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Crystal engineering using very short and linear C(sp)–H···N hydrogen bonds: formation of head-to-tail straight tapes and their assembly into nonlinear optical polar crystals

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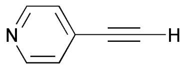
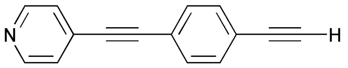
The crystallization of 4-ethynylpyridine (1) and 4-(4-ethynylphenyl)ethynylpyridine (2) leads to C(sp)-H···N hydrogen bonded straight tapes that further assemble into polar crystals, in the case of 2, and show intense powder SHG response, 8 times more efficient than crystalline urea.

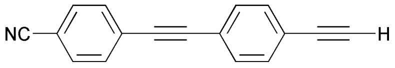
The aims of crystal engineering are to design crystal structures of molecular solids with specific topological features, chemical function, or physical properties.[1] One area of particular endeavor in this field is the design of non-centrosymmetric polar crystals[2] because of their importance for physical properties of bulk assemblies such as non-linear optical (NLO) activity.[3] In this study we introduce a new class of polar crystals in which the molecules are directed in a completely parallel orientation through C(sp)–H···N hydrogen bonds. Here we report the X-ray crystal structures of 4-ethynylpyridine (**1**) and 4-(4-ethynylphenyl)ethynylpyridine (**2**) as well as NLO properties of the polar crystals of **2**.



1



2



3

The crystal structural analysis† for **1**[4] revealed the formation of a linear tape structure formed by very short and linear C(sp)–H···N contacts (Fig. 1); the H···N distance (2.33 Å) found in the structure is about 0.4 Å shorter than the sum of their van der Waals (vdW) radii (2.75 Å) and is one of the shortest C–H···N contacts reported.[5] The C(sp)–H–N angle is 180° and the molecules in the tape are located on a crystallographic two-fold axis. The head-to-tail polar tapes of **1** are arranged in antiparallel fashion in the crystal, resulting in a centrosymmetric packing with space group *C*2/*c*.

The crystal structure analysis‡ for **2**§ also shows the formation of a tape structure through very short and linear C(sp)–H···N contacts (Fig. 2). Molecule **2** is almost planar in the crystal with the largest deviation of 0.21 Å from the least-square plane; the dihedral angle between the two aromatic rings is 19.0°. Interestingly, further packing analysis reveals that the unit cell of the crystal contains eight molecules of **2** in a non-centrosymmetric packing with space group *Fdd*2. Since the majority of achiral organic compounds tend to pack into centrosymmetric crystals,[3] this observation is rather unusual. Moreover, the dipole moments of the molecules are arranged perfectly in a parallel orientation in the crystal and, therefore, the vector parts of the first hyperpolarizabilities of the molecules are directed in a completely parallel orientation, which make this compound attractive for second-order NLO materials. In fact, the crystals of **2** show a strong second-harmonic generation (SHG) signal, 8 times more intense than that of crystalline urea, in the Kurtz powder test at 1907 nm. With this finding, we explored the SHG response in related compounds and found that the crystals of 4-(4-ethynylphenyl)ethynylbenzonitrile (**3**)¶ also exhibit an intense SHG signal, 16 times more efficient than crystalline urea, in the Kurtz powder test at 1907 nm. We surmise that molecules of **3** are also arranged linearly in the crystal, in a head-to-tail fashion directed by the C(sp)–H···N hydrogen bond.[6] Although it is not clear at present what factors are responsible for the polar organization of **2** and **3**, it can be pointed out that the *p*-phenylene units in **2** and **3**, which is absent in **1**, should play an important role in the polar assembly process.‖

In conclusion, we have found a unique assembly of directed polar crystals based on the C(sp)–H···N hydrogen bond, which has been little exploited in crystal engineering so far. The present results clearly demonstrate that the C–H···N weak

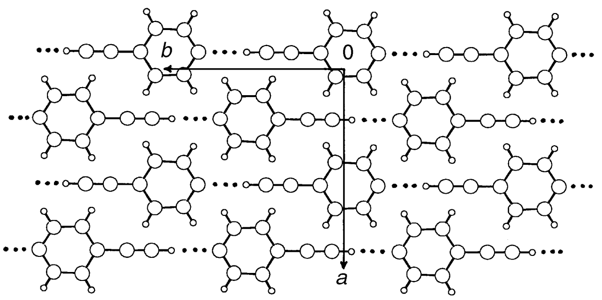


Fig. 1 Packing arrangement of **1** in the crystal. Short C(sp)–H···N contacts are shown by dotted lines; H···N 2.33 Å, C···N 3.28 Å, C–H–N 180°.

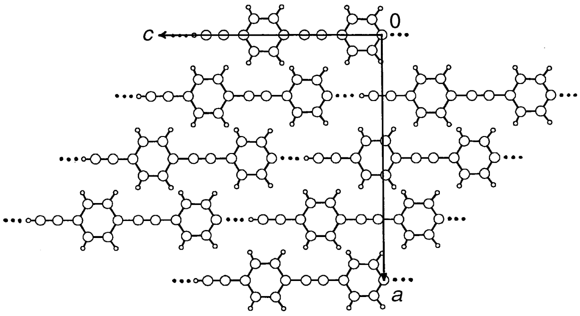


Fig. 2 Packing arrangement of **2** in the crystal. Short C(sp)–H···N contacts are shown by dotted lines; H···N 2.32 Å, C···N 3.27 Å, C–H–N 180°.

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hydrogen bond is capable of not only constructing well-defined crystal structures but also inducing functional properties (SHG response) to the resulting bulk assemblies.

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Notes and references

† *Crystal data* for **1**: C_7H_5N, M = 103.12, colorless rod, 0.60 × 0.20 × 0.20 mm, monoclinic, space group $C2/c$, a = 9.800(5), b = 8.684(5), c = 7.334(4) Å, β = 116.90(4)°, V = 556.6(6) Å^3, Z = 4, ρ_{calcd} = 1.231 g cm^{-3}, T = 193 K, Mo-Kα radiation. A total of 577 unique reflections ($2\theta_{max}$ = 54.2°) were collected, of which 456 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares) to give final R = 0.085 and R_w = 0.114. Residual electron density is 0.42 e Å^{-3}. CCDC 153071. See http://www.rsc.org/suppdata/cc/b1/b103689k/ for crystallographic data in .cif or other format.

‡ *Crystal data* for **2**: $C_{15}H_9N$, M = 203.24, colorless prism, 0.20 × 0.20 × 0.15 mm, orthorhombic, space group $Fdd2$, a = 17.491(1), b = 7.748(1), c = 15.5880(9) Å, V = 2112.5(4) Å^3, Z = 8, ρ_{calcd} = 1.278 g cm^{-3}, T = 123 K, Mo-Kα radiation. A total of 595 unique reflections ($2\theta_{max}$ = 55°) were collected, of which 513 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares) to give final R = 0.056 and R_w = 0.072. Residual electron density is 0.30 e Å^{-3}. CCDC 164007.

§ Compound **2** was prepared by successive Sonogashira coupling of 4-bromoiodobenzene with **1** and trimethylsilylacetylene followed by desilylation using Bu_4NF. *Spectroscopic data* for **2**; mp 180–181 °C (Found: M$^+$, 203.0733. $C_{15}H_9N$ requires M, 203.0735); ν_{max} (KBr)/cm^{-1} 3148, 2216, 2088, 1592, 1502, 1408 and 838; δ_H (300 MHz, $CDCl_3$) 3.21 (1 H, s), 7.38 (2 H, AA′XX′), 7.50 (4 H, s) and 8.61 (2 H, AA′XX′); δ_C (75 MHz, CDCl3) 79.53, 83.06, 88.49, 93.27, 122.55, 123.02, 125.56, 131.17, 131.81, 132.24 and 149.89; m/z (FD) 203 (M$^+$, 100%).

¶ Compound **3** was prepared by successive Sonogashira coupling of 4-bromoiodobenzene with 4-ethynylbenzonitrile and trimethylsilylacetylene followed by desilylation using Bu_4NF. *Spectroscopic data* for **3**; mp 196–198 °C (Found: M$^+$, 227.0753. $C_{17}H_9N$ requires M, 227.0735); ν_{max} (KBr)/cm^{-1} 3236, 2212, 1600, 1504 and 840; δ_H (300 MHz, $CDCl_3$) 3.21 (1 H, s), 7.49 (4 H, s), 7.60 (2 H, AA′BB′) and 7.64 (2 H, AA′BB′); δ_C (75 MHz, CDCl3) 79.45, 82.98, 89.48, 93.02, 111.73, 118.41, 122.58, 122.81, 127.82, 131.62, 132.56, 132.16 and 133.13; m/z (FD) 227 (M$^+$, 100%).

‖ Connection of the tapes of **2** by C(sp^2)–H···π contacts between the pyridine α-proton and the terminal acetylene moiety (H···π centroid distance 2.86 Å) might play a significant role in the polar assembly process. Although there are face-to-face overlaps between the pyridine ring and the *p*-phenylene unit of **2** in the crystal, the interplanar distance (3.80 Å) beyond the sum of vdW radii (3.40 Å), so that the π-stacking interaction would play a less important role in determining the packing.

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