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Controlling hydrogen-bond preferences in bipyridines with competing binding sites

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ABSTRACT

The design and synthesis of a family of supramolecular reagents (SRs) based on ethynyl-spaced substituted bipyridines are described, and their potential use as molecular 'hubs' for the predictable construction of binary and ternary co-crystals is explored. Each SR was synthesized in good yields through consecutive Pd-catalyzed Sonogashira cross-coupling reactions. Crystal structures of three binary co-crystals are presented with each structure clearly illustrating how accurate supramolecular assembly control can be achieved by increasing/decreasing the strength of the participating hydrogen-bond interactions.

1. Introduction

Organizing and constructing multi-component supermolecules from individual entities through reliable and versatile supramolecular synthetic strategies is an ever-increasing challenge in crystal engineering [1]. The hydrogen bond is the most widely used non-covalent interaction for synthesizing organic-based assemblies due to its strength and directionality, but also because it can be fine-tuned geometrically and electronically [2]. These attributes have been utilized recently in the design of co-crystals where multiple hydrogen bond donors and acceptors compete within a single crystallization reaction [3].

Isonicotinamide is a well-known supramolecular reagent (SR) capable of forming both binary and ternary co-crystals with expected connectivity and topology [4]. If isonicotinamide is combined with a monocarboxylic acid in a 1:1 ratio, the outcome is typically a binary co-crystal where the acid interacts through an O–H···N hydrogen-bond with the pyridine (the best hydrogen-bond acceptor), while an amide-amide homodimer creates a four-component supermolecule. When two different aromatic acids are combined with isonicotinamide in a 1:1:1 ratio, the pyridine site forms a hydrogen bond with the stronger carboxylic acid, while the amide functionality, second best acceptor, binds to the weaker acid. There are some limitations associated with isonicotinamide as a supramolecular building block, however, since its two binding sites reside on the same molecular backbone and they can, therefore, not be electrostatically altered independently, Scheme 1.

Another ditopic SR based on a combination of pyridyl- and benzimidazole binding sites can also form ternary co-crystals where the more basic benzimidazole site preferentially forms hydrogen bonds to a more acidic carboxylic acid while the pyridine site forms hydrogen bonds with the weaker of the two carboxylic acids [5]. However, in contrast to the situation in isonicotinamide, the two hydrogen-bond acceptors are electrostatically independent (*e.g.*, the addition of a substituent on one ring will not affect the inherent properties of the binding site on the other aromatic ring) which enables electrostatic fine-tuning of the individual hydrogen-bonding sites thereby increasing the versatility of the SR, Scheme 1.

Although the pyridyl and benzimidazole moieties are uncoupled, the comparison incorporates different heterocycles of varied basicity and shape, *i.e.*, 5-membered ring vs. 6-membered ring. In order to eliminate the possibility that ring-size and/or shape-complementary affects competitive intermolecular binding, we need to examine two similar *N*-heterocyclic moieties attached to the same uncoupled backbone.

Consequently, three different ethynyl-spaced substituted bipyridines were synthesized and characterized where the electrostatic nature of each binding site could be altered through the use of electron-donating (–OMe) or electron-withdrawing (–F) substituents around each pyridyl-heterocycle, Scheme 2.

Herein, we present the synthesis of three ethynyl-spaced bipyridines **1–3** and our initial efforts to construct binary co-crystals with predictable connectivities and stoichiometries.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. *Bis*(triphenylphos-

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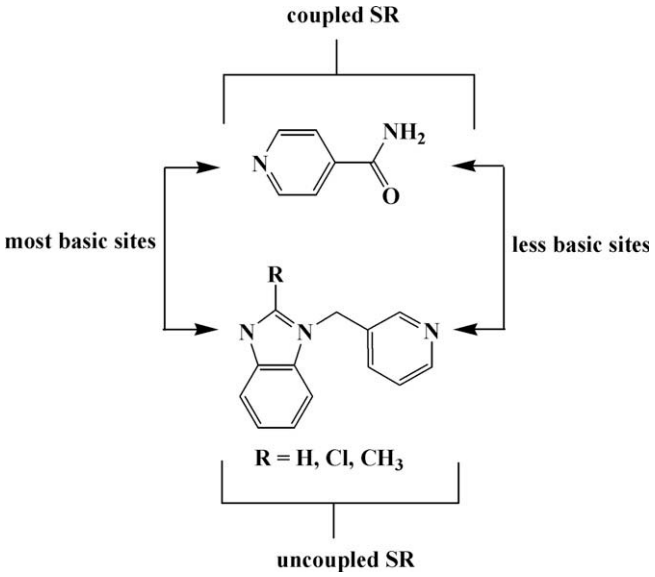
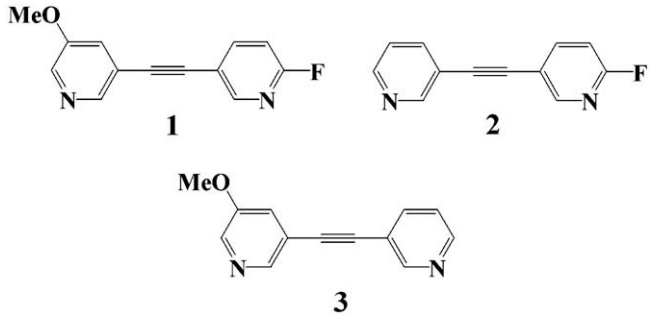


Scheme 1. Two ditopic SRs; isonicotinamide, has a coupled backbone, while pyridyl/benzimidazol-1-yl-based SRs display a decoupled framework.



Scheme 2. Three bifunctional SRs each possessing two different hydrogen-bonding moieties.

phine)palladium(II) dichloride was purchased from Strem while trimethylsilylacetylene was purchased from GFS chemicals. Melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected. Compounds were prepared for infared spectroscopic (IR) analysis as a mixture in KBr. ^{1}H NMR spectra were recorded on a Varian Unity plus 400 MHz spectrometer in $CDCl_3$.

2.2. Synthesis

2.2.1. [1-(2-Fluoropyrid-5-yl)-2-(3-methoxypyrid-5-yl)ethyne] (**1**)

2-Fluoro-5-bromopyridine (441 mg, 2.5 mmol), 3-methoxy-5-ethynylpyridine (400 mg, 3.01 mmol), copper iodide (16 mg, 0.084 mmol), triphenylphosphine (60 mg, 0.226 mmol), *bis*(triphenylphosphine)palladium(II) dichloride (60 mg, 0.086 mmol) were added to a round bottom flask. Tetrahydrofuran (20 mL) and triethylamine (20 mL) were added and dinitrogen bubbled through the resultant mixture for 10 min. A condenser was attached and the mixture heated at 70 °C under a dinitrogen atmosphere. The reaction was monitored by TLC and allowed to cool to room temperature upon completion (48 h). The solution was then diluted with 50 mL of ethyl acetate, washed with water (3 × 100 mL) then washed with saturated aqueous sodium chloride (1 × 100 mL). The organic layer was separated and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the residue chromatographed on silica with a hexanes/ethyl acetate mixture (10:1) as the eluant. The product was isolated as a light brown solid. The product **1** was recrystallized from toluene producing amber block shaped crystals (480 mg, 84%). M.p: 133–135 °C; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 8.41 (d, J = 1.6 Hz, 1H), 8.38 (s, 1H), 8.30 (d, J = 2.4 Hz, 1H), 7.95–7.90 (m, 1H), 7.31 (t, J = 1.4 Hz, 1H), 6.97 (dd, J = 8.4 Hz, J = 2.4 Hz, 3H), 3.88 (s, 3H); IR (KBr pellet) υ 3045, 1576, 1488, 1415, 1253, 1226 cm^{-1}.

2.2.2. [1-(2-Fluoropyrid-5-yl)-2-(3-pyrid-5-yl)ethyne] (**2**)

2-Fluoro-5-bromopyridine (1.60 g, 9.09 mmol), 3-ethynylpyridine (1.30 g, 12.6 mmol), copper iodide (45 mg, 0.237 mmol), triphenylphosphine (225 mg, 0.859 mmol), *bis*(triphenylphosphine) palladium(II) dichloride (130 mg, 0.185 mmol) were added to a round bottom flask. Tetrahydrofuran (30 mL) and triethylamine (30 mL) were added and dinitrogen bubbled through the resultant mixture for 10 min. A condenser was attached and the mixture heated at 70 °C under a dinitrogen atmosphere. The reaction was monitored by TLC and allowed to cool to room temperature upon completion (48 h). The solution was then diluted with 50 mL of ethyl acetate, washed with water (3 × 100 mL) then washed with saturated aqueous sodium chloride (1 × 100 mL). The organic layer was separated and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the residue chromatographed on silica with a hexanes/ethyl acetate mixture (10:1) as the eluant. The product **2** was isolated as a light orange solid (1.58 g, 88%). M.p: 63–65 °C; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 8.78 (d, J = 2 Hz, 1H), 8.59 (dd, J = 4.6 Hz, J = 1.4 Hz, 1H), 8.42 (d, J = 1.6 Hz, 1H), 7.95–7.91 (m, 1H), 7.82 (dt, J = 7.6 Hz, 1.8 Hz, 1H), 7.32 (dd, J = 7.8 Hz, J = 5 Hz, 1H), 6.97 (dd, J = 8.6 Hz, J = 3 Hz, 1H); IR (KBr pellet) υ 3065, 2223, 1576, 1487, 1247 cm^{-1}.

2.2.3. [1-(3-Methoxypyrid-5-yl)-2-(3-pyrid-5-yl)ethyne] (**3**)

3-Bromopyridine (396 mg, 2.51 mmol), 3-methoxy5-ethynylpyridine (400 mg, 3.01 mmol), copper iodide (16 mg, 0.084 mmol), triphenylphosphine (60 mg, 0.226 mmol), *bis*(triphenylphosphine)palladium(II) dichloride (60 mg, 0.086 mmol) were added to a round bottom flask. Tetrahydrofuran (20 mL) and triethylamine (20 mL) were added and dinitrogen bubbled through the resultant mixture for 10 min. A condenser was attached and the mixture heated at 70 °C under a dinitrogen atmosphere. The reaction was monitored by TLC and allowed to cool to room temperature upon completion (48 h). The solution was then diluted with 50 mL of ethyl acetate, washed with water (3 × 100 mL) then washed with saturated aqueous sodium chloride (1 × 100 mL). The organic layer was separated and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the residue chromatographed on silica with a hexanes/ethyl acetate mixture (10:1) as the eluant. The product **3** was isolated as an off-white solid (455 g, 87%). M.p: 100–102 °C; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 8.780(d, J = 1.2 Hz, 1H), 8.60 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 8.40 (d, J = 1.2 Hz, 1H), 8.31 (d, J = 8.31 Hz, 1H), 7.84 (dt, J = 7.6 Hz, 1.8 Hz, 1H), 7.34–7.32 (m, 1H), 3.90 (s, 3H); IR (KBr pellet) υ 3048, 2210, 1576, 1414, 1227, 700 cm^{-1}.

2.3. Supramolecular synthesis

2.3.1. [1-(2-Fluoropyrid-5-yl)-2-(3-methoxypyrid-5-yl)ethyne] · [4-nitrobenzoic acid] (**4**)

1-(2-Fluoropyrid-5-yl)-2-(3-methoxypyrid-5-yl)ethyne (10.0 mg, 0.044 mmol) and 4-nitrobenzoic acid (7.0 mg, 0.042 mmol) were added to a test tube and dissolved in 10 mL of acetonitrile. Upon slow evaporation of the solvent over 4 days, needle-shaped

crystals formed. M.p: 150–152 °C; IR (KBr pellet) υ 3098, 2419, 1911, 1707, 1534, 1341, 1253, 718 cm^{-1}.

*2.3.2. [1-(2-Fluoropyrid-5-yl)-2-(3-pyrid-5-yl)ethyne] · [4-nitrobenzoic acid] (**5**)*

1-(2-Fluoropyrid-5-yl)-2-(3-pyrid-5-yl)ethyne (9.0 mg, 0.045 mmol) and 4-nitrobenzoic acid (8.0 mg, 0.048 mmol) were added to a test tube and dissolved in 2 mL of ethanol. Upon slow evaporation of the solvent over 4 days, rod-shaped crystals formed. Dec. 165 °C; IR (KBr pellet) υ 3059, 2415, 1951, 1717, 1576, 1521, 1489, 1310, 717 cm^{-1}.

*2.3.3. [1-(3-Methoxypyrid-5-yl)-2-(3-pyrid-5-yl)ethyne] · [3,5-dinitrobenzoic acid] (**6**)*

1-(3-Methoxypyrid-5-yl)-2-(3-pyrid-5-yl)ethyne (10.0 mg, 0.048 mmol) and 3,5-dinitrobenzoic acid (20.0 mg, 0.094 mmol) were added to a test tube and dissolved in 5 mL of methanol. Upon slow evaporation of the solvent over 2 days, yellow rod-shaped crystals formed. M.p: 139–141 °C; IR (KBr pellet) υ 3098, 2419, 1911, 1707, 1534, 1341, 1253, 718 cm^{-1}.

Table 1
Crystal data and structure refinement parameters for **1** and **4–6.**

Compound	**1**	**4**	**5**	**6**
Emperical formula	$C_{13}H_9FN_2O$	$C_{13}H_9FN_2O$ $C_7H_5NO_3$	$C_{12}H_7FN_2O$ $C_7H_5NO_3$	$C_{13}H_{10}N_2O$ 2 ($C_7H_4N_2O_6$)
Formula weight	228.22	395.34	365.32	634.47
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group, Z	P2(1)/n, 4	P-1, 2	P-1, 2	P-1, 2
a (Å)	7.1841(16)	3.7993(5)	3.7472(4)	10.2937(14)
b (Å)	13.160(3)	11.3845(13)	13.1520(13)	10.6249(14)
c (Å)	11.410(2)	20.213(2)	16.3768(18)	13.8098(18)
α (°)	90	95.741(6)	87.566(7)	102.139(2)
β (°)	98.923(16)	92.251(8)	87.877(9)	110.992(3)
γ (°)	90	92.370(8)	88.320(5)	93.559(3)
V ($Å^3$)	1065.7(4)	868.30(18)	805.51(15)	1362.9(3)
T (°K)	203(2)	173(2)	173(2)	100(2)
D_c (g cm^{-3})	1.422	1.512	1.506	1.546
μ (mm^{-1})	0.104	0.118	0.116	0.126
Reflections				
Collected	6894	10,984	5440	15,651
Independent	2422	3934	3431	7774
Observed [$I > 2\sigma(I)$]	1569	1861	1992	6194
$R[I > 2\sigma(I)]$	0.0645	0.0661	0.0519	0.0675
wR_2	0.1575	0.1681	0.1457	0.1753

2.4. X-ray crystallography

All datasets were collected at low temperature using MoKα radiation, Table 1. Except for **6**, which was collected on a SMART APEX diffractometer, datasets were collected on Bruker SMART 100 equipment. Data were collected using SMART or APEXII software [6]. Initial cell constants were found by small widely separated "matrix" runs. An entire hemisphere of reciprocal space was collected. Scan speed and scan width were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT [7], using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Absorption corrections were not applied. The datasets for **4** and **5** were corrected for extinction; parameters for both datasets refined to values that were significantly different from zero.

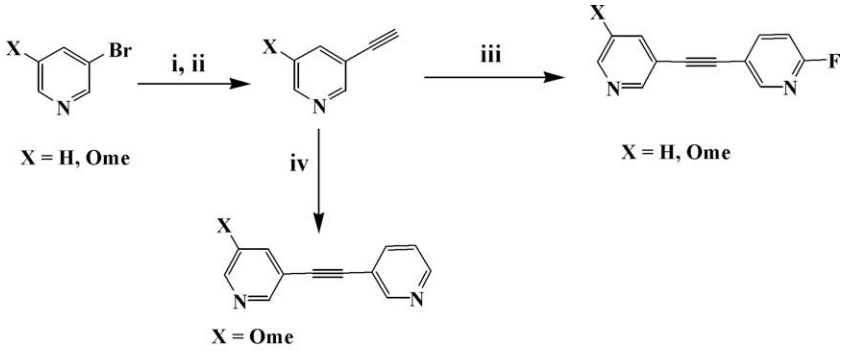
Data were reduced with SHELXTL [8]. The structures were solved in all cases by direct methods without incident. Positions of the carboxylic acid hydrogen atoms were allowed to refine; all other hydrogen atoms were assigned to idealized positions and were allowed to ride. Occupancy factors for partially occupied sites were allowed to refine until the last stages of data processing at which point they were assigned to fixed values.

3. Results and discussion

SRs **1–3** were prepared in good yields *via* multiple Pd-catalyzed Sonogashira [9] cross-coupling reactions, Scheme 3. The starting precursors, 3-methoxy-5-ethynylpyridine and 3-ethynylpyridine, were prepared as previously reported [10].

Recrystallizations were carried out for SRs **1–3** in a variety of solvents; however, crystals suitable for single-crystal X-ray diffraction were only obtained for **1**. The crystal structure of 1-(2-fluoropyrid-5-yl)-2-(3-methoxypyrid-5-yl)ethyne **1** contains one molecule in the asymmetric unit with both heterocycles alligned in a coplanar arrangement, Fig. 1. Relatively weak C–H···N and C–H···O hydrogen bonds extend the molecules into a 1-dimensional strand.

In an attempt to probe the importance of molecular electrostatics to direct co-crystal formation we prepared three co-crystals



(i) Me_3SiCCH, $Cl_2Pd(PPh_3)_2$, PPh_3, NEt_3, thf; (ii) K_2CO_3, MeOH;
(iii) 2-bromo-5-fluoropyridine, $Cl_2Pd(PPh_3)_2$, PPh_3, NEt_3, thf.
(iv) 3-bromopyridine, $Cl_2Pd(PPh_3)_2$, PPh_3, NEt_3, thf.

Scheme 3. Outlined synthetic route for SRs **1–3.**

4–6, by allowing **1** and **2** to react in a 1:1 stoichiometry and **3** to react in a 1:2 stoichiometry with aromatic carboxylic acids.

The primary motif in the crystal structure of **3** contains one SR **1** and one 4-nitrobenzoic acid molecule connected through the acid and methoxy-substituted pyridine moieties, Fig. 2. The primary synthon is an O–H···N hydrogen bond with O(31)···N(11) distance of 2.633(3) Å. Complementary C–H···O hydrogen bonds form between the proton of an aryl ring to the carbonyl of the acid moiety with a C(13)···O(32) distance of 3.240 Å. Secondary C–H···N hydrogen bonds, between the proton of the methoxy-substituted pyridine ring and the nitrogen atom of the fluoro-substituted ring, generates a 2:2 supermolecule, Fig. 3.

In the crystal structure of **5**, one SR **2** and one 4-nitrobenzoic acid are brought together by an O–H···N(py) hydrogen bond between the carboxylic acid and the non-fluorinated pyridine moiety, O(31)···N(21) distance of 2.611(2) Å, Fig. 4.

Complementary C–H···O hydrogen bonds are present between the proton of an aryl ring to the carbonyl of the acid moiety with a C(13)···O(32) distance of 3.141 Å. Secondary C–H···N hydrogen bonds, between the proton of the methoxy-substituted pyridine ring and the nitrogen atom of the fluoro-substituted ring, generate a 2:2 supermolecule, Fig. 5.

The formation of the 1:2 co-crystal of **6**, Fig. 6, is driven by two O–H···N hydrogen bonds with O(31)···N(11) and O(41)···N(21) distances of 2.567(2) and 2.579(2) Å, respectively. A complementary C–H···O hydrogen bond is formed between the proton of an aryl ring to the carbonyl of the acid moiety with a C(26)···O(42) distance of 3.165 Å, respectively.

In crystal structures **4** and **5**, 1:1 binary co-crystals are formed through carboxylic acid/pyridine hydrogen bonds. Both SRs **1** and **2** contain a pyridine ring substituted in the ortho-position with a fluorine substituent coupled to either a methoxy-substituted pyridine or simple pyridine in which the carboxylic acid can bind. In both cases the carboxylic acid forms a hydrogen bond to the pyridyl ring consisting of greater basicity, *i.e.,* methoxy-pyridine or pyridine (Fig. 1). Attempts at generating a 1:2 SR/acid co-crystal with either SR **4** or **5** and aromatic carboxylic acids, by increasing

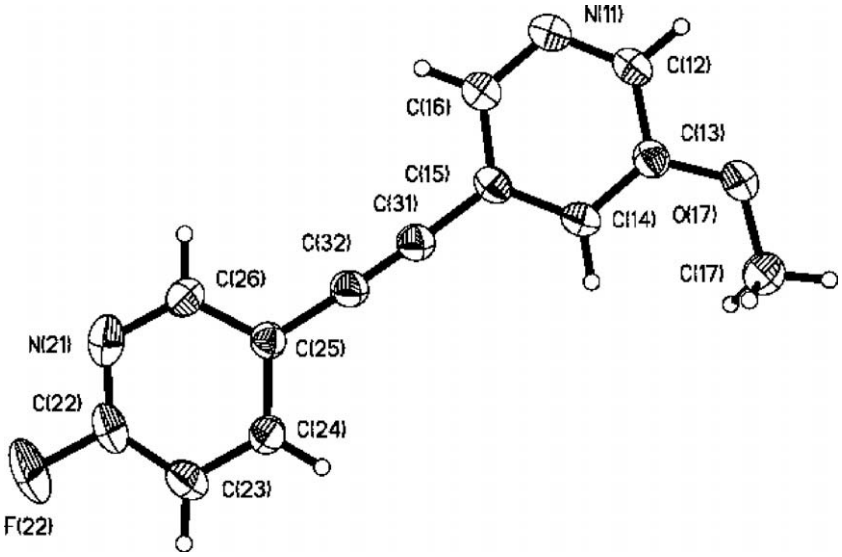


Fig. 1. Labeled thermal-ellipsoids plot (50% probability level) of SR **1**.

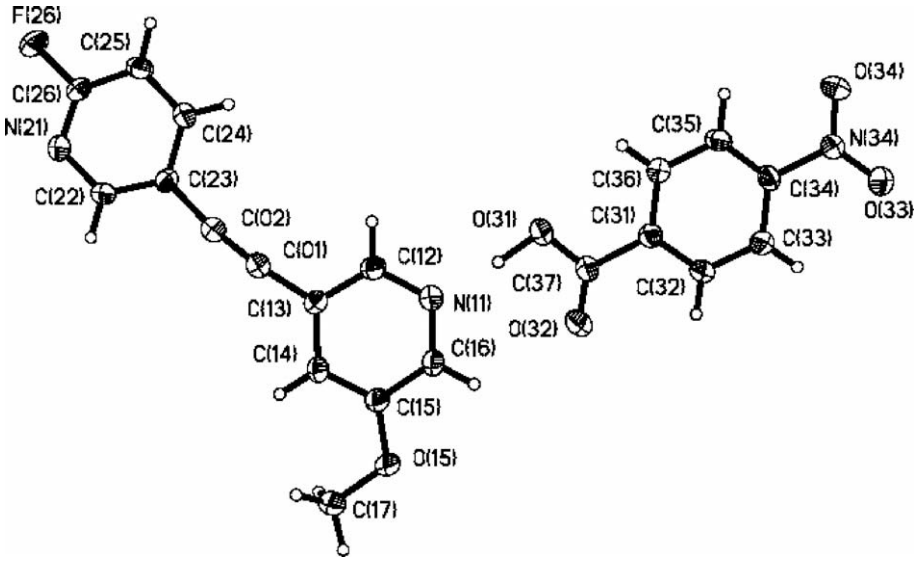


Fig. 2. Labeled thermal-ellipsoids plot (50% probability level) of the 1:1 binary co-crystal of **4**.

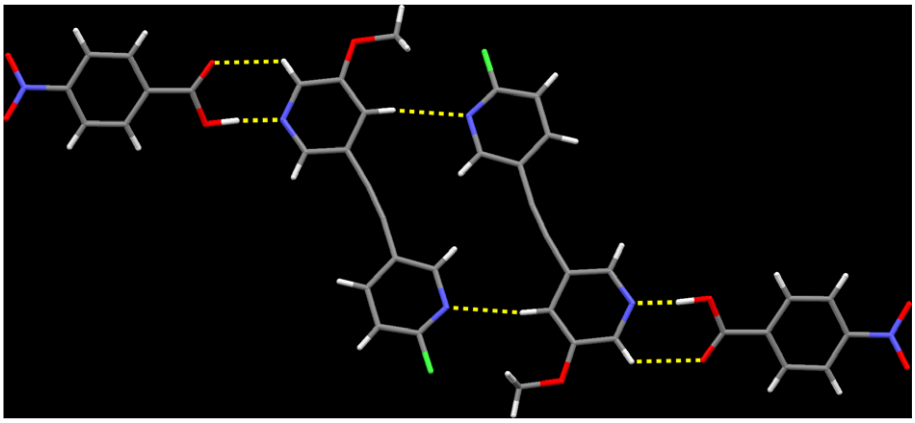


Fig. 3. Four component supermolecule formed through multiple O–H···N, C–H···O and C–H···N hydrogen bonds in **4** [12].

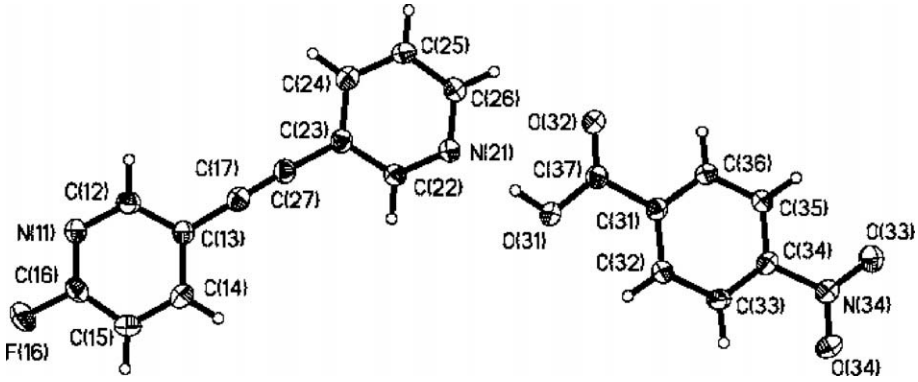


Fig. 4. Labeled thermal-ellipsoids plot (50% probability level) of the 1:1 binary co-crystal of **5**.

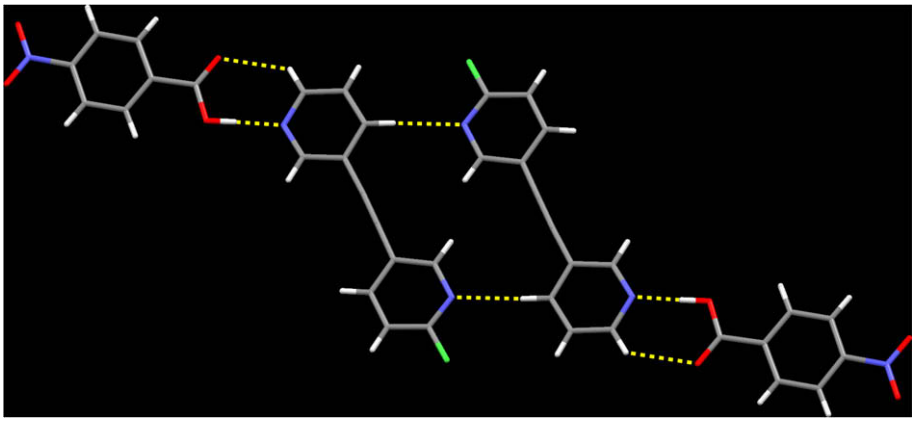


Fig. 5. Four component supermolecule of **5** formed through multiple O–H···N, C–H···O and C–H···N hydrogen bonds.

the ratio of acid, were unsuccessful. However, we do not believe that having the fluorine atom in the ortho-position hinders the nitrogen atom from participating in hydrogen bonding with a carboxylic acid, since it participates in forming C–H···N hydrogen bonds with a neighboring molecule. Furthermore, in the crystal structure of 1-(6-chloropyridin-3-ylmethyl)-3-phenyl-1H-pyrazole-5-carboxylic acid [11] the carboxylic acid forms an O–H···N to the pyridyl site despite the presence of a chlorine substituent ortho to the nitrogen atom.

The crystal structure **6** comprises a 1:2 SR/acid binary co-crystal in which both pyridine nitrogen atoms are acting as hydrogen-bond acceptors in the formation of O–H···N hydrogen bonds with two carboxylic acid molecules. Attempts were made to generate a 1:1 binary co-crystal, by reacting both components, *i.e.*, SR **3** and an aromatic carboxylic acid in a 1:1 ratio; however, suitable crystalline materials were not obtained.

4. Conclusions

Although only three co-crystals are presented herein, we have demonstrated that the electronic characteristic of an individual hydrogen-bond acceptor can be modified through covalent

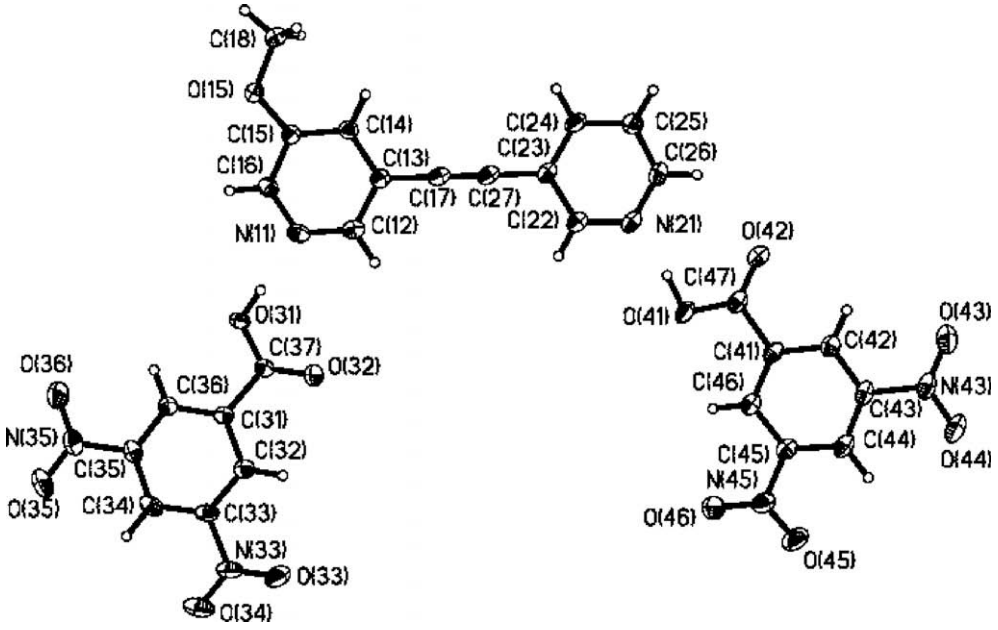


Fig. 6. Labeled thermal-ellipsoids plot (50% probability level) of the 1:2 binary co-crystal, **6**.

'switching' (achieved by covalently affixed substituents), which, in turn, drives the assembly of co-crystals. The primary hydrogen bonds and preferred interactions involving the ditopic acceptor molecules in these structures can be rationalized in the context of an electrostatic view of hydrogen-bond interactions. In the two cases, **4** and **5**, where a 1:1 binary co-crystal was obtained, the carboxylic acid did bind to the best hydrogen-bond acceptor (the site accompanied by the methoxy group), which is consistent with the hypothesis that the best donor will preferentially bind to the best acceptor. In the third case, **6**, both binding sites are involved in an interaction with a carboxylic acid. This may not be completely surprising since the potential differences between the two sites in **1**–**3** are relatively small. Due to the synthetic ease of cross-coupling functionalized pyridines, a variety of other suitable electron rich/deficient bipyridines are possible, allowing for a greater scope of functionalized SRs to be tested. The next logical step is to co-crystallize two carboxylic acids of varied acidity with SRs such as **1**–**3**, in an attempt to form ternary co-crystals with predictable and desirable connectivities and stoichiometries.

Supplementary materials

Crystallographic data for the structures reported have been deposited with the Cambridge Structural Data Centre (CCDC No. 750440-750443). These data can be obtained free of charge from www.ccdc.cam.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk.

Acknowledgements

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