Novel conjugated Schiff-Base compounds

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University of Durham

A Thesis Entitled

Novel Conjugated Schiff-Base Compounds

Submitted by

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To Mek and Wae
for love, courage and trust...

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Memorandum

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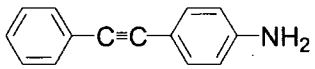
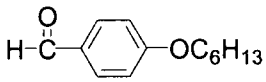
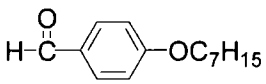
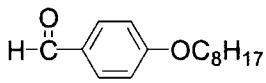
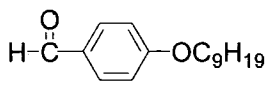
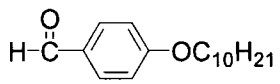
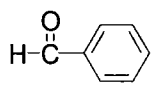
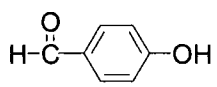
Statement of Copyright

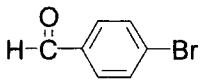
Abbreviations

λ	Wavelength
ε	Extinction coefficient
A	Acceptor
Cr	Crystalline phase
CTAB	Cetyltrimethylammonium bromide
D	Donor
DCM	Dichloromethane
DIPEA	Diisopropylethylamine
DME	Dimethoxyethane
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
Ed.	Edited
EI - MS	Electron Ionisation - Mass Spectrometry
Equiv	Equivalent
HOMO	Highest occupied molecular orbital
Hz	Hertz
I	Isotropic phase
IR	Infrared
LBTs	Langmuir-Blodgett Techniques
LCs	Liquid Crystals
LUMO	Lowest unoccupied molecular orbital

Max	Maximum
mM	milimolar
n	Vector quantity (director)
N	Nematic phase
nm	Nanometre
NMR	Nuclear Magnetic Resonance
OLEDs	Organic Light-Emitting Diodes
pKa	Acid dissociation constant
PPEs	Poly(aryleneethynylene)s
R	Alkyl
RT	Room temperature
SAMs	Self-Assembled Monolayers
SmA	Smectic A phase
SmB	Smectic B (hexatic B) phase
SmC	Smectic C phase
SN	Substitution nucleophilic bimolecular
TASF	Tris(dimethylamino)sulfonium trimethylsilyldifluoride
THF	Tetrahydrofuran
TMS	Trimethylsilyl
TMSA	Trimethylsilylacetylene
UV/Vis	Ultra Violet/Visible Light
X	Polar head groups
Y	Chain Length

Compound Numbering Scheme

Structure	No
 4-Phenylethynylaniline	1
 4-Hexyloxybenzaldehyde	2a
 4-Heptyloxybenzaldehyde	2b
 4-Octyloxybenzaldehyde	2c
 4-Nonyloxybenzaldehyde	2d
 4-Decyloxybenzaldehyde	2e
 Benzaldehyde	3a
 4-Hydroxybenzaldehyde	3b



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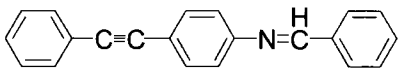

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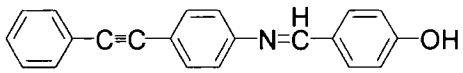

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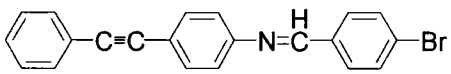

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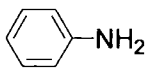

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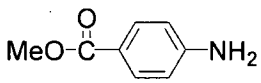

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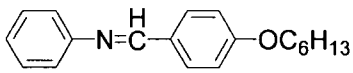

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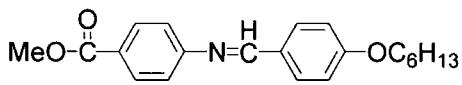

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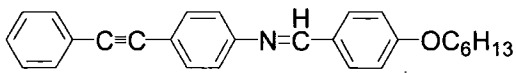

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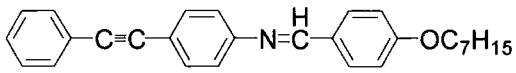

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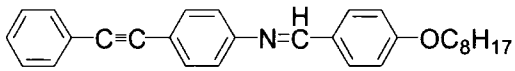

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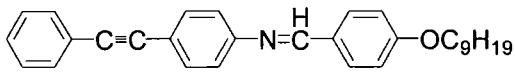

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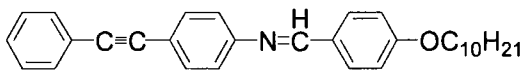

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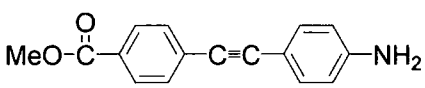

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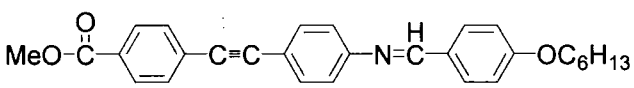

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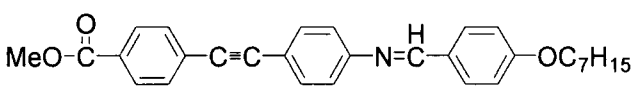

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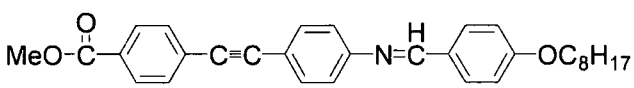

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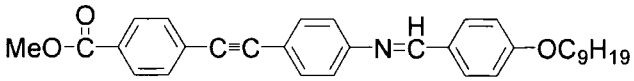

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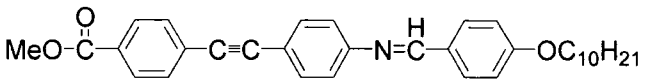

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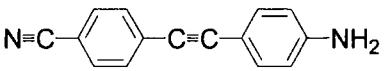

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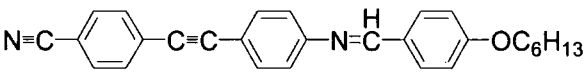

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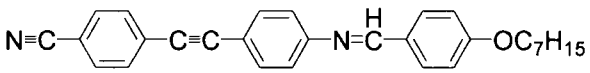

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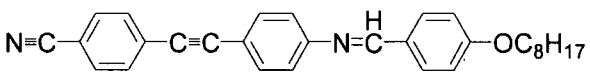

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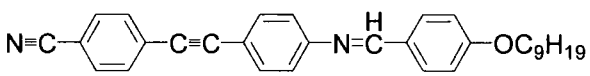

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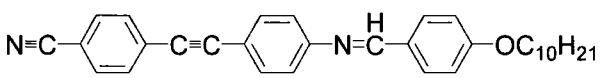

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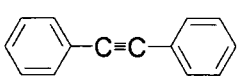


12

Diphenylacetylene

Abstract

To date conjugated ethynylated aromatic Schiff-Base systems are largely unexplored although the combination of two such well-known π-systems promises a wide range of electronic properties ranging from efficient electronic transmission to luminescent behaviour. The rigid linear nature of each group has led to the development of systems which exhibit liquid crystalline (LC) properties, and the combination of these motifs should be expected to lead to new materials with LC phases. This thesis describes the synthesis, molecular and electronic structure, as well as liquid crystalline behaviour, of a novel family of compounds featuring both acetylenic and imine (or Schiff-Base) functionalities.

Three series of ethynylated aromatic Schiff-Base systems were synthesised with a different polar head group (acceptor, A) namely; H, $MeCO_2$ and C≡N and various chain length alkoxy (donor, D) tails, to give rise to compounds which feature an unique D-C_6H_4-CH=N-C_6H_4-C≡C-C_6H_4-A substructure. Preliminary photophysical characteristics suggest that while the imine portion of the molecule dominates the electronic transitions the arylacetylene moiety must be involved to some extent.These new, conjugated ethynyl / Schiff-Base hybrid systems exhibit liquid crystalline properties at elevated temperatures. While all of the compounds examined have nematic phase, the compounds which feature longer alkyl tails or polar head groups also give rise to a Smectic A and/or Smectic B (hexatic B) phases.

Table of Contents

Chapter 3. Introduction to Liquid Crystalline Materials

Chapter 4. General Experimental Procedure

Accompanying Compact Disc

Associated .bmp files for the liquid crystalline textures of the selected synthesised compounds.

Chapter 1. Introduction

1.1 Introduction to Molecular Electronics

Molecular electronics is usually defined in one of two ways, either as the use of single molecular components to perform signal and information processing, or the use of the electronic properties of molecular materials to perform a bulk function. These two contrasting methods of applications are described as *molecular scale electronics* and *molecular materials for electronics*, respectively. [1-3]

Currently, the most well-known examples of molecular electronics technology are the molecular species incorporated in products featuring liquid crystal displays.[4] However, studies are ongoing right now to utilise molecules either singly or as aggregates of nanometre dimensions to provide the elementary active units of electronic systems with extremely high component density. It is this idea of building electronic circuits from molecular building blocks, either alone (unimolecular electronics) or in concert with solid state interfaces which promises to become a reality in future electronic systems. [5-10]

Molecular electronics is therefore a broad and interdisciplinary topic, and as such materials which are available for study within this area range from synthetic low molecular weight molecules to macromolecules, and their natural counterparts, and involve aspects of chemistry, biology and physics. Studies in molecular electronics usually begin with material synthesis, characterisation and manipulation, which then lead to the fabrication of devices and the

evaluation of their performance. Computational models can provide new concepts for devices and systems which employ the unique properties of molecular materials to the best effect. [11-13]

1.2 Molecular Materials for Electronics: The Challenge

The technological utilization of molecular materials depends on successfully engineering an overall set of properties that are either unique or superior to those of other materials. These properties include not only those essential for a particular device or application but also those required for the manufacturing process. In most instances a compromise between the demands of performance and processing is inevitable. Outstanding properties, for the examples, non-linear optical coefficients or electrical conductivity, are little use if the material is not stable under conditions appropriate for both processing and use.[14]

For example some materials are extremely sensitive to moisture and air, and this can make processing difficult and costly. Normal operation of electronics devices involves exposure to temperature of 60-100 °C over extended periods, while processing often results in brief excursions to temperatures in excess of 200 °C. If the material is intrinsically unstable under any of these conditions it is obviously of little use.[1]

The chemical and thermal stability of materials based on molecular compounds can also be adversely affected by reactive impurities. The preparation of highly

pure material is therefore of critical importance. Achieving high levels of purity is not easy, and a detailed knowledge of sample composition and structure provides the basis for distinguishing between artefacts that adversely affect properties and those whose presence is irrelevant. [15]

The need to produce high quality materials with tightly specified properties is one of the factors which accounts for the time required for the progression from the discovery of an interesting property to the marketing of a product based on it. For example, the existence of liquid crystalline (LC) phases was known since early last century, and the potential of LC materials for applications in displays were realized when the first patents for this application were filed in the 1930s. However, the first materials with the properties required to realize displays functioning at room temperature were not produced until 1960s and commercial displays not marketed until the 1970s.[1, 16]

The production of new molecular materials for application in the various areas summarised by the term "molecular electronics" is therefore a challenging process. In this thesis, the identification and synthesis of a new family of conjugated molecular building blocks is described, together with a preliminary study of the electronic and physical properties which characterise these materials.

1.3 Conjugated Rigid-Rod Molecular Systems

Many rigid rod conjugated systems such as 1,4-bis(phenylethynyl)benzene, 9,10-bis(phenylethynyl)anthracenes, 2,5-bis(phenylethynyl)thiophenes, and 2,5-bis(phenylethynyl) metallacyclopentadienes based on acetylenic substructures display interesting structural, electronic, nonlinear optical, and luminescent properties.[17 - 21] The conjugated π-system offered by these ethynyl-aromatic structures has led to the development of molecular wire architectures and these fascinating properties may be directly attributed to the extended, linear π-conjugation that runs along the principal molecular axis (**Figure 1.1**).[2, 22 - 24]

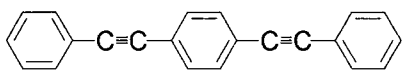
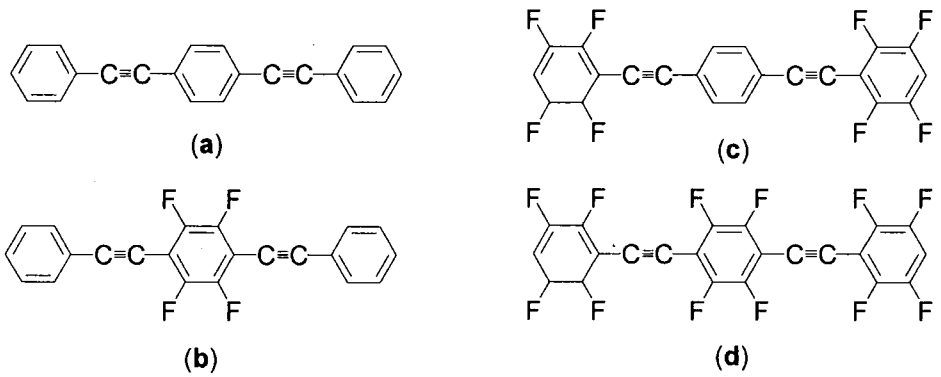


Figure 1.1: 1,4-bis(phenylethynyl)benzene

The relative conformation of the aryl rings within a single molecule is thought to influence the conductivity through that molecule, with the all co-planar form presumably being more conducting than the twisted motifs. Interestingly, the ability to switch conformations of these systems from a random set of intramolecular rotomers to a more conductive co-planar conformation would offer an attractive route by which to incorporate a molecular switch directly into wire. However Kim and Swanger [25] as well as Reinerth and co-workers[26] found that the barrier to rotation about the alkyne-aryl single bond is very low, and engineering control over

the molecular conformation in materials derived from the elementary work of 1,4-bis(phenylethynyl)benzene is a difficult challenge.

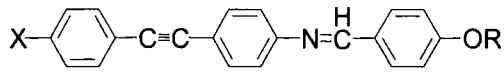
These compounds also exhibit the liquid-crystalline behaviour and interestingly many of the models used to rationalize the phase behaviour assume cylindrical symmetry along the ethynyl axis. In addition, Marder and co-workers[27] demonstrated the liquid crystalline (LC) behaviour of a series of 1,4-bis(phenylethynyl)benzene derivatives containing 0, 4, 10, and 14 fluorine atoms. These compounds were prepared via Pd/Cu catalysed cross-coupling reactions of appropriate terminal alkynes and iodoarenes (see the section *Synthesis of Alkynes: Cross coupling* below) as shown in **Figure 1.2**.



(**a**) 1,4-bis(phenylethynyl)benzene
(**b**) 1,4-bis(phenylethynyl)tetrafluorobenzene
(**c**) 1,4-bis (pentafluorophenylethynyl)benzene
(**d**) 1,4- bis(pentafluorophenylethynyl) tetrafluorobenzene

Figure 1.2: A series of 1,4-bis(phenylethynyl)benzene derivatives shown to have liquid crystalline phases. [27]

Given the intense interest in conjugated molecular systems based upon the 1,4-bis(phenylethynyl)benzene motif, we were interested in developing similar chemistry based upon the structure shown in **Figure 1.3**.



X = H, $MeCO_2$, CN
R = C_nH_{2n+1}; n = 6 (a), 7 (b), 8 (c), 9 (d), 10 (e)

Figure 1.3: Proposed ethynylated Schiff-Base aromatic systems.

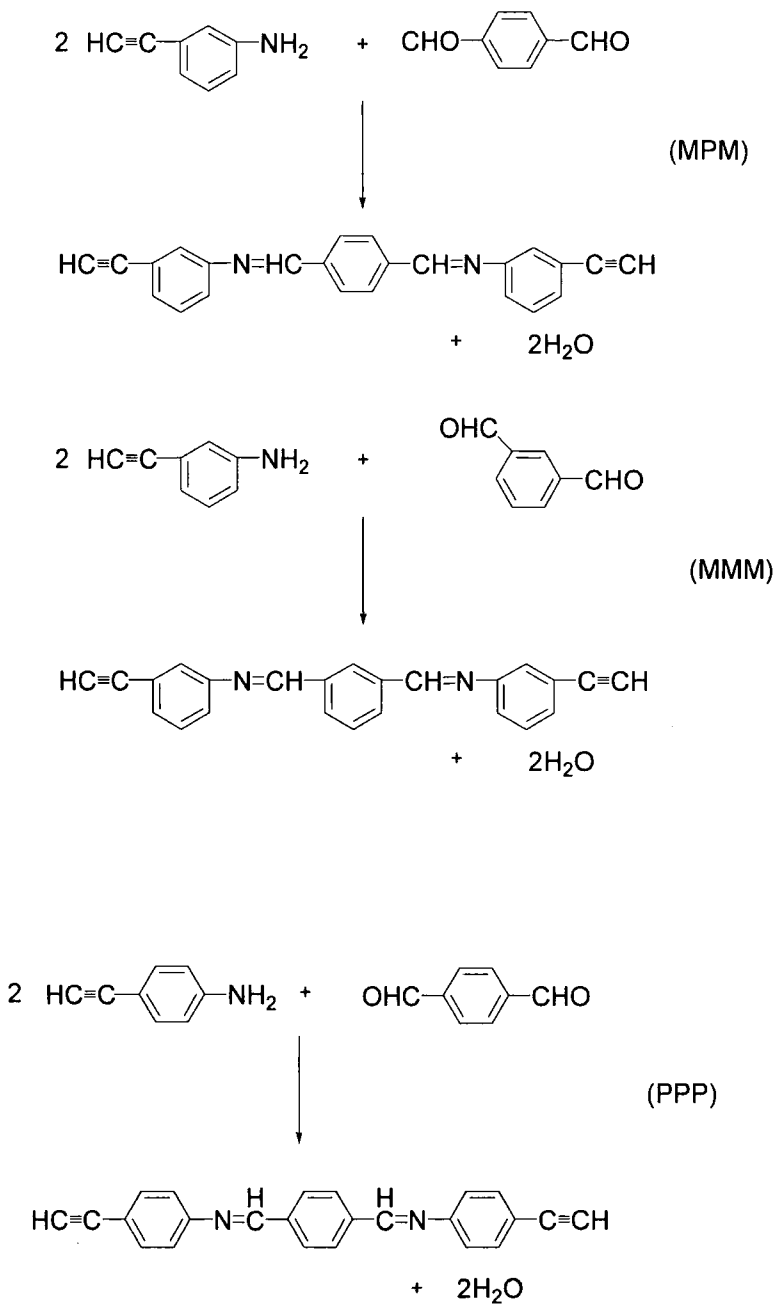
These systems could be readily assembled from amino-substitued tolanes, and an appropriate benzaldehyde (for more details on the general synthesis of imines, see **Section 1.4** and **Chapter 2** for more details of the synthesis of specific imines applied in this study.

Quite unexpectedly, conjugated Schiff-Base / acetylene hybrid compounds are virtually unknown, and despite the fact that each motif is known to offer useful properties such as a delocalised ground state electronic structure, rigid linear structure and relatively high thermal stabilities, these systems are unexplored for molecular materials applications. [28]

Of the work which has been carried out, most interest seems to have been generated by polymeric materials formed from oligo(imines) by the thermal cross-linking of terminal acetylene end-capping groups.[29 – 31] For example, condensation

of 1,3- or 1,4-phthaldehyde with 3- or 4-aminophenylacetylene gave the *meta-meta-meta* (MMM), *meta-para-meta* (MPM) or *para-para-para* (PPP) monomers as shown in **Scheme 1.1** which were polymerised by thermal curing at temperatures ranging from 150 °C to in excess of 400 °C. Depending on the precise details of the polymerisation process, the conductivity of the resulting cross-linked polymers could be engineered to be as high as 3.3 Ω cm^{-1}. [29]

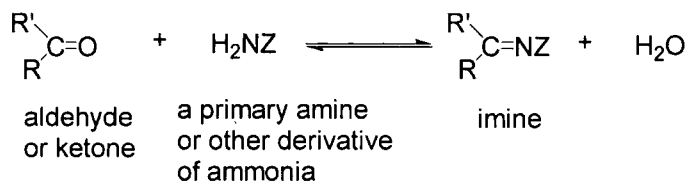
Before describing the results of this project in detail, it is useful to consider the synthetic chemistry which underpins the construction of molecular systems incorporating both imine and acetylenic functional groups. In the sections which follow, the chemistry of both these functional groups is summarised.



Scheme 1.1: The condensation of 1,3- or 1,4-phthaldehyde with 3- or 4-aminophenylacetylene gave the *meta-meta-meta* (MMM), *meta-para-meta* (MPM) or *para-para-para* (PPP) monomers. [29]

1.4 Introduction to the Chemistry of Imines

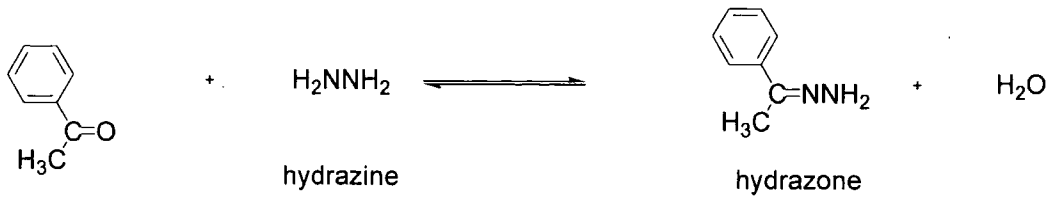
An imine is a compound with a carbon-nitrogen double bond. In general, aldehydes and ketones react with primary amines (R-NH_2) and with other ammonia derivatives (Z-NH_2) to form imines (**Scheme 1.2a and 1.2b**). The imine obtained from the reaction of a carbonyl compound and a primary amine (RNH_2) is called a Schiff-Base; the imine obtained from the reaction with hydroxylamine (NH_2OH) is called an oxime; the imine obtained from the reaction with hydrazine (NH_2NH_2) is called a hydrazone; and the imine obtained from the reaction with semicarbazide ($NH_2NHCONH_2$) is called a semicarbazone. Phenyl-substituted hydrazines react with aldehydes and ketones to form phenylhydrazones. All these reactions are shown in **Scheme 1.3**.[36, 37]



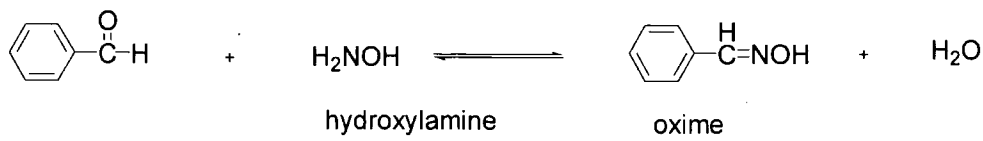
(**a**)

(**b**)

Scheme1.2: General reaction and example of imine formation.

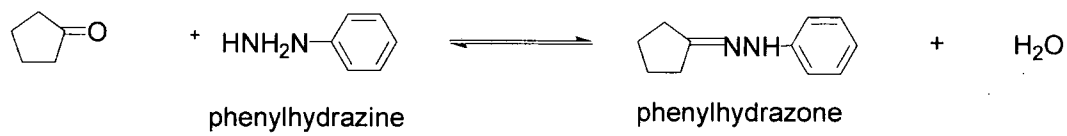


(**a**)



(**b**)

(**c**)



(**d**)

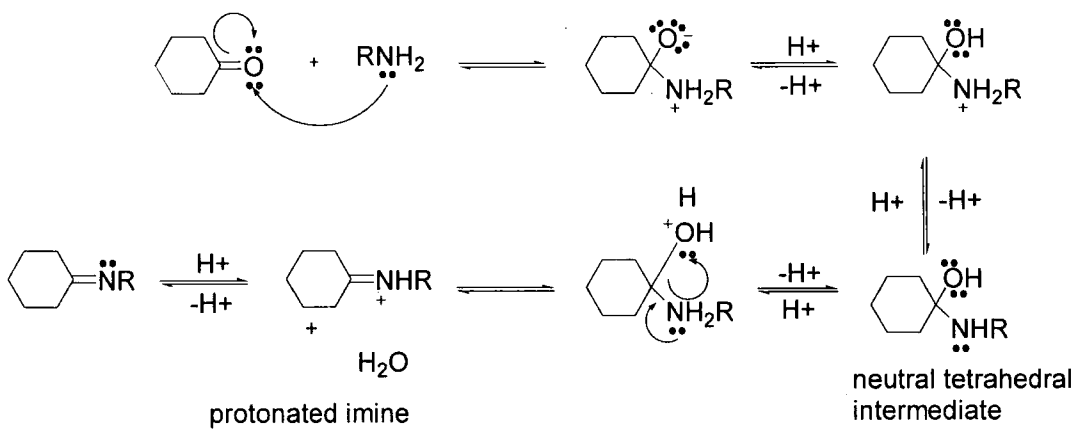
(**e**)

Scheme 1.3: Various examples of imine derivatives formed from the aldehydes or ketones.[36]

The molecular orbital description of the bonding in an imino group is similar to that of a carbonyl group. The imine nitrogen is sp^2 hybridized. One of its sp^2 orbital forms a σ bond with the imine carbon, one forms σ bond with substituent, and the third contains a pair of nonbonding electrons. The unhybridised p-orbitals of the nitrogen and carbon atoms overlap to form a π bond.

1.4.1 The Mechanism of Imine Formation

In the first step of the mechanism of imine formation, the nucleophilic amine attacks the carbonyl carbon. A proton transfer leads to the formation of a neutral intermediate tetrahedral at carbon which is in equilibrium with two protonated forms. Protonation can take place on either the nitrogen or the oxygen atom. Loss of water from the oxygen-protonated intermediate forms a protonated imine that loses a proton to yield the imine (**Scheme 1.4**).[36, 37]



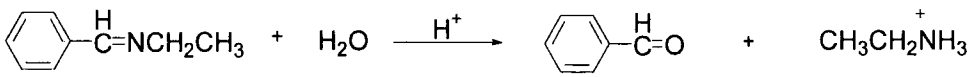
Scheme 1.4 : The mechanism of imine formation.

Because nitrogen is more basic than oxygen, the equilibrium favours the nitrogen-protonated tetrahedral intermediate. The equilibrium can be forced toward the imine by removing water as it is formed or by precipitation of the imine. The formation of all imines (Schiff-Bases, semicarbazones, oximes, hydrazones, and phenylhydrazones) follows the same general mechanism.

Overall, the addition of a nitrogen nucleophile to an aldehyde or a ketone is a nucleophilic addition-elimination reaction (that is, nucleophilic addition of an amine to form an unstable tetrahedral compound followed by elimination of water). On the other hand, when a carbon or hydrogen nucleophile adds to an aldehyde or a ketone, the reaction is a simple addition process and because there are no nonbonding electrons on the carbon or hydrogen in the tetrahedral compound, it is relatively stable. Thus, aldehydes and ketones undergo nucleophilic addition reactions with carbon and hydrogen nucleophiles, and undergo nucleophilic addition-elimination reactions with nitrogen nucleophiles. [38]

The pH at which imine formation is carried out must be carefully controlled. There must be moderate acid requirement to protonate the tetrahedral intermediate so that H_2O rather than the much more basic HO^- is the leaving group. However, if too much acid is present, it will protonate the reactant amine. Protonated amines are not nucleophiles, so they cannot react with carbonyl groups (**Scheme 1.4**).[37, 39]

In aqueous acidic solutions, imines are hydrolysed back to the carbonyl compound and amine, and imine hydrolysis plays an important role in the conversion of nitriles to ketones (**Scheme 1.5**).



Scheme 1.5: Imine hydrolysis in the conversion of nitriles to ketones.

Imine formation and hydrolysis are also important reactions in biological systems. In the protein enzyme catalysis process, imines are important to maintain the oxidation state of the carbonyl group and also to form a covalent bond to the substrate, so that the substrate cannot diffuse away in the middle of the reaction. [36, 40]

1.5 An Introduction to Alkyne chemistry

The alkyne moiety is characterised by the carbon-carbon triple bond. Each carbon is *sp* hybridised, so each has two *sp* orbitals and two *p* orbitals. One *sp* orbital overlaps with the σ orbital of the terminal substituent, and the other overlaps a *sp* orbital of the other carbon. Because the *sp* orbitals are oriented as far from each other as possible to minimize electron repulsion, alkynes are typically linear molecules with bond angles of close to 180 ° (**Figure 1.4**).

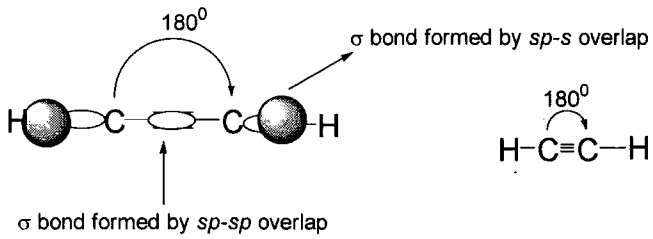
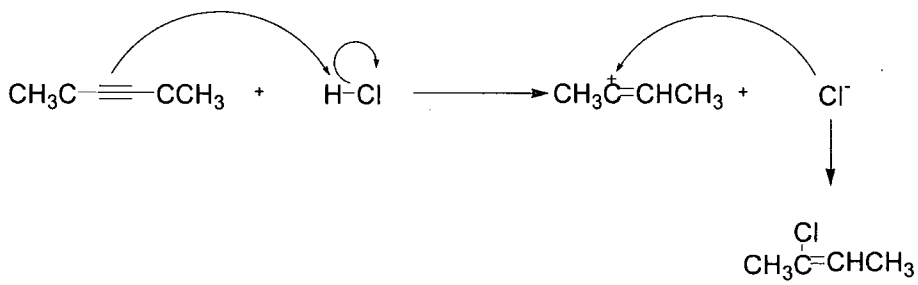


Figure 1.4: Alkyne is a linear molecule with bond angles of close to 180^0.

The two remaining *p* orbitals on each carbon are oriented at right angles to one another and to the *sp* orbitals. Each of the two *p* orbitals on one carbon overlaps with the parallel *p* orbital on the other carbon to form two π bonds.[36]

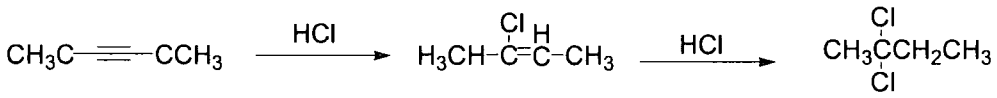
If we subtract the σ bond energy from the total bond energy of the triple bond (200 – 91 = 456 kJ/mol), we find that the average bond strength of each of the π bonds in the triple bond is less than 230 kJ/mol. (The value of 456 kJ/mol is that for σ bond formed by sp^2-sp^2 overlap. The σ bond formed by *sp*-*sp* overlap is expected to be somewhat stronger than that.) The π bonds, therefore, are much weaker than σ bond. The weak π bonds allow alkynes to react easily. Thermodynamically speaking, the carbon-carbon triple bond shows a marked tendency to open up and form addition compounds either with other reagents, or with itself, to give cyclic or polymeric products, even if the reaction rate may sometimes be slow, depending on the reaction mechanism available.

With a cloud of electrons completely surrounding the σ bond, an alkyne is an electron-rich molecule. In the other words, it is a nucleophile, so we expect it to react with electrophiles. Consequently, if a reagent such as HCl is added to an alkyne, a π bond will break because the π electrons are attracted to the electrophilic hydrogen. In the second step of the reaction, the positively charged carbocation intermediate reacts rapidly with the negatively charged chloride ion (**Scheme 1.6**).[38]



Scheme 1.6: The formation of 2-chloro-2-butene by an addition of HCl to 2-butyne.

Thus alkynes, like alkenes, undergo regioselective electrophilic addition reactions according to Markonikov's rule. There is however, an added complication in the reaction of alkynes. Because the product of the addition of an electrophilic reagent to an alkyne is an alkene, a second electrophilic addition reaction can occur (**Scheme 1.7**).

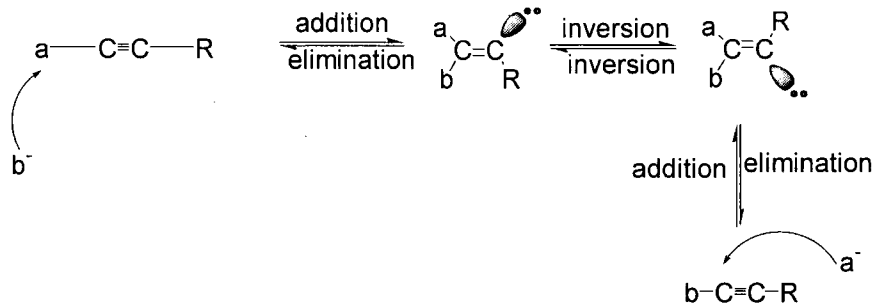


Scheme 1.7: The formation of 2-dichlorobutane by an addition of two equivalents of HCl to 2-butyne.

Since the carbon-carbon double bond is very readily attacked by electrophilic reagents and also only with nucleophilic reagents, it may come as a surprise that electrophilic attack (by halogens, peracids, ozone etc.) of the acetylenic bond occurs less readily and that nucleophilic attack (addition of water, alcohols, amines etc.) is relatively easy. [41]

To explain the increased susceptibility to nucleophilic attack, both steric and electronic factors may be invoked. Since three electrons pairs are bent back to form the triple bond, for simple steric reasons the nucleophile can approach the exposed carbon nucleus more closely, and the increased electronegativity of acetylenic carbon facilitates the process. Both the primarily attacked carbon atom and the adjacent carbon atom, which must carry the charge in the resulting vinyl anion, willingly take on a negative charge, since vinyl carbanions are more stable than alkyl carbanions, owing to the electronegative *sp* carbon. The charge is, of course, further stabilized when the carbon atom carries electron-withdrawing substituents, in particular electronegative resonance-stabilising groups.

Besides leading to olefins by addition, the mechanism is reversible and the reverse process is one of the steps in the formation of acetylenes by elimination from olefins. If the anion formed inmost cases by *trans*-addition undergoes *cis-trans* inversion before *trans*-elimination, the result is substitution (**Scheme 1.8**).



Scheme 1.8: The reversible mechanism of substitution formation of alkyne.

The geometry of the vinyl anion does not seem to be an important factor in explaining the greater ease of nucleophilic addition to the triple bonds, because the alkyl anion resulting from a nucleophilic attack on olefins would hardly be less stable, as far as angle strain is concerned, if judged from the analogous isoelectronic nitrogen derivatives (**Figure 1.5**):

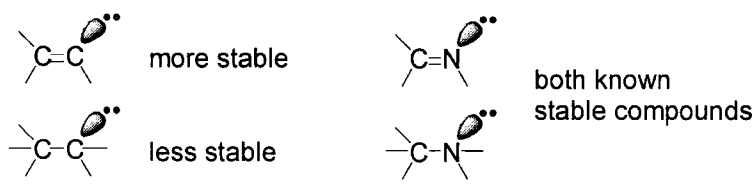


Figure 1.5: The analogous isoelectronic nitrogen derivatives of unsaturated carbon compounds.

The ease of nucleophilic attack on an acetylene also increases when the electronegative substituent is a second acetylenic group, RC≡CC≡CR'. Furthermore, conjugated polyynes even undergo reactions which are not possible with simple acetylenes. (**Figure 1.6**).

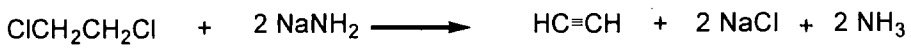
Figure 1.6: The resonance stabilised intermediate formed during reaction of buta-1,3-diynes with nucleophiles. Chemical reactivity indicates a dominant contribution from the eneyne form.

The mode of addition is always such that the nucleophile goes to the end of the polyynes system, placing the negative charge on the second carbon as to be stabilized by the rest of the acetylenic system and giving rise to 1,2-addition products. Thus cyanide, malonic ester, lithium alkyl, $LiAlH_4$ can be added to conjugated alkatetraynes and alkapentaynes, etc. Apparently mesomeric delocalization of the charge is unimportant in determining the course of these reactions.

The reason is possibly that, in valence-bond theoretical terms, the two resonance structures, of enynes and cumulene type, have widely different energies and geometries. Corresponding structures derived from polyenes are much more similar in both respects.

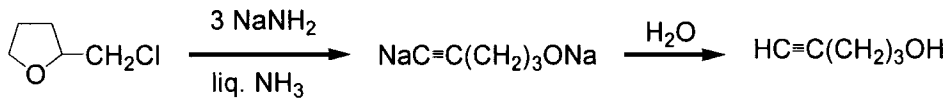
1.5.1 Synthesis of Alkynes: By Elimination

Numerous synthetic routes are known for the synthesis of acetylene-based systems. For an example, alkynes can be generated by elimination reactions, including dehydrohalogenation processes (**Scheme 1.9a**).[41]

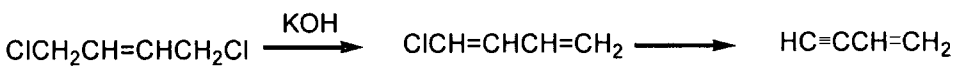


(a)

A related elimination is the formation of 4-pentyn-1-ol from tetrahydrofurfuryl chloride and sodamide (**Scheme 1.9b**). The readily available 1,4-dichloro-2-butene and 1,4-dichloro-2-butyne undergo 1,4-elimination upon heating with powdered and aqueous potassium hydroxide, respectively, giving vinylacetylene and butadiyne in excellent yields (**Scheme 1.9c**).



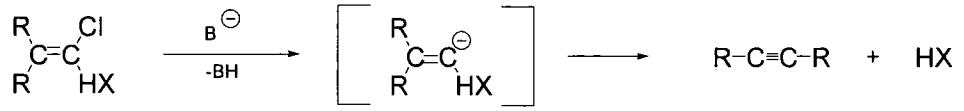
(b)



(c)

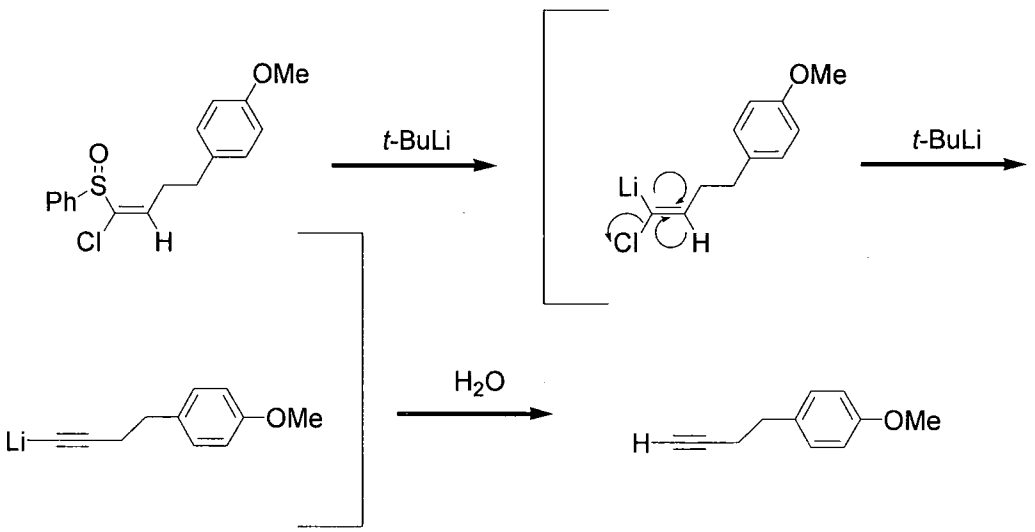
Scheme 1.9: The examples of alkyne elimination reactions via dehydrohalogenation process.[41]

The other well-known synthesis of alkynes by elimination is Fritsch-Buttenberg-Wiechell Rearrangement. Through this process olefins with hydrogen and halogen in vicinal positions as well as those bearing hydrogen and halogen at the same carbon atom can be converted into simple alkynes (**Scheme 1.11**).[38, 41]



Scheme 1.10: The mechanism of Fritsch-Buttenberg-Wiechell Rearrangement. [41]

Below is one of the examples of Fritsch-Buttenberg-Wiechell rearrangement:



Scheme 1.11: The examples of Fritsch-Buttenberg-Wiechell rearrangement. [41]

1.5.2 Synthesis of Alkynes: Cross-Coupling

In the past 60 years the synthetic chemistry involved in the preparation of acetylenes has been developed to a great extent and the most important preparative methods now consist of the metal catalysed couplings of acetylenes and their derivatives. Early processes developed by Glaser, and modified by people such as Eglington, Cadiot and Chodkiewicz, involved copper-catalysed coupling of terminal alkynes with halogenated olefins, alkynes and aryl systems.[41,42] In more recent times, palladium-based catalysts have been developed, and arguably these methods now form the basis for modern synthetic acetylene chemistry.[43]

1.5.3 Introduction to the Sonogashira reaction

The Sonogashira reaction, and palladium-catalysed cross-coupling reactions in general, are very useful synthetic tools for the production of acetylenic systems.[44] The Sonogashira protocol is a straightforward and powerful method for the construction of C(sp^2)-C(sp) bonds.[45-47] The reaction involves the palladium/copper catalysed cross-coupling of terminal alkynes with aryl halides, and has become one of the preferred methods for the preparation of ethynylarenes and their derivatives (**Scheme 1.12**).[48]

$$R^1C{\equiv}CH \quad + \quad XR^2 \xrightarrow[\text{base}]{\text{cat. } PdL_n,\ \text{cat. CuI}} R^1C{\equiv}CR^2$$

Scheme 1.12: The Sanogoshira Palladium-catalysed cross-coupling protocol.[43]

The Sonogoshira coupling reaction allows iterative assembly of extended molecules, although the step-wise assembly of large structures often employs alkynyl trialkylsilyl protecting groups and a rather tedious step-wise sequence consisting of:

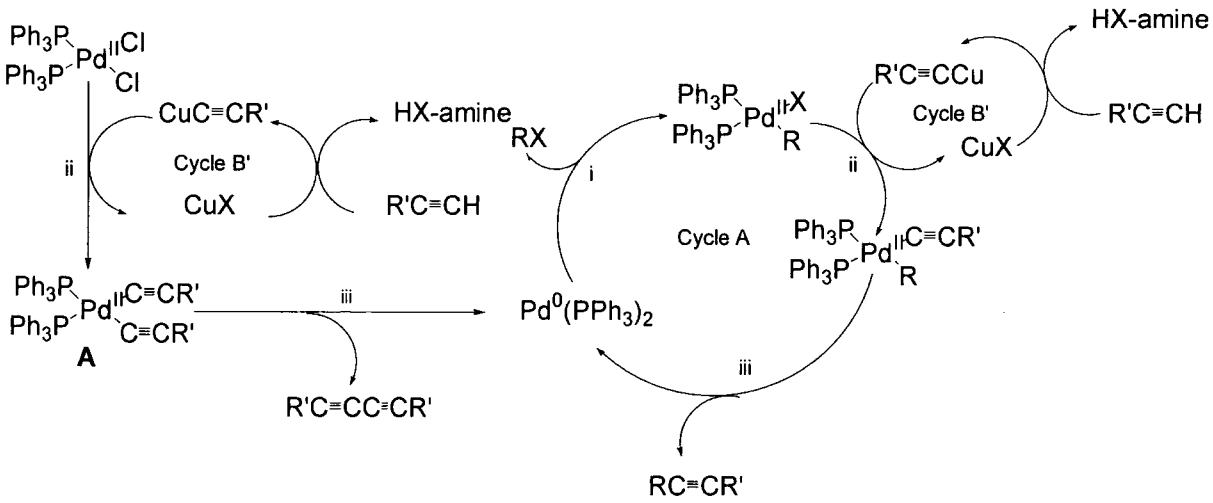
a) cross-coupling of the alkynyl silane,

b) protiodesilylation,

c) a second cross coupling step to afford the desired product.[49]

1.5.3.1 Mechanistic Considerations

There are three basic mechanistic steps involved in the Sonogashira process: oxidative addition, transmetallation, and reductive elimination (**Scheme 1.13**).



Scheme 1.13: Pd-catalysed cross-coupling reaction of terminal acetylene mechanism involving steps of i) oxidative addition, ii) transmetallation and iii) reductive elimination.[43]

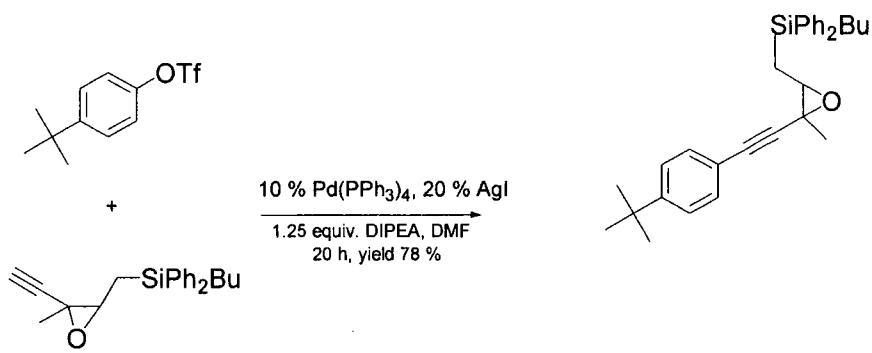
1.5.3.2 The Role of Palladium as a Catalyst

The Sonogoshira protocol is based on a combination of two catalytic cycles (A and B in **Scheme 1.13**).[43] Diethylamine or trimethylamine is commonly used both as a source of base and solvent. Copper (I) salts, usually CuI, provide a source of the copper catalyst.

Various complexes and salts may be used as the source of palladium, and common examples include palladium(0) complexes such as $[Pd_2(dba)_3]$ (dba=dibenzylideneacetone) and $[Pd(PPh_3)_4]$, and palladium(II) species such as $Pd(OAc)_2$, $Pd_2Cl_2(CNCH_3)_2$ and $PdCl_2(PPh_3)_2$. In each case these Pd(II) species are reduced in situ by reductive elimination of Pd-acetylide complex such as **A** which is in turn generated from the palladium(II) complex and the terminal acetylene, and substituted if necessary by appropriate donor ligands, L, usually a phosphine, to give the catalytically active 14-electron complexes, Pd^0L_2. $Pd(PPh_3)_4$ generates active species after the endergonic loss of excess triphenylphosphine, but the excess of PPh_3 ligand slows down the coupling in some cases. Commercial palladium-on-carbon (10 %) has also been used as a palladium source for the coupling with aryl bromides.[50]

In principle, all of the Pd^{II} salts are introduced with coordinating ligands that might interfere with the formation of the active species or act as a trap in the catalytic cycle. More active catalyst should be formed when Pd^{II} sources that contain ligands suitable primarily for the stabilization of Pd^{II} and not Pd^0 are used. Ideal compounds in this respect appear to be $Na_2[PdCl_4]$ or $PdCl_2$, since the hard Cl^- ion is not expected to show high affinity towards the soft Pd^0 centre. Furthermore, the solvent for the coupling reaction should not possess donor groups other than hard oxygen atoms, to avoid blocking the active sites on the Pd species although simple amine solvents an often employed in practice. The choice of catalyst precursor and supporting ligands is vital in the Sonogoshira reaction.[51]

The precise conditions employed depend on the reactivity of the halide, the alkynes and the base used. The reactivity order of coupling for organic halides is vinyl iodide ~ vinyl bromide > aryl iodide > vinyl chloride >> aryl bromide. Copper (I) iodide is a particularly effective cocatalyst although, occasionally copper (I) bromide also can be useful, as can other Group 11 metals. For an example, in the synthesis of internal acetylenes from coupling of ethynyloxiranes with alkenyl triflates, the use of $Pd(PPh_3)_4$ and AgI gives better results than the normal combination of $Pd(PPh_3)_4$ and CuI as shown in **Scheme 1.14**. [43]



Scheme 1.14: The synthesis of internal acetylenes from coupling of ethynyloxiranes with alkenyl triflates. [43]

The nature of the amine (or other base) has a critical role in the Palladium-catalysed coupling of the acetylene. The rate of the reaction is decreased in the order $nBuNH_2$ > Et_3N > $^iPr_2NH$ > Et_2NH > K_2CO_3, piperidine or pyrrolidine give better results in another combination of coupling reagents where the reactivity order of amines is piperidine pyrrolidine > $^iPr_2NH$ > Et_2NH.

Various improvements have been made to the Sonogashira protocol in recent times, and the development of more facile procedures has arisen from the identification of improved metal acetylide coupling partners, as well as more active palladium catalysts for cross coupling with unactivated arenes.[12] Sonogashira coupling of aryl bromides and iodides at room temperature is now possible, and steps are being made toward the activation of aryl chlorides.[43]

Other recent developments include:[42, 50]

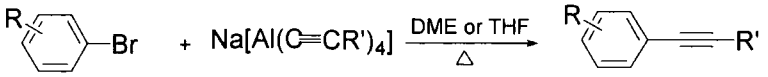
a) The use of various palladacycles which led to catalytic systems with higher turnover numbers,

b) Copper-free or silver catalysed protocols eliminated the undesired dimerization of terminal alkynes

c) reduced production of alkyne homodimerization by-products,

d) production of alkynes in practically useful yields in the cases where the starting alkynes are substituted with electron-withdrawing groups, such as carbonyl-containing groups and CF_3.

One example of newly developed and improved Sonogashira protocol is the use of tetraalkynyl aluminate salts ($Na[Al(C{\equiv}CR')_4]$) which are easily prepared in situ from $NaAlH_4$ and a terminal acetylene. They are quite effective in palladium-catalysed cross-coupling reactions with aryl or heteroaryl bromides. This newly improved method was introduced by Blum and co-workers (**Scheme1.15**).[52]



R' = Ph, Me_3Si, *n*Bu, $NC(CH_2)_3$

Scheme 1.15: Palladium-catalysed cross-coupling with tetraalkynyl aluminates according to Blum and co-workers. [52]

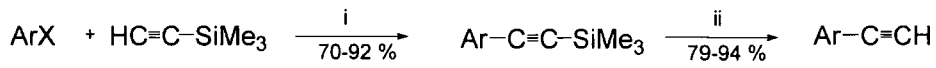
It is believed that the transformations are gratifyingly free from the oxidative homocoupling by-products that normally plague typical Sonogashira conditions.

1.5.4 Synthesis of Terminal Acetylenes

Conjugated terminal acetylenes are important intermediates in organic synthesis. The reaction of acetylene gas with organic halides under Sonogashira conditions preferentially gives only internal acetylenes because of the higher reactivity of monosubstituted acetylenes than that of acetylene gas. It is therefore necessary to use a protecting group if terminal acetylene products are to be obtained using Sonogashira protocols. The most commonly used protecting group for acetylene is the trimethylsilyl ($SiMe_3$, TMS) group and commercially available trimethylsilylacetylene ($HC{\equiv}CSiMe_3$, TMSA) provides an excellent starting material for the synthesis of various aryl and alkenylacetylenes.[43]

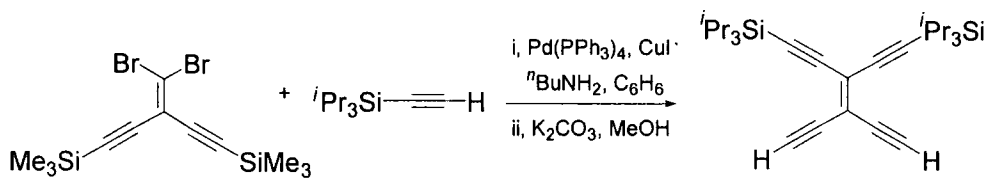
Generally, cross coupling of aryl or alkenyl halides with TMSA proceeds in the presence of a Pd catalyst and CuI followed by treatment with dilute aqueous KOH

or K_2CO_3 in MeOH or a source of fluorine such as KF, KF-crown ether, TASF, or nBu$_4$NF for the deprotection to give terminal acetylene (**Scheme 1.16**).



i. $PdCl_2(PPh_3)_2$, CuI cat., NEt_3 or pyridine, rt to 60 °C
ii. 1 *M* aq. KOH/MeOH, rt, 1 h

Scheme 1.16: Cross-coupling reaction of aryl or alkenyl halides with TMSA followed by the deprotection to give terminal acetylene.[43]

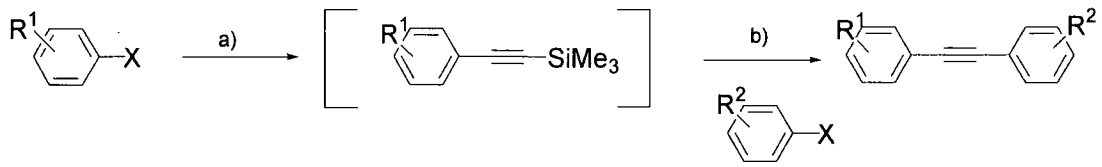


Scheme 1.17: The preparation of tetraethynylethene.[43]

One example of the synthesis of a rather unusual terminal acetylene is the preparation of tetraethynylethene which is prepared by Pd-catalysed alkynylation followed by deprotection with K_2CO_3 in MeOH which selectively cleaves the $SiMe_3$ groups to give the per ethynylated ethene as shown in **Scheme 1.17**.[43]

The terminal acetylenes which result are of course then suitable reagents for use in subsequent Sonogashira reactions and used in the synthesis of internal alkynes. The efficiency of this process can be substantially improved using the "sila"-Sonogashira coupling, which was introduced by Mori, Nishahara and co-

workers.[54-55] In their newly improved protocol, the trimethylsilyl protecting group is removed in-situ to afford the terminal acetylene which is coupled directly to afford the desired diaryl acetylene (**Scheme 1.18**).



X = OTf: a) $[Pd(PPh_3)_4]$, NEt_3/DMF, $HC{\equiv}CSiMe_3$, 60 °C, 6 h; b) CuCl, 80 °C, 12 h. and,

X = I: a) $[PdCl_2(PPh_3)_2]$, CuI, NEt_3, C_6H_6, $HC{\equiv}CSiMe_3$, RT, 18 h; b) H_2O, RT, 18 h.

Scheme 1.18: One pot synthesis of unsymmetrical bis-aryl ethynes, by sila-Sonogashira reaction. [54-55]

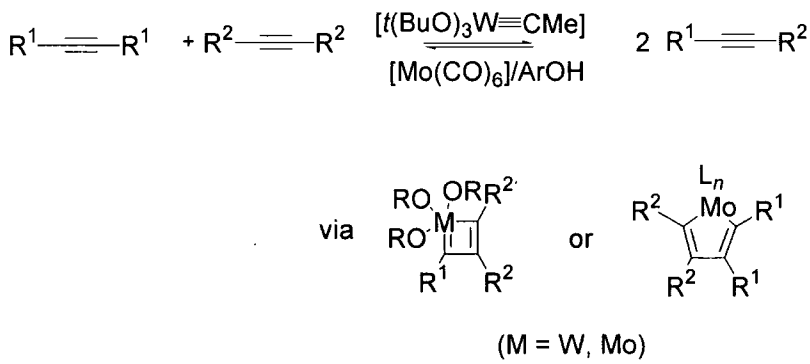
This one-pot coupling protocol still incorporates two distinct steps. First cross coupling of an aryl triflate with (trimethylsilyl)acetylene under copper free conditions gives the intermediate compound, which is followed by the addition of copper salt that promotes both in situ desilation and the second coupling event to an electron deficient aryl triflate. The scope of the sila-Sonogashira reaction has been substantially broadened recently by Brisbois, Grieco, and co-workers. Their procedure utilizes traditional Sonogashira conditions for the first coupling steps of a terminal alkyne to an aryl iodide. This is followed by addition of a sub-stoichiometric amount of water and 1,8-diazabicycloundec-7-ene (DBU, 6 equiv.),

which effect desilylation and cross-coupling to the second aryl iodide (**Scheme 1.18**).[49]

1.5.5 Synthesis of Alkynes: Metathesis

1.5.5.1 An Introduction of Alkynes Metathesis

Alkyne metathesis in homogeneous solution has been known since 1974, when it was discovered by Mortreux and Blanchard, who treated tolanes with a mixture of molybdenum hexacarbonyl and 4-chlorophenol. At elevated temperatures metathesis products were obtained.[56] Later, Schrock demonstrated that defined molybdenum-or tungsten-carbyne complexes are active in alkyne metathesis. Schrock and co-workers have reported several catalytic systems for acetylene metathesis,as shown in **Scheme 1.19**. [56-58]



Scheme 1.19: The ptotocol of catalytic systems for acetylene metathesis reported by Schrock and co workers.[57]

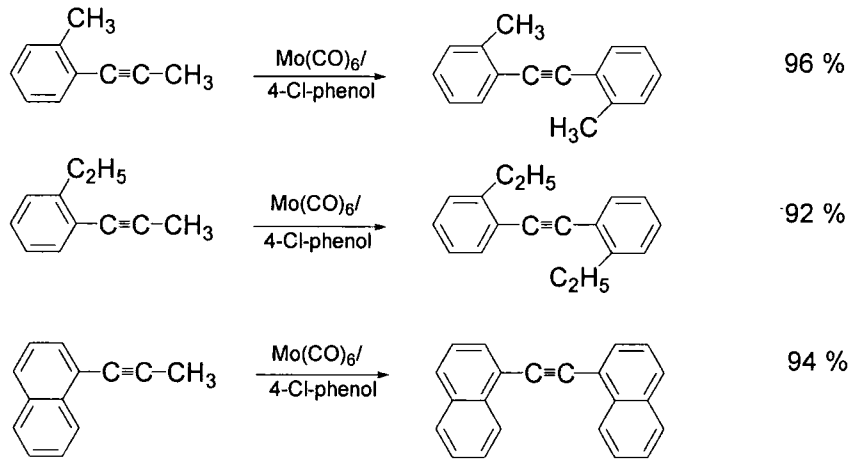
In 1995, Mori[59] showed that the Mortreux and Blanchard systems are valuable for preparative work, and metathesis of a series of substituted alkynes afforded their corresponding homo- and heterodimers. However, the yield was not always high.

In 1997 Bunz, Weiss and Mullen reported the first use of Shrock's tungsten-carbyne for the preparation of some poly(aryleneethynylene)s (PPEs) including 2,5-dihexyl-PPE and with a use of different monomers and reaction conditions involved. The dipropynylated monomer was treated with the tungsten-carbyne in carefully dried solvents under strict exclusion of air and water at elevated temperatures for 12-16 hours.[60]

Under these conditions, the PPEs formed via alkyne methathesis were obtained in good yield and high purity, which makes the method competitive with the Pd-catalysed coupling. While the Shrock catalyst ($tBuO)_3W{\equiv}C$-tBu) is very active, it is very sensitive toward air and particularly water. According to Bunz[19] the preparation of PPEs utilizing Shrock carbynes does not proceed smoothly in non-dried, non-purified, off-the-shelf solvents using commercially available precursors: the yield of the metathesis products was only moderate making this catalyst undesirable for the formation of PPEs. [59]

Kloppenburg, Pschirer and Bunz[61, 62] optimized the reaction conditions of alkyne metathesis essentially by returning to the original Mortreux system, utilizing $Mo(CO)_6$ and 4-chlorophenol and increasing the reaction temperature from 105 to

130-150 ^{0}C in order to cross couple derivatives of propyne. This reaction was coupled with a purge of nitrogen in order to remove the 2-butyne formed as a by-product. Yields obtained after the process of chromatography and crystallisation were above 90 %, with the product polymers obtained as bright yellow solids (**Scheme 1.20**).



Scheme 1.20: The reaction conditions of alkyne metathesis utilizing $Mo(CO)_6$ and 4-chlorophenol by increasing the reaction temperature producing more than 90 % yields. [19]

1.5.5.2 Comparison of the Schrock and the Mortreux-Bunz Alkyne Metathesis Systems

With a use of very active catalyst $(tBuO)_3W{\equiv}C\text{-}tBu$, alkyne methathesis can be performed at 80 ^{0}C.[57,60,63] This reaction, also shows good heteroatom tolerance. A significant disadvantage is the multi-step preparation of the catalyst which requires careful exclusion of air and water because the catalyst is very air and water sensitive. Furthermore, all the monomer reagents have to be rigorously dried and

purified to do successful metathesis and the whole reaction should be carried out carefully under controlled anhydrous conditions.[19]

For the alkyne metathesis systems of Mortreux-Bunz, $Mo(CO)_6$/4-chlorophenol in 1,2-dichlorophenol or 1,2-dichlorobenzene are used. The catalyst system forms in situ from its substituent at temperatures ranging from 130 to 150 °C, much higher than the system used by Schrock, but with a presence of the monomer in non-dried, off-the shelf solvents which available commercially and they are able to metathesise aromatic hydrocarbons in high yield and with unsurpassed ease. However, with exception of oxygen functionalities, this catalyst is not particularly tolerant to heteroatoms.

The simplicity of preparation gives these catalyst systems some superior and desirable advantages when compared with Pd-catalysed couplings of Heck-Cassar-Sonogashira type of synthesis. According to Mortreux and Bunz, PPEs prepared by Pd-catalysed methods contain diyne defects, which formed by either reduction of the Pd^{2+} catalyst precursor or the adventitious presence of atmospheric oxygen. [21]

High-molecular weight PPEs prepared by alkyne metathesis show promise as active layers in organic semiconductor devices, such as light emitting diodes, light emitting electrochemical cells, photovoltaic cell, and thin-film transistors despite delicate processing required to obtain device-quality material. This type of

metathesis- prepared PPE exhibits enhanced photophysical stability and their efficient fluorescence in solution point to exciting opportunities in the field of PPE semiconductors. [21]

1.6 An Introduction to the Chemistry of Ethers

The general structure for ethers is R-O-R'. Symmetrical ethers are ethers where the carbon groups, R and R' are the same. Asymmetrical ethers are ethers where the R and R' are different. In general, ethers are relatively unreactive compounds, and are frequently used as solvents given their combined hydrophobic (R) and hydrophilic properties. Ethers are fairly polar offering nonbonding pairs of electrons on the oxygen atom that can participate in hydrogen bonding with hydrogen-bond donors such as water, alcohols, and amines. Ethers also form stable complexes with Grignard reagents and Lewis acids like BH_3 and BF_3. [36]

The most general synthesis of these compounds is the Williamson ether synthesis, which involves the attack of an alkoxide ion on an unhindered alkyl halide. Ethers undergo a limited number of reactions, including cleavage by HBr and HI, and auto-oxidation to form peroxides. Sulfides are the sulfur analogs of ethers, general formula R-S-R'. Sulfur has an expandable valence, and sulfides can be oxidized to sulfoxides and sulfones. Sulfides are also more nucleophilic than ethers, undergoing alkylation to give sulfonium salts.

Epoxides (oxiranes) are three-membered cyclic ethers. They are commonly formed by the reaction of an alkene with a peroxy acid, which donates an oxygen atom to give a three-membered ring. Because of their ring strain, epoxides are much more reactive than other ethers. They can be opened by nucleophiles or electrophiles such as acids, alkoxides, and Grignard reagents. Many of these reactions give useful alcohols that are not easily obtained by other methods.

1.6.1 Synthesis of Ethers: The Williamson ether synthesis

In the most general terms, the Williamson synthesis of ethers involves reaction of an alkyl halide and alkoxide ion to produce an ether and halide anion.

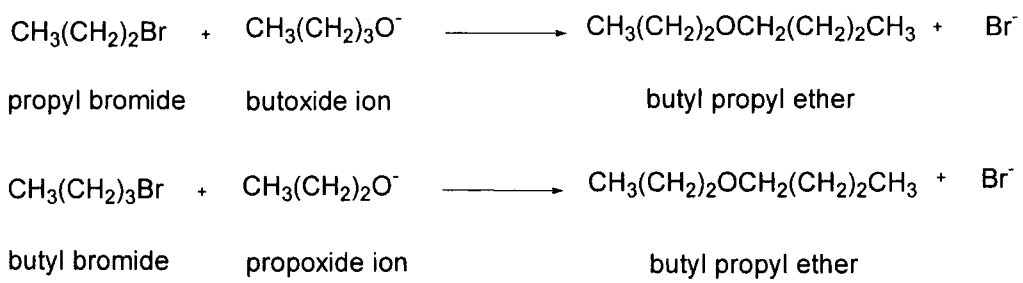
$$R\text{–}Br + R\text{–}O^- \longrightarrow R\text{–}O\text{–}R + Br^-$$

The alkoxide ion for the Williamson ether synthesis is usually prepared by using sodium metal or sodium hydride (NaH) to remove a proton from an alcohol.

$$2ROH + Na^+ \longrightarrow 2R\text{–}O^- + H_2$$

Alkoxide ion is a powerful nucleophile, and reacts well in an S_N2 reaction. The alkyl halide must be primary so that the backside attack is not sterically hindered. With secondary or tertiary halides, elimination usually results.

The Williamson ether synthesis is a substitution reaction and, because it requires a high concentration of a good nucleophile (the alkoxide ion), it is an S_N2 reaction. The examples of this type of synthesis are as follow (**Scheme 1.21**): [37, 38]



Scheme 1.21: The examples of Williamson ether synthesis.

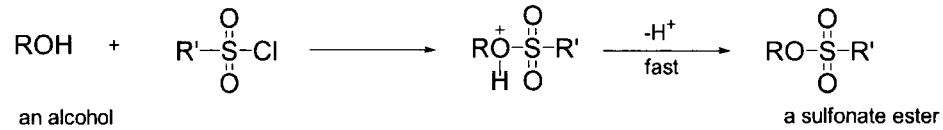
1.6.2 Substitution Reactions of Ethers

The leaving group of an ether (OR) and the leaving group of an alcohol (OH) have nearly the same basicity. For example, the pKa of MeOH is 15.5 and the pKa of water is 15.7. Both leaving groups are strong bases, so both are strong bases, so both are very poor leaving groups. Consequently, alcohols and ethers are equally unreactive toward nucleophilic substitution.

R-OH	R-O-R
an alcohol	an ether

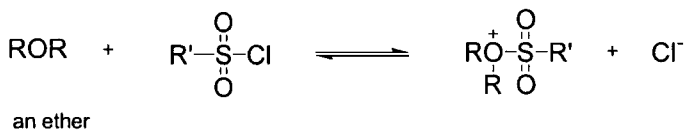
Many of the reagents that are used to activate alcohols towards nucleophilic substitution (e.g., $SOCl_2$, PCl_3) cannot be used to activate ethers. For example, when an alcohol reacts with an activating agent such as a sulfonyl chloride, a

proton is lost in the second step of the reaction and a stable sulfonate ester results as shown in **Scheme 1.22**.



Scheme 1.22: The formation of sulfonate ester.

When ether reacts with a sulfonyl chloride, however, the R group cannot be lost, so a stable sulfonate ester cannot be formed. Instead, the intermediate returns to be starting materials (**Scheme 1.23**).

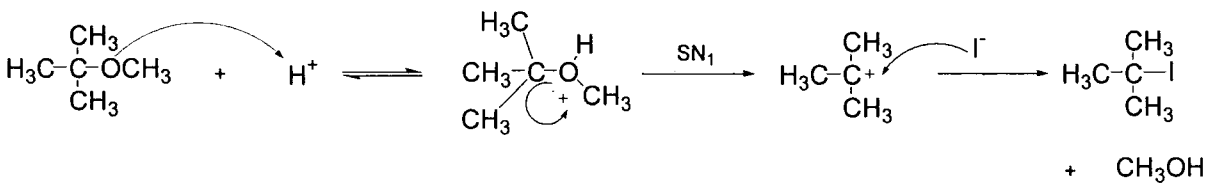


Scheme 1.23: The reaction of ether with sulfonyl chloride.

However, like alcohols, ethers can be activated by protonation. Therefore, in the presence of a high concentration of HI or HBr, ethers undergo a nucleophilic substitution reaction. Similar to the reaction of alcohols, the reaction of ethers with

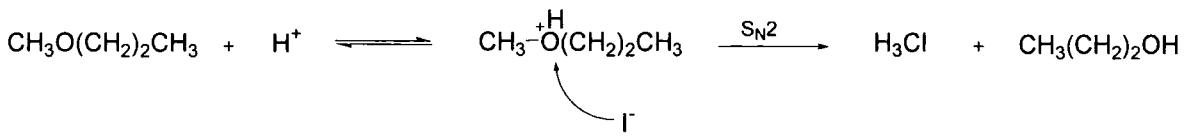
hydrogen halides is slow and the reaction mixture must be heated in order for the reaction to occur at a reasonable rate.

The first step in the cleavage of an ether (C-O) by HI or HBr is protonation of the ether oxygen. This converts the very basic RO^- leaving group into the less basic ROH leaving group. The next step in the mechanism depends on the structure of the ether. If departure of the leaving group creates a relatively stable carbocation, for example a tertiary carbocation, an S_N1 reaction occurs in which the leaving group departs, and the halide ion combines with the carbocation (**Scheme 1.24**).



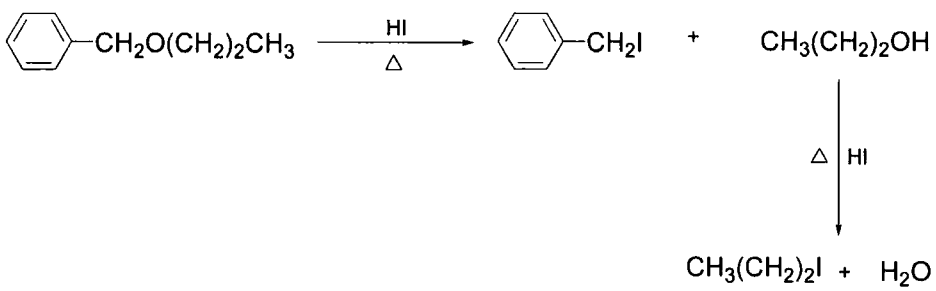
Scheme 1.24: The mechanism of ether cleavage by the protonation of ether oxygen as an initial step.

However, if the loss of the leaving group would create an unstable carbocation, for instance a methyl cation or a primary carbocation, the reaction cannot proceed via the S_N1 mechanism, and instead the leaving group must be displaced by the halide ion i.e. an S_N2 reaction occurs. The halide ion preferentially attacks the less strerically hindered of the two alkyl groups (**Scheme 1.25**).



Scheme 1.25: The displacement of S_N1 by S_N2 in the ether cleavage.

If an excess HI is used, the product alcohol will be converted into an alkyl halide. Cleavage of ethers by concentrated HI or HBr occurs more rapidly if the reaction can take place by an S_N1 pathway. If the instability of the carbocation causes the reaction to follow an S_N2 pathway, cleavage will be more rapid with HI than with HBr because I^- is a better nucleophile than Br^-. Only a substitution product is obtained because the bases present in the reaction mixture (halide ions and H_2O) are too weak to abstract a proton in an E_2 reaction, and any alkene formed in an E_1 reaction would react with HBr or HI to form the substitution product. S_N2 cleavage reactions would react with HBr or HI to form the substitution product. S_N2 cleavage reactions of ethers do not occur at all with concentrated HCl because Cl^- is too poor nucleophile (**scheme 1.26**). [37]



Scheme 1.26: The S_N2 cleavage reactions would react with HBr or HI to form the substitution product.

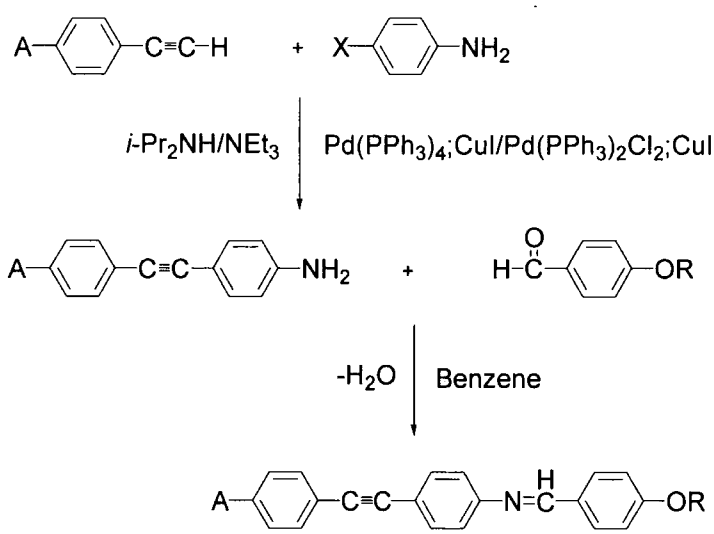
1.7 Work Described in This Thesis

In this thesis, the chemistry involving all functional groups mentioned above has been applied to produce a new series of conjugated molecular building blocks together with a preliminary study of the electronic and physical properties which characterise these materials. The syntheses and spectroscopic properties of these compounds are discussed in **Chapter 2**, their liquid crystalline and thermal properties are described in **Chapter 3**, and details of the experimental procedures are given in **Chapter 4**.

Chapter 2. Synthetic Chemistry and Characterisation

Conjugated molecular systems based on a combination of aromatic moieties with either acetylene or imine groups are well known. However, as indicated in the introductory chapter, simple linear compounds containing both of these moieties are virtually unknown. With a view to preparing a novel class of conjugated material, hybrid imine/acetylenic systems (**Figure 1.3**) were chosen as the subject of this thesis. By incorporating a flexible alkoxy tail group it was hoped to engineer liquid crystalline phases in these new materials.

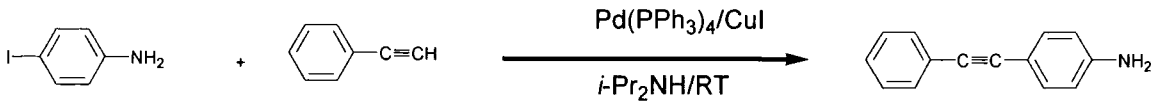
The general reaction scheme utilised in the production of the new family of compounds which form the subject of this thesis is given in outline form in **Scheme 2.1**.



A = H, $MeCO_2$, CN
X = I, Br
R = C_nH_{2n+1}; n = 6, 7, 8, 9, 10

Scheme 2.1: Synthetic approach adopted in this thesis.

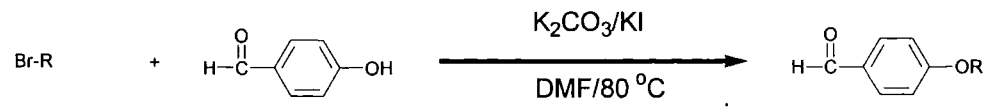
2.1 Synthesis of 4-Phenylethynylaniline[64]



1

The synthesis of **1** proceeded via $Pd(PPh_3)_4$/CuI catalysed coupling of 4-iodoaniline with ethynylbenzene. The reaction was carried out in dry *i*-Pr_2NH under nitrogen at room temperature forming a brown solution, from which the desired product was isolated in a good yield (75 %) as a brown solid after recrystallisation from DCM-hexane. The IR spectrum contained two strong absorption bands ν (NH_2) at 3377 cm^{-1} and 3476 cm^{-1} and a moderate ν (C≡C) band at 2212 cm^{-1}. The ^1H NMR spectrum showed the expected resonances in the appropriate regions: one broad peak occurred at δ 3.76 ppm representing two protons of the NH_2, two pseudo-doublets at δ 6.63 and 7.50 ppm arising from the *para*-substituted aromatic ring, and a broad, unresolved multiplet between δ 7.29 - 7.36 ppm from the mono-substituted phenyl moiety. The ^{13}C NMR spectrum contained two resonances at δ 87.99 and 91.33 ppm from the C≡C carbons and eight resonances in the aromatic region between δ 114.82 - 132.94 ppm. The EI-MS spectrum exhibited a molecular ion at *m/z* 193, and a fragment ion at *m/z* 176 representing the loss of NH_2

2.2 Synthesis of 4-Alkoxybenzaldehydes

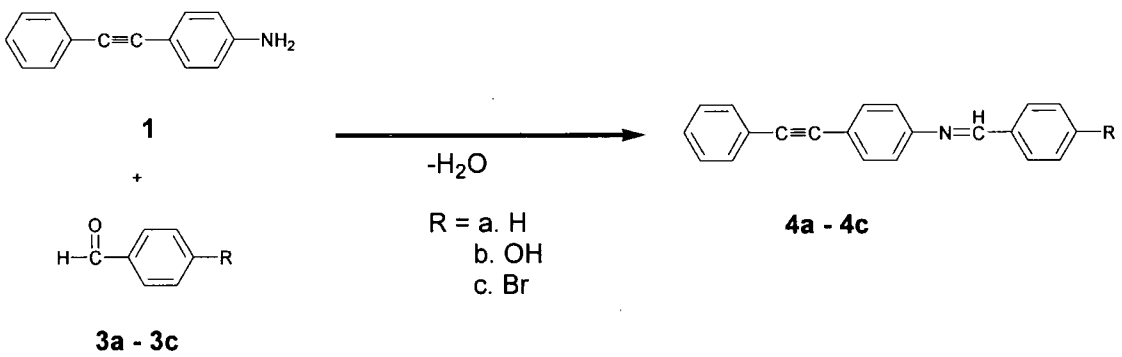


R= C_nH_{2n+1}; n = 6 (a), 7(b), 8 (c), 9 (d), 10 (e) **2a - 2e**

The preparation of **2a - 2e** was accomplished via the Williamson ether synthesis using different chain length bromoalkanes with 4-hydroxybenzaldehyde. The reaction was carried out in dry DMF forming an orange solution and a white precipitate of the inorganic salt by-products upon completion. The desired ethers were readily obtained as colourless oils following conventional organic workup and vacuum distillation in moderate to good yield (46 - 71 %). Generally for all compounds in the series, the IR spectra contained a strong ν (C=O) absorption band in the region 1705 -1722 cm^{-1} and a moderate ν (C(=O)-H) band at 2715 - 2731 cm^{-1} together with a moderate ν (C-O) (ether) absorption band at 1152 - 1174 cm^{-1}. The ^1H NMR spectra of **2a-2e** contained a triplet resonance (J_{HH} = 8.8 *Hz*) arising from the CH_3 moiety. An overlapping set of resonances in the region δ 1.21 - 1.84 ppm was attributed to the eight to sixteen CH_2 protons for each member of the series, while another triplet peak at δ 3.94 - 4.01 ppm (J_{HH} = 6.8 *Hz*) representing two protons was assigned to the OCH_2 linkage. Two pseudo-doublets in the aromatic region at δ 6.91 - 6.98 and δ 7.45 - 7.81 ppm were observed and assigned to the *para*-subsituted aromatic groups, while a singlet at δ 9.78 - 9.86 ppm indicated the presence of the aldehyde (C(=O)H). The ^{13}C NMR spectra show one resonance between δ 13.96 - 14.07 ppm from the methyl (CH_3) carbon, five to

nine resonances at δ 22.64 - 31.85 ppm from the appropriate number of CH_2 carbons, one resonance at δ 68.39 - 68.43 ppm from the alkyl ether carbon, while in the aromatic region four resonances at δ 114.37 - 132.24 ppm arise from carbon nuclei of the disubstituted-phenyl moieties. The carbonyl (aldehyde) carbon was observed as a singlet between δ 190.54 - 190.69 ppm. The EI-MS spectra of **2a - 2e** exhibited molecular ions at *m/z* 206, 220, 234, 249 and 262 respectively, and a fragment ion at *m/z* 121, arising from the loss of the alkyl chains.

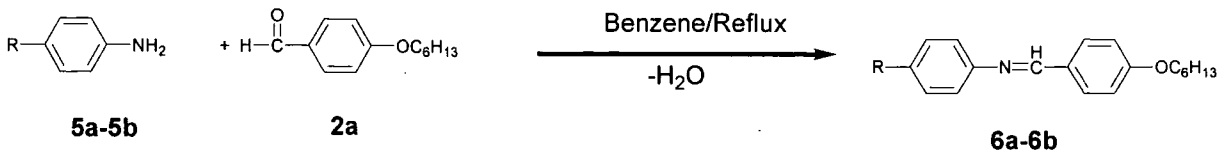
2.3 Synthesis of 4a-4e



The synthesis of the ethynyl substituted Schiff-Bases **4a-4c** involved elimination of water from three different *para*-substituted benzaldehydes, namely benzaldehyde, 4-hydroxybenzaldehyde and 4-bromobenzaldehyde, with 4-phenylethynylaniline (**1**). The brown oily solution formed was allowed to crystallise, then filtered and washed with EtOH followed by hexane to give the desired products as cream crystalline materials in moderate to good yield (56-87 %). Generally the IR spectra for all compounds were similar and contained the expected features. The weak ν

(C≡C) absorption band was found in the region 2210 - 2214 cm^{-1}, and a moderate intensity ν (C=N) absorption band at 1621 - 1627 cm^{-1}. In addition, a broad ν (OH) absorption band occurred at 3310 cm^{-1} for **4b**. The ^{1}H NMR spectrum for **4b** shows a broad resonance of the hydroxyl (OH) proton at δ 1.48 ppm. In addition to the aromatic resonances, a singlet occurred at δ 8.47 - 8.48 ppm indicating the presence of the imine proton (CH=N). The ^{13}C NMR spectra contained two resonances at *ca.* δ 90 ppm for the acetylenic C≡C carbons, while in the aromatic region, twelve resonances were observed between δ 121.02 - 134.99 ppm from the carbons of the substituted-phenyl rings. A singlet at δ 159.12 - 161.23 ppm was assigned to the imine (C=N) carbon. The EI-MS spectra for **4a**, exhibited a molecular ion at *m/z* 281 and fragment ions at *m/z* 203 indicating the loss of C_6H_6, and *m/z* 177 showing the loss of C_7H_6N. For **4b**, a molecular ion occurs at *m/z* 297 and a stable fragment peak at *m/z* 280 indicating the loss of OH. For **4c** a molecular ion occurred at *m/z* 360 together with the fragment peak at *m/z* 280 indicating the loss of bromide.

2.4 Synthesis of 6a and 6b



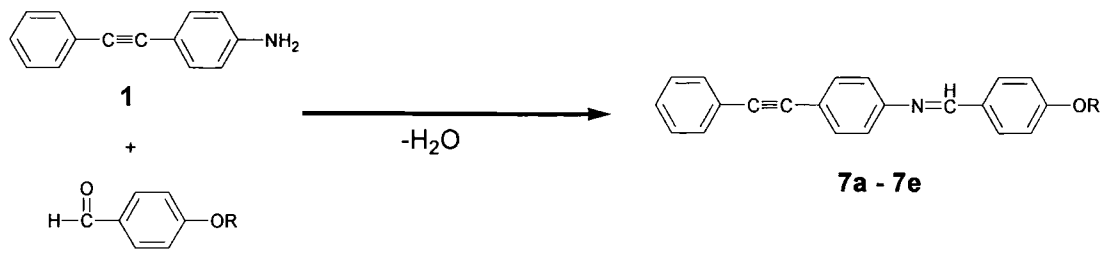
5a-5b **2a** **6a-6b**

R = a. H, b. $MeCO_2$

The synthesis of **6a-6b** involved elimination of water from **2a** and aniline or 4-aminomethylbenzoate respectively. The reactions were performed in refluxing benzene with the flasks fitted with a Dean-Stark condenser. Once the reaction was complete, the solvent was removed *in-vacuo* and the crude solid recrystallised from MeOH giving **6a** and **6b** in moderate to a very good yield 55 % and 89 %, respectively, as white crystalline solids. The IR spectra showed moderate ν (C=N) absorption bands at 1650 cm^{-1} (**6a**) and 1654 cm^{-1} (**6b**), and a strong ν (C-O) absorption bands at 1114 cm^{-1} (**6a**) and 1162 cm^{-1} (**6b**). In addition, **6b** showed a strong ν (C=O) absorption band from the ester carbonyl at 1725 cm^{-1}. The ^1H NMR spectra showed resonances clearly for all the functional groups, including one triplet (J_{HH} = 7.2 *Hz*) resonance at δ 0.92 ppm representing three protons of the CH_3 group. A set of overlapping resonances in the region δ 1.35 - 1.85 ppm with correct integrated area were assigned to the eight CH_2 protons, and another triplet (J_{HH} = 6.8 *Hz*) resonance at around δ 4.00 ppm was observed for the two protons of the OCH_2 link. Two pseudo-doublets at δ 6.97 and 7.85 ppm were assigned to the four protons of the disubstituted-phenyl rings and an unresolved multiplet at δ 7.19 - 7.40 ppm to the five protons of the C_6H_5 moiety in **6a**. Both compounds also

show a singlet peak near δ 8.30 ppm from the imine (CH=N) proton. The ^{13}C NMR spectra of **6a** and **6b** contain one resonance at around δ 14.00 ppm from the CH_3 carbon, and four resonances in the region of δ 22.59 - 31.57 ppm from the four CH_2 carbons. In addition, one resonance at δ 53.39 ppm indicated the methyl ester OCH_3 carbon of **6b**. Both compounds exhibited a resonance near at δ 68.00 ppm which is due to the ester (C-O) carbon. While eight resonances in the aromatic regions at δ 113.80 - 131.96 ppm indicated the carbons of mono- and disubstituted-phenyl rings, one resonance at δ 161.00 ppm was assigned to the imine carbon (C=N). In the case of **6b** an additional resonance was observed at δ 166.89 ppm and assigned to the ester (C=O) carbon. The EI-MS spectrum of **6a** exhibited a molecular ion at *m/z* 218 and a fragment ion at *m/z* 196 representing the loss of C_6H_{13}. For **6b** the molecular ion occured at *m/z* 339 and fragment ions at *m/z* 308 and *m/z* 255 representing the loss of MeO and C_6H_{13} respectively were also observed.

2.5 Synthesis of 7a-7e

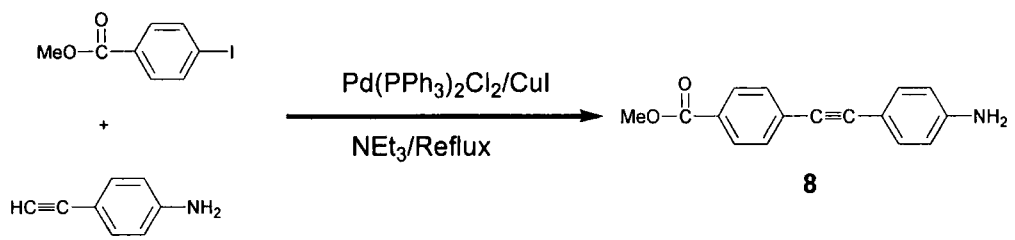


R = C_nH_{2n+1}; n = 6 (a), 7 (b), 8 (c), 9 (d), 10 (e)

The synthesis of **7a-7e** involved elimination of water from **1** with each of **2a-2e.** The brown oily solutions formed were allowed to crystallise and the crude product isolated by filtration and washed with EtOH followed by hexane. Pale yellow crystals were obtained after recrystallisation from DCM-hexane giving the desired compounds in moderate yield (44-61 %). In general, the spectroscopic data for all compounds showed the same characteristics. The IR spectra showed a weak ν (C≡C) absorption band at 2202 - 2212 cm^{-1}, a moderate ν (C=N) absorption band at 1653 -1668 cm^{-1} and a strong ν (C-O) absorption at 1168 - 1175 cm^{-1}. The ^1H NMR spectra show resonances clearly for all the functional groups: one triplet resonance at δ 0.89 - 0.92 ppm with coupling constant J_{HH} = 6.8 - 7.2 *Hz* representing three protons of the CH_3 group; a set of overlapping resonances in the region δ 1.22 - 1.97 ppm with correct integrated area which is assigned to the eight to sixteen CH_2 protons; a triplet at δ 3.98 - 4.04 ppm with coupling constant J_{HH} = 6.4 to 9.6 *Hz*, from the two protons of the OCH_2 link; four pseudo-doublet at δ 6.92 - 6.99, 7.18 - 7.20, 7.30 - 7.36 7.84 - 7.87 ppm from the *para*-disubstituted phenyl rings and a multiplet at δ 7.46 - 7.57 ppm from the mono-substituted-

phenyl rings. All compounds also show a singlet peak at δ 8.36 - 8.56 ppm which indicate one proton of the imine (CH=N). The ^{13}C NMR spectra of **7a-7e** showed resonances at δ 14.01 - 14.10 ppm from the CH_3 carbon and resonances in the region of δ 22.59 - 31.89 ppm indicated five to nine CH_2 carbons. One resonance around δ 68.30 ppm indicated the ether (C-O) carbon, Two resonances at δ 89.48 - 89.50 ppm and δ 89.50 - 89.57 ppm confirmed the presence of the C≡C carbons. Twelve resonances in the aromatic regions at δ 114.78 - 159.97 ppm were observed for the eighteen carbons (twelve of which are chemically and magnetically inequivalent) of the mono- and disubstituted-phenyl rings of **7a-7e** while the imine carbon (C=N) was observed around δ 162.00 ppm. The EI-MS spectra exhibited a molecular ion at *m/z* 381, 395, 409, 423, and 436 for **7a-7e** respectively, all fragment ions for all compounds exhibit the loss of alkyl chain; fragment ion at *m/z* 297, representing the loss of alkyl chains.

2.6 Synthesis of Methyl 4-[(aminophenyl)ethynyl]benzoate

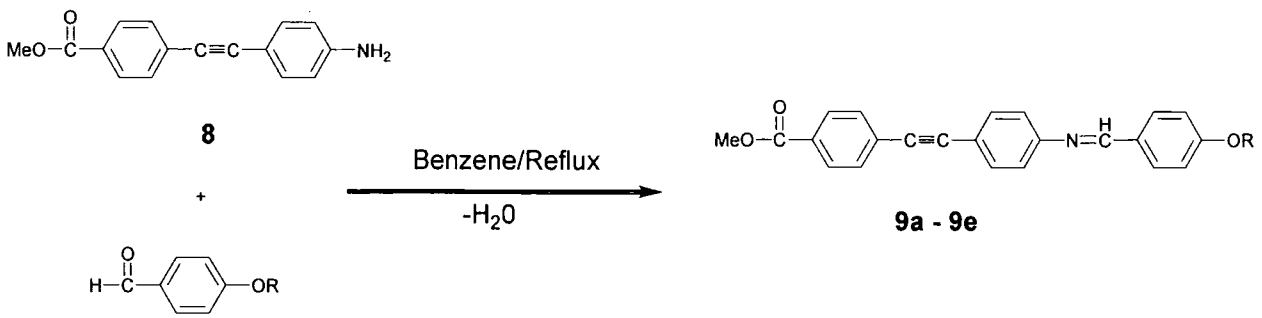


8

The synthesis of **8** proceeded via $Pd(PPh_3)_2Cl_2/CuI$ catalysed cross-coupling of 4-ethynylaniline and 4-iodomethylbenzoate. The reaction was carried out in dry NEt_3 and the solution mixture was heated at reflux (< 100 °C) under nitrogen overnight. The product formed as a yellow precipitate, which was purified by column chromatography, affording the desired pure material in a good yield (79 %) as a

yellow solid. The IR spectrum of **8** contained two strong ν (NH_2) absorption bands at 3367 cm^{-1} and 3458 cm^{-1}, a moderate ν (C≡C) band at 2208 cm^{-1}, and a strong ester ν (C=O) band at 1698 cm^{-1}. The ^1H NMR spectra show resonances clearly for all the functional groups, one broad peak occurred at δ 3.79 ppm representing two protons of the NH_2, one singlet peak at δ 3.84 ppm indicated the three protons of the CH_3 group and four pseudo-doublets at δ 6.65, 7.36, 7.55, and 8.00 ppm were observed and assigned to the disubstituted-phenyl groups. The ^{13}C NMR spectra show one resonance at δ 52.14 ppm of one OCH_3 carbon, two resonances at δ 86.89 and 93.52 ppm from the C≡C carbons and four resonances at δ 111.95 - 147.14 ppm from the disubstituted-phenyl groups and one resonance at δ 166.68 ppm from the ester (C=O) carbon. The EI-MS spectra of **8** exhibited a molecular ion at *m/z* 251, and a fragment ion at *m/z* 220 representing the loss of MeO and at *m/z* 192 indicates the loss of $MeCO_2$.

2.7 Synthesis of 9a - 9e

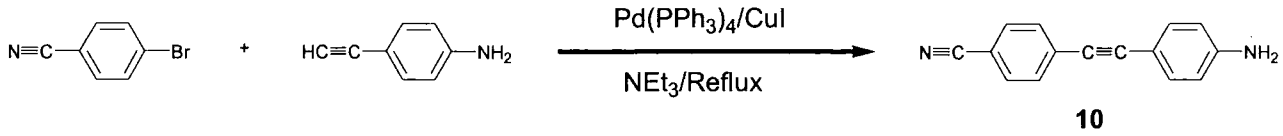


R = C_nH_{2n+1}; n = 6 (9), 7 (b), 8 (c), 9 (d), 10 (e)

The synthesis of **9a-9e** involved elimination of water from **8** with each of **2a-2e.** The reaction was performed in refluxing benzene and the flask fitted with Dean-Stark condenser. Recrystallisation of the crude material from DCM-hexane afforded the pale yellow crystalline product in moderate to good yield (45-78 %). The spectroscopic data for all compounds show the same characteristics. The IR spectra show a weak absorption ν (C≡C) band at 2186 - 2279 cm^{-1}, a strong ν (C=O) absorption band at 1716-1725 cm^{-1}, and a strong ν (C=N) absorption band at 1642-1657 cm^{-1}. Only one of the ν (C-O) absorption bands could be observed and assigned with confidence, falling in the region 1102 -1170 cm^{-1}. The ^1H NMR and ^{13}C spectra contained the expected, characteristic resonances including one triplet peak(J_{HH} = 6.4 - 7.2 *Hz*) at δ 0.89 - 0.90 ppm representing the alkyl CH_3 moiety. A set of overlapping resonances in the region δ 1.28 - 1.87 ppm with correct integrated area was assigned to the eight to sixteen protons of the CH_2 link, while a singlet resonance at δ 3.93 ppm was assigned to the and a triplet at δ 4.03 ppm (J_{HH} = 6.8 *Hz*) were assigned to the ester OCH_3 and the OCH_2 protons

respectively. Six pseudo-doublets at δ 6.99, 7.20 - 7.21, 7.48 - 7.58, 7.52 - 7.61, 7.60 - 7.87 and δ 7.90 - 8.04 ppm arising from the aromatic protons were observed. All compounds also showed a singlet peak at δ 8.38 - 8.39 ppm from the proton of imine (CH=N). The ^{13}C NMR spectra showed one resonance at δ 14.00 - 14.09 ppm from the alkyl CH_3 carbon, while resonances in the region of δ 22.58 - 32.70 ppm indicated five to nine CH_2 carbons. In addition to a resonance at δ 52.12 - 52.20 ppm (ester OCH_3), **9a - 9e** also exhibit a resonance at δ 68.28 - 68.45 ppm from the ether carbon and two resonances at δ 86.88 - 88.86 and δ 90.18 - 93.88 ppm from the acetylenic C≡C carbons. Twelve resonances at δ 114.70 - 132.76 ppm were observed for the distinct carbons of the three disubstituted-phenyls while at δ 160.17 - 162.84 ppm, one resonance occurred indicating a carbon of imine (C=N) and one resonance at δ 165.39 - 166.67 ppm which was assigned to the ester carbonyl carbon (C=O). EI-MS spectra exhibited molecular ions at *m/z* 439, 453, 467, 481, 495 for **9a-9e** respectively; all fragment ions exhibit the loss of MeO at *m/z* 408, 422, 436, 450 and *m/z* 464 respectively. All compounds also show the loss of an alkyl chain; fragment ions at *m/z* 355, representing the loss of alkyl chains.

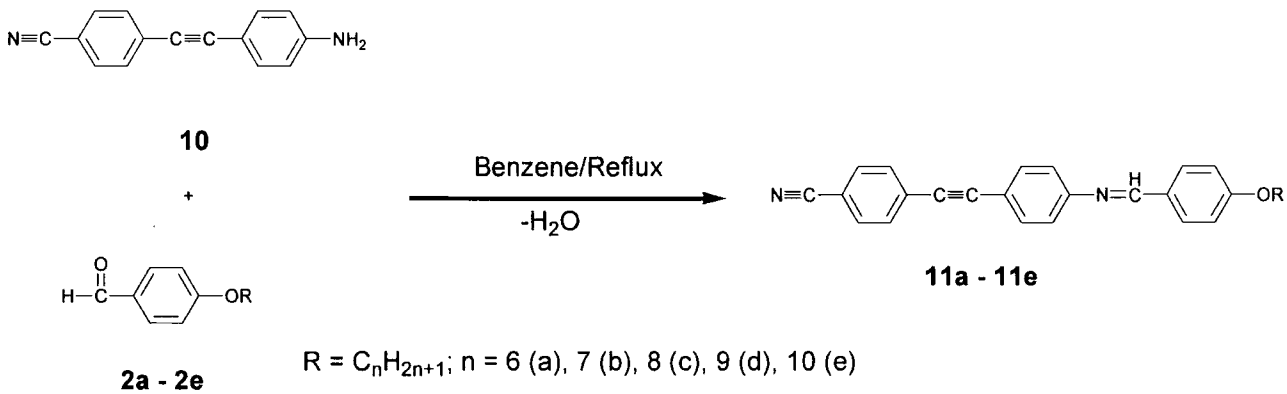
2.8 Synthesis of 4-[(4-Amino-phenyl)ethynyl]-benzonitrile



10

The synthesis of **10** proceeded via $Pd(PPh_3)_4$/CuI catalysed cross-coupling of 4-ethynylaniline and 4-bromobenzonitrile. The reaction was carried out in dry NEt_3 and the solution mixture was heated at reflux under nitrogen overnight forming a yellow solution, from which the desired product was isolated in a good yield (95 %) as a bright yellow solid. The IR spectrum contained two strong absorption ν (NH_2) bands at 3367 cm^{-1} and 3453 cm^{-1} and a moderate ν (C≡C) absorption at 2208 cm^{-1} and a strong ν (C≡N) absorption at 2230 cm^{-1}. The ^1H and ^{13}C NMR spectra contained the expected, characteristic resonances, including one broad resonance of (NH_2) at δ 3.90 ppm and four pseudo-doublets at δ 6.66, 7.36, 7.58, and 7.61 ppm from the two disubstituted-phenyl rings. The ^{13}C NMR spectrum showed two resonances at δ 86.11 and 95.11 ppm indicating the (C≡C) carbons, eight resonances in the aromatic regions at δ 110.66 – 133.31 ppm arising from the carbons of the two disubstituted-phenyl rings and one resonance at δ 147.45 ppm indicating the (C≡N) carbon. The EI-MS spectra exhibited a molecular ion at *m/z* 218, and two fragment ions shows a dominant peaks at *m/z* 202 representing the loss of NH_2 and at *m/z* 192 indicates the loss of C≡N.

2.9 Synthesis of 11a-11e



R = C_nH_{2n+1}; n = 6 (a), 7 (b), 8 (c), 9 (d), 10 (e)

The synthesis of **11a-11e** involved elimination of water from **10** with each of **2a-2e.** The reaction was performed in refluxing benzene and the flask fitted with Dean-Stark condenser. Recrystallisation of the crude material from DCM-hexane afforded the pale yellow crystalline products in moderate yield (46-64 %). The spectroscopic data show the same characteristics for all compounds. The IR spectra show a weak absorption ν (C≡C) band at 2167 - 2235 cm^{-1}, a strong ν (C≡N) absorption band at 2204 -2217 cm^{-1}, a moderate absorption ν (C=N) band at 1653-1680 cm^{-1} and another strong ν (C-O) absorption at 1106 -1172 cm^{-1}. The ^1H NMR and ^{13}C spectra contained the expected characteristic resonances, including one triplet peak at δ 0.84 - 0.90 ppm with coupling constant J_{HH} = 6.4 - 7.6 *Hz* representing three protons of the alkyl CH_3 moiety. An unresolved set of multiplets between δ 1.28 -1.86 ppm with the correct integrated area is assigned to the eight to sixteen protons of the CH_2 groups, while at δ 4.03 ppm, another triplet peak with coupling constant J_{HH} = 6.4 - 6.8 *Hz*, was observed and assigned to the two protons of the OCH_2 group. In addition to the aromatic resonances, all

compounds also show a singlet peak at δ 8.38 ppm from the imine (CH=N) proton. The ^{13}C NMR spectra show one resonance at δ 14.01 - 14.09 ppm from the CH_3 carbon, and resonances in the region of δ 22.58 - 31.89 ppm indicating the five to nine CH_2 carbons, as appropriate. Each compound also exhibited one resonance at δ 68.29 - 68.32 ppm (ether C-O) and two resonances from the acetylenic (C≡C) carbons between δ 87.97 - 95.13 ppm, while eight resonances in the aromatic regions at δ 111.32 - 132.83 ppm indicated the twelve carbons of three disubstituted-phenyl rings. A singlet resonance at δ 147.45 - 147.48 ppm was observed indicating the nitrile (C≡N) carbon and one resonance around δ 162 ppm indicating the imine (C=N) carbon. The EI-MS spectra exhibited molecular ions at *m/z* 406, 420, 434, 448, and 462 for **11a - 11e** respectively, and all fragment ions for all compounds exhibit the loss of their alkyl chain at *m/z* 322.

2.10 Electronic spectroscopy

Room temperature UV-Vis absorption spectra were recorded in dichloromethane at approximately 2.5 mM. Data are summarised in **Table 2.1**.

Table 2.1: UV-Vis data for selected compounds.

Sample Code	Absorption λ / nm (Extinction Coefficient ε / M^{-1} cm^{-1})		
	Peak 1	Peak 2	Peak 3
4a	295 (56500)	340 (48600)	-
4b	302 (30700)	337 (30800)	-
4c	294 (34800)	345 (28800)	-
6a	289 (25600)	321 (21800)	-
6b	324 (30800)	-	-
7a	306 (31700)	342 (36900)	-
7b	306 (31900)	343 (37100)	-
7c	306 (33900)	340 (40300)	-
7d	308 (38200)	343 (44900)	-
7e	306 (38400)	339 (44900)	-
9a	348 (50500)	-	-
9b	348 (51500)	-	-
9c	349 (38400)	-	-
9d	348 (33000)	-	-
9e	349 (37600)	-	-
11a	349 (31200)	-	-
11b	346 (58500)	-	-
11c	347 (42400)	-	-
11d	349 (50600)	-	-
11e	348 (38000)	-	-
12	282 (15700)	290 (11500)	299 (13700)

The UV-Vis spectrum of **4a**, which has a proton as an acceptor and no alkoxy chains as a donor, displayed two broad bands with λ_{max} = 295 nm (ε = 56500 M^{-1} cm^{-1}), and 340 nm (ε = 48600 M^{-1} cm^{-1}) (**Figure 2.1a**) The addition of a stronger acceptor group at the imine terminus, namely hydroxyl (OH) (**4b**) and bromine (**4c**),

had little effect on the spectral profile, with both compounds displaying two bands near λ_{max} 300 and 340 nm but with somewhat lower extinction coefficients (**Table 2.1**).

The alkoxy-substituted materials **7a** - **7e** displayed similar profiles to those of compounds **4a-4c**, with bands centred around 300 nm and 340 nm. However, in contrast to the compounds **4**, in the case of compounds **7**, the lower energy band was the more intense (**Figure 2.1b**, **Table 2.1**).

More significant changes in the spectral profile were observed in the case of compounds bearing both an acceptor and donor functional group at either end of the molecular framework. For the compounds (**9a** - **9e**), which contain both an electron withdrawing ester ($MeCO_2$) group at the "acetylenic" end of the molecule as well as inductively electron donating alkoxy chains at the "imine" end of the molecular backbone, only one broad band with λ_{max} around 350 nm (ε = 33000 - 50000 M^{-1} cm^{-1}) was observed (**Figure 2.1c**). Compounds (**11a** - **11e**) which are structurally similar, but feature a nitrile acceptor group rather than the ester moiety exhibit the same absorption characteristics, and only one broad shoulder band occurred around λ_{max} 348 nm with extinction coefficient (ε) around 31200 - 50600 M^{-1} cm^{-1} (**Figure 2.1d**).

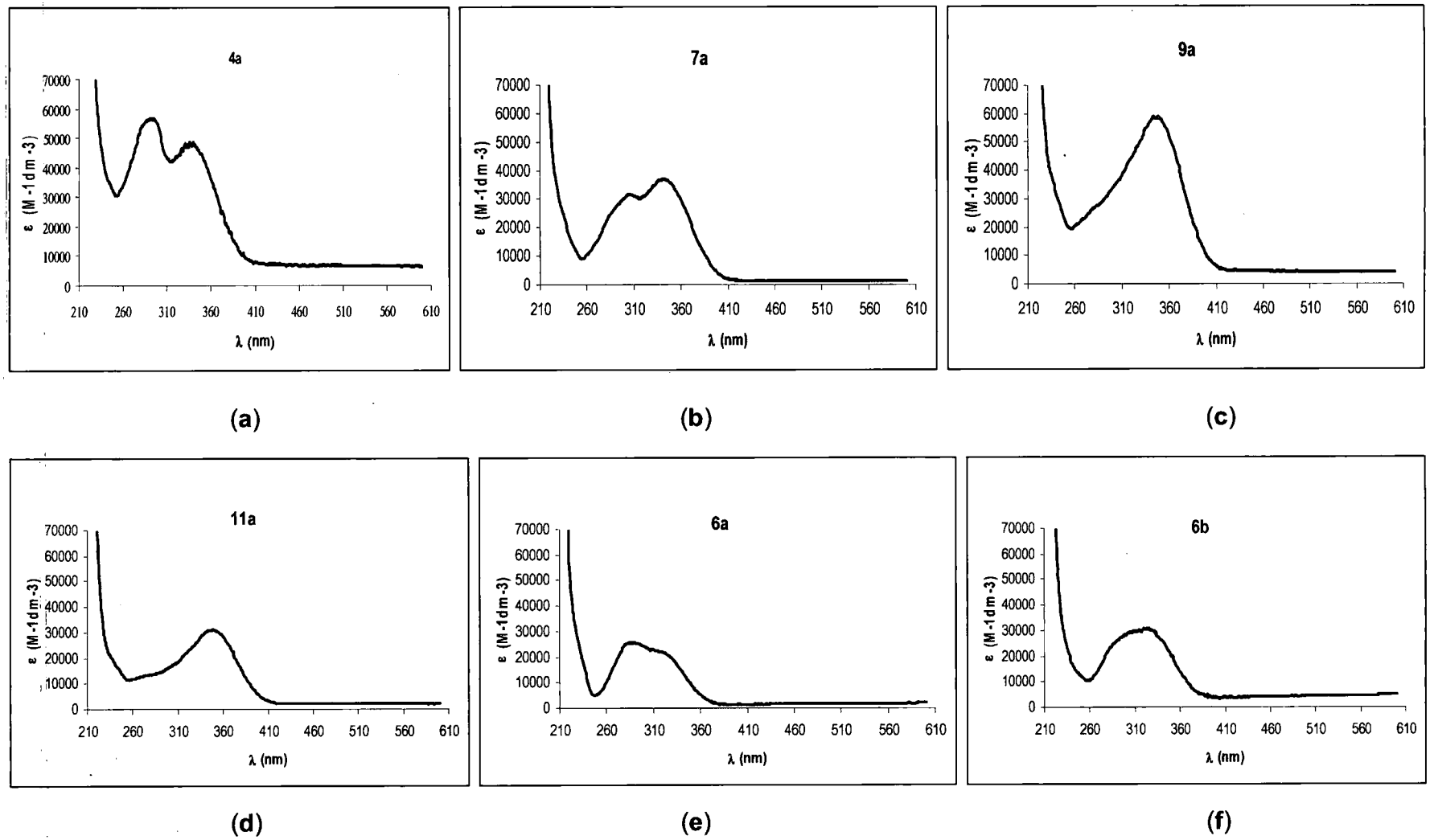


Figure 2.1: UV-vis absorption spectra for selected compounds in each series recorded in dichloromethane at 298 K.

The compounds **4**, **7**, **9** and **11** feature a common D-C_6H_4-CH=N-C_6H_4-C≡C-C_6H_4-A substructure. It was therefore of interest to compare the spectroscopic profiles observed for these hybrid imine/acetylene compounds with those of simple model materials such as **6a**, **6b** and diphenyl acetylene (tolane) to determine if the observed profiles were arising from a simple superposition of the spectra associated with each functional group in isolation, or from a more delocalised chromophore unique to the conjugated molecular framework.

The UV-Vis absorption spectrum of the simple hexyloxy substituted imine **6a** was characterised by two transitions with λ_{max} 289 (ε = 25600 $M^{-1}cm^{-1}$) and 321 (ε = 21800 $M^{-1}cm^{-1}$) nm (**Figure 2.1e**). Introduction of an additional electron withdrawing methyl ester group (**6b**) resulted in red-shift of the higher energy band which was then observed as a shoulder on the high energy side of the band at λ_{max} 324 nm, which had ε = 30800 $M^{-1}cm^{-1}$ (**Figure 2.1f**). In contrast to the relatively broad transitions observed in the imine derived materials, diphenylacetylene (**12**) gave an absorption spectrum with more vibrational structure. The lowest energy absorption band edge was found near 300 nm, and the structure of this spectrum has been described in considerable detail. [65 - 67]

While it is difficult, and unwise, to draw a definitive conclusion on electronic structure based solely upon a limited set of electronic spectral data, it appears on the basis of the similar profiles observed for **4a**, **7a** and the parent imine **6a** that the phenyl acetylene moiety has had more limited influence on the Ar-N=CH-Ar

portion of the molecule. However, the introduction of the additional electron withdrawing CO_2Me (**9a**) or CN (**11a**) groups gives spectral profiles which more closely resemble that to **6b**. It can be tentatively concluded that the imine portion of the molecule dominates the electronic transitions, but that the arylacetylene moiety must be involved to some extent. Further comment on this point must be reserved until an appropriate level computational study of the electronic structure is undertaken. Preliminary calculations (CACHE)[68] indicate that for a model system based on **4a** the HOMO is predominantly acetylene centred, and the LUMO more imine centred. Introduction of donor groups at the imine end of the molecule serves to increase the weight of the imine in the HOMO, whilst acceptor groups at the acetylenic end serve to increase the acetylenic contribution to the LUMO. In systems such as **11a** the HOMO and LUMO are both essentially delocalised over the molecular backbone. A graphical representation of the HOMO and LUMO orbitals and the optimised molecular structures of the model compounds **4-OMe** and **11-OMe** (in which the alkoxy group has been truncated to a methoxy group) are shown in **Figure 2.2** and **2.3**, respectively.

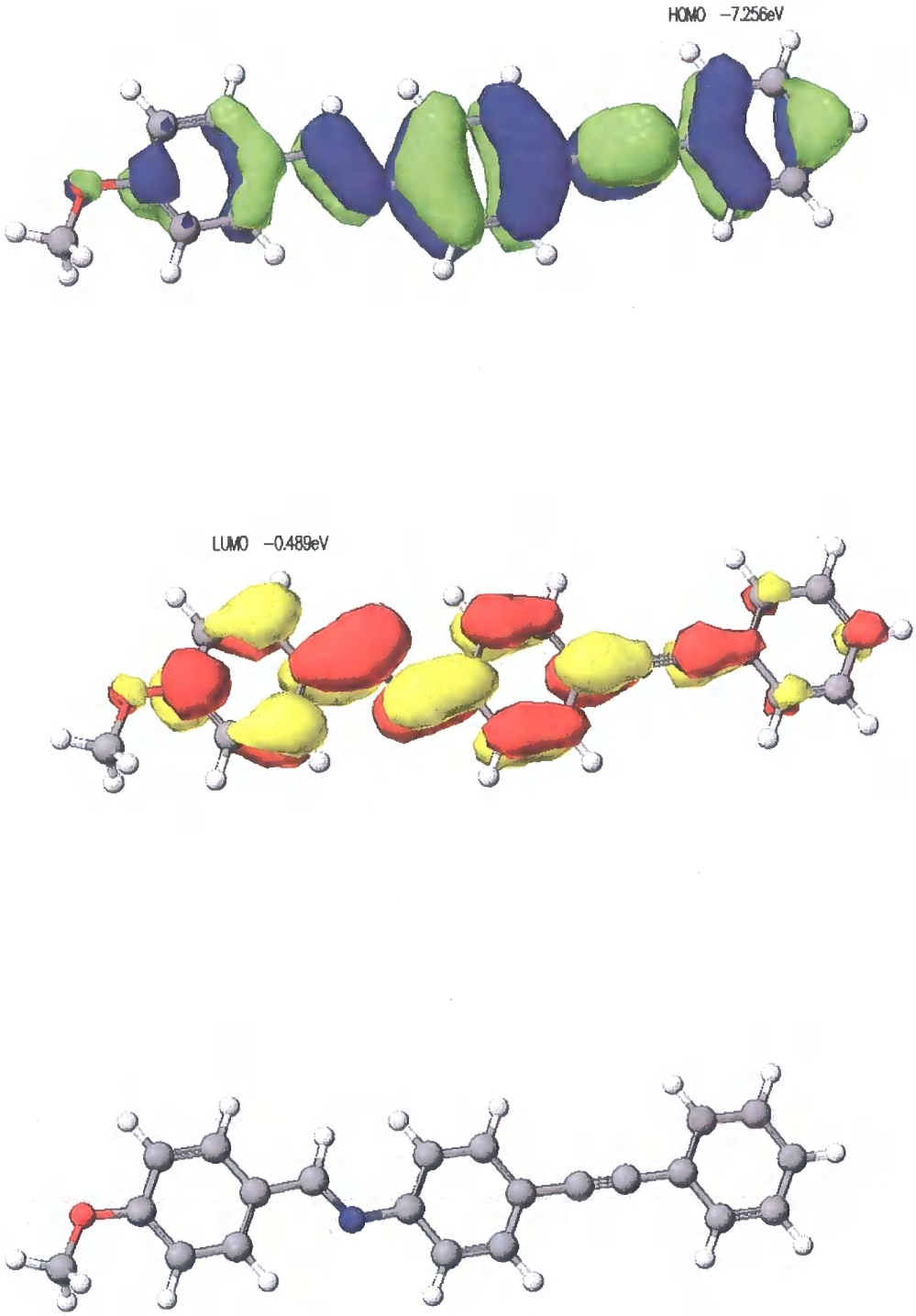


Figure 2.2: Graphical representation of the HOMO and LUMO orbitals, together with the optimised molecular structure of compound **4-OMe** (courtesy of Dr A. Beeby, Department of Chemistry, University of Durham).

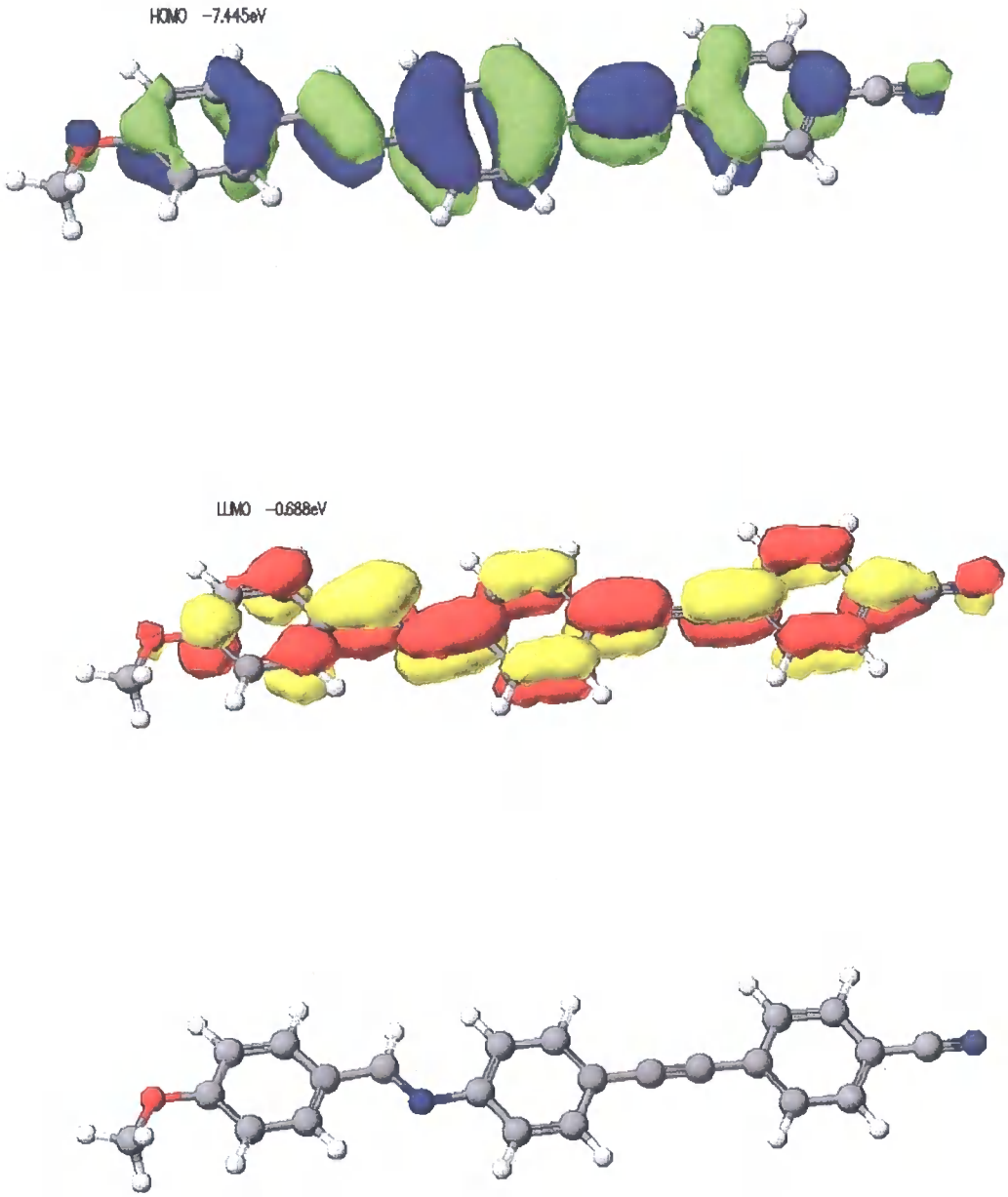


Figure 2.3: Graphical representation of the HOMO and LUMO orbitals, together with the optimised molecular structure of compound **11-OMe** (courtesy of Dr A. Beeby, Department of Chemistry, University of Durham).

2.11 Fluorescence spectroscopy

A considerable amount of interest in the 1,4-bis(phenylene)ethynylene system arises from the fluorescent properties of these compounds, both as a probe of molecular structure in the ground and excited states and as a molecular property which might be exploited in devices, such as OLEDs.[19, 20]

While time constraints prevented a detailed examination of the excited state properties of the hybrid compounds based upon the elementary structure of **4a**, preliminary measurements were undertaken. The emission spectra of **4a**, **4b**, **7a**, **9a** and **11a** were remarkably similar, and characterised by the observation of two emission maxima with shoulders on the low-energy side (**Figure 2.4**). These spectral profiles were quite distinct from the more vibrationally structured emission observed for the simple alkoxy imine **6a.** Although at the preliminary stage, these data support the supposition that the π-system in the mixed imine/acetylene systems is delocalised over both functional groups.

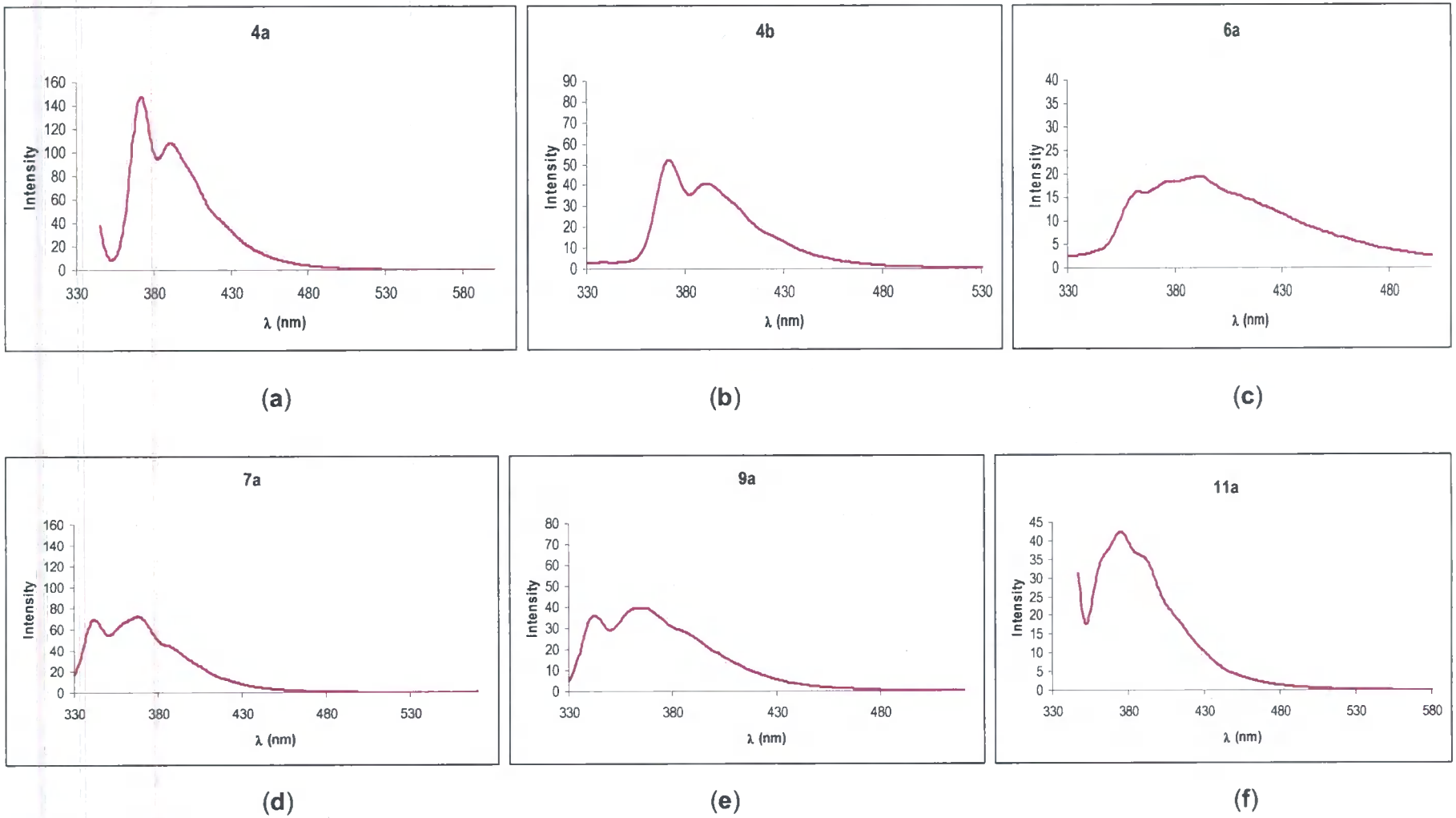


Figure 2.4: The emission spectra for selected compounds in each series recorded in cyclohexane at 298 K.

Chapter 3. Introduction to Liquid Crystalline Materials

The discovery of liquid crystal science is attributed to the Austrian botanist Friedrich Reinitzer, who in 1888 described cholesteryl benzoate as having two melting points.This double melting behaviour was found to be related to the formation of a liquid crystalline phase, now known as the cholesteric phase.[15, 32]

Liquid crystals are ordered, anisotropic fluids, which exist in certain materials between an ordered crystalline state and an isotropic liquid. Liquid crystalline materials (*mesogens*) possess *orientational* order in addition to the three-dimensional *translational* (positional) order present in conventional crystalline solids. The origin of this type of behaviour is the highly anisotropic molecular shape of liquid crystalline materials. The gradual loss of intermolecular interactions upon heating gives rise to a decrease in the translational and orientational order and the formation of various liquid crystal phases. When the material is heated beyond to its *clearing point*, and becomes a conventional isotropic liquid, all of the positional and orientational order in the material has been lost. This kind of material where the degree of order changes with increasing temperature is known as a *thermotropic liquid crystal*.

In addition, certain materials can be described as *lyotropic liquid crystalline materials*. In a lyotropic LC material the molecular system of interest is mixed with a solvent and the degree of order present in the system is dependent on the

concentration. These lyotropic materials are commonly surfactants and exhibit phases with lamellar, cubic or hexagonal structures. An example of a lyotropic liquid crystal is cetyltrimethylammonium bromide (CTAB), shown in **Figure 3.1**, which can exhibit liquid crystalline phases in the presence of water. It should be noted that lyotropic phases are also temperature dependent.

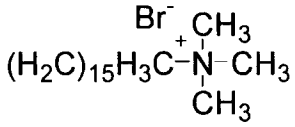


Figure 3.1 : cetyltrimethylammonium bromide (CTAB)

A mesogen may exhibit both lyotropic and thermotropic phase behaviour, and such systems are called *amphotropic*. To date, some 80,000 different compounds, low molecular mass as well as polymeric materials, exhibiting liquid crystal properties have been reported. [32]

3.1 Molecular Structure of Liquid Crystalline Materials

Thermotropic liquid crystals can be categorised with respect to their molecular shape as *calamitic* (rod-like) molecules, and *discotic* (disc-like) molecules. A common structural feature of calamitic mesogens is a rigid "mesogenic core", which are usually comprised of aromatic groups such as phenyl or biphenyl groups. Mesogens usually bear *at least one flexible aliphatic chain* which influences the melting point and the tendency of a molecule to form layered phases. A *polar end-*

group may also be present to increase the polarisation within the molecule, a common example being the cyano group in cyanobiphenyl liquid crystals. The components of the mesogen described are usually arranged in a linear fashion to give the anisotropic shape necessary for mesomorphic behaviour. Discotic mesogens generally have six flexible aliphatic chains symmetrically distributed around a rigid aromatic disc-shaped core (**Figure 3.2**). Numerous variations to these general molecular structures may be implemented, leading to the large variety of mesogenic compounds known today.

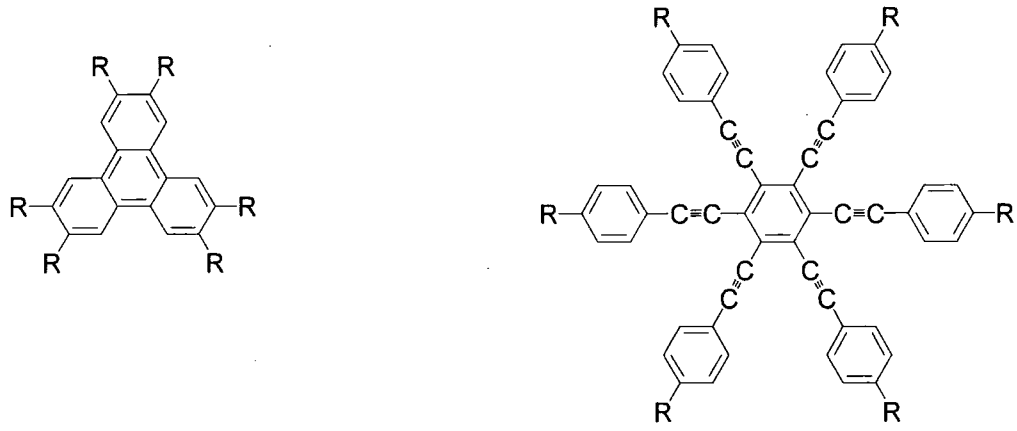


Figure 3.2: The examples of discotic mesogens[32]

3.2 Liquid Crystal Nomenclature

The initial classification system used to describe liquid crystal phases was introduced by Friedel in 1922. At that time not very many mesogenic compounds were known and broad generalised classifications were sufficient. Mesophases with long range orientational order were classified as *nematic phases*; the term

cholesteric was assigned to describe nematic phases exhibited by chiral compounds such as cholesterin. The term *smectic phase* was chosen to describe systems in which additional positional order is present with the formation of layered structures within the liquid crystal phase.

The large number of liquid crystalline materials that now exist and the more advanced techniques available for probing the structure of liquid crystal phases, such as X-ray and neutron diffraction, has necessitated a more systematic classification of the structure of liquid crystal phases. For example in the modern classification of achiral smectic phases, several classes exist namely smectic A (Sm A) and smectic C (Sm C), and these phases may be distinguished by their distinct, characteristic textures observed by polarised light microscopy.

3.3 Identification of Phases

There are numerous methods available nowadays to identify mesophases, including:

1. Thermal analysis.
2. Hot stage polarised optical microscopy.
3. X-ray diffraction and neutron scattering studies.
4. Miscibility studies.

and it is common for combinations of these techniques to be applied to the task of identifiying a given mesophase. A combination of thermal analysis, including

differential thermal analysis (DTA) and differential scanning calorimetry (DSC), and hot stage polarised optical microscopy is most commonly used for phase identification. In both DTA and DSC the heat evolved or absorbed by the compound in going from one state of matter to another is detected and plotted against temperature. The resulting plot is known as a *thermogram*, from which the temperature at which phase changes occur and the enthalpy associated with the transition can be obtained. The use of both heating and cooling cycles can be used to determine which of the transitions are reversible. [1, 33]

While thermal analysis provides information on the number and temperature ranges of individual mesophases, hot-stage polarised optical microscopy is used as the main technique for identifying individual mesophase structure for reasons of simplicity and convenience. Hot-stage polarised optical microscopy is an indirect method that relates characteristic optical textures to each phase with structural models of various phases. This technique requires a small quantity of the mesomorphic material to be sandwiched between a microscopic slide and cover-slip. The sandwiched assembly is then placed into the hot stage assembly of a polarizing microscope where it can be heated and cooled accurately in order to view the material at the required temperature. Different mesophases give rise to characteristic *optical textures* when viewed with polarised light. [16, 32]

The assignment based on these textures can be cross-checked with a direct structural analysis such as variable temperature X-ray diffraction. [34, 35]

Miscibility studies are also helpful in the identification of liquid crystal phases. A sample with an unknown liquid crystalline phase is mixed with a known and fully characterized liquid crystal, with complete miscibility across the phase diagram of the mixtures being taken as an indication that the known and unknown phases are identical.[1]

3.4 General Structure of Liquid Crystal Phases

With a view to later discussion, it is helpful at the present stage to consider the substructure and order associated with some of the most commonly encountered mesophases, and in particular those which will be encountered later in this thesis.

3.4.1 The Nematic Phase

The *nematic phase* is the least ordered mesophase. While individual molecules can adopt any orientation, on average molecules in the bulk ensemble are oriented in a particular direction. This direction can be described by the vector quantity *n*, known as the *director*. The director is the average local direction of the long molecular axis and represents the direction of the optic axis of the system (**Figure 3.3a**).

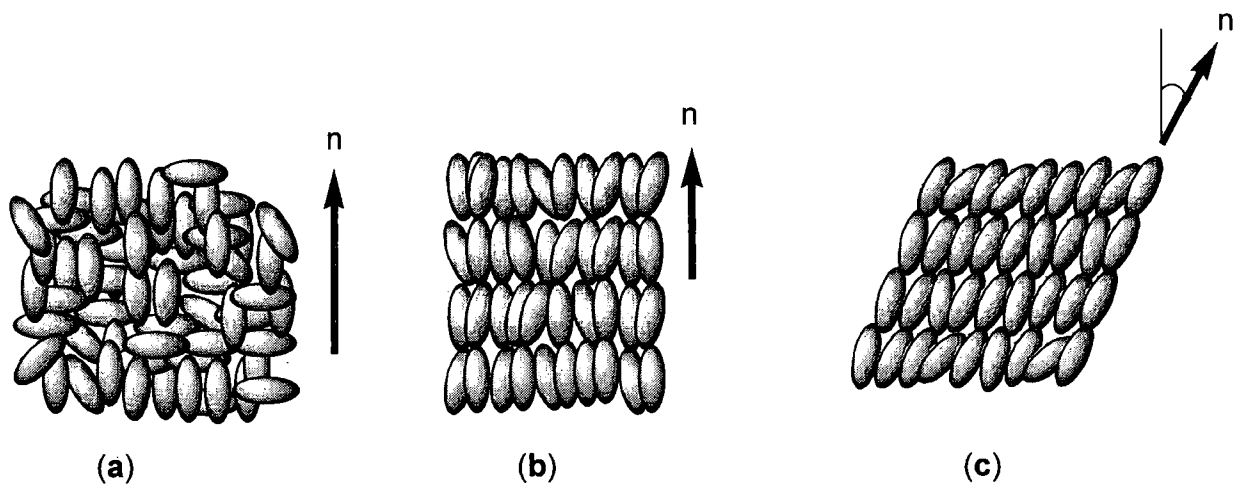


Figure 3.3: Generalized structure (**a**) nematic, (**b**) smectic A (**c**) smectic C.

3.4.2 The Fluid Smectic Phases

Lowering the temperature of a nematic phase can lead to a phase transition arising from the introduction of positional order about the molecules' centres of mass. These layered phases which feature both *orientational* and *positional* order are known as *Smectic phases.*

3.4.3 The Smectic A and Smectic C Phases

In the smectic A phase the director, and thus the optical axis, are perpendicular to the smectic layer plane, as shown in **Figure 3.3b**. It must of course be remembered that these are fluid phases with molecules able to diffuse readily between the layers, and as a consequence the orientational order within any layer is far from being perfect.

The smectic C phase has positional order similar to that of smectic A, but with the director tilted with respect to the smectic layer normal (**Figure 3.3c**).

3.4.4 Other phases

There are many other mesophases known, which feature higher degrees of order within and between layers. A complete description of these higher order phases falls out of the scope of this thesis, and for a complete description, the reader is referred to the excellent summaries given in the books by Demus[35], and Dierking[32] and their respective colleagues. However, for the reader's convenience, a summary of the terminology and structural characteristics of the mesophases most relevant to this work is given in **Tables 3.1 to 3.3**.

Table 3.1: General characteristic structural features of nematic and achiral smectic.[32]

Phase	Range of Orientational Order	Range of Positional Order	Orientation of Long Molecular Axis	Distribution of Molecular centers of Mass
N	Long	-	Angular	Isotropic
SmA	Short	Short	Orthogonal	Isotropic
SmC	Short	Short	Tilted	Isotropic
SmB (hexatic B)	Long	Short	Orthogonal	Hexagonal
SmI	Long	Short	Tilted (to apex)	Hexagonal
SmF	Long	Short	Tilted(to side)	Hexagonal

Most Ordered →

Iso < N < Sm A < Sm C < Sm B < Sm M < Sm I < Sm F < Crystal

← Least Ordered

Table 3.2: Most commonly observed natural textures of different liquid crystals phase (structural characteristics).[32]

Phase	Nematic	Smectic A	Smectic C
Textures	Schlieren Marble Thread-like Pseudo-isotropic	Fan-shaped Homogenous Focalconic Polygonal	Domain Focalconic Schlieren Broken-fan shaped

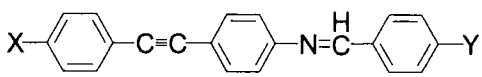
Table 3.3: The definitions of terminologies relevant to this work.[35]

Term	Definition
Thermotropic Liquid Crystals	a liquid crystalline materials formed by heating a solid or cooling an isotropic liquid, or by heating or cooling a thermodynamically stable mesophase
Lyotropic liquid crystalline materials	a liquid crystalline materials formed by dissolving an amphiphilic mesogen in suitable solvents, under appropriate conditions of concentration and temperature
Amphotropic Material	a compound which exhibits thermotropic as well as lyotropic mesophases
Calamitic Mesophase	a mesophase formed by molecules or macromolecules with rod or lath-like molecular structure
Discotic Mesogen	a mesogen composed of relatively flat, disc- or sheet shaped molecules
Mesogenic Compounds (mesomorphic compounds)	a compound that under suitable conditions of temperature, pressure and concentration can exist as mesophase

3.5 Thermal Analysis and Mesomorphic Behaviour of Compounds 7, 9 and 11

Three series of Schiff-Base compounds **7, 9** and **11** containing one of three different polar head groups (X) and an alkoxy tail of variable chain length (Y) have been synthesised (**Scheme 3.1**). The combination of rigid molecular framework and a flexible tail suggests that these systems might well exhibit liquid crystalline phases at elevated temperatures.

In general, liquid crystalline phase behaviour in linear molecular systems derived from multiple aromatic rings is enhanced by the incorporation of linking groups which promote a fully planar arrangement.[69, 70] In the present case, the imine CH=N unit confers a measure of rigidity to the molecule by conjugation between two aromatic rings and may increase the mesophase thermal stability of compounds such as **7**, **9** and **11** over more conventional systems based upon 1,4-bis(phenylethynyl)benzene. In these fully acetylenic derivatives the greater rotational distribution of the phenyl rings about the long molecular axis can reduce intermolecular interactions, ultimately giving rise to more limited thermal ranges associated with individual mesophases (see **Chapter 1**).



X = H (7), $MeCO_2$ (9), CN (11),

Y = OC_nH_{2n+1}; n = 6 (a), 7 (b), 8 (c), 9 (d), 10 (e),

Scheme 3.1: The Schiff-Base liquid crystals examined in this work

The identification of liquid crystalline phases in compounds **7**, **9** and **11** was undertaken using an Olympus BX51 polarising microscope fitted with a Linkam TMS 94 temperature controller and a Linkam THMS 600 hot stage, with expert help in interpretation of the optical textures from Dr D. P. Lydon of our research group. Thermal analysis was undertaken within the Department of Chemistry by Mr W. D. Carswell using a Perkin Elmer Pyris 1 DSC. All compounds were heated at 10 °C/min on the hot stage for the observation of liquid crystalline optical textures, and transition temperatures checked against DSC data.

Compound **7a** underwent a reversible crystalline transition (i.e a transition in the solid state between two crystal forms) at ca. 108 °C. A nematic phase was detected between 140-169 °C before clearing to the isotropic liquid. The observation of Schlieren textures with two- and four-point brushes which, when deformed with a mechanical probe, displayed flashing-type clearly indicated the liquid crystalline state to be a nematic mesophase.

The behaviour of **7b** was similar to that of **7a**, undergoing a reversible crystal-crystal phase transition at 96 °C. However, in addition to the nematic phase between 143-165 °C, an unidentified viscous phase was also detected at somewhat lower temperatures.

In compound **7c** the usual combination of DSC and polarised optical microscopy revealed both smectic and nematic phases the identification of which was more

obvious during the cooling cycle from the isotropic liquid. Below the isotropic liquid, a nematic phase exists between148 °C which clears to isotropic at 163 °C. The nematic nature of the LC phase was identified by the observation of four and two point brushes in conjunction with very fluid, flashing behaviour of this phase when pressed with a mechanical probe.

A sample of the material was cooled from the clearing at 10°C per minute to 148°C, where formation of a fan texture occurred, assigned as a smectic A phase (**Figure 3.4a**). Upon further cooling to 143 °C a transition occurs, punctuated by the appearance and disappearance of transition bars (**Figure 3.4b** and see sequence of micrographs on the accompanying CD), ultimately leading to a smoother fan texture. This is observation is consistent with smectic A to smectic B transition. There has been disagreement amongst experts regarding the significance of the transition bars in the smectic A to smectic B transition. The suggestion has been made that the presence of these transition bars indicates an impure sample, however, Gray and Goodby[15, 16, 35] state the changes are due to changes in the structure of the material and surface effects occurring at the transition point. At 93°C degrees the sample forms a crystal phase.

In compound **7d,** the material softened on heating to 99 °C which formed a viscous phase observed under microscope. At 134 °C an image was recorded of this phase as seen under the microscope for purpose of illustration, and is included in the accompanying CD. This soft phase transformed into a smectic A phase at 143

°C, identified by the fluid, homeotropic texture (viewed with crossed polarisers **Figure 3.4c** and parrallel polarisers **3.4d**). A further transition to a nematic phase occurred at 150 °C. This nematic phase clears to the isotropic phase above 159 °C

Compound **7e** which carries the longest alkoxyl chain in the series investigated here displayed a solid state transition (96 °C) which melted to give a smectic A phase at 142 °C which on further heating gave a nematic phase (152 °C) before clearing to the isotropic liquid at 157 °C.

To provide some comparison with the family of compounds **9** and **11** which feature polar head groups, the thermal behaviour of **9c** and **11c** were also examined. In general the properties of **9c** and **11c** were similar to those of **7**, but phase changes occurred at much higher temperatures, presumably as a consequence of the additional dipolar interactions in these cases.

Compound **9c** softens to undergo a crystal to crystal transition at 127 °C and softens to form a viscous phase at 146 °C. A smectic A phase is formed at 190 °C which exhibited a homeotropic texture (i.e. a dark film). The smectic A phase was found to persist over a considerably greater temperature range than the compounds **7** and the nematic phase, which exhibited the usual Schlieren textures and flashing type behaviour when the coverslip of the sample is probed with a

needle, was not formed until 242 °C. This ester functionalised material maintained good thermal stability until the clearing point at 268°C.

In this context it is worth noting the work of Yang et. al[70] who have examined the liquid crystalline states associated with alkoxy terminated fluoro-containing azobenzene derivatives. These workers found a similar enhancement of smectic phases as the length of the alkoxy tail was increased.[70]

The nitrile compound **11c** softened at 136 °C, to form an unidentified viscous phase. A transition to the smectic A phase was observed at 155 °C by the presence of focal conic texture (**Figure 3.4e**). The assignment as a smectic A phase was confirmed by the observation of fan textures and polygonal textures during the cooling cycle when the phase was approached from above 208 °C (**Figure 3.4f**). Above 210 °C a nematic phase was formed exhibiting two and four point Schlieren brushes. The onset of rapid decomposition above 246°C, prevented the determination of a precise clearing point, however no Schlieren texture was visible above 255°C.

In conclusion, compounds **7** display good thermal stability and well-defined nematic LC phases. The increase in length of the alkoxy tail or introduction of a polar head group as in **9c** and **11c** resulted in the observation of additional smectic A phases and a destabilisation of the nematic phase. Compound **9c** was remarkably thermally robust. For the purposes of comparison, all the data relating to the observed mesophases, transition temperatures and enthalpies of formation are summarised in **Table 3.4**.

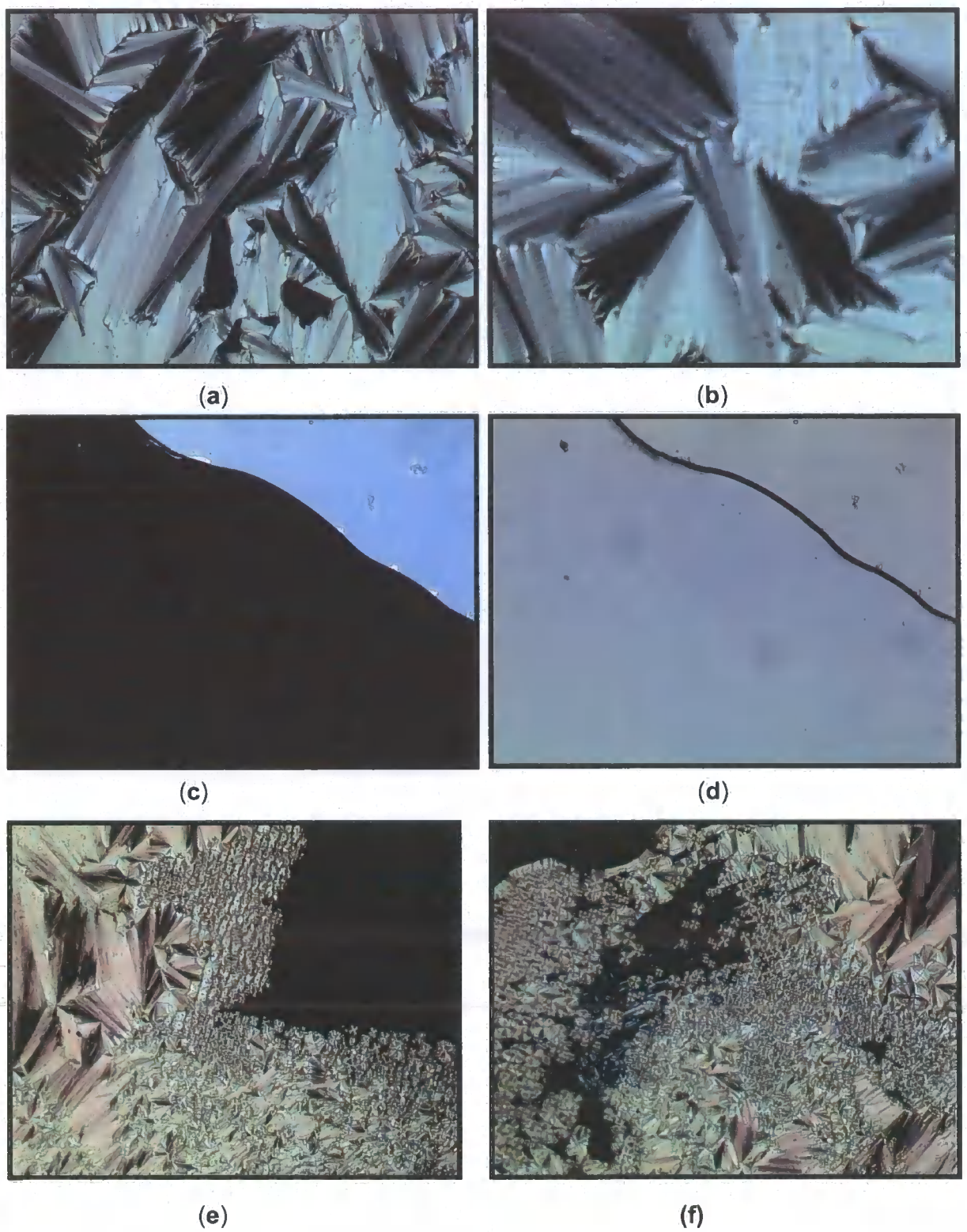


Figure 3.4: The different optical textures associated with the smectic A phase of (a) **7c** (b) **7c** (c) **7d** (d) **7d** (e) **11c**.(f) **11c**

Table 3.4 : The values of the transition temperature and the entalphy change associated with of the phases for the selected compounds.

Acceptor (X)	No. of Alkoxy Chain (n)	Transition temperatures °C, (ΔH, kJmol^{-1})					
		Cr	Viscous Phase	SmB	SmA	N	I
H	6	107.8 (9.02)				139.8 (9.58)	169.2 (0.76)
	7	96.0 (25.85)	140.8 (10.57)			143.2 (2.95)	164.6 (0.32)
	8			92.5 (21.87)	142.7 (5.26)	148.00 (2.81)	163.0 (0.92)
	9		99.0 (33.62)		142.9 (5.59)	150.2 (3.76)	159.2 (0.81)
	10		96.0 (33.96)		142.5 (5.54)	151.8 (4.00)	157.2 (0.96)
MeO(CO)	8	127.3 (7.33)	146.0 (32.24)		190.0 (52.52)	242.0 (2.26)	268.0 (0.91)
C≡N	8		136.0 (1.54)		155.5 (5.93)	208.0 (0.04)	246 (*)

* = decomposition point.

Chapter 4. General Experimental Procedure

4.1 Reagents, Materials, and Solvents

All experimental procedures involving air sensitive reagents were performed under an atmosphere of purified nitrogen using standard Schlenk techniques. All solvents in reactions were dried and distilled prior to use using standard methods.[71] Unless otherwise noted, all chemicals were purchased from commercial sources and used without further purification. Literature methods were used to prepare 4-phenylethynylaniline,[64] 4-hexyloxybenzaldehyde,[72] $Pd(PPh_3)_4$,[73] and $Pd(PPh_3)_2Cl_2$.[74]

4.2 NMR, Mass, UV-vis, Fluorescence Spectroscopy and Elemental Analysis

^1H and ^{13}C spectra were obtained using Bruker 400 Ultrashield B ACS 60 spectrometer from solution in either $CHCl_3$ or C_6H_6, using the solvent resonances as internal references. EI mass spectra were obtained using Micromass Autospec or Finigan Trace MS mass spectrometers. Infrared spectra were recorded from neat liquids, or as nujol mulls from samples mounted between NaCl discs using a Nicolet Avatar FT-IR spectrometer. UV-vis spectra were obtained in a 1 mm path length quartz cell with the ATI Unicam UV-2 spectrophotometer and the fluorescence spectra were obtained in a 1 cm path length quartz cell with a Perkin Elmer LS 50 B Luminescence Spectrometer.

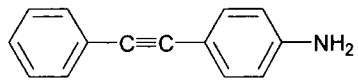
Elemental analyses were obtained using an Exeter Analytical CE-440 Elemental Analyser, by Mrs J. Dorstal of the Department of Chemistry University of Durham.

4.3 Thermal Analysis and LC Phase Identification

Thermal analysis was undertaken using a Perkin Elmer Pyris 1 DSC. While the identification of liquid crystalline phases of the synthesised compounds was undertaken using an Olympus BX51 polarising microscope fitted with a Linkam TMS 94 temperature controller and a Linkam THMS 600 hot stage.

4.4 Experimental

4.4.1. 4-Phenylethynylaniline[64]

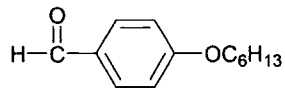


1

Dry *i*-Pr_2NH (45 ml) and THF (70 ml) were introduced to an oven-dried 250 ml Schlenk flask and rigorously deoxygenated by three freeze-pump-thaw sequences. Solid 4-iodoaniline (8.80 g, 40.0 mmol) and ethynylbenzene (9.0 g, 60 mmol) were added followed by $Pd(PPh_3)_4$ (2.31 g, 2.00 mmol) and CuI (0.38 g, 2.0 mmol). The solution was stirred under nitrogen for an hour at room temperature forming a brown solution which was filtered and filtrate obtained diluted with EtOAc (ca. 100 ml) and extracted with brine. The organic layer was separated and dried over $MgSO_4$ and solvent removed *in-vacuo*. The brown solid was then recrystallised from DCM-hexane to afford the title compound (6.59 g, 75 %). IR (nujol): ν (NH_2) 3377 s, 3476 s; ν (C≡C) 2212 m cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 3.76 (br, 2H, NH_2); 6.63, 7.50 (AB, 4H, C_6H_4); 7.29 - 7.36 (m, 5H, C_6H_5). ^{13}C NMR (100 MHz, C_6D_6): δ 87.99, 91.33 (2 x s, C≡C); 114.82, 121.08, 123.93, 125.73, 127.65, 128.25, 131.76, 132.94 (8 x s, Ar). EI^+ - MS (*m/z*): 193 [M^+]; 176 [$M-NH_2]^+$. Anal. Calcd. for $C_{14}H_{11}N$: C, 87.05; H, 5.70; N, 7.25. Found: C, 86.21 H, 5.65 N, 7.06.

4.4.2 4-Alkoxybenzaldehydes General Procedure:

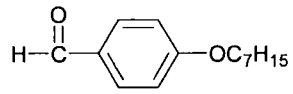
4-Hexyloxybenzaldehyde[72]



2a

Dry DMF (60.0 ml) was introduced to an oven-dried 100 ml round bottom flask, followed by 4-hydroxybenzaldehyde (13.30 g, 109.0 mmol), bromohexane (18.0 g, 109.0 mmol), K_2CO_3 (15.00 g, 109.00 mmol) and KI (1.00 g, 6.00 mmol). The solution was heated at 80 °C in the nitrogen atmosphere overnight forming an orange solution and a white precipitate of the inorganic salt by-products. The progress of the reaction was monitored with TLC (Hexane: EtOAc; 70:30) .Once the reaction was complete, the reaction mixture was cooled to room temperature, poured into ca. 150 ml cold water and extracted with diethylether (ca. 150ml). The organic layer was separated giving a brown solution which was dried over $MgSO_4$ and the solvent removed *in-vacuo.* Purification of the crude product was achieved by vacuum distillation (ca. 1mm Hg). Two fractions of colourless oil obtained, the first (80 °C - 110 °C) contained a mixture of reagents and some product whilst the second fraction (120 °C - 140 °C) was found to be the pure title compound. (10.4 g, 46.3 %). IR (neat): ν (C(=O)H) 2731 m; ν (C=O) 1705 s; ν (C-O) 1152 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=8.8 *Hz*, 3H, CH_3); 1.25 - 1.73 (m, 8H, CH_2); 3.94 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.91, 7.74 (AB, 4H, C_6H_4); 9.86 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.96 (s, CH_3); 22.70, 25.61, 29.00, 31.49 (4 x s, CH_2); 68.39 (s, C-O); 114.12, 115.05, 129.77, 132.15 (4 x s, C_6H_4); 190.61 (s, C=O). EI^+ - MS (*m/z*): 206 [M^+]; 121 [$M-C_6H_{13}$]$^+$.

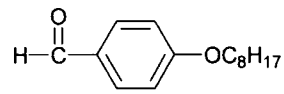
4-Heptyloxybenzaldehyde



2b

The compound **2b** (15.00 g, 67.8 %, b.p. 165 – 180 °C, 1mm Hg) was prepared in the general manner from 4-hydroxybenzaldehyde (12.3 g, 100.5 mmol), bromoheptane (18.0 g, 100.50 mmol), K_2CO_3 (13.9 g, 100.5 mmol) and KI (1.00 g, 6.00 mmol) in dry DMF (60 ml). IR (neat): ν (C(=O)H) 2731 m; ν (C=O) 1715 s; ν (C-O) 1174 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=8.8 *Hz*, 3H, CH_3); 1.30 - 1.84 (m, 10H, CH_2); 4.01 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.98, 7.81 (AB, 4H, C_6H_4); 9.86 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.02 (s, CH_3); 22.72, 25.90, 28.97, 29.21, 31.71 (5 x s, CH_2); 68.39 (s, C-O); 114.37, 115.05, 129.77, 132.15, (4 x s, Ar); 190.69 (s, C=O). EI^+ - MS (*m/z*): 220 $[M^+]$; 121 $[M\text{-}C_7H_{15}]^+$.

4-Octyloxybenzaldehyde

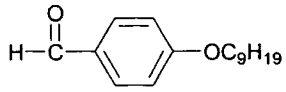


2c

The compound **2c** (12.70 g, 58.20 %, b.p. 193 °C – 210 °C 1 mm Hg) was prepared from 4-hydroxybenzaldehyde (11.4 g, 93.3 mmol,), bromooctane (18.0 g, 93.3 mmol), K_2CO_3 (12.9 g, 93.3 mmol) and KI (1.00 g, 6.00 mmol) in the manner described above. IR (neat): ν (C(=O)H) 2730 m; ν (C=O) 1716 s; ν (C-O) 1171 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.80 (t, *J*=8.8 *Hz*, 3H, CH_3); 1.20 - 1.79 (m, 12H, CH_2); 3.95 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.91, 7.46 (AB, 4H, C_6H_4); 9.79 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.07 (s, CH_3); 22.77, 23.01, 25.93, 26.09,

29.49, 31.59 (6 x s, CH_2); 68.43 (s, C-O); 114.00, 115.09, 129.75, 131.56 (4 x s, Ar); 190.54 (s, C=O). EI^+ - MS (*m/z*): 234 [M^+]; 121 [M-C_8H_{17}]$^+$.

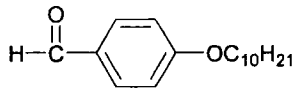
4-Nonyloxybenzaldehyde



2d

The compound **2d** (15.40 g, 71.12 % b.p. 222 °C - 245 °C 1 mm Hg) was prepared from 4-hydroxybenzaldehyde (10.6 g, 87.0 mmol), bromononane (18.0 g, 87.0 mmol), K_2CO_3 (12.0 g, 87.0 mmol) and KI (1.00 g, 6.00 mmol) in the manner described above. IR (neat): ν (C(=O)H) 2731 m; ν (C=O) 1716 s, ν (C-O) 1170 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.80 (t, *J*=8.8 *Hz*, 3H, CH_3); 1.20 - 1.80 (m, 14H, CH_2); 3.95 (t, *J*=6.8 *Hz*, 2H, OCH_2), 6.91, 7.46 (AB, 4H, C_6H_4); 9.79 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.07 (s, CH_3); 22.64, 25.95, 26.10, 29.22, 29.49, 31.68, 31.85 (7 x s, CH_2); 68.42 (s, C-O); 114.12, 115.05, 129.77, 132.15 (4 x s, Ar); 190.69 (s, C=O). EI^+ - MS (*m/z*): 249 [M^+]; 121 [M-C_9H_{19}]$^+$.

4-Decyloxybenzaldehyde

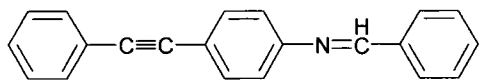


2e

The compound **2e** (10.20 g, 47.80 % b.p. 258 °C - 275 °C 1 mm Hg) was prepared from 4-hydroxybenzaldehyde (9.94 g, 81.5 mmol), bromodecane (18.0 g, 81.5 mmol), K_2CO_3 (11.2 g, 81.5 mmol) and KI (1.00 g, 6.00 mmol) in the manner described above. IR (neat): ν (C(=O)H) 2715 m; ν (C=O) 1722 s; ν (C-O) 1170 s

cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, *J*=8.8 *Hz*, 3H, CH_3); 1.21 - 1.80 (m, 16H, CH_2); 3.95 (t, *J*=6.8 *Hz*, 2H, OCH_2), 6.91, 7.45 (AB, 4H, C_6H_4); 9.78 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.07 (s, CH_3); 22.64, 22.76, 24.06, 25.95, 29.05, 29.22, 31.47, 31.85 (8 x s, CH_2); 68.43 (s, C-O); 114.32, 115.05, 129.74, 132.24 (4 x s, Ar); 190.69 (s, C=O). EI^+ - MS (*m/z*): 262 $[M^+]$; 121 $[M\text{-}C_{10}H_{21}]^+$.

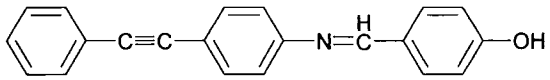
4.4.3. *N*-benzylidene-4-(phenylethynyl)aniline



4a

Benzaldehyde (0.25 g, 2.5 mmol) was added to 4-phenylethynylaniline (0.40 g, 2.1 mmol) and mixed to form a brown oily solution which was allowed to crystallise over 2 hours. The solid mass which formed was then filtered and washed with EtOH followed by hexane. Recrystallisation from DCM-Hexane afforded the title compound as cream coloured crystals. (0.51 g, 87 %). IR (nujol): ν (C≡C) 2212 w; ν (C=N) 1636 m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18, 7.65 (AB, 4H, C_6H_4); 7.32 - 7.52 (m, 5H, C_6H_5); 7.67 - 7.92 (m, 5H, C_6H_5); 8.47 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.51, 90.03 (2 x s, C≡C); 121.02, 121.15, 123.42, 125.66, 126.57, 128.25, 128.38, 130.23, 131.10, 132.11, 132.60, 133.98 (12 x s, Ar); 161.23 (s, C=N). EI^+ - MS (*m/z*): 281 $[M^+]$; 203 $[M\text{-}C_6H_6]^+$; 177 $[M\text{-}C_7H_6N]^+$. Anal. Calcd. for $C_{21}H_{15}N$: C, 89.68 H, 5.34 N, 4.98. Found C, 88.84 H, 5.32 N, 4.48.

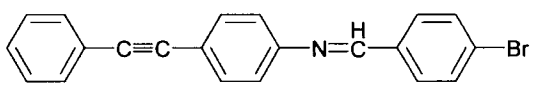
4.4.4. 4-({[4-Phenylethynyl)phenyl]imino}methyl)phenol



4b

The compound **4b** (0.42 g, 68.32 %) was prepared from 4-hydroxybenzaldehyde (0.30 g, 2.48 mmol) and (0.40 g, 2.07 mmol) in the manner described above. IR (nujol): ν (OH) 3310 br; ν (C≡C) 2214 w; ν (C=N) 1627 m cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (br, 1H, OH); 7.19, 7.79 (AB, 4H, C_6H_4); 7.28 - 7.35 (m, 5H, C_6H_5); 7.65, 7.79 (AB, 4H, C_6H_4); 8.48 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.88, 90.02 (2 x s, C≡C); 121.10, 121.56, 123.30, 125.55, 126.13, 128.25, 128.37, 130.03, 131.98, 133.12, 132.60, 133.87 (12 x s, Ar); 161.03 (s, C=N). EI^+ - MS (*m/z*): 297 $[M]^+$; 280 $[M\text{-}OH]^+$. Anal. Calcd for $C_{21}H_{15}NO$: C, 84.85 H, 5.05 N, 4.71. Found C, 83.79 H, 5.01 N, 4.69.

4.4.5. *N*-(4-bromobenzylidene)-4-(phenylethynyl)aniline

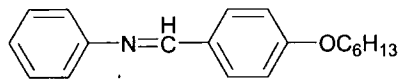


4c

The compound **4c** (0.42 g, 56.36 %) was prepared from 4-bromobenzaldehyde (0.46 g, 2.48 mmol) and 4-phenylethynylaniline (0.40 g, 2.07 mmol) in the manner described above. IR (nujol): ν (C≡C) 2210 w; ν (C=N) 1651 m cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20, 7.79 (AB, 4H, C_6H_4); 7.34 - 7.53 (m, 5H, C_6H_5); 7.56, 7.63 (AB, 4H, C_6H_4); 8.48 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 89.28, 89.92 (2 x

s, C≡C); 121.03, 121.17, 123.32, 125.77, 126.17, 128.25, 128.36, 130.24, 131.58, 132.11, 132.62, 134.99 (12 x C, Ar); 159.12 (s, C=N). EI^+ - MS (*m/z*): 360 $[M]^+$; 280 $[M\text{-}Br]^+$. Anal. Calcd for $C_{21}H_{14}NBr$: C, 70.00 H, 3.89 N, 3.89. Found C, 69.65 H, 3.81 N, 3.84.

4.4.6. *N*-(4-hexyloxybenzylidene)aniline

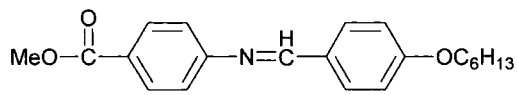


6a

Aniline (3.00 g, 32.2 mmol) and 4-hexyloxybenzaldehyde (6.65 g, 32.2 mmol) were introduced to an oven-dried 100 ml two-necked round bottom flask, followed by benzene (50.00 ml). The flask was fitted with a Dean-Stark condenser and heated at reflux for two hours under nitrogen at such a rate that ca. 25 ml of distillate was collected per hour forming a brown solution. Reaction progress was monitored with TLC and ^1H NMR spectroscopy. Once the reaction was complete, the solvent was removed *in-vacuo*. The crude product was recrystallised from MeOH to afford white crystals of the title compound. (4.97 g, 54.8 %). IR (nujol): ν (C=N) 1654 m; ν (C-O) 1114 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J*=7.2 *Hz*, 3H, CH_3); 1.35 -1.83 (m, 8H, CH_2); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.97, 7.84 (AB, 4H, C_6H_4); 7.19 - 7.40 (m, 5H, C_6H_5); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.00 (s, CH_3); 22.59, 25.69, 28.03, 31.57 (4 x s, CH_2); 68.24 (s, OCH_2); 114.73, 120.87, 123.42, 125.53, 129.10, 130.08, 130.56, 131.76, (8 x s, Ar); 161.96 (s, C=N). EI^+ - MS

(*m/z*): 218 $[M]^+$; 196 $[M\text{-}C_6H_{13}]^+$ Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.14; H, 8.19; N, 4.98. Found: C, 81.07 H, 8.20 N, 5.10.

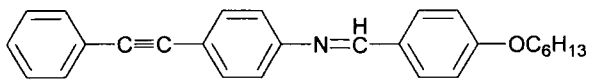
4.4.7. Methyl 4-[(4-hexyloxybenzylidene)amino]benzoate



6b

In the same manner as described for **6a** 4-aminomethylbenzoate (2.00 g, 13.3 mmol) and 4-hexyloxybenzaldehyde (2.73 g, 13.3 mmol) were allowed to react in a Dean-Stark equipped flask to give the desired compound after recrystallisation from MeOH (4.01 g, 89 %). IR (nujol): ν (CH_3CO_2) 1725 s; ν (C=N) 1650 m; ν (C-O) 1162 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J*=7.2 *Hz*, 3H, CH_3); 1.35 - 1.85 (m, 8H, CH_2); 3.92 (s, 3H, OCH_3); 4.01 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.97, 7.85 (AB, 4H, C_6H_4); 7.20, 8.07 (AB, 4H, C_6H_4); 8.35 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ13.99 (s, CH_3); 22.57, 25.67, 29.12, 31.55 (4 x s, CH_2); 53.39 (s, OCH_3); 68.44 (s, C-O); 113.80, 114.76, 120.73, 128.55, 129.80, 130.85, 130.91, 131.96 (8 x s, Ar); 160.90 (s, C=N); 166.89 (s, C=O). EI^+ - MS (*m/z*): 339 $[M]^+$; 308 $[M\text{-}MeO]^+$; 255 $[M\text{-}C_6H_{13}]^+$. Anal. Calcd. for $C_{21}H_{25}NO_3$: C, 74.34 H, 7.37 N, 4.13. Found: C, 74.03 H, 7.43 N, 3.94.

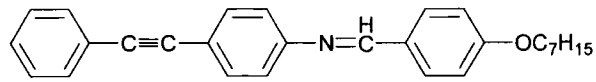
4.4.8. *N*-[(4-hexyloxyphenyl)methylene]-4-(phenylethynyl)aniline



7a

4-Phenylethynylaniline (0.55 g, 2.85 mmol) was added to 4-hexyloxybenzaldehyde (0.54 g, 2.85 mmol) to form a brown oily solution and was allowed to crystallise, then it was filtered and washed with EtOH followed by hexane. Pale yellow crystals were obtained after recrystallisation from DCM-hexane to afford the title compound (0.57 g, 52.49 %). IR (nujol): ν (C≡C) 2210 w; ν (C=N) 1668 m; ν (CO) 1173 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J*=6.8 *Hz*, 3H, CH_3); 1.36 - 1.97 (m, 8H, CH_2); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 7.85 (AB, 4H, C_6H_4); 7.19, 7.35 (AB, 4H, C_6H_4); 7.53 - 7.56 (m, 5H, C_6H_5); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.01 (s, CH_3), 22.59, 25.68, 29.13, 31.56 (4 x s, CH_2); 68.27 (s, C-O); 89.50, 89.57 (2 x s, C≡C); 114.78, 120.36, 121.07, 123.46, 127.63, 128.34, 128.85, 130.70, 131.56, 131.97, 152.15, 159.97 (12 x s, Ar); 162.16 (s, C=N). EI^+ - MS (m/z): 381 [M^+]; 297 [$M-C_6H_{13}]^+$. Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.04; H, 7.09: N, 3.67. Found: C, 84.84 H, 6.99 N, 3.50.

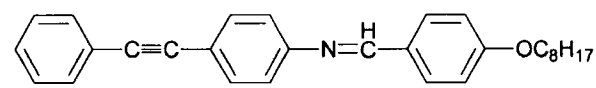
4.4.9. *N*-[(4-heptyloxyphenyl)methylene]-4-(phenylethynyl)aniline



7b

The compound **7b** (0.63 g, 61.34 %) was prepared from 4-phenylethynylaniline (0.50 g, 2.60 mmol) and 4-heptyloxybenzaldehyde (0.57 g, 2.60 mmol) in the manner described above. IR (nujol): ν (C≡C) 2210 w; ν (C=N) 1668 m; ν (CO) 1173 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J*=7.2 *Hz*, 3H, CH_3); 1.32 - 1.83 (m, 10H, CH_2); 4.04 (t, *J*=6.4 *Hz*, 2H, OCH_2); 6.92, 7.85 (AB, 4H, C_6H_4); 7.19, 7.30 (AB, 4H, C_6H_4); 7.46 - 7.56 (m, 5H, C_6H_5); 8.40 (s, 1H, NH): ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.07 (s, CH_3); 22.66, 26.01, 29.24, 29.38, 31.87 (5 x s, CH_2); 68.27 (s, C-O); 89.48, 89.56 (2 x s, C≡C); 114.78, 120.37, 121.06, 123.45, 127.64, 128.14, 128.33, 128.33, 130.70, 131.56, 131.97, 159.97 (12 x s, Ar); 162.16 (s, C=N). EI^+ - MS (m/z): 395 [M^+]; 297 [$M-C_7H_{15}]^+$. Anal. Calcd. for $C_{28}H_{29}NO$: C, 85.06; H, 7.34: N, 3.54. Found C, 84.47 H, 7.38 N, 3.47.

4.4.10. *N*-[(4-octyloxyphenyl)methylene]-4-(phenylethynyl)aniline

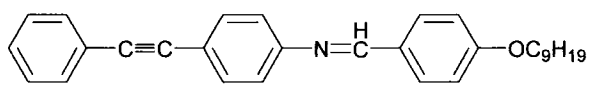


7c

The compound **7c** (0.67 g, 44.26 %) was prepared from 4-phenylethynylaniline (0.70 g, 3.63 mmol) and to 4-octyloxybenzaldehyde (0.84 g, 3.63 mmol) in the manner described above. IR (nujol): ν (C≡C) 2212 w; ν (C=N) 1664 m; ν (CO)

1175 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 *Hz*, 3H, CH_3); 1.22 -1.85 (m, 12H, CH_2); 4.02 (t, *J*=9.6 *Hz*, 2H, OCH_2); 6.99, 7.87 (AB, 4H, C_6H_4); 7.18, 7.36 (AB, 4H, C_6H_4); 7.49 - 7.57 (m, 5H, C_6H_5); 8.40 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.09 (s, CH_3); 22.65, 26.01, 29.17, 29.22, 29.34, 31.81 (6 x CH_2); 68.28 (s, C-O); 89.50, 89.57 (2 x s, C≡C); 114.78, 120.37, 121.06, 123.45, 127.63, 128.34, 128.82, 130.72, 131.56, 131.97, 146.65, 159.97 (12 x s, Ar); 162.17 (s, C=N). EI^+ - MS (m/z): 409 $[M^+]$; 297 $[M\text{-}C_8H_{17}]^+$. Anal. Calcd. for $C_{29}H_{31}NO$: C, 85.09; H, 7.58: N, 3.42. Found: C, 84.38 H, 7.54 N, 3.34.

4.4.11. *N*-[(4-nonyloxyphenyl)methylene]-4-(phenylethynyl)aniline

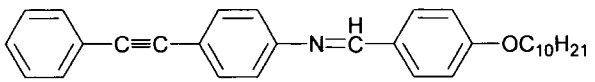


7d

The compound **7d** (0.54 g, 47.46 %) was prepared from 4-phenylethynylaniline (0.52 g, 2.69 mmol) and 4-nonyloxybenzaldehyde (0.67 g, 2.69 mmol) in the manner described above. IR (nujol): ν (C≡C) 2212 w; ν (C=N) 1682 m; ν (CO) 1168 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 *Hz*, 3H, CH_3); 1.25 -1.74 (m, 14H, CH_2) 3.98 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 7.85 (AB, 4H, C_6H_4); 7.20, 7.36 (AB, 4H, C_6H_4); 7.51 - 7.56 (m, 5H, C_6H_5); 8.56 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.09 (s, CH_3); 22.60, 25.93, 25.98, 29.00, 29.04, 29.18, 31.77 (7 x s, CH_2); 68.27 (s, C-O); 89.49, 89.56 (2 x s, C≡C); 114.78, 120.36, 121.05, 123.45, 127.63, 128.34, 128.82, 130.70, 131.56, 131.97, 152.16, 159.96 (12 x s, Ar);

162.16 (s, C=N). EI^+ - MS (m/z): 423 [M^+]; 297 [M-C_9H_{19}] $^+$. Anal. Calcd. for $C_{30}H_{33}NO$: C, 85.11; H, 7.80: N, 3.31. Found: C, 85.03 H, 7.92 N, 3.39.

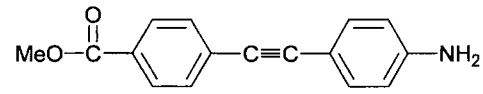
4.4.12. *N*-[(4-decyloxyphenyl)methylene]-4-(phenylethynyl)aniline



7e

The compound **7e** (0.62 g, 52.86 %) was prepared from 4-phenylethynylaniline (0.52 g, 2.69 mmol) and (0.70 g, 2.69 mmol) in the manner described above. IR (nujol): ν (C≡C) 2202 w; ν (C=N) 1653 m; ν (CO) 1174 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J*=6.8 *Hz*, 3H, CH_3); 1.33 - 1.83 (m, 16H, CH_2); 4.04 (t, *J*=6.4 *Hz*, 2H, OCH_2); 6.93, 7.84 (AB, 4H, C_6H_4); 7.20, 7.35 (AB, 4H, C_6H_4); 7.53 - 7.56 (m, 5H, C_6H_5); 8.39 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.10 (s, CH_3); 22.67, 26.01, 29.06, 29.18, 29.31, 29.55, 29.56, 31.89 (8 x s, CH_2); 68.27 (s, C-O); 89.49, 89.56 (2 x s, C≡C); 114.78, 120.36, 121.06, 123.45, 127.63, 128.34, 128.82, 130.70, 131.56, 131.97, 152.14, 159.97 (12 x s, Ar); 162.16 (s, C=N). EI^+ - MS (m/z): 436 [M^+]; 297 [M-$C_{10}H_{21}$]$^+$. Anal. Calcd. for $C_{31}H_{35}NO$: C, 85.13; H, 8.01; N, 3.20. Found: C, 84.68 H, 8.05 N, 3.21.

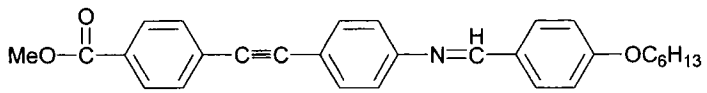
4.4.13. Methyl 4-[(4-aminophenyl)ethynyl]benzoate



8

Dry NEt_3 (180.00 ml) was introduced to an oven-dried 250 ml Schlenk flask and rigorously deoxygenated by three freeze-pump-thaw sequences. Then, 4-ethynylaniline (3.00 g, 26.00 mmol) was added followed by 4-iodomethylbenzoate (6.81 g, 26.00 mmol), $Pd(PPh_3)_2Cl_2$ (0.36 g, 0.52 mmol) and CuI (0.10 g, 0.52 mmol). The solution was heated at reflux under nitrogen with a mild temperature (< 100 °C) overnight forming a clear brown solution and yellow precipitate. The crude product was dried *in-vacuo* and purified by column chromatography (alumina, eluent: DCM) to afford the title compound as a yellow solid. (5.06 g, 78.75 %). IR (nujol); ν (NH_2) 3367 s; 3458 s; ν (C≡C) 2208 m; ν (CH_3CO_2) 1698 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.79 (br, 2H, NH_2); 3.84 (s, 3H, CH_3); 6.65, 8.00 (AB, 4H, C_6H_4); 7.36, 7.55 (AB, 4H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.14 (s, OCH_3); 86.89, 93.52 (2 x s, C≡C); 111.95, 114.72, 128.80, 129.47, 130.75, 131.15, 133.19, 147.14 (8 x s, Ar); 166.68 (s, C=O). EI^+ - MS (m/z): 251 [M^+]; 220 [M-MeO]$^+$; 192 [M-$MeCO_2$]$^+$. Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.49; H, 5.18: N, 5.58. Found: C, 76.28 H, 5.21 N, 4.18.

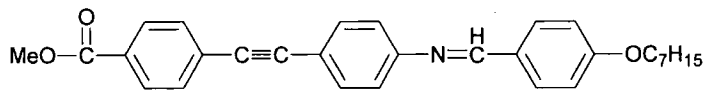
4.4.14. Methyl 4-[(4-{[(4-hexyloxyphenyl)metylene]amino}-phenyl)ethynyl]benzoate



9a

Methylbenzoate,4-ethynylaniline (0.50 g, 2.00 mmol) and 4-hexyloxybenzaldehyde (0.41 g, 2.00 mmol) were introduced to an oven-dried 100 ml two-necked round bottom flask, followed by benzene (50.00 ml). The flask was fitted with a Dean-Stark condenser and heated at reflux for two hours under nitrogen at such a rate that ca. 25 ml of distillate was collected per hour forming a brown solution. Reaction progress was monitored with TLC and ^{1}H NMR spectroscopy. Once the reaction was complete, the solvent was removed *in-vacuo*. The crude product was recrystallised from DCM, to afford pale yellow crystals of the title compound. (0.51 g, 58.1 %). IR (nujol): ν (C≡C) 2217 w; ν (CH_3CO_2) 1722 s; ν (C=N) 1657 m; ν (C-O) 1106 s cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=6.8 *Hz*, 3H, CH_3); 1.35 - 1.84 (m, 8H, CH_2); 3.93 (s, 3H, OCH_3); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 8.04 (AB, 4H, C_6H_4); 7.20, 7.78 (AB, 4H, C_6H_4); 7.48, 7.52 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.00 (s, CH_3); 22.58, 25.67, 28.90, 32.70 (4 x s, CH_2); 52.19 (1 x OCH_3); 68.28 (s, C-O); 88.86, 92.57 (2 x s, C≡C); 114.70, 114.69, 114.75, 119.70, 121.13, 128.19, 128.75, 129.37, 129.52, 130.75, 131.42, 131.95, 132.73 (12 x s, Ar); 162.24 (s, C=N); 166.58 (s, C=O). EI^{+} - MS (*m/z*): 439 $[M]^{+}$; 408 $[M\text{-}MeO]^{+}$; 355 $[M\text{-}C_6H_{15}]^{+}$. Anal. Calcd. for $C_{29}H_{29}NO_3$: C, 79.27; H, 6.61; N, 3.19. Found: C, 79.04 H, 6.57 N, 3.12.

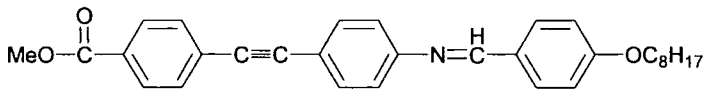
4.4.15. Methyl 4-[(4-{[(4-heptyloxyphenyl)metylene]amino}-phenyl)ethynyl]benzoate



9b

The compound **9b** (0.56 g, 77.8 %) was prepared from methylbenzoate,4-ethynylaniline (0.40 g, 1.59 mmol) and 4-heptyloxybenzaldehyde (0.35 g, 1.59 mmol) in the manner described above. IR (nujol): ν (C≡C) 2243 w; ν (CH_3CO_2) 1720 s; ν (C=N) 1652 s; ν (C-O) 1102 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=6.8 *Hz*, 3H, CH_3); 1.32 -1.86 (m, 10H, CH_2); 3.93 (s, 3H, OCH_3); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 8.03 (AB, 4H, C_6H_4); 7.20, 7.85 (AB, 4H, C_6H_4); 7.55, 7.60 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.06 (s, CH_3); 22.59, 25.96, 29.03, 29.16, 31.76 (5 x s, CH_2); 52.19 (s, OCH_3); 68.45 (s, C-O); 86.88, 90.18 (2 x s, C≡C); 114.72, 114.77, 114.82, 121.13, 129.37, 129.46, 129.79, 130.83, 131.14, 131.42, 131.97, 132.73 (12 x s, Ar); 162.29 (s, C=N); 166.67 (s, C=O). EI^+ - MS (*m/z*): 453 $[M]^+$; 422 $[M\text{-}MeO]^+$; 355 $[M\text{-}C_7H_{15}]^+$. Anal. Calcd. for $C_{30}H_{31}NO_3$: C, 79.47; H, 6.84; N,3.09. Found: C, 79.77 H, 7.02 N, 4.25.

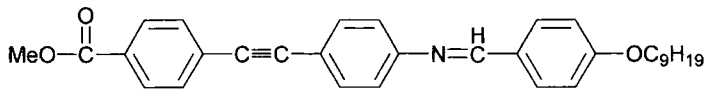
4.4.16. Methyl 4-[(4-{[(4-octyloxyphenyl)metylene]amino}-phenyl)ethynyl]benzoate



9c

The compound **9c** (0.41 g, 44.9 %) was prepared from methylbenzoate,4-ethynylaniline (0.50 g, 2.00 mmol) and 4-octyloxybenzaldehyde (0.47 g, 2.00 mmol) in the manner described above. IR (nujol): ν (C≡C) 2279 w; ν (CH_3CO_2) 1716 s; ν (C=N) 1657 s; ν (C-O) 1111 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$); δ 0.89 (t, *J*=6.8 *Hz*, 3H, CH_3); 1.31 -1.87 (m, 12H, CH_2); 3.93 (s, 3H, OCH_3); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 7.96 (AB, 4H, C_6H_4); 7.21, 7.86 (AB, 4H, C_6H_4); 7.57, 7.60 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.05 (s, CH_3); 22.65, 26.01, 29.16, 29.22, 29.34, 31.80 (6 x s, CH_2); 52.19 (s, OCH_3); 68.29 (s, C-O); 86.88, 93.51 (2 x s, C≡C); 114.72, 114.77, 114.81, 121.14, 129.37, 129.46, 129.79, 130.81, 131.14, 131.42, 131.96, 132.73 (12 x s, Ar); 160.17 (s, C=N); 166.67 (s, C=O). EI^+ - MS (m/z): 467 $[M]^+$; 436 $[M\text{-}MeO]^+$; 355 $[M\text{-}C_8H_{17}]^+$. Anal. Calcd. for $C_{31}H_{33}NO_3$: C, 79.66; H, 7.07: N, 3.00. Found: C, 79.53 H, 7.14 N, 3.00.

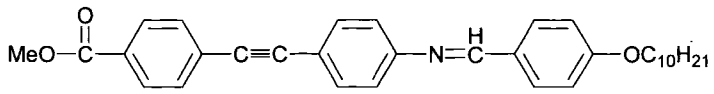
4.4.17. Methyl 4-[(4-{[(4-nonyloxyphenyl)metylene]amino}-phenyl)ethynyl]benzoate



9d

The compound **9d** (0.34 g, 50.4 %) was prepared from methylbenzoate,4-ethynylaniline (0.35 g, 1.40 mmol) and 4-nonyloxybenzaldehyde (0.35 g, 1.40 mmol) in the manner described above. IR (nujol): ν (C≡C) 2203 w; ν (CH_3CO_2) 1720 s; ν (C=N) 1648 s; ν (C-O) 1170 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 *Hz*, 3H, CH_3); 1.29 - 1.85 (m, 14H, CH_2) 3.93 (s, 3H, OCH_3); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 7.90 (AB, 4H, C_6H_4); 7.20, 7.60 (AB, 4H, C_6H_4); 7.57, 7.61 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08 (1 x CH_3); 22.66, 25.95, 29.06, 29.24, 29.33, 29.49, 31.86 (7 x s, CH_2); 52.12 (s, OCH_3); 68.45 (s, C-O); 86.89, 93.54 (2 x s, C≡C); 114.72, 114.77, 114.81, 121.14, 129.35, 129.46, 129.77, 129.83, 131.14, 131.43, 131.97, 132.76 (12 x s, Ar); 162.14 (s, C=N); 165.39 (s, C=O). EI^+ - MS (m/z): 481 $[M]^+$; 450 $[M\text{-}MeO]^+$; 355 $[M\text{-}C_9H_{19}]^+$. Anal. Calcd for $C_{32}H_{35}NO_3$: C, 79.83; H, 7.28: N, 2.91. Found: C, 79.04 H, 7.32 N, 2.82.

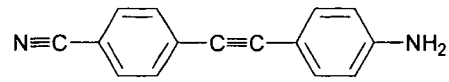
4.4.18. Methyl 4-[(4-{[(4-decyloxyphenyl)metylene]amino}-phenyl)ethynyl]benzoate



9e

The compound **9e** (0.27g, 50.5 %). was prepared from methylbenzoate,4-ethynylaniline (0.27 g, 1.08 mmol) and 4-decyloxybenzaldehyde (0.28 g, 1.08 mmol) in the manner described above. IR (nujol): ν (C≡C) 2186 w; ν (CH_3CO_2) 1725 s; ν (C=N) 1642 s; ν (C-O) 1106 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=6.4 *Hz*, 3H, CH_3); 1.28 - 1.86 (m, 16H, CH_2); 3.93 (s, 3H, OCH_3); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 8.03 (AB, 4H, C_6H_4); 7.21, 7.87 (AB, 4H, C_6H_4); 7.58, 7.61 (AB, 4H, C_6H_4); 8.39 (s, 1H, NH): ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.09 (s, CH_3); 22.67, 25.99, 29.12, 29.15, 29.30, 29.36, 29.54, 31.89 (8 x s, CH_2); 52.20 (s, OCH_3); 68.45 (s, C-O); 86.97, 93.88 (2 x s, C≡C); 114.72, 114.77, 114.82, 121.13, 129.33, 129.46, 129.52, 130.84, 131.14, 131.42, 131.96, 132.73 (12 x s, Ar); 162.54 (s, C=N); 166.13 (s, C=O). EI^+ - MS (m/z): 495 $[M]^+$; 464 $[M\text{-}MeO]^+$; 355 $[M\text{-}C_{10}H_{21}]^+$. Anal. Calcd. for $C_{33}H_{37}NO_3$: C, 80.00; H, 7.47: N, 2.83. Found: C, 79.78 H, 7.41 N, 2.78.

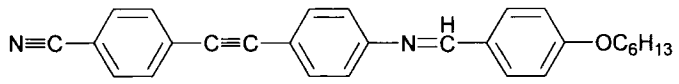
4.4.19. 4-[(4-Aminophenyl)ethynyl]benzonitrile



10

Dry NEt_3 (120 ml) was introduced to an oven-dried 250 ml Schlenk flask and rigorously deoxygenated by three freeze-pump-thaw sequences. To the solvent, 4-ethynylaniline (3.00 g, 25.60 mmol), 4-bromobenzonitrile (4.67 g, 25.60 mmol) were added followed by $Pd(PPh_3)_4$ (0.74 g, 0.64 mmol) and CuI (0.12 g, 0.64 mmol). The solution was heated at reflux under nitrogen overnight forming a yellow solution. The crude product was filtered and washed with hexane and dried *in-vacuo*. The solid obtained was dissolved in DCM and extracted with aqueous K_2CO_3. The organic layer was separated and dried over $MgSO_4$ and solvent was removed *in-vacuo* giving the title compound as a bright yellow solid (5.32 g, 95 %). IR (nujol): ν (NH_2) , 3367 s, 3453 s; ν (C≡C) 2208 m; ν (C≡N) 2230 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.90 (br, 2H, NH_2); 6.66, 7.36 (AB, 4H, C_6H_4); 7.58, 7.61 (AB, 4H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.11, 95.11 (2 x s, C≡C); 110.66, 111.40, 114.71, 118.72, 129.05, 131.69, 131.96, 133.31 (8 x s, Ar); 147.45 (s, C≡N);. EI^+ - MS (m/z): 218 $[M]^+$; 202 $[M\text{-}NH_2]^+$; 192 $[M\text{-}CN]^+$. Anal. Calcd. for $C_{15}H_{10}N_2$: C, 82.57; H, 4.59: N, 12.84. Found: C, 81.87 H, 4.51 N, 12.84.

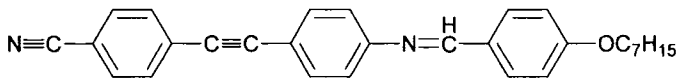
4.4.20. 4-[(4-{[(4-hexyloxyphenyl)methylene]amino} phenyl)ethynyl]benzonitrile



11a

4-Ethynylanilinebenzonitrile (0.50 g, 2.29 mmol) and 4-hexyloxybenzaldehyde (0.47 g, 2.29 mmol) were introduced to an oven-dried 100 ml two-necked round bottom flask, followed by the addition of benzene (50.00 ml). The flask was fitted with Dean-Stark condenser and heated at reflux under nitrogen for two hours forming a brown solution. Reaction progress was monitored with TLC and ^{1}H NMR, after an hour, 25 ml of distilled solution was collected. Once the reaction has completed, it was dried *in-vacuo*. The crude product was recrystallised from DCM, then it was filtered and washed with hexane. Pale yellow crystals obtained to afford the title compound. (0.59 g, 63.5 %). IR (nujol): ν (C≡C) 2167 w; ν (C≡N) 2212 s; ν (C=N) 1680,m; ν (C-O) 1165 s cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, *J*=7.2 *Hz*, 3H, CH_3); 1.31 -1.84 (m, 8H, CH_2); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 7.79 (AB, 4H, C_6H_4); 7.21, 7.63 (AB, 4H, C_6H_4); 7.57, 7.61 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.01 (s, CH_3); 22.58, 25.63, 29.03, 31.51 (4 x s, CH_2); 68.31 (s, C-O); 88.03, 94.02 (2 x s, C≡C); 111.34, 114.70, 114.77, 114.84, 118.56, 121.21, 128.42, 130.94, 131.69, 131.99, 132.05, 132.83 (12 x s, Ar); 147.45 (s, C≡N); 162.32 (s, C=N). EI^{+} - MS (m/z): 406 $[M]^{+}$; 322 $[M\text{-}C_6H_{13}]^{+}$. Anal. Calcd for $C_{28}H_{26}N_2O$: C, 82.76; H, 6.40: N, 6.90. Found: C, 82.23 H, 6.22 N, 6.45.

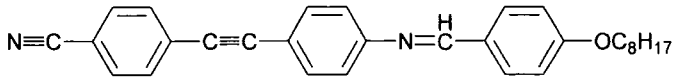
4.4.21. 4-[(4-{[(4-heptyloxyphenyl)methylene]amino} phenyl)ethynyl]benzonitrile



11b

The compound **11b** (0.58 g, 60.30 %) was prepared from 4-ethynylanilinebenzonitrile (0.50 g, 2.29 mmol) and 4-heptyloxybenzaldehyde (0.50 g, 2.29 mmol) in the manner described above. IR (nujol): ν (C≡C) 2168 w; ν (C≡N) 2208 s; ν (C=N) 1653 m; ν (C-O) 1172 s cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=6.8 *Hz*, 3H, CH_3); 1.32 - 1.83 (m, 10H, CH_2); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 7.84 (AB, 4H, C_6H_4); 7.25, 7.63 (AB, 4H, C_6H_4); 7.57, 7.61 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.06 (s, CH_3); 22.59, 25.96, 29.14, 31.76, 31.76 (5 x s, CH_2); 68.30 (s, C-O); 87.98, 95.13 (2 x s, C≡C); 111.37, 114.70, 114.77, 114.82, 118.56, 121.20, 128.44, 130.81, 131.68, 131.97, 132.04, 132.82 (12 x s, Ar) 147.47 (s, C≡N); 162.32 (s, C=N). EI^+ - MS (m/z): 420 $[M]^+$; 322 $[M-C_7H_{15}]^+$. Anal. Calcd for $C_{29}H_{28}N_2O$: C 82.86, H 6.67, N 6.67. Found: C, 82.12 H, 6.61 N, 6.49.

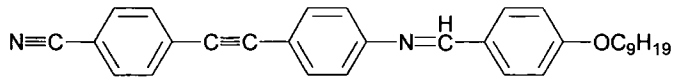
4.4.22. 4-[(4-{[(4-octyloxyphenyl)methylene]amino} phenyl)ethynyl]benzonitrile



11c

The compound **11c** (0.57 g, 57.35 %) was prepared from 4-ethynylanilinebenzonitrile (0.50 g, 2.29 mmol) and 4-octyloxybenzaldehyde (0.54 g, 2.29 mmol) in the manner described above. IR (nujol): ν (C≡C) 2206 w; ν (C≡N) 2213 s; ν (C=N) 1653 m; ν (C-O) 1168 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=6.8 *Hz*, 3H, CH_3); 1.30 - 1.83 (m, 12H, CH_2); 4.03 (t, *J*=6.4 *Hz*, 2H, OCH_2); 6.99, 7.86 (AB, 4H, C_6H_4); 7.21, 7.65 (AB, 4H, C_6H_4); 7.57, 7.61 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08 (s, CH_3); 22.65, 26.01, 29.16, 29.21, 29.33, 31.80 (6 x s, CH_2); 68.32 (s, C-O); 88.03, 94.02 (2 x s, C≡C); 111.38, 114.68, 114.72, 114.87, 118.55, 121.20, 128.42, 130.80, 131.66, 131.99, 132.04, 132.82 (12 x s, Ar); 147.48 (s, C≡N); 162.32 (s, C=N). EI^+ - MS, (m/z): 434 $[M]^+$; 322 $[M\text{-}C_8H_{17}]^+$. Anal. Calcd for $C_{30}H_{30}N_2O$: C, 82.95 H, 6.91 N, 6.45. Found: C, 82.33 H, 6.86 N, 6.29.

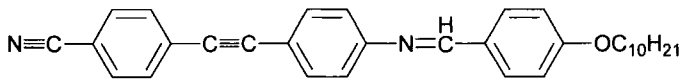
4.4.23. 4-[(4-{[(4-nonyloxyphenyl)methylene]amino} phenyl)ethynyl]benzonitrile



11d

The compound **11d** (0.47 g, 45.81 %) was prepared from 4-ethynylanilinebenzonitrile (0.50 g, 2.29 mmol) and 4-nonyloxybenzaldehyde (0.57 g, 2.29 mmol) in the manner described above. IR (nujol): ν (C≡C) 2235 w, ν (C≡N) 2217 s, ν (C=N) 1675 m, ν (C-O) 1106 s cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=6.4 *Hz*, 3H, CH_3); 1.29 - 1.86 (m, 14H, CH_2) 4.03 (t, *J*=6.4 *Hz*, 2H, OCH_2); 6.99, 7.87 (AB, 4H, C_6H_4); 7.21, 7.63 (AB, 4H, C_6H_4); 7.57, 7.59 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08 (s, CH_3); 22.66, 25.95, 29.06, 29.13, 29.24, 29.36, 31.86 (7 x s, CH_2); 68.30 (s, C-O); 87.97, 94.06 (2 x s, C≡C); 111.33, 114.70, 114.77, 114.82, 118.55, 121.20, 128.44, 130.79, 131.68, 131.98, 132.04,132.81 (18 x s, Ar); 147.48 (s, C≡N); 162.30 (s, C=N). EI^+ - MS (m/z): 448 $[M]^+$; 322 $[M-C_9H_{19}]^+$. Anal. Calcd for $C_{31}H_{32}N_2O$: C 83.04, H 7.14, N 6.25. Found: C, 82.12 H, 7.07 N, 5.99.

4.4.24. 4-[(4-{[(4-decyloxyphenyl)methylene]amino} phenyl)ethynyl]benzonitrile



11e

The compound **11e** (0.63 g, 59.55 %) was prepared from 4-ethynylanilinebenzonitrile (0.50 g, 2.29 mmol) and 4-decyloxybenzaldehyde (0.60 g, 2.29 mmol)) in the manner described above. IR (nujol): ν (C≡C) 2231 w, ν (C≡N) 2204 s, ν (C=N) 1680 m, ν (C-O) 1114 s cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.6 *Hz*, 3H, CH_3); 1.28 - 1.85 (m, 16H, CH_2); 4.03 (t, *J*=6.8 *Hz*, 2H, OCH_2); 6.99, 7.86 (AB, 4H, C_6H_4); 7.21, 7.63 (AB, 4H, C_6H_4); 7.57, 7.61 (AB, 4H, C_6H_4); 8.38 (s, 1H, NH): ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.09 (s, CH_3); 22.67, 25.99, 29.13, 29.30, 29.54, 29.33, 29.36, 31.89 (8 x s, CH_2); 68.29 (s, C-O); 87.97, 94.07 (2 x s, C≡C); 111.32, 114.70, 114.77, 114.81, 118.55, 121.20, 128.44, 130.79, 131.68, 131.98, 132.04, 132.81 (12 x s, Ar); 147.48 (s, C≡N); 162.30 (s, C=N). EI^+ - MS (m/z): 462 $[M]^+$; 322 $[M-C_{10}H_{21}]^+$. Anal. Calcd for $C_{32}H_{34}N_2O$: C 83.12, H 7.36, N 6.06. Found: C, 82.65 H, 7.40 N, 7.02.

Chapter 5. Conclusion and Future Work

5.1. Conclusion

A novel family of conjugated compounds featuring both acetylenic and imine functionalities with D-C_6H_4-CH=N-C_6H_4-C≡C-C_6H_4-A substructure bearing both polar head groups (acceptor, A) namely H, $MeCO_2$ and C≡N, and alkoxy tails of various chain lengths (donor, D) were synthesised. The synthetic methodology involved initial Pd-catalysed cross-coupling reaction of aryhalides with ethynylaniline followed by formation of the Schiff-Base via condensation with 4-alkoxybenzaldehydes. The compounds were spectroscopically characterised.

These compounds are fluorescent, with the imine portion of the molecule perhaps dominating the electronic transitions, with some contribution from the arylacetylene moiety. Low level electronic structure calculations on models of these compounds also showed that the π-system in the mixed imine/acetylene systems is delocalised over both functional groups.

These newly conjugated ethynyl/Schiff-Base hybrid systems exhibit liquid crystalline properties at elevated temperature. While all the examined compounds showed a nematic phase, the compounds which have longer alkoxy tails or polar head groups are also more likely to show a smectic A and/or smectic B (hexatic B) phases.

5.2. Future Work

Further studies on these ethynylated aromatic Schiff-Base compounds could focus on the fact that they exhibit liquid crystalline properties, with different techniques employed such as X-ray diffraction and neutron scattering for structural analysis and identification of the less well characterised viscous phase.

As a considerable amount of interest in the 1,4-bis(phenylene)ethylene system arises from the fluoresecent behaviour of these compounds, which may serve both as a probe of molecular structure in the ground and excited states and as a molecular property which might be exploited in devices, such as OLEDs. The use of the new compounds reported in this thesis, which have good thermal and environmental stability, in this areas should be investigated. Initial studies in this regard would involve full investigation of their luminescent behaviour. The photophysical studies should be coupled with computational analysis of the electronic structure. If the system proves to have an extensively delocalised π-system the use of similar frameworks in the development of conductive single molecules may also be of interest, given the ease of synthesis, purification and ability to introduce functional groups for surface attachment.

The combination of polar head groups (for surface binding) and alkoxy tails (for improved film forming characteristics) suggest these new conjugated ethynyl / Schiff-Base hybrid systems could find use in molecular wire-like studies. These rigid rod molecules should be ideal for assembly on an electrode by various

methods such as formation of Self-Assembled Monolayers (SAMs) or Langmuir-Blodgett Techniques (LBTs).

Studies carried out to identify and determine the possibility of bonding these conjugated molecular compounds to different surfaces in ordered arrays would represent a starting point for these further investigations and provide a link between the concepts of molecular materials for electronics, which often rely on molecule-molecule interactions, and molecular scale electronics, where the electronic structure of individual molecules holds the key to success.

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