Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

The effect of terminal chain modifications on the mesomorphic properties of 4,4'-disubstituted diphenyldiacetylenes

Mary E. Neubert Corresponding author[a]; Michael R. Fisch[a]; Sandra S. Keast[a]; Julie M. Kim[a]; Mark C. Lohman[a]; Rachel S. Murray[a]; Kyle J. Miller[a]; Raj A. Shenoy[a]; Michael J. Smith[a]; Ryan M. Stayshich[a]; Margaret E. Walsh[a]; Rolfe G. Petschek[b]; George A. Lorenzo[c]; Dena C. Burrows[c]; Shelly M. Oliver[c]
[a] Glenn H. Brown Liquid Crystal Intitute, Kent State University, Kent, OH 44242-0001, USA [b] Physics Department, Case Western Reserve University, Cleveland, OH 44106-7079, USA [c] Chemistry Department, Wheaton College, Wheaton, IL 60187-5593, USA

Online publication date: 25 May 2010

To cite this Article Neubert Corresponding author, Mary E. , Fisch, Michael R. , Keast, Sandra S. , Kim, Julie M. , Lohman, Mark C. , Murray, Rachel S. , Miller, Kyle J. , Shenoy, Raj A. , Smith, Michael J. , Stayshich, Ryan M. , Walsh, Margaret E. , Petschek, Rolfe G. , Lorenzo, George A. , Burrows, Dena C. and Oliver, Shelly M.(2004) 'The effect of terminal chain modifications on the mesomorphic properties of 4,4'-disubstituted diphenyldiacetylenes', Liquid Crystals, 31: 7, 941 — 963

To link to this Article: DOI: 10.1080/02678290410001666084
URL: http://dx.doi.org/10.1080/02678290410001666084

LIQUID CRYSTALS, VOL. 31, NO. 7, JULY 2004, 941–963

The effect of terminal chain modifications on the mesomorphic properties of 4,4′-disubstituted diphenyldiacetylenes

MARY E. NEUBERT*, MICHAEL R. FISCH, SANDRA S. KEAST, JULIE M. KIM, MARK C. LOHMAN, RACHEL S. MURRAY, KYLE J. MILLER, RAJ A. SHENOY, MICHAEL J. SMITH, RYAN M. STAYSHICH, and MARGARET E. WALSH

Glenn H. Brown Liquid Crystal Intitute, Kent State University, Kent, OH 44242-0001, USA

ROLFE G. PETSCHEK

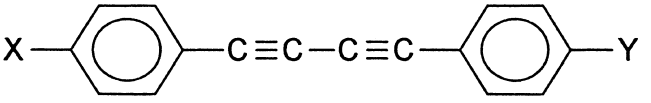
Physics Department, Case Western Reserve University, Cleveland, OH 44106-7079, USA

GEORGE A. LORENZO, DENA C. BURROWS and SHELLY M. OLIVER

Chemistry Department, Wheaton College, Wheaton, IL 60187-5593, USA

(*Received 6 October 2003; accepted 7 December 2003*)

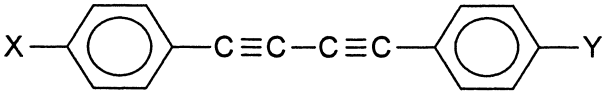
A variety of terminal chain modifications (*Y*) were made on the diacetylenes



in which $X = C_nH_{2n+1}$, $C_{12}H_{25}O$ and F, and $Y = CH_2CH(Me)C_2H_5$, $COCH_3$, $C{\equiv}CC_5H_{11}$, C_nF_{2n+1}—△—C_nH_{2n+1} and $CH{=}CHCO_2C_3H_7$. Mesomorphic properties were determined by hot stage polarizing microscopy and DSC. These were compared with those for the dialkyl analogues ($X = C_mH_{2m+1}$, $Y = C_nH_{2n+1}$) and a series of 1- and 2-olefins ($Y = CH{=}CHC_nH_{2n+1}$ and $CH_2CH{=}CHC_nH_{2n+1}$). The 1-olefin series showed wider range nematics than the dialkyl compounds, whereas the above modifications showed either narrow range nematic phases, no mesophase or higher melting temperatures. New transition temperature and enthalpy data are provided for some of the dialkyl and F-alkyl compounds previously reported, for comparisons. Preliminary birefringence data are also included along with the results of some heat and UV stability studies.

1. Introduction

Wide range room temperature nematic phases having a high birefringence and a low viscosity have previously been found in eutectic mixtures of the asymmetrically disubstituted diphenyldiacetylenes

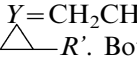


with $X = C_mH_{2m+1}$ and $Y = C_nH_{2n+1}$ or F [1]. These materials are useful for infrared applications and beam steering devices; gram quantities were needed to prepare devices for further testing. There was also interest in improving their properties by lowering the melting temperature, raising the clearing temperature and increasing the nematic range, birefringence and dielectric anisotropy. We have already reported on several structural modifications made to try to improve these properties substitution of one benzene ring with a pyrimidine [2] and replacing one terminal alkyl chain with either an amino group [3] or an olefin chain [4, 5]. Only the olefin chains gave improved properties.

In this paper, new data are provided for many of the dialkyl and F-alkyl diacetylenes that were prepared again on a larger scale, and the synthesis and mesomorphic properties are presented for a variety of chain modifications that were made, but which did not yield better properties. Two chain modifications were made to try to lower the melting temperature a branched

*Author for correspondence; e-mail: mail@lci.kent.edu

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001666084

chain, $Y=CH_2CH(Me)C_2H_5$ and a cyclopropane ring, $Y=$  R'. Both of these chains could also be made chiral, leading to chiral materials having a high birefringence. In order to extend core conjugation and attempt to increase the birefringence the following analogues were also synthesized $Y=C\equiv CC_5H_{11}$, $COCH_3$ and $CH=CHCO_2C_3H_7$. The diacetylenes show a strong preference for nematic phases. Two chains which favour the smectic A phase in other structures, $Y=COCH_3$ and C_nF_{2n+1}, were tried to determine if these would form a smectic A–nematic combination. Smectic phases have already been reported in some dialkoxydiacetylenes but none have been found in the dialkyl or alkyl–alkoxy series [6, 7]. Furthermore, the smectic phases occurred only in compounds having at least one long ($>C_6$) alkoxy chain.

2. Synthesis

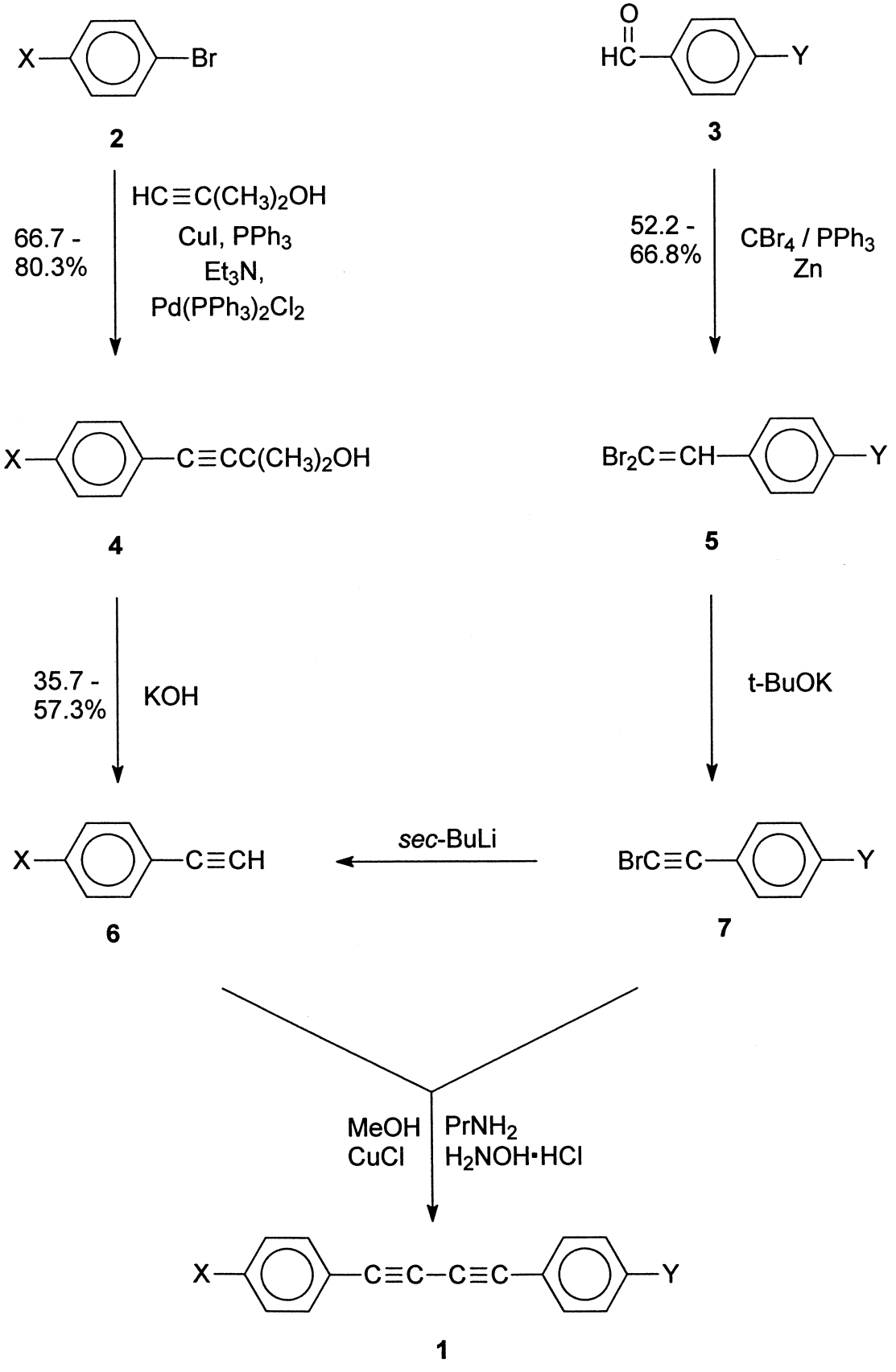
The synthesis of the asymmetrical diphenyldiacetylenes **1** (scheme 1) from a 4-substituted bromobenzene **2** and a 4-substituted benzaldehyde **3** has already been described adequately for alkyl/alkyl, alkoxy, F, CN [8, 9], and alkyl, F or amine [3] chains. These papers provide details for the preparation of both the acetylenes **6** and the bromoacetylenes **7** that need to be coupled to obtain the new diacetylenes **1**. Therefore, only the synthesis of the new chain intermediates will be discussed here. The acetylenes **6** with $X=CH_3$, C_5H_{11} and F are commercially available but expensive. Some of these were used while other homologues were synthesized. Usually, the chemistry for preparing the bromides **2** with the new chains was easier than for the aldehydes 3.

Synthesis of the new bromides **2** is given in scheme 2. Introduction of the triple bonded chain ($X=C\equiv CC_5H_{11}$) was straightforward using a coupling between the acetylene and 1-bromo-4-iodobenzene to give the bromide **8**. An attempt to use CuI as the coupling agent [10] was unsuccessful, but better results were achieved using $ZnCl_2$ [11]. Introduction of the α-keto chain ($X=CH_3CO$) was accomplished using the ketal protected ketobromide **10**. This ultimately yielded the protected ketodiacetylene **1** ($Y=$ ) which was then hydrolysed to the ketodiacetylene ($Y=COCH_3$). Esterification of 4-bromocinnamic acid gave the cinnamate bromide **11**. The perfluorinated chain ($X=C_nF_{2n+1}$) was attached to the benzene ring by a copper-catalysed coupling between the perfluorinated iodide and 1-bromo-4-iodobenzene giving the fluorinated chain bromide **12**. All of these bromides were converted to the acetylenes **6** using a copper–palladium-catalyzed coupling with a protected acetylene to give the protected acetylene 4 followed by a base-catalyzed removal of the protecting group.

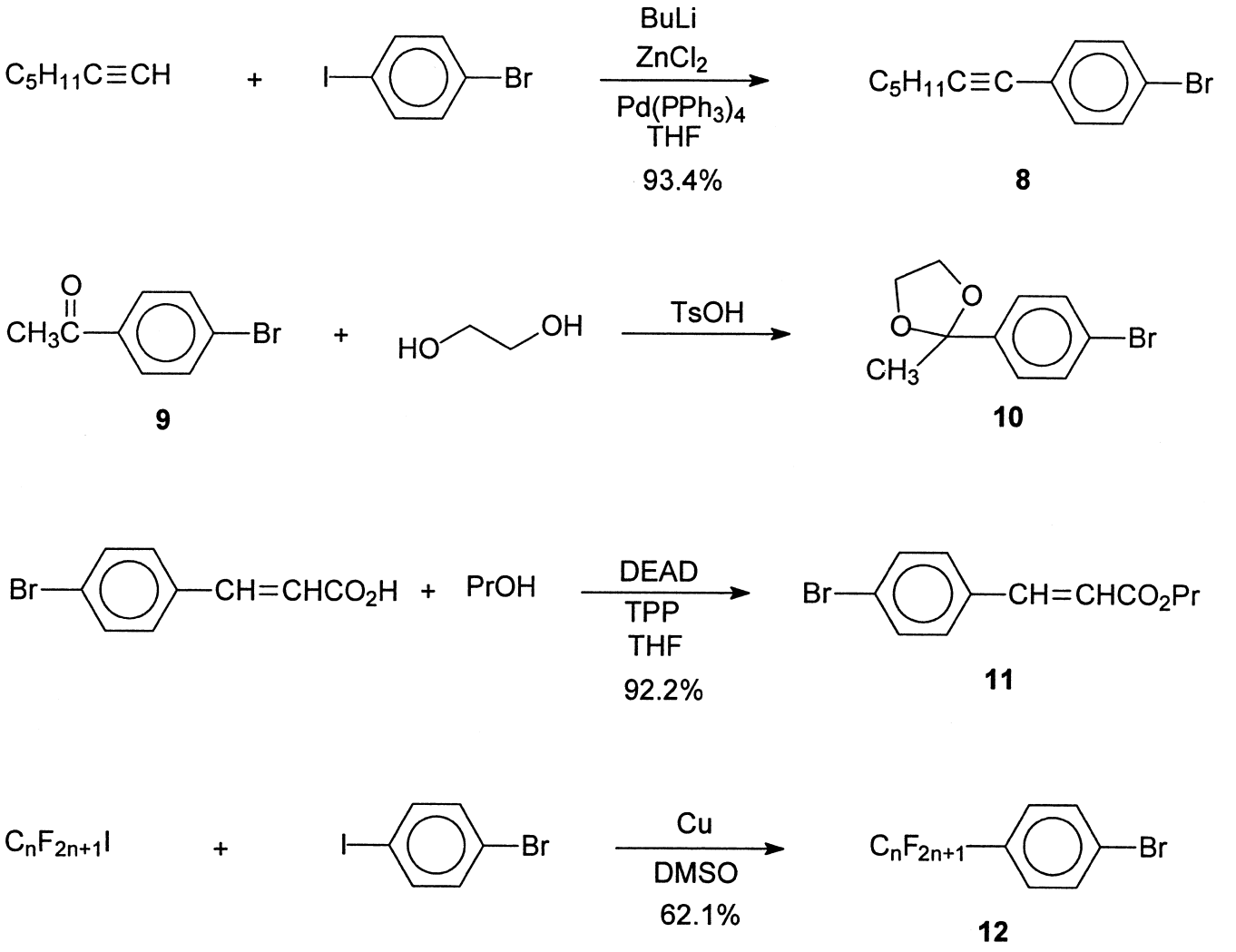
The branched chain ($Y=CH_2CH(Me)C_2H_5$) was incorporated using the aldehyde **19** (scheme 3). This required synthesis of the branched chain alkyl benzene **17**. Numerous methods have been reported for obtaining this compound, most were used to prepare optically pure isomers for the synthesis of chiral mesogens [12–14]. We chose to use a method used earlier to prepare chiral, branched chain benzoic acids (scheme 3) [15]. The racemic compound was made first to determine if the diacetylene had a mesophase before preparing the more expensive chiral material. A Friedel–Crafts acylation of benzene with the branched chain acid chloride **14** gave the ketone **15** in high yield. Several possible methods for reducing this ketone to the alkane **17** were available. With straight chain α-ketobenzenes, catalytic reduction gives the alkylbenzenes cleanly in high yields but we had found earlier that reduction is slower with the bulkier branched chain. A Wolff–Kishner reduction reportedly gave only the alcohol [12]. Since the reduction of biphenyl α-ketones with LAH-$AlCl_3$ reportedly gave the alkylbiphenyls [16], this method was chosen instead to reduce the ketone **15** to the alkylbenzene **17**. A purified yield of 79.4% of this compound was obtained. Treatment of this branched chain alkylbenzene with oxalyl chloride–$AlCl_3$ [17] followed by basic hydrolysis gave the acid **16** in a purified yield of about 84%. Reduction of this acid with LAH in THF gave the alcohol **18** in yields of 79–86%. Oxidation of this compound using pyridinium chlorochromate (PCC) [18] gave the desired aldehyde **19** ($Y=CH_2CH(Me)C_2H_5$) in a yield of 77%.

Synthesis of the *trans*-alkyl cyclopropylbenzaldehydes **22** was initially attempted by a two-step synthesis from terephthalic aldehyde **20** (scheme 4). The mono-olefins **21** with $R=C_2$ and C_3 (*cis*-*trans*-mixtures) had been reportedly isolated in high yields by treating this aldehyde with a Wittig reagent [19, 20]. Despite our attempts to follow the specific details given for the preparation of the *trans*-mono-olefin, we were able to isolate only impure material that was difficult to purify and characterize.

Another approach involved the preparation of the boronic acid olefin **27** which could be converted to the cyclopropyl boronic acid **31** and ultimately to the aldehyde **22** (scheme 5). A variety of problems was encountered in preparing this boronic acid. Initially, pinacol **28** seemed the obvious precursor via the pinacol borane olefin **26** but this compound was isolated only in low yields using two different literature methods [21, 22]. The olefin **27** was successfully prepared from the catechol borane olefin **24** [23, 24] but, because of the sensitivity of this olefin to air and moisture, it could not be purified by either recrystallization or chromatography. Additionally, the high temperature required to prepare this material was unfavourable for the starting acetylene. Still, some of the aldehyde **22** ($R=C_6H_{13}$)



Scheme 1.



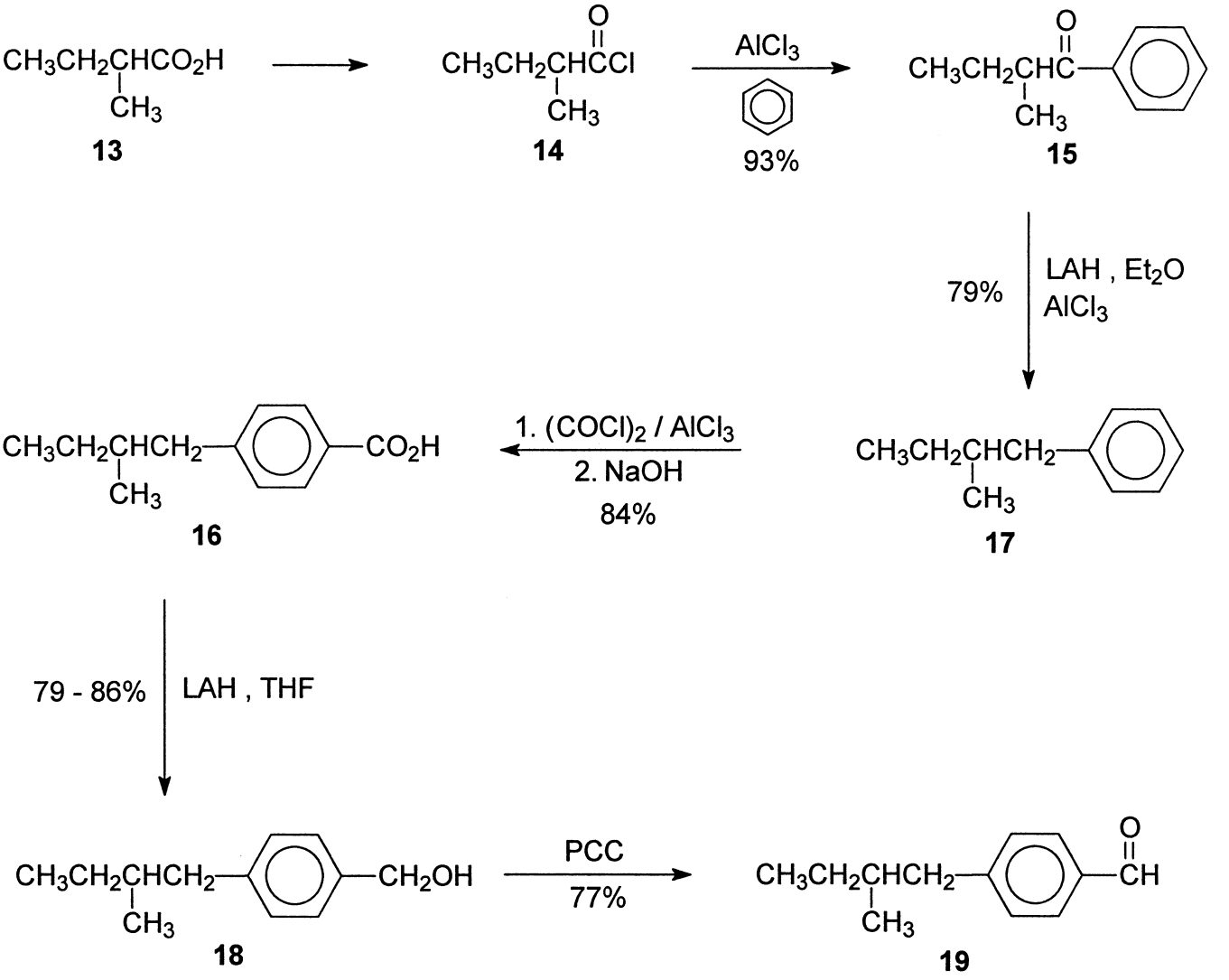
Scheme 2.

was prepared from this olefin by converting it to the methyl ester **29** [25], formation of the cyclopropyl ring **31** [26, 27], and then the aldehyde **22** [28].

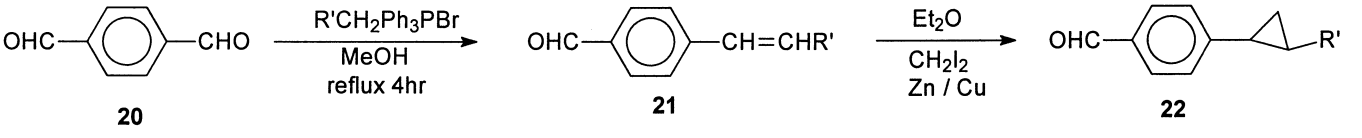
However, a much better approach through the intermediate olefin **30** was found. This olefin was converted to the pinacol borane olefin **26** ($R=C_5H_{11}$) in a yield of 85% [25]. The intermediate **30** was easily converted to the boronic acid olefin **27** ($R=C_7H_{15}$) by treatment with H_2O, or to the ester **29** ($R=C_{10}H_{21}$) by solvolysis with MeOH. The esters **29** from these various pathways were converted to the cyclopropyl esters **32** by the addition of CH_2I_2 [28] which hydrolysed to the boronic acid **31** ($R=C_6H_{13}$, C_7H_{15} and $C_{10}H_{21}$) during work-up. A Suzuki coupling of these with 4-bromobenzaldehyde gave the desired cyclopropylbenzaldehydes **22** ($R=C_6H_{13}$ and C_7H_{15}). The boronic acids **31** were difficult to purify. Converting this acid ($R=C_{10}H_{21}$) to the ester **33** ($R=C_{10}H_{21}$) gave a material that was easier to purify and which could be treated directly with 4-bromobenzaldehyde to give the cyclopropyl benzaldehyde **22** ($R=C_{10}H_{21}$). The pinacol olefin **26** ($R=C_5H_{11}$) could also be converted to the cyclopropyl compound **33** ($R=C_5H_{11}$) but an attempt to convert this to the aldehyde **22** was unsuccessful. Insufficient material was available for additional attempts, with the result that diacetylenes from this chain length on the cyclopropyl ring were never prepared.

The branched chain **19** and cyclopropylbenzaldehydes **22** were converted to the bromoacetylenes **7** through the dibromoolefin **5** obtained from a Wittig reaction (scheme 1) using the procedures reported earlier [3, 9]. These bromoacetylenes were coupled directly with the acetylenes **6** to give the diacetylenes **1** or converted to the acetylene **6** for coupling with another bromoacetylene depending on the desired acetylenes.

The acetylenes **6** can also be prepared by treating the



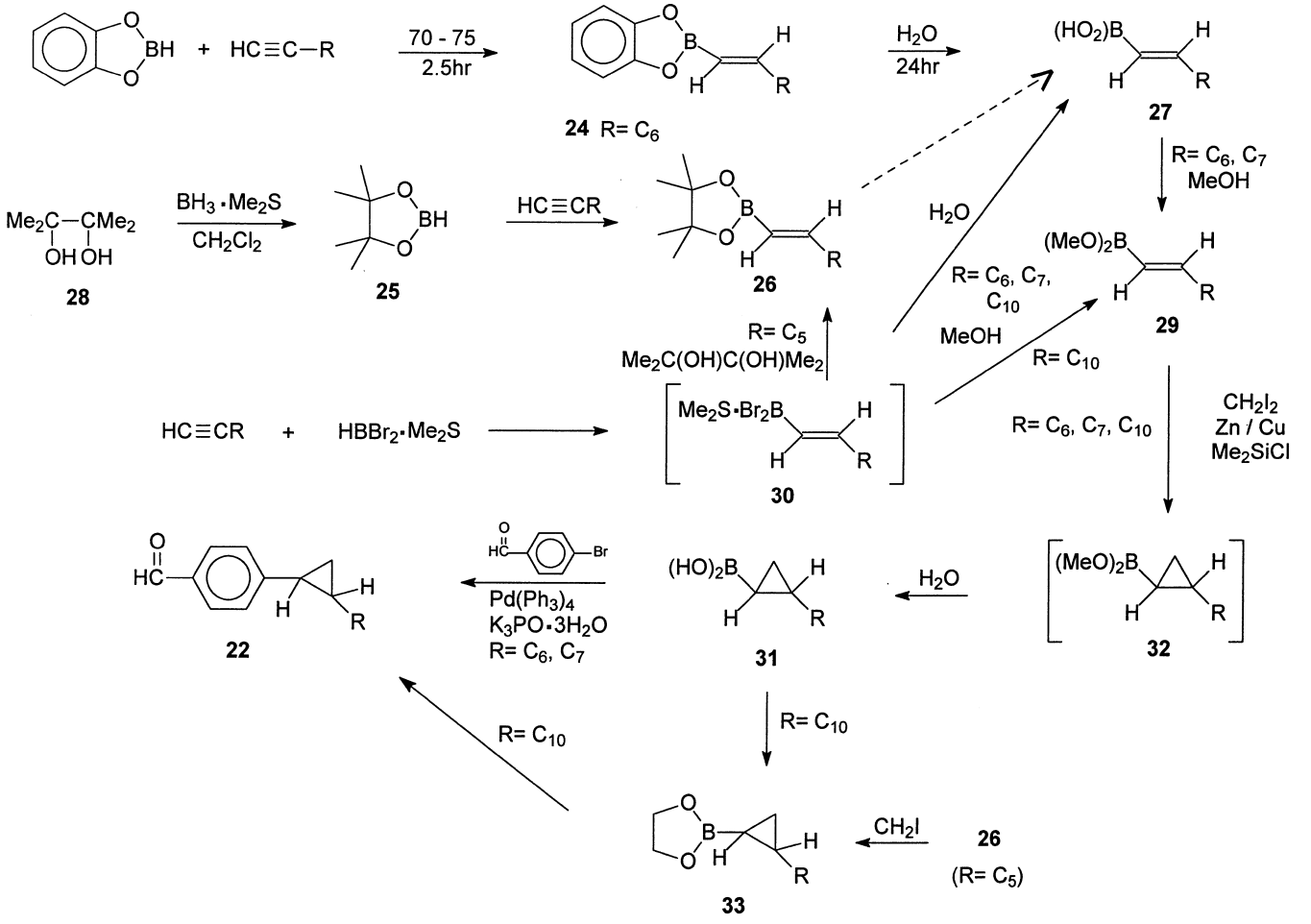
Scheme 3.



Scheme 4.

dibromoolefin with *n*-BuLi [8, 9]. The problem with these methods (from **6** or **7**) is that if total conversion does not occur, the mixture of starting material and product is difficult to separate. We found that the *t*-BuO^-K^+ used for the conversion of **6** to **7** must be freshly prepared with *t*-BuOH that has been freshly distilled. The use of a slight excess of the salt (1.1–1.2 equiv) in the reaction gave better results. Also, using *sec*- or *t*-butyl lithium rather than *n*-BuLi for the **7** to **6** conversion avoids the addition of *n*-BuLi to the triple bond forming ArC≡CBu. Minimizing exposure to light during all reactions involving a triple bond also improved results.

When the bromide **2** is available the acetylene **6** can be prepared from the protected acetylene **4** by basic hydrolysis which generally yields a cleaner product.



Scheme 5.

However, the bromoacetylene **7** is more stable than the acetylene **6** so it is the preferred intermediate for storage for long periods. Of course, which intermediate was prepared depended on the availability or ease of synthesis of the starting bromides **2** and aldehydes **3**, as well as the desired diacetylene **1**. With the branched chain compounds, we wanted to prepare both the mono- and di-substituted diacetylenes so the aldehyde was chosen as the branched chain intermediate. With most of the new chain modifications, the bromides were easier to prepare.

Coupling the acetylene **6** with the bromoacetylene **7** to form the diacetylenes **1** was best achieved if the CuCl was dried immediately before use. Using more $NH_2OH \cdot HCl$ did not improve the yield. The use of purer intermediates made purification easier; $CHCl_3$ was avoided as a solvent for recrystallization because it tended to result in pale yellow materials, whereas colourless products were isolated using other solvents.

All the diacetylenes **1** were purified by chromatography/recrystallization until they showed only one spot by TLC and had a clearing temperature range of 0.3°C or less. GC analysis proved to be the only method for detecting impurities since the dialkyl symmetrical analogues have the same TLC-R_f value as the unsymmetrical compounds. Those with only one alkyl group have a different R_f value but were sometimes contaminated with symmetrical dialkyl and di-X (or Y) compounds. Purities (GC) in the range from 96.07–100.00% were obtained for the unsymmetrical dialkyldiacetylenes. Those having similar chain lengths were more difficult to obtain pure because of the difficulty of removing the symmetrical compound, the most common impurity found. These trace amounts of symmetrical materials were posed no problem when mixed with other dialkyl diacetylenes, so when separation was difficult no further purification was done. Purities for the new diacetylenes fell in the range 98.16–100.00% except for the $X = CH_3$ and $Y =$ cyclopropyl analogue. Insufficient material was available to obtain a purer sample of this compound. As our skills improved both in purifying the diacetylenes and the intermediates, the purity increased, so that a typical GC purity is

now indistinguishable from 100.00%. The small amounts of impurities found here generally do not interfere with good characterization and mesomorphic properties, although in the olefin series they can affect the melting transition [5]. Characterization of all the compounds synthesized was by IR, ^{1}H NMR, sometimes ^{13}C NMR and in some instances, elemental analysis.

3. Mesomorphic properties

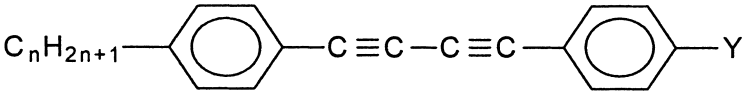
The transition temperatures (°C) for those diacetylenes **1** ($X=C_mH_{2m+1}$, $Y=C_nH_{2n+1}$ or F) which differed by at least 4°C in one of the transition temperatures from the values reported earlier [1] are given in table 1. Enthalpy values are also provided for both the melting and clearing temperatures along with the nematic phase temperature range. The temperatures were obtained by hot stage polarizing microscopy and the enthalpy values by DSC. These latter values were obtained from the first heating from virgin crystals unless otherwise noted.

Transition temperatures for the newly prepared diacetylenes are presented in table 2. A comparison of these properties with those of the alkyl analogue parent compound having the same or similar chain length is provided when possible, by comparing the differences in transition temperatures and in nematic (N) phase ranges. Data for the parent compounds are taken from table 1 and references [1, 8, 9]. When data for the exact homologues were unavailable, those for the two adjacent homologues were averaged to give an estimated value. Although this estimate is not accurate, other differences were large enough still to give an obvious trend GC purities are given in § 6.

A single branched chain, $Y=CH_2CH(Me)C_2H_5$ increased the melting temperatures both for $X=C_2H_5$ (compound no. 1) and F (no. 3) but two branched chains (no. 4) lowered it. Clearing temperatures decreased producing smaller N ranges. A long alkoxy chain combined with the branched chain (no. 2) gave a wide nematic and no smectic phase with transition temperatures that were similar to those for the ethyl analogue. A small amount of the symmetrical dialkoxy compound (no. 17) was also isolated. This showed both a N and smectic C (SmC) phases with the SmC having a wider range than the nematic. Transition temperatures were high, as expected. Data for numerous other symmetrical dialkoxydiacetylenes indicate that N phases occur at shorter chain lengths [6].

The cyclopropyl ring possesses a large amount of p-character and can serve to extend conjugation in appropriate molecules. The most favoured geometry for conjugation occurs when the plane of the benzene ring bisects the cyclopropyl C–C bonds [30]. This preferred configuration would alter the geometry of the

Table 1. Transition Temperatures (°C) and enthalpy values for some diacetylene.



n	Y	Cr[a]	N	I	N range	ΔH_m/kJ mol^{-1}	ΔH_c/kJ mol^{-1}	Purity/%
1	C_3H_7	104.3	109.5–110.9	122.6–122.7	11.8	25.07	1.23	98.24
1	C_5H_{11}	81.0	84.2–97.7	108.3–108.4	20.7	22.06[b]	1.01	97.76
3	C_6H_{13}	26.9	37.8–43.9	105.4–105.6	61.7	14.35	0.87	100.00
4	C_6H_{13}	23.9	26.7–28.0	91.4–91.5	63.5	10.56	0.71	97.70
4	C_8H_{17}	9.9	22.1–25.2	84.6	59.4	21.03	0.75	99.10
6	C_8H_{17}	36.8	38.4–39.4	82.6	43.2	12.05	0.69	96.07
2	F	67.5(Cr_2)[c]	(95.7–95.8)	95.7–95.9(Cr_1)	m	26.30	0.37	97.40
3	F	84.3	93.4–99.9	108.8–109.2	9.3	21.92	0.56	95.38[d]
4	F	64.5	89.2–90.5	91.1–91.2	0.7	26.39[e]	0.41	98.85
5	F	83.3	86.0–88.4	95.4–95.6	7.2	24.69	0.53	99.56
8	F	58.2	69.2–70.5	79.1–79.2	8.7	22.24[f]	0.32	97.48

[a]Cr = crystallization temperature obtained on cooling the melt at 2°C min^{-1} N = nematic phase, I = isotropic liquid, ΔH_m = enthalpy of melting from virgin crystals, ΔH_c = enthalpy of N–I obtained from the first heating scan, m = monotropic phase that occurs below the melting temperature. Purity determined by gas chromatography.

[b]Broad melting peak.

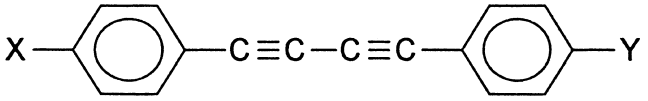
[c]Cr_2: first crystals formed on cooling converted to Cr_1 on heating to 90.5–92.6°C, which then melted to I $Cr_1 = Cr_{virgin}$ observed only by microscopy.

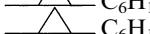
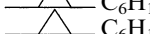
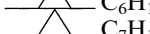
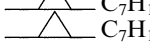
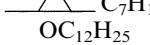
[d]Contains symmetrical diacetylene, $t_R = 3.91$.

[e]Only a broad peak occurred for melting so the ΔH for N–I was obtained from the cooling scan. This was subtracted from the total enthalpy of melting to give the ΔH for Cr–N. Microscopy showed the N phase was enantiotropic rather than monotropic.

[f]Melting occurred as a broad peak, whereas crystallization showed two peaks at 50.10°C (17.78 kJ mol^{-1}) and 46.72°C (5.25 kJ mol^{-1}).

Table 2. Mesomorphic properties for new diacetylenes.



Compound no	*X*	*Y*	Cr[a]	A or C	N	I	ΔH_m[b]	ΔH_c	Δm.p.[c]	Δcl.p.	ΔN
1	C_2H_5	$CH_2CH(Me)C_2H_5$	56.4[d]		63.6–65.4	85.6–85.9	17.50	0.58	21.0	−12.5	−33.5
2	$CH_2CH(Me)C_2H_5$	$C_{12}H_{25}O$	57.4[e]		63.6–65.2	95.8–95.9	31.92	0.70	f		
3	F	$CH_2CH(Me)C_2H_5$	104.8			108.3–109.6	20.99[g]		19.1		
4	$CH_2CH(Me)C_2H_5$	$CH_2CH(Me)C_2H_5$	60.8		68.1–68.5	78.4–78.5	26.05	0.68	−6.6	−22.5	−15.9
5	C_5H_{11}	CN	142.2		145.8–149.0	161.7–161.9	33.11	0.38	104.3		
6	$COCH_3$	C_5H_{11}	79.6		98.5–99.3	131.2–131.4	30.07	0.59	54.6	29.7	−25.0
7	$C_5H_{11}C\equiv C$	C_5H_{11}	87.5		94.5–96.7	106.3–106.5	36.32	1.34	~46.3	~13.3	~−33.0
8	$C_5H_{11}C\equiv C$	F	117.8			128.3–131.6	31.39		~60.1		~−10.1
9	C_3F_7	C_6H_{13}	49.9	65.7–66.1[h](A)		79.9–80.7	19.83[h]	4.10	22.2	−24.9	−61.7[I]
10	C_8F_{17}	C_6H_{13}	67.5	89.1–89.9 (A)		139.6–140.9	31.38	5.79	50.5	58.3	−43.2[I]
11	C_8F_{17}	C_2H_5	88.7	118.7–119.1 (A)		153.8–154.4	27.17	5.82	77.4	76.5	−32.6[I]
12	CH_3		31.2		(61.8–62.2)	71.5–75.9	30.90	0.51	−2.9	−20.3	m
13	C_5H_{11}		16.3 (Cr_2)[j]		43.5–44.2 (K_1)	77.2–77.3	26.49[j]	0.71	3.5	−11.2	−14.7
14	F		33.1		(57.7–57.9)	62.1–63.1	22.89	0.25	−7.4	−21.3	m
15	F		43.5		(48.4–48.7)	52.8–54.4	28.49	0.75			
16	F		43.3		47.3–49.2[k]	57.5–57.8	32.67	0.25	~−21.3	~−21.4	−0.1
17	$C_{12}H_{25}O$	$OC_{12}H_{25}$	81.1 (Cr_2)[l]	100.5–101.5 (Cr_1)(C)	107.4–107.6	122.1–122.2	43.59 (K–C)	1.63			
18	$CH=CHCO_2C_3H_7$	C_5H_{11}	87.9 (Cr_2)[m]		101.1–102.5 (K_1)	141.6–141.8	32.67[n]	0.58	~49.3	~48.7	−0.6[n]
									23.1	−14.1	−37.2[o]
19	$CH=CHCO_2C_3H_7$	F	128.2 (Cr_1)[p]		(144.5–144.7)	144.6–146.2 (Cr_2)	37.68		~84.7	~63.1	m[o]
									62.5	−5.3	m[q]
20	C_5H_{11}	CF_3[r]	96.6			101.6–102.7	24.53		15.0		

[a]Phase transitions (°C) obtained from microscopy. Cr = crystallization temperature obtained on cooling the melt at 2°C/min, C = smectic C, A = smectic A, N = nematic and I = isotropic liquid. Parentheses indicate a monotropic phase.

[b]Enthalpy values (kJ mol^{-1}) obtained from the first heating of virgin crystals DSC scan. ΔH_m = melting and ΔH_c = clearing temperature, Δcl.p. = clearing temperature (mesophase to isotropic).

[c]Differences (°C) from values reported for the parent compounds Δm.p. = melting temperature, Δcl.p. = clearing temperature and ΔN = nematic phase change. Negative values indicate a decrease.

[d]The first crystals formed on cooling converted to another form when cooled to 52.7°C. These crystals changed again on heating to 62.2°C, and then melted to the N phase. The cooling crystal change was observed by DSC ($\Delta H = -0.64$, 15.47 kJ mol^{-1}) but none was observed on heating.

[e]This material crystallized slowly giving a large flower-like texture. When this was reheated it started melting to the nematic phase at 62.0–62.9°C, but before all the crystals could melt some converted to needles which melted to the nematic phase at 64.7–65.0°C. Virgin crystals (needles) did showed no obvious change melting at 64.1–65.6°C. A DSC scan showed two peaks on reheating the cooled crystals. 59.2°C ($\Delta H = 20.53$ kJ mol^{-1}), 61.4°C ($\Delta H = 7.99$ kJ mol^{-1}) and only a very small peak at 58.6°C for the virgin crystals. When the cooled crystals were allowed to set for several days and reheated, they melted at 64.6–65.1°C and are therefore the same as the virgin and needle crystals.

[f]No data are available for the parent compound.

[g]A second broad peak was observed on heating at 102°C ($\Delta H = 0.36$) in the DSC scan. This is probably a crystal-to-crystal change. The major peak at 107.5°C had a $\Delta H = 20.63$. Both values were included in ΔH_m.

[h]Two peaks were observed for melting in the DSC scan. 57.17°C (10.12 kJ mol^{-1}) and 59.96°C (9.71 kJ mol^{-1}). This became one broad peak on reheating (60.09°C, 15.09 kJ mol^{-1}). In the microscope, the feathery crystals formed on cooling gradually became more mosaic on heating. Virgin crystals also showed some change at about 60°C.

[i]The total mesophase range, in this case only the SmA phase range, also decreases as compared with that in the parent compound (N only) for 6-3, 27.1°C and 2-8, 0.9°C but is larger for 6–8, 7.8°C.

[j]On cooling, crystals (Cr_2) formed at 16.3°C which converted to Cr_1 on further cooling to 13.4°C. On reheating, Cr_1 melted to the N phase. This was also seen in the DSC (9.30°C, $\Delta H = -16.83\,kJ\,mol^{-1}$ and 0.92°C, $\Delta H = 0.92$).

[k]This is the melting temperature for virgin crystals. Crystals obtained on cooling the N phase melted to the isotropic liquid at 57.5–59.0°C, making the nematic phase monotropic relative to this higher melting temperature. Difference values were calculated using the lower melting temperature.

[l]This compound showed a crystal change both on cooling and heating by microscopy and DSC microscopy Cr_2–Cr_1, 91.7–91.9°C (heating), virgin crystals are Cr_2, DSC. $\Delta H = 9.37$ (virgin Cr-Cr_1), 9.77 (Cr_1–Cr_2, on cooling). For the C–N transition $\Delta H = 2.86\,kJ\,mol^{-1}$. This compound was reported in reference [29] but no data were given.

[m]On cooling Cr_2 slowly changed to Cr_1.

[n]No crystal change was observed until the cooled crystals were reheated 98.27°C ($\Delta H = 1.90\,kJ\,mol^{-1}$) and 100.57°C ($\Delta H = 26.67\,kJ\,mol^{-1}$).

[o]An estimated value was calculated for $Y = C_7H_{15}$ using data for adjacent homologues. This was used as data for the parent compound.

[p]Crystals formed at 128.2° (Cr_1) on cooling which converted to Cr_2 on reheating to 137.2°C and then melted to the nematic phase. Virgin crystals = Cr_2. DSC showed a crystal change only on cooling. 125.82°C, $\Delta H = -10.63\,kJ\,mol^{-1}$ (I-Cr) and 124.74°C, $\Delta H = -30.50\,kJ\,mol^{-1}$ (Cr-Cr).

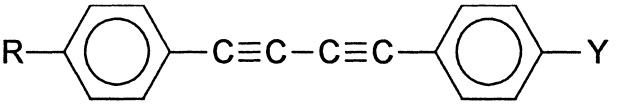
[q]The analogous $Y = CH{-}CHC_4H_9$ diacetylene was used as the parent compound in this comparison.

[r]Synthesis of this compound was reported earlier in reference [5].

diacetylene molecule. A terminal straight alkyl chain will tend to align with the central axis of the molecule and extends above the plane of the core part of the diacetylene molecule. With a *trans*-cyclopropyl group added between the benzene ring and the straight chain, the chain no longer lies on the molecular axis but lies outside the plane of the rest of the molecule. This could affect the molecular packing and lower the melting temperature much as a branched chain often does. Moreover, the cyclopropyl compounds we synthesized are a racemic mixture of enantiomers. Hence, if they form chiral crystals, the melting temperature could be depressed. Both the melting and clearing temperatures decreased in the cyclopropyl compounds (nos. 12–16) when compared with their alkyl analogues, but the melting temperatures were usually higher than in the branched chain compound (no. 1). The nematic properties were poor in compounds 12, 14 and 15, which showed only monotropic N phases, and in compound 16 which had only a short range enantiotropic phase. Only when $X = C_5H_{11}$ (no. 13) was the N phase of nearly the same temperature range as that found for the alkyl compounds. This result suggests that the investigation of additional modifications using the cyclopropyl ring, such as moving it to the second carbon atom in the chain, might be worthwhile.

An increase in the core length of a mesogen through extended conjugation with a terminal chain is often used to increase the mesophase range. Several functional groups were tried with this approach in mind. When $Y = COCH_3$ (no. 6), the nematic range decreased considerably because there is a larger increase in the melting than in the clearing temperature. A longer ketone chain might give lower temperatures and possibly a wider range nematic, but it would be unlikely to decrease the melting temperature enough to make it of interest for such applications as displays. In the α-ketophenylbenzoates, the smectic A (SmA) phase predominates over the nematic [31], whereas in the diacetylene the preference for the N phase seems to be stronger. However, without data for longer ketone chains, the possibility that this is true only for short chains cannot be eliminated. When Y is a long perfluorinated chain (nos. 9–11), only SmA phases were observed. A short perfluorinated chain, $Y = CF_3$ (no. 20) showed no mesophases. Although these perfluorinated chain diacetylenes are of little interest for nematic materials, they could be of interest for ferroelectric materials. Some feeling for the effect of replacing the hydrogen with a fluorine atom on mesomorphic properties can be obtained from comparing the properties of these two series (table 3). The effect of the fluorine atom on the melting temperature in these three homologues is to increase it, usually by a substantial amount, but the effect on the clearing temperature is less

Table 3. A comparison of mesomorphic properties of alkyl and fluoroalkyl acetylenes.



		Temperature/°C[a]					Temperature/°C[a]			
R	*Y*	N	I	Phase range/°C	ΔH_m/kJ mol^{-1}	*Y*	N	I	Phase range/°C	ΔH_c/kJ mol^{-1}
C_2H_5	C_8H_{17}[b]	41.7	77.4	36.2	18.39	C_8F_{17}	119.1	154.4	35.3	27.17
C_6H_{13}	C_3H_7	43.9	105.6	61.7	12.19	C_3F_7	66.1	80.7	14.6	19.83
C_6H_{13}	C_8H_{17}	39.4	82.6	43.2	10.64	C_8F_{17}	89.9	140.9	51.0	31.38

[a]Transition temperatures were determined by microscopy. N = crystal to smectic A, I = N or A to isotropic liquid. Enthalpies were obtained from DSC scans.
[b]Data for this compound is from reference [1].

consistent. A substantial decrease occurrs in the $Y = C_3F_7$ homologue while there are larger increases for the other two homologues. This could be due to the difference in chain length of the two fluorinated chains. This $Y = C_3F_7$ compound also has the shortest phase range and lowest enthalpy of melting of all the fluorinated analogues. Melting enthalpies for all the fluorinated analogues were higher than those for the parent compounds. Data for more homologues would be needed to determine whether consistent trends exist. The tendency to form SmA phases may be due to the immiscibility of the perfluoro chains and the other alkyl chain, or the phenyl rings. A completely fluorinated compound might be nematic.

A triple bond conjugated to the benzene ring (nos. 7 and 8) increased the transition temperatures as expected but decreased the N ranges considerably, with the $X = F$ analogue having no mesophase. Conjugation of a 1-olefin chain with the benzene ring also increases the transition temperatures but increases the clearing temperature much more than the melting temperature, giving wider N phases than in the dialkyl compounds. We have explored this modification more extensively in a separate publication [5]. Melting temperatures were usually below 100°C, making these the most interesting of the chain-modified diacetylenes. A 2-olefin chain lowers the transition temperatures and decreases the nematic range. Possibly it could be used to lower the melting temperature of a mixture of the 2-olefin diacetylenes. Conjugation of a cinnamate group with the benzene ring (nos. 18 and 19) gives transition temperatures above 100°C and narrower nematic phase ranges when compared with the 1-olefin analogues. These cinnamates also had higher melting but lower clearing temperatures. Branched chain cinnamate diacetylenes have been reported to have better photochemical stability than their alkyl counterparts [32]. However, a comparison of the mesomorphic properties for our alkyl cinnamate (no. 18) with those for a known branched chain analogue ($X = C_4H_9$, $Y = CH=CH(Me)Et$) 102° (Cr–I), 95°C (I–N) [32] shows that a branched chain in the cinnamate part is unlikely to lower the melting temperature significantly or widen the nematic phase range. Data for our limited number of branched chain compounds suggest that an attempt to use this chain modification to lower the melting temperatures in the diacetylenes is unlikely to succeed.

Using the terminal groups CN or CF_3 (nos. 5 and 20, respectively) to increase the dielectric anisotropy gave compounds with transition temperatures above 100°C and no N phase when $Y = CF_3$. This, coupled with the poor solubility of these compounds with the alkyl analogues, eliminates this approach for enhancing the dielectric anisotropy. A terminal F group offers some hope when it is coupled with a terminal 1-olefin chain but does not give a large increase in dielectric anisotropy. Significantly different types of structure modifications are needed to obtain larger $\Delta\varepsilon$ values while maintaining low transition temperatures and viscosities, and wide N phase ranges.

With the limited number of homologues studied for each *Y* modification, there is less certainty about the structure–property relationships than three homologues (short, medium and long) would give. Yet this limited number made it possible to screen a large number of modifications to find the one (olefins) that offers an obvious improvement. What has been learned in this work also serves as a guide for newer modifications which undoubtedly will be more difficult to synthesize.

4. Stability

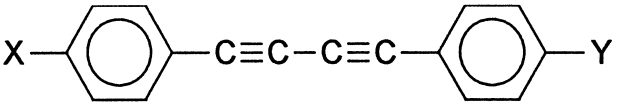
While working with all these diacetylenes, we noticed colouration occurring in the presence of light and heat. A simple study was made of the UV and thermal stability of selected samples of the dialkyl, alkyl 1-olefin and alkyl 2-olefin diacetylenes. Three properties were checked that would indicate degradation had occurred colour change, decrease in clearing temperature, and widening of the clearing transition. The test samples were placed on a microscope slide, a cover slip was

added and then either UV light or heat applied for a specified time. The clearing temperature was then determined by polarizing microscopy optical; two wavelengths (254, 366 nm) were available from the TLC detector UV lamp. Separate samples were used for each set of parameters. The lamp distance was held constant at approximately 5 cm. A hot plate served as a heat source for the thermal studies. Only one set of data was collected; obviously, experimental error would be high using this method. We believe, however, that at least some indication of the relative stability of these materials could be obtained; the data for these studies are given in tables 4 and 5.

The thermal studies (table 4) showed essentially no change in PTTP 24-36 (a eutectic mixture of the diacetylenes 52% $X=C_2H_5$, $Y=C_4H_9$ and 48% $X=C_3H_7$, $Y=C_6H_{13}$) up to 130°C, whereas the 1-olefin showed significant changes even at 80°C. Since only a small amount of the 2-olefin was available, no data were collected at the lower temperature for this compound. All three analogues showed obvious degradation above 130°C with the apparent instability being in the order 2-olefin > 1-olefin > alkyl. Data for the single dialkyl compound PTTP-36 is confusing. This could be due to the large experimental error in measuring small differences. One would expect this material to be perhaps a little better than the PTTP 24-36 mixture, or at least the same.

In the UV studies (table 5), little degradation occurred in either the 2-olefin or PTTP24-36 at short wavelength but some seemed to occur in the 1-olefin. At the longer wavelength, decomposition was obvious in all the samples. The 2-olefin seemed less stable than the alkyl and the 1-olefin showed the greatest degradation.

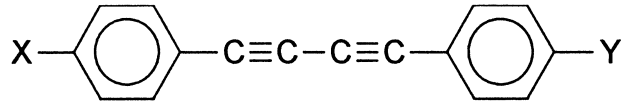
Table 4. Thermal stability studies.



Conditions		PTTP 24-36[a]			$X=C_3H_6$, $Y=C_6H_{13}$			$X=C_4H_9$, $Y=CH–CHC_4H_9$			$X=C_6H_{13}$, $Y=CH_2CH–CHC_2H_5$		
T/°C	t/min	Colour change	T_c[b] decrease	Range change	Colour change	T_c decrease	Range change	Colour change	T_c decrease	Range change	Colour change	T_c decrease	Range change
80	360	None	0.8	0.1				None	4.3	0.7			
100	190	None	0.3	0				Lt yel	6.3	1.9			
130	45	Lt yel	0.7	0	None	1.8	0.3	Lt yel	1.1	0.9	Yel	3.8	4.2
175	45	Dk yel	4.1	12.1	Yel	4.9	4.3	Yel	7.0	5.9	Dk yel	10.2	4.7
185	45	brown	8.1	32.1	Dk yel	6.9	16.0	Dk yel	7.1	6.7	Dk yel	11.5	4.1

[a]PTTP24-36 is a eutectic mixture of 52% $X=C_2H_5$, $Y=C_4H_9$ and 48% $X=C_3H_7$, $Y=C_6H_{13}$.
[b]Abbreviations. T = temperature, T_c = clearing temperature, t = time, range change = temperature at end of clearing transition – temperature at the beginning, all temperatures are in °C. Colour abbreviations. Lt = light, dk = dark, yel = yellow.

Table 5. Room temperature photochemical stability studies.



Conditions		PTTP 24-36[a]			$X=C_3H_6$, $Y=C_6H_{13}$			$X=C_4H_9$ $Y=CH–CHC_4H_9$			$X=C_6H_{13}$ $Y=CH_2CH–CHC_2H_5$		
Time/min	Light/nm	Colour change	T_c decrease	Range change	Colour change	T_c decrease	Range change	Colour change	T_c decrease	Range change	Colour change	T_c decrease	Range change
68	None	None	0.1	0.1				None	1.7	0.1	None	None	None
68	Lab	None	0.2	0.1				None	0.7	0.3			
1	254	Yel	0.7	0.5	Lt yel	1.8	−0.2	Lt yel	1.7	1.5	None	0.6	0.2
2	254	Yel	0.8	0.5	Lt yel	2.6	−0.1	Lt yel	1.3	1.1	None	0.7	0.6
3	254	Dk yel	1.0	0.6	Lt yel	2.9	−0.1	Lt yel	1.4	1.2	None	0.9	0
1	366	Brown	2.6	0.2	Yel	3.8	0.5	Yel	3.5	3.2	Yel	1.6	0.8
2	366	Brown	2.8	3.2	Yel	4.2	0.6	Yel	5.2	5.5	Yel	3.4	2.0
3	366	Brown	2.1	4.3	Yel	5.4	1.4	Yel	8.4	3.3	Yel	3.1	0.1

[a]Definitions as for table 4.

This may simply because the 1-olefin absorbs more strongly in both regions of the UV spectrum, especially in the longer wavelength regions [5]. Again, the single dialkyl diacetylene PTTP-36 seemed less stable than the PTTP24–36 mixture. In retrospect, there are numerous problems with this approach and a more thorough study is needed to determine more accurately the relative stability of these diacetylenes.

5. Optical birefringence

Various methods have been used to determine the optical birefringence (Δn) of liquid crystals [26, 27, 33], but only two of these are simple enough and involve equipment available in the liquid crystal synthesis laboratory. These are the refractometer and compensation methods. Recently, some data for typical known liquid crystals obtained using the refractometer method have been reported [33].

In designing new mesogens with a high birefringence, many structural modifications need to be tried to find the best materials. The rapid acquisition of Δn values is important for synthesis chemists so that decisions can be made as to future modifications. It is also important to determine the Δn values for all the compounds synthesized, and for these to be measured using the same method, so that values can be compared not only for the new modifications but also with values for known compounds. To the chemists, accurate values for Δn are less important than achieving a good comparison of these values. When compounds with the largest Δn values are found, more accurate determinations of the Δn value can be made. Of course, the best comparison can be made when all the compounds have the same purity (not always easily achieved) and minimal experimental error is involved. Ideally, the method used should use a minimal amount of material, a short period of time to avoid possible sample decomposition, and make the screening of a large number of compounds possible with easy to use equipment.

Initially, we felt that a good approach would be to use, with our polarizing microscope, the cells used for the DisplayTech APT instrument for determining dielectric anisotropy ($\Delta\varepsilon$) values, obtaining the Δn values with compensation methods [34]. These same cells could then be used to measure $\Delta\varepsilon$ values on the same sample. However, the cells were found not to have the thickness uniformity needed to determine Δn values accurately using the equation

$$\Delta n = \Gamma / d$$

where Γ = phase shift in nanometers and d = sample thickness. We next tried cells made by the LCI display group. These were 1 cm^2 capillary filled cells having a thickness of about 4 μm and anti-parallel alignment. For each cell, the exact thickness was measured at the centre of the cell. Since some variations occur throughout the cell, a holder was designed to make it possible to align the centre of the cell with the microscope objective.

Since all the new single diacetylenes were solids at room temperature, they materials had to be dissolved in a room temperature liquid crystal solvent. With the help of EM Industries, we chose first to use ZLI-2978-100 and later MLC6025-100 since these mixtures had a low Δn (0.083 and 0.085, respectively) and contained no cyanobiphenyls that could form complexes with the diacetylenes. Some solubility studies were made to determine the maximum amount of diacetylene that could be added to the liquid crystal solvent, usually about 15%. A few of the diacetylenes were insufficiently soluble to obtain Δn values, those having a terminal CN group and the F-cinnamate analogue.

In order to evaluate the method, Δn values were also obtained for several known materials and compared with reported values (table 6). Our value for the solvent ZLI2998-10 was essentially the same and the values for 5CB (4′-pentyl-4-biphenylcarbonitrile) were similar, but the value for PTTP24-36 was much higher and even higher than those for the single compounds.

By an error analysis using the following formulae

$$\Delta n_{\text{diacet}} = \frac{\Delta n_{\text{measure}} - \Delta n_{\text{host}}}{f} + \Delta n_{\text{host}}$$

$$\sigma^2_{\Delta n_{\text{diacet}}} = \frac{1}{f^2}\left[\sigma^2_{\Delta n_{\text{measure}}} + (1-f)^2\sigma^2_{\Delta n_{\text{host}}} + \left(\frac{\Delta n_{\text{measure}} - \Delta n_{\text{host}}}{f}\right)^2 \sigma_f^2\right]$$

where f is the fraction of material (typically 15%) added to the host compound, the uncertainty was obtained

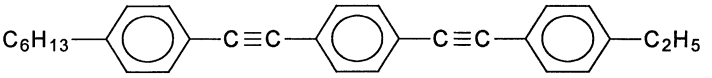
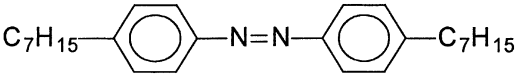
$$\sigma_{\Delta n_{\text{diacet}}} = 6.7\left[1.72\times10^{-4} + 6.4\times10^{-3}/225\right]^{\frac{1}{2}} \approx 095.$$

Thus, only differences larger than this can be considered valid in comparing our Δn values for different structures.

The Δn values determined using this method are presented in table 7. Only the 1-olefin chain increased the Δn values. The 2-olefin, cyclopropyl ring and amino groups gave values similar to those for the alkyl chain. The combination of a nitro and an amino group ($X = NO_2$, $Y = NR_2$) or two alkoxy groups gave a large decrease, but a perfluorinated chain decreased the birefringence even more. The birefringence seemed to increase when A and $X = F$, $Y =$ 1-olefin, but decrease when A, $B = F$.

Two physical properties determine the apparent birefringence of a mesogen in a liquid crystalline solvent (i) the molecular polarizability (slightly modified by local field effects in the solvent), (ii) the mean orientation or the order parameter of the mesogen. It is difficult, even with the errors in our measurements, to

Table 6. Optical birefringence values (Δn) for 15% solutions of some known liquid crystals.

Liquid crystal	Δn Reported	Δn Found
Solvent A—EM Industries ZLI2978-10	0.083	0.084
Solvent B—EM industries MLC6025-100	0.085	
Eutectic diacetylene mixture PTTP 24-36 (solvent A)	0.347[a]	0.514
5CB in solvent A	0.18[b]	0.215
5CB in solvent B		0.207
	~0.38[c]	0.214
		0.221

[a]Data are from reference [1].
[b]Data from reference [33].
[c]Data for the symmetrical C_3 analogue from reference [35].

rationalize all of these data in terms simply of the molecular polarizability. We believe, therefore, that at least some of this variation is due to changes in the molecular order parameter.

6. Experimental

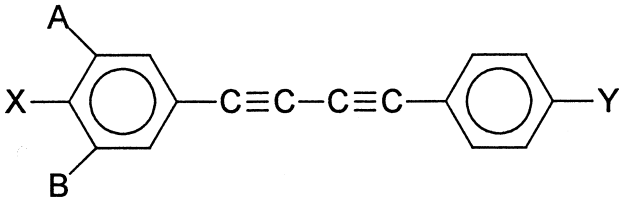
6.1. *Characterization*

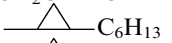
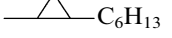
TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as the detectors. Purifications by chromatography were carried out by flash chromatography on silica gel (Fisher EM Science, 230–400 mesh). Capillary GC analysis was obtained using a Hewlett-Packard 5-m or 10-m methylsilicone gum column. Temperature programming was from 100°C(0) at 20°C min^{-1} to 250°C(0–15) with detector and injector temperatures set at 270°C, using a split valve rate of 182 ml min^{-1} and a column head pressure set at 16.22 ml min^{-1} unless otherwise noted. For GC analysis of the dialkyl diphenyldiacetylenes, see reference [36]. All gradient GCs were run at 20°C min^{-1}, retention times (t_R) are in minutes. Melting points were determined using a Hoover–Thomas melting point apparatus and are corrected. These are not provided for compounds for which transition temperatures were determined by microscopy (tables 1 and 2).

A Nicolet-Magna FTIR spectrophotometer was used to record IR spectra in cm^{-1} using NaCl plates. We were unable to obtain intense IR spectra for the compounds containing a perfluorinated chain when these were run in Nujol. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ 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. Data are recorded in the order of chemical shift (δ), multiplicity, number of protons, coupling constant (Hz), and identification. In order to maximize the amount of information obtained from a spectrum, sample solutions were made as concentrated as possible and overlapping proton regions expanded whenever possible. ^{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 acetylene carbon atoms of the diphenyldiacetylene group occurred at different chemical shifts whereas calculations showed only two different carbon chemical shifts.

Transitions 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°C min^{-1}. Discussions of mesophase identification by texture can be found in the literature [37]. Crystallization temperatures were obtained by cooling the melt at 2°C min^{-1} until crystals 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 they were not mesophases. Monotropic mesophases (those that occur below the melting temperature) were reheated immediately once formed to obtain the more accurate heating transition temperature. DSC scans were run using a Perkin-Elmer DSC 7 equipped with a TAC 7/PC instrument controller at the rate of 5°C min^{-1}, calibrated using indium and zinc. During the course of the research, Perkin-Elmer Pyris software was installed. A few scans were obtained using a Perkin-Elmer Pyris 1 DSC instrument equipped with a TAC 7/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 reheating this

Table 7. Optical birefringence values (Δn) from 15% solutions.



X	*Y*	Solvent	Δn
A,*B* = H			
C_2H_5	C_4H_9	A	0.404
C_3H_7	C_6H_{13}	A	0.344
C_2H_5	$CH_2CH(Me)Et$	A	0.358
$EtCH(Me)CH_2$	$CH_2CH(Me)Et$	A	0.274
F	$CH_2CH(Me)Et$	A	0.261
C_5H_{11}	COMe	A	0.237
$C_8H_{17}O$	O C_8H_{17}	A	0.154
C_5H_{11}	F	A	0.288
C_6H_{13}	C_3F_7	A	0.261
C_6H_{13}	C_8F_{17}	A	0.097
C_2H_5	C_8F_{17}	A	0.098
C_5H_{11}	$C\equiv CC_5H_{11}$	A	0.317
F	$C\equiv CC_5H_{11}$	A	0.151
C_5H_{11}	NMe_2	A	0.318
C_5H_{11}	NEtBu	A	0.348
F	NMeBu	A	0.298
NO_2	NHC_5H_{11}	A	0.117
NO_2	NBu_2	A	0.128
C_2H_5	CH=CHEt	A	0.381
F	CH=CHEt	A	0.441
CH_3	CH=CHPr	A	0.271
C_2H_5	CH=CHPr	A	0.354
C_6H_{13}	CH=CHPr	B	0.447
CF_3	CH=CHPr	A	0.328
F	CH=CHPr	A	0.438
C_3H_7	CH=CHBu	A	0.447
C_4H_9	CH=CHBu	A	0.444
C_5H_{11}	CH=CHBu	A	0.411
F	CH=CHBu	B	0.417
C_5H_{11}	$CH=CHCO_2Pr$	B	0.303
C_6H_{13}	$CH_2CH=CHEt$	B	0.323
F	$CH_2CH=CHEt$	B	0.369
C_6H_{13}	$CH_2CH=CHPr$	B	0.318
F	$CH_2CH=CHPr$	B	0.295
CH_3		A	0.317
F		A	0.301
A = F, *B* = H			
F	$CH_2CH=CHPr$	A	0.444
F	$CH_2CH=CHBu$	A	0.384
A, *B* = F			
F	C_5H_{11}	A	0.262
F	C_6H_{13}	A	0.283
F	CH=CHPr	A	0.291
F	CH=CHBu	A	0.354

crystallized material. Enthalpy values were obtained from the first heating run from virgin crystals.

Birefringence data were collected using the Leitz microscope fitted with a Leitz tilting compensator having 1–30 orders, a 10× reticle eyepiece, and a rotating stage. The tilt angle on the compensator was adjusted to near 0° and inserted into the compensator slot on the microscope. With the polarizers crossed and the iris diaphragm wide open, the sample was rotated 45° from the maximally dark position with the compensator. After closing the diaphragm to a few mm, the dial of the compensator was rotated showing a series of various coloured bands. There should be a black or dark purple band and sometimes two. The compensator dial was rotated until the first (darkest) black band was centred in the crosshairs and then the degrees were read using the black drum markings (rotation angle counter clockwise). Measurements were taken on the red band after clockwise rotation using the red drum markings. These should be the same. Red and black values were totaled, averaged, and at least three measurements of both were made and all the values added to give a more accurate number.

6.2. *Synthesis*

Commercially available starting materials were used without further purification except for some of the aldehydes, which were purified by vacuum distillation. Exposure to light in all reactions was minimized by avoiding illumination and wrapping the reaction flask with aluminum foil. Anhydrous reactions were carried out in 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°C when not in use. Organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate. To avoid low yields, tertiary butanol, used in preparing the bromoacetylenes, was always distilled within a day of its use and stored over Linde #4A sieves.

6.2.1. *4-Bromo-1-hept-1-ynylbenzene* ***8***

To a stirred solution of 1-heptyne (5.0 g, 52.0 mmol) in anhydrous THF (50 ml) at 0°C under N_2 was added from a syringe a 2.5M solution of *n*-BuLi in hexane (21.0 ml, 52.5 mmol) over a 15 min period. After stirring at 0°C for 1 h, a solution of anhydrous $ZnCl_2$ in THF (20 ml) was added quickly, stirring continued for an additional hour and the mixture allowed to warm to room temperature. A solution of 1-bromo-4-iodobenzene (14.7 g, 52.0 mmol) and $Pd(PPh_3)_4$ (2.93 g, 2.53 mmol) in THF (50 ml) was added dropwise and stirring continued at room temperature for an additional 20 h. The solvent was removed *in vacuo*, an equal volume of hexane added and the solution washed with 1.5N HCl, H_2O, saturated $NaHCO_3$ solution and saturated NaCl solution. The dried organic layer was filtered and the

solvent removed from the filtrate *in vacuo* to give the crude product (14.2 g). Purification of this material by chromatography using hexane gave 12.1 g (93.4%) of **8** as a yellow liquid. TLC (5% EtOAc in hexane), $R_f = 0.70$; GC $t_R = 3.48$ (96.41%, product), 1.29 (3.07%) and 2.70 (0.52%), IR(film) 2243 (wk d, alkyne), 1657 (wk., Ar) and 1493 (str d, Ar). ^{1}H NMR 7.40 (d, 2, $J = 8.22$, ArH *ortho* to Br), 7.24 (d, 2, $J = 8.42$, ArH *ortho* to alkyne), 7.38 (t, 2, $J = 7.00$, alkyne CH_2), 1.70–1.50 (m, 2, β-CH_2), 1.50–1.25 (m, 4, 2 CH_2), and 0.90 (t, 3, 6.94, CH_3). This material was used without further purification.

6.2.2. *2-(4-Bromophenyl)-2-methyl-1,3-dioxolane* ***10***

A mixture of the keto bromide **9** (40.0 g, 0.20 mol), ethylene glycol (13.7 g, 0.22 mol) and *p*-TSA (a few crystals) in benzene (75 ml) was heated under reflux for 17 h using a Dean–Stark trap. The cooled reaction mixture was extracted with Et_2O and the organic layer washed with 5% Na_2CO_3 solution and H_2O, and then dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave 37.1 g of the crude product. Both IR and ^{1}H NMR showed that this material contained both the ketal **10** and some of the starting ketone, but it was used without purification to prepare the acetylene **4**.

6.2.3. *Propyl-3-(4-bromophenyl)acrylate* ***11***

To a stirred mixture of 4-bromocinnamic acid (12.0 g, 52.8 mmol) and diethylazodicarboxylate (DEAD, 9.20 g, 52.8 mmol) in dry THF (53 ml) under N_2, cooled slightly below room temperature by an ice bath, was added dropwise a solution of PPh_3 (13.9 g, 52.8 mmol) and *n*-PrOH (4.76 g, 79.3 mmol) in THF (53 ml). This mixture was stirred at room temperature for 20 h and then the solvent was removed *in vacuo*. The remaining material was triturated with hexane and the insoluble solids removed by filtration. Removal of the solvent from the filtrate *in vacuo* gave 14.7 g of the crude solid product. Purification of this material by chromatography using increasing percentages of CH_2Cl_2 in hexane, up to 50%, gave 13.1 g (92.2%) of the ester **11** as a colourless solid. GC showed that this material was 99.4% pure ($t_R = 5.20$ min) which was sufficient for preparing the acetylene **4**. A purer sample of **11** was obtained, with difficulty, by recrystallization from 15% H_2O in EtOH m.p. 35.8–39.8°C, TLC ($CHCl_3$), $R_f = 0.611$, IR(Nujol) 1723 (str, CO_2R), 1644 (str, alkyne), 1598 (m, Ar), and 1173 (str, OR). ^{1}H NMR 7.62 (d, 1, $J = 16.03$, ArCH), 7.52 (d, 2, $J = 8.59$, ArH *ortho* to Br), 7.39 (d, 2, $J = 8.46$, ArH *ortho* to CH), 6.44 (d, 1, $J = 15.83$, $CHCO_2$), 4.17 (t, 2, $J = 6.76$, CO_2CH_2), 1.73 (sext, 2, $J = 7.14$, β-CH_2), and 0.99 (t, 3, $J = 7.41$, CH_3).

6.2.4. *1-Bromo-4-heptafluoropropylbenezene* ***12*** *($n = 3$)*

To a stirred solution of 1-bromo-4-iodobenzene (17.0 g, 0.06 mol) in DMSO (120 ml) containing Cu powder (12.9 g) at room temperature was added dropwise perfluoropropyl iodide (17.7 g, 0.06 mol). This mixture was heated at 100°C for 17 h, cooled to room temperature, poured into H_2O (300 ml) and then extracted with Et_2O (4×300 ml). The organic layer was separated, washed with H_2O (4×500 ml), dried, and filtered. Removal of the solvent from the filtrate *in vacuo* gave 28.6 g of the crude product **12** ($n = 3$). TLC ($CHCl_3$), $R_f = 0.70$, 0.59, IR(film) 1601 (med, Ar). ^{1}H NMR 7.67 (d, 2, $J = 8.71$, ArH *ortho* to Br).

The $n = 8$ homologue was prepared in the same manner to give a yellow solid (62.1%), m.p. 77–81.0°C. ^{13}C NMR 139.1, 138.0, 133.4, 133.1, 132.1, 128.6, 128.5, 128.3, 127.9, 127.0, 121.1, and 114.2. An attempt to purify this compound by chromatography using hexanes was unsuccessful. Both bromides ($n = 3$, 8) were used to prepare the acetylenes **4** without further purification.

6.2.5. *2-Methylbutanoyl chloride* ***14***

Oxalyl chloride (67.6 ml, 0.53 mol) was added dropwise to a stirred solution of 2-methylbutyric acid (45.4 g, 0.44 mol) in CH_2Cl_2 (500 ml) and the mixture stirred at room temperature for 9 h. Excess oxalyl chloride was removed by distillation to give 44.0 g (82.9%) of the crude acid chloride **14** which was used without further purification; IR(film) 1798 (str, COCl).

6.2.6. *2-Methylbutanoylbenzene* ***15***

To a stirred mixture of $AlCl_3$ (67.7 g, 0.51 mol) in benzene (169 ml) at 0°C was added dropwise the crude acid chloride **14** (51.0 g, 0.42 mol) during 1 h. The resulting mixture was heated at reflux for 2 h, cooled to room temperature and then poured slowly into a mixture of ice (525 g) in HCl (175 ml). After stirring this mixture for 30 min, it was extracted with Et_2O. The organic layer was separated, washed twice with H_2O, dried and filtered. Removal of the solvent from the filtrate followed by distillation *in vacuo* at 61°C (0.32 mmHg) [lit [13] b.p. for *S*-isomer 132–133°C (32 mmHg)] gave 63.9 g (93.2%) of the ketone **15** TLC ($CHCl_3$), $R_f = 0.63$, GC $t_R = 3.47$ (95.32%, ketone) and 0.26 (4.67%), IR(film) 1691 (str, C–O), and 1597, 1584 (med, Ar). ^{1}H NMR 7.96 (d, 2, $J = 6.67$, Ar H *ortho* to C–O), 7.60–7.40 (m, 3, Ar H), 3.41 (sext, 1, $J = 6.74$, CH), 1.83 (sept, 1, $J = 7.07$, CH_2 proton closest to

CH_3), 1.51 (sept, 1, $J=7.28$, CH_2 proton closest to H), 1.20 (d, 3, $J=6.88$, α-CH_3), and 0.92 (t, 3, $J=7.41$, CH_3).

6.2.7. *2-Methyl-1-phenylbutane* ***17***

To a stirred mixture of LAH (24.3 g, 0.64 mol) in anhydrous Et_2O (579 ml) cooled in an ice bath was slowly added $AlCl_3$ (128.1 g, 0.96 mol) over 40 min, keeping the temperature at 5°C or under. A solution of the ketone **15** (53.2 g, 0.32 mol) in $CHCl_3$ (965 ml) was added dropwise allowing the reaction temperature to increase to room temperature. This mixture was then heated at reflux for 13 h, cooled to room temperature, and a saturated solution of Na_2SO_4 added dropwise until all the LAH became white and a clear organic layer became visible. Extraction of this mixture twice with $CHCl_3$ and separation of the layers gave an organic extract that was washed twice with H_2O, dried, and filtered. Removal of the solvent from the filtrate *in vacuo* gave the crude product. Distillation of this liquid at 44°C (0.35 mmHg) [lit [12], b.p. 101.5–102°C (40 mm)] gave 37.7 g (79.4%) of the alkylbenzene **17** TLC($CHCl_3$), $R_f=0.75$, GC $t_R=2.58$ (96.60%, product) and 0.29 (3.40%), IR(film) showed no C=O at 1690. ^{1}H NMR 7.32–7.10 (m, 5, Ar H), 2.64 (dd, 1, $J=6.20$, 13.41, $ArCH_2$ proton closest to CH_3), 2.36 (dd, 1, $J=7.99$, 12.87, $ArCH_2$ proton closest to H), 1.63 (2 app sexts, 1, $J=6.50$, CH), 1.51–1.28 (m, 1, CH_2 proton closest to β-CH_3), 0.91 (t, 3, $J=7.92$, terminal CH_3), and 0.85 (d, 3, $J=6.63$, β-CH_3). Proton assignments for these 2-methylbutyl compounds were based on spectra for 2-methylbutanol [38]. Similar data were reported earlier for compound **17** [39].

6.2.8. *4-(2-Methylbutyl)benzoic acid* ***16***

To a stirred solution of $AlCl_3$ (13.47 g, 0.10 mol) in CH_2Cl_2 (39 ml) at room temperature was added dropwise $(COCl)_2$ (25.7 g, 0.20 mol) followed by a solution of the alkylbenzene **17** (15.0 g, 0.10 mol) in CH_2Cl_2 (57 ml) over a 40 min period. The volume of the reaction mixture was reduced to half by distillation to remove $(COCl)_2$. An equal volume of CH_2Cl_2 was then added to the cooled remaining liquid and the solution poured into a mixture of ice (250 g) and $CaCl_2$ (15 g). The organic layer was separated, washed with H_2O, dried, and filtered. Removal of the solvent from the filtrate *in vacuo* gave 18.0 g (84.3%) of the crude acid chloride. IR(film) 1778.9, 1740 (str dbl, COCl), 1700 (wk, CO_2H), and 1600 (str, Ar). This liquid was heated under reflux in a solution of NaOH (27 g, 0.68 mol), EtOH (370 ml), and H_2O (180 ml) for 24 h and then cooled to room temperature. The EtOH was removed *in vacuo*, H_2O (1.5 l) added, the mixture cooled in an ice bath and made acidic with conc HCl. The resulting precipitate was collected by filtration, washed with water, and dried to give the crude product. Recrystallization of this solid from hexane gave 22.0 g (84.3%) of the purified acid **16** m.p. 130–132°C (lit [14] m.p. 130°C), TLC($CHCl_3$), $R_f=0.04$; IR(Nujol) 3200–2400 (br, acid OH), 1697 (str, CO_2H), and 1607 (str, Ar). ^{1}H NMR 8.03 (d, 2, $J=8.14$, Ar H *ortho* to CO_2H), 7.25 (d, 2, $J=8.06$, ArH *ortho* to CH_2), 2.72 (dd, 1, $J=13.18$, 6.22, $ArCH_2$ proton closest to CH_3), 2.44 (dd, 1, $J=13.26$, 8.08, $ArCH_2$ proton closest to H), 1.68–1.71 (sext, 1, $J=6.51$, CH), 1.33–1.40 (m, 1, CH_2 proton closest to CH_3), 1.01–1.26 (m, 1, CH_2 proton closest to H), 0.90 (t, 3, $J=7.24$, terminal CH_3), and 0.85 (d, 3, $J=6.59$, β-CH_3).

6.2.9. *4-(2-Methylbutyl)phenylmethanol* ***18***

To a stirred solution of LAH (2.95 g, 77.6 mmol) in THF (64 ml) under N_2 at 0°C was added dropwise a solution of the acid **16** (15.0 g, 77.6 mmol) in THF (24 ml) during 1.5 h. This mixture was allowed to warm to room temperature and stirred for 72 h. The LAH was slowly decomposed by a dropwise addition of H_2O (125 ml) followed by 20% NaOH in H_2O (9.5 ml) and H_2O (12.5 ml) until the grey suspension turned white. The resulting precipitate was collected by filtration and washed thoroughly with THF. The THF was removed from the filtrate *in vacuo*, H_2O (200 ml) added and the solution extracted with Et_2O. The Et_2O layer was washed with H_2O, dried, and filtered. Removal of the solvent from the filtrate *in vacuo* gave a liquid which was chromatographed using 1/1 CH_2Cl_2/hexane to give 11.9 g (85.6%) of the liquid alcohol **18**. TLC ($CHCl_3$), $R_f=0.53$, IR(film) 3357 (str br, OH), 1619 (med, Ar), and no carbonyl absorption. ^{1}H NMR 7.28 (d, 2, $J=7.86$, Ar H *ortho* to CH_2OH), 7.15 (d, 2, $J=8.06$, Ar H *ortho* to CH_2), 4.64 (s, 2, CH_2O), 2.65 (dd, 1, $J=13.48$, 6.22, $ArCH_2$ proton closest to CH_3), 2.38 (dd, 1, $J=13.72$, 7.99, Ar CH_2 proton closest to H), 2.00 (s, 1, OH), 1.64 (app sext, 1, $J=6.52$, CH), 1.50–1.30 (m, 1, CH_2 proton closest to CH_3), 1.30–1.05 (m, 1, CH_2 proton closest to H), 0.92 (t, 3, $J=7.24$, terminal CH_3), and 0.86 (d, 3, $J=6.67$, β-CH_3).

Another batch of this compound was purified by distillation at 95–110°C (0.6 mmHg) giving a yield of 78.9%, GC $t_R=3.07$ (99.43%).

6.2.10. *4-(2-Methylbutyl)benzaldehyde* ***19***

To a stirred mixture of pyridinium chlorochromate (PCC, 73.8 g, 0.34 mol) in CH_2Cl_2 (456 ml) under N_2 at room temperature, was added dropwise a freshly prepared solution of the alcohol **18** (40.7 g, 0.23 mol) in CH_2Cl_2 (43 ml), and stirring was continued for 30 min. A TLC ($CHCl_3$) of the reaction mixture showed

that no starting alcohol was present. Ether (250 ml) was added to the reaction mixture and the resulting mixture filtered through alternating layers of Celite and Florosil (total weight = 158 g, 12.5 cm Buchner funnel) twice to remove the chromium salts and dark colour. Removal of the solvent from the filtrate *in vacuo* followed by distillation of the residue at 85–88°C (0.4 mmHg) gave 31.1 g (77.5%) of the aldehyde **19** as a thick yellow liquid. TLC ($CHCl_3$), $R_f = 0.55$ and 0.41 (trace), GC $t_R = 2.82$ (93.13%, product), 2.67 (2.23%), and 3.83 (3.78%); IR(film) 2875, 2730 (med, CHO), 1709 (str, CHO), 1608, 1582 (str, wk, Ar). ^{1}H NMR 9.97 (s, 1, CHO), 7.80 (d, 2, $J = 8.42$, ArH *ortho* to CHO), 7.31 (d, 2, $J = 7.69$, ArH *ortho* to *R*), 2.72 (dd, 1, $J = 13.18$, 6.23, $ArCH_2$ proton nearest to CH_3), 2.44 (dd, 1, $J = 13.18$, 8.06, $ArCH_2$ proton nearest to H), 1.70 (app sext, 1, $J = 6.59$, CH), 1.60–1.10 (m, 2, CH_2), 0.92 (t, 3, $J = 7.33$, terminal CH_3), and 0.85 (d, 3, $J = 6.59$, β-CH_3).

6.2.11. *Synthesis of the protected acetylenes* ***4***

These compounds were prepared from the bromides **2** using the procedures reported earlier for other *X* substituents [3]. Characterization data for the new analogues and any variations from these procedures are given here.

$X = C_5H_{11}–C\equiv C$. Reflux time was 0.5 h, purification was by chromatography using 20% EtOAc in hexane, yield = 80.3%, pale yellow liquid. TLC ($CHCl_3$), $R_f =$ 0.14, IR(film) 3353 (med, br, OH), 2228 (wk, alkyne), 1516 (str, $C\equiv C\cdot C_6H_4\ C\equiv C$). ^{1}H NMR 7.32 (s, 4, Ar H), 2.41 (t, 2, $J = 7.08$, α-CH_2), 2.05 (s, 1, OH), 1.61 (s, m, 8, 2 CH_3, β-CH_2), 1.50-1.20 (m, 4, 2 CH_2), and 0.92 (t, 3, $J = 6.92$, terminal CH_3).

$X =$. Purification of the crude product was by chromatography using CH_2Cl_2, yield = 66.7% of a liquid TLC ($CHCl_3$), $R_f = 0.18$, IR(film) 3411 (str, br, OH), 2226 (v wk, alkyne), 1588 (str, Ar), and 1592 (str, Ar), and no C=O absorption. ^{1}H NMR 7.90 (d, 2, $J = 8.05$, Ar H *ortho* to alkyne), 7.50 (d, 2, $J = 8.06$, Ar H *ortho* to C), 4.03 (t, 2, $J = 3.46$, OCH_2 closest to Ar), 3.77 (t, 2, $J = 3.48$, OCH_2 closest to CH_3), 2.61 (s, 3, terminal CH_3), and 1.60 (s, 6, 2 CH_3).

$X = C_3H_7O_2CH=CH$. Purification was by chromatography using EtOAc/hexane followed by recrystallization from hexane (tends to form an oil when the concentration is too high) gave 8.6 g (67.3%) of compound **4** as a colourless solid. TLC ($CHCl_3$), $R_f = 0.057$, IR(Nujol) 3283 (OH), 1710 (m, CO_2R), and 1644 (med, Ar alkyne). ^{1}H NMR 7.64 (d, 1, $J = 16.11$, ArCH), 7.47 (d, 2, $J = 8.79$, Ar H *ortho* to C), 7.41 (d, 2, $J = 8.79$, ArH *ortho* to CH), 6.44 (d, 1, $J = 16.12$, β-CH), 4.17 (t, 2, $J = 6.59$, CO_2CH_2), 2.10 (s, 1, OH), 1.73 (sext, 2, $J = 7.14$, CH_2), 1.63 (s, 6, 2 CH_3) and 0.99 (t, 3, $J = 7.33$, terminal CH_3).

$X = C_nF_{2n+1}$. $n = 3$: crude yield = 93.8%. Purification of this material by chromatography using 5–10% EtOAc/hexane gave 9.75 g (33.7%) of the acetylene **4** as a yellow liquid. TLC (10% EtOAc/hexane), $R_f = 0.12$, GC $t_R = 1.62$ (92.4%, product), 1.26 (7.60%). ^{1}H NMR 7.53 (s, 4, ArH), 2.02 (s, 1, OH), and 1.64 (s, 6, 2 CH_3) $n = 8$: purification of this material by chromatography using 10–15% EtOAc in hexane gave a yield of 80.0% of the acetylene **4** as a yellow solid m.p. 80.5–82.0°C. ^{13}C NMR 133.1, 131.7, 131.5, 128.9, 128.4, 128.0, 126.9, 126.8, 126.6, 110.8, 96.5, 80.8, 65.6, and 31.3.

6.2.12. *Synthesis of the acetylenes* ***6*** *from the protected acetylenes* ***4***

Removal of the protecting group from the acetylenes **4** was achieved using the same method as reported earlier [3]. Variations from these procedures and characterization data for these new analogues are given here.

$X = C_5H_{11}–C\equiv C$. Reflux time 4 h. Purification by chromatography using CH_2Cl_2 gave 57.3% of a yellow liquid TLC ($CHCl_3$), $R_f = 0.79$, GC $t_R = 4.34$ (100%); IR(film) 3296 (str, alkyne H), 2115 (wk, alkyne), and 1518 (ArH). ^{1}H NMR 7.40 (d, 2, $J = 8.50$, ArH *ortho* to alkyne), 7.32 (d, 2, $J = 8.50$, ArH *ortho* to C_5 alkyne), 3.13 (s, 1, alkyne H), 2.40 (t, 2, $J = 6.96$, α-CH_2), 1.69–1.52 (m, 2, β-CH_2), 1.50–1.30 (m, 4, 2 CH_2) and 0.92 (t, 3, $J = 7.24$, CH_3).

$X =$. Reflux time was 17 h, crude yield 27.8%, then used without purification. ^{1}H NMR supported this structure.

$X = C_3F_7$. Purification by chromatography using hexane gave a yield of 36.4% of the acetylene **6** as a yellow liquid TLC (hexane), $R_f = 0.55$, GC $t_R = 0.28$ (96.9%, product) and 1.73 (3.09%); IR(film) 3317 (str, alkyne H), 2380, 2340 (wk, alkyne), and 1613 (med, Ar). ^{1}H NMR 7.63 (d, 2, $J = 8.42$, ArH *ortho* to R_f), 7.56 (d, 2, $J = 8.42$, Ar H *ortho* to C_3F_7), 3.23 (s, 1, alkyne H), and no aliphatic chain protons.

$X = C_8F_{17}$. Preparation was in the same manner as for $X = C_3F_7$. Reflux time was 6 h, yield 35.7% of a colourless liquid, GC $t_R = 1.04$ (100%). Characterization data were the same as for the C_3 homologue.

$X = C_3H_7O_2CCH=CH–$. This acetylene was prepared using the NaH method [40] to avoid ester hydrolysis. To stirred solution of the protected acetylene **4** (8.40 g, 30.8 mmol) in dry toluene (2 ml) under N_2 at room temperature, was slowly added 60% NaH in oil (164 mg). This mixture was heated to reflux using a short path distillation head to collect liquids distilling

below *c* 106°C. After the temperature remained steady for 20 min, the reaction mixture was cooled to room temperature, filtered, and the insoluble material washed thoroughly with toluene followed by a small amount of acetone. The solvents were removed from the filtrate *in vacuo* and the remaining material dissolved in CH_2Cl_2 (150 ml). This solution was extracted with 5% $NaHCO_3$ solution (100 ml), washed with H_2O (150 ml), dried, and filtered. Removal of the solvent from the filtrate gave 5.98 g (98.6%) of the crude product. Purification of this material by chromatography using 40% CH_2Cl_2/hexane gave 5.18 g (78.4%) of the acetylene **6** as a yellow solid m.p. 41.8–47.2°C, GC $t_R = 4.72$ (99.18%), IR(Nujol) 3224 (med, acetylene H), 2105 (wk, alkyne), 1704 (str, CO_2R), 1645 (str, Ar C=C), 1560, 1513 (str, med, Ar). ^{1}H NMR 7.65 (d, 1, $J = 16.11$, ArCH), 7.51 (d, 2, $J = 8.79$, ArH *ortho* to C), 7.47 (d, 2, $J = 9.16$, ArH *ortho* to CH), 6.45 (d, 1, $J = 16.12$, COCH), 4.17 (t, 2, $J = 6.59$, α-CH_2), 3.19 (s, 1, acetylene H), 1.73 (sext, 2, $J = 7.10$, β-CH_2), and 1.00 (t, 3, $J = 7.51$, terminal CH_3).

6.2.13. *Preparation of the dibromoolefins* **5**

These compounds were prepared from the aldehydes **3** using method 2 described earlier [3]. Purification, reaction variations, and characterization data are provided here.

$Y = CH_2CH(CH_3)C_2H_5$. Purified yield was 66.8%, yellow liquid GC $t_R = 5.49$ (96.16%, product), 1.53 (0.78%), and 5.21 (2.28%), IR(film) 1614 and 1515 (wk, ArC=C), and ^{1}H NMR 7.46 (d, 2, $J = 7.69$, ArH *ortho* to C=C), 7.44 (s, 1, CH=CBr), 7.14 (d, 2, $J = 8.06$, ArH *ortho* to CH_2), 2.62 (dd, 1, $J = 13.55$, 6.23, $ArCH_2$ proton closest to CH_3), 2.35 (dd, 1, $J = 13.19$, 8.06, $ArCH_2$ proton closest to H), 1.65 (app sext, 1, $J = 6.50$, CH), 1.51–1.05 (m, 2, CH_2), 0.90 (t, 3, $J = 7.33$, terminal CH_3), and 0.84 (d, 3, $J = 6.59$, β-CH_3).

Y=CN. Purification was by chromatography using 35% CH_2Cl_2/hexane followed by recrystallization from abs EtOH, yield was 76.0%: m.p. 90.0–91.5°C, IR(Nujol) 2228 (wk, CN) and 1600 (wk, C–C). ^{1}H NMR 7.68 (d, 2, $J = 9.16$, ArH *ortho* to CN), 7.63 (d, 2, $J = 9.16$, ArH *ortho* to CH), and 7.50 (s, 1, CH).

$Y = OC_{12}H_{25}$. Purified by recrystallization from abs EtOH, yield 52.2% pale yellow solid: m.p. 39.3–41.3°C, GC $t_R = 11.62$ (99.21%, product), 10.22 (0.42%), and 10.41 (0.37%). ^{1}H NMR 7.63 (d, 2, $J = 9.16$, ArH *ortho* to CH), 7.40 (s, 1, CH), 6.87 (d, 2, $J = 8.79$, ArH *ortho* to O*R*), 3.96 (t, 2, $J = 6.41$, OCH_2), 1.78 (q, 2, $J = 6.96$, β-CH_2), 1.54–1.21 (m, 18, 9 CH_2), and 0.88 (t, 3, $J = 6.59$, CH_3).

6.2.14. *Preparation of the 1-Bromoacetylenes 7*

These compounds were prepared from the dibromoolefins using method 2 as described earlier [3]. Variations from this procedure and characterization are provided here.

$Y = CH_2CH(CH_3)C_2H_5$. This compound was prepared several times. GC of the crude materials showed the bromoacetylene **7** ($t_R = 3.15$) contaminated with the acetylene **6** ($t_R = 1.50$) and sometimes the starting dibromoolefin **5** ($t_R = 4.45$). Attempts to separate these cleanly by column chromatography were unsuccessful. Since all these compounds can yield the acetylene **6**, this mixture was converted to the acetylene without further purification. One sample gave the following characterization data. GC $t_R = 3.18$ (92.84%, **7**), 1.49 (3.8%, **6**), 2.60 (0.94%), and 3.05 (1.63%), IR(film) 2203 (wk, alkyne), 1611 (wk, Ar), and 1512 (med, Ar). ^{1}H NMR 7.35 (d, 2, $J = 8.31$, ArH *ortho* to Br), 7.08 (d, 2, $J = 8.30$, ArH *ortho* to CH_2), 2.62 (dd, 1, $J = 13.43$, 6.18, $ArCH_2$ proton closest to CH_3), 2.34 (dd, 1, $J = 13.31$, 8.02, $ArCH_2$ proton closest to H), 1.64–1.56 (m, 1, CH), 1.40–1.00 (m, 2, CH_2), 0.89 (t, 3, $J = 7.33$, terminal CH_3), and 0.82 (d, 3, $J = 7.41$, β-CH_3). Samples such as this, which did not contain the dibromoolefin **5**, were used to prepare the diacetylenes.

$Y = OC_{12}H_{25}$. Reflux time was 6 h: pale yellow solid, GC $t_R = 8.88$ (100.0%). ^{1}H NMR 7.36 (d, 2, $J = 8.79$, ArH *ortho* to alkyne), 6.81 (d, 2, $J = 8.79$, ArH *ortho* to O*R*), 3.93 (t, 2, $J = 6.59$, OCH_2), 1.77 (quint, 2, $J = 7.20$, β-CH_2), 1.70–1.05 (m, 18, 9 CH_2), and 0.88 (t, 3, $J = 6.41$, CH_3).

Y=CN. Reflux time was 9 h, purification from abs EtOH gave a yellow solid (40.6%) m.p. 146–147°C, TLC (5% EtOAc/hexane) $R_f = 0.39$. ^{1}H NMR 7.61 (d, 2, $J = 8.79$, ArH *ortho* to CN), and 7.51 (d, 2, $J = 8.42$, ArH *ortho* to alkyne).

6.2.15. *4-Ethynyl-(2-methylbutyl)benzene* **6** *X* = $CH_2CH(CH_3)C_2H_5$

To a stirred solution of the impure bromoacetylene **7** (3.76 g, about 15.0 mol) in dry THF (15 ml) at −78°C under N_2, was added dropwise a solution of *sec*-BuLi in THF (15.0 ml, 19.5 mol). Stirring was continued at this temperature for 1 h. The reaction mixture was allowed to warm to room temperature, stirred for 1 h, then H_2O was slowly added (40 ml), and the mixture extracted with Et_2O (50 ml). The Et_2O extract was washed 3 times with H_2O (75 ml), dried, filtered, and the solvent removed from the filtrate *in vacuo* to give 3.1 g of the crude product. Purification of this material by chromatography gave 2.87 g of the liquid acetylene **6** TLC (hexane), $R_f = 0.40$, GC $t_R = 1.50$ (99.52%, product) and 0.65 (0.11%), IR(film) 3302 (med, alkyne H), 2111 (med, alkyne), 1610 (wk, Ar), and 1509 (med, Ar). ^{1}H NMR 7.40 (d, 2, $J = 8.18$, ArH *ortho* to alkyne), 7.10 (d, 2, $J = 8.30$, ArH *ortho* to CH_2), 3.03 (s, 1, acetyl H),

2.63 (dd, 1, $J=13.27$, 6.23, $ArCH_2$ proton closest to CH_3), 2.35 (dd, 1, $J=13.29$, 8.06, $ArCH_2$ proton closest to H), 1.75–1.50 (m, 1, CH), 1.50–1.05 (m, 2, CH_2), 0.90 (t, 3, $J=7.33$, terminal CH_3), and 0.83 (d, 3, $J=6.64$, β-CH_3).

6.2.16. *Preparation of the cyclopropyl intermediates*

For this work the following equipment was used for characterization. Aldrich silica gel TLC plates #Z12278-5, Perkin-Elmer 1430 ratio recording infrared spectrophotometer or a Bowman MB-122 Michelson series FTIR, and a GE QE-300. ^{1}H FTNMR with Tecmag Aquarius modifications. The Zn–Cu couple was prepared using a method described earlier [42]. The salt $K_3PO_4 \cdot 3H_2O$ was prepared by placing anhydrous K_3PO_4 in a dessicator (without dessicant) along with an open container of H_2O (3 mol/mol salt) and allowing the salt to absorb the H_2O during 48 h. The resulting solid was ground to a powder for addition to the reaction mixture.

Synthesis of the precursors **24**–**27**, **29**, and **30** for the cyclopropylbenzaldehydes **22** by the pathways shown in scheme 5 are adequately described in the literature for $R=C_6H_{13}$ [24, 25]. The remaining homologues ($R=C_5H_7$, C_7H_{15} and $C_{10}H_{21}$) were prepared using the same methods. Characterization data for our materials agreed with those reported. This section will concentrate on the synthesis of the cyclopropyl intermediates. Typical examples of the procedures used and characterizations are given here.

6.2.16.1. *trans-(2-Heptyl)cyclopropylboronic acid **31**.* To a stirred solution of a Zn-Cu couple (7.74 g, 118 mmol) in anhydrous Et_2O (925 ml) under anhydrous conditions at room temperature, was carefully added CH_2I_2 (15.86 g, 59.2 mmol) followed by Me_3SiCl (0.40 ml). Once this mixture began to reflux, a solution of the freshly prepared boronic ester **29** ($R=C_7H_{15}$, 5.85 g, 29.6 mmol) in Et_2O (15 ml) was added dropwise during 1 h. Heating at reflux was continued for 24 h and then the reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was washed with a saturated NH_4Cl solution (25 ml) and then 3 times with H_2O (15 ml). The solvent was removed *in vacuo* from the dried organic layer to give 2.84 g (35.0%) of the cyclopropylboronic acid **31** ($R=C_7H_{15}$) IR(film) 3080, 3000, 1450, 1400, 1360, 1280, 1260, 1160 and 1100. ^{1}H NMR showed a broad multiplet at 2.50 to 0.5.

The C_6 and C_{10} homologues were prepared in the same manner. The C_6 homologue was purified further by converting it to the methyl ester **32** and then hydrolysing this back to the acid; yield was 29.3%. The yield for the C_{10} homologue was *c* 52%.

6.2.16.2. *trans-(2-Decyl)cyclopropylpinacolboronate **33**.* To a stirred solution of pinacol (**28**, 1.83 g, 15.4 mmol) in pentane (20 ml) was added the boronic acid **31** ($R=C_{10}H_{21}$, 3.55 g, 15.4 mmol). Stirring was continued for another 30 min and then the reaction mixture was filtered. The filtrate was dried and the solvent evaporated to give 4.98 g of a yellow oil. Chromatographic purification of this material using 5% Et_2O/hexane gave 1.78 g, (37.6%) of the ester **33** as a yellow oil. IR 3060, 3000, 1640, 1450, 1380, 1010, 990 and 900. and ^{1}H NMR 1.27 (m, alkane), 0.88 (m, CH_3), and 0.42 (m, cyclopropyl). These data agree with those for the $R=C_4$ analogue [40].

6.2.16.3. *4-(trans-2-Hexylcyclopropyl)benzaldehyde 22 ($R=C_6H_{13}$).* A mixture of the boronic acid **31** ($R=C_6H_{13}$, 3.55 g, 21 mmol), K_3PO_4 $3H_2O$ (17.3 g, 21 mmol) and $Pd(PPh_3)_4$ (670 mg, 21 mmol) was added to a stirred solution of 4-bromobenzaldehyde (3.55 g, 9 mmol) in dry toluene (77 ml) under N_2 at room temperature. This mixture was heated to 100°C for 21 h and cooled to room temperature; H_2O (200 ml) was then added and the mixture extracted twice with hexane. The organic layer was washed 3 times with saturated NaCl solution, filtered through silica gel (10 g), and the solvent removed *in vacuo* from the filtrate. Chromatography of the remaining material on silica gel (175 g) using 15% Et_2O/hexane gave 3.91 g (80.5%) of the aldehyde **22** ($R=C_6H_{13}$) as a yellow oil. TLC (15% Et_2O/hexane) showed minor spots at $R_f=0.51$ (4-bromobenzaldehyde), 0.20 (boronic acid **31**), and a major spot with $R_f=0.62$ for the aldehyde **22**; IR 2920, 2855, 1700, 1605, 1570, 1212 and 1167. ^{1}H NMR 9.95 (s, 1, CHO), 8.80 (d, 2, ArH *ortho* to CHO), 8.20 (d, 2, ArH *ortho* to cyclopropyl), and 0.80–1.70 (m, 17, alkyl and cyclopropyl).

The $R=C_7$ homologue was prepared in a similar manner, with a 57.8% yield. This material was slightly impure after two chromatographic treatments. The C_{10} homologue was prepared by treating the ester **33** ($R=C_{10}H_{21}$) in the same manner, the yield was 42.3% (after two chromatographic treatments). The aldehydes **22** were converted to the bromoacetylenes **7** ($Y=$cyclopropyl-*R*) via the dibromoacetylenes **5** ($Y=$cyclopropyl-*R*) using the methods 2 previously described [3].

6.2.17. *Preparation of the diacetylenes **1***

These compounds were prepared by coupling the acetylenes **6** with the bromoacetylenes **7** in the same manner as described earlier. Experimental details varying from those reported and representative characterization data for the new analogs prepared are given here.

$X=C_2H_5$, $Y=CH_2CH(CH_3)C_2H_5$. Purification was

by recrystallization from MeOH, yield 29.8%. GC $t_R = 7.16$ (0.33%, possibly PTTP-22) and 8.56 (99.67%, product). ^{1}H NMR 7.45 (d, 2, $J = 8.18$, ArH *meta* to Et), 7.43 (d, 2, $J = 8.18$, ArH *meta* to branched chain), 7.16 (d, 2, $J = 8.42$, ArH *ortho* to Et), 7.11 (d, 2, $J = 8.42$, ArH *ortho* to branched chain), 2.67 (q, 2, $J = 7.55$, $ArCH_2$), 2.64 (dd, 1, $J = 13.18$, 6.21, $ArCH_2$ proton closest to CH_3), 2.36 (dd, 1, $J = 13.23$, 8.06, $ArCH_2$ proton closest to H), 1.64 (t, 1, $J = 6.36$, CH), 1.50–1.06 (m, 2, γ-CH_2), 1.23 (t, 3, $J = 6.0$, ethyl CH_3), 0.90 (t, 3, $J = 7.31$, branched chain terminal CH_3), and 0.84 (d, 3, $J = 6.58$, CH_3).

$X = CH_2CH(CH_3)C_2H_5$, $Y = C_{12}H_{25}O$. Since the bromoacetylene **7** ($Y = C_{12}H_{25}O$) was not very soluble in MeOH, a 1/1 mixture of MeOH/THF was used as the solvent for this compound and three times the amount of MeOH was used as the reaction solvent; reaction time was 1 h. The crude product, isolated by filtration of the reaction mixture, was dried *in vacuo*, a small amount of hexane added and the mixture filtered to remove copper salts. The solid isolated from the filtrate was purified by chromatography using hexane. The desired asymmetrical diacetylene **1** ($X = CH_2CH(CH_3)C_2H_5$, $Y = C_{12}H_{25}O$) was eluted first and recrystallized from CH_3CN to give a yield of 53.6% of a colourless solid. TLC (hexane), $R_f = 0.06$. ^{1}H NMR 7.45 (d, 2, $J = 9.16$, ArH *meta* to OR), 7.43 (d, 2, $J = 8.42$, ArH *meta* to branched chain), 7.10 (d, 2, $J = 8.42$, ArH *ortho* to branched chain), 6.83 (d, 2, $J = 9.16$, ArH *ortho* to OR), 3.95 (t, 2, $J = 6.59$, OCH_2), 2.64 (dd, 1, $J = 13.55$, 6.23, $ArCH_2$ proton closest to CH_3), 2.36 (dd, 1, $J = 13.55$, 8.06, $ArCH_2$ proton nearest to H), 1.78 (quint, 2, $J = 6.84$, β-alkoxy CH_2), 1.68–1.00 (m, 21, $CHCH_2$ and 9 CH_2), 0.90 (t, 3, $J = 7.33$, terminal branched chain CH_3), 0.88 (t, 3, $J = 5.86$, alkoxy CH_3), and 0.84 (d, 3, $J = 6.59$, methane CH_3).

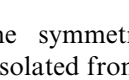
Some of the symmetrical diacetylene **1** ($X, Y = C_{12}H_{25}O$) was isolated from the recrystallization solvent and recrystallized from hexane. TLC (30% CH_2Cl_2-hexane), $R_f = 0.51$. ^{1}H NMR 7.44 (d, 4, $J = 9.16$, ArH *ortho* to alkyne), 6.83 (d, 4, $J = 9.16$, ArH *ortho* to OR), 3.95 (t, 4, $J = 6.59$, OCH_2), 1.78 (quint, 4, $J = 6.84$, β-CH_2), 1.60–1.50 (m, 36, $2 \times 9\,CH_2$), and 0.88 (t, 6, $J = 6.41$, 2 CH_3).

$X = F$, $Y = CH_2CH(CH_3)C_2H_5$. Reaction time was 3.5 h at room temperature, recrystallization from MeOH; yield was 39.5%. TLC (hexane), $R_f = 0.28$, GC $t_R = 6.00$ (0.86%) and 8.92 (98.49%). ^{1}H NMR 7.51 (dd, 2, $J = 8.96$, 5.33, ArH *meta* to F), 7.44 (d, 2, $J = 8.26$, ArH *meta* to CH_2), 7.12 (d, 2, $J = 8.22$, ArH *ortho* to CH_2), 7.03 (t, 2, $J = 8.73$, ArH *ortho* to F), 2.64 (dd, 1, $J = 13.49$, 6.20, $ArCH_2$ proton closest to CH_3), 2.37 (dd, 1, $J = 13.45$, 8.05, $ArCH_2$ proton closest to H), 1.64 (sext, 1, $J = 6.78$, CH), 1.50–1.05 (m, 2, aliph CH_2), 0.90 (t, 3, $J = 7.28$, γ-CH_3), and 0.84 (d, 3, $J = 6.64$, β-CH_3).

$X = C_5H_{11}$, $Y = CN$. Reaction time was 17 h at room temperature, recrystallization from abs EtOH. GC $t_R = 11.42$ (99.70%); IR(Nujol) 2228 (wk, alkyne, CN), 2223 (med, CN, alkyne). ^{1}H NMR 7.63 (d, 2, $J = 8.22$, ArH *ortho* to CN), 7.58 (d, 2, $J = 8.63$, ArH *meta* to CN), 7.45 (d, 2, $J = 8.10$, ArH *meta* to CH_2), 7.16 (d, 2, $J = 8.06$, ArH *ortho* to CH_2), 2.62 (t, 2, $J = 7.59$, α-CH_2), 1.61 (quint, 2, $J = 7.44$, β-CH_2), 1.45–1.20 (m, 4, 2 CH_2), and 0.89 (t, 3, $J = 6.74$, CH_3).

$X = C_5H_{11}$–C≡C, $Y = C_5H_{11}$. Reaction time was 14 h at room temperature; the crude product was purified by three recrystallizations from abs EtOH, chromatography using hexane and a final recrystallization from abs EtOH. The yield was 26.1%. TLC (hexane), $R_f = 0.30$, GC (200 to 270°C at 2°C min^{-1}, injector and detector temperatures were 290°C) $t_R = 12.75$ (99.4%, product) and 15.50 (0.60%), IR(Nujol) 2216, 2145 (wk, alkyne) and 1465 (str, Ar). ^{1}H NMR 7.44 (d, 2, $J = 8.05$, ArH *meta* to chain alkyne), 7.43 (d, 2, $J = 8.14$, ArH *meta* to C_5H_{11}), 7.34 (d, 2, $J = 8.35$, ArH *ortho* to chain alkyne), 7.15 (d, 2, $J = 8.10$, ArH *ortho* to C_5), 2.61 (t, 2, $J = 7.65$, $ArCH_2$), 2.41 (t, 2, $J = 6.96$, alkyne CH_2), 1.70–1.50 (m, 4, 2 β-CH_2), 0.92 (t, 3, $J = 6.92$, CH_3), and 0.89 (t, 3, $J = 7.06$, CH_3).

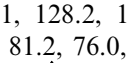
$X = C_5H_{11}$–C≡C, $Y = F$. Reaction time was 17 h at room temperature; the crude product was purified by chromatography (0.5% CH_2Cl_2 in hexane) followed by two recrystallizations from abs EtOH. The yield was 47.0%. TLC (hexane), $R_f = 0.38$, GC $t_R = 4.83$ (99.93%). ^{1}H NMR 7.52 (dd, 2, $J = 8.84$, 5.38, ArH *meta* to F), 7.44 (d, 2, $J = 8.50$, ArH *meta* to chain alkyne), 7.36 (d, 2, $J = 8.46$, ArH *ortho* to chain alkyne), 7.04 (t, 2, $J = 6.98$, ArH *ortho* to F), 1.70–1.55 (m, 2, β-CH_2), 1.55–1.25 (m, 4, 2 CH_2), and 0.93 (t, 3, $J = 6.94$, CH_3).

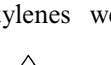
$X =$  , $Y = C_5H_{11}$. Purified by chromatography (20% CH_2Cl_2/hexane), yield was 52.6%. ^{1}H NMR 7.89 (d, 2, $J = 8.10$, ArH *meta* to ketal), 7.59 (d, 2, $J = 8.08$, ArH *ortho* to ketal), 7.47 (d, 2, $J = 8.01$, ArH *meta* to C_5H_{11}), 7.21 (d, 2, $J = 8.03$, ArH *ortho* to C_5H_{11}), 4.02 (t, 2, $J = 3.46$, OCH_2 closest to phenyl), 3.80 (t, 2, $J = 3.42$, OCH_2 farthest from phenyl), 1.70 (s, 3, CCH_3), 1.60–1.20 (m, 8, 4 CH_2), and 0.90 (t, 3, $J = 6.80$, CH_3). Transition temperatures 105.5–108.8°C (Cr–I) and 98.5–98.3°C (I–Cr).

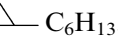
$X = CH=CHCO_2C_3H_7$, $Y = C_5H_{11}$. Reaction time was 3 h, purification by chromatography (40% hexane/CH_2Cl_2) followed by recrystallization from hexane; yield was 31.3%. TLC (20% hexane/CH_2Cl_2), $R_f = 0.68$, GC $t_R = 36.04$ (100.00%); IR 2216, 2215 (wk, alkyne), 1710 (str, CO_2R), and 1630 (str, ArCH=CH). ^{1}H NMR 7.65 (d, 1, $J = 16.12$, ArH *ortho* to CH), 7.53 (d, 2,

$J=8.79$, ArH *meta* to alkyne), 7.48 (d, 2, J *c* 8.79, ArH *ortho* to alkyne), 7.45 (d, 2, $J=8.42$, ArH *meta* to C_5H_{11}), 7.15 (d, 2, $J=8.43$, ArH *ortho* to C_5H_{11}), 6.45 (d, 1, $J=16.11$, olefin CH), 4.17 (t, 2, $J=6.77$, ester α-CH_2), 2.61 (t, 2, $J=7.69$, $ArCH_2$), 1.73 (sext, 2, $J=7.14$, ester β-CH_2), 1.65–1.50 (m, 2, alkyl β-CH_2), 1.46–1.24 (m, 2 CH_2), 1.00 (t, 3, $J=7.32$, ester CH_3), and 0.89 (t, 3, $J=6.59$, alkyl CH_3).

$X=CH=CHCO_2C_3H_7$, $Y=F$. Reaction time was 1 h, purification by chromatography (20% hexane/CH_2Cl_2) followed by recrystallization from MeCN; yield was 10.1%. TLC (hexane), $R_f=0.49$, GC $t_R=13.11$ (100.00%), IR(Nujol) 2216, 2151 (v. wk, alkyne), 1716 (str, CO_2R), and 1600 (str, C=C). ^{1}H NMR 7.65 (d, 1, $J=16.11$, ArH *ortho* to CH), 7.60–7.48 (m, 6, Ar H), 7.04 (t, 2, $J=8.79$, ArH *ortho* to F), 6.46 (d, 1, $J=16.11$, olefin CH), 4.17 (t, 2, $J=6.78$, OCH_2), 1.74 (app sext, 2, $J=7.14$, CH_2) and 1.10 (t, 3, $J=7.51$, CH_3). ^{13}C NMR 166.9, 165.8, 160.8, 143.4, 135.3, 134.8, 134.7, 133.1, 128.2, 123.6, 119.7, 117.9, 117.8, 116.3, 115.9, 81.8, 81.2, 76.0, 73.8, 66.5, 22.3 and 10.7.

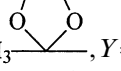
$X=C_5F_{11}$, $Y=$  C_6H_{13}. Reaction time was 4.5 h at 0°C, 1 h at room temperature, recrystallized from abs EtOH/MeOH, yield was 16.2%. GC $t_R=23.31$ (100.00%). ^{1}H NMR 7.43 (d, 2, $J=7.33$, ArH *meta* to CH_2), 7.39 (d, 2, $J=8.05$, ArH *meta* to CH), 7.14 (d, 2, $J=8.42$, ArH *ortho* to CH_2), 6.98 (d, 2, $J=8.43$, ArH *ortho* to CH), 2.60 (t, 2, $J=7.69$, $ArCH_2$), 1.70–1.50 (m, 1, ArCH), 1.50–1.12 (m, 14, 7 CH_2), 1.12–0.96 (m, 3, cyclopropyl), 0.89 (t, 3, $J=6.59$, C_5-CH_3), and 0.88 (t, 3, J *c* 6.23, cyclopropyl chain CH_3). The following two cyclopropyl diacetylenes were purified in the same manner.

$X=CH_3$, $Y=$  C_6H_{13}. Purified yield was *c* 29.9% GC $t_R=21.60$ (72.50%, product), 11.41 (27.09%), 7.60 (0.40%).

$X=F$, $Y=$  C_6H_{13}. Purified yield *c* 14.3%, GC $t_R=16.04$ (98.72%) and 6.02 (1.12%). $X=C_3F_7$, $Y=C_6H_{13}$. Reaction time was 3.25 h at 0°C, purified by chromatography (hexane) followed by recrystallization from MeOH; yield was 22.4%. TLC (hexane), $R_f=0.41$, GC $t_R=9.50$ (99.67%). ^{1}H NMR 7.64 (d, 2, $J=8.81$, ArH *ortho* to CF_2), 7.56 (d, 2, $J=8.71$, ArH *meta* to CF_2), 7.46 (d, 2, $J=8.34$, ArH *meta* to CH_2), 7.16 (d, 2, $J=8.34$, ArH *ortho* to CH_2), 2.62, (t, 2, $J=7.63$, $ArCH_2$), 1.63–1.57 (m, 2, –CH_2), 1.31–1.25 (m, 6, 3 CH_2) and 0.88 (t, 3, $J=6.33$, CH_3). ^{13}C NMR 145.1, 132.6, 132.5, 130.0, 129.1, 128.7, 127.1, 126.9, 126.8, 126.1, 118.4, 83.4, 79.4, 76.8, 72.8, 36.0, 31.7, 31.1, 28.9, 22.6 and 14.1.

$X=C_8F_{17}$, $Y=C_2H_5$. Reaction time was 4 h at 0°C, purified by recrystallization from MeCN; yield was 42.0%. GC $t_R=8.35$ (99.27%), 2.23 (0.62%). ^{1}H NMR 7.62 (d, 2, $J=8.71$, ArH *ortho* to CF_2), 7.56 (d, 2, $J=8.90$, ArH *meta* to CF_2), 7.47 (d, 2, $J=8.17$, ArH *meta* to CH_2), 7.23 (d, 2, $J=8.94$, ArH *ortho* to CH_2), 2.67 (q, 2, $J=7.76$, CH_2), and 1.24 (t, 3, $J=7.56$, CH_3). ^{13}C NMR 146.3, 132.6, 132.5, 127.5, 129.1, 128.1, 127.1, 126.9, 126.8, 126.1, 118.4, 83.4, 79.4, 72.8, 29.0 and 15.2.

$X=C_8F_{17}$, $Y=C_6H_{13}$. Reaction time was 4 h at 0°C, 17 h at room temperature, it was purified by recrystallization from MeOH; yield was 51.2%: GC $t_R=12.46$ (98.16%), 2.21 (1.13%), and 8.37 (0.71%). ^{1}H NMR 7.64 (d, 2, $J=8.42$, ArH *ortho* to CF_2), 7.55 (d, 2, $J=8.42$, ArH *meta* to CF_2), 7.45 (d, 2, $J=8.06$, ArH *meta* to CH_2), 7.16 (d, 2, $J=8.06$, ArH *ortho* to CH_2), 2.61 (t, 2, $J=7.69$, $ArCH_2$), 1.58–1.56 (m, 2, β-CH_2), 1.30–1.28 (m, 6, 3 CH_2), and 0.88 (t, 3, $J=6.76$, CH_3), and ^{13}C NMR 145.1, 132.5, 132.5, 129.5, 129.1, 128.6, 127.1, 126.9, 126.8, 126.1, 118.4, 83.4, 79.4, 76.4, 72.8, 36.0, 31.7, 31.1, 28.9, 22.6 and 14.1.

$X=COCH_3$, $Y=C_5H_{11}$. A solution of the ketal diacetylene **1** (X =  , $Y=C_5H_{11}$, 1.00 g, 2.79 mmol) in acetone (30 ml) containing *p*-TSA (160 mg, 0.84 mmol) and H_2O (10 drops) was heated under reflux for 3 h. The reaction mixture was cooled to room temperature, the solvent removed *in vacuo*, and the remaining material dissolved in Et_2O (50 ml). This solution was washed with saturated $NaHCO_3$ solution, dried, filtered, and the solvent removed *in vacuo* from the filtrate to give the crude product. Recrystallization of this material from MeOH gave 461 mg (52.39%) of the diacetylene **1** ($X=COCH_3$, $Y=C_5H_{11}$): GC $t_R=3.87$ (100.00%); IR 2216 (wk, alkyne), 1676 (str, C=O) and 1610 (med, Ar). ^{1}H NMR 7.93 (d, 2, $J=8.14$, ArH *ortho* to CO), 7.60 (d, 2, $J=8.14$, ArH *meta* to CO), 7.46 (d, 2, $J=7.94$, ArH *meta* to CH_2), 7.16 (d, 2, $J=8.06$, ArH *ortho* to CH_2), 2.62 (t, 2, $J=7.56$, α-CH_2), 2.61 (s, 3, $COCH_3$), 1.70–1.50 (m, 2, β-CH_2), 1.40–1.20 (m, 4, 2 CH_2), and 0.89 (t, 3, CH_3). Elemental analysis calcd for $C_{23}H_{28}O$, C 86.20, H 8.81, found C 86.00, H 8.41%.

6.2.18. *Synthesis of the symmetrical diacetylene* ***1****, X = Y = CH$_2$CH(CH$_3$)C$_2$H$_5$*

To a stirred solution of the bromoacetylene **7** ($Y=CH_2CH(CH_3)C_2H_5$, 4.81 g, 19.2 mmol) in MeOH (43 ml) at *c* 0°C under N_2, was added dropwise a solution of CuCl (38 mg) in $PrNH_2$ (19.2 ml) followed by $NH_2OH\cdot HCl$ in 320 mg increments (960 mg). This reaction mixture was allowed to warm from the heat of the reaction and stirring continued for 1 h; it was then cooled in an ice bath. The resulting precipitate was removed by filtration and the solvent removed from the filtrate *in vacuo*. The remaining material was dissolved

in CH_2Cl_2, washed with 3 M HCl (100 ml), H_2O (100 ml), dried, and filtered. Removal of the solvent from the filtrate *in vacuo* gave 1.19 g (36.3%) of the crude product. Recrystallization of this material from EtOH/H_2O gave 850 mg (25.9%) of the diacetylene **1** ($X = Y = CH_2CH(CH_3)C_2H_5$). TLC (hexane), $R_f = 0.31$, GC $t_R = 17.80$ (100.00%), IR(Nujol) 2151 (med, alkyne), 1604 (med, Ar), and 1503 (str, Ar), and ^{1}H NMR 7.43 (d, 2, $J = 7.93$, Ar H *ortho* to alkyne), 7.11 (d, 2, $J = 8.06$, ArH *ortho* to CH_2), 2.64 (dd, 1, $J = 13.37$, 6.13, $ArCH_2$ proton nearest to CH_3), 2.36 (dd, 1, $J = 13.49$, 8.04, $ArCH_2$ proton closest to H), 1.62 (m, 1, CH), 1.30–1.00 (m, 2, CH_2), 0.90 (t, 3, $J = 7.29$, terminal CH_3), and 0.83 (d, 3, $J = 6.73$, β-CH_3).

7. Conclusions

Some diphenyldiacetylenes, with one of the terminal alkyl chains of the parent *R*/*RO*/F series replaced with a variety of new chain modifications, have been synthesized and their mesomorphic properties determined by hot stage polarizing microscopy and DSC. All of these modifications decreased the nematic phase range. Terminal chains conjugated to the benzene ring, and expected to be more rigid giving wider mesophases (α-ketone, 1-alkyne and cinnamate), increased both melting and clearing temperatures. A chain with increased rigidity but without conjugation (C_nF_{2n+1}) also gave higher transition temperatures but favoured a smectic A phase over a nematic phase even though the diacetylene core has a strong preference for nematic phases. Chains with increased bulkiness and *gauche* conformers (branched and cyclopropyl chains) which tend to give lower melting temperatures gave higher ones with the branched chain, lower melting temperatures were found with the cyclopropyl chains. Only the 1-olefin chain gave wider nematic phases but also with higher transition temperatures. Simple heat and UV stability studies showed that the dialkyldiacetylenes undergo some decomposition above 130°C or when exposed to long wavelength UV light. Both 1- and 2-olefin chains showed less stability, decomposing at lower temperatures and with the 1-olefin even degrading at a short UV wavelength.

Optical birefringences were determined using the compensation method for nearly all of the chain modifications studied. A comparison of these data indicated that molecular polarizability has the largest effect on the birefringence values, but variations suggested that changes in the molecular order parameter also play a role.

We are grateful for the following essential contributions: partial financial assistance from NSF Science and Technology Center, ALCOM, DMF 89-20147, Air Force AFOSRF 49620-98-C0019, and Wheaton College undergraduate summer research grants, assistance in the stability studies by C. Webster and helpful suggestions made by M. Niemczyk and T. Wilkinson.

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] 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.*, **22,** 957.
[5] Neubert, M. E., Abdallah, jr, D. G., Keast, S. S., Kim, J. M., Lee, S. N., Stayshich, R. M., Walsh, M. E., Petschek, R. G., and Wu, S.-T., 2003, *Liq. Cryst.*, **30,** 711.
[6] Grant, B., 1978, *Mol. Cryst. liq. Cryst.*, **48,** 175.
[7] Kitamura, T., Lee, C. H., Taniguchi, Y., Fujiwara, Y., Matsumoto, M., and Sano, Y., 1997, *J. Am. chem. Soc.*, **119,** 619.
[8] Juang, T. M., Chen, Y. N., Lung, S. H., Lu, Y. H., and Hsu, C. S., 1993, *Liq. Cryst.*, **15,** 529.
[9] Meng, H.-H. B., Dalton, L. R., and Wu, S.-T., 1994, *Mol. Cryst. liq. Cryst.*, **250,** 303.
[10] Melissaris, A. P., and Litt, M. H., 1994, *J. org. Chem.*, **59,** 5818.
[11] Cross, G. J., Seed, A. J., Toyne, K. J., Goodby, J. W, Hird, M., and Artal, M. C., 2000, *J. Mater. Chem.*, **10**, 1555; Seed, A. J., Toyne, K. J., Goodby, J. W., and Hird, M., 2000, *J. Mater. Chem.*, **10**, 2069.
[12] Smolingky, G., and Feuer, B. I., 1964, *J. Am. chem. Soc.*, **86,** 3085.
[13] Dolphin, D., Muljiani, Z., Cheng, J., and Meyer, R. B., 1973, *J. chem. Phys.*, **38,** 413.
[14] Gray, G. W., and McDonnell, D. G., 1976, *Mol. Cryst. liq. Cryst.*, **37,** 189.
[15] Neubert, M. E., Leonhardt, D., and Sabol-Keast, S., 1989, *Mol. Cryst. liq. Cryst.*, **172,** 227.
[16] Gray, G. W., and Mosley, A., 1976, *J. chem. Soc., Perkin II*, 97.
[17] Neubert, M. E., and Fishel, D. L., 1979, *Mol. Cryst. liq. Cryst.*, **53,** 101; Neubert, M. E., and Fishel, D. L., 1983 *Org. Synth.*, **61,** 8; Neubert, M. E., and Fishel, D. L., 1990, Org. Synth. Coll., **7,** 420.
[18] Corey, E. J., and Suggs, J. W., 1975, *Tetrahedron Lett.*, **31,** 2647.
[19] LeBigot, Y., Delmas, M., and Gaset, A., 1982, *Synth Commun.*, **12,** 1115.
[20] LeBigot, Y., Delmas, M., and Gaset, A., 1983, *Synth Commun.*, **13,** 177.
[21] Tucker, C. E., Davidson, J., and Knochel, P., 1992, *J. org. Chem.*, **57,** 3482.
[22] Pereira, S., and Srebnik, M., 1996, *Tetrahedron Lett.*, **37,** 3283.
[23] Brown, H. C., and Gupta, S. K., 1972, *J. Am. chem. Soc.*, **94,** 4370.
[24] Brown, H. C., Hamaokra, T., and Ravindran, N., 1973, *J. Am. chem. Soc.*, **95**, 5786; Brown, H. C., 1975,

Organic Synthesis via Boranes (New York: John Wiley), pp. 104–105.
[25] BROWN, H. C., BHAT, N. G., and SOMAYAJI, V., 1983, *Organometallics*, **2**, 1311; BROWN, H. C., and IMAI, T., 1984, *Organometallics*, **3**, 1392.
[26] PELZL, G. in 1998, *Handbook of Liquid Crystals*, Vol 2A, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (New York: Wiley-VCH), pp. 128–141.
[27] PHOTINOS, P., 2001, in *Liquid Crystals, Experimental Study of Physical Properties and Phase Transitions*, edited by S. Kumar (Cambridge: Cambridge University Press), pp. 112–121.
[28] WANG, X.-Z., and DENG, M.-Z., 1996, *J. chem. Soc., Perkin Trans.*, **1,** 2663.
[29] KITAMURA, T., LEE, C. H., TANIGUCHI, Y., FUJIWARA, Y., SANO, Y., and MATSUMOTO, M., 1996, *Mol. Cryst. liq. Cryst.*, **287,** 93.
[30] MARCH, J., 1992, *Advanced Organic Chemistry*, 4th Edn (New York: John Wiley), pp. 151–153.
[31] NEUBERT, M. E., HERLINGER, F. C., JIROUSEK, M. R., and DEVRIES, A., 1986, *Mol. Cryst. liq. Cryst.*, **139,** 299.
[32] THURMES, W. N., WAND, M. D., VOHRA, R. T., and MORE, K. M., 1997, *Proc. SPIE*, **3015,** 2.
[33] OHTSUKA, T., OHNISHI, H., and TAKATSU, H., 2001, in *Physical Properties of Liquid Crystals Nematics*, edited by D. Dunmur, A. Fukuda and G. Luckhurst (IEE-INSPEC), pp. 515–522.
[34] HARTSHORNE, N. H., and STUART, A., 1970, *Crystals and the Polarizing Microscope*, 4th Edn (London: Edward Arnold), pp. 295–300.
[35] TANAKA, T., SEKINE, C., ASHIDA, T., ISHITOBI, M., KONYA, N., MINAI, M., and FUJISAWA, K. *Mol. Cryst. liq. Cryst.*, 2000, **346**, 209.
[36] SHERMAN, E., LACHNER, A. M., and WU, S.-T., 1995, *Mol. Cryst liq. Cryst.*, **265,** 669.
[37] NEUBERT, M. E., 2001, in *Liquid Crystals, Experimental Study of Physical Properties and Phase Transitions*, edited by S. Kumar (Cambridge: Cambridge University Press), Chap. 2, Demus, D., and Richter, L., 1978, *Textures of Liquid Crystals*, (New York: Verlag Chemie); Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals, Textures and Structures* (Leonard Hill).
[38] CHAMBERLAIN, N. F., 1974, *The Practice of NMR Spectroscopy with Spectra-Structure Correlations for Hydrogen-1* (New York: Plenum Press), p. 370.
[39] GELIN, R., CHANTEGREL, B., and GELIN, S., 1969, *Bull. Soc. Chim. Fr.*, 4136.
[40] HAVENS, J., and HERGENROTHER, P. M., 1985, *J. org. Chem.*, **50,** 1763.
[41] FONTANI, P., CARBONI, B., VAULTIER, M., and MAAS, G., 1991, *Synthesis*, 605.
[42] LAMBERT, J. P., KOENG, F. R., and HAMERSMA, J. W., 1971, *J. org. Chem.*, **36,** 2941.