

Aryl–perfluoroaryl stacking interactions, hydrogen bonding and steric effects in controlling the structure of supramolecular assemblies of *N,N'*-diaryloxalamides†‡

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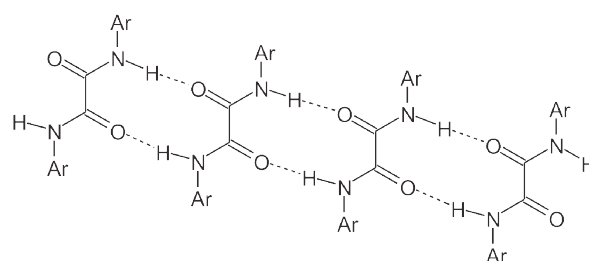
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Cocrystallization of *N,N'*-diaryloxalamides with pentafluorophenol (pfp) leads to 1 : 2 molecular complexes, which were characterized by X-ray crystallography. The non-planar oxalamide molecules and pfp assemble into polymeric tapes with use of the N–H···O and O–H···O hydrogen bonds and phenyl–perfluorophenyl interactions, whereas the molecules adopting planar conformations form with pfp flat trimers held together by intermolecular hydrogen bonds creating two 7-membered rings.

Hydrogen bonds and π – π stacking between aromatic rings belong to the most common directional forces responsible for self-assembly of molecules within the crystal. Because of their strength and directionality hydrogen bonds play a key role in the construction of supramolecular architectures.^{1,2} Also, attractive interactions between π -systems belong to major forces directing the aggregation of aromatic compounds and can be used to manipulate the organization of molecular subunits in the solid state.³ Particularly, the electron-deficient aromatic rings interact most strongly with electron-rich aromatic groups. A good example is provided by π -stacking interactions between aryl and perfluoroaryl rings.^{3,4} There is increasing interest in such systems and many 1 : 1 complexes of perfluoro aromatic compounds with their non-fluorinated analogues have been designed and prepared.⁵ Due to the attractive electrostatic quadrupole–quadrupole interactions their crystal structures are characterized by stacks of alternating component molecules.⁶

Recently, we have demonstrated that aryl–perfluoroaryl stacking combined with hydrogen bonding interactions can be used to control the crystal structures of supramolecular assemblies.⁷ Continuing our efforts in this field, we focused our attention on *N,N'*-diaryloxalamides. Simple oxalamides, due to their ability of self-complementary hydrogen-bonding interactions, have found wide application as supramolecular building blocks for construction of ordered solid state assemblies,⁸ helical structures⁹ and gelators yielding thermo-reversible gels.¹⁰ Symmetrical *N,N'*-disubstituted diamides of oxalic acid are known to form robust

infinite tapes through the centrosymmetric dimeric hydrogen-bond motifs (Scheme 1).⁸ However, the translational parameter along the oxalamide tape, being of *ca.* 5.0 Å,^{8c} is not compatible with the effective π – π stacking interactions of the neighbouring *N*-aryl substituents (Fig. 1). Therefore our initial attempts of co-crystallization of *N,N'*-diphenyloxalamide (**1**) with its pentafluorophenyl analogue were unsuccessful. Thus we tried complexation of *N,N'*-diaryloxalamides **1–4** with pentafluorophenol (pfp) or pentafluorobenzoic acid (pfba). We expected that these strong hydrogen bond donors could disrupt relatively weak homomeric hydrogen bonds between the oxalamide units¹² creating new heteromeric interactions. One of the possible motifs generated in this way would be a one-dimensional (1D) tape composed of the alternating oxalamide and pfp molecules connected by the N–H···O and O–H···O hydrogen bonds and stabilized by aromatic ring interactions, as shown in Scheme 3.



Scheme 1

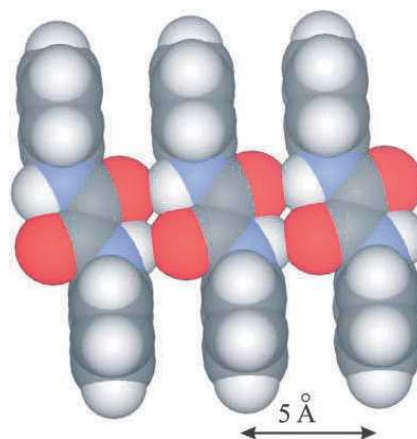


Fig. 1 A hypothetical *N,N'*-diaryloxalamides tape with the aryl ring perpendicular to the oxalamide units.

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‡ Electronic supplementary information (ESI) available: ORTEP drawings and hydrogen-bond geometry for **2**, **4**, **1·pfp**, **2·pfp**, **3·pfp**, **4·pfp** and **4·pfba**. See DOI: 10.1039/b709654b