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Strong phenyl–perfluorophenyl π–π stacking and C–H···F–C hydrogen bonding interactions in the crystals of the corresponding aromatic aldimines

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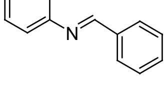
Abstract—The X-ray diffraction analysis of two co-crystals, **1·2** (aldimines **1** and **2**) and **3·4** (aldimines **3** and **4**), reveals that there are strong phenyl–perfluorophenyl π–π stacking and intermolecular hydrogen bonding interactions. The new perfluoroaryl–aryl face-to-face interaction of the crystalline aldimines provides a design motif for a new class of self-assembling system.

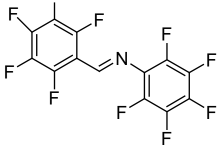
Noncovalent interactions between aromatic units play a significant role in determining the structures and properties of molecular assemblies in biology, chemistry, and materials science.[1] Although a considerable amount of work studying the stacking of aromatic rings has concentrated on phenyl–phenyl interaction, there is a growing interest in the interactions between aryl and perfluoroaryl units.[2–6] Patrick and Prosser first reported that a 1:1 mixture of benzene (mp = 5.5 °C) and hexafluorobenzene (mp = 4 °C) forms a complex, that melts at 24 °C.[3] In the past decade, the intermolecular interactions in hydroaromatic and perfluoroaromatic molecules, such as aryl–perfluoroaryl stacking synthon (Ar–Ar^F), C–H···F, C–F···π, and F···F interactions have been the focus of structural, photophysical, topochemical, and differential scanning calorimeter (DSC) studies.[4–6] Coates et al. reported the alternating stacking interactions of monoolefines and diolefines substituted with phenyl and perfluorophenyl groups, and can undergo photochemically induced [2+2] reactions in the solid state to lead to cyclobutane products.[5] Many aryl–perfluoroaryl stackings have also been observed at low temperature.[6] Here we first report the face-to-face and head-to-tail or head-to-head stacking between the phenyl and perfluorophenyl rings in the co-crystals of aldimines $Ar^1CH{=}NAr^2$ (Ar^1, $Ar^2 = C_6H_5$, C_6F_5) at room temperature.

Aldimines $Ar^1CH = NAr^2$ (Ar^1, $Ar^2 = C_6H_5, C_6F_5$) were prepared from the corresponding amines and aldehydes in high yields (Scheme 1).

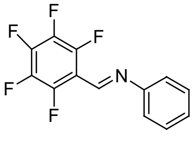
After a benzene and dichloromethane solution of an equal molar mixture **1** and **2** was slowly evaporated, the 1:1 co-crystals **1·2** were isolated as a colorless crystalline solid that is stable in air at room temperature. The strength of the aromatic π–π stacking interactions was revealed by the melting point increase of the co-crystals **1·2** (98–100 °C) compared with the pure starting materials **1** and **2** (51–56 °C, and 88–90 °C). The structure and



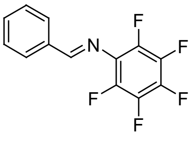
1 (mp = 51-56 °C)



2 (mp = 88-90 °C)



3 (mp = 115-117 °C)



4 (mp = 114-115 °C)

Keywords: Non-covalent interactions; π–π Stacking; Hydrogen bond.

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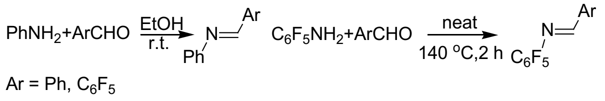

Scheme 1.

the packing arrangement of **1** and **2** in the co-crystals were determined by single-crystal X-ray diffraction analysis.

As can been seen in Figure 1, co-crystal **1·2**[8] stacks in vertical columns in an alternating fashion, face-to-face and head-to-tail, which could reduce the repulsion force of the lone pair electrons of the nitrogen atom in the imines. The alternating arrangement can be attributed to a quadrupolar interaction between electron-rich and electron-deficient aromatic rings.[7] The torsional angle of the two phenyl rings in imines **1** is ~36°, which is less than that of imines **2** (~44°). The phenyl rings in the imines **1** and the pentafluorophenyl rings in the imines **2** are almost parallel to each other, with dihedral angles of only ~7° and ~4°, respectively. The mean perpendicular distance of the phenyl ring to the neighboring pentafluorophenyl ring is 3.44 Å, which indicates that there are significant intermolecular π–π interactions between the phenyl rings and the pentafluorophenyl rings.[2–6] The structure of the complex **1·2** is further stabilized by H···F hydrogen bonding (C20A–H···F5, as shown by the dashed lines in Fig. 1b) between **1** and **2** from the stacking layer of two adjacent columns. The H···F distance is 2.59 Å, and the C–H···F angle is 154.6°. There are also numerous weak C–H···F interactions[4] between the phenyl rings and pentafluorophenyl rings in the neighboring column molecules (~2.80 Å, 146°), which also can stabilize the co-crystals. The shortest intermolecular H3···F3 hydrogen bond distance is 2.720 Å. All of these interactions cause the elevation of the melting point of the co-crystal.

Slow evaporation of an equal molar solution of imines **3** and **4** in hexane also afforded a colorless co-crystal with melting point of 110–112 °C. This is lower than those of pure starting compounds. We propose that there could

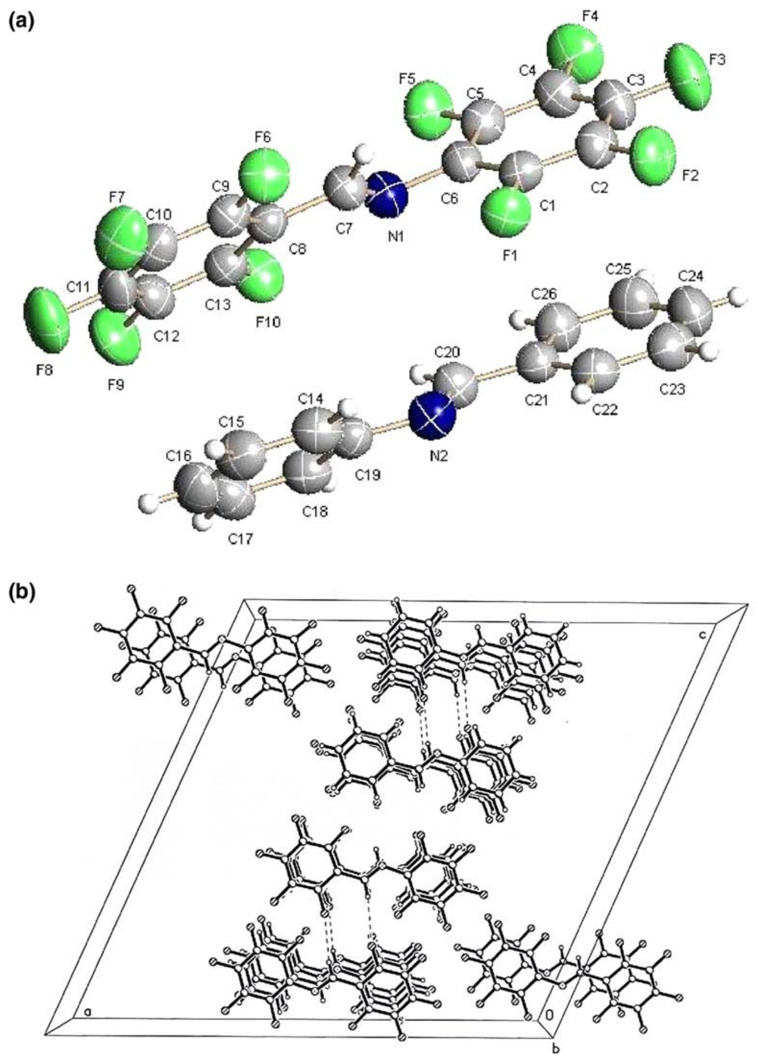

Figure 1. (a) Molecular structure of the complex **1·2**. (b) Molecular packing map of **1·2**. The hydrogen bonding between the fluorine atoms and the hydrogen atoms is indicated using dashed lines.

be two possible stacking patterns, head-to-head or head-to-tail, based on the structures of imines **3** and **4**. The π–π interactions would dominate in the former stacking manner, however, there would also be lone pair electrons repulsion interactions between the nitrogen atoms, which are oriented in the same direction. If stacking in the latter manner, lone pair electrons repulsion could be avoided, but there would be electrostatic repulsion interactions between the neighboring aromatic rings.

X-ray analysis of complex **3·4**[8] shows that the crystals are stacked in the head-to-head, face-to-face fashion, which permits the phenyl rings and pentafluorophenyl rings to stack alternatingly. The electrostatic attraction interactions of the aromatic rings are enhanced by the lone pair electron repulsion. The torsion angles of imines **3** and **4** are ~48°. Due to the neighboring phenyl–perfluorophenyl face-to-face orientation, the corresponding two aromatic rings are parallel each other, with a dihedral angle only ~4°. The mean perpendicular distance of the phenyl rings to the neighboring perfluorophenyl rings is ~3.4 Å, which is close to that of **1·2** (~3.44 Å). The packing map data of the **3·4** co-crystal reveals that there is no intermolecular hydrogen bonding between the imines C–H···F, but that there are numerous weak C–H··· F interactions between the phenyl rings and pentafluorophenyl rings in the neighboring column molecules (~2.70 Å, ~131°). The shortest intermolecular H22···F5 hydrogen bond distance is 2.749 Å. The electrostatic repulsion of the lone pair electrons of the imine nitrogen atoms and the absence of intermolecular hydrogen bonding may account for the lower melting point of the **3·4** co-crystal than those of pure starting molecules **3** or **4** (Fig. 2).

To conclude, X-ray diffraction analysis of two closely related crystal structures of phenyl and perfluorophenyl aldimines **1** and **2** at room temperature disclosed that there exist significant π–π stacking interactions between the phenyl and perfluorophenyl rings. The molecules are stacked in vertical columns, face-to-face and head-to-tail. The phenyl and perfluorophenyl rings, which stack

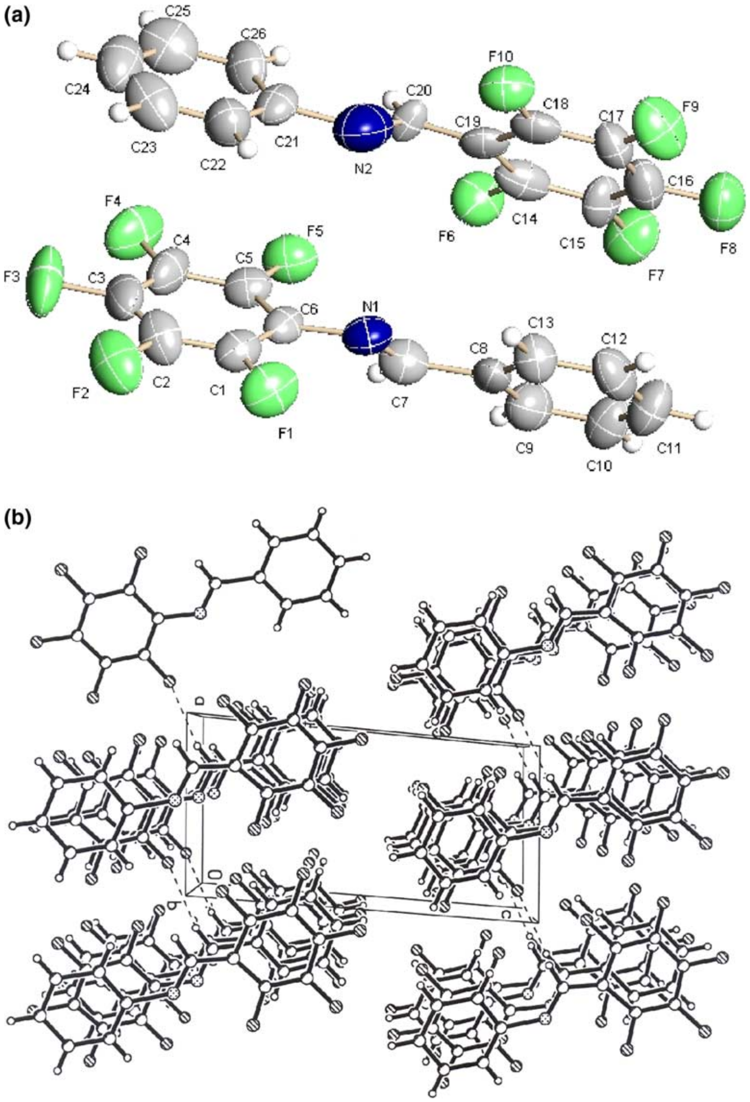

Figure 2. (a) Molecular structure of complex **3·4**. (b) Molecular packing diagram of the **3·4** co-crystal. The fluorine atoms are green, and the nitrogen atoms are azure. The intermolecular C–H···F–C interactions are shown using dashed lines.

alternatingly, π–π stacking interactions, electrostatic attractions and intermolecular hydrogen bonding in the co-crystals of **1·2**, work together to increase its melting point. In complex of **3·4** the π–π stacking interactions dominated the electrostatic repulsions of the lone pair of the imines nitrogen atoms, which forces the molecules to align in a head-to-head manner. The co-crystals **3·4**, however, have a lower melting point than the corresponding starting materials, which could be attributed to the electrostatic repulsion interactions and the absence of intermolecular hydrogen bonds. The work reported here provides strong evidence for the power of fluoroaryl–aryl face-to-face interactions as a design motif for a new class of self-assembling systems. The potential applications of these new fluoroaldimines structures are the subject of the on-going investigations.

Acknowledgements

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8. *Crystal data*: **1·2** (1:1): CCDC No. 241887 $C_{26}H_{12}F_{10}N_2$, $M = 542.38$; monoclinic, spacegroup $C2/c$, $a = 26.736(2)$, $b = 7.4098(6)$, $c = 25.102(2)$ Å, $\alpha = 90$, $\beta = 114.213(2)$, $\gamma = 90°$, $V = 4535.3(7)$ Å^3, $Z = 8$, $D_c = 1.589$ Mg/m^3, $\mu = 0.152$ mm^{-1}, 5248 [$R_{(int)} = 0.0744$] unique reflections, $F(000) = 2176$, final $R_1 = 0.0472$, $wR_2 = 0.1011$, [$I > 2\delta(I)$]. **3 · 4** (1:1): CCDC No. 241888 $C_{26}H_{12}F_{10}N_2$, $M = 542.38$; triclinic, $P1$, $a = 6.142(4)$, $b = 7.556(5)$, $c = 12.347(8)$ Å, $V = 560.6(6)$ Å,[3] $Z = 1$, $D_c = 1.607$ Mg/m^3, $\mu = 0.154$ mm^{-1}, 2848 [$R_{(int)} = 0.0900$] unique reflections, $F(000) = 272$, final $R_1 = 0.0521$, $wR_2 = 0.1208$, [$I > 2\delta(I)$]. Intensity data was collected at 293(2) K with a Bruker P4 four-circle diffractometer; with equipped a graphite monochromator, and Mo Kα radiation [λ (Mo Kα) = 0.71073 Å)]. A total of 13,276 and 3311 independent reflections were measured in range $1.69 < \theta < 28.35°$ and $1.88 < \theta < 28.30°$, respectively. The structures were solved by directed methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-square refinement was based on $F^{\wedge 2}$. All calculations were performed using the program SHELX-97.