

Molecular structure–thermal behaviour relationship of dimers consisting of different terminal substituents and sulphur–sulphur linking group



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HIGHLIGHTS

- New disulphide dimers containing various terminal substituents (CH₃, C₂H₅, Cl and Br).
- Influence of molecular structure upon thermal behaviour and substituent effect are reported.
- Disulphide dimers with terminal aliphatic chain exhibit monotropic N phase.
- Cl-dimer (enantiotropic N and monotropic SmA) and Br-dimer (enantiotropic SmA and mosaic B).
- The derivative with terminal Br exhibits higher stability of SmA due to higher polarizability.

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ABSTRACT

A new series of dimers 6-(4-oxybenzylidene-4'-substituted-aniline)hexyldisulphides containing various terminal substituents (CH₃, C₂H₅, Cl and Br) have been synthesized. The correlation between the molecular structure and the properties of all the ultimate compounds has been made on the basis of their thermal behaviour. The dimers with CH₃ and C₂H₅ substituents exhibit predominantly the monotropic N phase of which the C₂H₅-containing derivative possesses more stable nematogenic temperature range in comparison to its methyl-containing analogue. As for the member with Cl substituent, it exhibits enantiotropic N and monotropic smectic A phase. However, the dimer in which the Cl was substituted by Br exhibits purely enantiotropic smectic A phase. Upon cooling all of the final compounds show the transition from isotropic to mesophase prior to the change from mesophase to crystal except the member with Br substituent which displays mosaic B phase even at room temperature. An extensive study to further substantiate the relationship between the stability of the phase and associated transition temperatures due to different terminal substituent is also studied. This study reveals that the terminal Br increases the clearing temperature and polarizability which enhances the formation and stability of SmA and mosaic B phases.

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Introduction

Liquid crystal dimers have been the focus of many researchers as their properties are quite different from conventional liquid crystals [1] and they could also act as the model compounds for main chain polymeric liquid crystals [2]. There are two types of liquid crystal dimers: Symmetric and non-symmetric dimers. Symmetric dimers consist of two identical mesogenic units connected

by a single spacer whilst non-symmetric dimers consist of two different mesogenic units linked by a single spacer.

It has also been revealed that for typical dimers in which the two individual mesogenic groups attached to each other via a flexible polymethylene spacer unit, the stability of mesophase can be varied through the change in the linking group and substituent. For instance, the aromatic imine-based dimers are well known for their abilities to exhibit mesomorphic behaviour resulted from their high-shape anisotropy and the presence of terminal halogen which helped to increase the molecular polarizability [3–5]. Furthermore, previous researchers had also reported that the

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linking group such as disulphide (S–S) reduced the transitional properties of the dimers [6,7].

In this report, we present a comprehensive study on a series of symmetric dimer with sulphur–sulphur linkage in the hexamethylene spacer. In these dimers the substituents CH₃, C₂H₅, Cl and Br are attached to the aniline fragments at both terminal ends. Hence, the effect of different terminal substituents on the thermal behaviour of the aniline fragments and their relationship with its molecular structure will be presented. The synthetic routes for the preparation of intermediates and title compounds with atomic numbering scheme are summarized in Scheme 1.

Experimental details

Materials

4-hydroxybenzaldehyde, 4-substituted-aniline, 1,6-dibromohexane, potassium thioacetate and potassium metabisulphide were purchased from Acros Organics (Belgium). Sodium hydroxide and concentrated hydrochloric acid were purchased from Fischer Scientific (United Kingdom) whilst sodium iodide was purchased

from R&M Chemicals (United Kingdom). All solvents and reagents were used without further purification.

Characterization

Physical measurements

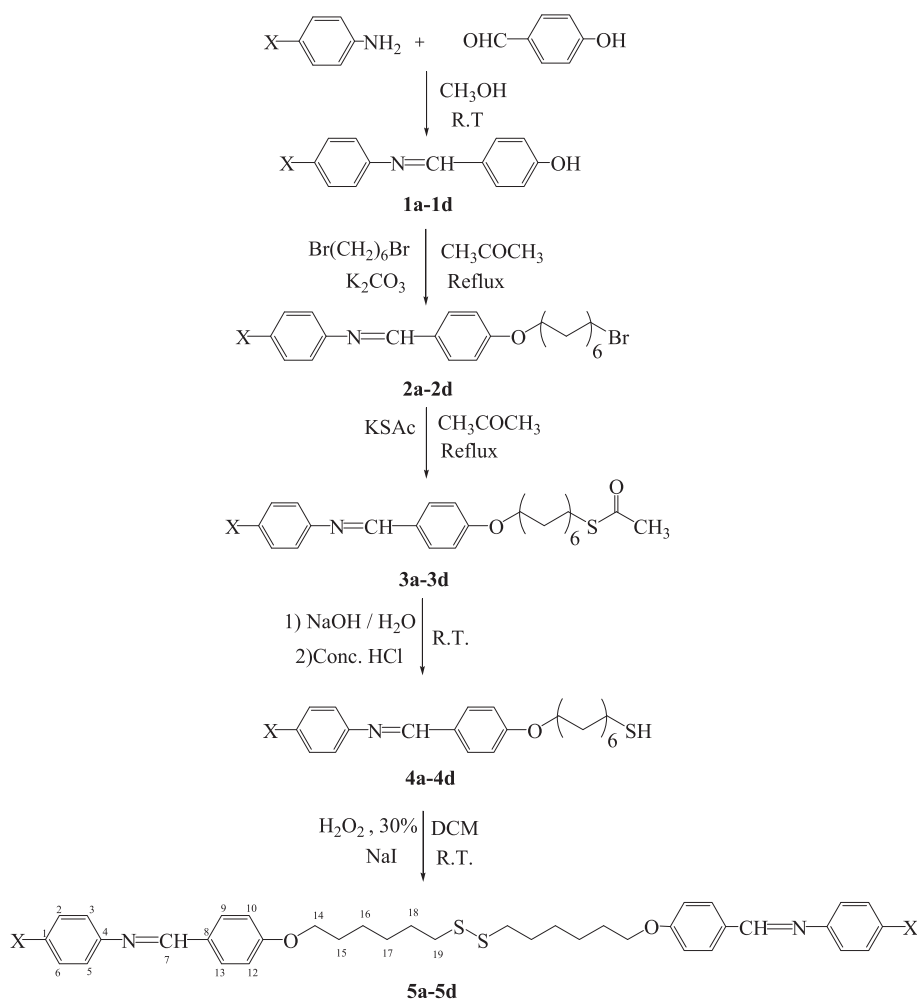
Melting points were determined by Gallenkamp melting point apparatus. The CHN microanalyses were performed on a Perkin Elmer 2400 LS Series CHN/O analyzer.

FTIR measurement

Fourier transform infrared (FT-IR) data were recorded by a Perkin Elmer 2000-FTIR spectrophotometer in which the samples were mixed with KBr. The frequency range used for recording the IR spectra was set at 4000–400 cm⁻¹.

NMR measurement

The ¹H and ¹³C NMR spectra were recorded on Bruker Avance 500 Ultrashield spectrometer. The 1D NMR data were supported by the aids of 2D ¹H–¹H correlation spectroscopy (COSY), ¹H–¹³C



Scheme 1. Synthetic pathway towards the formation of compounds **5a–5d**.

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