Polar Assembly of 2,6-Diethynylpyridine through C(sp^2)–H···N, C(sp)–H··π and π–π Stacking Interactions: Crystal Structure and Nonlinear Optical Properties

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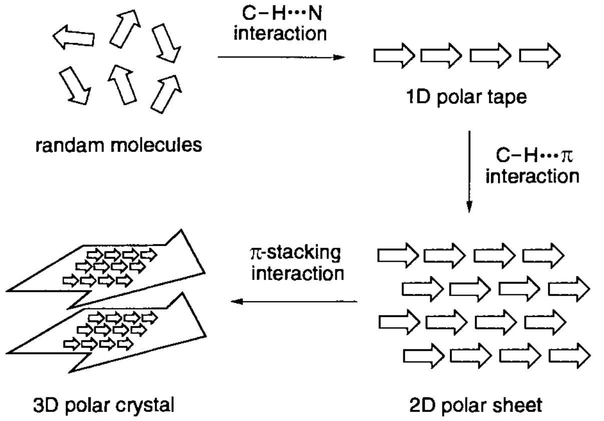
The crystallization of 2,6-diethynylpyridine **1** leads to C(sp^2)–H···N hydrogen bonded head-to-tail tapes which are held together by C(sp)–H··π hydrogen bridges to form 2D polar sheets; further assembly through π–π stacking interaction results in 3D polar crystals which show intense powder SHG response, 5-fold stronger than crystalline urea.

Crystal engineering aims at the design of 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 the bulk assemblies such as second-order non-linear optical (NLO) activity.[3] In this study we found that 2,6-diethynylpyridine **1** formed unique and well-defined polar crystals through C(sp^2)–H···N, C(sp)–H··π and π–π stacking interactions (Scheme 1). In contrast to the well-established C–H···O[4] interaction, which has been proven to be a useful tool to obtain supramolecular synthons,[5] weak hydrogen bondings through short C–H···N[6] and C–H··π[7] contacts have been little exploited in crystal engineering so far. Moreover, only limited structures formed by C–H···Y (Y = O, N, π) attractive forces have been discussed in terms of the functional properties of the resulting assemblies, e.g., NLO activity[8] or selective complexation with guest molecules.[9] Here we report the C–H···N and C–H··π bonded polar structure of **1** determined by X-ray study together with its NLO properties.



Scheme 1. Schematic representation of the polar organization of **1**; the order of assembling is tentative.

The crystal structural analysis[10] of a single crystal of **1**[11] obtained by slow sublimation revealed that the unit cell of the crystal contains two molecules of **1** in a non-centrosymmetric packing with space group *Cm*. Since the majority of achiral organic compounds tend to pack into centrosymmetric crystals,[3] this observation is rather unusual and it is interesting to elucidate the factors responsible for the polar organization of **1**. Packing analysis reveals the formation of a polar tape structure formed by short and linear C(sp^2)–H···N contacts (Figure 1); the H···N distance (2.43 Å) is shorter than the sum of their van der Waals radii (2.5 Å) and the C–H–N angle is 180°. The head-to-tail tapes are held together by C(sp)–H··π hydrogen bridges with a T-shaped geometry to form polar sheet structure (Figure 1); the H··π (centroid) distance is 2.78 Å and the C–H–π (centroid) angle is 162.2°. Moreover, further packing analysis reveals that there is a face-to-face overlap between the pyridine units of **1** in the crystal (Figure 2) with the interplanar distance (3.31 Å) shorter than the sum of van der Waals radii (3.4 Å). Therefore, the π–π stacking interaction would also play an important role in determining the polar packing, though it is difficult to clarify the origin[12] of the geometrical preference observed for the overlap. In this respect, however, it is interest-

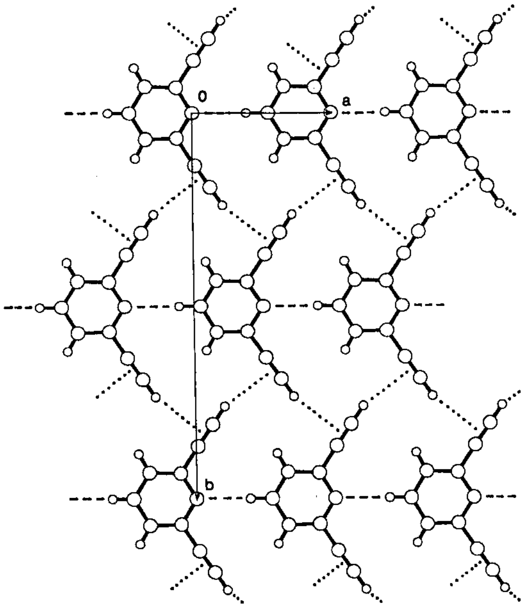


Figure 1. Packing arrangement of **1** in the crystal. Short C(sp^2)–H---N contacts are shown by dashed lines; H---N 2.43 Å, C---N 3.38 Å, C–H–N 180°. Short C(sp) – H··· π contacts are shown by dotted lines; H··· π (centroid) 2.78 Å, C–H–π (centroid) 162.2°.

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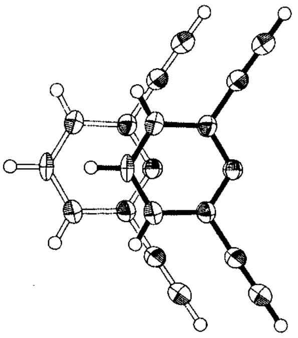

Figure 2. A face-to-face overlap between molecules of **1** in the crystal. The interplanar distance and dihedral angle are 3.31 Å and 0°.

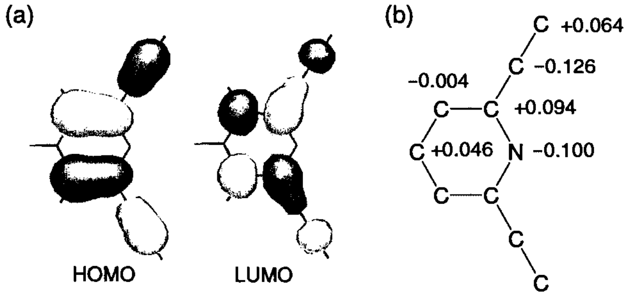

Figure 3. AM1 calculated frontier molecular orbitals of **1** (a) and total atomic charges in **1** (b); those of hydrogen atoms are summed into the connected carbon atoms.

ing to point out that both favorable orbital and electrostatic interactions are able to operate simultaneously in the observed parallel overlap while only one of them is available in the hypothetical antiparallel overlap, according to the frontier molecular orbitals and ground state atomic charges shown in Figure 3. Thus, it seems that the C(sp^2)–H···N and C(sp)–H··π attractive forces coupled with the π–π stacking interaction are responsible for the polar organization of **1** (Scheme 1).

Interestingly, the dipole moments of the molecules are arranged perfectly in a parallel orientation in the crystal of **1** and, therefore, the vector parts of the first hyperpolarizabilities of the molecules are directed in a completely parallel orientation, which makes this compound attractive for second-order NLO materials. In fact, the crystals of **1** show a strong second-harmonic generation (SHG) signal, 5-fold larger than crystalline urea, in the Kurtz powder test at 1907 nm.

In conclusion, we have shown a simple model for the construction of polar assembly based on cooperative C(sp^2)–H···N, C(sp)–H··π and π–π stacking interactions. The present results clearly demonstrate that these weak interactions are 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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