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Hydrogen Bond–Aromaticity Cooperativity in Self-Assembling 4-Pyridone Chains

Megha Anand,^[a] Israel Fernández,^{*,[b]} Henry F. Schaefer III,^[a] and Judy I-Chia Wu^{†[a]}

Self-assembling building blocks like the 4-pyridone can exhibit extraordinary H-bond–aromaticity coupling effects. Computed dissected nucleus independent chemical shifts (NICS(1)_{zz}), natural bond orbital (NBO) charges, and energy decomposition analyses (EDA) for a series of hydrogen (H-) bonded 4-pyridone chains (4-py)_n (n = 2 to 8) reveal that H-bonding interactions can polarize the 4-pyridone exocyclic C=O bonds and increase 4n+2 π -electron delocalization in the six-membered ring. The resulting H-bonded 4-pyridone units dis-

play enhanced π -aromatic character (both magnetically and energetically) and their corresponding N–H...O=C interactions are strengthened. These π -electron polarization effects do not depend on the relative orientations (co-planar or perpendicular) of the neighboring 4-pyridone units, but increase with the number of H-bonded units. © 2015 Wiley Periodicals, Inc.

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Introduction

Amidic (N–H...O=C) hydrogen (H-) bonding interactions play important roles in many natural and synthetic self-assembling systems.^[1–3] But these basic interactions can display very different strengths depending on the local molecular context. For example, in the formamide dimer (see Fig. 1a), a single N–H...O=C interaction is worth ca. –4.5 kcal/mol, but the strongest H-bond in the formamide octamer (–11.6 kcal/mol) is *twice* as strong, while that of the 4-pyridone octamer (–21.3 kcal/mol) is *five times stronger*!^[4–6]

These nonadditive effects usually are attributed to π -bond cooperativity, i.e., the “positive synergism between H-bond strengthening and increased delocalization of the π -conjugated system,” and the resulting stronger than expected H-bonds are called resonance assisted H-bonds (RAHB).^[7–10] Enhanced H-bonding interactions result when the H-bond donors and acceptors are interlinked by a *pseudo- π* -conjugative interaction (see formamide and 4-pyridone dimer examples in Figs. 1a and 1b). Nevertheless, several studies have argued that π -resonance assistance may not always be required to achieve high degrees of H-bond cooperativity in π -conjugated substrates.^[11–20]

Surprisingly, Chen and Dannenberg’s computational survey of H-bonding in 4-pyridone chains, (4-py)_n (n = 2–10), revealed that the cooperative effects observed in *co-planar* H-bonded chains persisted even when each of the individual 4-pyridone rings were twisted to adopt a mutually perpendicular (*perp*-) conformation (see *perp*-4-pyridone dimer in Fig. 1c).^[6] Since the π -systems of each of the neighboring H-bonded units are orthogonal to each other, no π -overlap and therefore no π -resonance assistance is possible between the H-bonded units (see Fig. 1c).^[6] Thus, these authors commented, that “the main contributions to cooperativity in these systems must be some

combination of polarization and mutual polarization”^[6] and that “resonance within the π -systems certainly must contribute to the large polarizability of 4-pyridone.”^[6]

We now unravel the origin of this cooperative effect and highlight the broader impact of such principles for tuning amidic (N–H...O=C) H-bonding interactions. Computed nucleus independent chemical shifts (NICS),^[21–23] natural bond orbital (NBO) charges,^[24] and energy decomposition analyses (EDA)^[25,26] for a series of H-bonded *co-planar* and *perp*- (4-py)_n chains (n = 2–8) are illustrative.

Methods

All geometry optimizations and NBO calculations were performed at the B3LYP/D95(d,p) level employing Gaussian 09 (Revision D.01).^[27] The *co-planar*-(4-py)_n chains (n = 2–8) were constrained to C_{2v} symmetry. The *perp*-(4-py)_n chains (n = 2–8) were restricted to have $\Phi = 90^\circ$ C^a–N^b–C^c–C^d (see Fig. 1c) dihedral angles; even (odd) numbered chains have D_{2d} (D_{2h}) symmetry. These geometric constraints resulted only in small imaginary frequencies (less than 21 cm^{–1}) corresponding to

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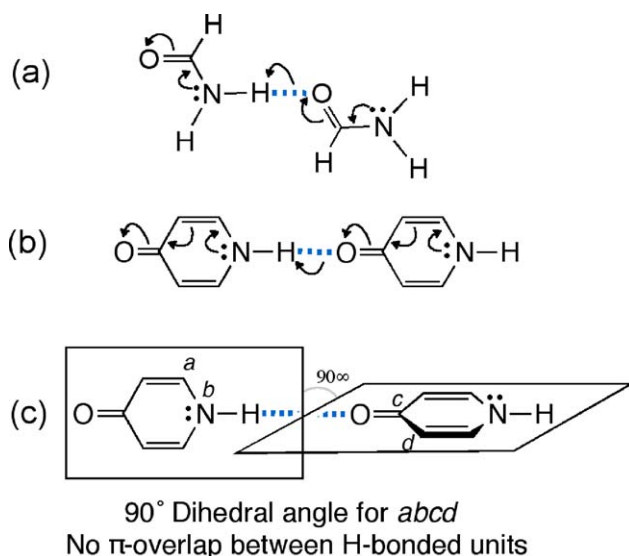


Figure 1. Pseudo π -conjugative interactions in the *co-planar* (a) formamide dimer and (b) 4-pyridone dimer. (c) In *perp*-4-pyridone, no π overlap and thus no π -resonance assistance is operative between the H-bonded units. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the twisting motions of the 4-pyridone units around the C_2 axis parallel to the H-bonds.

The $N-H\cdots O=C$ interaction energies (E_{HB} , in kcal/mol) for the *co-planar* and *perp*- (4-py) $_n$ chains were computed at B3LYP/D95(d,p) with no zero point vibrational energy (ZPVE) or counterpoise corrections (see Supporting Information, Table S1). The E_{HB} values for each of the individual H-bonds were evaluated by the total electronic energy of the (4-py) $_n$ system considered minus the energy of the interacting fragments. For

example, in (4-py) $_8$, the central $N-H\cdots O=C$ interaction is evaluated by the energy of (4-py) $_8$ minus that of two (4-py) $_4$ structures (see Supporting Information Figure S1).

Dissected NICS(1) $_{zz}$ ^[22,23] were computed at 1 Å above the heavy atom ring center of the 4-pyridone rings (at PW91/IGLOIII) to evaluate their aromatic character. The NICS $_{zz}$ index extracts the out-of-plane ("zz") tensor component of the isotropic NICS. When computed at 1 Å above the ring system considered, contributions from the sigma framework are minimized, and the resulting NICS(1) $_{zz}$ values reflect the degree of π -aromaticity. More negative NICS(1) $_{zz}$ values indicate more aromatic character.

EDA^[25,26] were employed to evaluate the π -conjugative interactions in the six-membered rings of the 4-pyridone monomer, dimer, and octamer ring π -systems. Each of the 4-pyridone rings considered was divided into four (triplet state) fragments: two $HC=CH$ units, one $N-H$, and one exocyclic $C=O$. The resulting total interaction energies (ΔE_{int}) were divided into the following components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp}$$

ΔE_{elstat} , ΔE_{Pauli} , ΔE_{orb} , and ΔE_{disp} represent the electrostatic, Pauli repulsion, orbital interaction, and dispersion contributions to the total ΔE_{int} value.^[26] The ΔE_{orb} term can be further partitioned into contributions from the σ - and π - orbitals ($\Delta E_{orb} = \Delta E_{\sigma} + \Delta E_{\pi}$). (Since the 4-pyridone chains considered here have at least one mirror plane, the ΔE_{orb} term can be partitioned into contributions from the σ - and π - orbitals. Thus, the contributions from the a' (in-plane) orbitals evaluate the π -orbital interactions; contributions from the a'' (out-of-plane) orbitals evaluate the π -orbital interactions.). In this article, our analysis

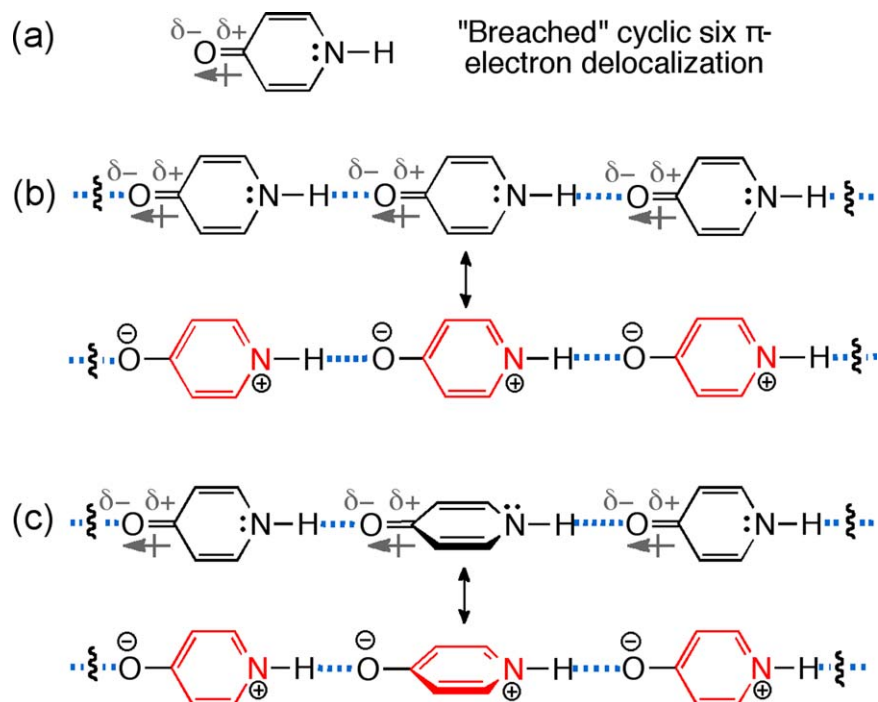


Figure 2. (a) 4-Pyridone is only modestly aromatic, but the H-bonded (b) *co-planar*- and (c) *perp*- 4-pyridone chains display enhanced aromatic character due to ring π -electron polarization (see resonance structures in red).

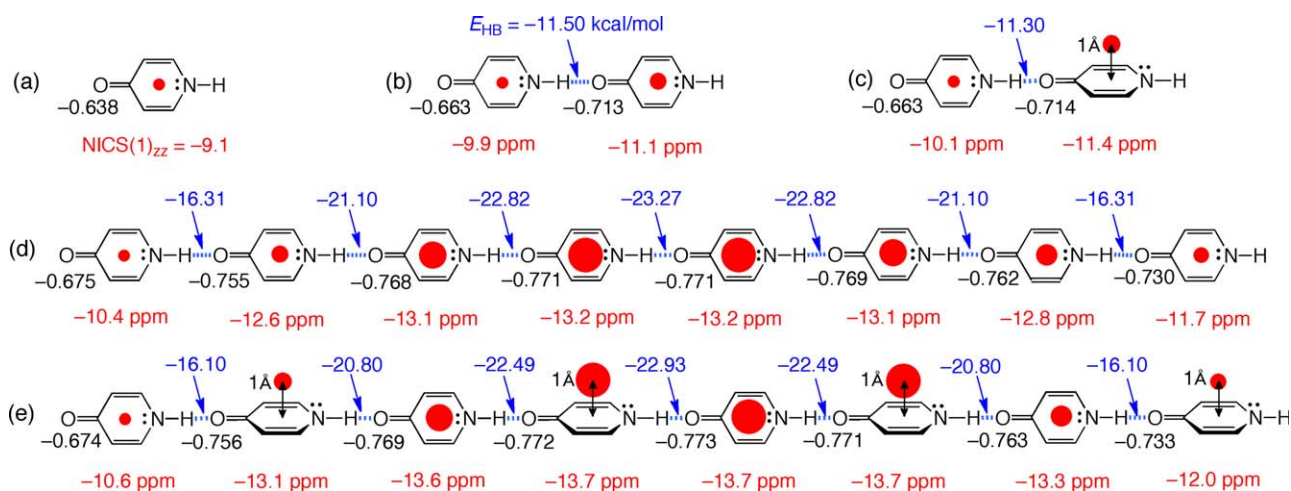


Figure 3. Computed NBO charges for the O atoms (values in black), H-bonding interaction energies (E_{HB} in kcal/mol, blue) and dissected NICS(1)_{zz} values (at 1 Å above each of the 4-pyridone ring planes, in ppm, red) for the 4-pyridone monomer, dimers (*co-planar* and *perp-*), and octamers (*co-planar* and *perp-*).

focuses on the ΔE_{π} term, which provides a measure of the π -conjugation effect (see selected examples in Ref. 28 and also Ref. 29) within the π -system of the 4-pyridone rings considered.

All EDA calculations were computed at BP86-D3^[30]/TZ2P//B3LYP/D95(d,p), employing the Amsterdam density functional program.^[31] The molecular orbitals of each fragment were expanded in a large uncontracted set of Slater-type orbitals (STOs) containing diffuse TZ2P functions. This triple- ζ basis set is augmented by two sets of polarization functions (p and d for hydrogen atoms; d and f for all other heavy atoms). An auxiliary set of s, p, d, f, and g STOs was employed to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each SCF cycle.

Results and Discussions

Our computations reveal that H-bond–aromaticity cooperativity underlies the strong N–H...O=C interactions of *co-planar*- and *perp-* (4-py)_n systems. H-bonding interactions that increase cyclic 4n+2 π -electron delocalization enhance the aromatic character of the H-bonded units, and the corresponding H-bonds are strengthened.^[32,33]

Thus, 4-pyridone is only moderately aromatic but becomes increasingly more so upon H-bonding. As shown in Figure 2a, the exocyclic C=O bond disrupts the cyclic six π -electron delocalization in the ring, but is polarized toward the more electronegative O atom; this allows modest π -aromatic character in the six-membered ring. In the (4-py)_n systems, the H-bonded C=O moieties are increasingly polarized (and become even more so for the longer (4-py)_n chains); this enhances cyclic 4n+2 π -electron delocalization and increases π -aromaticity in the 4-pyridone rings (see Figs. 2b and 2c, resonance structures in red). Such H-bond–aromaticity coupling effects cannot occur in analogous H-bonded formamide chains, but are operative in both the *co-planar* and *perp-* (4-py)_n systems. Note the nearly identical *co-planar* vs. *perp-* E_{HB} values for the 4-pyridone dimers (Figs. 3b and 3c) and octamers (Figs. 3d and 3e).

Since H-bonding increases the polarity of the C=O π bonds, the computed NBO charges for the H-bonded O atoms in the dimer and octamer (−0.71 to −0.77) are more negative than the non-H-bonded O atoms in the 4-pyridone monomer (−0.64), dimer(s) (terminal O: −0.66), and octamer(s) (terminal O: −0.67) (see Fig. 3 and Supporting Information, Table S2). As shown in Figure 3, the inner 4-pyridone rings of extended (4-py)_n chains display more negatively charged O atoms (see values in black), have stronger N–H...O=C interactions (see E_{HB} values in blue), and are increasingly more π -aromatic (see NICS(1)_{zz} values in red).

Direct comparisons of the computed dissected NICS(1)_{zz} for the 4-pyridone monomer (−9.2 ppm), dimer(s) (−9.9 to −11.4 ppm), and octamer(s) (−10.6 to −13.7 ppm) reveal the expected aromaticity enhancement (see Fig. 3). In (4-py)₈, the NICS(1)_{zz} values of the central 4-pyridones are 2–3 ppm more negative compared to the terminal rings, and 4–5 ppm more negative compared to the 4-pyridone monomer. This 4–5 ppm change is very significant, especially when compared in

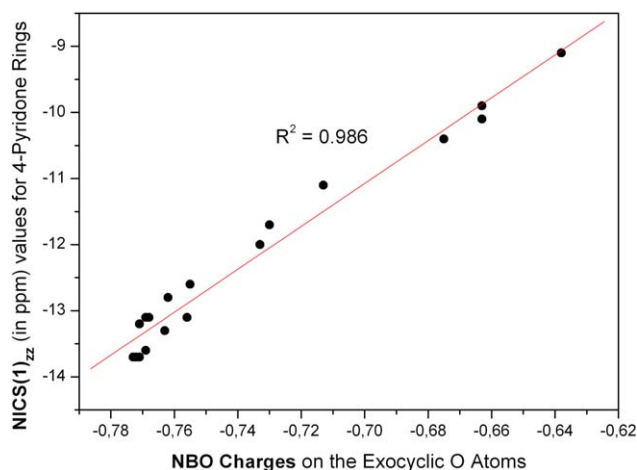



Figure 4. Computed NICS(1)_{zz} (in ppm) vs. NBO charges on the exocyclic O atoms for the individual 4-pyridone rings in the monomer and (4-py)_n ($n = 2$ and 8) systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

Table 1. EDA energies (in kcal/mol) for pyridone chains

Monomer	Dimer		Octamer	
	(Coplanar)	(Perpendicular)	(Coplanar)	(Perpendicular)
ΔE_{int}	−605.8	−606.3	−606.1	−606.1
ΔE_{Pauli}	1072.6	1094.1	1132.3	1131.8
$\Delta E_{\text{elstat}}^{[a]}$	−676.6 (40.3%)	−686.9 (40.4%)	−702.7 (40.4%)	−702.4 (40.4%)
$\Delta E_{\text{orb}}^{[a]}$	−997.8 (59.4%)	−1009.5 (59.4%)	−1031.8 (59.4%)	−1031.5 (59.4%)
$\Delta E_{\pi}^{[b]}$	−891.4 (89.3%)	−900.2 (89.2%)	−917.2 (88.9%)	−917.0 (88.9%)
$\Delta E_{\pi}^{[b]}$	−106.5 (10.7%)	−109.3 (10.8%)	−114.5 (11.1%)	−114.5 (11.1%)
$\Delta E_{\text{disp}}^{[a]}$	−4.0 (0.3%)	−4.0 (0.2%)	−4.0 (0.2%)	−4.0 (0.2%)
Fragments	 Four triplet fragments: (C=O) + (HC=CH) + (N—H) + (HC=CH)			

All data have been computed at the BP86-D3/TZ2P+//B3LYP/D95(d,p) level. [a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb} . [c] These bold values highlight the DeltaEpi values, which are the focus of this study.

context with the computed 6.7 ppm NICS(1)_{zz} difference for benzene (−29.2 ppm) vs. a hypothetical “1,3,5-cyclohexatriene” ring (−22.5 ppm) with restricted alternating single (1.53 Å) and double (1.33 Å) CC bonds. Note also the excellent correlation between the computed NICS(1)_{zz} values vs. NBO charges on the O atoms of the (4-py)_n chains ($R^2 = 0.986$) (see Fig. 4).

Indeed, computed EDA results for the 4-pyridone monomer, dimer(s), and octamer(s) (in both *co-planar* and *perp-* forms) reveal that H-bonded 4-pyridones do exhibit increased π -conjugation, as expected by their enhanced aromatic character. As shown in Table 1, the computed ΔE_{π} values for the 4-pyridone rings increase significantly going from the monomer (−106.5 kcal/mol), to the dimer(s) (−109.3 kcal/mol), and to the central 4-pyridone ring of the octamer(s) (−114.5 kcal/mol). Changes in the orientations of the neighboring 4-pyridone units, *co-planar* or *perp-*, have essentially no effect on the degree of π -conjugation increase. These findings along with the NBO and NICS(1)_{zz} results presented above confirm Dannenberg et al.'s earlier speculation and further show that changes in the aromatic character in H-bonded 4-pyridone rings underlie the enormous H-bond cooperativity of extended (4-py)_n chains.

Conclusions


H-bonding interactions can polarize the π -clouds of 4-pyridone rings and increase their aromatic character significantly. Rather than RAHB, this increased “resonance within the π -system”^[6] underlies the extraordinary amidic (N—H...O=C) H-bond cooperativity of extended *co-planar* and *perp-* (4-py)_n chains.^[6] Comparable H-bonded formamide chains exhibit weaker N—H...O=C interactions,^[4,5] since no H-bond-aromaticity coupling is possible. These cooperative relationships are important for understanding the wide range of N—H...O=C hydrogen bond strengths present in many functional organic and biological systems.

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Keywords: self-assembly · hydrogen bonding · aromaticity · nucleus independent chemical shifts · energy decomposition analysis

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