Persistent One-Dimensional Face-to-Face π-Stacks within Organic Cocrystals.

Anatoliy N. Sokolov,[a] Tomislav Friščić,[a] Steven P. Blais,[b] John A. Ripmeester[b] and Leonard R. MacGillivray[a,]*

[a] Department of Chemistry, University of Iowa, Iowa City, IA 52242-1294 (USA)

[b] Steacie Institute for Molecular Science, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

SUPPLEMENTARY MATERIAL

S1. General Information:

For the synthesis of the co-crystals: 4,4'-dipyridyl and *trans*-1,2-bis-(4-pyridyl)ethylene, were commercially available (Aldrich Co.). *Trans*-1,2-bis-(4-pyridyl)acetylene was prepared according to the literature.[1] *Trans*-1,2-bis-(4-pyridyl)ethylene was purified by the addition of activated carbon to a solution of *trans*-1,2-bis-(4-pyridyl)ethylene in hot EtOH, stirring for 30 min, filtration and re-crystallization from EtOH.

S2. Thermogravimetric Analysis:

Thermogravimetric analysis shows that all three samples experience a single mass loss that begins at 100° (1), 110° (2), and 125° (3). The hydrogen bond distances for 1, 2 and 3 are reflected in the stabilities of the solids, as revealed by the onset of the mass loss.

S3. X-ray Crystallography:

Crystal data for **1**: monoclinic, $P\ 2_1/c$, a = 7.609(1) Å, b = 19.338(2) Å, c = 9.911(1) Å, β = 110.09(1)°, V = 1369.7(3) Å^3, Z = 4, ρ_{calc} = 1.29 g/cm^3, R_1 = 0.047 for 2480 reflections with $I > 2\sigma(I)$.

Crystal data for **2**: triclinic, $P\ \bar{1}$, a = 7.731(1) Å, b = 9.582(1) Å, c = 11.110(1) Å, α = 75.67(1)°, β = 80.77(1)°, γ= 74.24 (1)°, V = 763.6(1) Å^3, Z = 2, ρ_{calc} = 1.26 g/cm^3, R_1 = 0.052 for 1905 reflections with $I > 2\sigma(I)$.

Crystal data for **3**: monoclinic, $P\ 2_1/n$, a = 7.721(1) Å, b = 9.152(1) Å, c = 21.737(2) Å, β = 91.74(1)°, V = 1535.2(1) Å^3, Z = 2, ρ_{calc} = 1.15 g/cm^3, R_1 = 0.045 for 2083 reflections with $I > 2\sigma(I)$.

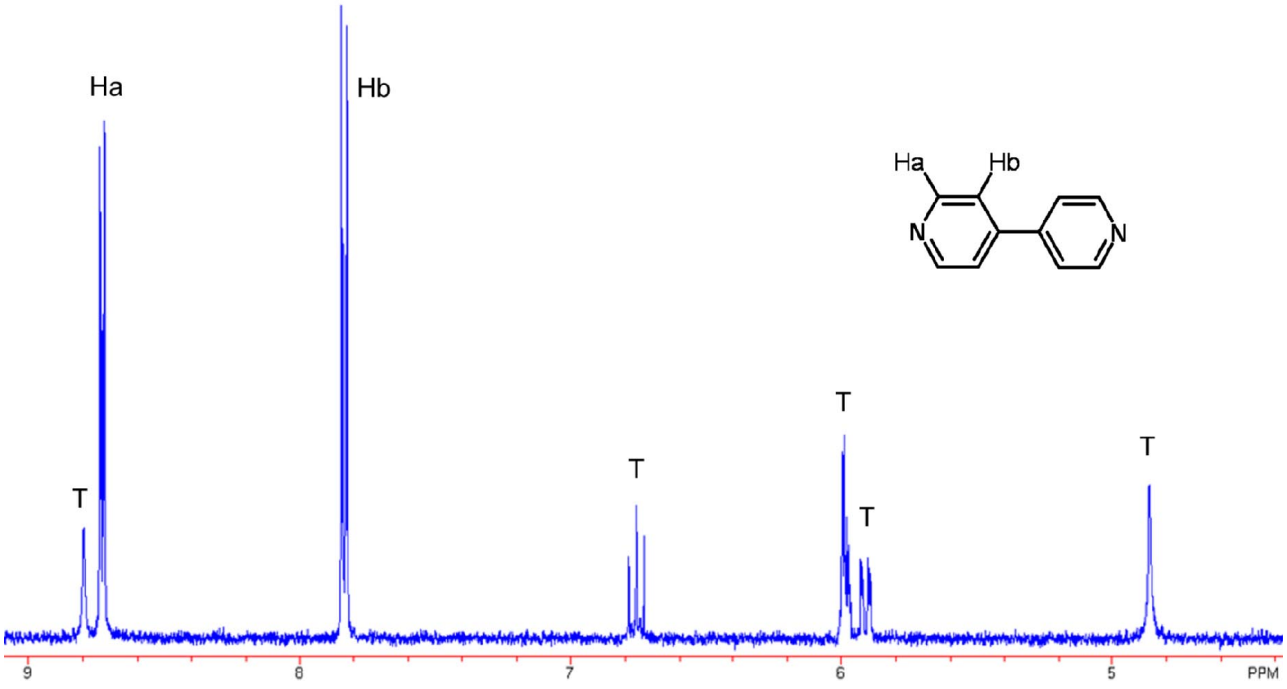
All crystal data were measured on a Nonius Kappa CCD single-crystal X-ray diffractometer at liquid nitrogen temperature. After anisotropic refinement of non-hydrogen atoms, hydrogen atoms bonded to sp^2 hybridized atoms, hydroxyl and amine groups were placed in idealized positions and allowed to ride on the atom to which they are attached. The ladder inclination angle, θ, was based on the angle between three points as defined by N2, N1, and N1 of the next crystallographically identical pyridine-based rung. Structure solution was accomplished with the aid of SHELXS-97 and refinement was conducted using SHELXL-97 locally implemented on a Pentium-based IBM compatible computer.[2] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-295847 (1), CCDC-295848 (2), CCDC-295849 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

References:

Champness, N. R.; Khlobystov, A. N.; Majuga, A. G.; Schroder, M.; Zyk, N. V. *Tetrahedron Lett.* **1999**, *40*, 5413.
(1) Sheldrick, G. M. *SHELXL-97*, University of Göttingen, Germany, **1997**.

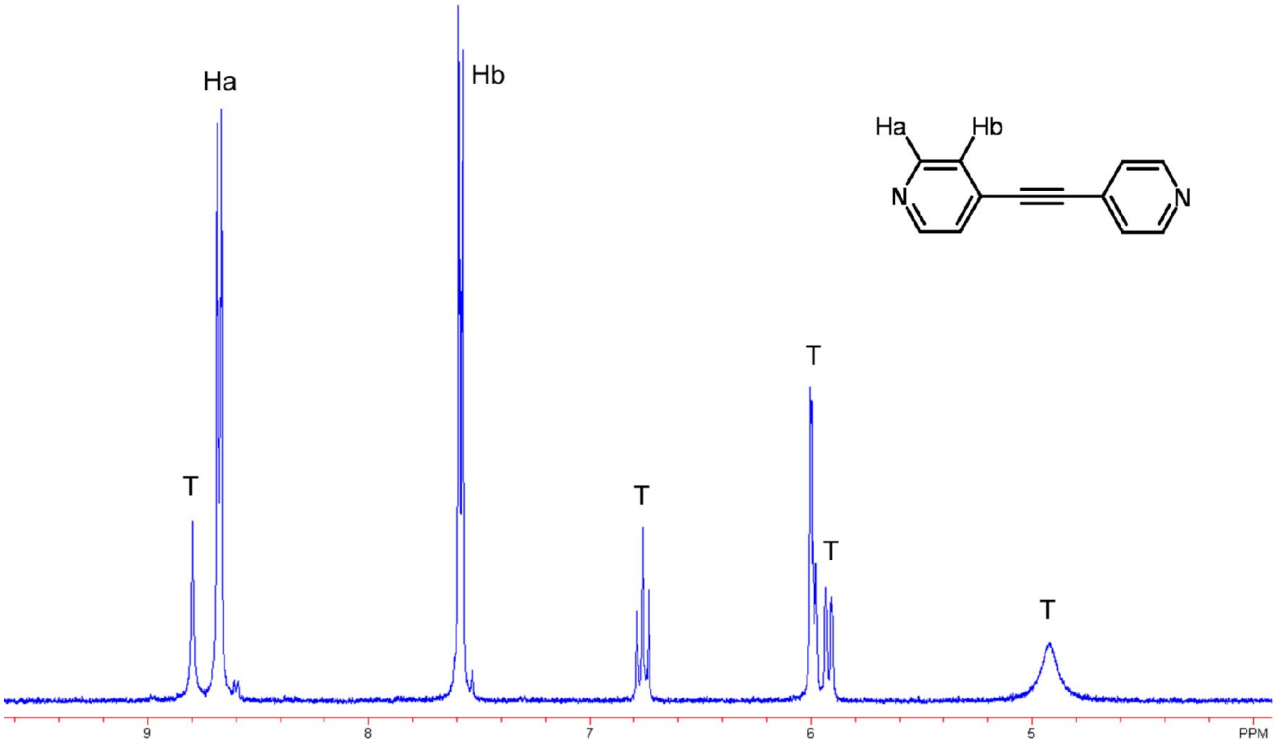
S4. ^{1}H NMR spectra of **1**, **2**, and **3**.

1



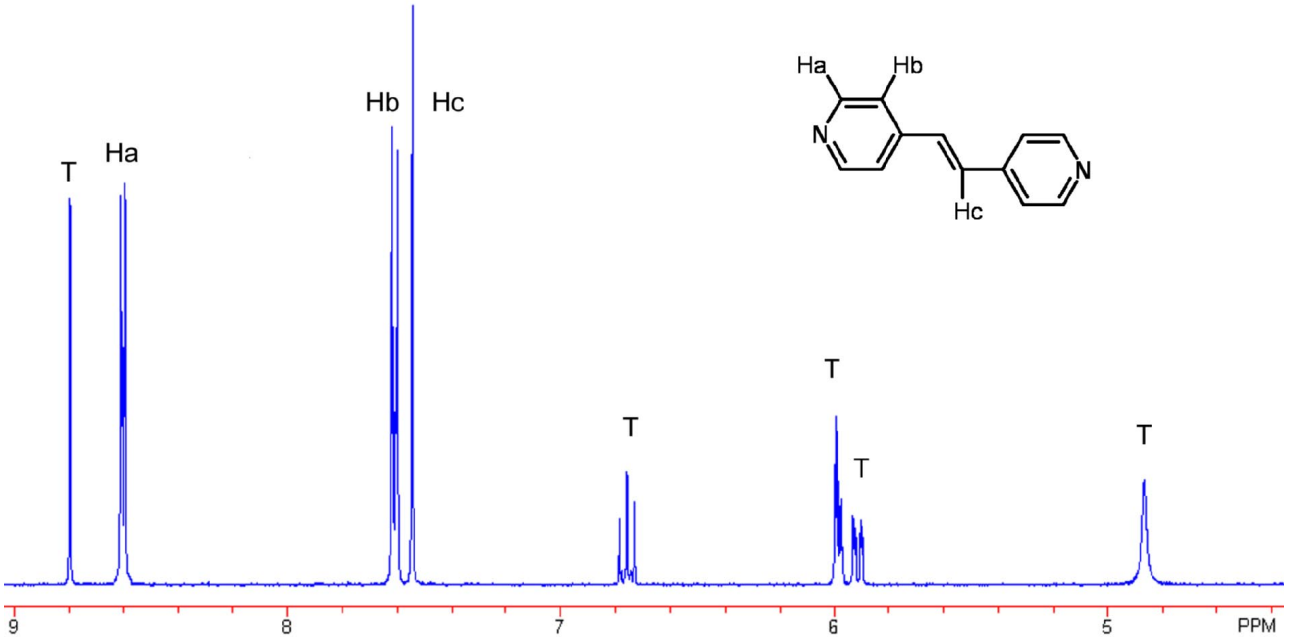
T = 3-aminophenol

2



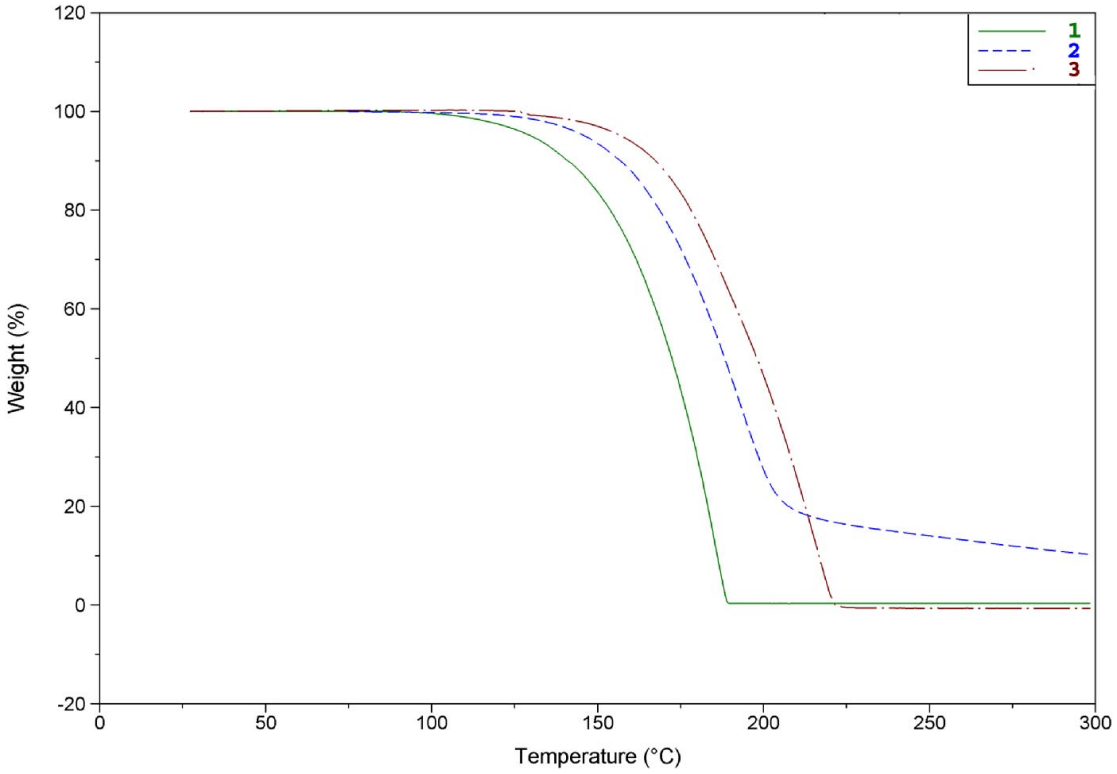
T = 3-aminophenol

3



T = 3-aminophenol

S5. TGA thermograms of **1**, **2**, and **3**.



S6. FTIR spectra of samples **1**, **2**, and **3** (KBr).

A) – 3

B) – 2

C) – 1