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High order stacking of a perfluoro 'Y-enyne'†

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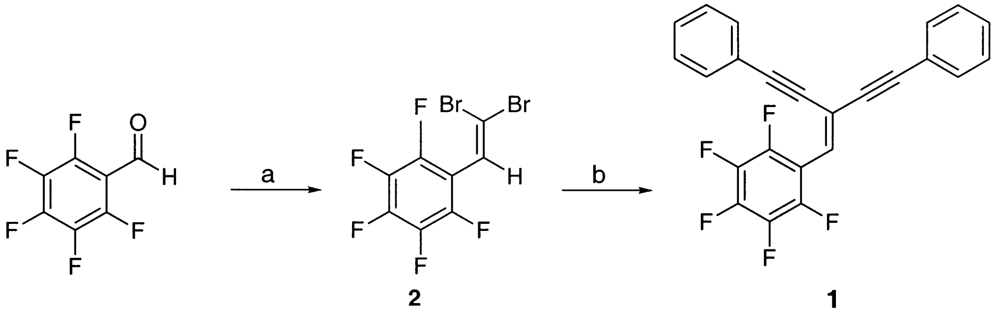
Abstract—The X-ray structure of perfluorophenyl substituted Y-enyne **1** reveals a face-to-face stacking interaction between phenyl and perfluorophenyl groups of different molecules resulting in a high order in the solid state. Acetylene–arene and acetylene–fluorine interactions also contribute to the high order stacking. The X-ray structure suggests a distorted conjugation of the chromophore. © 2001 Elsevier Science Ltd. All rights reserved.

Interest in crystal engineering and solid-state architecture to design and generate networks has grown in recent years.[1,2] Recently, Schröder et al.[3] reported a new approach to inorganic crystal engineering developing three dimensional arrays with silver (I). Roberts et al.[4] reported two-step ring-forming reactions leading to 'ladder' polymers that were thought to have unusual and interesting properties. Stacking controlled by hydrogen bonding,[2,5] coulombic attraction,[6] as well as charge transfer[7] has been used to order π-conjugated systems. Coates et al.[6] have reported that phenyl-perfluorophenyl stacking interactions can be used to align crystals for the topochemical [2+2] photodimerization and photopolymerization of olefinic compounds, as well as the polymerization of diynes.[8] These reactions have many applications in designing new materials for use as photoresists[9] and in photoalignment layers for liquid crystal devices.[10]

We previously introduced a simple way to synthesize branched enynes ('Y-enynes') and reported the photocyclization of a naphthyl substituted 'Y-enyne'.[11] In order to study the effect of fluorine substitution on stacking behavior in these systems, as well as in an attempt to engineer their photophysical properties and photochemical behavior, we have synthesized fluorine substituted 'Y-enynes'. In this paper, we report the synthesis of 2-(ethynylphenyl)-1-(pentafluorophenyl)-4-phenyl-1-buten-3-yne **1** and its stacking in the crystal as revealed by X-ray measurement. To the best of our knowledge, this is the first report of stacking in enynes.

Pentafluorobenzaldehyde was converted via Corey–Fuchs[12] reaction to 1,1-dibromo-2-(pentafluorophenyl)-ethene **2**, followed by Sonogashira coupling[13] with phenylacetylene affording 'Y-enyne', **1**[14] (Scheme 1).



Scheme 1. Synthesis of 'Y-enyne' **1**. (a) CBr_4, PPh_3, CH_2Cl_2, argon, 0°C, 8 h; (b) $Pd(PPh_3)_2Cl_2$, CuI, THF, NEt_3, phenylacetylene, argon, 70°C, 24 h.

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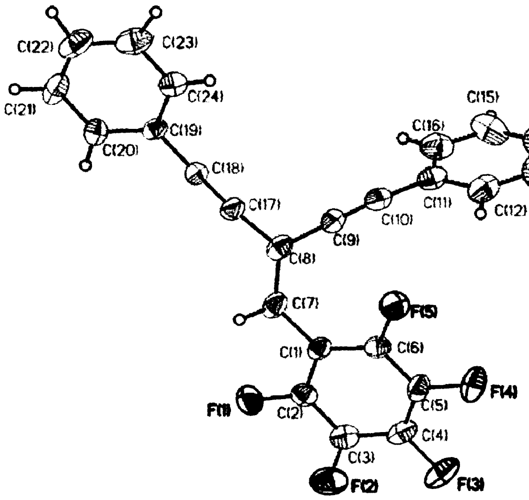


Figure 1. ORTEP of **1** at 150 K (ellipsoids at 50% probability).

The X-ray crystal structure of **1**[15] (Fig. 1) confirms its chemical structure. The structure shows that the pentafluoro phenyl ring is almost parallel to one of the two remaining phenyl rings (dihedral angle of the mean plane of the pentafluorophenyl ring and that having C_{19} is 1.3°), and it is almost perpendicular to the third phenyl ring (dihedral angle of the mean plane of the pentafluorophenyl ring and that having C_{11} is 94.1°).

Also, the X-ray structure reveals face-to-face stacking interactions between the phenyl and perfluorophenyl groups of different molecules. These interactions result in high order stacking of the molecules in the solid state. The pentafluoro phenyl ring of one molecule stacks above a phenyl ring from another molecule forming a 'ladder' (Fig. 2(a)). Several 'ladders' stack so that a phenyl ring is stacked between two pentafluorophenyl rings, while a pentafluorophenyl ring is stacked between two phenyl rings (Fig. 2(b)) leading to the formation of hollow hexagonal channels through the aromatic rings, 2.76 Å in diagonal (Fig. 2(c)).

Moore et al.[16] first reported acetylene–arene π–π interactions as a driving force for aggregation of phenylacetylene macrocycles. These authors reported that π–π interactions maximized when the triple bond lies parallel to the aromatic plane (tilt angle, θ, is 90°), and the distance between the aromatic centroid and the center of the carbon–carbon triple bond lies within 10 Å.[16] Solid stacking of **1**, as revealed by the X-ray measurement, predicts such interactions. One of the two acetylene carbon–carbon triple bonds in molecule A has a tilt angle $\theta_1 = 88.7°$ with respect the pentafluorophenyl ring of molecule B[17] (Fig. 2(d)); this triple bond has the

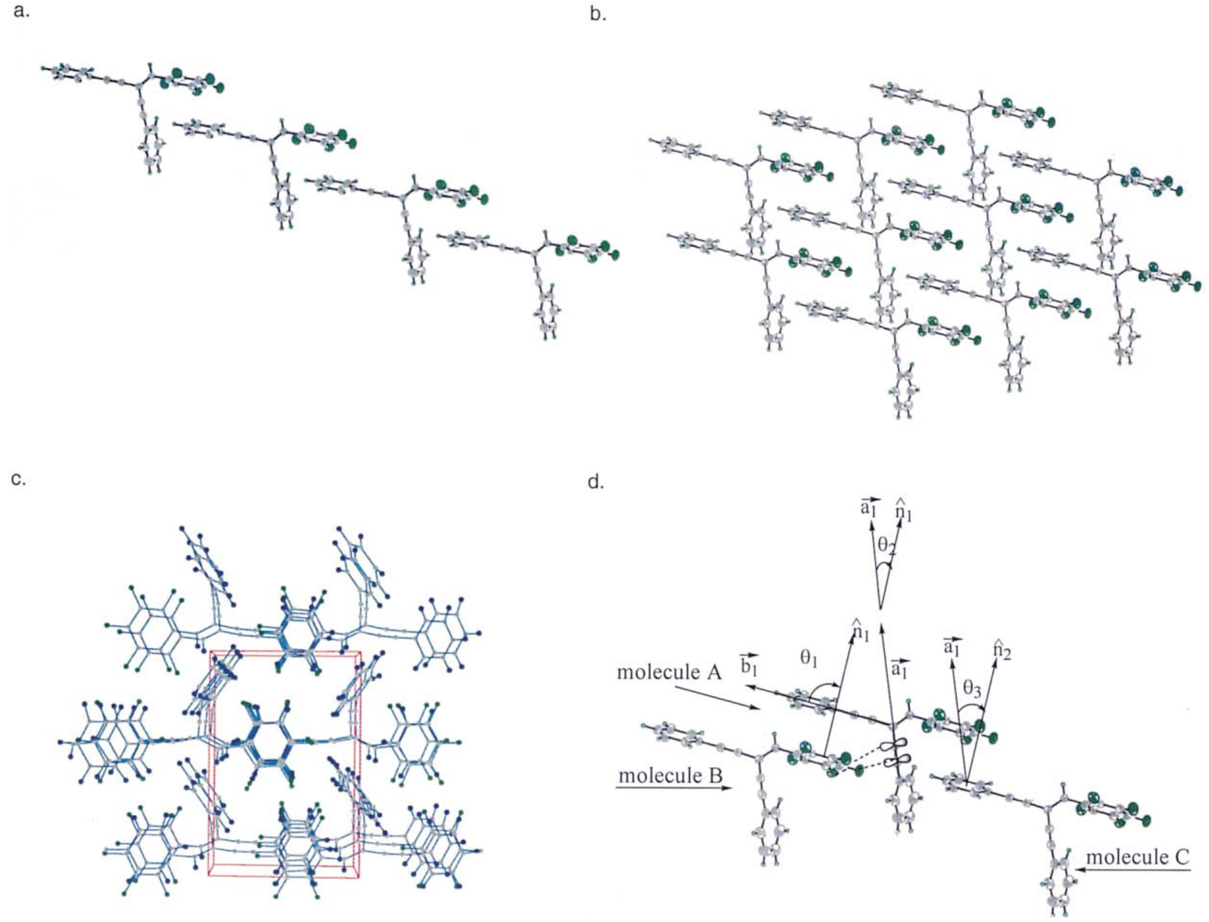
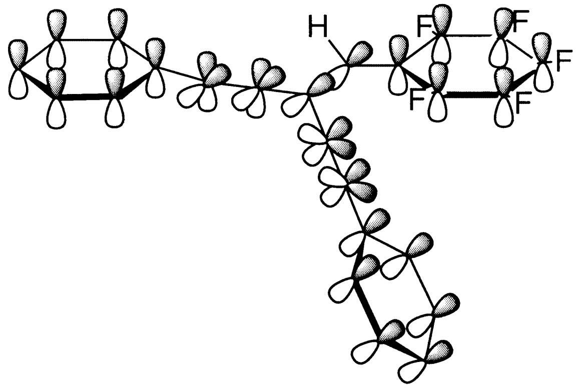


Figure 2. Stacking of **1**. (a) Layer of molecules; (b) multiple layers; (c) view of the unit cell along the *a* axis; (d) acetylene–arene π–π interactions.



1

Figure 3. The proposed distorted conjugation of **1**.

same tilt angle with the molecule above it (not shown for simplicity). The other carbon–carbon triple bond in molecule A has a tilt angle $\theta_2 = 30.2°$ with the pentafluorophenyl ring of molecule B and tilt angle $\theta_3 = 31.5°$ with the phenyl ring of molecule C. Moreover, we think interactions between the fluorine atoms in molecule B with the *p*-orbitals of the acetylene in molecule A also contribute to the solid stacking. Therefore, the coulombic interactions and the acetylene–arene π–π interactions, in addition to the fluorine–π interactions, contribute to the high order stacking of **1**.

Though aggregation was not evident from the ^{1}H NMR spectrum of **1** [32.5 and 155 mM in $CDCl_3$], a red shift in the UV-spectrum (hexane and acetonitrile) does suggest aggregation in less polar solvents as the concentration is increased.

The X-ray confirms that the conjugation of the chromophore of **1** is distorted. The hydrogen bonded to C_7 (H_7) is 45° out of the plane of the pentafluoro ring (dihedral angle of ($H_7C_7C_1$) and the mean plane of the pentafluorophenyl ring is 135°). This requires the *p*-orbital of C_7 to be at 45° with that of C_1 (Fig. 3). Therefore, the pentafluoro ring is in 'semi' conjugation with the rest of the chromophore.

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14. Pure product **1** (yellow solid) was isolated in 55%: mp 135–137°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.92–6.93 (dd, 1H, $J_1 = 2.4$ Hz, $J_2 = 1.1$ Hz), 7.32–7.45 (m, 8H), 7.54–7.59 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −136.2 (sm, 2F), −154.2 (m, 1F), −162.9 (sm, 2F). ^{13}C NMR (50 MHz, $CDCl_3$) δ 84.95 (C), 87.03 (C), 90.58 (C), 93.67 (C), 95.53 (C), 110.79–111.52 (C, dt, $J_1 = 3.3$, $J_2 = 17.3$ Hz), 121.97–122.07 (C, d, $J = 5.45$ Hz), 126.61 (CH), 129.41 (CH), 129.08 (CH), 129.21 (CH), 131.74 (CH), 131.88 (CH) and a series of broad peaks in the aromatic region (Ar C-F). HR-MS: calcd for m/z 394.078092, found m/z 394.077464.
15. Single-crystal X-ray diffraction analysis of **1**. Crystal structure data for **1** (single crystal from dichloromethane/isopropanol): formula $C_{24}H_{11}F_5$, $M = 394.33$, crystal dimensions 0.3×0.2×0.25 mm, monoclinic, space group $P2_1$, $a = 7.6530(4)$, $b = 13.4288(8)$, $c = 8.9323(4)$ Å, $\beta = 94.340(2)°$, $V = 915.35(8)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.431$ g cm^{-3}. Bruker AXS SMART platform diffractomator (Ag-Kα, $\lambda = 0.56086$ Å), three different ϕ settings and 0.3° increment ω scan, $2\theta < 40°$, $T = 150$ K. 5804 measured reflections, all 3144 independent reflections were used in the refinement. Data integration was carried out with SAINT, corrections for absorption and decay were applied using SADABS. Structure solution and refinement: direct methods, non-hydrogen atoms were refined including anisotropic thermal parameters, hydrogen atoms were refined isotropically, $R = 0.0553$ [$I > 2\sigma(I)$].
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17. The distance between the aromatic centroid of the pentafluoro phenyl ring in molecule A and the center of the carbon–carbon triple bond in molecule B is 4.097 Å.