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Synthesis and mesomorphic properties of 4-alkylamino-4′-substituted diphenyldiacetylenes

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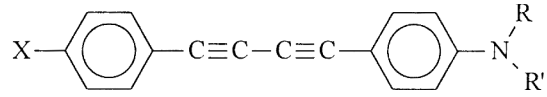
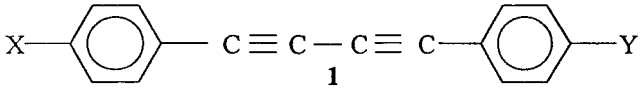
Various substituted aminodiphenyldiacetylenes of the type with X=C_3H_7,



C_5H_{11}, F or NO_2 and R, R' = H, CH_3–C_6H_{13} were synthesized and their mesomorphic properties determined. Semi-empirical and *ab initio* quantum chemical calculations using AM1, 421G and 631G* suggested that the amino group would increase the dielectric anisotropy and optical birefringence as compared to the alkyl chain. Mesomorphic properties were found to be poor with the maximum nematic phase range being 44.8°C and many of the compounds having no nematic phase. Both melting temperatures and enthalpies for those having nematic phases were too high to form good eutectic mixtures.

1. Introduction

In recent years, numerous unsymmetrical 4,4′-disubstituted diphenyldiacetylenes **1** have been synthesized [1–7]. Many of these compounds have wide range, low



1

temperature nematic phases with low viscosity and large optical birefringence Δn (*c.* 0.28 in the IR region [8]); they usually have small positive dielectric anisotropies $\Delta\varepsilon$, although appreciable negative dielectric anisotropies are possible. We were interested in modifying the structure of these diacetylenes to increase both the Δn and $\Delta\varepsilon$ values while maintaining the wide nematic phases and the low viscosities.

Large positive values of $\Delta\varepsilon$ typically result from large dipoles along the long axis of the molecule, i.e. large longitudinal dipoles. Rather small dielectric anisotropies result from the intrinsic polarizabilities of the molecules, while much larger dielectric anisotropies result from the reorientation of dipoles. Longitudinal dipoles contribute to the positive $\Delta\varepsilon$, transverse dipoles contribute to the negative $\Delta\varepsilon$. Known practical diacetylene compounds have either alkyl or alkoxy substituents. The dipoles associated with alkyl substituents are small; those associated with alkoxy substituents are larger but are at an appreciable angle to the molecular long axis, typically at a large enough angle that they are expected to contribute more to the negative than to the positive dielectric anisotropy. This accounts for the rather low dielectric anisotropies in these materials.

We set out to test whether molecules with substituted amines but without strong acceptors might resolve this difficulty. Systems with substituted amines are known that have liquid crystal properties, although this moiety does decrease the tendency to show these properties relative to an alkyl or alkoxy group. This is to some extent counteracted by the possibility of attaching two different chains to the amine, resulting in less symmetric and therefore less crystallizable molecules. However, unlike alkoxy and alkyl substituents, amines, particularly disubstituted amines, have small transverse and significant longitudinal dipoles. Similarly, the push–pull nature of the diacetylene-amine phenyl ring was expected to increase the electronic polarizability. Semi-empirical and *ab initio* quantum chemical calculations using AMI,

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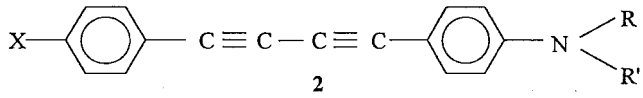
421G and 631G* confirmed this chemical intuition. This suggests that an amino substituent ($Y = NRR'$) along with an alkyl substituent (X = alkyl) should produce large Δn and $\Delta\varepsilon$ values. Consequently, various amino analogues of the type **2** were synthesized and their



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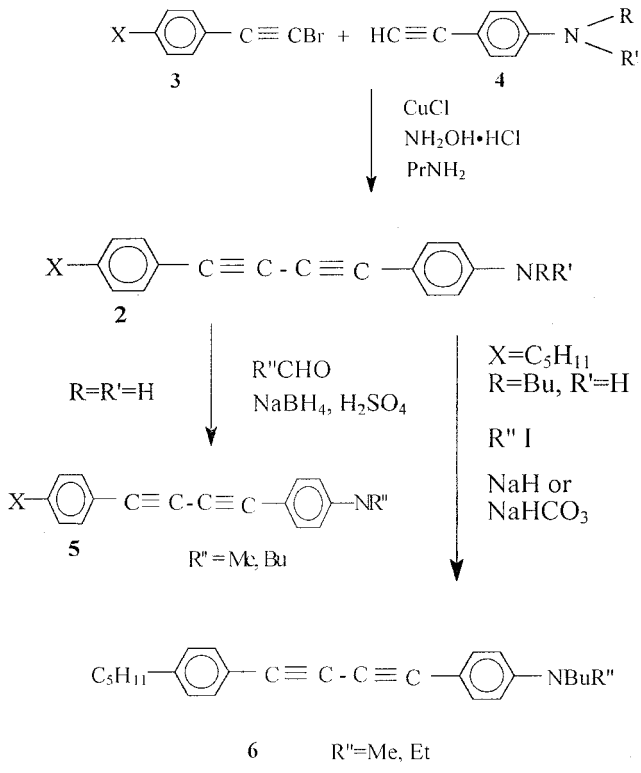
mesomorphic properties determined. Syntheses of the compounds with $X = O_2N$, $R = R' = H$ [3–5]; $R = H$; $R' = Me$ [5, 9]; $R = R' = Me$, and $R = H$, $R' = C_6H_{15}$ have already been reported [3]. Transition temperatures were reported only for the last compound (Cr 127.5°C N 146°C I). We repeated the preparation of some of these to determine their mesomorphic properties and to use in comparisons. Although diacetylenes in general are not stable to UV light, many of the applications for large birefringence liquid crystals are for the manipulation of infrared light. Hence, with appropriate optical shielding, these materials could be practical for these purposes.

2. Synthesis

The synthesis of these aminodiacetylenes was based on methods reported earlier for preparing various asymmetrical diacetylenes [1, 2, 5–7]. A copper-catalysed coupling of the bromoacetylene **3** with the amino acetylene **4** readily produced the diacetylenes **2** (scheme 1). The amino alkyl groups, R and R', can be incorporated into the amino acetylene **4** as was done in the synthesis of the diacetylenes **2** with $R = H$, $R' = C_4H_9$ ($X = C_5H_{11}$, F) and C_5H_{11}, C_6H_{13} ($X = NO_2$), and $R = R' = CH_3$ ($X = C_5H_{11}$) or by alkylating the amino diacetylene **2** ($R = R' = H$, prepared from **3** and **4**); this method was used also to prepare both the dimethyl and dibutylamino-diacetylene **5** and the butyl-methyl or ethyl analogues **6**.

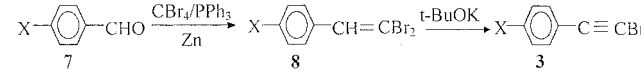


Scheme 1.

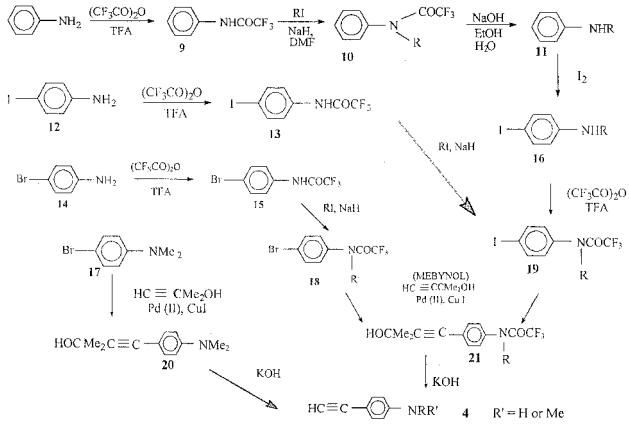
A variety of methods has been used to prepare the bromoacetylenes **3** [1, 6, 7, 9–13]. Our approach (scheme 2) converted the aldehyde **7** to the dibromo-olefin **8** which was then dehydrobrominated to the bromoacetylene **3**. A major problem in the synthesis of the dibromo-olefin was to separate the product from the by-product triphenylphosphine oxide. We found that the best way to remove this was to filter the crude material once or twice through a short silica gel column. This also removed any unreacted aldehyde. Final purification was achieved by a more careful chromatography on silica gel. Vacuum distillation was also tried but GC indicated that the product was less pure than the chromatographed olefin. This distilled material could, however, be used to prepare the acetylene **3**. Two solvent systems, *t*-BuOH and toluene were used for the conversion of the olefin **8** to the acetylene **3**. Both gave comparable yields. Low yields of the bromoacetylene **3** with $X = F$ appeared to be due to co-distillation or sublimation of this material with *t*-BuOH during its removal. Perhaps toluene would be a better solvent to use for preparing this analogue.

Many of the acetylene intermediates in this work seemed to be sensitive to light; this was also true of the iodide intermediates. Consequently, every effort was made to protect these materials from light. An attempt to distil the bromoacetylene led to decomposition, suggesting a sensitivity to heat as well.

The syntheses for two of the aminoacetylenes **4** ($R = R' = H$ or Me) were reported earlier [14–19]. In our work on the synthesis of alkylaminoazo dyes, alkylation of aniline with one equivalent of an alkyl bromide gave a mixture of aniline and both mono and disubstituted aniline which was difficult to separate [20]. Thus, we chose to use the trifluoroacetyl group for protection when only one *N*-alkyl substituent was needed. This protecting group is easy to add and remove [21, 22]; the resulting amide can be alkylated, and it has been used to prepare the aminoacetylene **4** ($R = R' = NH_2$) [23]. Before this work became known to us, we had already prepared the alkylated anilines **11** via the amides



Scheme 2.



Scheme 3.

9 and **10** (scheme 3) for use in preparing azo dyes. Iodination converted these anilines to the iodides **16**, which then gave the amides **19**. However, iodination never was complete, giving a mixture of amines that were difficult to separate. Starting with the iodoaniline **12** gave the same intermediate **19** in only two steps, making this the method of choice. The corresponding bromoaniline **14** was also tried. Both the halides **13** and **15** could be alkylated to the amides **18** and **19** but complete conversion was never achieved; longer reaction times did not improve the yields. The amides isolated could, however, be purified by chromatography.

Two methods were available to introduce the triple bond onto the benzene ring. Both involved using a protected acetylene, either with a CMe_2OH [16, 17] or a $SiMe_3$ [14, 15, 16(*a*)] group. In one instance, removing the CMe_2OH group reportedly led to decomposition, and better results were obtained by using the $SiMe_3$ [16(*b*)] group. We were able to prepare the aminoacetylenes **4** using either group but came to prefer CMe_2OH (scheme 3). Both the iodide **19** and the bromide **18** gave high yields in this reaction. Using bromoaniline **14** has the advantages that it is less expensive and not light sensitive. Chloroaniline was also tried; the resulting amide analogous to **15** was synthesized but poor results were obtained in the coupling reaction. Hydrolysis of the acetylene **21** gave the aminoacetylenes **4** ($R' = H$) in good yields. Since the bromodimethylaniline **17** is commercially available, it was converted to the aminoacetylene **4** ($R = R' = Me$) via the intermediate **20**.

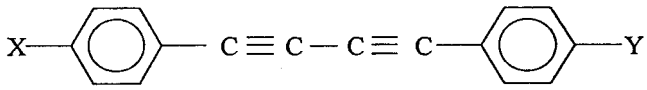
3. Quantum chemical calculations

Quantum chemistry calculations were performed on several of these molecules, using the GAMESS general atomic and molecular electronic structure system. The structures of the various molecules were optimized using the semi-empirical basis set AM1, usually followed by an *ab initio* basis set such as 421G or 631G*. The molecular dipoles were then calculated using the *ab initio* basis, 631G*. The molecular polarizabilities were calculated by applying a finite static field, using the same 631G* *ab initio* basis set, and comparing the results for the dipole moments with and without the field. This should yield a good estimate for the polarizability at frequencies high compared with the rate at which the molecules re-orient but low in comparison with the electronic excitations of the molecules. Thus these are a conservative estimate for the polarizabilities in the infrared. All calculations where done using simple restricted Hartree–Fock (RHF) calculations. The effect of this approximation on the results is expected to be small (but is hard to assess immediately). All non-zero components of the polarizability were calculated, and are reported. In addition, we report the difference between the polarizability along the long axis of the molecule and average of the polarizabilities perpendicular thereto. This latter parameter is expected to be the most important in determining the birefringence.

It is known that there is relatively little energy involved in rotating the phenyl rings attached to a diacetylene relative to each other. However, we report here only on calculations in which the two phenyl rings were parallel to each other. Presumably, this overstates somewhat the molecular polarizability anisotropy. Similarly, the nitro and dialkylamine groups were constrained to be in the same plane as the phenyl rings to which they are attached. This will again tend to overstate the molecular polarizability anisotropy and molecular dipole. Finally, no molecule with $X =$ alkyl was examined, $X = H$ was used instead. As $X =$ alkyl is a better donor than $X = H$, this is again likely to overstate the molecular polarizability anisotropy and molecular dipole. All of these approximations allow some simplifications in the calculations as they allow them to be made with higher symmetry, C_{2v} or higher. However, we believe that all of these effects are relatively small and that our results reasonably reflect the trends in these series.

The molecular dipoles, molecular polarizabilities and polarizability anisotropy from these calculations are given in table 1. In the calculations, the geometries were all constrained to have at least C_{2v} symmetry so that the dipole is along the long axis of the molecule and the polarizability tensor is diagonal when the coordinates are chosen to be along the special axes of this group. The z direction is the long axis of the molecule, the x direction is perpendicular thereto but in the plane of the phenyl rings, the y direction is perpendicular to the phenyl rings. It is expected that the long axis of the molecule should align primarily along the director and that the degree of order along other molecular axes should be relatively small. Hence the birefringence

Table 1. Calculated dipoles, components of the electronic polarizability tensor, and the most relevant electronic polarizability anisotropy for compounds **1**.



X	Y	Dipole /Debye	α_{zz}	α_{xx}	α_{yy}	$\Delta\alpha$
H	H	0	0.8819	0.3554	0.1284	0.6398
H	NMe_2	3.060	1.0768	0.4104	0.1822	0.7905
F	NMe_2	5.1161	1.0764	0.4080	0.1848	0.7900
NO_2	NH_2	9.9354	1.1116	0.3906	0.0988	0.8669

is controlled primarily by $\Delta\alpha = \alpha_{zz}^{-1/2}(\alpha_{xx} + \alpha_{yy})$. The molecular dipoles in this table are given in Debye and the polarizabilities in 10^3 Debye/au.

The dielectric anisotropy is difficult to predict from the dipole moment of a material, particularly if the dipole moment is large. This is because inter-molecular interactions between the molecules significantly affect the dielectric anisotropy. However, if the dipole moment along the long axis of the molecule is more than about 2 or 3 Debye (or about this much larger than the dipole(s) transverse to the long axis of the molecule), then the dielectric anisotropy is usually positive and acceptably larger. Thus it would seem that all these molecules have significant positive dielectric anisotropies. Determination of the $\Delta\varepsilon$ and Δn values are in progress and will be reported later.

We also see that the addition of the strong amine donor appreciably increases the optical polarizability and the polarizability anisotropy. Using the strong π acceptor $X = NO_2$ further increases the polarization anisotropy. However, changing $X = H$ to $X = F$, which is a strong σ acceptor but moderate π donor has surprisingly little effect on the polarizability. A larger change would be expected on replacing alkyl (a π donor) by F. In any case, $X = F$ does very appreciably increase the size of the electric dipole, which in turn would be expected to increase the dielectric anisotropy.

Given these calculations, it is expected that the amines should all have appreciably better dielectric anisotropies than the diacetylene **1** with $X = Y = H$, roughly in the order X = alkyl, F, NO_2. It is also expected that the amines should have somewhat larger birefringences. This effect is marginal, however, except for $X = NO_2$ and might be overwhelmed by changes in the order parameter, which also effects the birefringence.

4. Mesomorphic properties

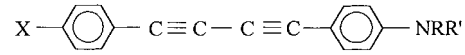
Transition temperature (°C) for the aminodiacetylenes prepared, as determined by hot stage polarizing microscopy, along with some enthalpy values obtained from DSC scans are presented in table 2. There seems to be little consistency in the effect of the substituents X, R, and R' on mesomorphic properties. When $X = C_3$ [$C_3 = C_3H_7$, etc], and $R = R' = H$, a monotropic nematic phase was observed but no mesophases occurred when $X = C_5$ or NO_2. However, when $R = R' = Me$ and $X = C_3$, C_5 the opposite is true, with $X = C_5$ having an enantiotropic nematic phase and $X = C_3$ showing no mesophase. Longer chain lengths for all the substituents in any combination produced much lower melting temperatures but no nematic phases. On the other hand, when $R = H$ with $R' = C_4$–C_6 ($X = C_5$, F, NO_2), melting temperatures were high and nematic ranges were wider (18.5–44.8°C) making these the best mesogens of the entire group. Surprisingly, the combination of $R = CH_3$, $R' = Bu$ and $X = F$ lowers the melting temperature 60°C but also destroys all mesophases, despite the fact that the isotropic liquid can be supercooled by an additional 60°C. Enthalpy of melting values for all the mesogens were, however, too high for them to be useful in eutectic mixtures. Still, it is possible that a disubstituted fluoro analogue (expected to have an even lower melting temperature, an appreciable dipole moment and a low heat of melting) could be useful in mixtures despite having a low tendency to mesophase formation.

5. UV-Vis absorption

The UV-Vis spectra were obtained in solution but the solvent curve was subtracted to give only spectra of the diacetylenes. Some typical curves are shown in figure 1. We did not carefully measure the path length or concentration so these curves are in arbitrary units and only the shapes should be compared. As can be readily seen, the amine, the alkyl amine and most strongly the dialkylated amines shift the lowest lying absorption to longer wavelengths. This is expected, as going from amine to alkylamine to dialkylamine results in an increasingly strong donor *para* to the electron-accepting diacetylene. Also, note that the absorptions in figures 1(*a*–*c*) extend slightly into the visible (in 1(*d*) when $X = NO_2$ there is a major absorption in the visible). It is difficult to know if this is a result of trace impurities (e.g. oxidized amines) in the sample, or if it is an intrinsic property of these materials.

It is also expected, on the basis of 'ordinary chemical reasoning', that the transition dipole matrix element from the ground state to this lowest lying state is along the long axis of the molecule. The smaller the energy difference between the ground state and excited state, the higher the expected contribution of this state to the polarizability (provided the transition matrix element does not change dramatically, as systematized e.g. by its sum-over-states formula) [24]. It is expected that this

Table 2. Transition temperatures (°C) for compounds **2**.



						ΔH/kJ mol^{-1}	
X	*R*	*R'*	Cr[a]	N	I	Melting	Clearing
C_3	H	H	75.9[b]	(89.2–89.3)[c]	117.1–118.5	32.7	
C_5	H	H	110.0[d]		110.5–110.9		
NO_2	H	H			246.6–247.3 dec		
NO_2	H	C_5	113.6	127.1–127.8	152.4–152.5		
F	H	C_4	93.4	102.0–105.8	133.1–133.5[e]	33.5[f]	
NO_2	H	C_6	121.9	129.0–131.0	149.2–149.5	39.8	0.33
C_5	H	C_4	97.4	97.7–101.1	143.0–145.9[g]	23.9	1.16
C_3	Me	Me	146.9		151.2–152.3	25.2	
C_5	Me	Me	125.1	128.1–128.9	133.3–133.6	27.9	1.24
C_5	Me	C_4	7.4	(30.5–30.9)[c]	43.9–44.6	29.0	
F	Me	C_4	− 4.0		61.3–62.1	23.1	
C_5	C_2	C_4	41.8		52.9–55.2	31.1	
C_5	C_4	C_4	28.1		44.5–45.9	27.6	
NO_2	C_4	C_4	134.0		134.5–139.0	29.9	

[a] Cr = crystallization temperature on cooling at 2° min^{-1}, N = nematic phase, I = isotropic liquid, dec. = decomposes.
[b] A crystal-to-crystal change occurred at 104.5–106.9°C on reheating these crystals.
[c] Parentheses indicate a monotropic phase.
[d] These crystals (Cr_1) converted to another form (Cr_2) on cooling. Cr_2 converted to Cr_1 on reheating at 86.8–87.0 which melted to the isotropic liquid.
[e] Shifting of the clearing temperature in repeated runs suggests this material is unstable at this temperature.
[f] Showed a crystal change at 90.7° on heating.
[g] The broad clearing temperature may be due to hydrogen bond formation.

should result in a larger electronic polarizability anisotropy for the molecule. With similar order parameters, this would translate into an increased birefringence. Relatively little change in the absorptions are seen upon addition of a fluorine *para* to the acetylene, while rather significant changes are seen on addition of a *para*-nitro group. This suggests that such a *para*-fluorine atom does not increase the molecular polarizability anisotropy, but that the nitro group does. This is consistent with the results of the quantum chemical calculations. Unfortunately, the nitro group also results in unacceptably high melting temperatures for the liquid crystal phases.

6. Conclusions

A variety of mono- and di-alkylated aminodiphenyldiacetylenes were prepared. Some of these compounds had enantiotropic nematic phases but usually with melting temperatures above 100°C. A few had much lower melting temperatures but showed either no mesophases or only monotropic nematic phases.

7. Experimental

All temperatures are given in °C. Commercially available starting materials were used without purification unless otherwise indicated. All reactions using iodides were protected from light due to the light instability of these materials. Acetylenes and diacetylenes were stored at 5° when not in use. Anhydrous reactions were run in flame- or oven-dried glassware using solvents dried over Linde 4A molecular sieves. Organic extracts were dried over anhydrous Na_2SO_4 or $MgSO_4$. The NaH used was a 60% suspension in mineral oil, and was usually washed with hexane immediately before addition to the reaction mixture. The amount used is that for the oil suspension.

TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as the detectors. Flash chromatography and silica gel filtrations were done using Mallinckrodt silica gel (230–400 mesh). Capillary GC analysis was obtained using a Hewlett-Packard 5890 instrument equipped with a HP3395 Integrator, a FID detector and a Hewlett Packard 5 m methylsilicone gum column. All gradient GCs were run at 20° min^{-1}. 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

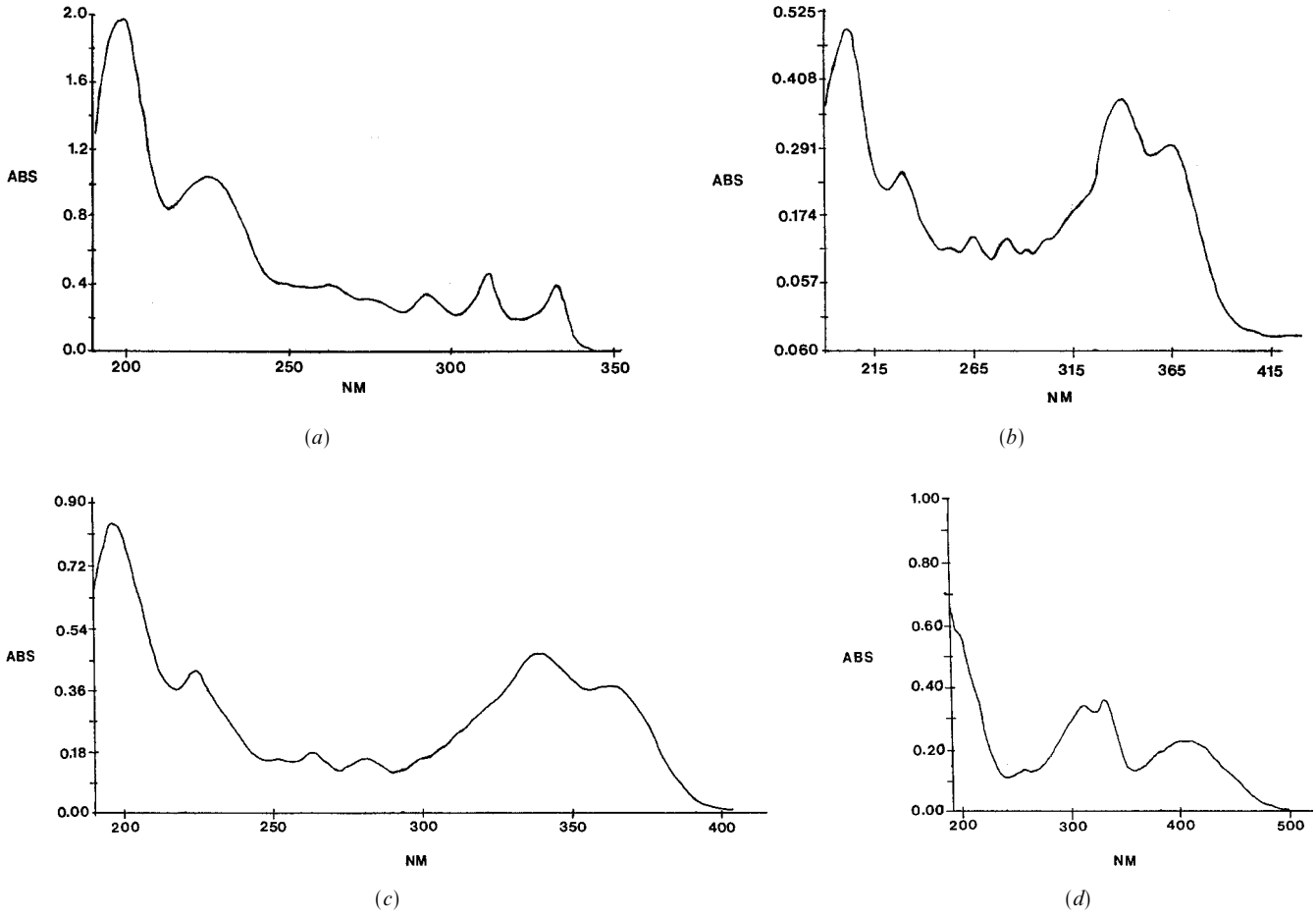


Figure 1. UV-Vis absorption spectra for compounds **2**. (*a*) $X = C_5H_{11}$, $R = R' = H$; (*b*) $X = C_5H_{11}$, $R = CH_3$, $R' = C_4H_9$; (*c*) $X = F$, $R = CH_3$, $R' = C_4H_9$; (*d*) $X = O_2N$, $R = H$, $R = C_4H_9$.

spectrometer equipped with a VXR-400 data station at 200 and 50 MHz respectively. Chemical shifts are given in δ units and coupling constants in Hz. ^{13}C NMR chemical shifts were compared with those values calculated using a softshell ^{13}C NMR Module. UV solution spectra were obtained in a 1 cm cell using a Perkin-Elmer lambda 4B instrument. The solvent curve was subtracted from all spectra.

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}. Crystallization temperatures were obtained by cooling the melt at 2° min^{-1} until crystals were formed, to ensure that all mesophases had been observed before this temperature. These crystals were reheated to obtain the melting temperatures and to confirm that these were not mesophases. DSC scans were run using a Perkin-Elmer DSC7 equipped with a TAC 7/PC instrument controller at a rate of 5° min^{-1}; indium was used for calibration.

7.1. *1-(2,2-Dibromoethenyl)-4-alkylbenzene* ***8***

Method 1 ($X = C_5H_{11}$). A solution of CBr_4 (131.7 g, 0.40 mol) in CH_2Cl_2 was added dropwise over a 2 h period to a stirred suspension of PPh_3 (114.6 g, 0.44 mol) and Zn dust (26.0 g, 0.40 mol) in CH_2Cl_2 (450 ml) at 0° under N_2. The reaction mixture was stirred at r.t. for 24 h and then cooled to 0°. A solution of the aldehyde **7** with $X = C_5H_{11}$ (35.0 g, 0.20 ml) in CH_2Cl_2 (60 ml) was added dropwise to this pink mixture and stirring was continued for 3.5 h. The reaction mixture was filtered twice through silica gel (*c.* 250 g) and the silica gel washed thoroughly with 1 : 1 CH_2Cl_2/hexane; the solvent was removed from the filtrate *in vacuo*. The remaining liquid could be purified by distillation as described here or by flash chromatography as described below in method 2. Distillation at 135–140° (0.6 mm Hg) gave 61.1 g (92.7%) of the dibromoolefin **8** ($X = C_5H_{11}$) as a pale yellow liquid. TLC (10% hexane/CH_2Cl_2), $R_f = 0.71$; GC (100–250°) major peaks at $t_R = 5.76$ (94.86%, product), 5.51 (1.01%), 6.71 (1.82%) and numerous

minor peaks; IR (film) 1616 with sh (med, ArC=CBr_2) and 1514 (med, Ar); ^{1}H NMR 7.50 (d, 2, J = 7.86, ArH *ortho* to C=C), 7.45 (s, 1, C=CH), 7.18 (d, 2, J = 8.22, ArH *ortho* to C_5), 2.60 (t, 2, J = 7.69, Ar–CH_2), 1.58 (quint, 2, J = 7.78, β-CH_2), 1.36–1.29 (m, 4, 2 CH_2) and 0.90 (t, 3, J = 6.60, CH_3).

Method 2 ($X = C_3H_7$). The reaction mixture obtained as in method 1 was filtered twice through silica gel (*c.* 250 g) using first CH_2Cl_2 and then 1:1 CH_2Cl_2/hexane as the eluting solvents until TLC indicated that no additional product was eluted. The second filtrate was allowed to evaporate to near but not complete dryness and hexane (10 × product volume) added. The precipitated solid was removed by filtration and washed thoroughly with hexane. Removal of the solvent from the filtrate *in vacuo* gave a material which was flash chromatographed on silica gel using hexane to give the purified dibromoolefin **8** ($X = C_3H_7$) as a pale yellow liquid in 68.4 g (99.9%) yield. TLC (hexane) R_f = 0.58; GC t_R = 3.88 (100%, 100–250°); ^{1}H NMR aliph region: 2.57 (t, 2, J = 7.65, $ArCH_2$), 1.63 (quint, 2, J = 7.44, β-CH_2) and 0.93 (t, 3, J = 7.33, CH_3).

$X = F$. Yellow liquid, purified yield = 95.6%. GC t_R = 4.10 (100%, 50–250°); IR (film) 1603, 1584 (str, ArC=CBr_2) and 1507 (str, Ar); ^{1}H NMR δ 7.54 (dd, 2, J = 9.08, 5.45, ArH *ortho* to C=C), 7.46 (s, 1, CH) and 7.08 (t, 2, J = 8.61, ArH *ortho* to F).

$X = NO_2$. The starting aldehyde did not dissolve easily in CH_2Cl_2 so THF (*c.* 50% of the CH_2Cl_2 volume) was added. The crude product was purified directly by flash chromatography through silica gel using CH_2Cl_2 followed by recrystallization from abs. EtOH to give 63.1 g (88.8%) of the dibromoolefin **3** ($X = NO_2$) as a yellow solid. TLC (1:1 CH_2Cl_2/hexane) R_f = 0.65; m.p. 104–105°; IR (Nujol) 1603 (med), 1587 (med) and 1518 (str, ArC=CBr_2); ^{1}H NMR 8.24 (d, 2, J = 8.87, ArH *ortho* to NO_2), 7.71 (d, 2, J = 9.12, ArH *ortho* to CH) and 7.56 (s, 1, CH).

7.2. *1-(Bromoethynyl-4-pentylbenzene* **3** *($X = C_5H_{11}$)*

Method 1. To a stirred solution of the dibromoolefin **8** ($X = C_5H_{11}$, 3.00 g, 9.03 mmol) in toluene (75 ml) at r.t. under anhydrous conditions, was added in small portions *t*-BuOK (1.02 g, 9.03 mmol). This mixture was heated under reflux for 6 h, stirred at r.t. for 17 h and then quenched by the addition of H_2O (20 ml). Toluene was removed *in vacuo* and the remaining material dissolved in H_2O (75 ml) and extracted with hexane (2 × 150 ml). The organic layer was separated, dried, filtered, and the solvent removed from the filtrate *in vacuo* to give the crude product. Purification of this material by flash chromatography on silica gel using hexane gave the purified bromoacetylene **3** ($X = C_5H_{11}$) as a pale yellow liquid (2.0 g, 90.3%). TLC (hexane) R_f = 0.60; IR (film) 2208 (wk C≡C) 1607 (wk, Ar) and 1517 (str, ArH); ^{1}H NMR 7.37 (d, 2, J = 8.22, ArH *ortho* to C≡C), 7.12 (d, 2, J = 8.10, ArH *ortho* to alkyl), 2.59 (t, 2, J = 7.70, $ArCH_2$), 1.59 (quint, 2, J = 7.55, β-CH_2), 1.33–1.24 (m, 4, $2CH_2$) and 0.88 (t, 3, J = 6.78, CH_3).

Method 2. To a stirred solution of the dibromoolefin **8** ($X = C_5H_{11}$, 25.4 g, 76.7 mmol) in *t*-BuOH at r.t. under N_2, was added in small portions *t*-BuOK (8.61 g, 76.2 mmol). This mixture was heated under reflux for 4.25 h, cooled to r.t., H_2O (125 ml) added and the solvents removed *in vacuo*. The remaining material was dissolved in hexane, washed with H_2O, dried, filtered, and the filtrate evaporated to give 20.1 g of the crude product. TLC (hexane) showed 3 spots with R_f = 0.00, 0.55, and 0.65. Purification of this material by flash chromatography through a 5″ column of silica gel using hexane gave the bromoacetylene **3** ($X = C_5H_{11}$, 2.05 g, 90.3%). TLC (hexane) R_f = 0.60°; GC (100–220°) t_R = 2.75 (2.85%), 3.21 (0.82%) and 3.31 (96.34%, bromoacetylene).

The following analogues of **3** were prepared using the methods indicated.

$X = C_3H_7$. Method 1 ~92.8%; method 2 ~89.5%.

$X = F$. Method 2, yield 57.0–77.6%, colourless solid with m.p. 42–43°. TLC (hexane) R_f = 0.47; GC (100–250°) t_R = 0.51 (0.5%) and 0.78 (99.5% product); IR (Nujol) 2200 (wk C≡C), 1605 (med with sh, Ar) and 1512 (str, Ar); ^{1}H NMR 7.43 (dd, 2, J = 8.45, 5.48, 2, ArH *ortho* to C≡C), 7.01 (t, 2, J = 8.49, ArH *ortho* to F). This material seemed to azeotrope with *t*-BuOH making it difficult to obtain a good yield. Thus, method 1 might be better for preparing this analogue.

$X = NO_2$. Method 2, the reaction time was 8 h. The reaction mixture was cooled to r.t., H_2O added and the mixture extracted three times with CH_2Cl_2. The organic layer yielded a solid which was recrystallized from CH_3CN to give 38.2 g (92.5%) of the bromoacetylene **3** ($X = NO_2$), m.p. 169.1–173.1° dec (lit. [12] 173–175°); TLC ($CHCl_3$) R_f = 0.63; IR (Nujol) 2195 (wk, C≡C), 1594 and 1510 (str, Ar); ^{1}H NMR 8.19 (d, 2, J = 8.99, ArH *ortho* to NO_2) and 7.60 (d, 2, J = 8.96, ArH *ortho* to C≡C).

7.3. *2,2,2-Trifluoro-N-phenylacetamide* **9**

To the stirred aniline (10.0 g, 0.11 mol) cooled in an ice bath was added dropwise a mixture of $(CF_3CO)_2O$ (80 g, 0.38 mol) and CF_3CO_2H (44 g, 0.38 mole). The reaction mixture was heated under reflux for 24 h, cooled to r.t. and Et_2O added. This mixture was washed thoroughly with H_2O, dried, filtered and the solvent evaporated from the filtrate to give 18.2 g (89.5%) of the crude amide. This material was purified by flash chromatography on silica gel using 1:1 CH_2Cl_2/hexane to give the amide **9**, yield 17.5 g (86.0%), m.p. 88.5–89.5°

(lit. [25] 88.5–90°). TLC ($CHCl_3$), $R_f = 0.44$; IR (Nujol) 3335 (str NH), 1709 (str amide) and 1607 (str, Ar); ^{1}H NMR 11.26 (s, 1, NH), 7.68 (d, 2, $J = 8.59$, ArH *ortho* to N), 7.42 (t, 2, $J = 7.70$, ArH *meta* to N) and 7.23 (t, 1, $J = 7.37$, ArH *para* to N).

7.4. *2,2,2-Trifluoro-N-pentyl-N-phenylacetamide* ***10*** *($R = C_5H_{11}$)*

To a stirred suspension of NaH (1.55 g) in anhyd. DMF (dried 17 h over 4A molecular sieves) at r.t under N_2, was added dropwise a solution of the amide **9** (7.00 g, 37.0 mmol) in DMF (40 ml) over a 15 min period. Stirring was continued for 40 h and then a solution of *n*-pentyl iodide (8.06 g, 40.7 mmol) in DMF (25 ml) was added over one min. After stirring at r.t. for 70 h, the solvent was removed *in vacuo*. The remaining material was dissolved in Et_2O and the solution washed with H_2O (3 × 200 ml), dried and filtered. The solvent was removed from the filtrate *in vacuo* to give 8.45 g (87.7%) of the crude product. TLC of this material in $CHCl_3$ showed 3 spots with $R_f = 0.39$, 0.58 and 0.78. This material was flash chromatographed on silica gel. Elution with increasing amounts of CH_2Cl_2 in hexane gave the following fractions: TLC ($CHCl_3$) $R_f = 0.81$ (hexane, trace amount), $R_f = 0.59$ (25% CH_2Cl_2), 5.53 g liquid; $R_f = 0.37$ (95% CH_2Cl_2), 0.86 solid with m.p. 83–84 (starting amide) and $R_f = 0.80$, 0.60 (CH_2Cl_2), 1.56 g liquid product plus $C_5H_{11}I$. The second fraction was found to be the desired alkylated amide **10** ($R = C_5H_{11}$), 57.4%: IR (film) 1703 (str, amide) and 1613 (med Ar); ^{1}H NMR 7.46–7.39 (m, 3, *meta* and *para* ArH), 7.27 (d, 2, $J = 8.02$, ArH *ortho* to N), 3.72 (t, 2, $J = 7.65$, NCH_2), 1.65–1.50 (m, 2, N β-CH_2), 1.36–1.21 (m, 4, 2 CH_2) and 0.88 (t, 3, $J = 6.70$, CH_3). The third fraction was rechromatographed on silica gel using 1 : 1 CH_2Cl_2/hexane to give a liquid (791 mg) shown to be the alkylated aniline **11** ($R = C_5H_{11}$). TLC ($CHCl_3$) $R_f = 0.61$; IR (film) 2423 (wk, NH) and 1608 (str, ArH); ^{1}H NMR ($CDCl_3$) 7.17 (t, 2, $J = 7.94$, ArH *meta* to NHR), 6.68 (t, 1, $J = 7.31$, ArH *para* to NHR), 6.60 (d, 2, $J = 7.57$, ArH *ortho* to NHR), 3.60 (br s, 1, NH) 3.10 (t, 2, $J = 7.02$, NCH_2) and 1.61 (quint, 2, $J = 6.66$, N β-CH_2), 1.43–1.26 (m, 6, 3 CH_2) and 0.90 (t, 3, $J = 6.55$, 3 CH_3). This aniline represents 13.0% of the amide **10**, giving a corrected amide yield of 70.4%.

The amide **10** with $R = C_6H_{13}$ was prepared in the same manner in 94.0% yield but was used without purification to obtain the aniline **11**.

7.5. *N-Hexylbenzenamine* ***11*** *($R = C_6H_{13}$)*

A mixture of the amide **10** ($R = C_6H_{13}$, 22.5 g, 0.08 mol) and NaOH (16.5 g, 0.41 mol) in EtOH (50 ml) and H_2O (50 ml) was heated under reflux for 20 h. The pH of the cooled (r.t.) reaction mixture was adjusted to *c*. 6 with 3M aq HCl. Water (200 ml) was added and the mixture extracted with Et_2O (300 ml). The Et_2O layer was washed with H_2O (4 × 100 ml), dried, filtered, and the solvent removed from the filtrate to give 14.0 g, 95.5% of the crude product. This material was purified by flash chromatography on silica gel using increasing concentrations of CH_2Cl_2 in hexane. A 1 : 1 mixture gave 10.9 g (74.5%) of the purified aniline as a colourless liquid **11** ($R = C_6H_{13}$). TLC ($CHCl_3$) $R_f = 0.65$; IR (film) 3411 (med, NH) and 1607 (str, Ar); ^{1}H NMR 7.17 (t, 2, $J = 7.92$, ArH *meta* to N), 6.69 (t, 1, $J = 7.33$, ArH *para* to N), 6.61 (d, 2, $J = 7.65$, ArH *ortho* to N), 3.60 (s, 1, NH), 3.10 (t, 2, $J = 7.00$, NCH_2), 1.02 (quint, 2, $J = 7.33$, N β-CH_2), 1.44–1.28 (m, 6, 3 CH_2) and 0.90 (t, 3, $J = 6.37$, CH_3).

7.6. *N-(Hexyl)-4-iodobenzenamine* ***16*** *($R = C_6H_{13}$)*

To a stirred mixture of the aniline **11** ($R = C_6H_{13}$, 500 mg, 2.82 mmol) and $NaHCO_3$ (360 mg, 4.28 mmol) in 80% aq. EtOH at r.t. in the dark, was added I_2 (1.35 g, 8.44 mmol) in 150 mg portions every 10 min. The reaction mixture was stirred for 1 h, poured into a solution of $Na_2S_2O_3$ (2 g) in H_2O (100 ml) and extracted with CH_2Cl_2. The organic layer was washed with more of the $Na_2S_2O_3$ solution followed by H_2O; it was then dried, and filtered through silica gel, washing with CH_2Cl_2 (100 ml). The solvent was evaporated from the filtrate to give 780 mg (90.7%) of the crude liquid iodo compound **11** ($R = C_6H_{13}$). TLC ($CHCl_3$) $R_f = 0.59$, 0.74 and 0.86; GC (50–200°) $T_R = 6.25$ (6.0%, starting aniline) and 8.72 (94.0%, product); IR (film) 3424 (med, NH) and 1607 (str, Ar); ^{1}H NMR 7.40 (d, 2, $J = 8.79$, ArH *ortho* to I), 6.38 (d, 2, $J = 8.79$, ArH *ortho* to N), 3.06 (t, 2, $J = 7.00$, NCH_2), 1.59 (quint, 2, $J \sim 6.27$, N β-CH_2), 1.41–1.27 (m, 6, 3 CH_2) and 0.90 (t, 3, $J = 6.41$, CH_3). This material was used without further purification.

7.7. *2,2,2-Trifluoro-N-(4-iodophenyl)acetamide* ***13***

This compound was prepared in the same manner as described in [23], our characterization data agreeing with that previously reported.

7.8. *2,2,2,-Trifluoro-N-(4-bromophenyl)acetamide* ***15***

This compound was prepared from 4-bromoaniline in the same manner as the iodo analogue **13** in a 99.5% yield, m.p. 121–123°. IR (Nujol) 3407 (med, NH), 1704 (str C=0) and 1597 (str, Ar); ^{1}H NMR 8.02 (br s, 1, NH), 7.52 (d, 2, $J = 9.68$, ArH *ortho* to Br) and 7.49 (d, 2, $J = 9.63$, ArH *ortho* to N).

7.9. *2,2,2-Trifluoro-N-(4-chlorophenyl)acetamide*

This compound was prepared from 4-chloroaniline in the same manner as the iodo analogue **13** in a 98.8%

yield, m.p. 122.8–126.3°. ^{1}H NMR 8.06 (br s, 1, NH), 7.53 (d, 2, $J = 8.95$, ArH *ortho* to N) and 7.36 (d, 2, $J = 8.95$, ArH *ortho* to Cl).

7.10. *2,2,2-Trifluoro-N-alkyl-N-(4-iodophenyl)acetamide* ***19***

Method 1. $R = C_6H_{13}$. To a stirred solution of the iodoaniline **16** (780 mg, 2.57 mmol) in CF_3CO_2H (1.0 ml) in an ice bath was added quickly $(CF_3CO)_2O$ (2.70 g, 12.8 mmol). This mixture was warmed to *c.* 50°, stirred for 15 min, poured into H_2O (40 ml) and extracted with CH_2Cl_2 (50 ml). The organic layer was washed with H_2O (2 × 50 ml), dried, filtered, and the solvent removed from the filtrate *in vacuo* to give 910 mg (88.3%) of the product **19** ($R = C_6H_{13}$) as a liquid. TLC ($CHCl_3$) $R_f = 0.05$; GC (50–200°) $t_R = 8.41$ (99.6% product) and 8.72 (0.4%) starting aniline; ^{1}H NMR showed trace amounts of impurities at 7.2–7.5. This material was used without further purification.

Method 2 ($R = C_4H_9$). To a stirred suspension of NaH (800 mg, 20.0 mmol) in DMF (20 ml) at r.t., using anhydrous conditions, was added dropwise a solution of the iodoamide **13** (6.0 g, 19.1 mmol) in DMF (10 ml). The reaction mixture was stirred for 3.0 h and then *n*-butyl iodide (3.86 g, 21.0 mmol) was added dropwise. Stirring was continued at 60° for 72 h and the mixture was then cooled to r.t., diluted with Et_2O (200 ml) and washed with H_2O (5 × 30 ml). The organic layer was dried, filtered, and the solvent removed from the filtrate *in vacuo* to give the crude product. TLC ($CHCl_3$) showed 3 spots with $R_f = 0.60$, 0.57 and 0.43. Purification of this material by flash chromatography using 1:1 hexane in CH_2Cl_2 with increasing amounts of CH_2Cl_2 gave 3.44 g (48.6%) of the amide **19** ($R = C_4H_9$). IR (film) 1704 (sh, amide) and ~1600 (wk Ar); ^{1}H NMR 7.77 (d, 2, $J = 8.67$, ArH *ortho* to I), 6.96 (d, 2, $J = 8.14$, ArH *ortho* to N), 3.70 (t, 2, $J = 7.50$, NCH_2), 1.53 (quint, 2, $J = 7.78$, N β-CH_2), 1.32 (sext, 2, $J \sim 6.68$, N γ-CH_2) and 0.91 (t, 3, $J = 7.14$, CH_3); ^{13}C NMR 139.0, 130.5, 119.0, 113.5, 94.5, 51.9, 29.5, 20.0 and 19.4.

The $R = C_5$ homologue was also prepared using this method, purified yield = 75.4%.

7.11. *2,2,2-Trifluoro-N-(bromophenyl)-N-butylacetamide* ***18*** *(*$R = C_4H_9$*)*

This compound was prepared by alkylating the bromoamide **15** using the same procedure as used for the alkylation of the iodoaniline **13** (method 2) except that the reaction mixture was stirred at 50° for 24 h. Yield after chromatography = 59.3%, (22.8% of **15** was recovered). ^{1}H NMR 7.57 (d, 2, $J = 8.67$, ArH *ortho* to Br), 7.09 (d, 2, $J = 8.10$, ArH *ortho* to N), 3.21 (t, $J = 7.51$, 2, N–CH_2), 1.60–1.42 (m, 2, N β-CH_2), 1.33 (sext, 2, $J = 6.96$ γ-CH_2) and 0.91 (t, 3, $J = 7.15$, CH_3).

The $R = C_6H_{13}$ homologue was prepared in a similar manner. The reaction mixture was stirred for 96 h at 50°, yield = 77.9% (21.0% of **15** was recovered).

7.12. *2,2,2-Trifluoro-N-butyl-N-[4-(3-hydroxy-3-methyl-1-butynyl)phenyl]-acetamide* ***21*** *(*$R = C_4H_9$*)*

To stirred solution of the bromoamide **18** (R = Bu, 10.76 g, 33.2 mmol) and MEBYNOL (6.98 g, 83 mmol) in Et_3N (130 ml) at r.t. were added PPh_3 (0.21 g, 0.8 mmol), CuI (0.05 g, 0.29 mmol) and $(PPh_3)_2PdCl_2$ (500 mg, 0.08 mmol). The reaction mixture was heated under reflux for 17 h and the insoluble solids removed by filtration and washed thoroughly with Et_2O. Removal of the solvent *in vacuo* from the filtrate gave 9.50 g (87.4%) of the product **21** (R = Bu) as a dark yellow oil. This material was used without further purification.

The following homologues were prepared from the iodides **19** in the same manner.

$R = H$. The crude product was stirred in glac. HOAC (10 ml, 74.6 mmol) at 0° for 10 min, and then r.t. for 1 h; the solvent was then removed *in vacuo*. The remaining material was stirred in H_2O (2 × 200 ml) and the solid removed from the filtrate *in vacuo* to give a light tan solid (97.3%) as the product **21** (R = H), m.p. = 132.3–135.3°. IR (Nujol) 3411 (wk, d, NH), 3251 (wk, OH), 2362, 2330 (wk C≡C), 1716 (str, amide) and 1607 (str, Ar); ^{1}H NMR 7.95 (br s, 1, NH), 7.52 (d, 2, $J = 8.88$, ArH *ortho* to amide), 7.41 (d, 2, $J = 8.92$, ArH *ortho* to C≡C), 1.90 (br, s, 1, OH) and 1.60 (s, 6, 2 CH_3). This material was used without further purification.

$R = C_5H_{11}$. The crude product was purified by flash chromatography on silica gel using 10% hexane/CH_2Cl_2 to give 67.1% of the product **21** ($R = C_5H_{11}$) as a colourless solid, m.p. 68–70°. ^{1}H NMR 7.48 (d, 2, $J = 8.54$, ArH *ortho* to C≡C), 7.15 (d, 2, $J = 8.34$, ArH *ortho* to amide), 3.71 (t, 2, $J = 7.55$, NCH_2), 2.09 (s, 1, OH), 1.63 (s, 6, 2 CH_3), 1.55 (quint, 2, $J = 5.96$, N β-CH_2), 1.31–1.24 (m, 4, 2 CH_2) and 0.87 (t, 3, $J = 6.59$, CH_3). NMR spectra for $R = C_4$ and C_6 were similar.

$R = C_6H_{13}$. The crude product was purified by flash chromatography on silica gel using a 5% hexane in $CHCl_3$ solution to give the product as a pale yellow liquid in 79.7% yield. GC (100–200° gradient) $t_R = 7.46$ min. (100%).

7.13. *4-Ethynylbenzenamine* ***4*** *(*$R = R' = H$*)*

To a refluxing solution of the hydroxy compound **21** (R = H, 9.8 g, 36 mmol) in *i*-PrOH (100 ml) was quickly added KOH (5.6 g, 101 mmol). This mixture was heated under reflux for 3 h, cooled to r.t. and the solvent removed *in vacuo*. The remaining material was stirred in cold hexane (20 ml) to remove traces of *i*-PrOH, the solvent decanted, CH_2Cl_2 added to the remaining solid and the resulting solution filtered through silica gel.

Removal of the solvents from the filtrate *in vacuo* gave 2.53 g (96.9%) of the aniline **4** ($R = R' = H$) as a yellow solid, m.p. 99.5–101.4°. IR (Nujol) 3487, 3401 (wk, NH_2) 3263 (wk, C≡CH), 2104 (wk, C≡C) and 1630 (str, Ar); ^{1}H NMR 7.30 (d, 2, $J = 8.63$, ArH *ortho* to C≡C), 6.60 (d, 2, $J = 8.14$, ArH *ortho* to N), 2.96 (s, 1, C≡CH), and 2.41 (br s, 2, NH_2).

$R = n$-*Bu* was prepared in the same manner, as a yellow liquid in 79.7% yield. TLC (CH_2Cl_2) $R_f = 0.5$; IR (film) 3418 (wk, NH), 3218 (med, C≡CH), 2110 (med, C≡C) and 1624 (str, Ar); ^{1}H NMR 7.29 (d, 2, $J = 8.75$ *ortho* to C≡C), 6.48 (d, 2, $J = 8.75$, ArH *ortho* to N), 3.78 (br s, 1, NH), 3.09 (t, 2, $J = 6.96$, NCH_2), 2.94 (s, 1, C≡CH), 1.65–1.50 (quint, 2, $J = 6.39$, N β-CH_2), 1.50–1.20 (m, 2, N γ-CH_2) and 0.94 (t, 3, $J = 7.24$, CH_3).

The $R = C_5$ and C_6 homologues were prepared in the same manner except that the remaining material after removal of the solvent from the reaction mixture was dissolved in EtOAC. This solution was washed with H_2O, dried, filtered and the solvent removed from the filtrate *in vacuo*. The remaining material was purified by flash chromatography on silica gel using 1:1 hexane/CH_2Cl_2 to give the colourless liquids of $R = C_5$ (67.6%) and C_6 (82.7%). ^{1}H NMR spectra were similar to that given for $R = C_4$.

7.14 *2,2,2-Trifluoro-N,N-dimethyl-N-[4(3-hydroxy-3-methyl-1-butynl)phenyl]acetamide* ***20***

This compound was prepared using the same procedure as described for the synthesis of the amide **21**. Purification of the crude product by chromatography on silica gel using CH_2Cl_2 gave 38.5% of the amide **20**. IR (film) 3373 (med br, OH), 2215 (wk, C≡C) and 1610 (str, Ar); ^{1}H NMR 7.29 (d, 2, $J = 9.56$, ArH *ortho* to C≡C), 6.61 (d, 2, $J = 9.00$, ArH *ortho* to N), 2.96 (s, 6, 2 N−Me), and 1.61 (s, 6, 2, CH_3); ^{13}C NMR 149.8, 132.5, 111.7, 109.6, 91.6, 82.7, 65.4, 40.0.

7.15. *4-Ethynyl-N,N-dimethylbenzenamine* ***4*** *(R = R′ = Me)*

Powdered NaOH (0.76 g, 18.9 mmol) was added to a stirred solution of the alkynol **20** (1.8 g, 9.0 mmol) in toluene (250 ml). This reaction mixture was heated under reflux for 17 h, cooled to r.t. and filtered. The solvent was removed from the filtrate *in vacuo* and the remaining material chromatographed on silica gel using 50% CH_2Cl_2/hexane to give the aminoalkyne **4** ($R = R' =$ Me, 500 mg, 38.2%). TLC (1:1 CH_2Cl_2/hexane, $R_f = 0.50$; IR (film) 3248 (str C≡CH), 2111 (med, C≡C) and 1624 (med, Ar); ^{1}H NMR 7.29 (d, $J = 9.00$, 2, ArH *ortho* to C≡C), 6.62 (d, $J = 9.03$, 2, ArH *ortho* to N) and 2.98 (s, 7, C≡CH and 2 N−CH_3); ^{13}C NMR 149.95, 132.8, 111.3, 108.3, 84.7, 74.8, and 39.6.

7.16. *Diacetylenes* ***2*** *($X = C_5H_{11}$, $R = R' = H$)*

To a stirred solution of the acetylene **4** ($R = R' = H$, 2.53 g, 21.6 mmol), $CuCl_2$ (40 mg), NH_2OH HCl (1.50 g = 21.6 mmol) and $BuNH_2$ (40 ml) in MeOH (100 ml) under N_2 at 0°, was added dropwise a solution of the bromoacetylene **3** ($X = C_5H_{11}$, 15.15 g, 20.5 mmol) in MeOH (50 ml). The mixture was stirred at 0° for 6 h, at r.t. for 17 h and then cooled to 0°. The resulting precipitate was removed by filtration, washed with cold MeOH and then recrystallized from MeOH to give 3.79 g (61.0%) of the purified diacetylene **2** ($X = C_5H_{11}$, $R = R' = H$). IR (Nujol) 3430, 3400, 3335 (med, NH_2), 2222, 2137 (wk, C≡C) and 1631, 1605 (str, Ar); ^{1}H NMR 7.42 (d, $J = 8.47$, 2, ArH *meta* to C_5), 7.33 (d, 2, $J = 8.55$, ArH *meta* to NH_2), 7.13 (d, 2, $J = 8.14$, ArH *ortho* to C_5), 6.59 (d, 2, $J = 8.50$, ArH *ortho* to NH_2), 3.89 (br s, 2, NH_2), 2.60 (t, 2, $J = 7.65$, $ArCH_2$), 1.58 (quint, 2, $J = 7.48$, β-CH_2), 1.35–1.25 (m, 4, 2 CH_2) and 0.89 (t, 3, $J = 6.60$, CH_3), and ^{13}C NMR 144.2, 134.0, 132.3, 132.2, 128.5, 119.2, 114.6, 110.8, 82.4, 81.1, 73.8, 72.2, 35.9, 31.4, 30.8, 22.5, and 14.0.

The following analogues were prepared in the same manner.

$X = C_3H_7$, $R = R' = H$. This was purified by chromatography on silica gel using 1:1 CH_2Cl_2 in hexane (R_f in $CH_2Cl_2 = 0.42$) and then recrystallized from MeOH, yield 50.2%.

$X = NO_2$, $R = R' = H$. This was purified by chromatography on silica gel using 1:1 CH_2Cl_2/hexane ($R_f = 0.40$), yield 38.7%, and then recrystallized from MeOH. IR (Nujol) 3487, 3381 (med, NH_2), 2196 (str, C≡C), 1643 (med, Ar) and 1597, 1347 (str, NO_2); ^{1}H NMR 8.23 (d, 2, $J = 8.96$, ArH *ortho* to NO_2), 7.80 (d, 2, $J = 8.88$, ArH *meta* to NO_2), 7.28 (d, 2, $J = 8.52$, ArH *meta* to NH_2), 6.54 (d, 2, $J = 8.54$, ArH *ortho* to NH_2) and 5.93 (br s, 2, NH_2).

$X = C_5H_{11}$, $R = R' = Me$. Crude yield = 76.3%; purified by recrystallization from MeOH, yield = 45.3%. IR (Nujol) 2190, 2130 (wk, C≡C) and 1603 (str, Ar); ^{1}H NMR 7.41 (d, 2, $J = 8.30$, ArH *meta* to C_5), 7.39 (d, 2, $J = 8.95$, ArH *meta* to N), 7.13 (d, 2, $J = 8.38$, ArH *ortho* to C_5), 6.60 (d, 2, $J = 9.12$, ArH *ortho* to N), 2.98 (s, 6, $N(CH_3)_2$), 2.59 (t, 2, $J = 7.66$, $ArCH_2$), 1.70–1.50 (m, 2, β-CH_2), 1.40–1.20 (m, 4, 2 CH_2) and 0.89 (t, 3, $J = 6.63$, CH_3); ^{13}C NMR 150.5, 144.1, 133.8, 132.4, 132.2, 128.5, 119.4, 111.6, 108.0, 83.1, 81.1, 74.0, ~72.0, 40.7, 35.9, 31.4, 30.9, 29.7, 22.5, and 14.0.

$X = C_5H_{11}$, $R = H$, $R' = C_4H_9$. Crude yield = 71.1%; purified by recrystallization from MeOH, yield = 50.0%. IR (Nujol) 3443 (wk, NH), 2208, 2138 (wk, C≡C), and 1620 (str, Ar); ^{1}H NMR 7.42 (d, 2, $J = 8.01$, ArH *meta* to C_5), 7.34 (d, 2, $J = 8.89$, ArH *meta* to N), 7.13 (d, 2, $J = 8.14$, ArH *ortho* to C_5), 6.50 (d, 2, $J = 8.55$, ArH *ortho* to N), 3.90 (br s, 1, NH), 3.12 (t, 2, $J = 7.65$,

NCH_2), 2.60 (t, 2, $J = 7.65$, $ArCH_2$), 1.68–1.20 (m, 10, 5 CH_2), 0.96 (t, 3, $J = 6.74$, amino CH_3) and 0.89 (t, 3, $J = 6.56$, alkyl CH_3).

X = F, R = H, R′ = C_4H_9. Purification was by chromatography on silica gel using 1:1 hexane/MeOH, yield = 53.9%. ^{1}H NMR 7.49 (dd, 2, $J = 8.96$, 5.33, ArH *meta* to F), 7.35 (d, 2, $J = 8.79$, ArH *meta* to N), 7.02 (t, 2, $J = 8.75$, ArH *ortho* to F), 6.51 (d, 2, $J = 8.83$, ArH *ortho* to N), 3.91 (br s, 1, NH), 3.14 (q, 2, $J = 6.92$, NCH_2), 1.66–1.10 (m, 4, 2 CH_2) and 0.96 (t, 2, $J = 7.18$, CH_3).

X = NO_2, R = H, R′ = C_5H_{11}. The solvent was removed from the cooled reaction mixture *in vacuo*. The residue was dissolved in a 1:1 mixture (200 ml) of Et_2O/THF. This solution was washed with H_2O (2 × 100 ml), dried, filtered, and the solvent removed from the filtrate to give 86.7% of the crude product. Purification was by flash chromatography on silica gel using 5% EtOAC in hexane; the product was rechromatographed using 25% CH_2Cl_2 in hexane and then recrystallized from CH_2Cl_2/hexane to give 46.7% of the purified diacetylene. Characterization data were nearly identical to those for $R' = C_6H_{13}$.

X = NO_2, R = H, R′ = C_6H_{13}. This was prepared in the same manner as for $R' = C_5H_{11}$. Purification was by flash chromatography (2×) on silical gel using 25% CH_2Cl_2/hexane followed by recrystallization from CH_2Cl_2/hexane, yield = 43.8%. TLC ($CHCl_3$) $R_f = 0.70$; IR (Nujol) 3411 (wk, NH), 2196 (str, C≡C) and 1607 (str doublet, Ar); ^{1}H NMR 8.18 (d, 2, $J = 8.87$, ArH *ortho* to NO_2), 7.62 (d, 2, $J = 8.50$, ArH *meta* to NO_2), 7.36 (d, 2, $J = 8.50$, ArH *meta* to N), 6.51 (d, 2, $J = 8.54$, ArH *ortho* to N), 4.00 (s, 1, NH), 3.13 (t, 2, $J = 2.96$, NCH_2), 1.62 (quint, 2, $J = 6.72$, β-CH_2), 1.43–1.34 (m, 6, 3 CH_2) and 0.90 (t, 3, $J = 6.41$, CH_3); ^{13}C NMR 149.6, 147.0, 134.3, 129.5, 123.6, 112.1, 107.7, 86.8, 80.2, 78.6, 71.5, 43.4, 31.5, 29.2, 26.7, 22.6 and 14.0.

7.17. *N,N-Dibutyl-4-[4-(4-pentylpheny l)-1,3-butadiynylbenzamine* **5** *(X = C_5H_{11})*

A slurry of the aminodiacetylene **2** (*R = R′* = H, 0.96 g, 3.34 mmol) and $NaBH_4$ (0.89 g, 23.4 mmol) in anhyd. THF (25 ml) was added dropwise to a vigorously stirred mixture of 3M H_2SO_4 (1.5 ml) and PrCHO (1.69 g, 23.4 mmol in 20 ml anhyd. THF at − 20°). The reaction was stirred at − 20° for 30 min; 3–4 pellets of NaOH were added and the mixture warmed to r.t. Insoluble materials were allowed to settle and the liquid was decanted and retained. The remaining material was extracted with Et_2O (2 × 50 ml) and the Et_2O layer combined with the decanted liquid. The combined Et_2O solution was washed with brine (30 ml), dried, filtered and the solvent removed from the filtrate *in vacuo*. The remaining material was purified by chromatography using CH_2Cl_2 followed by recrystallization from MeOH to give the diacetylene **5** (*X* = C_5H_{11}) in a 73.14% yield (0.98 g). TLC (CH_2Cl_2) $R_f = 0.65$; IR (Nujol) 2203, 2130 (wk, C≡C) and 1603 (str, Ar); ^{1}H NMR 7.42 (d, 2, $J = 8.06$, ArH *meta* to C_5), 7.36 (d, 2, $J = 8.79$, ArH *meta* to N), 7.13 (d, 2, $J = 7.77$, ArH *ortho* to C_5), 6.54 (d, 2, $J = 8.79$, ArH *ortho* to N), 3.28 (t, 4, $J = 7.51$, 2 NCH_2), 2.60 (t, 2, $J = 7.69$, $ArCH_2$), 1.70–1.20 (m, 14, 7 CH_2), 0.96 (t, 6, $J = 7.14$, amino CH_3), 0.89 (t, 3, $J = 6.78$, CH_3); ^{13}C NMR 148.4, 144.0, 133.9, 132.2, 119.5, 111.1, 106.7, 83.4, 81.0, 74.2, 71.9, 50.7, 36.9, 31.4, 30.9, 29.3, 22.5, 20.3 and 14.0.

The following analogues were prepared in the same manner:

Compound **2** (*X = NO_2, R = R′ = Bu*). Purified yield = 47.7%. TLC (hexane) $R_f = 0.65$; IR (Nujol) 2203 (str, C≡C) and 1604 (str, Ar); ^{1}H NMR 8.19 (d, 2, $J = 8.96$, ArH *ortho* to NO_2), 7.62 (d, 2, $J = 8.95$, ArH *meta* to NO_2), 7.38 (d, 2, $J = 8.99$, ArH *meta* to N), 6.55 (d, 2, $J = 9.07$, ArH *ortho* to N), 3.29 (t, 4, 2 NCH_2), 1.65–1.49 (quint, 4, $J = 7.37$, 2 β-CH_2), 1.49–1.28 (sext, 4, $J = 6.82$, 2 γ-CH_2) and 0.96 (t, 6, $J = 7.14$, 2 CH_3).

Compound **5** (*X = C_3H_7R'' = Me*). Purified yield = 27.1%, recrystallized from MeOH. ^{1}N NMR 7.43 (d, 2, $J = 8.22$, ArH *meta* to C_3), 7.39 (d, 2, $J = 8.99$, ArH *meta* to N), 7.13 (d, 2, $J = 8.14$, ArH *ortho* to C_3), 6.61 (d, 2, $J = 9.08$, ArH *ortho* to N), 3.00 (s, 6, 2 NMe), 2.58 (t, 2, $J = 7.55$, $ArCH_2$), 1.61 (sext, 2, $J = 7.44$, β-CH_2) and 0.91 (t, 3, $J = 7.31$, CH_3).

7.18. *N-Butyl-N-methyl-4-[4-(4-pentylpheny l)-1,3-butadiynyl]benzenamine* **6** *(R″ = Me)*

To a solution of the diacetylene **2** (*X* = C_5H_{11}, *R* = Bu, *R′* = H, 1.20 g, 3.50 mmol) in dry DMF (10 ml) was added NaH (160 mg, 3.84 mmol). After stirring this mixture for 2 h, MeI (0.75 g, 5.24 mmol) was added. The reaction mixture was warmed to 40°, stirred for 40 h, cooled to r.t., diluted with Et_2O, washed with H_2O, dried, filtered, and the solvent removed from the filtrate *in vacuo*. Chromatography of this material on silica gel using 10% CH_2Cl_2/hexane gave 520 mg (41.6%) of the product. Further purification was achieved by recrystallization from MeOH to give the diacetylene **6** (*R″* = Me). TLC (10% CH_2Cl_2/hexane) $R_f = 0.20$; IR (Nujol) 2216, 2144 (med, C≡C) and 1617 (str, Ar); ^{1}H NMR 7.44 (d, 2, $J = 8.06$, ArH *meta* to C_5), 7.40 (d, 2, $J = 7.69$, ArH *meta* to N), 7.15 (d, 2, $J = 8.01$, ArH *ortho* to C_5), 6.60 (d, 2, $J = 9.00$, ArH *ortho* to N), 3.36 (t, 3, $J = 7.25$, NCH_2), 2.99 (s, 3, NCH_3), 2.62 (t, 2, $J = 7.55$, $ArCH_2$), 1.62–1.55 (m, 6, 3 CH_2), 1.55–1.29 (m, 4, 2 CH_2 in C_5), 0.97 (t, 3, $J = 7.00$, C_4CH_3) and 0.91 (t, 3, $J = 6.96$, C_5CH_3).

Compound **2** (*X = F, R = Bu, R″ = Me*) was prepared in the same manner. Purification was by chromatography on silica gel using hexane as the solvent followed

by recrystallization from MeOH, yield = 12.7%. ^{1}H NMR 7.50 (dd, 2, J = 8.97, 5.35, ArH *meta* to F), 7.39 (d, 2, J = 9.08, ArH *meta* to N), 7.03 (t, 2, J = 8.79, ArH *ortho* to F), 6.59 (d, 2, J = 9.08, ArH *ortho* to N), 3.35 (t, 2, J = 7.37, NCH_2), 2.98 (s, 3, N CH_3), 1.65–1.50 (m, 2, β-CH_2), 1.45–1.25 (m, 2, γ-CH_2) and 0.96 (t, 3, J = 7.14, CH_3).

7.19. *N-Butyl-N-ethyl-4-[4-(4-pentylphenyl)-1,3-butadiynyl]benzenamine* **6** *($R'' = C_5H_5$)*

A mixture of the aminodiacetylene **2** ($X = C_5H_{11}$, R = H, 900 mg, 2.62 mmol) and $NaHCO_3$ (1.10 g, 13.1 mmol) in EtI (30 ml) was heated under reflux for 120 h. The cooled reaction mixture was dissolved in Et_2O (*c.* 50 ml), washed with H_2O, dried, filtered and the solvent removed from the filtrate to give the crude product. Purification of this material by chromatography on silica gel using 20% CH_2Cl_2/hexane gave 560 mg (57.7%) of the product. It was further purified by recrystallization from MeOH to give the dialkylaminodiacetylene **6** ($R' = C_2H_5$). TLC (1:1 MeOH/hexane) R_f = 0.22; IR (Nujol) 2210, 2144 (wk, C≡C), and 1611 (str, Ar); ^{1}H NMR 7.41 (d, 2, J = 8.10, ArH *meta* to C_5), 7.36 (d, 2, J = 8.79, ArH *meta* to N), 7.12 (d, 2, J = 7.94, ArH *ortho* to C_5), 6.55 (d, 2, J = 8.87, ArH *ortho* to N), 3.37 (q, 2, J = 7.04, NCH_2Me), 3.26 (t, 2, J = 7.59, NCH_2Pr), 2.59 (t, 2, $ArCH_2$), 1.70–1.45 (m, 4, 2 β-CH_2), 1.45–1.15 (m, 8, 4 CH_2), 1.15 (t, 3, J = 6.96, C_2CH_3), 0.95 (t, 3, J = 7.33, C_4CH_3) and 0.85 (t, 3, J = 6.96, C_5CH_3); ^{13}C NMR 148.8, 144.5, 134.5, 132.7, 129.0, 120.0, 111.6, 107.3, 83.8, 81.5, 74.7, 72.5, 50.6 and 45.4.

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