



Specific interaction modes in the crystal structures of oligofluorinated tolanes featuring additional electron donor and acceptor groups

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ABSTRACT

A series of partially fluorinated and specifically *para*-substituted tolanes (**1–4**) have been synthesized via palladium-catalyzed Sonogashira cross-coupling reaction. The single-crystal structures have been determined by X-ray diffraction. The molecules adopt a geometry being more or less disturbed from planarity due to crystal packing effects. The packing structures are characterized by the formation of molecular stacks achieved through different modes of $\pi \cdots \pi$ interaction and being accomplished by other types of weak interactions including hydrogen bonds as well as bromo and in particular fluoro involved contacts.

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1. Introduction

Compounds showing a simple basic structure with clear molecular geometry and having well defined substituents and functional groups are most desirable testing systems in order to increase the knowledge on non-covalent intermolecular interactions [1,2]. Corresponding weak intermolecular contacts are a fundamental tool in the field of crystal engineering, aiming at the control of a crystal structure from molecular construction [3,4]. This is of paramount importance in organic materials science since macroscopic properties of a solid such as electric and optical behaviour [5,6] as well as structural polymorphism [7] and catalysis [8], having widespread commercial implications, can be selectively influenced this way. In the course of these studies, different packing motifs in crystals including strong and weaker hydrogen bonding [9,10] or π -stacking interactions [11], giving rise to the formation of specific supramolecular synthons [1,12], have been discussed in detail. Making a more profound understanding of the nature and strength of organic halogen promoted non-covalent interactions [13] accessible, especially involving organic bound fluorine atoms in competition with other weak contacts [2,14], is another current challenge [15]. A motive for it is that fluorinated organic compounds often show uncommon and unique physical and chemical properties [16]. With relevance to

molecules intended for the formation of metal–ligand network structures [17], liquid crystal behaviour [18] or crystals suitable for non-linear optical properties like second harmonic generation (SHG) [19], fluorination has been considered to control the strength of neighbouring donor and acceptor groups and thus affect their behaviour of supramolecular interaction. In this connection, partially fluorinated tolanes [20] and hetero derivatives of tolanes [21] have recently been synthesized and studied with reference to their crystalline packing structures.

Herein we report the synthesis of a series of similarly fluorinated tolanes **1–4** (Scheme 1) featuring, however, selected donor and acceptor groups in the *para* positions of the aryl rings and discuss their crystal structures in the light of the consequences coming from the fluorine substitution.

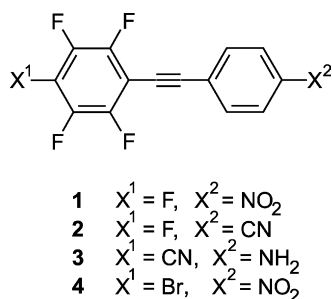
2. Results and discussion

2.1. Compounds studied

All the compounds **1–4** being substituted derivatives of tolane were synthesized following a common protocol in the key preparation step. This involves a Sonogashira–Hagihara cross-coupling reaction between a halogenated arene and an aryl substituted ethyne in the presence of a standard palladium(II)/copper(I) catalytic system [22]. The respective aryl halides (**5a**, **5b**) and corresponding aryethynes (**6a–6c**) are specified in Scheme 2. A complete synthetic route, exemplary shown for the preparation

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Scheme 1. Formula structures of compounds studied.

of compound **1**, is detailed in **Scheme 3**. Single crystals of the compounds **1–4** were obtained by slow evaporation of solutions of **1** and **4** in acetone, **2** in chloroform and **3** in dimethylsulfoxide.

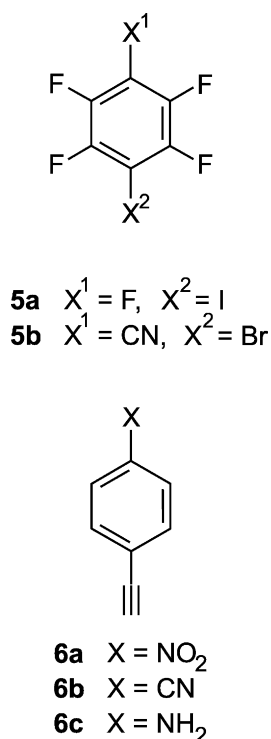
2.2. X-ray single crystal structures

The crystallographic data and structure refinement parameters for the studied compounds (**1–4**) are summarized in **Table 1**. For the description of the crystal structures, intermolecular contacts within the sum of the van der Waals radii [23] have been used. Corresponding hydrogen bond type interactions (C–H···O, C–H···N, C–H···F, N–H···N) as well as C–F··· π , N–O···O, N–O···N, Br···O and F···F contacts are presented in **Table 2**.

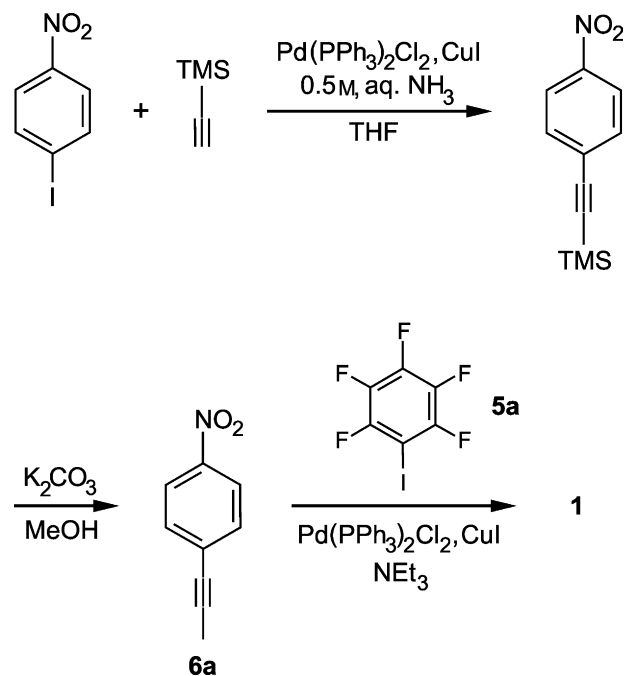
2.2.1. Nitropentafluoro-substituted tolane 1

Crystallization of **1** from acetone yielded yellow plates of the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit of the cell. The molecule (**Fig. 1(a)**) deviates from planarity and adopts a dihedral angle of nearly 9.9° between the mean planes of the aromatic rings. The nitro substituent is slightly tilted (ca. 2.5°) with respect to the aromatic ring to which it is attached.

In the crystal structure, the molecules are stacked along the *b*-axis in a head-to-head fashion. Within a given stack, consecutive molecules are strictly parallel but displaced by 3.64 Å in direction



Scheme 2. Formula structures of fluoroarene and ethynylarene intermediates.



Scheme 3. Synthetic route exemplary demonstrated for compound **1**.

of their longitudinal axes. In this arrangement, the ethynyl moiety of each molecule is sandwiched in a distance of 3.50 Å between the perfluorophenyl and nitrophenyl rings of two neighbouring molecules which suggests the presence of $\pi(\text{C}\equiv\text{C})\cdots\pi(\text{arene})$ interactions [20,21] (**Fig. 2**). These findings are consistent with a recently arisen theoretical interaction model based on molecular electrostatic potentials [24] which provides a new view for simple explanation of the packing behaviour of molecules in crystalline perfluoroarene–arene complexes [25,26]. In this model, the geometries of arene stacking are induced by local substituent effects with the proximal vertex of the other ring rather than being caused by traditional π -polarization or quadrupole interaction [27,28] that was already questioned before [29]. The electron-withdrawing nature of the ring substituents in **1** relieves electrostatic repulsion between the aryl π -clouds which in the present case produces a longitudinal displacement of neighbouring molecules. The molecular planes of adjacent stacks are oriented approximately orthogonal thus forming an overall herringbone pattern. There appears to be no significant non-covalent bonding based on fluorine interactions [15]. The shortest C–H···F contact [C(2)–H(2)···F(1) 2.68 Å, 142°] is beyond the sum of the van der Waals radii (2.67), whereas the F···F distance (2.94 Å) represents the van der Waals limit. This suggests that fluorine involved interactions hardly contribute to crystal stabilization of **1**. However, an unusual feature of the crystal structure is the short distance between the nitro substituents of two adjacent molecules in the structure, showing O···O separations of 2.82 and 2.91 Å, which is less than twice the van der Waals radius of oxygen (3.04 Å). The structure excerpt displayed in **Fig. 3** shows the contact mode between the nitro substituents. Due to the orthogonal orientation of the interacting molecules *I* and *II*, their nitro substituents approach each other in a perpendicular fashion with N–O···O and N–O···N angles (symmetry: $-x, 0.5 + y, 0.5 - z$) being 136.1 and 113.4° , respectively. The N–O···O angle between the symmetry related molecules *I* and *III* which adopt a coplanar arrangement (symmetry: $-x, 1 - y, 1 + z$) is 131.3° . In this context, it should be noted that similar close O···O contacts have also been observed in the crystal structures of a picric acid complex [30] and of 2,4,6-trinitrotoluene [31].

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