LIQUID CRYSTALS, 2003, VOL. 30, NO. 6, 711–731

The effect of olefinic terminal chains on the mesomorphic properties of 4,4′-disubstituted diphenyldiacetylenes

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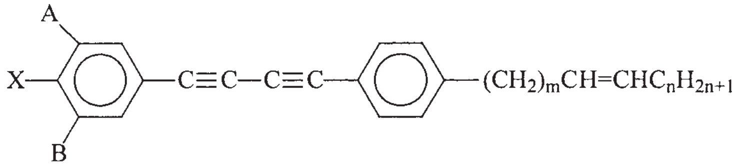
(*Received 30 June 2002; accepted 21 January 2003*)

New diphenyldiacetylenes of the type

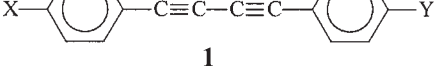


with A, B=H and/or F; $m=0$, 1; $n=1$–4; and $X=C_nH_{2n+1}$, F, CF_3 or CN were synthesized and their mesomorphic properties determined by hot stage polarizing microscopy and DSC. When $m=0$, all of these compounds showed only a nematic phase except when $X=CF_3$ when both nematic and smectic A phases were seen. Both clearing and melting temperatures were higher than those reported for substitution with the corresponding alkyl chains but the much larger increase in clearing temperatures produced considerably wider nematic phases. Eutectic mixtures of a few of these olefins yielded nematic materials also having much wider temperature ranges and higher clearing temperatures than the eutectic mixtures of the alkyl compounds, while retaining their high birefringence and low viscosities. Such materials are of interest for beam-steering devices.

Four of the diacetylenes with $m=1$ (A, B=H) were also prepared ($X=C_6H_{13}$, F, $n=2$, 3). When X was C_6H_{13} ($n=2$), the nematic range was smaller in the 2- than in the 1-olefin but wider than in the alkyl series. When X=F, either no nematic phase or a monotropic one was observed, whereas the 1-olefins gave a much wider nematic phase. Both transition temperatures were lower than those for the corresponding 1-olefin and alkyl analogues. The compound with $X=C_6H_{13}$ and $n=2$ had a melting temperature below room temperature.

1. Introduction

Asymmetrically disubstituted diphenyldiacetylenes, 1 are of interest in electro-optical applications as wide range nematic materials having a large optical birefringence and a low viscosity [1]. We have been interested in improving the properties of these materials by increasing the nematic range, dielectric anisotropy and optical birefringence [2, 3]. A simple method for improving the dielectric anisotropy would be to add



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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
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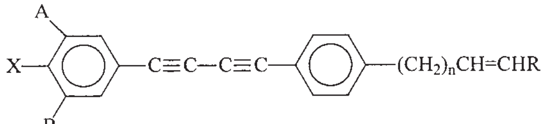
DOI: 10.1080/0267829031000111432

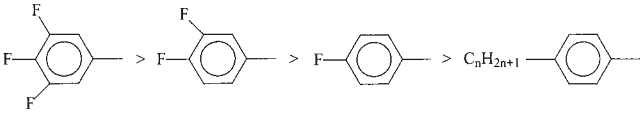
a cyanobiphenyl to a eutectic mixture of the dialkyl diacetylenes (X, $Y=C_nH_{2n+1}$). However, such mixtures form complexes having decreased solubilities, much higher transition temperatures, and decreased nematic ranges [4]. Some complexes even show a preference for smectic phases. This work also showed that the polar diacetylenes do not mix well with the non-polar compounds. Thus, structure modification was the only approach left for improving properties. Basically, only two possible modifications to the diacetylenes are possible; a change in the ring system or a change in the terminal chains. We have investigated both types. Some ring modifications have been reported [2], others will be published later. The incorporation of amino groups into the terminal chains has also been reported [3]. Other chain modifications will be included in a future paper discussing structure–property relationships in these compounds [5]. In this paper, only the olefin chain compounds will be discussed.

The effect on mesomorphic properties of placing a double bond within an alkyl terminal chain has been studied in a variety of mesogens [6]. In some, the melting temperature was lowered but no strong obvious trend was found. Most of this work was done using mesogens having two or more rings attached directly to each other without a connecting group. In our experience, the trends observed in such series are not very useful for predicting mesomorphic properties for two-ring systems having a connecting group between them. Additionally, the olefinic chain was attached either to a cyclohexane ring or to a benzene ring as an alkenyloxy group. These trends would not necessarily apply to an olefin chain attached directly to the benzene ring of the diacetylenes **1**. Such a chain would be expected to produce lower transition temperatures than would an alkenyloxy group.

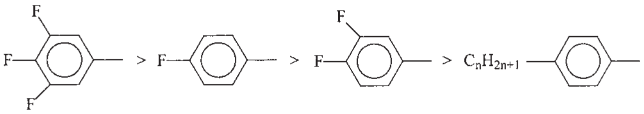


2

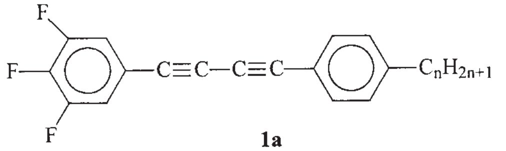
More applicable are the few studies made of two-ring mesogens with connecting groups and a terminal group containing an olefin group [7]. In these compounds, the double bond was attached directly to a benzene ring (1-olefin) or at the end of an alkyl chain. A few diphenyldiacetylenes of this type have been studied [8, 9]. The 1-olefins showed higher transition temperatures and an increase in the nematic phase range. Birefringence is also enhanced in the 1-olefin. Moving a double bond from the 1-position to the 2- or 3-positions should lower the melting temperature but would be expected to decrease the nematic phase range and the birefringence. A double bond at the end of the terminal chain is favourable for polymerization and, therefore, less desirable in terms of stability. Thus, initially, we felt that the 2- or 3-olefinic ($n=1$ or 2) diacetylenes **2** offered more promising variations for improving the mesomorphic properties of the diphenyldiacetylenes. Different terminal X and lateral A and B substituents could be used to increase the dielectric anisotropy. Because the fluorine atom is both a π-donor and a σ-acceptor, its effect on the dipole moment and polarizability anisotropy are somewhat complicated. To assess these, we have made calculations of the dipole moments and static electrical polarizabilities of the compounds similar to those of compound **2** with the olefin chain replaced by a hydrogen. This allows us to assess the relative importance of various substituents to the anisotropic polarizability, which is expected to be related to the birefringence. It also allows us to assess the importance of various substituents' dipole moments and hence to the dielectric anisotropy. The most important contributions to the dielectric anisotropy are proportional to the square of the components of the dipole moments, and the birefringence is proportional to the anisotropic polarizability. Both are proportional to the order parameter. The relevant molecular direction is determined by the molecular director which is along the long axis of the molecule (or the line which goes though the –yne carbons), or the C2 rotation axis in the molecules we calculated. However, with alkyl or olefin chains the molecular director will be slightly different because of the steric interactions of the alkyl chain(s). Also, for X, $A=F$, $B=Y$ both the steric and dipolar interactions of the fluorine will make small changes in this direction. The results for the dipoles, however, seem reasonably unambiguous so that the dielectric anisotropy should be in the following order:



The results for polarizability are less clear. There seems to be relatively little (only a few percent) change in the low frequency anisotropy in the polarizability dependent on the fluorine or alkyl substitutions. This polarizability is primarily anisotropic along the –yne connector. Thus it is expected that the size and direction of the order parameter will primarily determine the birefringence. The theoretical suggestion is that the birefringence should be in the following order:



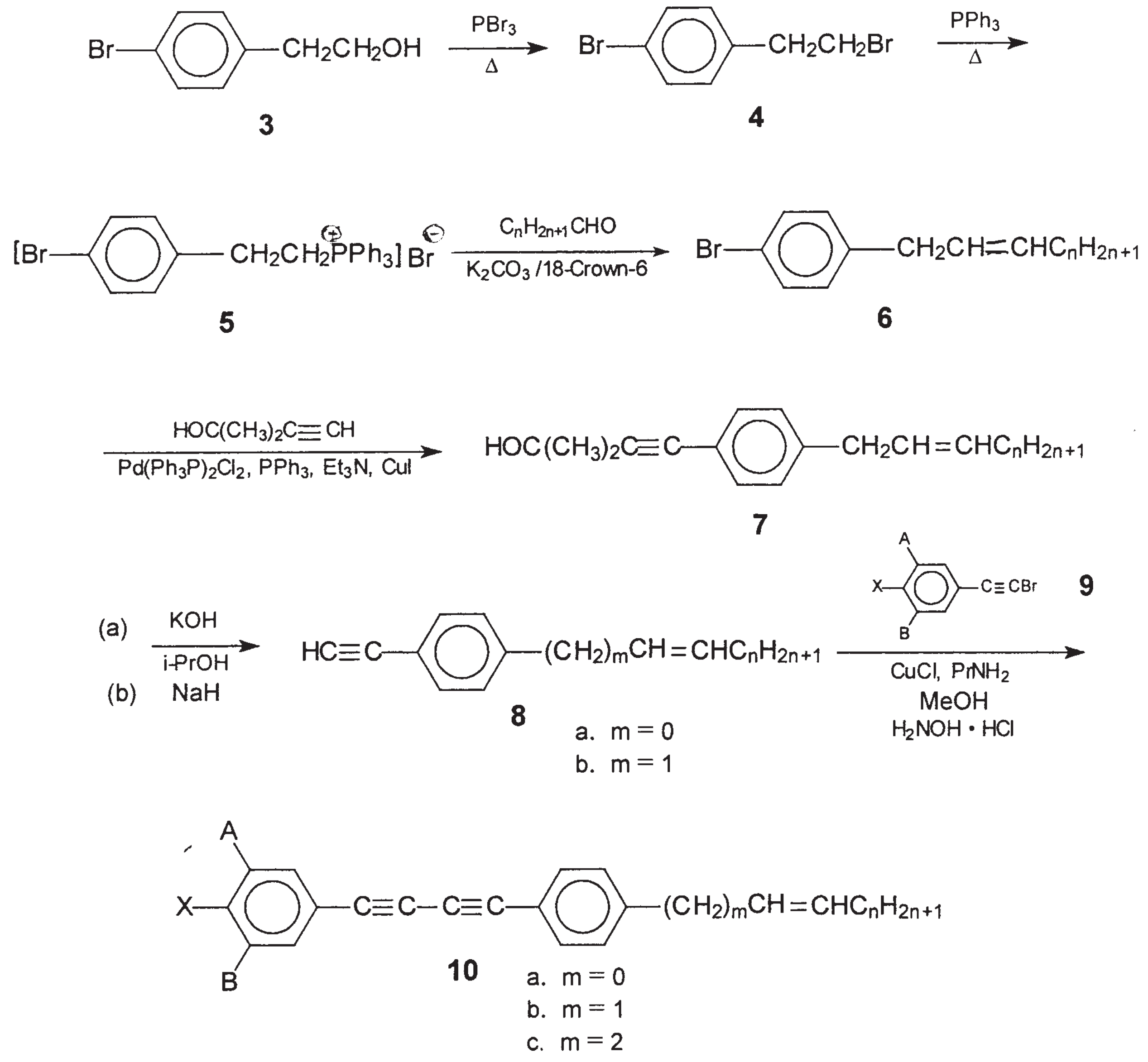
Another possibility for adjusting the properties would be to mix these compounds with the dialkyl compounds or the 1-olefin analogues. We were also interested in preparing the 3-olefin analogues but thus far have been unable to prepare an appropriate 3-olefin intermediate. In this paper, we report our synthesis of the $n=1$ and $n=2$ olefin diacetylenes **2** and their mesomorphic properties. A few of the alkyl trifluoro compounds **1a** were also synthesized for comparing properties with the olefinic analogues.



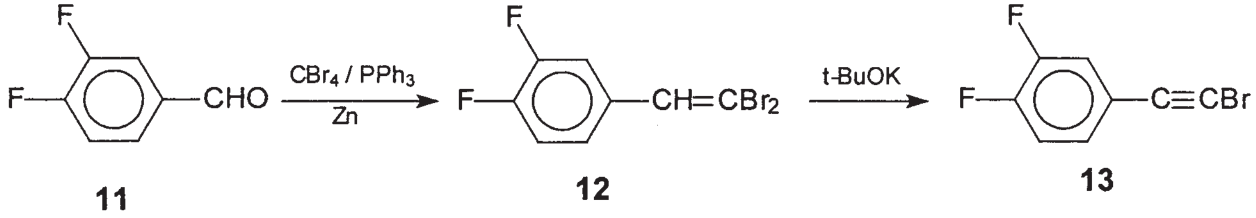
1a

2. Synthesis

A popular method for preparing the alkyldiphenyldiacetylenes involves a coupling reaction between a substituted phenylacetylene and a substituted bromoacetylene [8, 9]. Use of this method for synthesizing the olefinic diacetylenes **10** (scheme 1) would involve the coupling of the olefinic acetylene **8** with the bromoacetylene **9**. The synthesis of the bromoacetylenes **9** is well documented [3, 8, 9] and, therefore, does not need to be described here. Only the one with $X=A=\mathrm{F}$, **13**, has not been reported previously. This compound was prepared in the manner shown in scheme 2. The only new development in preparing the diacetylenes **10** was the synthesis of the olefinic acetylenes **8**. Previously, 4-bromo- and iodo-(alkyl/alkoxy) benzenes were converted



Scheme 1.



Scheme 2.

to the acetylenes by displacement of the halide with a protected acetylene [8, 9]. We used the same method to convert the bromo-olefins **6** to the acetylenes **8**. Synthesis of the bromo-olefins **6** was achieved using a Wittig reaction between the bromide **4** and the appropriate alkyl aldehydes. The alcohol **3** is commercially available or can be prepared by LAH reduction of 4-bromophenylacetic acid [10]. Conversion of this alcohol to the bromide **4** was achieved using PBr_3; HBr has also been used [10].

Many conditions that can be used for Wittig reactions; some can be used to control which isomer, *cis* or *trans*, will predominate in the olefin. We chose to use a method described earlier to give a high *trans*/*cis*-ratio by using a crown ether as catalyst [11] since the *trans*-chain would produce a more linear structure. No problems were encountered in preparing the salt **5** but numerous experiments were required before the optimum conditions for converting this salt to the olefin **6** were determined. Yields of 80–90% were finally achieved for $n = 1$–3. Especially difficult was the synthesis of the $n = 1$ analogue since the aldehyde had a lower boiling point than did the reaction mixture. This problem was solved using a large excess of the aldehyde. GC analysis usually showed one major peak and several minor ones. Samples with at least 80% of the major peak were used to prepare the acetylenes **8** via the protected acetylenes **7**. GC analysis again showed one major and several minor peaks, although NMR spectra suggested these were of higher purity. These compounds were unstable to light, requiring that they be stored in the dark and used under minimal light conditions. Samples containing at least 80% of the major component were coupled with the bromoacetylenes **9** to give the diacetylenes **10** in the same manner as described earlier [3]. Gram quantities of many of these diacetylenes have been prepared in average yields of 40–50%.

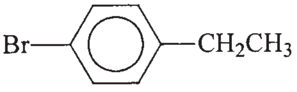
All these diacetylenes were purified by recrystallization or flash chromatography followed by recrystallization until their clearing temperatures had a range of 0.30° or less. The use of CH_2Cl_2 or $CHCl_3$ as solvent was avoided since these tended to produce materials that were pale yellow instead of colourless. All of the purified compounds were colourless solids when recrystallized.

Since the symmetrical diacetylenes can also form in the coupling reaction, all samples were checked for these materials by capillary GC using a previously reported method [12]. Both the dialkyl- and alkyl-olefinic diacetylenes had the same TLC-R_f values and could only be separated by capillary GC. None of the symmetrical dialkyl compounds were detected in the purified materials. Although the diolefinic diacetylene should have a different TLC-R_f value, none of this material was detected. This could be because the olefin chain is on the acetylene intermediate rather than on the bromoacetylene. Our experience has shown that the bromoacetylene is more likely to react with itself than does the acetylene [5]. Usually some symmetrical F, di-F and tri-F diacetylenes were isolated when these bromoacetylenes were used. This was also true in the preparation of the diacetylene **1a** having no olefinic chains. The presence of both types of symmetrical material with similar solubilities made purification of these olefins difficult. This is reflected in their low purified yield. As experience was gained in purifying both the intermediates and the final diacetylenes, the GC purities of the diacetylenes increased to a range of 99.8–100%. However, some of the fluorinated ring diacetylenes were obtained in purities as low as 99.12%.

The low yields and purification difficulties provided an incentive to obtain a higher purity in the bromo-olefin **6**. There also was the desire to know the *trans*/*cis*-ratio resulting from the Wittig reaction and if the final diacetylenes contained the *cis*-isomer. Attempts to determine the *trans*/*cis*-ratio from interpretation of the olefin protons of the ^{1}H NMR spectra for the bromo-olefin **6** were unsuccessful. Unlike in an olefin chain attached directly to the benzene ring, the two olefinic protons have similar chemical shifts. The intervening CH_2 group causes an additional splitting so that both olefinic protons would be expected to give at least a doublet of triplets, which would overlap with similar chemical shifts. Long range coupling (1, 3) through the double bond would add an additional splitting. Thus, interpreting the olefinic protons for the pure *trans*-isomer alone would be difficult. Although ^{1}H

NMR spectra have been reported for both pure *cis*- and trans-isomers for but-1-enylbenzene, no interpretation of the olefin proton splitting was provided [13]. Spin decoupling experiments reportedly gave two coupling constants of 6.25 and 15.4 Hz for the *trans*-isomer [14].

A better approach was found when a new, larger batch of the bromo-olefin **6** ($n=2$) was prepared, using the experience obtained from previous reactions to obtain purer material. The crude product showed only three peaks on the GC scan: $t_R=1.22$ (5.28%), 1.61 (0.89%) and 2.94 (93.63%). An attempt to separate these three components by careful chromatography on silica gel gave several fractions, none of which showed only one or two components. The fraction showing the most peaks by GC—but with primarily three peaks at $t_R=1.22$ min (17.53%), 1.61 min (0.57%) and 2.94 min (81.34%)—was submitted for GC/MS analysis. The two peaks at $t_R=1.61$ and 2.94 min had the same mass spectra and were found to be the *cis*- and *trans*-isomers, respectively, of the olefin. The peak with $t_R=1.22$ min showed parent peaks at 186 and 184 which suggested the structure for 1-bromo-4-ethylbenzene **14**. This compound could form by hydrolysis of the salt **5**. Eliminating it from the crude product mix gave a *trans*/*cis*-ratio of 99.1 to 0.9% formed in the Wittig reaction.



14

This latest batch of primarily *trans*-olefin **6**, containing none of the ethyl compound **14**, was converted to the protected acetylene **7** ($n=2$). An attempt to remove the protecting group from this compound by reflux with KOH in MeOH for 48 h gave a mixture of two olefins. This differed from our earlier results in which reflux times of either 24 or 48 h had yielded primarily only one olefin. We have no explanation for why a mixture was formed in this case. GC analysis of the crude mixture from this reaction showed that it contained 44.82% of the 2-olefin **8b** ($n=3$), 23.55% of the 1-olefin **8a** ($n=2$) and 20.10% of starting material. The two olefins could not be separated by chromatography on silica gel in hexane but fractions from this chromatography were clean enough to show the presence of two olefins in the ^{1}H NMR spectra. A comparison of these spectra with that for the material made earlier showed that this actually was the 1-olefin **8a** rather than what was thought to be the 2-olefin **8b**. Such a bond migration was reported earlier to occur in 1-phenylbutene-2-ene in the presence of KOH in an aprotic solvent [15].

The ^{1}H NMR spectra for the olefin mixtures made it possible to resolve the confusion that occurred earlier in interpreting the olefin protons for the bromo-olefin **6**, acetylene intermediates **7** and **8** and the diacetylenes **10**. The olefin protons for the bromo-olefin **6** and for the protected acetylene **7** showed an essentially symmetrical complex multiplet as shown in figure 1; whereas, these protons for the acetylene **8** and the diacetylenes **10** showed an unsymmetrical multiplet like that shown in figure 2. For the 1-isomer, the olefin proton nearest to the ring occurs at a higher chemical shift and is a simple doublet with a large coupling constant. The other olefin proton is a doublet of triplets with some overlap at the lower chemical shift, which would agree with figure 2. Also, our ^{1}H NMR data for the acetylene **8** isolated earlier agrees with the data reported for *trans*-1-phenyl-1-pentene [16] which give a *trans*-coupling constant = 15.9 Hz, supporting the 1-olefin **8a** structure (figure 2). A trans-coupling constant of about 16 was observed. Although GC analysis showed the presence of some of this 1-isomer in the sample of the bromo-olefin **6** ($n=2$), this could not be detected in the NMR spectra. With the complexity of the splitting pattern (figure 1) this is not surprising. We did not feel that the complex splitting pattern in this curve could be interpreted accurately. In hindsight, the differences in the NMR spectra for the 1- and 2-olefins should have been noticed earlier, but on seeing them both in a mixture it was realized that isomerization had occurred in the deprotection step. Thus, all the acetylenes **8** and the diacetylenes **10** prepared up to this point contained the 1-olefin, i.e. they are actually **8a** and **10a**.

An easier route to the 1-olefin acetylene **8a** ($n=3$) shown in scheme 3 was tried, using a method described earlier for the synthesis of *trans*-1-phenyl-1-pentene [16]. No problems were encountered in preparing the olefin **15** but GC analysis of the purified product showed two peaks at $t_R=2.90$ min (5.51%) and 3.27 min (94.30%). The 2.90 min peak has the same retention time found for the 2-olefin acetylene **8b**. No *cis*-olefin was detected. This method avoided the Wittig reaction but still required forming the protected acetylene **16** and deprotecting it to obtain the 1-olefin **8a**. GC analysis of the protected acetylene **16** isolated showed the presence of a small amount of the 2-olefin ($t_R=5.01$ min, 4.40%) as well as the 1-olefin ($t_R=5.31$ min, 93.17% 1-olefin). To try to avoid isomerization in the deprotection reaction, the NaH method was tried [17]. The olefin acetylene isolated showed a smaller amount of the 2-olefin ($t_R=2.52$ min, 0.56%), as well as the 1-olefin ($t_R=2.85$ min, 99.11%).

The 2-olefin acetylene **8b** was still of interest for preparing the diacetylenes. All that was needed was to find a way to avoid double bond migration during removal of the protecting group. Several attempts were made to do this by treating the 2-olefin acetylene **7**

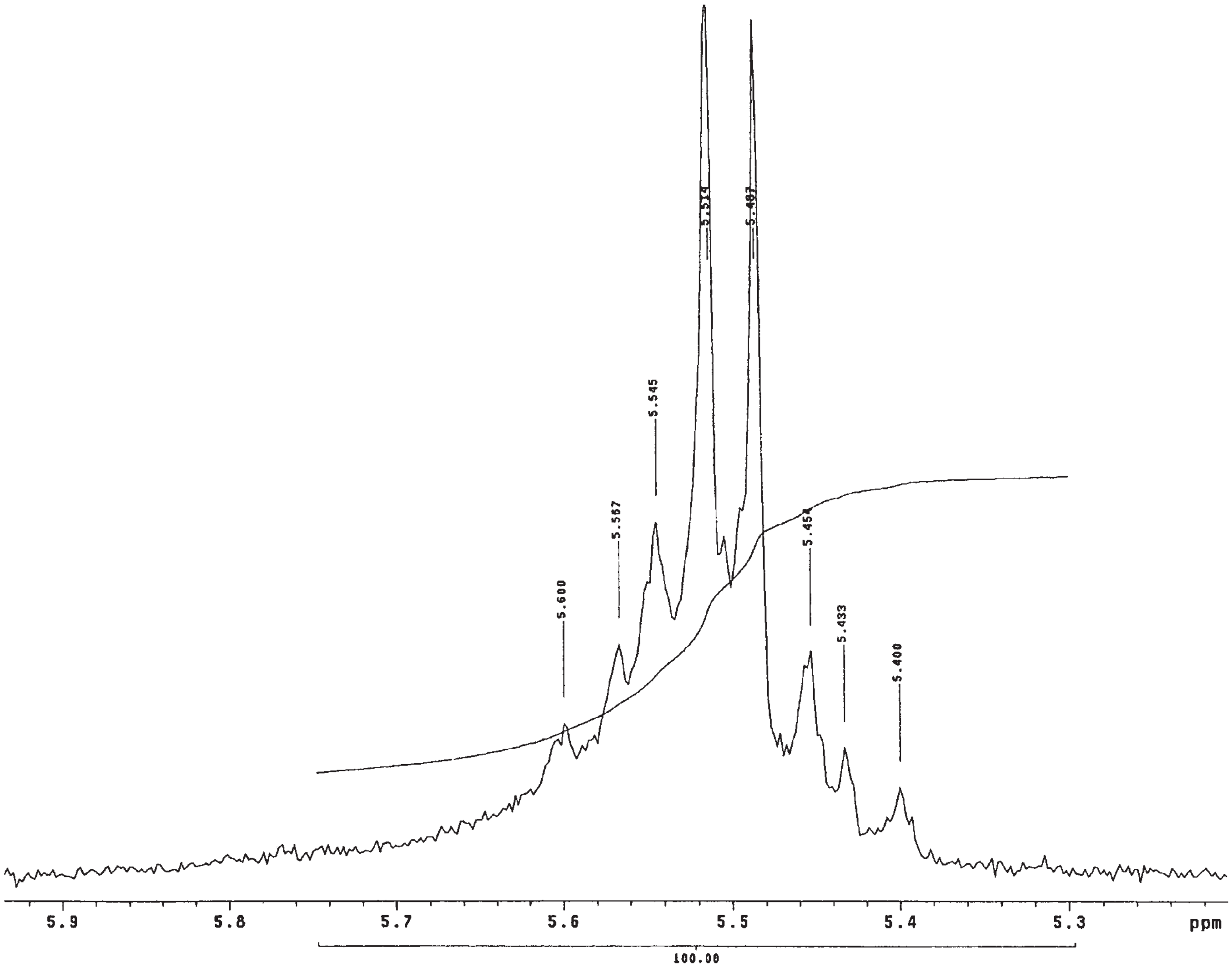
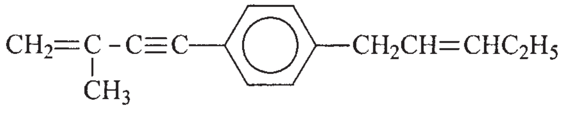


Figure 1. Olefin proton region of the ^1H NMR spectrum for the 2-bromo-olefin **6** ($n=2$).

($n=2$) with potassium *t*-butoxide in toluene or benzene. The best material isolated contained 98.03% of the 2-olefin acetylene **8b** and 0.94% of the 1-olefin **8a**. In one of these attempts, in which molecular sieves were added to the reaction mixture a compound was isolated which had a GC $t_R=4.6$ min and a ^1H NMR spectrum that showed no $C{\equiv}CH$ peak but additional peaks in the olefin area (figure 3) along with a new methyl peak at 1.98 min. These data fit the olefin-acetylene structure **17**. This could conceivably form by base-catalyzed dehydration. Literature data [18] for an analogous mesityl compound without the 2-olefin chain supports this structure.



17

Both the 1-olefin acetylene **8a** ($n=3$) prepared using the scheme 3 method and the 2-olefin acetylenes **8b** ($n=2$ and 3) were used to prepare a few diacetylenes **10**. The 2-olefin diacetylenes **10b** were more difficult to purify than the 1-olefin analogues due to their greater solubility. High purities were obtained but yields were low.

^{13}C NMR spectra were obtained for a representative sampling of the prepared diacetylenes **10**. Those having ring fluorine atoms showed additional splittings due to ^{13}C–F coupling, with the coupling constants decreasing with increasing distance from the fluorine atoms as is typical in ^{13}C NMR spectra for fluorine-substituted benzene rings. In the spectra for nearly all these compounds, the chemical shifts for the two outer diacetylene carbons differ from each other as well as from the two internal carbon atoms, which also differ from each other. This indicates that some substituent effects differentiate these carbon atom pairs.

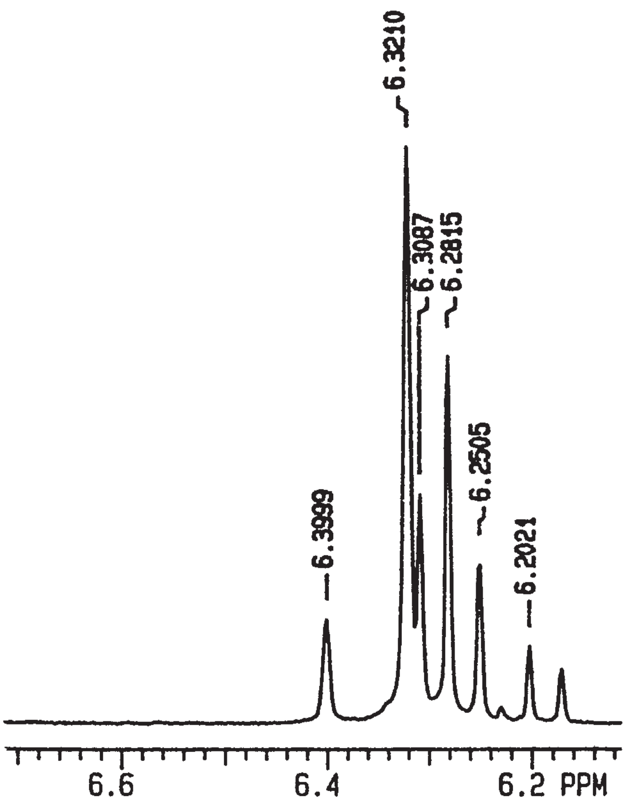
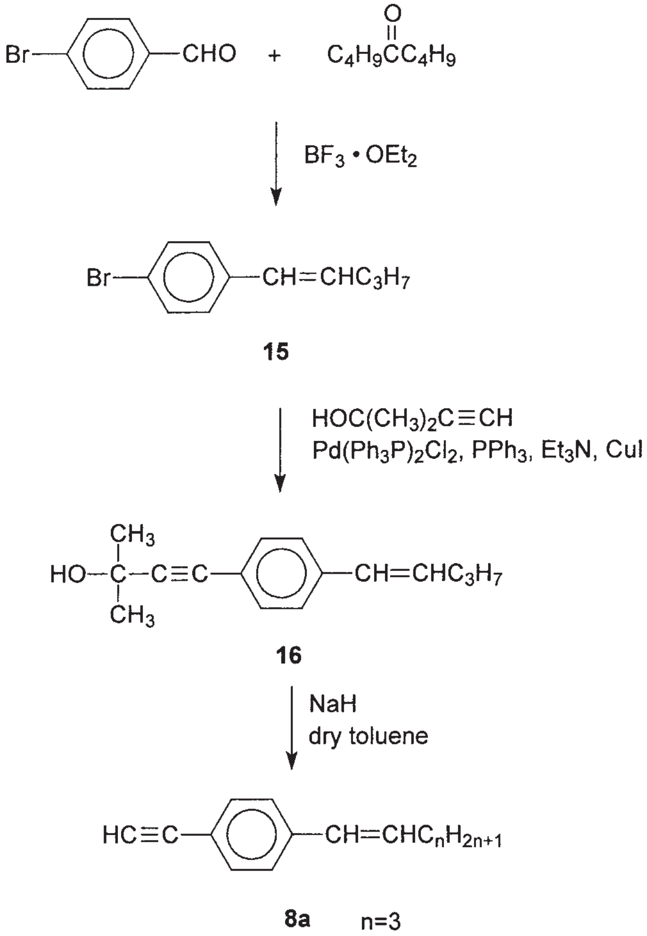


Figure 2. Olefin proton region of the ^{1}H NMR spectrum for the acetylene **8a** ($n=4$).

3. Mesomorphic properties

Transition temperatures (°C) for the new 1-olefinic diphenyldiacetylenes were determined by both hot stage polarizing microscopy and DSC. A comparison of these temperatures, as determined by microscopy along with nematic phase ranges, with those for the corresponding alkyl chain analogues is given in tables 1 and 2. Many of the dialkyldiacetylenes first reported by Wu and co-workers [1] were remade to obtain larger amounts of materials for further studies. Our data are used for the homologues that were remade, whereas Wu's data are used for those that were not. Many of the olefinic diacetylenes showed crystal to crystal changes; some showed different crystals having slightly different melting temperatures. For this comparison, the more stable or more likely to be seen crystal form was used for the melting temperatures.

All of these compounds showed only a nematic phase, except when $X=\mathrm{CF_3}$ ($n=3$) when both a nematic and a short range smectic A phase were seen. This suggests a strong preference for the nematic phase in these diacetylenes but that smectic phases can be observed with the proper structure modification. Both the melting and clearing temperatures increased in all the olefinic compounds except the melting temperature for $X=\mathrm{F}$, $n=3$ which decreased by 2.8°. However, the increase in clearing temperature was much greater (average increase $=68.9°$) than the increase in melting temperatures (average increase $=22.1°$). This gave mesogens with a much wider nematic phase range. A comparison of the nematic ranges in table 1 shows large increases, with the largest occurring when $X=\mathrm{F}$, $n=3$ (76.7°). Both the olefins with $X=\mathrm{F}$ or $\mathrm{CF_3}$ showed mesophases when none occurred in the alkyl analogues. Even some of the laterally substituted analogues showed large increases in the nematic phase range (table 2), although this seemed to decrease both with an additional substituent and with a longer olefinic chain. The extended nematic range and higher temperatures are probably due to the extended conjugation that occurs in the 1-olefins.



Scheme 3.

Enthalpies of melting, as determined by DSC (table 3), varied from 9.70 kJ mol^{-1} for $X=\mathrm{C_4H_9}$, $A=B=\mathrm{H}$, $n=4$ to 30.88 for $X=\mathrm{CN}$, $A=B=\mathrm{H}$, $n=3$. There appears to be no consistent trend in comparing these values for the olefins versus those for the alkyl chain.

Some crystal-to-crystal changes were also observed in a few of these 1-olefin diacetylenes **10a**. This is not

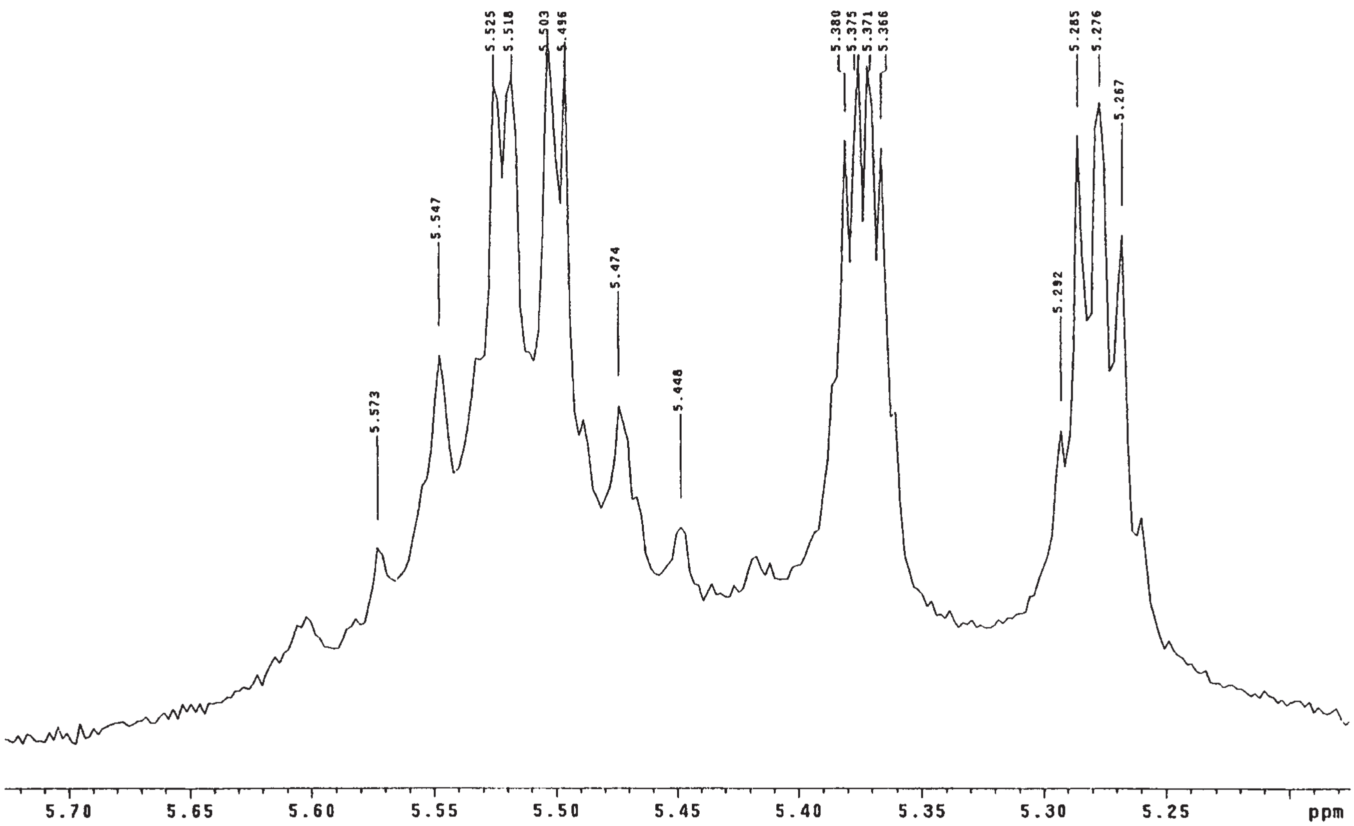


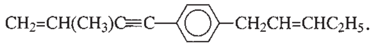
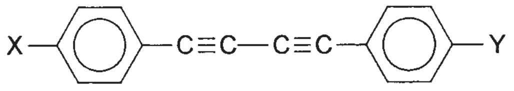
Figure 3. Olefin proton region of the ^{1}H NMR spectrum for .

Table 1. A comparison of mesomorphic Properties for:



	$Y = C_nH_{2n+1}$[a]					$Y = CH{=}CHC_nH_{2n+1}$[a]					
X	*n*	Cr	N	I	N range	*n*	Cr	N[c]	I	N range	Increase in N range
C_2H_5	4	40.3	44.4	98.4	54.0	2	98.6	104.4	174.1	69.7	15.7
F	4	65.5	90.1	90.7	0.6	2	69.2	93.0	165.7	72.7	72.1
CH_3	5	81.0	87.7	108.4	20.7	3	101.5	114.0	180.8	66.8	46.1
C_2H_5	5	[b]	44.7	101.7	57.0	3	64.1	82.3	177.0	94.7	37.7
C_6H_{13}	5	[b]	60.0	97.8	37.8	3	68.3	72.6	159.8	87.2	49.4
NC	5	142.2	149.0	161.9	12.9	3	156.7	174.8	227.8[d]	53.0	40.1
F	5	83.3	88.4	95.6	7.2	3	80.3	85.6	169.5	83.9	76.7
CF_3	5	96.6	—	102.7	0.0	3	123.1	130.6	140.4[e]	9.8	9.8
C_3H_7	6	28.4	44.8	104.0	59.2	4	47.2	53.6	163.3	109.7	50.5
C_4H_9	6	36.5	39.1	82.6	43.5	4	42.8	54.8	153.2	98.4	54.9
C_5H_{11}	6	[b]	60.0	97.8	37.8	4	76.0	79.4	155.9	76.5	38.7
F	6	[b]	76.0	80.1	4.1	4	68.0	82.7	150.0	67.3	63.2

[a] Data obtained by hot stage microscopy in °C: Cr = crystallization temperature on cooling at 2°C min^{-1}; N = crystal to nematic, unless otherwise indicated; I = nematic to isotropic liquid.

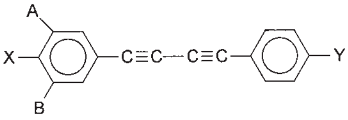
[b] These data from reference [1] were obtained by DSC; no crystallization temperatures were reported.

[c] Some crystal changes were observed; these are discussed in the text.

[d] This material decomposed rapidly near the clearing temperature, as shown by the brown sample colour and large shift in the temperature for this transition.

[e] Melts to smectic A phase at 127.8°C, A–N at 130.6°C.

Table 2. A comparison of mesomorphic properties for:



			$Y = C_nH_{2n+1}$					$Y = CH=CHC_nH_{2n+1}$					
X	*A*	*B*	*n*	Cr[a]	N	I	N range	*n*	Cr	N	I	N range	Increase in N range
F	F	H	5		—	81.9[b]	0	3	80.0	88.6	131.2	42.6	42.6
F	F	H	6		(48.5)	65.3[b]	m[c]	4	67.3	78.9	117.2	38.3	38.3
F	F	F	5	25.2	—	43.3	0	3	63.8	69.0	91.2	22.2	22.2
F	F	F	6	16.9	—	29.5	0	4	73.4	79.1	80.3	1.2	1.2

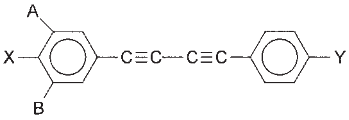
[a] Cr = Crystallization temperature on cooling the sample at 2°C min^{-1}; N = crystal to nematic transition; I = nematic to isotropic liquid; parentheses indicate a monotropic transition. Temperatures are in °C; data obtained by hot stage microscopy.

[b] Data are from references [8, 9].

[c] The normal N range could not be determined in a monotropic phase.

surprising since some of these had also been seen in the dialkyl analogues [5]. Such transitions were studied by microscopy and DSC but differentiating these from the effect of impurities on the melting/crystallization transitions was difficult. Many of these compounds had been made using the initial impure batches of the olefin acetylene **8a** containing the ethyl by-product **14** and the *cis*-olefin, which could be carried on to the synthesis of

Table 3. A comparison of enthalpy values (kJ mol^{-1}) for:



			$Y = C_nH_{2n+1}$			$Y = CH=CHC_nH_{2n+1}$		
X	*A*	*B*	*n*	ΔH_m[a]	ΔH_c[a]	*n*	ΔH_m	ΔH_c
C_2H_5	H	H	4	22.34	0.60	2	19.37	0.85
F	H	H	4	26.56[b]	0.37	2	23.68	0.62
CH_3	H	H	5	22.06	1.01	3	27.90	1.28
C_2H_5	H	H	5	17.85[c]		3	23.17	1.12
C_6H_{13}	H	H	5	14.62[c]		3	11.85	1.13
NC	H	H	5	33.11	0.38	3	30.88	[d]
F	H	H	5	24.69	0.53	3	19.56	0.79
CF_3	H	H	5	24.53		3	17.43[e]	0.92
F	F	H	5	30.86[f]		3	21.03	0.36
F	F	F	5	24.16[g]		3	26.72	0.24
C_3H_7	H	H	6	14.35	0.87	4	24.89	1.09
C_4H_9	H	H	6	10.26		4	9.70	1.00
C_5H_{11}	H	H	6	14.62[c]		4	17.29	1.66
F	H	H	6	31.10	0.21	4	24.28	0.77
F	F	H	6	24.99[f]		3	22.36	0.29
F	F	F	6	22.59		3	28.73	0.26

[a] Values were obtained from the first heating of virgin crystals. Melting may include crystal to crystal changes.

[b] A single broad peak was observed for Cr–N–I but I–N was observed on cooling.

[c] Values are from reference [1].

[d] Clearing temperature was too high to obtain value.

[e] Has an enantiotropic smectic A phase, enthalpy for A–N = 0.59.

[f] Values are from reference [8].

[g] Two peaks were observed on melting and recrystallization.

the diacetylenes to give trace amounts of similar analogues that might not be detected by GC. Therefore, it was necessary to consider impurities as a source for complex melting. Among the diacetylenes with $X=F$, complex melting involving different crystal forms was apparent by microscopy but not observed by DSC. These compounds were more difficult to purify than the other analogues suggesting that their complex melting may be due to impurities not detected by GC. One compound **10a** ($X=C_6H_{13}$, $n=3$, $A=B=H$) was resynthesized using the 1-olefin acetylene **8a** prepared using the reaction scheme 3. The clearing temperature did not change nor did it sharpen but an increase of about 2° in the melting temperature occurred along with some simplification of the melting. This compound showed no crystal changes by DSC but did show a rapid one on cooling in the microscope. One crystal form started to grow at 67.7° on cooling the nematic phase at $2^\circ\,\mathrm{min}^{-1}$. This converted to a second form at about 66.9°, or the second form started to appear in another area while the first one formed and then converted to the second. Such a rapid change would be difficult to see by DSC. No change was seen on reheating the second crystal form.

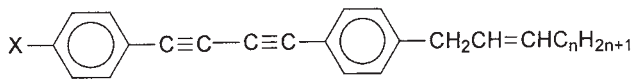
Two crystal forms were also observed in the diacetylenes with $A=B=H$ and $X=C_2H_5$, $n=2$ or $X=C_5H_{11}$, $n=4$. In the $n=2$ analogue, both virgin crystals and those formed on cooling converted to another form on heating at about 104°. This was also observed by DSC ($\Delta H_m=4.29$, $15.08\,\mathrm{kJ\,mol^{-1}}$). The $n=4$ analogue showed a crystal change on heating the virgin crystals at 73.7–74.6°, which was also observed by DSC. The first crystals formed on cooling melted at the same temperature as the second crystals formed on heating, but if these were cooled to room temperature and allowed to set overnight, they changed to the virgin crystals.

When $X=F$ and $n=2$, 3 or 4 ($A=B=H$), a mixture of large, flat plates and long, thin needles were observed by microscopy at the crystallization and melting transitions. These went through a variety of changes depending on sample history. While observing these, it appeared that the samples were acting like mixtures. One homologue ($n=2$) was repurified and showed some simplification in these transitions. No crystal changes were observed in the DSC. We now feel that these changes are probably due to the presence of trace amounts of impurities and that purer samples would show either no crystal changes or a rapid one such as that observed for $X=C_6H_{13}$, $n=3$.

Mesomorphic properties for the two 2-olefin diacetylenes (**10b** $A=B=H$) prepared are given in table 4. A comparison of the data for $X=C_6$ or F and $Y=C_5H_{11}$, $CH=CHC_3H_7$ or $CH_2CH=CHC_2H_5$ shows that both the melting and clearing transition temperatures for the 2-olefin compounds are lower than for either the alkyl or the 1-olefin chains. The range of the nematic phase is shorter than that for the 1-olefin but can be either longer ($X=C_6$) or shorter ($X=F$) than that for the alkyl chain. A limited comparison of the effect of the total chain length on mesomorphic properties (table 5) suggests that increasing the olefin chain length from 4 to 5 improves these properties (lower melting temperatures, wider nematic phase ranges), whereas, increasing the chain length from 5 to 6 provides no additional improvement.

In table 6 a comparison of the mesomorphic properties of these olefinic diphenyldiacetylenes (compounds 19 and 21–23) with those for other mesogens containing triple bonded connectors indicates that the olefinic diacetylenes are better in a number of properties than those for the other mesogens. The tolanes (compounds **1** and **2**) show no mesophases, although their melting temperatures are in the acceptable region. Increasing the core length by incorporating a triple bond into one of the terminal chains (compound **3**) increases the

Table 4. Mesomorphic properties for:

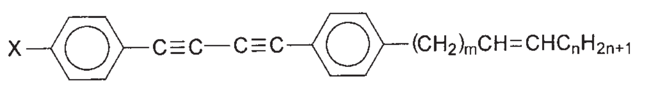


		Transition temperature °C					
X	*n*	Cr[a]	N	I	N range °C	ΔH_m kJ mol^{-1}	ΔH_c kJ mol^{-1}
C_6H_5	2	17.6	23.4	75.5	52.1	11.85	0.49
C_6H_5	3	18.2	45.0	64.0	19.0	19.44	0.48
F	2	16.9	66.6	67.5	0.9	23.43	0.21[b]
F	3	28.7	(55.1)	74.2	m	25.62	0.20[b]

[a] Microscopy: Cr = crystallization temperature obtained on cooling at $2^\circ\,\mathrm{min}^{-1}$, N = nematic phase, I = isotropic liquid, parentheses or m indicates a monotropic phase; DSC enthalpy values: ΔH_m = melting, ΔH_c = clearing.

[b] Value taken from the cooling curve.

Table 5. Effect of olefin chain length on mesomorphic properties for:



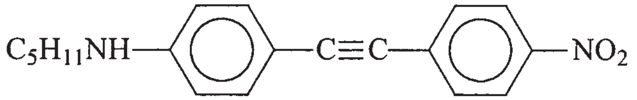
			Transition temperatures °C		
X	*m*	*n*	N[a]	I	N range
C_2	0	2	104.4	174.1	69.7
C_2	0	3	82.3	177.0	94.7
F	0	2	93.0	165.7	72.7
F	0	3	85.6	169.5	83.9
F	0	4	82.7	150.0	67.3
C_6	1	2	23.4	75.5	52.1
C_6	1	3	45.0	64.0	19.0
F	1	2	66.1	67.5	1.4
F	1	3	(55.1)	74.2	m

[a] N = nematic, I = isotropic liquid, and ( ) or m indicates a monotropic phase.

birefringence but also the melting temperature and still produces no mesophase. A nematic phase does occur when a nitrogen atom is incorporated into one of the phenyl rings (compound **4**) but again, the melting temperature is too high. Adding another triple bonded chain (compound **5**) simply increases the melting temperature but also destabilizes the nematic phase. A double bond-triple bond connector (compound **6**) gives an unstable material. Using a connector having a double bond flanked by two triple bonds (compounds **7** and **8**) produces wide range nematics with a high birefringence. Melting temperatures are below 100° but are still a little too high and there is the problem of isomer interconversion at the double bond. Isolating two triple bonds with a benzene ring giving the ditolanes (compounds **9**, **10**) yields unacceptably high melting temperatures and an increased chance for a smectic phase to form. Adding a triple-bonded terminal chain (compound **11**) only increases the melting temperature. Adding a nitrogen atom to the central ring of a ditolane (compound **12**) lowers the melting temperature but it is still above 100° and a smectic phase also occurs. This modification, however, does yield a wide range nematic phase. Adding a lateral methyl group to the central phenyl ring can decrease the melting temperature below 100° (compounds **13**–**15**) but the viscosity is too high. Some of the dialkyldiacetylenes (compounds **16**–**18**) have even lower melting temperatures but with reduced nematic ranges. These, however, have the advantage of having low viscosities and ΔH_m values while still having a large birefringence. Replacing one of the terminal alkyl chains with a 1-olefinic chain (compounds **19** and **21**) yields melting temperatures and nematic phases with ranges similar to those of the ditolanes but with lower viscosities. Particularly interesting is the compound **21** with $R = F$, $R' = CH{=}CHPr$, which has a much wider nematic phase range than its alkyl analogue (compound **20**), making it more useful in mixtures for increasing the dielectric constant. The 2-olefin analogues **22** and **23** have the advantage of lower melting temperatures than the 1-olefin analogues but with shorter nematic ranges. However, all of these diacetylenes have some instability to heat and UV light.

The problem in designing high birefringence nematic mesogens is not that a high birefringence cannot be obtained. It is a matter of designing such a structure which will incorporate the extended conjugation needed to obtain the high birefringence and still have a low melting temperature, a wide range nematic phase, low viscosity and be stable to heat and UV light.

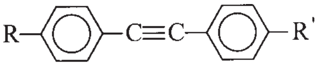
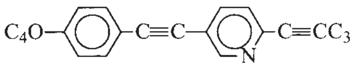
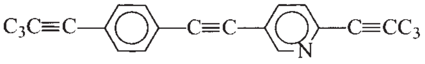
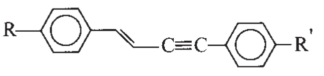
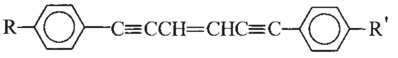
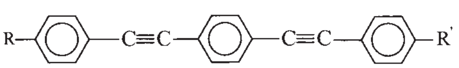
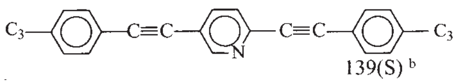
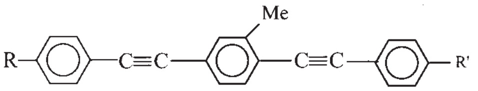
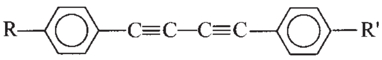
A simple comparison of the stability of the olefin **10a** ($n = 4$, $X = C_4H_9$, $A = B = H$) with that of PTTP 24/36 (eutectic mixture of **1** with $X = C_2$, $Y = C_4$ and $X = C_3$, $Y = C_6$) [1] suggests that the olefinic diacetylenes are less stable to light and heat than the dialkyl ones [5]. Such instability is undesirable for any application, making it essential to find a way to improve the stability of these materials. One way to do this is to add a dopant to prevent the reactions that occur during decomposition. Possible types of reactions occurring are auto-oxidation and polymerization. The addition of 4-methoxyphenol, a free radical scavenger, seemed to improve thermal stability but not UV stability. Since the mechanism of the polymerization of diacetylenes reportedly occurs through a carbene triplet state [26], it seemed reasonable that the addition of a non-fluorescent positive dichroism dye, absorbing in the blue and near UV, to the diacetylene mixture could inhibit polymerization and improve stability. One possibility is the tolane dyes such as *N*-methylamino-4-nitrotolane [27].



The addition of this material to the olefinic diacetylene mixture improved stability but 10–15% of it was needed which increased the viscosity. Nevertheless, these olefinic diacetylenes are of interest for beam-steering devices [28, 29].

Birefringence values for these materials will be reported elsewhere [5]. A comparison of the UV curves for the olefins **10a** and **10b** with that for PTTP-24 is shown in figure 4. The curve for the 2-olefin is essentially the same as that for PTTP-24, indicating that the double-bond is not conjugated to the benzene

Table 6. A comparison of the olefinic diacetylenes with some other related compounds having a connector containing a triple bond.

Compound	N[a]	I	N range °C	Δn	ΔH_m kJ mol^{-1}	Reference
						
1. $R = R' = C_3$		72.5	0	0.26		[19]
2. $R = F$, $R' = C_5$		64.2	0	0.18		[20]
3. $R = C_3$, $R' = C \equiv CC_3$		98.8	0	0.35		[19]
4. 	92.5	115.0	22.5			[21]
5. 	(100.5)	119.0	m			[21]
6. 	unstable					[22]
				~0.42		[23]
7. $R = R' = C_3$	95.3	162.3	67.0		22.0	
8. $R = C_3$, $R' = C_2$	81.4	148.8	67.4			
						
9. $R = R' = C_3$ 169.7(S)[b]	178.3	244.5	66.2	0.50		[19]
10. $R = R' = C_5$	151.1	212.3	61.2			[19]
11. $R = C_3$, $R' = C \equiv CC_3$	193.5	264.6	71.1			[19]
12.  139(S)[b]	144.0	237.0	93.0			[8]
				~0.38		[24][25]
13. $R = R' = C_3$	123.4	200.4	77.0		21.0	
14. $R = C_3$, $R' = C_5$	86.2	182.8	96.6		15.1	
15. $R = F$, $R' = C_5$	88.1	174.0	85.9		24.2	
				~0.28		[1]
16. $R = R' = C_3$	107.5	131.9	24.4		25.1	[1]
17. $R = C_3$, $R' = C_5$	62.0	115.3	53.3		14.3	[1]
18. $R = C_2$, $R' = C_5$	44.7	101.7	57.0		17.8	[1]
19. $R = C_2$, $R' = CH{=}CHPr$	82.3	177.0	94.7		23.2	
20. $R = F$, $R' = C_5$	88.4	95.6	7.2		24.7	
21. $R = F$, $R' = CH{=}CHPr$	85.6	169.5	83.9		22.9	
22. $R = C_6H_{13}$, $R' = CH_2CH{=}CHC_2H_5$	23.4	75.5	52.1		11.9	
23. $R = F$, $R' = CH_2CH{=}CHC_2H_5$	66.6	67.5	0.9		23.4	

[a] Abbreviations for transition temperatures (°C): S = crystal to smectic, N = crystal or smectic to nematic, I = nematic to isotropic liquid; Δn = optical birefringence obtained from the literature using different methods; ΔH_m enthalpy of melting.

[b] This compound melts to an unidentified smectic phase phase before forming the nematic phase.

ring; whereas, the tail of the curve for the 1-olefin is longer, supporting the 1-olefin structure.

A eutectic mixture of just the two fluorinated olefins **10a** ($X = F$, $A = B = H$, $n = 2$ and 3) (mixture B) gave a nematic phase of about the same range as the standard alkyl mixture (table 7) [28] but a much higher figure of merit and a higher clearing temperature. This figure of merit ($FoM = K_{11}\Delta n^2/\gamma_1$), where K_{11} is the bend elastic constant, Δn is the birfringence and γ_1, is an appropriate rotational viscosity, gives the approximate

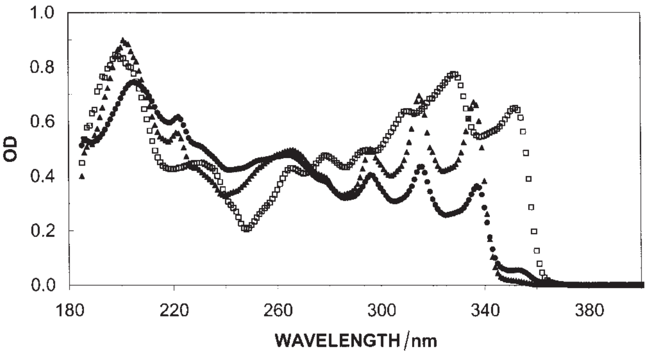
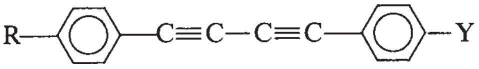


Figure 4. A comparison of the UV spectra for



▲ Blue: 1% $R=C_2H_5$, $Y=C_4H_9$ in ZLI-2359; ○ pink: 1% $R=C_6H_{13}$, $Y=CH_2CH=CHC_2H_5$ in MLC-6815; and □ black: 1% $R=C_2H_5$, $Y=CH=CHC_2H_5$ in ZLI-2359.

time-response performance of an LC modulator. Several alkyl-olefins ($X=C_nH_{2n+1}$) had to be added to obtain a room temperature nematic phase (mixture C) with a much wider nematic range and a figure of merit value about twice that of the standard mixture.

4. Conclusions

In an attempt to synthesize a series of asymmetrically disubstituted diphenyldiacetylenes having a 2-olefinic chain, a series of the 1-olefin analogues was isolated. The olefin chain was attached to a substituted benzene ring through a Wittig reaction that gave the 2-olefin in a *trans/cis*-ratio of *c.* 99.1/0.9%. Some of the ethyl analogue of this intermediate was formed but could be removed by vacuum distillation. This intermediate was converted to the 2-olefin protected acetylene, but removal of the protecting group caused double bond migration to the 1-olefin. The use of NaH in toluene to remove the protecting group avoided this migration giving only the 2-olefin acetylene. Introduction of the 1-olefin was more easily achieved by treating 4-bromobenzaldehyde with a ketone in the presence of $BF_3 \cdot OEt_2$. Both the 1- and 2-olefin acetylenes were coupled with a variety of 4-substituted bromophenyl acetylenes to give a series of 1- and 2-olefin diacetylenes.

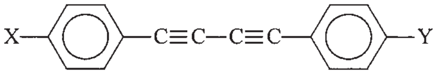
All the 1-olefin diacetylenes had higher melting and clearing temperatures than the alkyl analogues. A much larger increase in the clearing than in the melting temperature produced much wider nematic ranges. These mesogens have the advantage of wider nematic ranges, higher clearing temperatures, low viscosities and low enthalpies of melting. Their higher melting temperatures eliminate them as candidates for display materials but they are of interest for beam-steering applications. Instability to heat and light is the major disadvantage but this problem can be eliminated by the addition of a dopant. The 2-olefin diacetylenes had transition temperatures lower than those for both the 1-olefin and the alkyl analogues. The nematic ranges were narrower than those for the 1-olefins but could be wider or narrower than those for the alkyl analogues.

5. Experimental

5.1. *Characterization*

TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as the detectors.

Table 7. Eutectic Mixtures of:



Component	*X*	*Y*	T_m[a]	T_c	N range	FoM[b] $\mu m^2 s^{-1}$
Mixture A *(standard)*			~10	90	80	20
1	C_2	C_4				
2	C_3	C_6				
3	C_4	F				
4	C_6	F				
Mixture B			78	163	85	80
1	F	$CH=CHC_2H_5$(47%)				
2	F	$CH=CHC_3H_7$(53%)				
Mixture C			6	156	150	40
1	Mixture B					
2	C_2	$CH=CHC_2H_5$				
3	C_2	$CH=CHC_3H_7$				
4	C_3	$CH=CHC_4H_9$				

[a] Transition temperatures (°C): T_m = melting, T_c = clearing, N = nematic.
[b] Figure of merit; for definition see text.

Chromatographic purifications were done using flash chromatography on Fisher or EM Science silica gel (230–400 mesh). This absorbent was also used for silica gel filtrations. Capillary GC analysis was obtained using a Hewlett-Packard 5890 instrument equipped with a HP3395 Integrator, a FID detector and a Hewlett Packard 5 m ($n=3$) or 10 m ($n=2$, 4) methylsilicone gum column.

Temperature programming was from 100° at $20^\circ\,\mathrm{min}^{-1}$ to 250–270°, with a detector and injector temperature = 270–290° using a split valve rate of $182\,\mathrm{ml\,min}^{-1}$ and a column head pressure = $16.22\,\mathrm{ml\,min}^{-1}$ unless otherwise noted. For GC analysis of the dialkyldiphenyldiacetylenes, see reference [12]. All gradient GCs were run at $20^\circ\,\mathrm{min}^{-1}$. Retention times ($t_\mathrm{R}$) are in minutes. Melting points were determined using a Hoover–Thomas melting point apparatus and are corrected. These are not reported for compounds for which transition temperatures are given in tables 1, 2 and 4.

A Nicolet Magna FT/IR spectrophotometer was used to record IR spectra in cm^{-1} using NaCl plates. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ (unless otherwise indicated) with TMS as the internal standard, using a Varian Gemini-200 spectrometer equipped with a VXR-400 data station at 200 and 50 MHz, respectively. Chemical shifts are given in δ units and coupling constants in Hz. In order to achieve as complete an analysis of the data as possible for those compounds containing an olefinic chain, the olefin and neighbouring proton regions were expanded both vertically and horizontally. This was not done for all the spectra observed but for various representative compounds. When good resolution was possible, multiplicity and coupling constants are given; otherwise, complex peaks are indicated as a multiplet. Discussion of the 1- and 2-olefin proton regions is given in the text. ^{13}C NMR chemical shifts were compared with those values calculated using a Softshell ^{13}C NMR Module. Most variations from the calculated values were small. All four carbon atoms of the diacetylene group occurred at different chemical shifts whereas calculations showed only two different carbon chemical shifts. Ring-fluorinated compounds showed an additional splitting for some of the ring carbon atoms due to the ^{13}C–F coupling. UV spectra were obtained using a dual beam Perkin-Elmer lambda 9 photospectrometer. Two cells were used having 6 μm SiO_2 spacer posts with quartz substrates having no ITO coatings. Homogeneous alignments were obtained but the input UV light was unpolarized. The sample cell contained a 10% concentration of the diacetylene in the liquid crystal ZLI-2359 or MLC-6815 (EM Industries, Inc.). A reference cell containing only the solvent gave automatic reduction of its UV from that of the sample.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 POL polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of $2^\circ\mathrm{C\,min}^{-1}$. Discussions of texture identification of mesophases can be found in three books [30]. Crystallization temperatures were obtained by cooling the melt at $2^\circ\,\mathrm{min}^{-1}$ until crystals were formed, to ensure that all mesophases had been observed before this temperature. These crystals were reheated to obtain the melting temperatures and to confirm that these were not mesophases. DSC scans were run using a Perkin-Elmer DSC7 equipped with a TAC 7/PC instrument controller at a rate of $5^\circ\,\mathrm{min}^{-1}$, and calibrated using indium and zinc. During the course of this research, Perkin-Elmer Pyris Software was installed. A few scans were done using a Perkin-Elmer Pyris/DSC equipped with a TAC7/DX Controller. At least three scans were obtained for each compound: heating from virgin crystals to isotropic liquid, cooling this liquid until crystals formed and re-heating this crystallized material. Deviations from this approach or additional scans are indicated. The melting and clearing enthalpies recorded in table 3 were obtained by heating the virgin crystals. This usually gives the largest melting enthalpy value obtained from the most stable crystal formed.

The GC-Mass spectrum was obtained by Oneida Research Services, Inc., Whitesboro, NY, using a Finnigan Mass Spec 4500-SSQ Quadropole at 70 ev and a Hewlett Packard GC HP 5890A equipped with an Auto Sampler 7673, a J & W DB-1 30 m high resolution capillary column using a temperature program of 40° (2 min), 270° (5 min), 4 psig head pressure of He and an injector temperature of 270°C. Elemental analyses were also obtained from Oneida.

5.2. *Synthesis*

All temperatures are given in °C. Commercially available starting materials were used without purification except for some of the aldehydes, which were purified either by vacuum distillation or by extraction with a dilute KOH solution to remove any acid present. Exposure to light in all reactions involving a triple bond was minimized by keeping the hood lights off and the reaction flask wrapped with Al foil. Anhydrous reactions were run using flame-dried glassware under dry N_2 using newly dried solvents (Linde #4A molecular sieves). All acetylenes and diacetylenes were stored under argon in sealed containers at 5° when not in use. Organic extracts were dried over anhyd. Na_2SO_4 or $MgSO_4$. Tertiary butanol used in making the bromoacetylene was always distilled within a day of its use and stored over Linde 4A molecular sieves. Otherwise, yields were low.

5.2.1. 1-Bromoethynyl 4-substitutedbenzenes 9

The syntheses of all these compounds were reported earlier [3, 9], except for the trifluoro analogue **9** ($A = B = C = \mathrm{F}$). This was prepared in the same manner. Data for the precursor dibromolefin: purified yield = 90.9%. TLC ($\mathrm{CHCl_3}$) $R_\mathrm{f} = 0.86$, GC $t_\mathrm{R} = 2.54$ min (98.7%); IR (film) 3098, 3026 (v wk ArCH) and 1611, 1529 (med, str, ArC=C); ^{1}H NMR 7.34 (s, 1, $\mathrm{CH{=}CBr_2}$), 7.25–7.15 (m, 2, ArH). For the bromoacetylene **9**: purified yield = 62.0%, TLC (hexane) $R_\mathrm{f} = 0.59$, GC $t_\mathrm{R} = 1.15$ (99.7%), IR (film) 3085 (v wk, ArCH), 2210 (med, C≡C), 1615 (med, Ar) and 1589 (str, Ar); ^{1}H NMR 7.07 (dd, 2, 7.04 and 7.65, ArH).

5.2.2. 4-Bromophenethyl bromide 4

To a stirred solution of the alcohol **3** (49.2 g, 0.24 mol) at r.t. was added dropwise $\mathrm{PBr_3}$ (66.2 g, 0.24 mol). The reaction mixture was heated under reflux for 20 min in an oil bath (170°), stirred for 16 h at r.t. and then poured onto crushed ice (400 g). This mixture was diluted with $\mathrm{H_2O}$ (1.5 l) and extracted with $\mathrm{Et_2O}$. The organic layer was separated, washed with $\mathrm{H_2O}$, filtered to remove some insoluble material, dried and filtered. The solvent was removed from the filtrate *in vacuo* to give 65.7 g of the crude product. Purification of this material by chromatoraphy using EtOAc/hexane (1/10) gave the dibromide **4** as a colourless liquid (64.3 g, 96.5%). TLC (hexane) $R_\mathrm{f} = 0.54$, GC $t_\mathrm{R} = 4.52$ (99.78%); IR (film) 1597 (str Ar) and no OH; ^{1}H NMR 7.45 (d, 2, $J = 8.39$, ArH *ortho* to Br), 7.10 (d, 2, $J = 8.42$, ArH *ortho* to $\mathrm{CH_2}$), 3.55 (t, 2, $J = 7.35$, β-$\mathrm{CH_2}$) and 3.12 (t, 2, $J = 7.37$, $\mathrm{ArCH_2}$).

5.2.3. 2-(4-Bromophenyl)ethyltriphenylphosphonium bromide 5

A stirred mixture of the dibromide **4** (64.2 g, 0.24 mol), $\mathrm{PPh_3}$ (64.4 g, 0.24 mol) was heated at reflux for 40 min, cooled to r.t. and dissolved in $\mathrm{CH_2Cl_2}$ (450 ml). This solution was added dropwise to vigorously stirred $\mathrm{Et_2O}$ (4 l). The resulting white precipitate was collected by filtration, washed with $\mathrm{Et_2O}$ and dried *in vacuo* to give 127.3 g (99.4%) of the crude salt **5** as a colorless solid. IR (KBr) 1591 (wk, Ar), 1485 (str, Ar) and 1453 (str, $\mathrm{PCH_2}$ stretch); ^{1}H NMR (DMSO-d_6) 7.99–7.72 (m, 15, 3 $\mathrm{C_6H_5}$), 7.53 (d, $J = 8.38$, ArH *ortho* to Br), 7.30 (d, 2, $J = 8.26$, ArH *ortho* to $\mathrm{CH_2}$), 4.08–3.88 (m, 2, β-$\mathrm{CH_2}$) and 2.97–2.81 (m, 2, $\mathrm{ArCH_2}$). This material was used without further purification.

5.2.4. 4-(2-Hexen-2-yl)bromobenzene 6 *(n = 3)*

A mixture of the phosphonium bromide **5** (120.0 g, 0.23 mol), $\mathrm{K_2CO_3}$ (63.0 g, 0.46 mol) and 18-crown-6 (3.0 g, 0.011 mol) in dry $\mathrm{CH_2Cl_2}$ (1.5 l) under $\mathrm{N_2}$ was heated under reflux for 24 h. Then butyraldehyde (65.8 g, 0.91 mol) was added dropwise over 30 min and the mixture heated at reflux for 70 h. Insoluble material was removed from the hot reaction mixture by filtration and the solvent removed from the cooled filtrate *in vacuo* to give 89.5 g of the crude product. Purification by chromatography using hexane gave 45.8 g (83.9%) of the olefin **6** ($n = 3$) as a colourless liquid. IR (film) 1657 (wk, C=C), 1492 and 1460 (str, med, Ar). GC analysis showed the following peaks: $t_\mathrm{R} = 2.23$, (7.71%), 2.80 (1.07%) and 5.05 (90.49%) indicating that this material was not analytically pure. However, it was used successfully to prepare the olefinacetylene **8**. Some of this material (5.9 g) was distilled to obtain a purer sample. Two major fractions were collected: b.p. 95° (1.0 mm), 2.26 g, GC $t_\mathrm{R} = 3.54$ (99.26%) and b.p. 100° (1.5 mm), 2.12 g (total recovery 73.6%), GC 99.82%. ^{1}H NMR spectra for both these samples were the same and identical to that for the impure material: 7.40 (d, 2, $J = 8.42$, ArH *ortho* to Br), 7.06 (d, 2, $J = 8.79$, ArH *ortho* to $\mathrm{CH_2}$), 5.62–5.43 (m, 2, CH=CH), 3,35 (d, 2, 5.86, $\mathrm{ArCH_2}$), 2.11 (2, dt, $J = 7.32$, 5.49, δ-$\mathrm{CH_2}$), 1.41 (app sext, 2, $J = 7.45$, $\mathrm{CH_2}$) and 0.94 (t, 3, $J = 7.32$, $\mathrm{CH_3}$). ^{13}C NMR 140.4, 131.6, 130.3, 127.6, 119.7, 33.1, 29.5, 23.0 and 14.0.

The bromo-olefins **6** ($n = 1$ and 2) were prepared in the same manner:

n = 1. Twice the amount of aldehyde was used to compensate for losses due to its low boiling point, purified yield 62.0%. GC $t_\mathrm{R} = 1.17$ (5.78%), 2.24 (7.62%) and 2.33 (84.39%); ^{1}H NMR 7.39 (d, 2, $J = 8.38$, ArH *ortho* to Br), 7.06 (d, 2, $J = 8.14$, ArH *ortho* to $\mathrm{CH_2}$), 5.71–5.46 (m, 2, CH=CH), 3.35 (d, 2, $J = 6.22$, $\mathrm{ArCH_2}$) and 1.71 (d, 3, $J = 6.75$, $\mathrm{CH_3}$).

n = 2. Synthesis of this homologue was done many times to obtain enough material for preparing larger quantities of various olefin diacetylenes **10a**. As was true with the $n = 1$ and 3 homologues, a GC analysis of the crude product showed three major peaks: $t_\mathrm{R} = 1.22$ (5.28%), 1.61 (0.89%) and 2.94 (93.63%). These components could not be separated by chromatography using hexane; TLC (hexane) R_f values were the same. A MS-GC analysis of a chromatography fraction containing all three components indicated that the GC peak with $t_\mathrm{R} = 1.22$ had two parent peaks at 184, 186 which suggests the structure for 1-bromo-4-ethylbenzene *m*/*z* (ID, % relative abundance) 186 ($\mathrm{MBr^{81}}+$, 55.28), 184 ($\mathrm{MBr^{79}}+$, 58.50), 171 ($\mathrm{C_7H_6Br^{81}}+$, 98.39), 1.69 ($\mathrm{C_7H_6Br^{79}}+$, 100.00), 105

($C_6H_5CH_2CH_3$, 84, 79), 90 (C_7H_6+, 25.13), 77 (26.57), 63 (6.70) and 51 (31.13).

The two peaks at $t_R = 1.61$ and 2.94 showed the same molecular weight and fragmentation patterns indicating that these are the *cis*- and *trans*-isomers of the bromo-olefin **6** ($n = 2$) respectively: *m*/*z* (ID, % relative abundance of *trans*, *cis*, respectively) 226 ($MBr^{81}+$, 38.80, 34.37), 224 ($MBr^{79}+$, 37.62, 33.25), 197, 195 ($MBr^{81,79}+\text{-}C_2H_5$ 23.47, 20.01; 22.88, 20.51), 184, 182 ($Br^{81,79}$–$C_6H_4CH_2CH$, 24.48, 22.30; 25.38, 23.21), 171 ($Br^{81,79}C_7H_6+$, 16.88, 15.10), 169, (17.51, 15.38), 145 ($\cdot C_6H_4CH_2CH{=}CHC_2H_5$, 13.21, 13.92), 116 ($\cdot C_6H_4CH_2CH{=}CHCH_2+$, 100.00, 100.00), 90 (11.74, 11.50), 77 (7.81, 7.76), 63 (7.78, 7.83) and 51 (7.10, 7.65).

The *trans*-isomer was separated from both the *cis*-isomer and the ethyl compound by a careful vacuum distillation of a larger batch of material: crude wt = 48.0 g. TLC (hexane) $R_f = 0.53$, 0.34 and 0; GC showed many peaks with the major ones at $t_R = 1.21$ (1.54%), 1.60 (0.89%), 2.92 (71.05%) and 8.16 (12.18%). Removal of the triphenylphosphene oxide by chromatography (hexane) left 27.21 g of material. Vacuum distillation of this material at an oil bath temperature of 120° gave the following fractions: b.p. 25–79 (2–1.5 mm), 693 mg, GC $t_R = 1.23$ (51.62% ethyl), 1.62 (20.92% *cis*-olefin) and 2.94 (73.39% *trans*-olefin); b.p. 77–80° (1.5 mm), 4.31 g, GC $t_R = 1.22$ (0.38% ethyl), 1.61 (4.24% *cis*) and 2.96 (93.17% *trans*); b.p. 97–99 (3 mm), 12.21 g, GC $t_R = 1.61$ (0.65% *cis*) and 2.97 (99.25% *trans*); 89° (1.5 mm), 2.50 g, GC $t_R = 2.95$ (99.96% *trans*) and pot residue 1.56 g, GC $t_R = 2.95$ (99.10% *trans*). Characterization for the 99.96% *trans*-olefin is as follows: TLC (hexane) $R_f = 0.53$; IR (film) 1670 (wk, C=C) and 1486 (strAr); ^{1}H NMR 7.39 (d, 2, $J = 8.42$, ArH *ortho* to Br), 7.06 (d, 2, $J = 8.06$, ArH *ortho* to CH_2), 5.65–5.38 (m, 2, CH=CH), 3.34 (d, 2, $J = 5.82$, $ArCH_2$), 2.12 (dq, 2, $J = 6.60$, 6.96, δ-CH_2) and 0.97 (t, 3, $J = 7.51$, CH_3); ^{13}C NMR 140.4, 133.4, 131.6, 130.3, 126.9, 119.8, 33.0, 25.8, 20.8 and 14.5; elemental analysis calculated for $C_{11}H_{13}$ Br: C 58.69, H 5.82, Br 35.49; found C 58.61, H 5.82, Br 35.78. Fractions 4 and 5 represent a yield of 36.9% of the olefin **6** ($n = 2$). These were used to prepare the acetylene **8** ($m = 0$, $n = 3$). Less pure materials were used earlier.

Subtraction of the % ethyl compound from the crude product gives a *trans*/*cis* ratio = 94.06 to 0.94%; ^{1}H NMR for the 89.9% pure (GC) 1-bromo-4-ethylbenzene isolated from the distillation: 7.39 (d, 2, $J = 8.42$, ArH *ortho* to Br), 7.07 (d, 2, $J = 8.42$, ArH *ortho* to CH_2), 2.60 (q, 2, $J = 7.69$, CH_2) and 1.21 (t, 3, $J = 7.51$, CH_3).

5.2.5. *4-(3-Methyl-3-hydroxybut-1-ynyl)-hexen-2-ylbenzene 7 (n = 3)*

To a stirred mixture of the olefin **6** ($n = 3$, 38.6 g, 0.16 mol), 2-methyl-3-butyn-2-ol (34.0 g, 0.40 mol), CuI (267.4 mg, 1.40 mmol), PPh_3 (1.00 g, 3.84 mmol) and Et_3N (470 ml) under N_2 at r.t. was added $Pd(Ph_3P)_2Cl_2$ (267.2 mg, 0.38 mmol). This mixture was heated under reflux for 48 h, cooled to r.t., and the insoluble solids removed by filtration and washed with Et_2O. The solvent was removed from the filtrate *in vacuo*, the remaining material dissolved in Et_2O (500 ml) and washed with H_2O. The organic layer was dried, filtered and the solvent removed from the filtrate *in vacuo* to give 51.8 g of the crude product. Purification of this material by chromatography using 1/3 hexane CH_2Cl_2 gave 33.4 g (85.3%) of the protected acetylene **7** ($n = 3$) as a pale yellow liquid: TLC (1/3 hexane CH_2Cl_2) $R_f = 0.30$; IR (film) 3348 (str, broad OH), 2242 (wk, C≡C), 1657 (wk, C=CAr) and 1512, 1459 (str, med, Ar); ^{1}H NMR 7.33 (d, 2, $J = 8.05$, ArH *ortho* to C≡C), 7.11 (d, 2, $J = 7.77$, ArH *ortho* to CH_2), 5.60–5.45 (m, 2, CH=CH), 3.38 (d, 2, $J = 5.21$, $ArCH_2$), 2.20–2.16 (m, 2, δ-CH_2), 2.13 (s, 1, OH), 1.61 (s, 6, 2 CH_3), 1.42 (sext, 2, $J = 7.32$, CH_2) and 0.93 (*t*, 3, $J = 7.36$, CH_3).

The analogues with $n = 1$ and 2 were prepared in the same manner:

$n = 1$. Purified yield = 86.0%; ^{1}H NMR 7.33 (d, 2, $J = 8.05$, ArH *ortho* to C≡C), 7.12 (d, 2, $J = 7.78$, ArH *ortho* to CH_2), 5.66–5.51 (m, 2, CH=CH), 3.39 (d, 2, $J = 5.94$, $ArCH_2$), 2.11 (s, 1, OH), 1.71 (d, 3, $J = 5.62$, CH_3) and 1.61 (s, 6, 2 CH_3).

$n = 2$. Purified yield = 86.0%; ^{1}H NMR 7.34 (d, 2, $J = 8.19$, ArH *ortho* to C≡C), 7.12 (d, 2, $J = 7.77$, ArH *ortho* to CH_2), 5.57–5.45 (m, 2, CH=CH), 3.37 (d, 2, $J = 5.86$, $ArCH_2$), 2.15 (quint, 2, $J = 7.14$, δ-CH_2), 2.02 (s, 1, OH), 1.62 (s, 6, 2 CH_3) and 1.01 (t, 3, $J = 7.53$, CH_3). Use of the bromo-olefin purified by distillation gave this compound in a yield of 67.9%; GC showed primarily two peaks: $t_R = 4.56$ (1.99%) and 5.01 (97.18%). This material was converted to the acetylene **8a** ($n = 3$) without further purification.

5.2.6. *4-(3-Methyl-3-buten-1-ynl)-penten-2-ylbenzene* **17**

This compound was isolated as a liquid from the attempt to obtain the 2-olefin acetylene (**8b**, $n = 2$) by hydrolysis of the protected acetylene **7** ($n = 2$) in KO_t-Bu/toluene containing molecular sieves. Characterization data are as follows: GC $t_R = 2.57$ (1.81%), 4.6 (93.17%) and 5.73 (3.68%); IR (film) 2213 (wk, C≡C), 1618 (med, Ar and C=C) and 1508 (str, Ar); ^{1}H NMR 7.36 (d, 2, $J = 8.06$, ArH *ortho* to C≡C), 7.13 (d, 2, $J = 8.42$, ArH *ortho* to CH_2), 5.57–5.44 (m, 2, CH=CH, see figure 3), 5.38 (q, 1, $J=0.97$, CH_2 proton *cis* to CH_3), 5.28 (q, 1, $J=1.67$, CH_2 proton *trans* to CH_3), 3.38 (d, 2, $J=5.86$, $ArCH_2$), 2.15 (app. quint, 2, $J=6.59$, CH_2), 1.98 (t, 3, $J=0.73$, CCH_3) and 1.01 (t, 3, $J=6.04$, ethyl CH_3); ^{13}C NMR 141.7, 133.2, 131.8, 128.5, 127.1, 127.0, 121.9, 121.8, 121.7, 120.8, 112.5, 90.2, 88.7, 33.5, 23.7, 23.8, 20.8 and 14.5.

*5.2.7. 4-Ethynyl(hexen-1-yl)benzene **8a** (n=4), Method 1*

A mixture of the protected acetylene **7** ($n=3$, 33.2 g, 0.14 mol) and KOH (23.1 g, 0.41 mol) in 2-propanol (450 ml) was heated under reflux for 48 h, cooled to r.t. and the solvent removed *in vacuo*. The remaining material was dissolved in Et_2O (300 ml), washed twice with H_2O (300 ml), dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave the crude product (23.8 g, 94.0%). Purification of this material by chromatography using hexane gave 20.1 g (79.4%) of the alkyne **8a** ($n=4$) as a colourless liquid: TLC (hexane) $R_f=0.53$; IR (film) 3289 (str, $C\equiv CH$), 2111 (med, $C\equiv C$) and 1651, 1611 (med, $ArC=C$); ^1H NMR 7.41 (d, 2, $J=8.22$, ArH *ortho* to $C\equiv C$), 7.28 (d, 2, $J=8.42$, ArH *ortho* to CH), 6.36 (d, 1, $J=15.80$, ArCH), 6.24 (dt, 1, $J=15.87$, 5.82, β-CH), 3.08 (s, 1, $C\equiv CH$), 2.21 (dt, 2, $J=5.94$, 7.00, γ-CH_2), 1.53–1.20 (m, 4, 2 CH_2) and 0.92 (t, 3, $J=7.22$, CH_3). GC analysis showed two peaks at $t_R=4.51$ (7.43% 2-olefin) and 4.99 (92.12% 1-olefin) (starting temperature = 70°). This material was used successfully to prepare the diacetylenes **10a**. With fewer impurities to remove, these materials were easier to purify to analytical purity.

The analogues with $n=2$ and 3 were prepared in the same manner:

n=2. Reflux time 24 h, purified yield = 73.7%; ^1H NMR 7.42 (d, 2, $J=8.39$, ArH *ortho* to $C\equiv C$), 7.38 (d, 2, $J=8.34$, ArH *ortho* to CH), 6.41–6.20 (m, 2, CH=CH), 3.08 (s, 1, $C\equiv CH$), 2.24 (dq, 2, $J=7.39$, 7.39, CH_2) and 1.08 (t, 3, $J=7.42$, CH_3), GC $t_R=1.84$ (1.38%), 3.22 (4.37%), 3.32 (1.77%) and 3.62 (91.13% 1-olefin) (starting temperature = 70°).

n=3. Purified yield = 80.3%; GC $t_R=2.70$ (3.90%), 2.94 (5.72%, 2-olefin) and 3.10 (86.58%, 1-olefin); ^1H NMR data is the same as given in the following method 2 preparation.

*5.2.8. 4-(Penten-1-yl)bromobenzene **15***

To a stirred solution of 4-bromobenzaldehyde (20.36 g, 0.110 mol) and 5-nonanone (14.23 g, 0.10 mol) in hexane (200 ml) under N_2 at r.t. was slowly added $BF_3{\cdot}OEt_2$ (10.22 g, 0.72 mol). The reaction mixture was heated under reflux for 1 h, cooled to r.t., H_2O (500 ml) slowly added and then extracted with Et_2O (4 × 400 ml). The organic layer was separated, dried, filtered and the solvent removed from the filtrate to give 38.3 g of the crude product. Chromatography of this material using hexane gave 17.1 g (75.9%) of the liquid bromo-olefin **15**: TLC (hexane) $R_f=0.75$ (major) and 0.62 (minor); GC $t_R=2.90$ (5.51%) and 3.27 (94.30%); IR (film) 1657.0 (med, $ArC=C$), and 1597.8 (wk, Ar); ^1H NMR 7.40 (d, 2, $J=8.43$, ArH *ortho* to Br), 7.19 (d, 2, $J=8.42$, ArH *ortho* to CH), 6.32 (d, 1, $J=16.12$, ArCH), 6.20 (dt, 1, $J=15.75$, 5.87, β-CH), 2.17 (dt, 2, $J=6.59$, 7.41, γ-CH_2), 1.48 (app. sext, 2, $J=7.32$, δ-CH_2) and 0.94 (t, 3, $J=7.32$, CH_3); ^{13}C NMR 137.0, 132.0, 131.7, 129.0, 127.6, 120.5, 35.3, 22.6 and 13.9; elemental analysis calculated for $C_{11}H_{13}Br$: C 58.69, H 5.82; found C 56.44, H 5.67%.

*5.2.9. 4-(3-Methyl-3-hydroxybut-1-ynyl)-penten-1-ylbenzene **16***

This compound was prepared in the same manner as the 2-olefin analogue 7 ($n=2$) using a reflux time of 42 h. Chromatography of the crude product (29.2 g) using CH_2Cl_2 gave 15.0 g (86.8%) of the protected acetylene **16** as a yellow solid: m.p. 59.0–62.0°; TLC (hexane) $R_f=0.18$; GC $t_R=4.88$ (2.09%), 5.01 (4.40%) and 5.30 (93.17%); IR (Nujol) 3217 (str, OH), 2230 (v wk, $C\equiv C$), 1664 (v wk, C=C) and 1512 (med Ar); ^1H NMR 7.34 (d, 2, $J=8.79$, ArH to $C\equiv C$), 7.26 (d, 2, $J=8.79$, ArH *ortho* to CH), 6.36 (d, 1, $J=16.11$, ArCH), 6.23 (dt, 1, $J=15.75$, 5.95, olefin CH), 2.19 (dt, 2, $J=5.86$, 7.32, γ-CH_2), 2.07 (s, 1, OH), 1.61 (s, 6, 2 CH_3), 1.49 (app. sext, 2, $J=7.32$, δ-CH_2) and 0.95 (t, 3, $J=7.14$, CH_3).

*5.2.10. 4-Ethynyl(penten-1-yl)benzene **8a** (n=3), Method 2*

A stirred mixture of the protected acetylene **16** (14.0 g, 61.3 mmol) and NaH (60% in mineral oil, 349 mg, 14.5 mmol) in dry toluene (150 ml) under N_2 was heated to reflux in a short path distillation apparatus until the boiling point was reached (*c.* 110°) and 70 ml of distillate collected. The reaction mixture was cooled to r.t., filtered and the solvent removed from the filtrate *in vacuo*. The remaining material was dissolved in CH_2Cl_2 (400 ml) and washed three times with H_2O (400 ml). The organic extracts were combined, dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave 12.4 g of the crude product. Purification of this material by chromatography using hexane gave 6.50 g (62.3%) of the acetylene **8a** as a colourless liquid: TLC (hexane) $R_f=0.50$; GC $t_R=2.85$ (99.11% 1-olefin) and 2.52 (0.56% 2-olefin); IR (film) 3309 (str, $C\equiv CH$) 2112 (med, $C\equiv C$), 1658 (med, $C\equiv C$), 1613 (med, Ar) and 1511 (str, Ar); ^{1}H NMR 7.41 (d, 2, $J=8.79$, ArH *ortho* to C≡C), 7.28 (d, 2, $J=8.43$, ArH *ortho* to CH), 6.36 (d, 1, $J=15.75$, ArCH), 6.24 (dt, 1, $J=15.97$, 6.04, β-CH), 3.08 (s, 1, C≡CH), 2.19 (dt, 2, $J=5.49$, 7.50, γ-CH$_2$), 1.60 (m, 2, δ-CH$_2$) and 0.95 (t, 3, $J=7.14$, CH$_3$); ^{13}C NMR 138.6, 132.7, 132.5, 129.5, 126.0, 120.4, 84.1, 76.6, 35.4, 22.7 and 14.0.

5.2.11. *4-Ethynyl(penten-2-yl)benzene* ***8b*** *(n=2)*

The protected acetylene 7 ($n=2$) was treated with NaH in the same manner as compound **16** to give 745 mg (99.9%) of the crude product. Only the 2-isomer was detected by GC and ^{1}H NMR. Purification of this material by chromatography using hexane gave the following fractions: 101 mg; GC $t_R=2.08$ (2.54%), 2.51 (96.46%, *trans*-2-olefin), 2.68 (0.64%, *cis*-2-olefin) and 2.82 (0.11%, 1-olefin); 300 mg, GC $t_R=2.50$ (99.27%, *trans*-2-olefin), 2.67 (0.38%, *cis*-2-olefin) and 2.81 (0.84%, 1-olefin); 300 mg, GC $t_R=2.49$ (99.67%, *trans*-2-olefin), 2.66 (0.24%, *cis*-2-olefin) and 2.81 (0.05%, 1-olefin). The total weight for fractions 2 and 3 was 547 mg (73.3%). Data for fraction 3 were as follows: IR (film) 3289 (str, C≡CH), 2104 (wk, C≡C) and 1663 (wk, Ar); ^{1}H NMR 7.41 (d, 2, $J=8.42$, ArH *ortho* to C≡C), 7.14 (d, 2, $J=8.42$, ArH *ortho* to CH$_2$), 5.65–5.38 (m, 2, CH=CH), 3.39 (d, 2, $J=5.86$, ArCH$_2$), 3.01 (s, 1, C≡CH), 2.15 (app. quint, 2, $J=6.96$, δ-CH$_2$), and 1.00 (t, 3, $J=7.51$, CH$_3$).

This same method was used to prepare **8b** ($n=3$). Purification was by chromatography using hexane, yield=97.0%; GC $t_R=3.40$ (99.13% *trans*-2-olefin). IR and ^{1}H NMR data were essentially the same as for **8b** ($n=2$). ^{13}C NMR 142.4, 132.4, 131.5, 128.5, 127.6, 119.7, 84.0, 81.4, 33.6, 29.5, 23.0 and 14.0.

5.2.12. *4-[4-(Hexen-1-yl)phenyl-1,3-butadiynyl]-4-pentylbenzene* ***10a*** *(A=B=H, X=C$_5$H$_{11}$, n=4)*

A mixture of the acetylene **8** ($m=0$, $n=4$, 1.47 g, 7.96 mmol), CuCl (6.31 mg, 0.06 mmol) and *n*-propylamine (4.71 g, 79.63 mmol) in MeOH (45 ml) was stirred at r.t. for 10 min under N$_2$. To this mixture was added NH$_2$OH·HCl (390 mg, 5.57 mmol); stirring was continued at r.t. for 10 min and the mixture was cooled to 0°. A solution of the bromoacetylene **9** ($A=B=$H, $X=$C$_5$H$_{11}$, 2.00 g, 7.96 mmol) in MeOH (45 ml) was added dropwise, and the reaction mixture was stirred at 0° for 3 h and then filtered. The collected solid was washed with MeOH and dissolved in hexane. This solution was washed three times with H$_2$O (100 ml), dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave 1.77 g (63.0%) of the crude product. Recrystallization of this material twice from CH$_3$CN gave 1.51 g (53.0%) of a colourless solid identified as the diacetylene **10a** ($A=B=$H, $X=$ C$_5$H$_{11}$, $m=0$, $n=4$): TLC (hexane) $R_f=0.35$; GC $t_R=12.5$ (99.92%); IR (Nujol) 2220 (wk, C≡C), 1650 (wk, C=C), 1604 (wk, Ar) and 1506 (med, Ar); ^{1}H NMR 7.44 (d, 2, $J=8.26$, ArH *meta* to olefin), 7.43 (d, 2, $J=8.06$, ArH *meta* to C$_5$), 7.28 (d, 2, $J=8.42$, ArH *ortho* to olefin), 7.14 (d, 2, $J=8.06$, ArH *ortho* to C$_5$), 6.37 (d, 1, $J=16.12$, ArCH), 6.26 (dt, 1, $J=15.84$, 5.90, olefin β-CH), 2.60 (t, 2, $J=7.33$, ArCH$_2$C$_4$), 2.22 (dt, 2, $J=5.87$, 6.81 olefin γ-CH$_2$), 1.68–1.50 (m, 2, olefin δ-CH$_2$), 1.50–1.24 (m, 8, 4 CH$_2$), 0.92 (t, 3, $J=6.95$, olefin CH$_3$) and 0.89 (t, 3, $J=6.79$, alkyl CH$_3$); ^{13}C NMR 144.7, 139.0, 133.3, 132.9, 132.6, 129.3, 128.8, 126.1, 120.1, 119.2, 82.4, 81.8, 77.5, 74.7, 73.7, 36.2, 33.1, 31.7, 31.1, 22.8, 22.5, 14.25, and 14.21; elemental analysis calcd for C$_{27}$H$_{30}$: C 91.47, H 8.53; found C 91.17, H 8.51%.

The following analogues (**10a**) were prepared in the same manner. Experimental details, which differ from those given above, are provided:

A=B=H, n=2

X=C$_2$H$_5$. Purified by chromatography using hexane followed by recrystallization from CH$_3$CN, yield= 31.0%: GC $t_R=10.4$ (100.00%); ^{1}H NMR 7.44 (d, 4, $J=8.14$, ArH *ortho* to C≡C), 7.30 (d, 2, $J=8.26$, ArH *ortho* to olefin), 7.16 (d, 2, $J=7.77$, ArH *ortho* to C$_2$), 6.42–6.22 (m, 2, CH=CH), 2.56 (q, 2, $J=7.64$, ArCH$_2$), 2.25 (dq, 2, $J=4.76$, 7.32, olefin γ-CH$_2$), 1.23 (t, 3, $J=7.60$, olefin CH$_3$), and 1.09 (t, 3, $J=7.43$, alkyl CH$_3$); ^{13}C NMR 146.0, 139.0, 134.7, 132.9, 132.7, 128.4, 128.2, 126.1, 120.1, 119.2, 82.3, 81.8, 74.6, 73.7, 29.1, 26.4, 15.5, 13.7.

X=F. Purified yield=37.0%: GC $t_R=8.19$ (99.15%); ^{1}H NMR 7.51 (dd, 2, $J=8.83$, 5.58, ArH *meta* to F), 7.45 (d, 2, $J=8.47$, ArH *meta* to olefin), 7.30 (d, 2, $J=8.31$, ArH *ortho* to olefin), 7.03 (t, 2, $J=8.57$, ArH *ortho* to F), 6.39–6.20 (m, 2, CH=CH), 2.25 (dq, 2, $J=7.33$, 4.76, γ-CH$_2$) and 1.10 (t, 3, $J=7.47$, CH$_3$).

A=B=H, n=3

X=CH$_3$. Purified yield=49.4%: GC $t_R=10.89$ (98.57%); and ^{1}H NMR 7.43 (d, 2, $J=8.35$, ArH *meta* to olefin), 7.41 (d, 2, $J=8.18$, ArH *meta* to CH$_3$), 7.28 (d, 2, $J=8.43$, ArH *ortho* to olefin), 7.13 (d, 2, $J=7.77$, ArH *ortho* to CH$_3$), 6.36 (d, 1, $J=15.83$, ArCH), 6.25 (dt, 1, $J=15.87$, 6.17, β-CH), 2.35 (s, 3, ArCH$_3$), 2.19 (app. sext, 2, $J=7.29$, γ-CH$_2$), 1.48 (app. sext, 2, $J=7.29$, δ-CH$_2$) and 0.94 (t, 3, $J=7.33$, CH$_3$).

X=C$_2$H$_5$. Purified yield=29.8%: GC $t_R=11.78$ (97.89%) decomposes when heated, 20.17 (1.60%); ^{1}H NMR 7.45 (d, 4, $J=8.06$, ArH *ortho* to C≡C), 7.30 (d, 2, $J=8.10$, ArH *ortho* to olefin), 7.17 (d, 2, $J=7.97$, ArH *ortho* to C$_2$), 6.38 (d, 1, $J=16.11$, ArCH), 6.26 (dt, 1, $J=16.03$, 6.26, β-CH), 2.66 (q, 2, $J=7.57$, ArCH$_2$), 2.20 (dt, 2, $J=6.23$, 7.14, olefin γ-CH$_2$), 1.50 (app. sext, 2, $J=7.33$, δ-CH_2), 1.23 (t, 3, $J=7.51$, ethyl CH_3) and 0.95 (t, 3, $J=7.33$, olefin CH_3).

$X=C_6H_{13}$. Purified yield = 44.0%: GC $t_R=26.66$ (100.00%); ^{1}H NMR 7.44 (d, 4, $J=8.06$, ArH *meta* to olefin and CH_2), 7.29 (d, 2, $J=8.42$, ArH *ortho* to olefin), 7.14 (d, 2, $J=7.69$, ArH *ortho* to CH_2), 6.55–6.18 (m, 2, CH=CH), 2.60 (t, 2, $J=7.87$, $ArCH_2$), 2.20 (app. quint, 2, $J=6.59$, olefin γ-CH_2), 1.90–1.44 (m, 4, alkyl β-CH_2 and olefin δ-CH_2), 1.44–1.20 (m, 6, 3 CH_2), 0.95 (t, 3, $J=6.96$, olefin CH_3) and 0.91 (t, 3, $J=6.59$, alkyl CH_3); ^{13}C NMR 114.7, 138.9, 132.1, 132.9, 132.6, 129.5, 128.8, 126.1, 120.1, 119.1, 82.3, 81.8, 74.6, 73.7, 36.2, 35.4, 31.9, 31.4, 29.1, 22.8, 22.6, 14.3 and 14.0; elemental analysis calcd for $C_{27}H_{30}$ C 91.47, H 8.53, found C 91.20, H 8.54.

$X=CF_3$. Purified by chromatography using hexane followed by recrystallization from abs EtOH, yield = 28.6%: GC $t_R=8.80$ (99.82%); ^{1}H NMR 7.63 (d, 2, $J=9.52$, ArH *meta* to CF_3), 7.58 (d, 2, $J=9.52$, ArH *ortho* to CF_3), 7.46 (d, 2, $J=8.42$, ArH, *meta* to olefin), 7.29 (d, 2, $J=8.42$, ArH, *ortho* to olefin), 6.38 (d, 1, $J=16.11$, ArCH), 6.25 (dt, 1, $J=15.75$, 5.86, β-CH), 2.21 (dt, 2, $J=5.49$, 7.32, γ-CH_2), 1.60–1.40 (m, 2, δ-CH_2) and 0.96 (t, 3, $J=7.32$, CH_3); ^{13}C NMR 139.4, 133.4, 133.0, 132.8, 131.2, 130.5, 129.4, 126.7, 126.1, 126.0, 125.6, 125.5, 121.3, 119.5, 83.5, 80.2, 76.6 (possibly overlaps with $CDCl_3$), 73.9, 35.4, 22.6 and 13.9.

$X=CN$. Purified by chromatography using hexane followed by recrystallization from abs EtOH, yield = 54.5%: GC $t_R=14.02$ (100.00%); ^{1}H NMR 7.63 (d, 2, $J=7.70$, ArH *ortho* to CN), 7.59 (d, 2, $J=8.05$, ArH *meta* to CN), 7.46 (d, 2, $J=8.42$, ArH *meta* to olefin), 7.32 (d, 2, $J=8.42$, ArH *ortho* to olefin), 6.45–6.20 (m, 2, CH=CH), 2.21 (dt, 2, $J=5.49$, 7.32, γ-CH_2), 1.51 (m, 2, δ-CH_2) and 0.96 (t, 3, $J=7.32$, CH_3); ^{13}C NMR 139.6, 133.6, 133.0, 132.3, 129.3, 127.1, 126.2, 119.2, 118.5, 112.4, 84.6, 79.7, 78.5, 73.8, 35.4, 22.6, and 14.0.

$X=F$. During removal of the solvent from the filtered reaction mixture, an insoluble solid precipitated and was removed by filtration. Work-up was then continued in the usual manner, purified yield = 27.8%: TLC (hexane) $R_f=0.27$, GC $t_R=9.10$ (99.89%); IR (Nujol) 2151 (w, C≡C), 1648 (v wk) 1598 (med, ArC=C), 1505 (str, Ar) and 1159 (med, C–F); ^{1}H NMR 7.50 (dd, 2, $J=7.73$, 5.33, ArH *meta* to F), 7.44 (d, 2 $J=8.34$, ArH *ortho* to olefin), 7.29 (d, 2, $J=8.30$, ArH *meta* to olefin), 7.02 (t, 2, $J=8.50$, ArH *ortho* to F), 6.37 (d, 1, $J=15.83$, ArCH), 6.28 (dt, 1 $J=15.83$, 6.01, β-CH), 2.20 (dt, 2, $J=5.41$, 7.36, olefin γ-CH_2), 1.49 (app. sext, 2, $J=7.31$, CH_2) and 0.95 (t, 3, $J=7.33$, CH_3); ^{13}C NMR 165.6, 160.7, 139.1, 134.8, 134.6, 133.2, 132.9, 129.4, 119.8, 118.20, 118.17, 116.3, 115.8, 82.1, 80.8, 74.3, 74.11, 74.08, 35.4, 22.6 and 14.0.

A = B = H, n = 4

$X=C_3H_7$. Purified by chromatography using hexane and recrystallized from CH_3CN, yield = 36.0%: GC $t_R=16.72$ (100.00%); ^{1}H NMR 7.44 (d, 4, $J=7.24$, ArH *ortho* to C≡C), 7.29 (d, 2, $J=8.30$, ArH *ortho* to olefin), 7.14 (d, 2, $J=8.19$, ArH *ortho* to C_3H_7), 6.37 (d, 1, $J=15.87$, ArCH), 6.26 (dt, 1, 15.84, 5.97, olefin β-CH), 2.59 (t, 2, $J=7.32$, $ArCH_2$), 2.22 (dt, 2, $J=5.86$, 6.96, olefin γ-CH_2) 1.63 (app. sext, 2, $J=7.57$, olefin δ-CH_2), 1.51–1.22 (m, 4, 2 CH_2), 0.93 (t, $J=7.33$, olefin CH_3) and 0.92 (t, 2, $J=7.12$, alkyl CH_3).

$X=C_4H_9$. Purified by chromatography using hexane and recrystallized from CH_3CN, yield = 43.7%: GC $t_R=18.89$ (99.83%); ^{1}H NMR 7.44 (d, 2, $J=8.26$, ArH *meta* to olefin), 7.43 (d, 2, $J=8.06$, ArH *meta* to C_4H_9), 7.29 (d, 2, $J=8.43$, ArH *ortho* to olefin), 7.14 (d, 2, $J=8.14$, ArH *ortho* to C_4H_9), 6.37 (d, 1, $J=15.83$, ArCH), 6.26 (dt, 1, $J=15.79$, 5.55, olefin β-CH), 2.51 (t, 2, $J=7.33$, $ArCH_2$), 2.22 (dt, 2, $J=5.86$, 6.90 olefin γ-CH_2), 1.68–1.23 (m, 8, 4 CH_2) and 0.92 (t, 6, $J=7.04$, 2 CH_3).

$X=F$. Purified yield = 33.0%: $t_R=11.10$ (99.69%); ^{1}H NMR 7.51 (dd, 2, $J=5.54$, 9.09, ArH *meta* to F), 7.45 (d, 2, $J=8.56$, ArH *meta* to olefin), 7.30 (d, 2, $J=8.38$, ArH *ortho* to olefin), 7.03 (t, 2, $J=8.73$, ArH *ortho* to F), 6.37 (d, 1, 15.75, ArCH), 6.27 (dt, 1, $J=16.11$, 5.74, olefin β-CH), 2.22 (dt, 2, $J=5.86$, 6.86, olefin γ-CH_2), 1.52–1.24 (m, 4, 2 CH_2) and 0.92 (t, 3, $J=6.96$, CH_3); ^{13}C NMR 165.6, 160.6, 139.1, 134.8, 133.5, 132.9, 129.2, 126.1, 119.8, 118.1, 116.3, 115.8, 112.5, 82.1, 80.8, 74.2, 74.0, 74.1, 33.0, 31.6, 22.5 and 14.2.

A = X = F, B = H

n = 3. Purified by recrystallization from abs EtOH, yield = 5.0%: TLC (hexane) $R_f=0.38$; GC $t_R=8.87$ (99.12%); ^{1}H NMR 7.45 (d, 2, $J=8.18$, ArH *meta* to olefin), 7.30 (d, 2, $J=8.30$, ArH *ortho* to olefin), 7.38–7.04 (m, 3, ArF_2H_3), 6.38 (d, 1, $J=15.80$, ArCH), 6.27 (dt, 1, $J=16.08$, 5.68, olefin β-CH), 2.21 (dt, 2, $J=7.20$, 5.50, olefin γ-CH_2), 1.50 (app. sext, 2, $J=7.33$, CH_2) and 0.95 (t, 3, $J=7.32$, CH_3).

A small amount of symmetrical difluordiacetylene was isolated from the filtrate and recrystallized from 93% EtOH: transition temperatures 125.7–127.6 (Cr–I) and 114.7 (I–Cr); GC $t_R=5.58$ min (95.89%); ^{1}H NMR 7.35 (dd, 2, $J=7.35$, 2.20 ArH *ortho* to F and C≡C), 7.30–7.22 (m, 2, ArH *meta* to F and *ortho* to C≡C) and 7.22–7.06 (m, 2, ArH *meta* to C≡C); ^{13}C NMR (ID based on calculated values): 154.2, 153.9, 152.8, 152.5 (benzene 4-C), 149.1, 148.9, 147.8, 147.5 (benzene 3-C), 129.7, 129.6, 129.56, 129.48 (benzene ring 6-C), 121.8, 121.4 (benzene 2-C), 118.6, 118.54, 118.46, 118.4 (benzene 1-C), 118.2, 117.8 (benzene 5-C), 79.9 (Ph–C≡) and 74.1 (cent alkyne C). A DSC scan showed only a broad singlet for both melting and crystallization,

$\Delta H_m = 19.88$ kJ mol^{-1}. A small amount of symmetrical fluorodiacetylene was isolated earlier in the synthesis of an aminodiacetylene: transition temperatures 194.2–195.8 (Cr–I dec) and 185.3 (I–Cr) (recrystallized from CH_3CN); DSC 190.60° (br, Cr–I), $\Delta H = 34.75$ kJ mol^{-1} and ^{1}H NMR 7.51 (dd, 4, $J = 5.33$, 8.96, ArH *ortho* to $C{\equiv}C$) and 7.04 (t, 4, $J = 8.77$, ArH *ortho* to F). A large amount of this symmetrical diacetylene was isolated when 4-fluoro-bromoacetylene was accidentally added to the Cu/NH2OH·HCl, instead of the alkyl acetylene.

n = 4. Purified yield = 21.0%: GC $t_R = 10.08$ (99.83%); ^{1}H NMR 7.46 (d, 2, $J = 8.18$, ArH *meta* to olefin), 7.31 (d, 2, $J = 8.75$, ArH *ortho* to olefin), 7.38–7.05 (m, 3, ArF_2H_3), 6.38 (d, 1, $J = 15.75$, ArCH), 6.27 (dt, l, $J = 15.74$, 5.49 olefin β-CH), 2.24 (dt, 2, $J = 6.77$, 5.78, olefin γ-CH_2), 1.56–1.24 (m, 4, 2 CH_2) and 0.93 (t, 3, $J = 6.90$, CH_3); ^{13}C NMR 154.0, 153.7, 152.8, 152.5, 148.9, 148.7, 147.8, 147.5, 139.3, 133.6, 132.9, 129.5, 129.48, 129.4, 129.3, 129.2, 126.1, 121.7, 121.3, 119.5, 119.1, 119.0, 118.9, 118.1, 117.7, 82.7, 79.5, 74.9, 73.9, 33.0, 31.6, 22.5 and 14.2.

A = B = X = F, n = 3.

Purified by recrystallization from MeOH, yield = 24.9%: GC $t_R = 8.58$ min (99.60%); ^{1}H NMR 7.45 (d, 2, $J = 8.26$, ArH *meta* to olefin), 7.31 (d, 2, $J = 8.34$, ArH *ortho* to olefin), 7.12 (t, 2, $J = 6.86$, ArF_3H_2), 6.38 (d, 1, $J = 15.75$, ArCH) 6.28 (dt, 1, $J = 16.11$, 5.86, β-CH), 2.20 (dt, 2, $J = 7.10$, 5.86, γ-CH_2), 1.50 (app. sext, 2, $J = 7.33$, δ-CH_2) and 0.95 (t, 3, $J = 7.32$, CH_3); ^{13}C NMR 157.8, 148.8, 143.7, 139.5, 138.6, 133.5, 133.0, 129.3, 126.1, 118.1, 117.2, 117.0, 116.9, 116.7, 83.4, 75.9, 73.6, 35.4, 20.6 and 13.9.

n = 4. Purified yield = 45.0%: GC $t_R = 9.51$ (99.79%); ^{1}H NMR 7.45 (d, 2, $J = 8.30$, ArH *meta* to olefin), 7.30 (d, 2, $J = 8.42$, ArH *ortho* to CH_2), 7.13 (t, 2, $J = 7.16$, ArF_3H_2), 6.37 (d, 1, $J = 15.38$, ArCH), 6.28 (dt, 1, $J = 15.75$, 5.37 olefin β-CH), 2.23 (dt, 2, $J = 6.58$, 6.92, γ-CH_2), 1.70–1.20 (m, 4, 2 CH_2) and 0.93 (t, 3, $J = 7.00$, CH_3).

*5.2.13. 4-[4-(Penten-2-yl)phenyl-1,3-butadiynl]-4-hexylbenzene **10b** (A = B = H, X = C_6H_{13}, n = 2)*

Purified by recrystallization from MeOH, yield = 11.0%: GC $t_R = 24.82$ (100.00%); IR (film) 2157 (med, $C{\equiv}C$), 1664 (wk, Ar) and 1611 (med, Ar); ^{1}H NMR 7.45 (d, 2, $J = 8.43$, ArH *meta* to C_6H_{13}), 7.43 (d, 2, $J = 8.42$, ArH *meta* to olefin chain), 7.15 (d, 2, $J = 8.42$, ArH *ortho* to C_6H_{13}), 7.14 (d, 2, $J = 8.06$, ArH *ortho* to olefin chain), 5.65–5.36 (m, 2, CH=CH), 3.40 (d, 2, $J = 5.86$, olefin α-CH_2), 2.60 (t, 2, $J = 7.29$, $ArCH_2$), 2.15 (app. quint, 2, $J = 6.87$, olefin δ-CH_2), 1.78-1.50 (m, 2, C_6-β-CH_2), 1.50–1.18 (m, 6, 3 CH_2), 1.01 (t, 3, $J = 7.51$, olefin CH_3) and 0.88 (t, 3, $J = 6.41$, alkyl CH_3); ^{13}C NMR 144.7, 142.9, 133.4, 132.7, 132.6, 128.7, 128.6, 126.6, 119.5, 119.1, 81.9, 81.6, 73.8, 73.6, 36.2, 33.6, 31.9, 31.3, 29.1, 22.8, 20.8, 14.31 and 14.30.

n = 3. This homologue was prepared in the same manner and purified by chromatography using hexane followed by recrystallization twice from MeOH, yield = 49.4%: GC $t_R = 29.30$ (100.00%); ^{13}C NMR 144.7, 142.9, 132.7, 132.6, 131.7, 128.7, 128.67, 127.4, 119.5, 119.1, 81.9, 81.7, 73.8, 73.6, 36.2, 33.7, 31.9, 31.4, 29.5, 29.1, 23.0, 22.8, 14.3 and 14.0.

The two analogs with X = F were prepared similarly.

n = 2. Purified by chromatography followed by recrystallization from MeOH, yield = 11.0%: GC $t_R = 8.67$ (100.00%); ^{1}H NMR was similar to that for the following $n = 3$ homologue: ^{13}C NMR 165.6, 160.6, 143.1, 134.7, 134.6, 133.5, 132.8, 128.7, 126.6, 119.2, 118.2, 116.3, 115.8, 81.0, 80.4, 33.6, 20.8 and 14.5; elemental analysis. calcd for $C_{21}H_{17}$ F C 87.47, H 5.94; found C 87.16, H 5.95%.

n = 3. Purified by recrystallization three times from MeOH, chromatography using hexane and recrystallization once again from MeOH, yield = 48.3%: GC $t_R = 10.18$ (99.89%); ^{1}H NMR 7.50 (dd, 2, $J = 5.30$, 8.98, ArH *meta* to F), 7.45 (d, 2, $J = 8.79$, ArH *meta* to CH_2), 7.16 (d, 2, $J = 8.05$, ArH *ortho* to CH_2), 7.03 (t, 2, $J = 8.79$, ArH *ortho* to F), 5.65–5.44 (m, 2, CH=CH), 3.34 (d, 2, $J = 5.86$, $ArCH_2$), 2.20–2.00 (m, 2, δ-CH_2), 1.41 (app. sext, 2, $J = 7.32$, CH_2) and 0.93 (t, 3, CH_3); ^{13}C NMR 165.6, 160.6, 143.1, 134.8, 134.6, 132.8, 131.7, 128.7, 127.3, 119.2, 118.2, 116.3, 115.8, 82.0, 80.4, 74.1, 73.4, 33.7, 29.5, 23.0 and 14.0.

*5.2.14. Synthesis of compound **1a***

n = 5. This material was difficult to purify due to its high solubility. It was purified by chromatography using hexane followed by recrystallization twice from abs EtOH, chromatographed again and recrystallized twice from MeOH; yield = 7.0%: GC $t_R = 8.14$ (99.88%); ^{1}H NMR similar to that with $n = 6$.

n = 6. Purification was by chromatography using hexane followed by recrystallization from abs EtOH and then MeOH; yield = 23.0%: TLC (hexane) $R_f = 0.34$, GC $t_R = 8.83$ (99.87%); ^{1}H NMR 7.44 (d, 2, $J = 8.42$, ArH *para* to C_6H_{13}), 7.14 (d, 2, $J = 8.42$, ArH *ortho* to C_6H_{13}), 7.13 (dd, 2, $J = 7.69$, 6.59, ArH *ortho* to F), 2.62 (t, 2, $J = 7.69$, $ArCH_2$), 1.80–1.50 (m, 2, β-CH_2), 1.50–1.10 (m, 6, 3 CH_2) and 0.88 (t, 3, $J = 6.23$, CH_3).

The diacetylene **1** with $X = CF_3$, $Y = C_5H_{11}$ was also synthesized. Purification was by chromatography using hexane followed by recrystallization from MeOH; yield = 26.6%: TLC $R_f = 0.34$ (hexane); GC t_R 8.40 (100.00%); ^{1}H NMR 7.63 (d, 2, $J = 9.52$, ArH *meta* to

CF_3), 7.58 (d, 2, $J=9.52$, ArH *ortho* to CF_3), 7.45 (d, 2, $J=8.42$, ArH *meta* to C_5H_{11}), 7.16 (d, 2, $J=8.42$, ArH *ortho* to C_5H_{11}), 2.61 (t, 2, $J=7.33$, $ArCH_2$), 1.61 (q, 2, $J=7.08$, β-CH_2), 1.50–1.20 (m, 4, 2 CH_2) and 0.89 (t, 3, $J=6.59$, CH_3).

We are grateful for the essential contributions made by many others: partial financial assistance from NSF Science and Technology Center DMF89-20147 (ALCOM), AFOSRF 49620-98-C-0019, JPL Contract 961621 and additional assistance in the synthesis work by S. Grooms, M. Lohman, M. Smith, T. Vetman, and C. Webster.

References

[1] Wu, S.-T., Margerum, J. D., Meng, H. B., Dalton, L. R., Hsu, C.-S., and Lung, S.-H., 1992, *Appl. Phys. Lett.*, **61**, 630.
[2] Hudson, C. M., Shenoy, R. A., Neubert, M. E., and Petschek, R. G., 1999, *Liq. Cryst.*, **26**, 241.
[3] Shenoy, R. A., Neubert, M. E., Abdallah, Jr. D. G., Keast, S. S., and Petschek, R. G., 2000, *Liq. Cryst.*, **27**, 801.
[4] Neubert, M. E., Keast, S. S., Humeniuk, E. E., Walsh, M. E., and Petschek, R. G., 1999, *Liq. Cryst.*, **26**, 1695.
[5] Neubert, M. E., unpublished results.
[6] Kelly, S. M., 1996, *Liq. Cryst.*, **20**, 493.
[7] Vill, V., 1992, *Transition Temperatures and Related Properties of Two-Ring Systems with Bridging Group* in Landolt-Bornstein Group IV, Vol. 7, Liquid Crystals, b, edited by J. Thiem (Berlin: Springer Verlag).
[8] Juang, T. M., Chen, Y. N., Lung, S. H., Lu, Y. H., Hsu, C. S., and Wu, S.-T., 1993, *Liq. Cryst.*, **15**, 529.
[9] Meng, H. B., Dalton, L. R., and Wu, S.-T., 1994, *Mol. Cryst. liq. Cryst.*, **250**, 303.
[10] Griffin, Jr., R. W., Gass, J. D., Berwick, M. A., Shulman, R. S., 1964, *J. org., Chem.*, **29**, 2109; Glover, S. A., Rowbottom, C. A., Scott, A. P., and Schoonroad J. L., 1990, *Tetrahedron*, **46**, 7247.
[11] Boden, R. M., 1975, *Synthesis*, 784.
[12] Sherman, E., Lackner, A. M., and Wu, S.-T., 1995, *Mol. Cryst. liq. Cryst.*, **265**, 669.
[13] Romesberg, F. E., Flanagan, M. E., Uno, T., and Schultz, P. G., 1998, *J. Am. chem. Soc.*, **120**, 5160.
[14] Crociani, B., Antonardi, S., Di bianca, F., and Fontana, A., 1993, *J. organomet. Chem.*, **450**, 21.
[15] D'Incan, E., and Viout, P., 1984, *Tetrahedron*, 3421.
[16] Kabalka, G. W., Tejedor, D., Li, N.-S., Malladi, R. R., Trotman, S., 1998, *Tetrahedron*, **54**, 15525; Kabalka, G. W., Li, N.-S., Tejedor, D., Malladi, R. R., and Trotman, S., 1999, *J. org. Chem.*, **64**, 3157.
[17] Havens, S. J., and Hergenrother, P. M., 1985, *J. org. Chem.*, **50**, 1763.
[18] Dehmlow, E. V., and Winterfeldt, A., 1989, *Tetrahedron*, **45**, 2925.
[19] Sekine, C., Fujisawa, K., Fujimoto, Y., and Minai, M., 1999, *Mol. Cryst. liq. Cryst.*, **332**, 235.
[20] Wu, S.-T., Hsu, C.-S., Chen, Y.-N., Wang, S.-R., and Lung, S.-H., 1993, *Opt. Eng.*, **32**, 1792.
[21] Hird, M., Toyne, K. J., and Gray, G. W., 1993, *Liq. Cryst.*, **14**, 741.
[22] Fujita, A., Goto, Y., and Nahagawa, E., 1994, *Liq. Cryst.*, **17**, 699.
[23] Goto, Y., Inukai, T., Fujita, A., and Demus, D., 1995, *Mol. Cryst. liq. Cryst.*, **260**, 23.
[24] Wu, S.-T., Hsu, C.-S., and Shyu, K.-F., 1999, *Appl. Phys. Lett.*, **74**, 344.
[25] Hsu, C.-S., Shyu, K.-F., Chuang, Y. Y., and Wu, S.-T., 2000, *Liq. Cryst.*, **27**, 283.
[26] Wegner, W., 1977, *Pure appl. Chem.*, **49**, 443.
[27] Wu, S.-T., Sherman, E., Margerum, J. D., Funkhouser, K., and Fung, B. M., 1995, *SID-ASIAN DISPLAY*, 567.
[28] Wu, S.-T., Neubert, M. E., Keast, S. S., Abdallah, D. G., Lee, S. N., Walsh, M. E., and Dorschner, T. A., 2000, *Appl. Phys. Lett.*, **77**, 957.
[29] Wu, S.-T., and Neubert, M. E., 2001, U.S. Patent 6312618 B1.
[30] Neubert, M. E., 2001, in *Liquid Crystals, Experimental Study of Physical Properties and Phase Transitions,* edited by S. Kumar, Chap. 2 (Cambridge University Press); Demus D., and Richter, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie); Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals, Textures and Structures* (Leonard Hill).