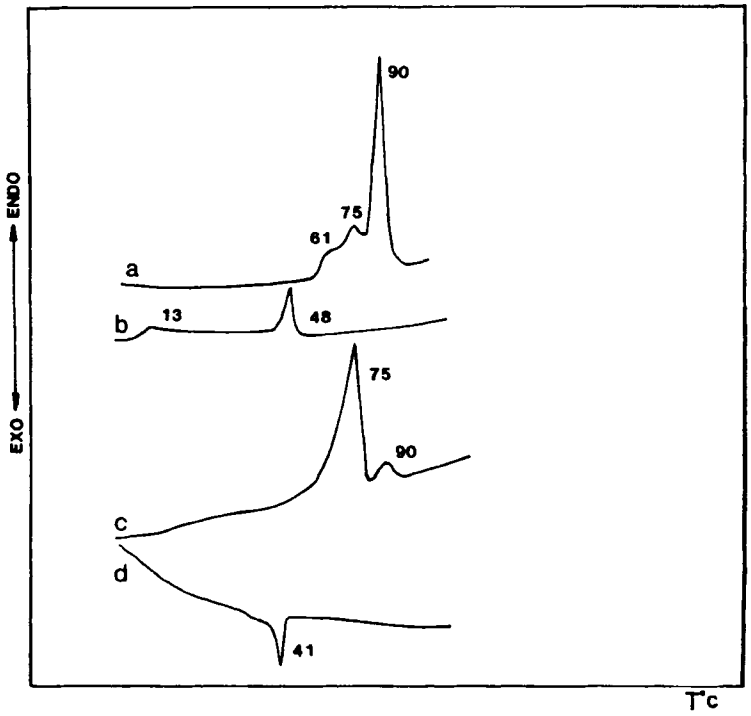


FIGURE 3 DSC scan of diacetylenic diester III (heating and cooling rate 20°C/min); a) first heating, b) second and further heatings, c) rerun after 24 hours, d) cooling.

ature crystallized slowly as is apparent from Figure 3c (slow development of the peak at 90°C), and Figure 4 in which a slow formation of spherulites from the nematic melt can be seen.

The diester III was also relatively unresponsive to light with no visible color changes on exposure to daylight. Only a slight color change was observed on U.V. irradiation.

Comparing the behavior of the three diesters one can see that the *p*-methoxybiphenyl terminated diester shows a different behavior from the azoxybenzene terminated compounds. It is not mesomorphic and is much more radiation sensitive in its crystalline form. This may be due to the molecular conformation within the crystal because the molecules seem to be packed into a layered lattice with a relatively

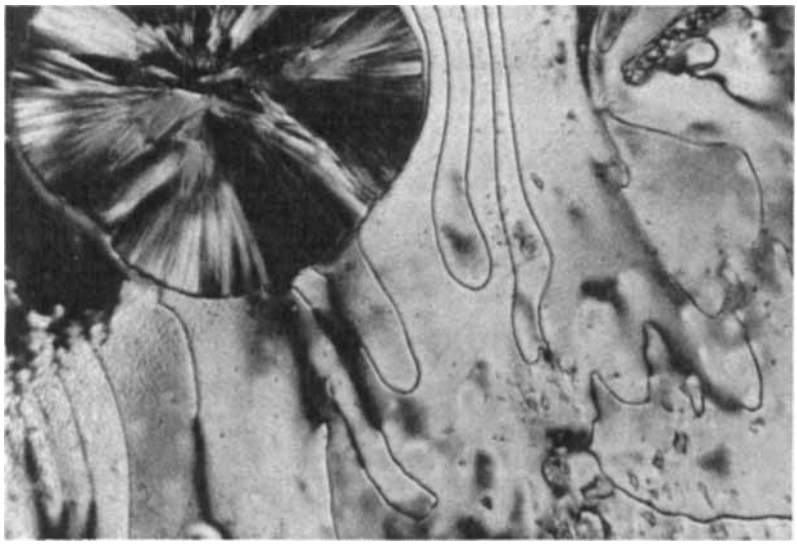


FIGURE 4 Photomicrograph of compound III at room temperature with spherulitic growth in nematic phase (max. × 320).
See Color Plate III.

upright conformation as is apparent from the SAX scattering: the spacing of 40.0 Å is relatively close to the length of the extended molecule of *I* of 46.5 Å. This gives a rather small tilt angle of some 30° for the molecules of ester *I* in the layers of the lattice.

In contrast to *I* compounds II and III are nematic and much less sensitive to irradiation. The reason for this behavior may well be due to different molecular packing in the crystals of compound II and III as can be seen from the data in Table III.

The difference in mesomorphic behavior between compounds II and III is due to the distorted configuration of the two benzene rings in the mesogen of compound III. This distortion is introduced by the steric repulsion between the substituted methyl groups[9] which slows the crystallization and allows for easy supercooling of compound III. On the other hand the methyl substitution broadens the mesogen thereby weakening its mesogenic properties. Compound III is thus monotropic while II is enanthiotropic. This result is in agreement with the behavior of twin compounds based on both types of mesogens and dodecanedioic acid spacer.[10]

Further work on diacetylenic diesters is in progress and will be reported elsewhere.

Acknowledgment

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