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The effect of replacing a benzene ring with a saturated six-membered ring on the mesomorphic properties of 4,4′-disubstituted diphenyldiacetylenes

MARY E. NEUBERT*, SANDRA S. KEAST, JULIE M. KIM, KYLE J. MILLER, RACHEL M. MURRAY, AARON G. NORTON, RAJ A. SHENOY, MARGARET E. WALSH

Glenn H. Brown Liquid Crystal Institute, Kent State University, Kent, Ohio 44242-2001, USA

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

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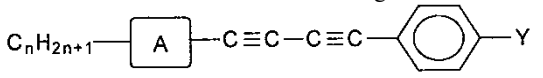
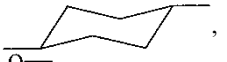
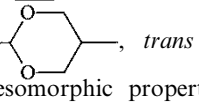
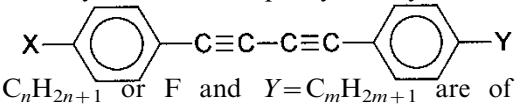
A limited selection of ring modified diphenyldiacetylenes of the type  where $A=$  , $Y=$ C_nH_{2n+1}, CF_3, F, COMe, NH_2, and NMe_2, and $A=$  , *trans* and *cis* with $Y=F$ and *trans* with $Y=C_3H_7$, were synthesized. Mesomorphic properties were determined by hot stage polarizing microscopy and DSC. These properties were generally poorer than those found in the parent benzene compounds. This was also true of some pyrimidine analogues reported earlier. Birefringence values also decreased as expected.

1. Introduction

Unsymmetrically substituted diphenyldiacetylenes of the type  where $X=C_nH_{2n+1}$ or F and $Y=C_mH_{2m+1}$ are of interest as wide temperature range nematics having a large birefringence and low viscosity for broad beam steering devices [1]. We have been studying structural modifications of these systems to try to improve their properties. Lower melting temperatures, larger birefringences and larger dielectric anisotropies are needed for broader applications. Two types of structural modification are possible: chain and ring. We have already reported results with amino [2], olefin [3] and other chain modifications [4], as well as replacing one benzene ring with a pyrimidine ring [5]. In this paper, some additional ring substitutions using 1,4-*trans*-cyclohexane **1a** and 2,5-*trans*-dioxane **1b** will be discussed. These were chosen because a cyclohexane ring often lowers melting temperatures in other systems and the dioxane ring should increase the dielectric anisotropy.

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2. Synthesis

Many of the diacetylenes reported earlier were synthesized by coupling an acetylene with a bromoacetylene. Our new ring-modified diacetylenes were prepared in the same manner. The cyclohexyldiacetylenes were prepared by coupling a *trans*-cyclohexylacetylene **8** with an aromatic bromoacetylene **7** to obtain the diacetylene **9** with one cyclohexyl ring (scheme 1). Coupling of the intermediate bromocyclohexylacetylene **6** with the acetylene **8** gave the symmetrical dicyclohexyldiacetylene **10**. Detailed procedures for preparing the aromatic bromoacetylenes from the aldehydes **3** via the dibromoolefin are adequately described in the literature [2, 6, 7]. The cyclohexylbromoacetylene **6** was prepared in the same manner from the *trans*-cyclohexylaldehyde **2**. The acetylene **8** was obtained by treating the bromoacetylene with *sec*-BuLi. A different approach was used to prepare the dioxane-acetylene **14** from the aldehyde **12** by treating it with

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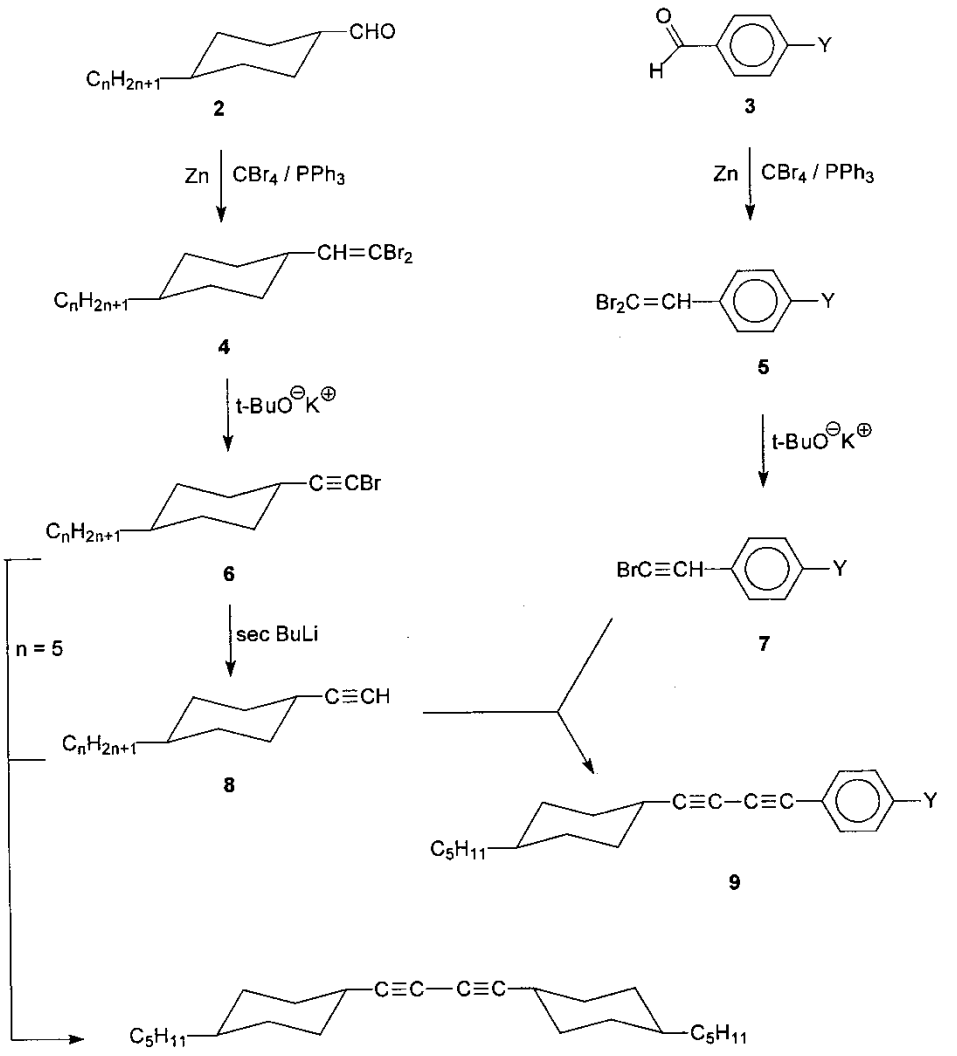
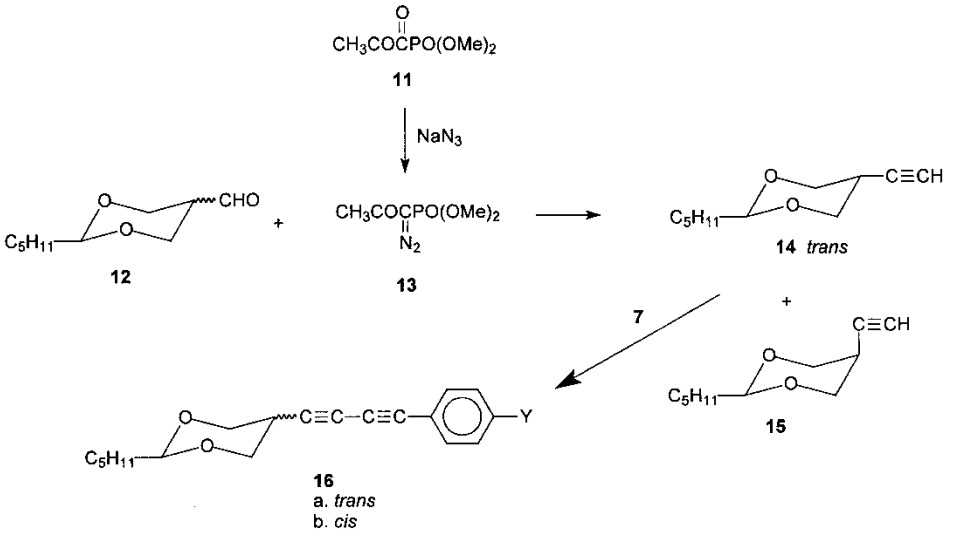
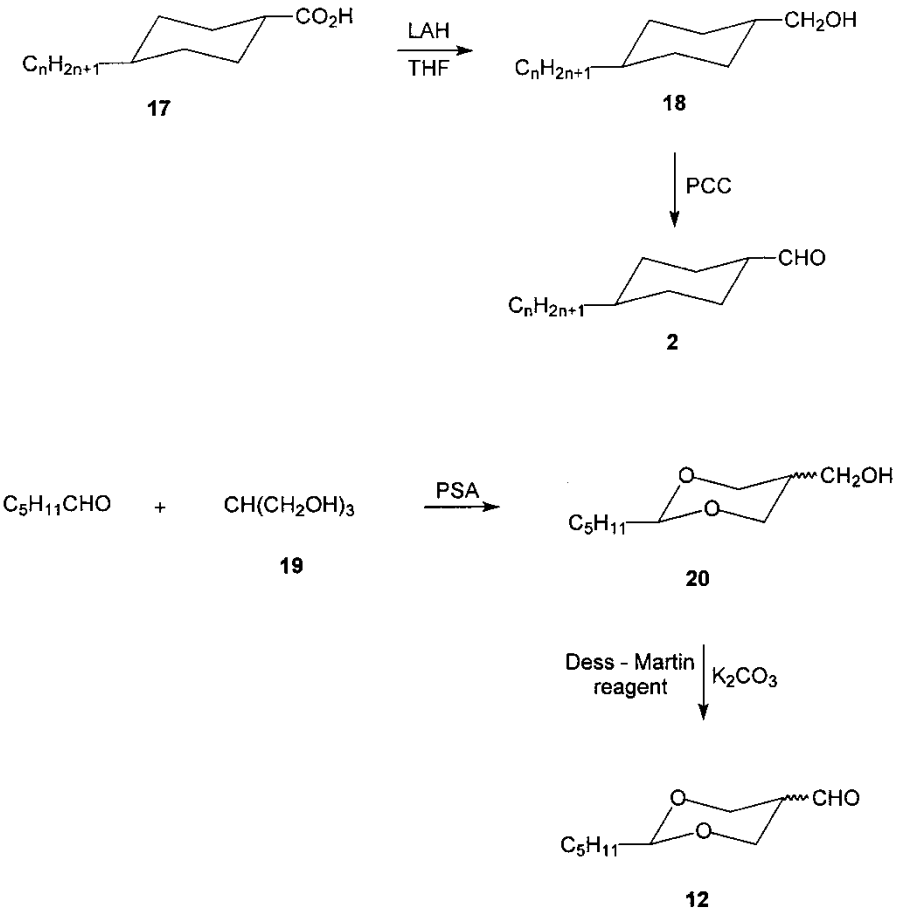


Scheme 1



Scheme 2



Scheme 3

the phosphonate diazo reagent **13** (scheme 2) [8, 9]. A mixture of *trans*-**14** and *cis*-**15** isomers was isolated but these were separated by chromatography and were converted to the *trans*-**16a** and *cis*-**16b** diacetylenes, respectively.

Synthesis of the *trans*-aldehydes **2** and **12** is illustrated in scheme **3**. The commercially available *trans*-cyclohexyl acids **17** were reduced to the alcohols **18** using LAH. Oxidation of these with pyridinium chlorochromate (PCC) gave the desired *trans*-aldehydes **2**. The dioxane ring was formed by treating hexanal with the triol **19** giving a mixture of the *trans* and *cis* isomers of the alcohol **20** [10]. These two isomers were not separated until the acetylene was prepared. Oxidation of this alcohol using the Dess–Martin reagent gave the aldehyde **12** [11, 12].

These new diacetylenes were purified by chromatography and recrystallization until they were colourless solids, had sharp melting and clearing temperatures and GC purities were nearly 100%. Our goal was to obtain the diacetylenes having a high purity to determine accurate mesomorphic properties rather than high yields.

3. Mesomorphic properties

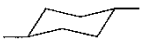
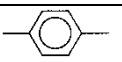
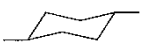
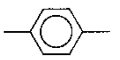
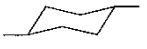
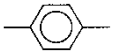
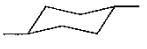
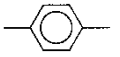
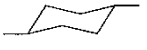
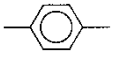
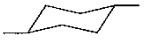
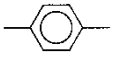
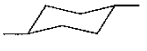
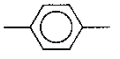
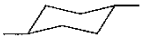
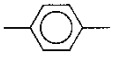
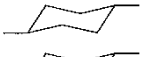
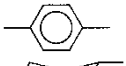
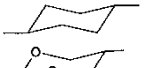
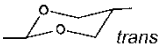
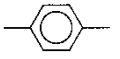
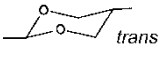
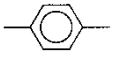
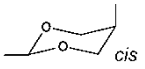
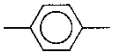
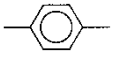
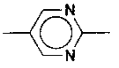
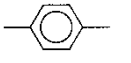
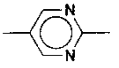
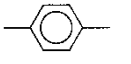
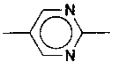
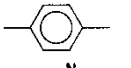
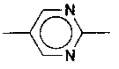
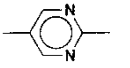
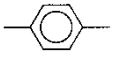
Transition temperatures were determined by hot stage polarizing microscopy and DSC provided the associated enthalpy changes. These are listed in table 1. Data for several pyrimidine analogues prepared earlier [5] are included for comparison. Only nematic phases were observed when mesophasic behaviour was found. The widest nematic temperature range was observed in the cyclohexyl 5-3 compound (2), while the lowest melting temperature and enthalpy of melting were found for the *trans*-dioxane 5-F compound (12). Of the ring systems tried, the pyrimidine one showed the least desirable properties although the same Y groups were not studied. In contrast to that observed in the diphenyl series, the dialkyldioxane (11) had poorer mesomorphic properties than the alkyl-F compound (12). This fluoro compound had a melting temperature of 60.4°C, a nematic range of 13.8°C and a ΔH of melting of only 12.95 kJ mol^{-1}, making it the most interesting of these ring-modified diacetylenes.

A comparison of these properties with those of the analogous benzene compounds is given in table 2. The effect of replacing a benzene ring with a saturated

6-membered ring on the melting temperature varies as it does for most structural modifications. It usually decreases, but with the amount varying over a wide range. From this limited information, it would not be possible to predict the effect these rings would have on the properties in other similar structures. In all the compounds studied here, the clearing temperature decreased when nematic phases occurred. The nematic phase temperature ranges usually also decreased. Thus, nothing was gained in improved mesomorphic properties using these ring modifications.

Replacing a benzene ring with a saturated ring was

Table 1. Mesomorphic Properties for C_nH_{2n+1}—A—C≡C—C≡C—B—Y.

Compound	*n*	*A*	*B*	*Y*	Transition Temperatures[a]/°C Cr[a]	N	I	N range/°C	ΔH_m[b]/ kJ mol^{-1}	ΔH_c/ kJ mol^{-1}
1	4			C_2H_5	32.4	60.6–61.4	82.6–82.7	21.3	27.43	0.48
2	5			C_3H_7	57.5	64.9–65.6	104.0–104.1	38.5		
3	5			F	75.9	82.8–84.3	91.4–91.6	7.3	21.25	0.40
4	5			CF_3	92.5		99.0–99.2	0	21.20	
5	5			CN	124.1	132.0–132.3	153.6–158.9	26.6	24.33	0.71
6	5			NH_2	90.4[c]		133.8–134.9	0		
7	5			NMe_2	122.9		128.9–129.8	0	30.97	
8	5				94.7		112.0–114.0	0		
9	5			$COCH_3$	93.8	96.5–97.6	113.4–113.6	16.0	24.22	0.54
10	5			C_5H_{11}	57.9[d]	70.0–70.1	92.7–92.9	20.8	29.88	0.97
11	5			C_3H_7	61.4	(74.1–74.3)	74.1–74.5		23.24[e]	0.42
12	5			F	46.0	56.5–60.4	74.1–74.2	13.8	12.95[f]	0.42
13	5			F	68.1		80.6–82.6	0	26.28	
14	6			OC_4H_9	80.4	90.7	99.4	8.7		
15	6			—C≡CC_5H_{11}	152.8		159.1	0	39.0	
16	6			—C≡C$C_{10}H_{21}$	141.7		146.3	0		
17	6			CN	125.7	129.2	142.7dec	13.5	21.9	
18	6			CN			~100°dec	0		

[a]Cr = crystallization temperature obtained on cooling the melt at 2°C min^{-1}, N = nematic, I = isotropic liquid.

[b]ΔH_m = enthalpy of melting, ΔH_c = enthalpy for clearing transition.

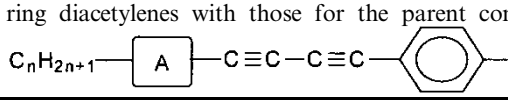
[c]The first crystals formed on cooling at 90.4°C (Cr_1) converted to another form Cr_2 on cooling to 87.8°C. On reheating, Cr_2 melted to the isotropic liquid.

[d]The first crystals formed on cooling (Cr_1) converted to another form on cooling to 51.5°C (Cr_2). Cr_2 melted to the nematic phase on reheating to 70.1°C.

[e]A crystal to crystal change was observed at 72.59°C on heating ($\Delta H = 2.30$ kJ mol^{-1}) and was also seen on cooling.

[f]In the DSC, two peaks were observed for melting in all three scans at 50.25°C ($\Delta H = 5.26$ kJ mol^{-1}) and 55.30°C ($\Delta H = 7.69$ kJ mol^{-1}).

Table 2. A comparison of mesomorphic properties of modified ring diacetylenes with those for the parent compounds

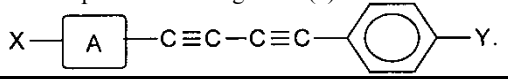


n	*Y*	A	ΔT_m[a]/°C	ΔT_C/°C	ΔN/°C
4	C_2H_5		−17.0	−15.7	−32.7
5	C_3H_7		3.6	−7.4	−11.0
5	F		−4.1	−4.0	0.1
5	CF_3		−3.5		
5	CN		−20.2	−3.0	13.7
5	NH_2		24.0		
5	NMe_2		0.9		−4.7
5	COMe		−1.7	−17.8	−16.1
5	F	*trans*	−28.0	−21.4	6.6
5	F	*cis*	−5.8		−7.2
5	C_3	*trans*	12.5	−43.0	−53.3

[a] T_m = melting temperature, T_c = clearing temperature, N = nematic, Δ represents the difference between the benzene parent compound and the saturated ring compound.

expected to decrease the optical birefringence and this was found, see table 3; for data for the analogous benzene compounds and procedure see [4]. The dicyclohexyldiacetylene had a $\Delta n = 0.124$ (solvent A).

Table 3. Optical birefringence (n) in 15% solutions for



X	*A*	*Y*	Solvent[a]	Δn
C_4H_9		C_2H_5	A	0.231
C_5H_{11}		C_3H_7	A	0.228
C_5H_{11}		CF_3	A	0.201
C_5H_{11}		F	A	0.151
C_5H_{11}		COMe	A	0.171
C_5H_{11}		NH_2	A	0.168
C_5H_{11}		NMe_2	A	0.202
C_5H_{11}	*trans*	F	A	0.221
C_5H_{11}	*cis*	F	A	0.071
C_5H_{11}	*trans*	C_3H_7	B	0.212

[a] Solvent A = ZLI 2978-100 (EM Merck) $n = 0.084$; solvent B = MLC6025-100.

4. Experimental

4.1. *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 performed on Fisher or EM Science silica gel (230–400 mesh). Capillary GC analysis was obtained using a Hewlett Packard 5890 instrument equipped with a HP 3395 integrator, a FID detector and a Hewlett Packard 5 m ($n = 3$) or 10 m ($n = 2,4$) methylsilicone gum column. Temperature programming was from 100°C (0) at 20°C min^{-1} to 250–270°C (0 to 15) with a detector and injector temperature of 270–290°C using a split valve rate of 182 ml min^{-1} and a column head pressure of 16.22 ml min^{-1} unless otherwise noted. 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 reported for compounds for which transition temperatures are given in table 1.

A Nicolet Magna FTIR spectrophotometer was used to record IR spectra in cm^{-1} using NaCl plates. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ with TMS as the internal standard, using a Varian Gemini-200 spectrometer equipped with a VXR-400 data station at 200 and 50 MHz, respectively. Chemical shifts are given in PPM and coupling constants in Hz; ^{13}C NMR chemical shifts were compared with values calculated using a Softshell ^{13}C NMR Module. Most variations from the calculated values were small. The following abbreviations are used to identify protons: cyh = cyclohexyl, dio = dioxanyl and C_2 indicates which carbon atom.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 POL polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°C min^{-1}. Discussions of texture identification of nematic phases can be found in two books [13]. Crystallization temperatures were obtained by cooling the melt at 2°C min^{-1} until crystals were formed, to ensure that all mesophases had been observed before this temperature. These crystals were reheated to obtain the melting temperatures and to confirm that these were not mesophases. DSC scans were run at a rate of 5°C min^{-1} using a Perkin-Elmer DSC7 equipped with a TAC7/PC instrument controller which had been calibrated using indium and zinc. During the course of this research, Perkin-Elmer Pyris software was installed. A few scans were performed using a Perkin-Elmer Pyris/DSC equipped with a TAC7/DX controller. At least three scans were obtained for each compound: heating from virgin crystals to isotropic liquid, cooling this liquid until crystals formed, and re-heating this crystallized

material. The melting and clearing enthalpies recorded in table 1 were obtained by heating the virgin crystals. This usually gives the largest melting enthalpy value obtained from the most stable crystal formed. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, N.Y.

4.2. *Synthesis*

Commercially available starting materials were used without purification. Exposure to ambient light in all reactions involving a triple bond was minimized by keeping the fume hood lights switched off and the reaction flask wrapped with Al foil. Anhydrous reactions were performed using flame-dried glassware under dry N_2 using freshly 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 anhydous Na_2SO_4 or $MgSO_4$. Tertiary butanol used in making the bromoacetylenes was always distilled within a day of its use and stored over Linde 4A molecular sieves; otherwise, yields were low.

4.2.1. *(4-Pentyl-trans-cyclohexyl)methanol,* ***18*** *(n=5)*

To a stirred suspension of $LiAlH_4$ (9.18 g, 0.24 mol) in dried THF (200 ml) under N_2 at r.t. was added dropwise within 3 h, a solution of the cyclohexyl acid **17** (40.0 g, 0.20 mol) and stirring continued at r.t. for 13 h. The LAH was decomposed by a slow dropwise addition of H_2O (40 ml) followed by a 20% aq. NaOH solution (35 ml) and H_2O (70 ml). The white precipitate was removed by vacuum filtration and then rinsed with THF and H_2O. Removal of THF from the filtrate *in vacuo* gave a liquid which was extracted 3 times 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 36.0 g (97.7%) of the crude product. Chromatography of this material using 10% EtOAc in hexane gave 34.1 g (92.3%) of the purified liquid alcohol **18**. TLC (10% EtOAc/hexane) $R_f=0.45$; GC $t_R=2.26$ (100.00%); IR (film) 3654 (str, br OH). ^{1}H NMR 3.45 (d, 2, $J=6.25$, CH_2O), 1.78 (d, 4, $J=6.67$, cyh-H_e), 1.50–1.10 (m, 10, $4CH_2$, cyh-1,4-H_a), 1.00–0.75 (m, 4, cyh-H_e) and 0.88 (t, 3, $J=6.63$, CH_3).

The butyl analogue, **18** ($n=4$), was prepared in the same manner: GC $t_R=1.73$ (99.56%), 2.46 (0.36%). This material was used without further purification.

4.2.2. *(4-Pentyl-trans-cyclohexyl)carboxaldehyde,* ***2*** *(n=5)*

A solution of the cyclohexyl alcohol **18** ($n=5$, 18.1 g, 98.2 mmol) in CH_2Cl_2 (196 ml) was added dropwise to a stirred mixture of pyridinium chlorochromate (PCC, 31.7 g, 147.3 mmol) in CH_2Cl_2 (19 ml) at r.t. Stirring was continued for 30 min, then Et_2O (200 ml) was added and the mixture filtered though Celite^{TM} to remove the thick, insoluble, black gum which was then washed thoroughly with H_2O. Removal of the solvents from the filtrate *in vacuo* gave the crude product. Chromatography of this material using 1.5% EtOAc in hexane gave 13.0 g (72.6%) of the liquid aldehyde **13** ($n=2$). TLC ($CHCl_3$) $R_f=0.60$; IR (film) 2707 (str, aldehyde CH) and 1727 (str, C–O). ^{1}H NMR 9.61 (t, 1, $J=1.63$, CHO), 2.30–2.05 (m, 1, cyhC-H), 2.05–1.70 (m, 4, cyh-H_e), 1.70–1.10 (m, 11, $4CH_2$, cyhC_2, C_4, C_6–H_a), 1.10–0.70 (m, 2, cyhC_3, C_5–H_a) and 0.88 (t, 3, $J=6.70$, CH_3).

The $n=4$ homologue was prepared in the same manner but using PDC and a reaction time = 4.0 h; yield 73.7%. Purification was by chromatography on silica gel treated with 1% Et_3N using 35% CH_2Cl_2/hexane.

4.2.3. *(4-Pentyl-3,5-dioxanyl)methan-1-ol,* ***20***

To a stirred solution of hexanal (10.2 g, 102.4 mmol) and 2-hydroxymethyl-1,3-propanediol (8.7 g, 81.9 mmol) at r.t. was added dropwise a solution of PTSA (200 mg) in toluene (300 ml). The reaction mixture was heated at reflux for 3 h using a Dean–Stark trap. After cooling to r.t., it was washed with 5% Na_2CO_3 (75 ml) and H_2O, dried and filtered. Removal of the solvent from the filtrate followed by chromatography of the remaining liquid using 20% EtOAc/hexane (TLC $R_f=0.2$) gave 14.5 g (93.8%) of a mixture of the *cis* and *trans* alcohols **20** as a yellow liquid. IR (film) 3434 (str, br OH). ^{1}H NMR showed a mixture of *cis* and *trans* isomers: 4.54 (t, 1, $J=4.94$, dioC_2-H_a, *cis*), 4.43 (t, 1, $J=5.13$, dioC_2-H_a, *trans*), 4.20–4.02 (m, 2, dioC_4, C_6–H_e), 4.02–3.80 (m, 2, dioC_4, C_6–H_a), 3.60–3.40 (m, 2, OCH_2), 2.50–2.00 (m, 1, dioC_5–$H_{a,e}$), 1.56–1.50 (m, 2, α-CH_2), 1.50–1.20 (m, 6, $3CH_2$) and 0.88 (t, 3, $J=3.59$, CH_3). ^{13}C NMR:102.8, 102.4, 69.2, 67.5, 62.2, 61.4, 37.1, 36.5, 36.1, 34.9, 31.7, 23.7, 22.6 and 14.0.

4.2.4. *2-Pentyl-5-formyl-1,3-dioxane,* ***12***

To a solution of the dioxane-alcohol **20** (12.0 g, 63.7 mmol) in CH_2Cl_2 (500 ml) at r.t. was added the Dess–Martin reagent [11] (40.5 g, 95.6 mmol). After stirring this mixture for 17 h at r.t., a solution of $Na_2S_2O_3$ (55 g) in 1M $NaHCO_3$ solution (160 ml) was added dropwise and stirring continued for 30 min. Diethyl ether (500 ml) was added and the layers separated. The aqueous layer was extracted with Et_2O (200 ml), and the Et_2O layer was added to the

first Et_2O extract, washed with a saturated $NaHCO_3$ solution (200 ml), H_2O (300 ml), and then dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave the crude product which was purified by chromatography using 20% EtOAc/hexane to give 7.1 g (59.8%) of the aldehyde **12** as a colourless liquid. IR (film) 2730 (wk, CHO), 1729 (str, C–O) and no OH absorption. ^{1}H NMR showed a mixture of *cis* and *trans* isomers: ca 9.99 (s, 1, *cis* CHO, ~11.6%), 9.62 (s, 1, *trans* CHO), 4.55 (app t, 1, $J=5.31$, *cis* and *trans*-dioC_2–H_a), 4.49–4.28 (m, 2, *cis* and *trans*-dioC_4, C_6–He), 4.00–3.67 (m, 2, *cis* and *trans*-dioC_4, C_6–H_a), 3.20–2.90 (m, 1, *trans*-dioC_5–H_a), 2.50–2.20 (m, 1, *cis*-dioC_5–H_e), 1.80–1.50 (m, 2, α-CH_2), 1.45–1.20 (m, 6, 3CH_2) and 0.89, 0.88 (2t, 3, $J=4.03$, 4.40, CH_3).

4.2.5. *trans-1-(2,2-Dibromoethenyl)-4-pentylcyclohexane, **4** (n=5)*

This compound was prepared from the aldehyde **2** ($n=5$) using the procedure (method A) described earlier [2]. The reaction mixture was stirred for 16 h and the crude product purified by chromatography using hexane to give 24.7 g (73.1%) of the dibromoolefin **2** ($n=5$). TLC ($CHCl_3$) $R_f=0.72$; GC $t_R=4.28$ (98.7%), 0.93 (0.46%) and 3.8 (0.62%); IR (film) 1617 (wk, C–C) and 1500 (str, Ar). ^{1}H NMR 6.20 (d, 1, $J=9.08$, CH–C), 2.35–2.10 (m, 1, cyhC_1–H), 1.79 (s, 2, cyhC_2, C_6–H_e), 1.74 (s, 2, cyhC_3, C_5–H_e), 1.40–1.00 (m, 11, cyhC_2, C_4, C_6–H_a and 4CH_2), 1.00–0.80 (m, 2, cyhC_3, C_5–H).

The $n=4$ homologue was prepared in the same manner. Purified yield of a yellow liquid was 87.5%.

4.2.6. *trans-1-(Bromoethynyl)-4-pentylcyclohexane, **6** (n=5)*

This compound was prepared from the dibromoolefin **4** ($n=5$) in the same manner (method 2) as described earlier [1]. Reflux time was 18 h. GC $t_R=3.22$ (97.33%); IR (film) 1452 (str), alkyne was not detected. ^{1}H NMR 2.18 (t, t, 1, $J=11.84$, 3.6, cyhC_1–H), 1.95 (app dd, 2, $J=14.41$, 3.54, cyhC_2, C_6–H_e), 1.74 (app d, 2, $J=11.92$, cyhC_3, C_5–H_e), 1.44–1.05 (m, 12, 4CH_2, cyhC_3, C_5–H_e), 1.44–1.05 (m, 12, 4CH_2, cyhC_2, C_3, C_5, C_6–H_a), 0.91–0.76 (m, 1, cyhC_4–H_a) and 0.88 (t, 3, $J=6.65$, CH_3). This compound was also prepared using method 1 [2]; crude product yield = 93.1%. This material was used without purification.

The $n=4$ homologue was prepared in the same manner but using a reflux time of 6.5 h; purified yield = 95.5%, TLC $R_f=0.78$.

4.2.7. *trans-4-Pentyl-1-ethynylcyclohexane, **8** (n=5)*

To a stirred solution of the dibromoolefin **7** ($n=5$, 24.0 g, 71.0 mmol) in THF (41 ml) cooled in a dry ice/acetone bath under N_2, was added dropwise a solution of 1.3M *sec*-BuLi in THF (136.5 ml) within 45 min. Stirring was continued for 1 h and then the mixture allowed to warm to r.t. and stirred for another hour. After adding H_2O (130 ml) dropwise, the organic layer was separated, the H_2O layer extracted 3 times with Et_2O (200 ml) and the Et_2O layers combined. This Et_2O solution was washed with H_2O, dried, filtered and the solvent removed from the filtrate *in vacuo* to give the crude product. Chromatography of this material using hexane gave 9.67 g (76.5%) of the acetylene **8** ($n=5$). TLC (hexane) $R_f=0.52$; GC $t_R=1.48$ (100.00%); IR (film) 3322 (str, alkyneCH), 2117 (med, alkyne). ^{1}H NMR 2.16 (tt, 1, $J=11.72$, 2.56, cyhC_1–H_a), 2.04 (s, 1, alkyneCH), 1.98 (app dd, 2, $J=$ ~13.92, 3.66, cyhC_2, C_6–H_e), 1.75 (d, 2, $J=11.89$, cyhC_3, C_5–H_e), 1.50–1.05 (m, 12, cyhC_2, C_3, C_5, C_6–H_a and 4CH_2), 0.96–0.84 (m, 1, cyhC_4–H_a) and 0.9 (t, 3, $J=6.64$, CH_3).

4.2.8. *Dimethyl(2-azopropyl)phosphonate, **13***

To a stirred mixture of 60% NaH dispersion (1.27 g, 31.6 mmol) in benzene (90 ml) and THF (15 ml) at 0°C was added a solution of the ketophosphonate **11** (5.0 g, 30.1 mmol) in benzene (30 ml) and the reaction mixture stirred for 1 h. A solution of TsN_3 (2.50 g, 12.64 mmol) in benzene (6 ml) added dropwise, and the reaction mixture was allowed to warm to r.t. and stirred for 2 h. It was then filtered through Celite™ which was washed thoroughly with Et_2O. Removal of the solvent from the filtrate *in vacuo* gave the crude product which was chromatographed using 50% EtOAc/hexane to give 5.75 g (99.3%) of the purified azophosphonate **13** as a yellow liquid. IR (film) 2130 (str, C–N) and 1665 (str, C–O). ^{1}H NMR 3.83, 2.99 (2s, 6, 2-OCH_3) and 2.99 (s, CH_3, CH_3CO).

4.2.9. *2-Pentyl-5-ethynyl-1,3-dioxane, **14** and **15***

To a stirred solution of the aldehyde **12** (6.5 g, 36.9 mmol) in MeOH (600 ml) containing K_2CO_3 (10.2 g, 73.6 mmol) was added all at once the azidophosphonate **4** (8.5 g, 44.3 mmol). After stirring at r.t. for 17 h, this reaction mixture was diluted with Et_2O, and extracted with a 5% $NaHCO_3$ solution (250 ml) and H_2O (200 ml). The combined aqueous layers were extracted again with Et_2O (200 ml) and the organic layers combined. This Et_2O solution was washed with brine (250 ml), dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave the crude product. Chromatography of this material using 5% EtOAc/hexane gave 2.78 g (43.71%) of the

trans-acetylene **14** followed by 2.3 g (33.5%) of the *cis*-isomer **15**, both as liquids, total yield = 77.2%.

trans-Isomer **14** (C_5H_{11} and C≡CH are equatorial): TLC (5% EtOAc/hexane) $R_f = 0.63$; IR (film) 3316 (str, alkyne), 2124 (wk, alkyne), 1471 (med) and 1160 (str). ^{1}H NMR 4.46 (t, 1, $J = 5.13$, cyh C_2–H_a), 4.21 (dd, 2, $J = 11.72$, 4.76, cyh C_4, C_6–H_e), 3.61 (t, 2, $J = 11.35$, cyh C_4, C_6–H_a), 3.00–2.90 (m, 1, cyh C_5–H_a), 2.09 (d, 1, $J = 2.56$, alkyneCH), 1.78–1.52 (m, 2, CH_2), 1.52–1.16 (m, 6, $3CH_2$) and 0.89 (t, 3, $J = 6.59$, CH_3). ^{13}C NMR 102.3, 79.6, 71.7, 70.1, 34.7, 31.6, 27.6, 23.6, 22.5 and 14.0.

cis-Isomer **15** (C_5 equatorial, C≡CH axial): GC $t_R = 1.97$ (6.85%), 2.21 (91.93%), TLC (5% EtOAc/hexane) $R_f = 0.34$; IR (film) 3316 (str, alkyneCH), 2117 (wk, alkyne), 1477, 1388 (med) and 1160 (str). ^{1}H NMR (a trace amount of *trans* was also observed) 4.51 (t, 1, $J = 5.13$, cyh C_2–H_a), 4.16 (dd, 2, $J = 11.35$, 1.46, dioC_4, C_6–H_e), 3.89 (dt, 2, $J = 11.35$, 1.28, dioC_4, C_6–H_a), 2.45 (q, 1, $J = 1.46$, dioC_5–H_e), 2.17 (d, 1, $J = 2.56$, alkyneCH), 1.80–1.65 (m, 2, α-CH_2), 1.52–1.18 (m, 6, $3CH_2$) and 0.89 (t, 3, CH_3). ^{13}C NMR 103.1, 84.2, 70.1, 69.8, 69.5, 34.9, 31.6, 27.9, 23.6, 22.7 and 14.0.

4.2.10. *Synthesis of diacetylenes,* ***9***

These compounds were prepared by a copper-catalysed coupling between the acetylene **8** and the bromoacetylene **7** using the previously described method [2–4]. Experimental details that differ from those described earlier are recorded here along with characterization data.

4.2.10.1. *$X = C_4H_9$, $Y = C_2H_5$.* Reaction time = 17 h at r.t., chromatographed material was recrystallized from cold CH_3CN, yield = 26.6%; TLC (hexane) $R_f = 0.32$; GC $t_R = 9.89$ (100%). ^{1}H NMR 7.38 (d, 2, $J = 8.22$, ArH *ortho* to alkyne), 7.12 (d, 2, $J = 8.18$, ArH *ortho* to C_2H_5), 2.63 (q, 2, $J = 7.60$, $ArCH_2$), 2.32 (tt, 1, $J = 11.77$, 3.62, cyhC_1–H_a), 2.00 (app dd, 2, $J = 13.56$, 3.50, cyhC_2, C_6–H_e), 1.76 (app d, 2, $J = 14.20$, cyhC_3,C_5–H_e), 1.45 (dd, 2, $J = 12.91$, 3.02, cyhC_6, C_6–H_a), 1.32 (dd, 2, $J = 16.16$, 3.26, cyhC_3, C_5–H_a), 1.40–1.10 (m, 6, $3CH_2$), 1.21 (t, 3, $J = 7.59$, ethylCH_3) 1.00–0.70 (m, 1, cyhC_4–H_a) and 0.88 (t, 3, $J = 6.51$, butylCH_3). ^{13}C NMR 144.9, 132.0, 75.3, 64.3, 36.4, 36.3, 32.1, 32.0, 30.1, 28.7, 22.6, 14.9, 13.7. Elemental analysis: calcd for $C_{22}H_{28}$, C 90.35, H 9.65; found, C 90.35, H 9.52%.

4.2.10.2. *$X = C_5H_{11}$, $Y = C_3H_7$.* Reaction time = 4.5 h at r.t., chromatographed material was recrystallized from abs. EtOH, yield = 51.0%; TLC ($CHCl_3$) $R_f = 0.85$, GC $t_R = 12.35$ (98.92%). ^{1}H NMR data were similar to that for $X = C_4$, $Y = C_2$.

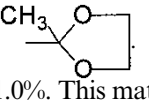
4.2.10.3. *$X = C_5H_{11}$, $Y = F$.* The reaction mixture was stirred in an ice bath for 4 h, then at room temperature for 11 h; the chromatographed product was recrystallized from CH_3CN, yield = 30.0%; TLC (hexane) $R_f = 0.40$; GC $t_R = 8.46$ (97.34%). ^{1}H NMR 7.45 (dd, 2, $J = 8.89$, 5.39, ArH *ortho* to alkyne), 6.99 (t, 2, $J = 8.77$, ArH *ortho* to F), 2.25–2.40 (m, 1, cyhC_1–H_a), 2.00 (dd, 2, $J = 13.55$, 3.50, cyhC_2, C_6–H_e), 1.77 (d, 2, $J = 11.64$, cyhC_3, C_5–H_e), 1.50–1.00 (m, 12, $4CH_2$ and 4cyh–H_a), 1.00–0.70 (m, 1, cyhC_4–H_a) and 0.88 (t, 3, $J = 6.65$, CH_3).

4.2.10.4. *$X = C_5H_{11}$, $Y = CF_3$.* Reaction time = 17 h at r.t., chromatographed material recrystallized from cold MeCN, yield = 28.6%; TLC (hexane) $R_f = 0.43$, GC $t_R = 8.37$ (100%); IR (mineral oil) 2244 (med alkyne) and 1617 (med, Ar). ^{1}H NMR 7.56 (s, 4ArH), 2.34 (tt, 1, $J = 11.81$, 3.54, cyhC_1–H_a), 2.01 (app dd, 2, $J = 13.80$, 2.34, cyhC_2, C_6–H_e), 1.78 (app d, 2, $J = 11.72$, cyhC_3, C_5–H_e), 1.47 (dd, 2, $J = 12.72$, 3.20, cyhC_2, C_6–H_a), 1.40–1.10 (m, 8, $4CH_2$), 1.34 (dd, 2, $J = 12.82$,3.01, cyhC_3, C_5–H_a), 1.00–0.79 (m, 1, cyhC_4–H_a) and 0.88 (t, 3, $J = 6.69$, CH_3).

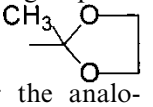
4.2.10.5. *$X = C_5H_{11}$, $Y = CN$.* This reaction was run twice using different reaction conditions: stirred in an ice bath for 4 h and then at r.t. for 60 h, or stirred in an ice bath for 3 h, then at r.t. for 17 h. In this second reaction, TLC showed the reaction was incomplete, therefore additional Cu and $PrNH_2$ were added and stirring continued for 24 h at r.t. The crude products from both reactions were purified by chromatography using 20% CH_2Cl_2/hexane followed by recrystallization from MeCN. Yields were 11.0 and 15.0%, respectively. TLC ($CHCl_3$) 0.67; IR (mineral oil) 2235 (str, CN and alkyne), 1606 (med Ar). ^{1}H NMR 7.60 (d, 2, $J = 8.59$, ArH *ortho* to CN), 7.53 (d, 2, $J = 8.63$, ArH *ortho* to alkyne), 2.35 (tt, 1, $J = 11.74$, 3.60, cyhC_1–H_a), 2.01 (dd, 2, $J = 13.59$, 3.34, cyhC_2, C_6–H_e), 1.78 (d, 2, $J = 14.49$, cyhC_3, C_5–H_e), 1.55–1.10 (m, 12, $4CH_3$ and 4cyh–H_a) and 0.88 (t, 3, $J = 6.54$, CH_3).

4.2.10.6. $X = C_5H_{11}$, $Y = NH_2$. Reaction time = 1 h at r.t., crude yield = 55.2%. A small amount of this material was recrystallized from MeOH for characterization; the remaining materials were converted to $Y = NMe_2$. TLC ($CHCl_3$) $R_f = 0.58$; m.p. 130–132°; IR (mineral oil) 3440, 3416 (wk, NH_2), 3331 (med, NH_2

hydrogen-bonded) and 1625, 1605 (med, Ar). ^{1}H NMR 7.28 (d, 2, $J=7.73$, ArH *ortho* to C), 6.56 (d, 2, $J=7.57$, ArH *ortho* to N), 3.84 (s, 2, NH_2), 2.30 (tt, 1, $J=11.72$, $\sim$3.38, cyhC_1–H_a), 2.00 (dd, 2, $J=12.68$, 2.93, cyhC_2, C_6–H_e), 1.76 (d, 2, $J=13.71$, cyhC_3, C_5–H_e), 1.50–1.10 (m, 12, 4CH_2 and 4cyh–H_a), 1.00–0.75 (m, 1, cyhC_4–H_a) and 0.88 (t, 3, $J=6.41$, CH_3).

4.2.10.7. $X=C_5H_{11}$, $Y=$  Reaction time = 17 h at r.t., crude yield = 41.0%. This material was not purified: m.p. 108–110°; IR showed no C=O peaks. ^{1}H NMR 7.41 (s, 4, ArH), 4.03 (t, 2, $J=3.44$, ketal CH_2), 3.52 (t, 2, $J=3.52$, ketal CH_2) and 1.63 (s, 3, ketal CH_3). Cyclohexyl and the remaining alkyl protons matched those given above.

4.2.10.8. *$X=C_5H_{11}$, $Y=NMe_2$.* This compound was prepared by alkylation of the amino compound **9** ($Y=NH_2$) in the same manner as described previously for alkylation of the phenyl analogue [2]. The crude product was isolated from MeOH: yield = 89.4%; GC $t_R=4.78$ (100%); IR (mineral oil) showed no NH_2, 2131 (wk alkyne), 1611 (med, Ar). ^{1}H NMR 7.36 (d, 2, $J=9.08$, ArH *ortho* to C), 6.60 (d, 2, $J=9.08$, ArH *ortho* to N) and 2.99 (s, 6, NMe_2); remaining protons were as above.

4.2.10.9. *$X=C_5H_{11}$, $Y=COCH_3$.* The ketal group was removed from the diacetylene **9** with $Y=$  using *p*-TSA as described previously for the analogous phenyl diacetylene [4]. The crude product was recrystallized from MeOH: yield = 51.1%; GC $t_R=3.17$ (100%); IR (mineral oil) 2236 (wk, alkyne), 1703 (str, C–O) and 1618 (med, Ar). ^{1}H NMR 7.90 (d, 2, $J=8.43$, ArH *ortho* to C–O), 7.55 (d, 2, $J=8.26$, ArH *ortho* to alkyne) and 2.61 (s, 3, $COCH_3$), Elemental analysis: calcd for $C_{23}H_{22}O$, C 86.20, H 8.81; found C 86.00, H 8.41%.

4.2.11. *Synthesis of the dioxane diacetylenes,* ***16***

These were prepared in the same manner as the diacetylenes **9** but using the dioxane acetylenes **14** and **15** in place of the cyclohexylacetylenes.

4.2.11.1. *$Y=F$, trans.* The chromatographed product (from the *trans*-acetylene **14**) was recrystallized from 95% EtOH: yield = 16.2%; TLC (10% EtOAc/hexane) $R_f=0.60$, GC $t_R=5.01$ (100%). ^{1}H NMR 7.47 (dd, 2, $J=8.93$, 5.32, ArH *ortho* to alkyne), 7.02 (app t, 2, $J=8.77$, ArH *ortho* to F), 4.47 (t, 1, $J=5.09$, dioC_2–H_a), 4.24 (t, 1, $J=11.30$, dio C_4, C_6–H_a), 3.65 (t, 2, $J=11.30$, dioC_4, C_6–H_a), 3.00–2.90 (m, 1, dio C_5–H_a), 1.70–1.50 (m, 2, α-CH_2), 1.50–1.20 (m, 6, 3CH_2) and 0.89 (t, 3, $J=6.62$, CH_3). ^{13}C NMR 165.6, 160.3, 134.7, 134.5, 116.1, 115.7, 102.4, 78.8, 78.0, 77.7–76.3 ($CHCl_3$ cluster includes diacetylene carbons), 69.8, 34.7, 31.6, 28.6, 23.6, 22.6 and 14.0.

4.2.11.2. *$Y=C_3H_7$, trans.* The chromatographed product was recrystallized from MeOH: yield = 18.5%; GC $t_R=10.81$ (100.00%). ^{1}H NMR 7.38 (d, 2, $J=8.42$, ArH *ortho* to alkyne), 7.11 (d, 2, $J=8.42$, ArH *ortho* to C_3H_7), 4.46 (t, 1, $J=9.90$, dioC_2–H_a), 4.23 (dd, 2, $J=11.72$, 4.57, dioC_4, C_6–H_e), 3.64 (t, 2, $J=11.35$, dioC_4, C_6–H_a), 2.57 (t, 2, $J=7.51$, $ArCH_2$), 1.59 (m, 4, *gem* CH_2), dioCH_2), 1.30 (m, 6, dio3CH_2), 0.92 (t, 3, $J=7.32$, $ArCH_3$) and 0.88 (t, 3, $J=7.14$, dioCH_3). Elemental analysis: calcd for $C_{22}H_{28}O_2$, C 86.20, H 8.81; found C 86.00, H 8.41; found C 81.52, H 8.51%.

4.2.11.3. *$Y=F$, cis.* This isomer was prepared from the *cis*-acetylene **15** and was purified in the same manner as the *trans*-isomer: yield = 77.5%; GC $t_R=5.13$ (100%). ^{1}H NMR 7.47 (dd, 2, $J=9.03$, 5.40, ArH *ortho* to alkyne), 7.01 (app t, 2, $J=8.73$, ArH *ortho* to F), 4.52 (t, 1, $J=5.19$, dioC_7–H_a), 4.20 (dd, 2, $J=11.40$, 1.27, dioC_4, C_6–H_e), 3.92 (dd, 2, $J=11.41$, 2.83, dioC_4, C_6–H_a), 2.60 (t, 1, $J=1.57$, dioC_5–H_e), 1.80–1.60 (m, 2, α-CH_2), 1.50–1.20 (m, 6, 3CH_2) and 0.90 (t, 3, $J=6.45$, CH_3).

4.2.12. *Dicyclohexyldiacetylene,* ***10***

This compound was prepared in the same manner as the diacetylenes **9** but using the bromoacetylene **6** with the acetylene **8**. Reaction conditions were 3 h in an ice bath, then at r.t. for 24 h. It was recrystallized from abs. EtOH: yield = 46.0%; TLC $R_f=0.45$; GC $t_R=14.69$ (99.17%). ^{1}H NMR 2.22 (tt, 2, $J=11.86$, 3.60, cyhC_1–H_a), 1.95 (dd, $J=13.65$, 3.40, cyhC_2, C_6–H_e), 1.50–1.15 (m, 4, CH_2 and 4cyh–H_a), 1.15–0.70 (m, 2, cyhC_4–Ha) and 0.88 (t, 6, $J=6.63$, CH_3).

5. Conclusions

It is clear that the use of a cyclohexyl or a dioxanyl ring to lower melting temperatures while maintaining a wide temperature range nematic phase did not work for these diacetylenes. A 2-olefin terminal chain seems to be more effective in lowering melting temperatures [3]. Neither do pyrimidine rings seem to improve the mesomorphic properties of these diacetylenes. Of

course, there are many more ring systems that could be used to replace a benzene ring; among these may be some that will improve mesomorphic properties.

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