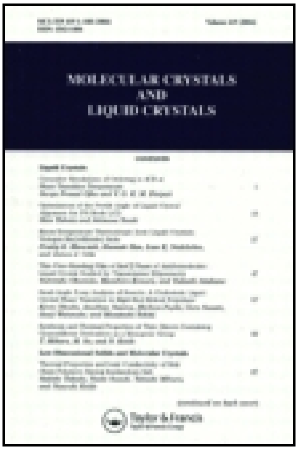

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Phase Transfer Pd(O) Catalyzed Polymerization Reactions. 5. Synthesis and Thermal Characterization of 1,2-{4,4′-di[S(-)-2-methylbutyloxy]phenyl}acetylene and 1-(4-n-alkoxyphenyl)-2-{4′-[S(-)-2-methylbutyloxy]phenyl}acetylene Monomers

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Phase Transfer Pd(O) Catalyzed Polymerization Reactions. 5. Synthesis and Thermal Characterization of 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene and 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene Monomers†

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1,2-{4,4′-Di[S(−)-2-methylbutyloxy]phenyl}acetylene and 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxyl]phenyl}acetylene monomers were prepared by a one pot phase transfer Pd(O)/Cu(I) catalyzed three step coupling of the appropriate aryl halides with 2-methyl-3-butyn-2-ol. 1,2-{4,4′-Di[S(−)-2-methylbutyloxy]phenyl}acetylene is crystalline. The 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes with $n = 8–10$ present enantiotropic cholesteric mesophases, and those with $n = 11, 12$ present monotropic cholesteric mesophases. The chiral derivative with $n = 6$ is crystalline with either a second crystalline phase or a highly ordered monotropic smectic mesophase.

INTRODUCTION

In the first papers in this series,[1-3] we described the synthesis and thermotropic behavior of both symmetrically and asymmetrically substituted 1,2-(4,4′-dialkoxyaryl)acetylene monomers. The linear 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes can be divided into three groups.[2] The lower homologues with $n = 1–3$ are crystalline. Those with $n = 4–8$ present crystalline polymorphism in addition to a nematic mesophase. The higher homologues with $n = 10–12$ display an enantiotropic smectic C phase directly below the nematic mesophase. Upon further cooling, these higher homologues and 1,2-(di-*n*-nonyloxyphenyl)acetylene also exhibit an additional monotropic smectic phase, possibly smectic B, before crystallizing.

In addition to the symmetrically substituted, linear 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes, diarylacetylenes with both symmetric and asymmetric methyl

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branching in either the alkoxy substituents or in the aromatic ring(s) of the mesogen were examined.[1,2] In general, both symmetry and methyl branching destabilize liquid crystallinity, such that only the asymmetrically branched derivatives display a nematic mesophase in addition to melting/crystallization. However, if the mesogen is extended by one phenylethynyl unit, an enantiotropic nematic mesophase is also realized in the symmetrically branched derivatives.[3]

Because the above blank experiments on achiral methyl branched diphenylacetylenes demonstrated that liquid crystalline mesophases form in asymetrically substituted compounds, we have now synthesized the analogous chiral derivatives. This paper presents the synthesis and characterization of 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene and 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes with $n = 6, 8-12$. The corresponding 1-(4-*n*-alkoxyphenyl)-2-{4-[S(+)-2-methylbutyl]phenyl}acetylenes with $n = 1-8$, 10 have been reported previously.[4,5] In addition to crystalline melting at 26–57°C, those compounds with $n \geqslant 1$ present enantiotropic cholesteric mesophases ($T_i = 41-63$°C). Even 1-(4-methyloxyphenyl)-2-{4′-[S(+)-2-methylbutyl]phenyl}acetylene presents a monotropic cholesteric mesophase.

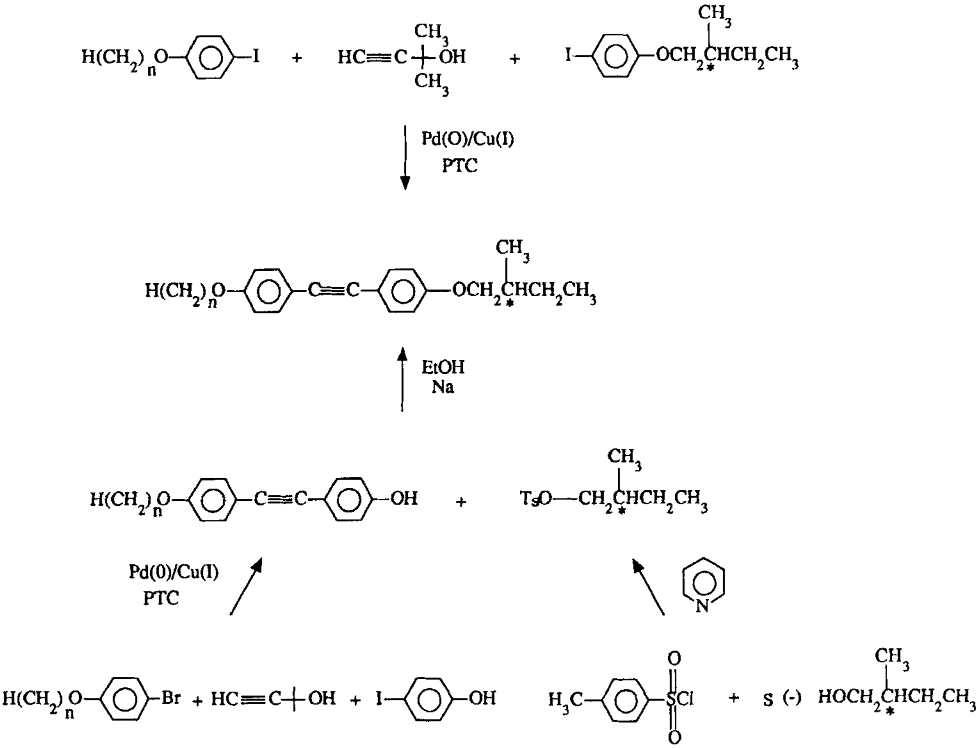
RESULTS AND DISCUSSION

Synthesis of 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxyl]phenyl}acetylenes and 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene

The 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes were prepared by the two routes outlined in Scheme I. In most cases, the chiral alkoxy substituent was introduced in the first step of the reaction sequence by reaction of 4-iodophenol with S(−)-2-methyl-1-butyl tosylate. The resulting 1-iodo-4-[S(−)-2-methylbutyloxy]benzene was then coupled with 2-methyl-3-butyn-2-ol and 1-iodo-4-(*n*-alkoxy)benzene by the three step, one pot phase transfer Pd(O)/Cu(I) catalyzed procedure described in the first paper in this series (Method C).[1] Alternatively, 1-(4-*n*-hexyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene was synthesized by introducing the chiral alkoxy substituent in the last step of the reaction sequence. That is, 1-(4-*n*-hexyloxyphenyl)-2-(4′-hydroxyphenyl)acetylene was first prepared by coupling 1-iodophenol with 2-methyl-3-butyn-2-ol and 1-bromo-4-hexyloxybenzene as above. The chiral substituent was then introduced by reaction of 1-(4-*n*-hexyloxyphenyl)-2-(4′-hydroxyphenyl)acetylene with S(−)-2-methyl-1-butyl tosylate.

The results of the phase transfer Pd(O)/Cu(I) catalyzed coupling reactions using 1-iodo-4-[S(−)-2-methylbutyloxy]benzene are presented in Table I. The yield is low in all cases. While up to 68% yield was previously obtained using this procedure (Method C),[1] these reactions resulted in an average of 15% yield. However, in this case, we used less palladium catalyst (2% vs. 4.5% of the aryl halide). We are currently finding that this is below the minimum amount of catalyst required to give the maximum yield.[6] In addition, when the (chiral) methyl branch is in the 2-position, prolonged reaction times which favor increased diphenylacetylene formation, also result in partial cleavage of the alkoxy side chain under these strongly basic conditions.[1]

The yields reported in Table I are corrected for minor side products of the



SCHEME I Two route synthesis of 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}-acetylenes.

corresponding 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes. When present, these impurities were removed by fractional recrystallization at room temperature from very dilute ethanol solutions. Their formation is possible because a slight excess of both 2-methyl-3-butyn-2-ol and the 1-iodo-4-*n*-alkoxybenzene was used, such that 1-iodo-4-[S(−)-2-methylbutyloxy]benzene was always the limiting reagent. Such contaminants are not formed when the second aryl halide used in the 3-step coupling procedure is an aryl bromide rather than an aryl iodide.

Although the conditions of both reaction sequences were not optimized, the cleaner and preferable route to these 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes is by reaction of a 1-(4-*n*-alkoxyphenyl)-2-(4′-hydroxyphenyl)acetylene with the chiral tosylate. Following the recently reported synthesis of 2,4,6-(triphenylethynyl)phenol by Heck *et al.*,[7] this is the second reported Pd(O) catalyzed coupling of a hydroxy containing aryl halide with an acetylene. The phenol functionality evidently has no effect on the reaction(s) except to deactivate the aryl halide towards oxidative addition to Pd(O) by electron donation.

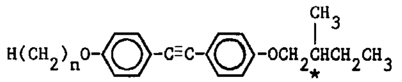
The synthesis of dichiral 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene resulted in a yield similar to those reported previously (Method B).[1]

Thermal Characterization

The DSC traces observed on heating and cooling 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene and the 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyl-

TABLE I

Synthesis of 1-(4-*n*-alkoxyphenyl)-2-{4'[S(−)-2-methylbutyloxy]phenyl}acetylenes by phase transfer Pd(O)/Cu(I) catalyzed coupling reactions.⁺



n	Reaction Time (h) after Ar^1X addition	 after Ar^2X addition	Yield (%)	Purity (%)
8	3	15.5	9.1	99.9
9	4	16	12.6	98.0
10	3	17.5	16.8	99.2
11	3	28	16.1	99.9
12	3.5	17	19.4	99.9

⁺Ar^1X (first addition) = 1-iodo-4-[S(−)-2-methylbutyloxy]benzene. Ar^2X (2nd addition) = 1-iodo-(4-n-alkoxy)benzene. Reaction conditions of first addition: 2.8 mmol Ar^1X, 3.1-3.3 mmol 2-methyl-3-butyn-2-ol, 6.1-6.3 mmol NEt_3, 3 ml benzene, 1.9-2.0 mol% $PdCl_2(PPh_3)_2$ vs. Ar^1X, CuI: Pd: PPh_3 = 3.8-4.1 : 1 : 5.3-6.4, reflux. Second addition: 3.0-3.4 mmol Ar^2X, 2 ml THF, 8.2-9.4 mol% TBAH and 2.2-3.4X KOH vs. 2-methyl-3-butyn-2-ol, reflux.

oxy]phenyl}acetylenes are presented in Figure 1. Their complete thermal transitions are summarized in Table I. At first glance, 1-(4-*n*-hexyloxyphenyl)-2-{4'-[S(−)-2-methylbutyloxy]phenyl}acetylene appears to undergo simple melting and recrystallization. Although liquid crystalline mesophase(s) were realized once the linear 1,2-(4,4'-di-*n*-alkoxyphenyl)acetylenes contained at least four methylenic units in the alkoxy substituents,[2] it would not be surprising if the chiral derivative with *n* = 6 is crystalline since methyl branching destabilizes liquid crystallinity.[2,3] However, the enthalpy of the sharp exotherm observed on cooling is less than half (4.47 kcal/mol) that of the melting endotherm (11.0 kcal/mol). A small exotherm centered at 9°C is also observed on cooling to 0°C. Because crystallization is not complete at 0°C, recrystallization occurs slowly upon reheating, with a very broad exotherm centered at 12°C. (This exotherm is too broad to accurately measure its enthalpy.) The difference in enthalpies and the fact that the sharp exotherm is supercooled from melting by only 8°C indicates that a monotropic smectic mesophase forms. This is supported by the fact that if the sample is cooled from the isotropic state to 50°C and reheated, no recrystallization occurs, and the enthalpy of the 80°C isotropization endotherm corresponds to that of the 73°C cooling exotherm (4.46 kcal/mol). A mosaic texture with lancet shaped regions as is typical of smectic B and smectic G mesophases is observed by optical microscopy upon cooling from the isotropic melt. However, this phase is quite viscous and can be sheared only with difficulty, whereupon the sample crystallizes completely. Therefore, although 1-(4-*n*-hexyloxyphenyl)-2-{4'-[S(−)-2-methylbutyloxyl]phenyl}acetylene displays two distinct phases upon cooling in which the isotropic to solid transition is supercooled very little and has a relatively small enthalpy change, the high viscosity of this

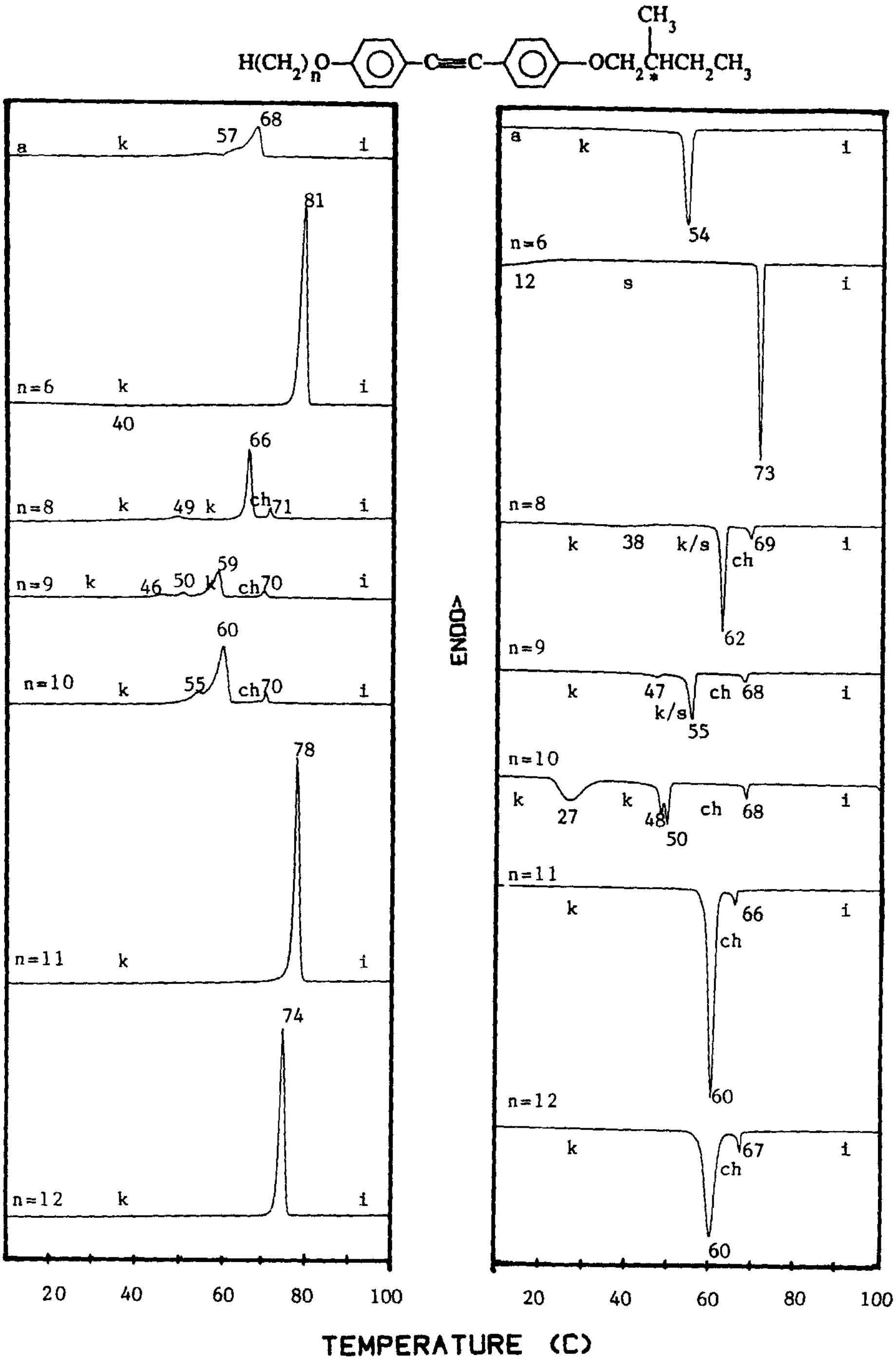
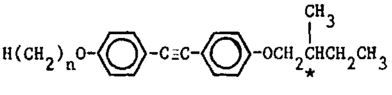


FIGURE 1 DSC heating and cooling scans of 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes and (a) 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene.

TABLE II

Thermal transitions and thermodynamic parameters of 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene and 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes.[+]



$H(CH_2)_nO-C_6H_4-C{\equiv}C-C_6H_4-OCH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

n	Phase Transitions (°C) and the Corresponding Enthalpy Changes (in parentheses, kcal/mol)
-[++]	k 57 k 68 (4.29)[**] i i 54 (4.28) k
6	s/k 40 (1.26) k 81 (11.0) i i 73 (4.47) s 12 (0.96) k
8	k 49 (0.32) k 66 (3.18) ch 71 (0.32) i i 69 (0.38) ch 62 (3.14) s/k 38 (0.46) k
9	k 46 k 50 k 59 (3.05)[**] ch 70 (0.36) i i 68 (0.39) ch 55 s/k 47 (2.74)[**] k
10	k 55 k 60 (7.79)[**] ch 70 (0.45) i i 68 (0.51) ch 50 k 48 (2.66)[**] k 27 (3.56) k
11	k 78 (12.4) i i 66 (0.35) ch 60 (10.6) k
12	k 74 (10.3) i i 67 (0.47) ch 60 (8.71) k

[+] k = crystalline, s = smectic, n = nematic, i = isotropic melt; first line of data obtained on heating, second line on cooling

[++] 1,2-{4,4′-di[S(−)-2-methylbutyl]oxy}phenyl acetylene

[**] overlapping with previous transition(s)

phase does not allow us to positively differentiate between a highly ordered smectic mesophase and a crystalline phase.

Cholesteric mesophases are realized once the *n*-alkoxy substituent reaches eight methylenic units in length. The 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes with $n = 8-10$ present thermodynamically stable, enantiotropic cholesteric mesophases. Those with $n = 11$, 12 present monotropic cholesteric mesophases in addition to a stable crystalline phase. Because the cholesteric phase of the chiral derivatives with $n = 11$, 12 is monotropic, crystals grow in the isotropic melt if the cholesteric mesophase is reheated to isotropization, but below the crystalline melting temperature (Figure 2).

Figure 3 shows two optical micrographs typical of the cholesteric textures exhibited by these compounds. Figure 3A shows the oily streaks which are observed when 1-(4-*n*-octyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene is initially melted during slide preparation, and are therefore typical of thick sample preparations. Figure 3B shows the same sample after a thin film has formed. This fan shaped cholesteric texture is observed in all subsequent heating and/or cooling scans. However, if this texture is sheared and reheated, oily streaks are again observed. Although fan shaped textures are also exhibited by smectic *A* (s_A) me-

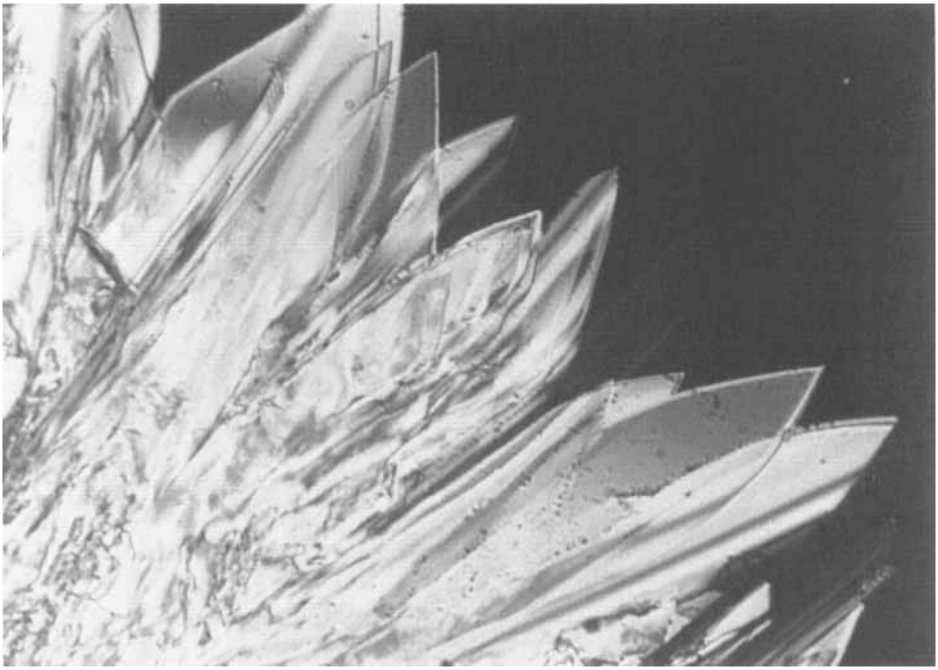


FIGURE 2 Microscopic texture (100 ×) observed on heating 1-(4-*n*-dodecyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]pheny}acetylene from the cholesteric mesophase, 73.0°C. See Color Plate VII.

sophases, cholesteric and s_A textures can be differentiated by the initial development of the anisotropic texture observed upon cooling from the isotropic state, by the difference between the isotropic-anisotropic phase transition enthalpies, and by miscibility studies. In addition to the observation of oily streaks, the second evidence that these compounds form cholesteric mesophases is that the anisotropic texture first develops in the shape of droplets; the fan texture is seen within the cholesteric droplets. Thirdly, their isotropic-mesomorphic phase transition enthalpies are within the range expected for nematic or cholesteric mesophases. In addition, mixtures with the corresponding linear 1,2-(4,4′-di-*n*-alkoxyphenyl)-acetylenes which display nematic mesophases exhibit cholesteric mesophases with broader thermal stability windows since nematic and cholesteric mesophases are miscible in all proportions, and since mixing suppresses crystallization.

The chiral derivatives with $n = 8, 9$ resemble the linear 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylenes with $n = 4-8$ in that they present enantiotropic (chiral) nematic mesophases and solidify from the nematic mesophase in multi-steps with very little supercooling (4°C) of the first, large exotherm. As shown in Figure 4 for 1-(4-*n*-octyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene, solidification from the cholesteric phase also presents a mosaic texture which appears to involve more than one, immiscible phases. As discussed previously,[2,3] it is questionable as to whether the immiscible phases involve only crystalline polymorphs as in 1(4-decylphenyl)-2-(4′-cyanophenyl)acetylene,[8] or both crystalline and smectic phase(s). While the small supercooling indicates that a nematic/smectic transition occurs, the

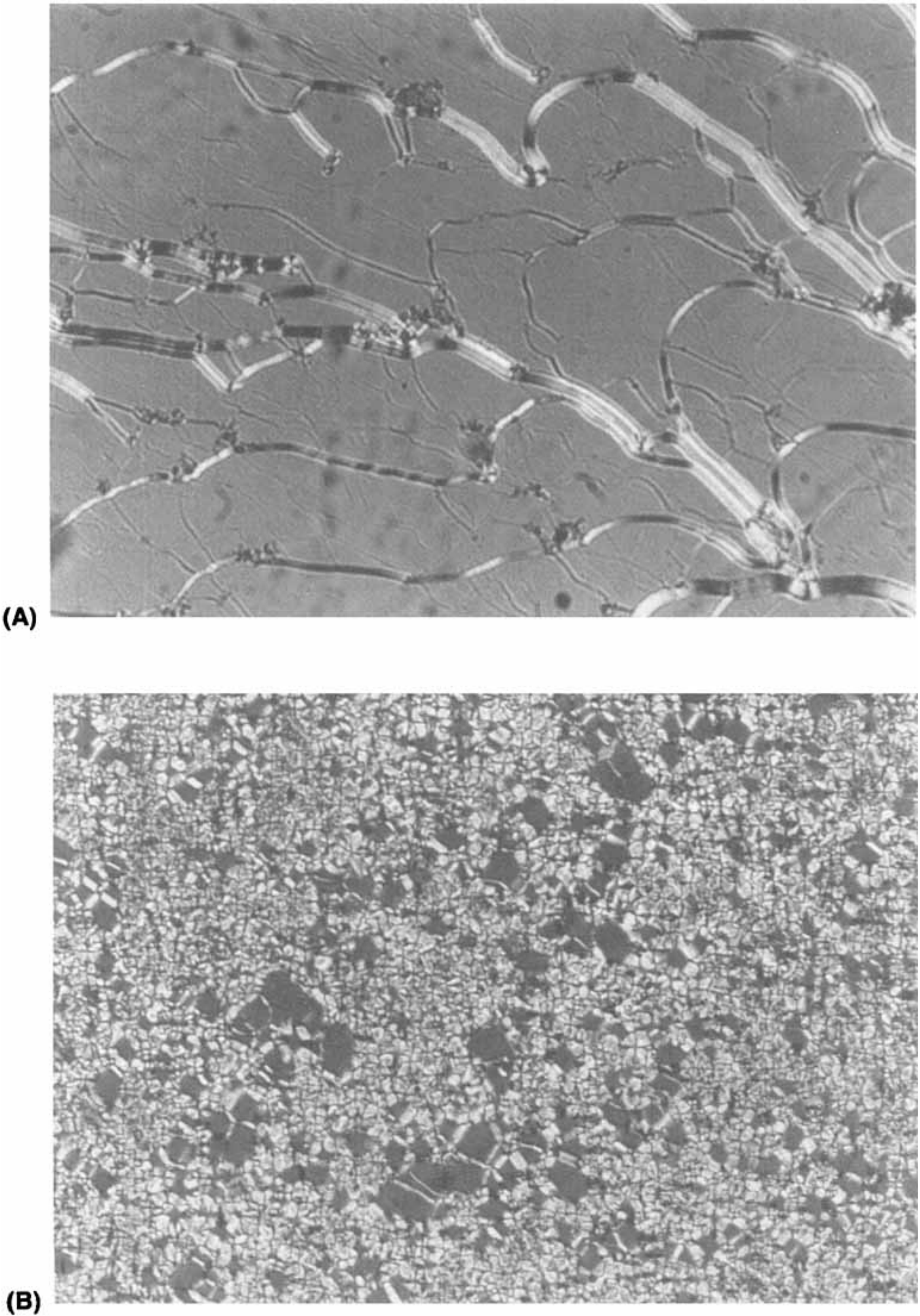


FIGURE 3 Microscopic textures (100 ×) observed on (A) the initial heating, 69.0°C, and (B) cooling, 70.1°C, the cholesteric mesophase of 1-(4-*n*-octyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}-acetylene. See Color Plate VIII.

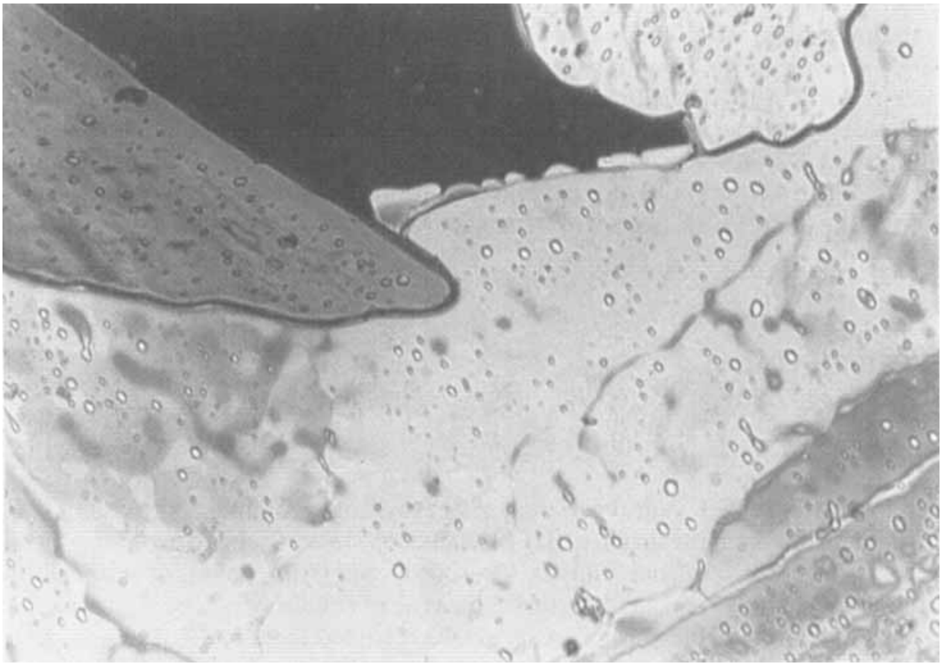


FIGURE 4 Microscopic texture (100 ×) observed on cooling 1-(4-*n*-octyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene from the cholesteric state; 63.5°C. See Color Plate IX.

total enthalpy change upon cooling from the cholesteric state to 0°C is indicative of multi-step crystallization. At the time,[2] we made the conservative conclusion that all the immiscible phases were probably crystalline, with only crystalline polymorphism occurring in addition to the nematic mesophases of the 1,2-(4,4′-di-*n*-alkoxyphenyl)acetylene series with $n = 4–8$. However, now that a monotropic smectic mesophase has been observed before the very slow crystallization of 1-(4-*n*-hexyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene, it is apparent that a monotropic smectic mesophase must be involved in the immiscible phases observed on cooling both the chiral derivatives with $n = 8$, 9 and the linear derivatives with $n = 4–8$. This is consistent with the conclusion reached on the phase transitions of 1,4-bis[2-(4,4′-diheptyoxyphenyl)ethynyl]benzene, and by analogy, 1,2-(4,4′-di-*n*-heptyloxyphenyl)acetylene.[3]

1-(4-*n*-Decyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene presents DSC traces similar to the chiral derivatives with $n = 8$, 9, except that the first large exotherm observed on cooling is supercooled by 10°C, and multi-step crystallization is more resolved. In addition, only subtle textural changes of a single phase material are observed upon cooling to the stable room temperature crystalline phase. 1-(4-*n*-Decyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene apparently undergoes only multi-step crystallization/melting transitions in addition to isotropization. Its behavior is therefore intermediate between that of $n = 8$, 9 and that of $n = 11$, 12.

The dichiral 1,2-{4,4′-di[S(−)-2-methylbutyloxy]phenyl}acetylene presents a broad endotherm on heating, and a sharp exotherm on cooling (Figure 1). Although the enthalpy change is relatively low (4.3 kcal/mol), the exotherm is supercooled by 14°C, which is in the same range as the crystalline transitions of the 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes with $n = 11, 12$. Therefore, although this sample is crystalline, it does not crystallize well. Symmetrically substituted 1,2-(4,4′-dipentyloxyphenyl)acetylenes with a methyl branch in either the 2-, 3- or 4-position of the pentyloxy substituents are also crystalline ($\Delta H =$ 5.4–6.7 kcal/mol) with from 9 to 42°C supercooling.[2]

EXPERIMENTAL

Materials

4-Iodophenol (99%), tetrabutylammonium hydrogen sulfate (TBAH) (97%), bis(triphenylphosphine)palladium (II) chloride (99%) and triphenylphosphine (99%) were used as received from Aldrich. Cuprous iodide (Alfa, 98%), S(−)-2-methyl-1-butanol (Fluka, 95%) and 2-methyl-3-butyn-2-ol (Fluka, 99%) were also used as received. Triethylamine (Fisher, reagent) was distilled from KOH. Benzene (Aldrich, 99+ % spectrograde) and tetrahydrofuran (THF) (distilled from $LiAlH_4$) were deaerated before each use by bubbling argon through the solvent for at least 30 min. S(−)-2-Methyl-1-butyl tosylate was prepared as described previously,[9] except that the reaction mixture was allowed to warm to room temperature following the addition of S(−)-2-methyl-1-butanol at 0°C.

Techniques

200 MHz ^{1}H-NMR spectra (δ, ppm) were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as the internal standard.

Purity was determined by high pressure liquid chromatography (HPLC) with a Perkin-Elmer Series 10 LC instrument equipped with an LC-100 column oven (40°C), an LC-600 autosampler, and a Nelson Analytical 900 Series data station. Measurements were made using a UV detector after ^{1}H-NMR demonstrated that non-UV-absorbing impurities were absent, with $CHCl_3$ as solvent and a 100 Å PL gel column (1.0 ml/min).

A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were read as the maximum or minimum of the endothermic or exothermic peaks. All heating and cooling rates were 10°C/min. Tabulated thermal transitions were read from reproducible second or later heating scans, and from first or later cooling scans. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard.

A Carl-Zeiss optical polarized microscope (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[10,11]

Etherification of 4-Iodophenol and 1-(4-Hexyloxyphenyl)-2-(4′hydroxyphenyl)acetylene

The etherification of 4-iodophenol with *n*-bromoalkanes, and of 4-iodophenol and 1-(4-hexyloxyphenyl)-2-(4′-hydroxyphenyl)acetylene with S(−)-2-methyl-1-butyl tosylate followed the procedures used to etherify 4-bromophenol.[1] All resulting compounds were >99% pure. The ^{1}H-NMR spectra of 1-(4-*n*-hexyloxyphenyl)-2-{4′-[S(−)2-methylbutyloxy]phenyl}acetylene (45% yield) is presented in the next section.

1-Iodo-4-[S(−)-2-methylbutyloxy]benzene (66–88% Yield). ^{1}H-NMR: 0.9 (*m*, $—C\underline{H}_3$, 6 protons), 1.2 and 1.4 (2 *m*, $—C\underline{H}_2CH_3$, 2 protons), 1.8 (*m*, $—C\underline{H}—$), 3.6 (*m*, $—OC\underline{H}_2—$), 6.6 (*d*, 2 aromatic protons ortho to —OR), 7.4 (*d*, 2 aromatic protons ortho to —I).

1-Iodo-4-(*n*-alkoxy)benzenes (53–79% Yield). All 1-iodo-4-(*n*-alkoxy)benzenes ($n = 8–12$) have identical ^{1}H-NMR chemical shifts: 0.9 (*t*, $—C\underline{H}_3$), 1.0–1.6 (*m*, $—[C\underline{H}_2]—_{n-3}$), 1.7 (*m*, $—OCH_2C\underline{H}_2—$), 3.9 (*t*, $—OC\underline{H}_2—$), 6.6 (*d*, 2 aromatic protons ortho to —OR), 7.5 (*d*, 2 aromatic protons ortho to —I).

Phase Transfer Pd(O)/Cu(I) Catalyzed Acetylene Coupling Reactions

1) Synthesis of 1,2-{4,4′-di[S(−)-2-methylbutyloxyphenyl]}acetylene

Potassium hydroxide (1.4 g, 26 mmol) and TBAH (0.31 g, 0.91 mmol) were ground together in a mortar and added to a mixture of cuprous iodide (0.15 g, 0.78 mmol), triphenylphosphine (0.29 g, 1.1 mmol) and $PdCl_2(PPh_3)_2$ (0.15 g, 0.21 mmol) in a round bottom flask equipped with a condenser connected to an argon inlet/outlet. A solution of 2-methyl-3-butyn-2-ol (0.49 g, 5.8 mmol) and 1-iodo-4-[S(−)-2-methylbutyloxy]benzene (3.0 g, 10 mmol) in deaerated THF (15 ml) was then added at room temperature. After the oil bath had heated to 80°C, the reaction mixture was stirred for 23 h. Once cooled to room temperature, 100 ml of saturated aqueous ammonium chloride was added and the reaction mixture was stirred for 1 h, and then extracted eight times with toluene, leaving a very blue aqueous phase. The toluene extracts were dried over $MgSO_4$. This was then filtered and the solvent was removed on a rotary evaporator. Purification by two chromatographic separations on silica gel using hexane as eluent followed by recrystallization from ethanol (75 ml) yielded 0.82 g (45%) white crystals in two fractions (purity 99.2%). ^{1}H-NMR: 0.95 (*m*, $—C\underline{H}_3$, 12 protons), 1.2 and 1.3 (2 *m*, $—C\underline{H}_2CH_3$, 4 protons), 1.8 (*m*, $—C\underline{H}—$, 2 protons), 3.8 (*m*, $—OC\underline{H}_2—$, 4 protons), 6.8 (*d*, 4 aromatic protons ortho to —OR), 7.4 (*d*, 4 aromatic protons ortho to $—C{\equiv}C—$).

2) Synthesis of 1-(4-n-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxyl]phenyl}acetylenes

In a typical procedure, a solution of 2-methyl-3-butyn-2-ol (0.27 g, 3.2 mmol), triethylamine (0.62 g, 6.1 mmol) and 1-iodo-4-[S(−)-2-methylbutyloxy]benzene (0.81 g, 2.8 mmol) in deaerated benzene (3 ml) was added via an addition funnel to a mixture of cuprous iodide (0.038 g, 0.20 mmol), triphenylphosphine (0.088 g, 0.34 mmol) and $PdCl_2(PPh_3)_2$ (0.037 g, 0.053 mmol) in a round bottom flask equipped with a reflux condenser connected to an argon inlet/outlet. The reaction mixture was heated to reflux for 3 h. ^{1}H-NMR demonstrated that the aryl iodide was completely reacted after 2 h. 1-Iodo-4-decyloxybenzene (1.2 g, 3.4 mmol) in deaerated THF (2 ml), and an intimately ground mixture of TBAH (0.09 g, 0.27 mmol) and KOH (0.39 g, 7.0 mmol) were then successively added. After refluxing 17.5 h, the reaction mixture was allowed to cool to room temperature, and a saturated aqueous solution of ammonium chloride (100 ml) was added. This was stirred 1 h and then extracted five times with toluene, leaving a very blue aqueous phase. The toluene extracts were dried over $MgSO_4$. The filtered and condensed product was purified by column chromatography on silica gel using hexane as eluent. Recrystallization from ethanol (100 ml) yielded 0.20 g (17%) of 1-(4-*n*-decyloxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylene; purity >99%. The results of the acetylene coupling reactions using Method C of reference 2 are presented in Table I. The ^{1}H-NMR chemical shifts of the 1-(4-*n*-alkoxyphenyl)-2-{4′-[S(−)-2-methylbutyloxy]phenyl}acetylenes (n = 6, 8–12) are identical: 0.8 (*t*, —$CH_2C\underline{H}_3$), 0.9 (*m*, —$C\underline{H}_3$, 6 protons), 1.1–1.6 (*m*, —$[C\underline{H}_2]$—$_{n-3}$, —$CHC\underline{H}_2$—, $2n$–4 protons), 1.8 (*m*, —$OCH_2C\underline{H}_2$—, —$OCH_2C\underline{H}$, 3 protons), 3.7 (*m*, —$OC\underline{H}_2$ CH—), 3.9 (*t*, —$OC\underline{H}_2$—), 6.8 (*d*, 4 aromatic protons ortho to —OR), 7.4 (*d*, 4 aromatic protons ortho to —C≡C—).

3) Synthesis of 1-(4-*n*-hexyloxyphenyl)-2-(4′-hydroxyphenyl)acetylene

A solution of 2-methyl-3-butyn-2-ol (1.3 g, 15 mmol) and triethylamine (5.5 g, 55 mmol) in deaerated THF (15 ml) was added via an addition funnel to a mixture of cuprous iodide (0.20 g, 1.0 mmol), triphenylphosphine (0.39 g, 1.5 mmol), $PdCl_2(PPh_3)_2$ (0.19 g, 0.27 mmol) and 4-iodophenol (3.0 g, 14 mmol) in a round bottom flask equipped with a reflux condenser connected to an argon inlet/outlet. The reaction mixture was heated to reflux until 4-iodophenol had completely reacted (3.5 h). 1-Bromo-4-hexyloxybenzene (3.9 g, 15 mmol) in deaerated THF (10 ml), and an intimately ground mixture of TBAH (0.38 g, 1.1 mmol) and KOH (2.4 g, 43 mmol) were then successively added. After refluxing 37 h, the reaction mixture was allowed to cool to room temperature, and water (150 ml) and toluene (20 ml) were added. The aqueous phase was then neutralized with HCl, and approximately 6 g ammonium chloride was added. After stirring for over 1 h, the two phase mixture was filtered to remove solids (0.40 g) and extracted five times with toluene, leaving a light brown aqueous phase. The toluene extracts were dried over $MgSO_4$, filtered and concentrated. After two chromatographic separations on a silica gel column using toluene as eluent, 1-(4-*n*-hexyloxyphenyl)-2-(4′-hydroxyphenyl)acetylene was recrystallized from hexane (100 ml) to yield 1.1 g (27%) light beige colored crystals; purity >99.9%. ^{1}H-NMR: 0.9 (*t*, —$C\underline{H}_3$), 1.0–1.6 (*m*, —$[C\underline{H}_2]_3$—), 4.0 (*t*, —$OC\underline{H}_2$—), 5.0 (*s*, $ArO\underline{H}$), 6.76 and 6.83 (two overlapping doublets, 2 aromatic protons ortho to —OH and 2 aromatic protons ortho to —OR, respectively), 7.34 and 7.41 (two overlapping doublets, 2 aromatic protons ortho to —C≡C—ArOR and 2 aromatic protons ortho to —C≡C—ArOH, respectively.)

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