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Synthesis, characterization and comparative study of a series of fluorinated Schiff bases containing different orientation —CH=N— spacers

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HIGHLIGHTS

- Three pairs of fluorinated Schiff bases isomers **1a–b**, **2a–b** and **3a–b** were synthesized and characterized.
- Their conformations are determined by different orientation —CH=N— spacers.
- Each pair of isomers has different supramolecular stackings.

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ABSTRACT

Investigation of the crystal structures of three pairs of multi-fluorinated compounds with bridge-flipped isomeric character, which on the molecular level differ only in the orientation of the bridging bond —CH=N— connecting two larger parts of the molecule, offers a useful context for the examination and evaluation of supramolecular assembly in the case. The results show that the orientation of the bridging bond —CH=N— determines the conformation of six organic molecules **1a–b**, **2a–b** and **3a–b**, thus further influencing intermolecular weak interactions and final supramolecular arrangements. Accordingly, each molecule of six multi-fluorinated compounds as supramolecular building block unit, via strong intermolecular interactions, including interactions between fluorine atoms and aromatic ring hydrogen atoms, between fluorine atoms, and between hydroxyl groups and fluorine atoms, as well as interaromatic $\pi\cdots\pi$ stacking interactions etc., constructs a series of different and attractive crystal packings. These results demonstrate that by changing —CH=N— orientation, we can obtain different hydrogen-bonded supramolecular structures through different interactions.

Introduction

Organic crystals have been attracting much attention for decades due to their superiority for understanding of intermolecular interactions and potential applications in optoelectronics and pharmaceutical products [1–2]. Detailed understanding of the electronic structure of the molecules and the specific intermolecular interaction terms would enable us to engineer better molecular structures and control their physic-chemical properties for targeted applications [3–5]. The driving force for the molecular packing arrangements largely arises from non-covalent interaction between molecules, such as hydrogen bonding, $\pi\cdots\pi$ stacking interactions as well as van der Waals force. Most relevant of these non-covalent interactions are stacking interactions and hydrogen bonds, which have been subjects of extensive study in the last two decades. In recent literature, due to the unique properties of fluorinated compounds, substantial efforts have been put in by various researchers towards the understanding of interactions involving organic fluorine and the role they play in generating different packing motifs which guides assembling of molecules in the crystal lattice [3,6–9].

Schiff base is an interesting compound with a functional group that contains a carbon–nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. The chain on the nitrogen makes the Schiff base a stable imine. They can form stable

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complexes with transition metals and tend to exhibit potent in the fields of biochemistry [10–12], catalyst chemistry [13], organometallic chemistry [14,15] and material chemistry [16–18]. It has been found that the non-covalent interactions, such as N···H hydrogen bonds, $\pi\cdots\pi$ stacking have a significant influence on the properties of the Schiff bases especially in the cases of fluorine atoms. The small size of the fluoro-substituent enables its incorporation into crystal structures without undue disruption, and hence the crystal structures can still be exhibited. Moreover, it is the combination of the small size and high polarity of F atom which serves as proton acceptor can create strong intra/intermolecular actions in the form of C—H···F, F···F, F···π, F···π^F, and $\pi\cdots\pi^F$. All this weak interactions play an important role in generating different packing motifs and related properties of fluorinated compounds.

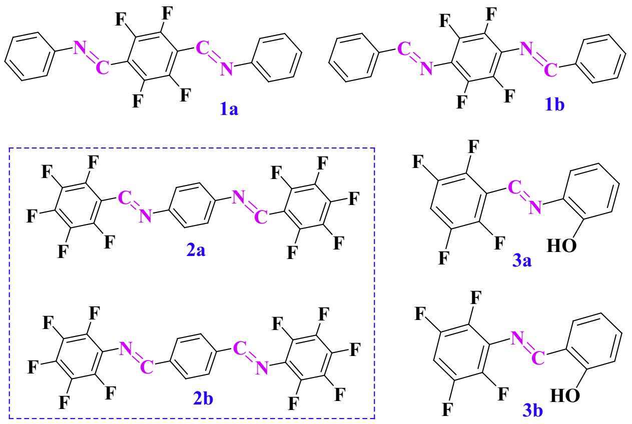
In this paper, we report synthesis and crystal structures of four new fluorinated Schiff base compounds (**1a–b**, **3a–b**) as well as the supramolecular chemistry of three pairs of multi-fluorinated Schiff bases (**1a–b**, **2a–b**, **3a–b**) with different orientation of the bridging bond —CH=N—/—N=CH— spacers in the solid state (Scheme 1). Obviously, this is an excellent opportunity to elucidate the difference of supramolecular assembly in the orientation isomers, though two crystal structures (**2a–b**) of six compounds (**1a–b**, **2a–b**, **3a–b**) have been reported [6]. To the best of our knowledge, this firstly systematically investigate the supramolecular organization in series of fluorinated Schiff base molecules with different orientations of

Results and discussion

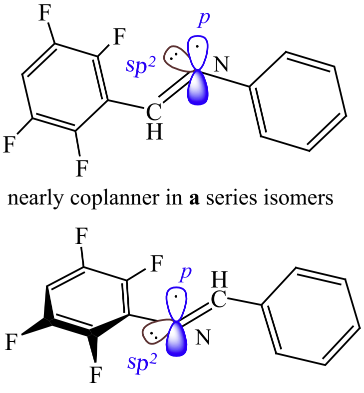
Synthesis and general characterization of six compounds

Although two compounds **2a–b** were once reported by Collas et al. [6], their syntheses and characterization as well as structural analyses are still C=N spacers. This opens the possibility to explore the effect of fluorine atoms and C=N spacers in the Schiff base molecular on formation of the crystal packing, and may be good in industrial and pharmaceutical applications.

Briefly mentioned here and below for comparative study. Four symmetrical Schiff base compounds **1a–b** and **2a–b** as well as two unsymmetrical ones **3a–b** (Scheme 1) were respectively synthesized by the condensation of the corresponding aldehydes with the corresponding benzene-1,4-diamines/aniline in EtOH/CH_2Cl_2, in which **a** series' isomers present dark yellow crystalline solid and **b** series' ones pale yellow crystalline solid, being in agreement with their structures (see structural discussion section below), namely the better coplanar in **a** series' molecules makes them have the better delocalization effect and become the rigid-rod-type conjugated chromophore molecules. However, reversing the orientation of bridging —CH=N— bond in molecules gives **b** series' isomers without coplannarity from the electron repulsion between the substituted electron-riched fluorine atoms and the lone-pairs in nitrogen atoms (Scheme 2).



Scheme 1. The chemical structures of six fluorinated Schiff base compounds.



nearly coplanner in **a** series isomers

have 30-50° dihedral angles in **b** series isomers

Scheme 2. Difference in conformation between bridge-flipped isomeric fluorinated benzylideneanilines from electron repulsion of electron-riched F atoms and lone-pair in sp^2 orbit of N atom.

General description of six crystal structures

All single crystals were obtained from EtOH or CH_2Cl_2 solution after slow evaporation of the solvent at ambient conditions and examined using single crystal X-ray diffraction method. It gave a triclinic crystal lattice with a *P*-1 space group for **2a** and **3a**, monoclinic crystal system with $P2_1/c$ space group for **1b** and **2b**, an orthorhombic crystal lattice with *Pbca* for **1a** and with $P2_12_12_1$ for **3b**, respectively. All bond distances and angles of the molecules are normal. Figs. 1–16 give the diagrams of all six compounds including the intramolecular features of the C—H···F interaction in six compounds, O—H···F and O—H···N in **3b** as well as F···F interactions in **1a–b** and $\pi\cdots\pi$ stacking in **2a–b**, **3a–b** [19–25]. Table 1 lists the relevant crystallographic and refinement data,

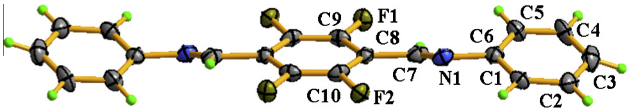


Fig. 1. Molecular structure of **1a** with thermal ellipsoids at the 20% level. The atom-numbering scheme is shown only for one-half of the molecule as the other half is generated by (−1 − *x*, −*y*, 1 − *z*).

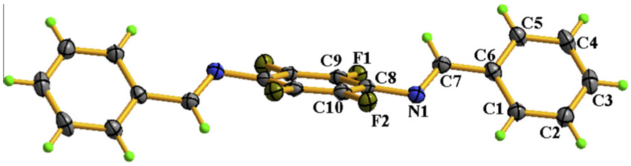


Fig. 2. Molecular structure of **1b** with thermal ellipsoids at the 25% level. The atom-numbering scheme is shown only for one-half of the molecule as the other half is generated by (2 − *x*, 2 − *y*, 1 − *z*).