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Metric engineering of perfluorocarbon-hydrocarbon layered solids driven by the halogen bonding†

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Electronic Supplementary Information

General Formation of co-crystals 3-6 involving starting materials 1a-d and 2a-b. Equimolar amounts of diiodoalkane **1a-d** and the dicyano alkane **2a-b** were dissolved in a vial of clear borosilicate glass at room temperature. Chloroform was used as solvent. The open vial was placed in a closed cylindrical wide-mouth bottle containing vaseline oil. $CHCl_3$ was allowed to diffuse at room temperature and after 24 hours co-crystals **3-6** were obtained.

X-ray diffraction analysis. Data were collected with a SMART diffractometer, Mo-Kα radiation [λ = 0.71073 Å]. The temperature was controlled by the Bruker KRIOFLEX low temperature device. All structures were refined by full-matrix least-squares on F^2, with anisotropic heavy atoms and isotropic H atoms.

X-ray diffraction data refinement. Structure solutions by SIR92[1] and refinement on F^2 by SHELX97[2] program packages.

1. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Applied Cryst.* 1994, **27**, 435.
2. G. M. Sheldrick, *SHELX*97 Program for the Refinement of Crystal Structures 1997, University of Göttingen, Germany.

3a) CCDC 230372

$C_8H_8F_4I_2N_2$, M = 461.96, monoclinic, $P2_1/n$, a = 7.752(2), b = 6.3557(14), c = 12.991(3) Å, β = 95.15(3) °, U = 637.5(3) Å^3, Z = 2, T = 90(2) K, μ(Mo-Kα) = 4.958 mm^{-1}, crystal dimensions 0.20x0.10x0.05; $2\theta_{max}$ = 72.42, 11423 reflections collected, 2935 unique, 2246 with $I > 2\sigma(I)$, R_{ave} = 0.0508, absorption corrections: Tmin/Tmax=0.582. 89 parameters refined, final R(all) = 0.0684, R(obs) = 0.0464, wR = 0.0904, G.o.F. 1.012, difference Fourier residues -2.24 < ρ < 3.04 eÅ^{-3}.

6a) CCDC 230373

$C_{14}H_8F_{16}I_2N_2$, M = 762.02, triclinic, P(-1), a = 5.3349(6) b = 7.3918(8)), c = 14.6816(18) Å, α = 93.480(14) β = 97.835(15) γ = 110.882(13) °, U = 532.13(11) Å^3, Z = 1, T = 90(2) K, μ(Mo-Kα) = 3.099 mm^{-1}, crystal dimensions 0.29x0.22x0.12; $2\theta_{max}$ = 72.38, 15685 reflections collected, 4825 unique, 4625 with $I > 2\sigma(I)$, R_{ave} = 0.0247, absorption corrections: Tmin = 0.565, Tmax=0.680. 170 parameters refined, final R(all) = 0.352, R(obs) = 0.0332, wR = 0.0791, G.o.F. 1.199, difference Fourier residues -1.31 < ρ < 2.44 eÅ^{-3}.

4a) CCDC 230374

$C_{10}H_8F_8I_2N_2$, M = 561.98, triclinic, *P*(-1), *a* = 5.2447(5), *b* = 7.9197(6), *c* = 9.6803(10) Å, α = 84.078(12), β = 85.711(11), γ = 75.147(9) °, *U* = 386.09(6) Å^3, *Z* = 1, *T* = 90(2) K, μ(Mo-Kα) = 4.152 mm^{-1}, crystal dimensions 0.19x0.13x0.10; $2\theta_{max}$ = 72.36, 14301 reflections collected, 3586 unique, 3427 with $I > 2\sigma(I)$, R_{ave} = 0.0209, absorption corrections: Tmin = 0.563, Tmax=0.660. 116 parameters refined, final *R*(all) = 0.0201, *R*(obs) = 0.0184, w*R* = 0.0448, G.o.F. 1.068, difference Fourier residues $-0.63 < \rho < 1.41$ eÅ^{-3}.

5a) CCDC 230375

$C_{12}H_8F_{12}I_2N_2$, M = 662.00, triclinic, *P*(-1), *a* = 5.3183(8), *b* = 7.0369(11), *c* = 13.415(2) Å, α = 75.865(8), β = 86.012(12), γ = 71.855(9) °, *U* = 462.63(12) Å^3, *Z* = 1, *T* = 90(2) K, μ(Mo-Kα) = 3.515 mm^{-1}, crystal dimensions 0.30x0.20x0.11; $2\theta_{max}$ = 71.86, 11424 reflections collected, 4056 unique, 3722 with $I > 2\sigma(I)$, R_{ave} = 0.0271, absorption corrections: Tmin = 0.559, Tmax=0.670. 143 parameters refined, final *R*(all) = 0.0446, *R*(obs) = 0.0388, w*R* = 0.1029, G.o.F. 1.137, difference Fourier residues $-2.32 < \rho < 2.71$ eÅ^{-3}.

4b) re107 CCDC 230376

$C_{12}H_{12}F_8I_2N_2$, M = 590.04, monoclinic, $P2_1/n$, *a* = 7.8842(8), *b* = 6.3141(6), *c* = 17.377(2) Å, β = 92.886(8) °, *U* = 863.96(16) Å^3, *Z* = 2, *T* = 90(2) K, μ(Mo-Kα) = 3.717 mm^{-1}. crystal dimensions 0.16x0.11x0.04. $2\theta_{max}$ = 72.82, 17631 reflections collected, 4048 unique, 3553 with $I > 2\sigma(I)$, R_{ave} = 0.0359, absorption corrections: Tmin/ Tmax = 0.824, 133 parameters refined, final *R*(all) = 0.0419, *R*(obs) = 0.0344, w*R* = 0.0728, G.o.F. 1.091, difference Fourier residues $-1.88 < \rho < 1.80$ eÅ^{-3}.

5b) CCDC 230377

$C_{14}H_{12}F_{12}I_2N_2$, M = 690.06, triclinic, *P*(-1), *a* = 5.2409(6), *b* = 9.7393(9), *c* = 10.3874(102) Å, α = 79.665(10), β = 76.972(11), γ = 84.691(10) °, *U* = 507.42(9) Å^3, *Z* = 1, *T* = 90(2) K, μ(Mo-Kα) =

3.209 mm^{-1}, crystal dimensions 0.28x0.16x0.13; $2\theta_{max}$ = 72.48, 4644 unique, 4351 with $I > 2\sigma(I)$, absorption corrections: Tmin = 0.501, Tmax=0.607. 160 parameters refined, final R(all) = 0.0214, R(obs) = 0.0195, wR = 0.0489, G.o.F. 1.051, difference Fourier residues $-1.15 < \rho < 1.24$ e$Å^{-3}$.

6b) CCDC 230378

$C_{16}H_{12}F_{16}I_2N_2$, M = 790.08, triclinic, $P(-1)$, a = 5.4008(16), b = 7.214(2), c = 16.065(4) Å, α = 88.713(8), β = 87.854(6), γ = 72.453(10) °, U = 596.3(3) $Å^3$, Z = 1, T = 200(2) K, μ(Mo-Kα) = 2.769 mm^{-1}, crystal dimensions 0.22x0.13x0.04; $2\theta_{max}$ = 55.22, 10182 reflections collected, 2756 unique, 2116 with $I > 2\sigma(I)$, R_{ave} = 0.0425, no absorption corrections. 187 parameters refined, final R(all) = 0.0431, R(obs) = 0.0338, wR = 0.0712, G.o.F. 0.876, difference Fourier residues $-0.42 < \rho < 0.93$ e$Å^{-3}$.

Figure 3 Crystal packing of **5a** viewed down the *b* crystallographic axis.

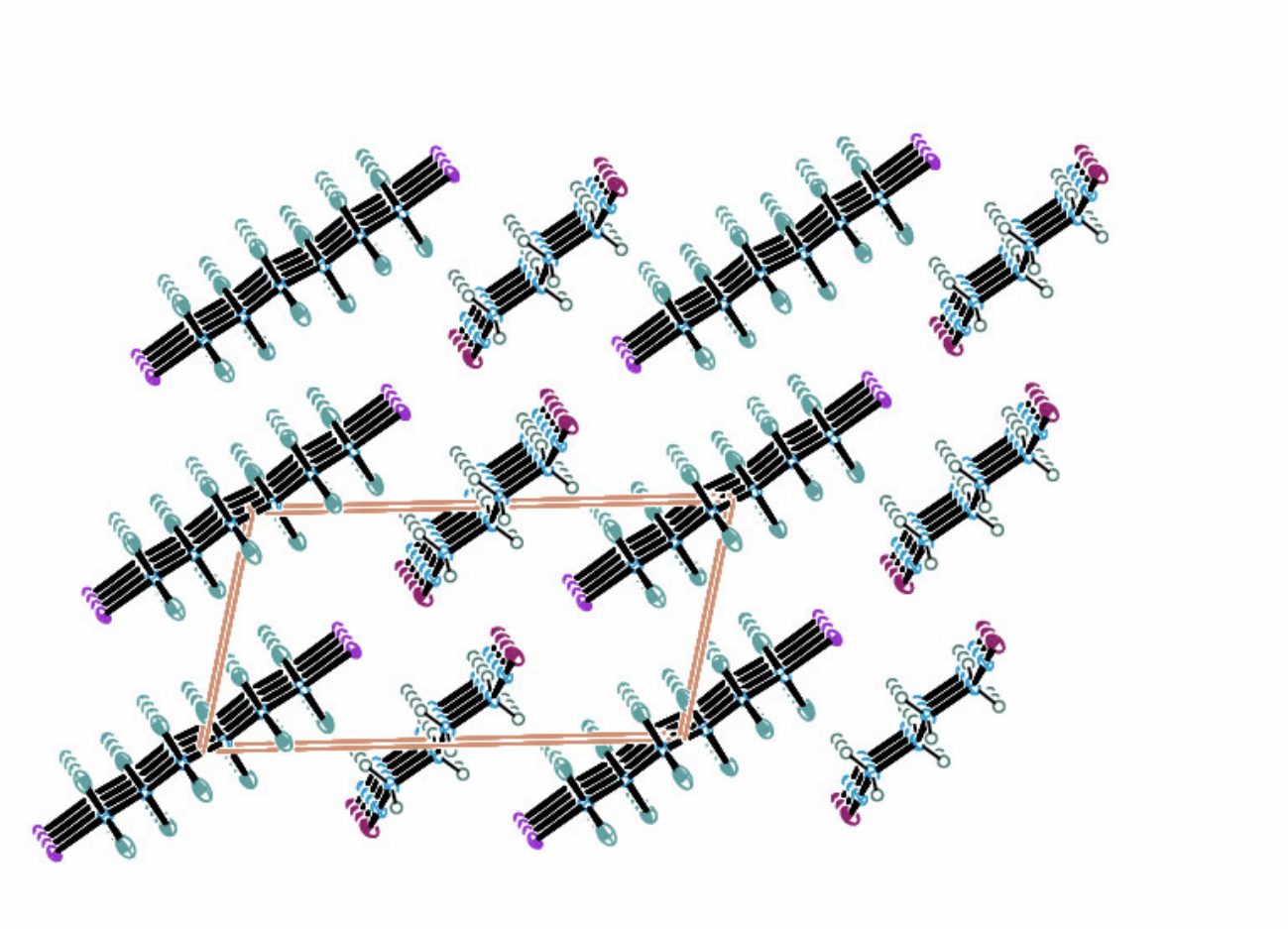

Figure 4 Crystal packing of **4b** viewed down the *a* crystallographic axis.

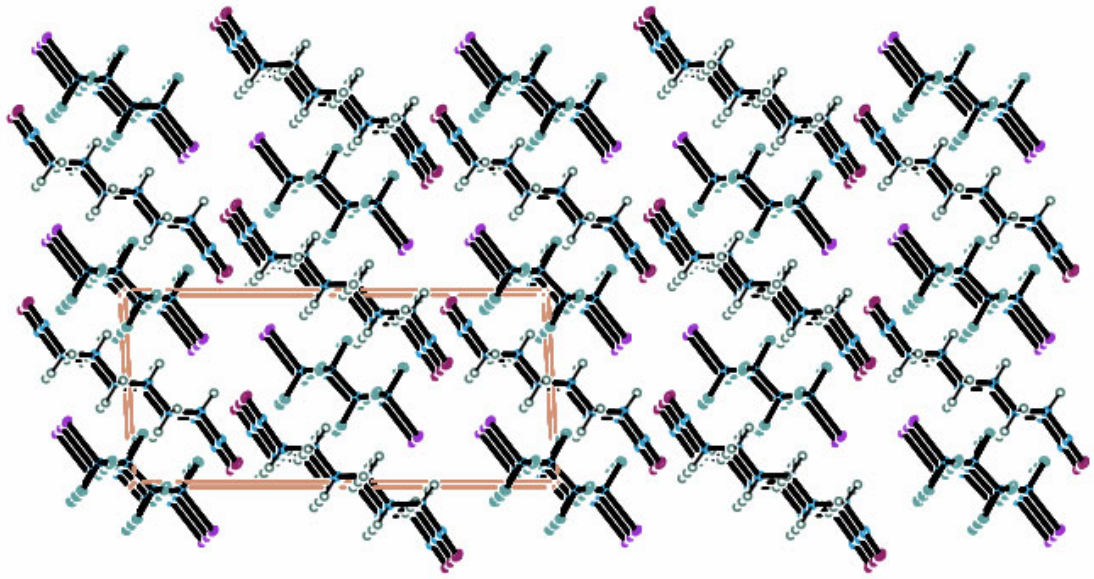

Figure 5 Crystal packing of **5b** viewed down the *b* crystallographic axis.

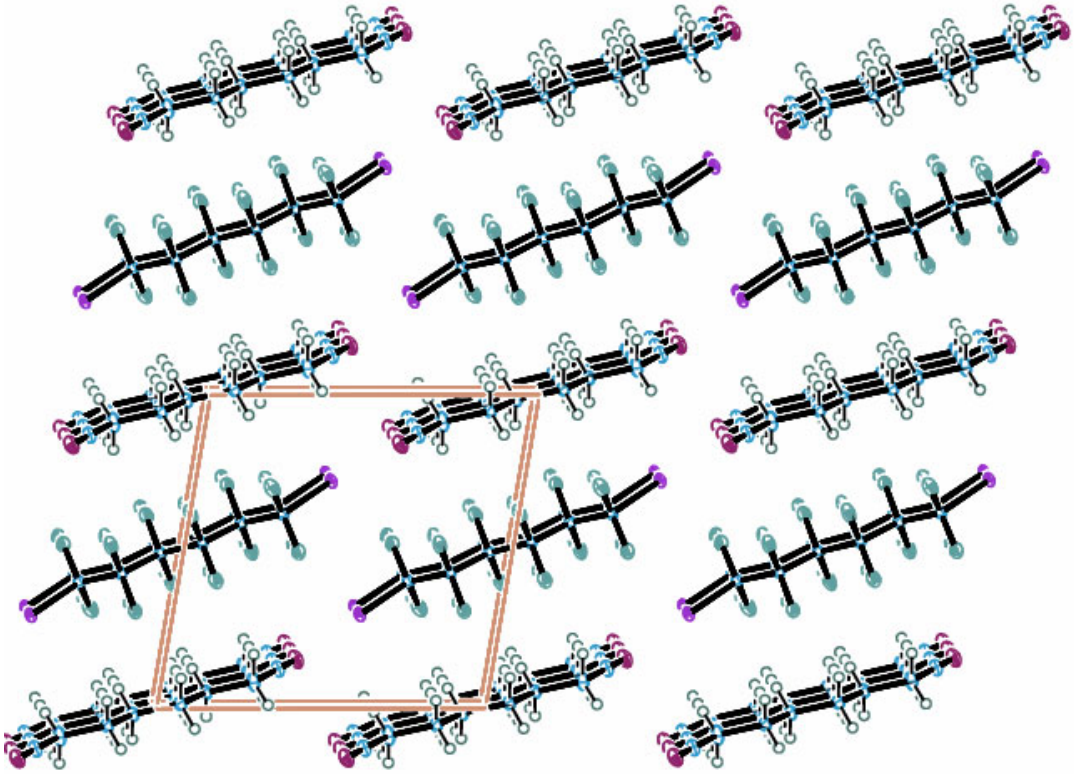

Figure 6 Crystal packing of **6b** viewed down the *b* crystallographic axis.

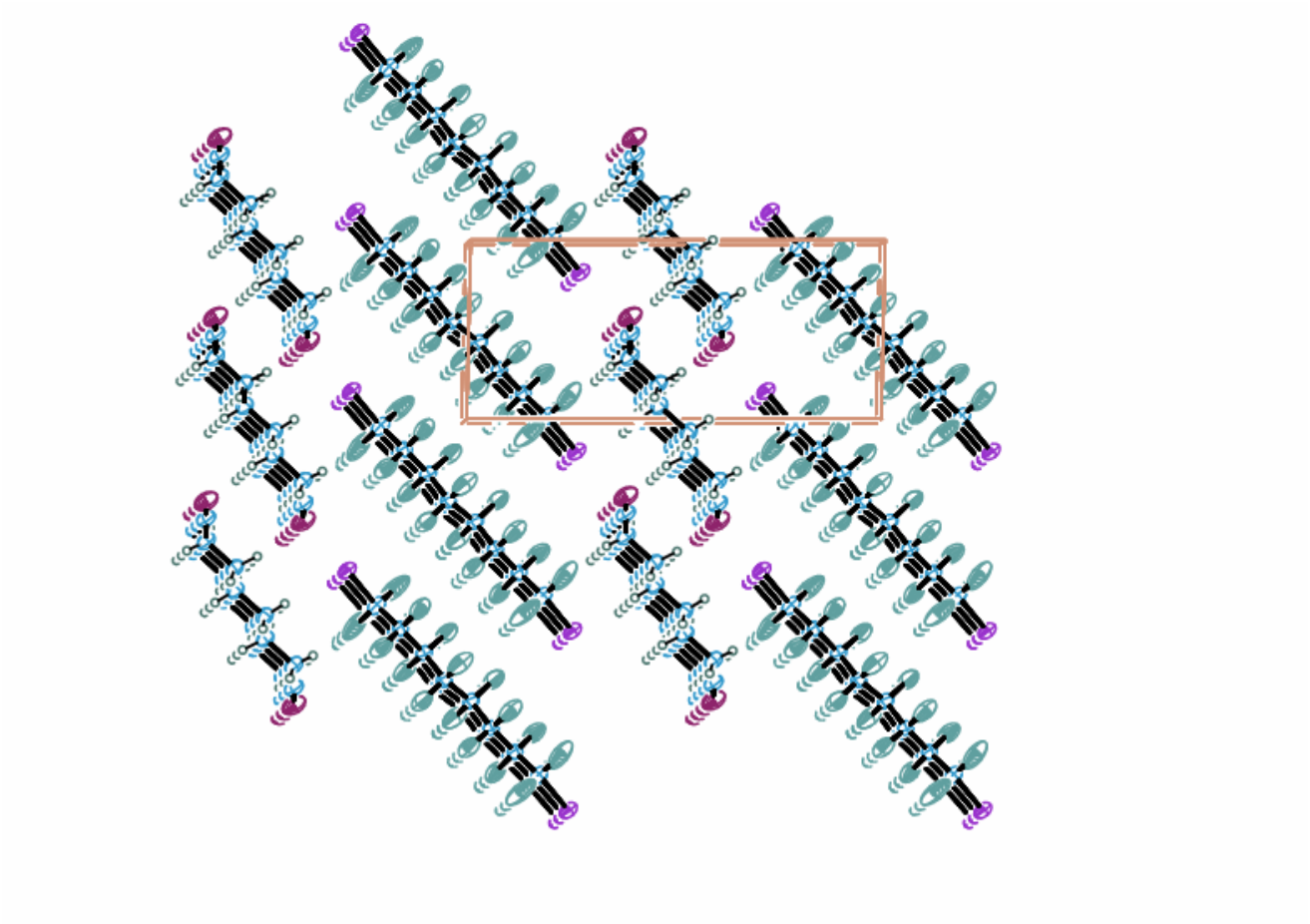

Figure 7 Crystal packing of **3a** viewed down the *a* crystallographic axis.

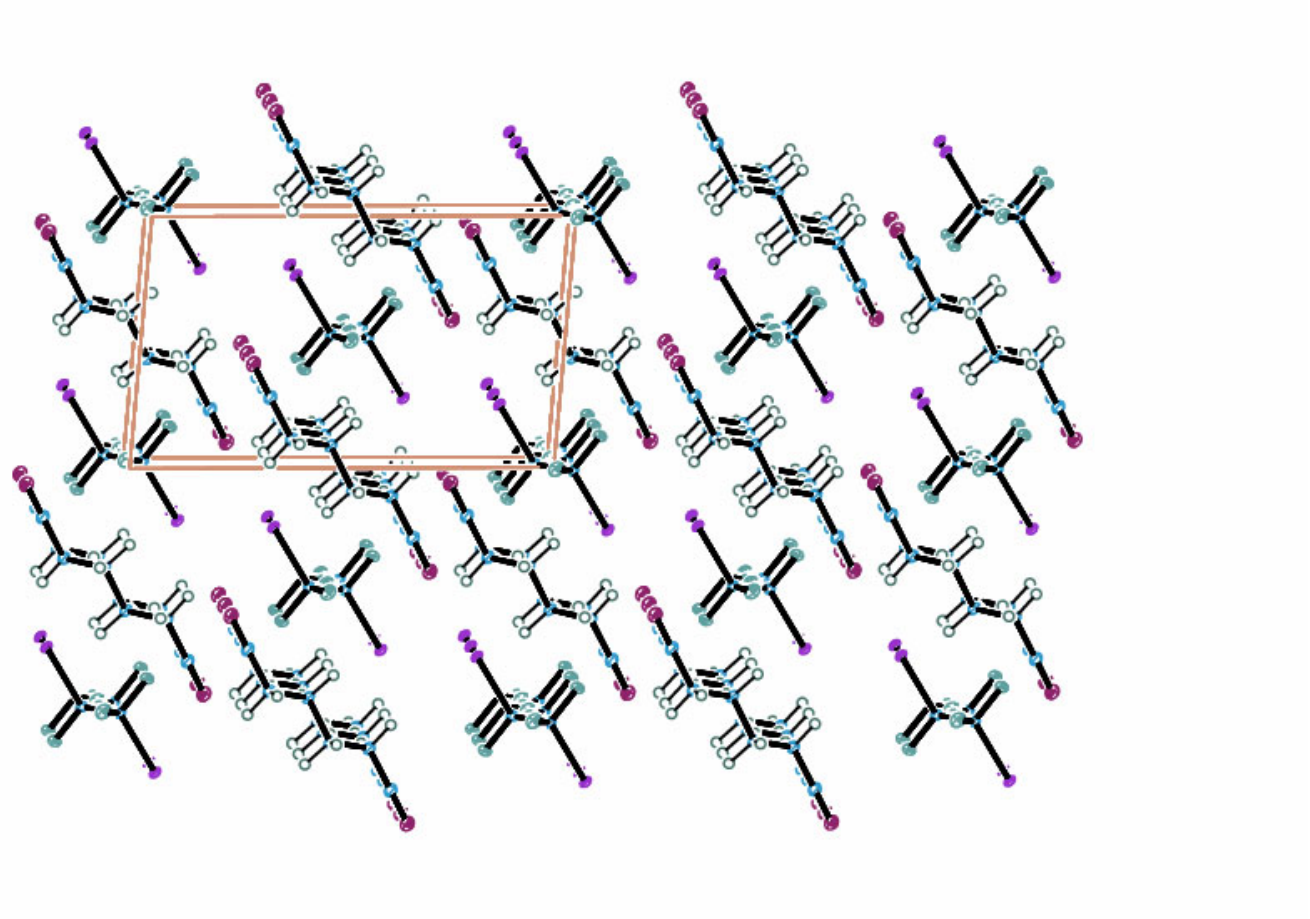

Figure 8 Crystal packing of **6a** viewed down the *b* crystallographic axis.

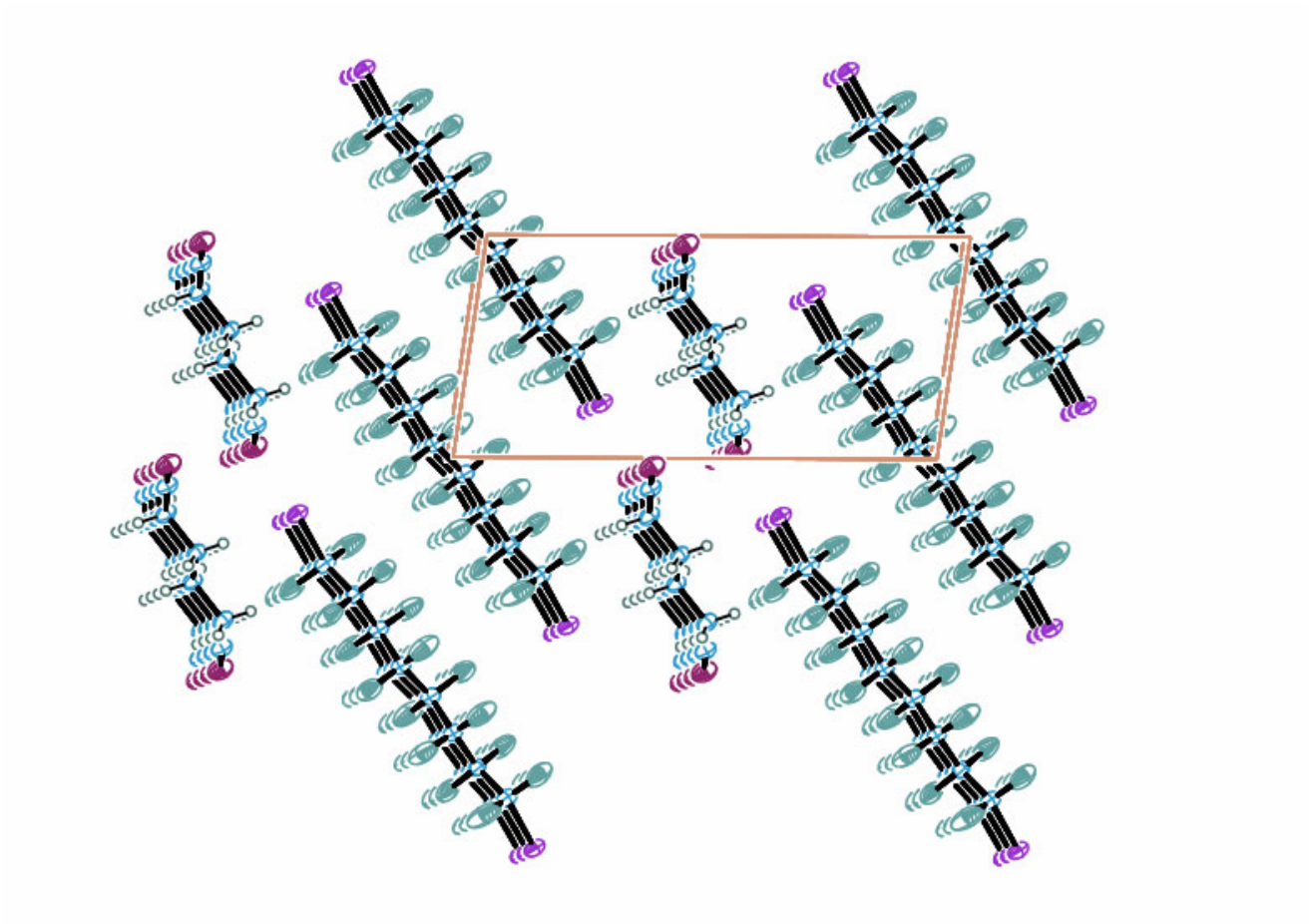

Figure 9 Crystal packing of **4a** viewed down the *b* crystallographic axis.