# NOVEL CONJUGATED SCHIFF-BASE COMPOUNDS

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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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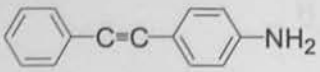
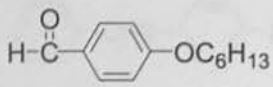
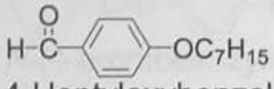
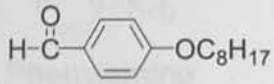
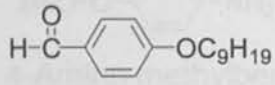
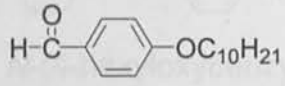
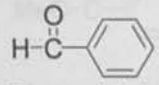
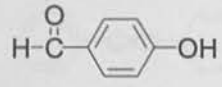
## Statement of Copyright

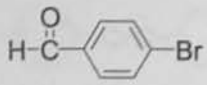
## Abbreviations

| | |
|---|---|
| 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 |



4-Bromobenzaldehyde 3c

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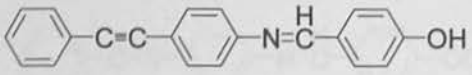

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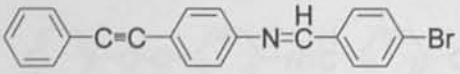

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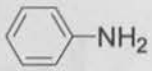

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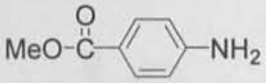
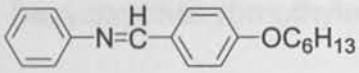


4-Amino methylbenzoate 5b



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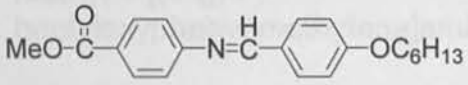

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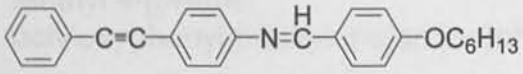

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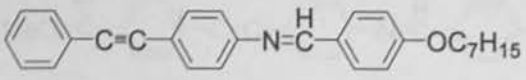

7b

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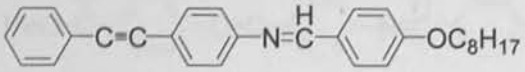

7c

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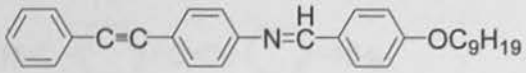

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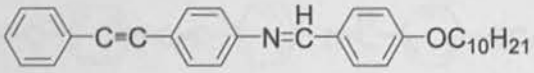

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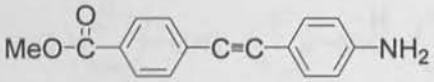

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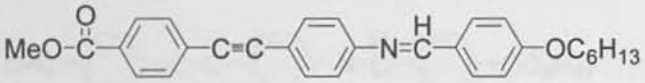
Methyl 4-[(4-aminophenyl)ethynyl]benzoate



9a

Methyl 4-[(4-{[(4-hexyloxyphenyl)methylene]amino}phenyl)ethynyl]benzoate

9b

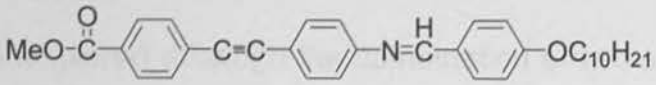
Methyl 4-[(4-{[(4-heptyloxyphenyl)methylene]amino}phenyl)ethynyl]benzoate

9c

Methyl 4-[(4-{[(4-octyloxyphenyl)methylene]amino}phenyl)ethynyl]benzoate

9d

Methyl 4-[(4-{[(4-nonyloxyphenyl)methylene]amino}phenyl)ethynyl]benzoate



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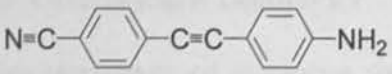

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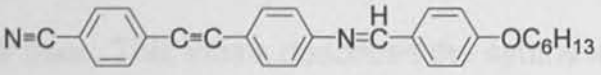
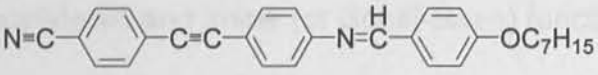


11a

4-[(4-{[(4-Hexyloxyphenyl)methylene]amino}phenyl)ethynyl]benzonitrile



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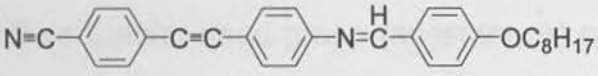

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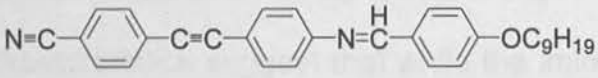

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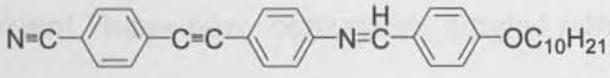

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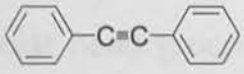
4-[(4-{[(4-Decyloxyphenyl)methylene]amino}phenyl)ethynyl]benzonitrile



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.