

A Renaissance of the (Anti)Aromaticity Concept in Modern Applications of Organic Chemistry

By

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Abstract

This dissertation focuses on applying computational quantum chemical tools to explore modern applications of aromaticity and antiaromaticity in organic chemistry. Even though all sophomore organic chemistry students learn about the concepts of aromaticity and antiaromaticity, these ideas continue to find exciting applications in active areas of research. The topics covered in this dissertation include understanding the effects of supramolecular self-assembly on the electronic properties of organic pigments and understanding the origin of acidity differences in popular photoacids. We found that organic pigments with bifunctional hydrogen bonding sites, such as indigo, isoindigo, diketopyrrolopyrrole, and naphthodipyrrolidone, can self-assemble through hydrogen bonding interactions, showing increased $[4n]$ π -electron antiaromaticity and lower LUMO energy levels. The reciprocal relationship between hydrogen bonding and antiaromaticity gain makes them good candidates for components of n -type organic field-effect transistor (OFET) materials. We found that π -polarization of acridone compounds can perturb the numbers and positions of Clar sextet rings. Decreasing numbers of Clar sextets are connected to experimental observations of a narrowing HOMO-LUMO gap and increased charge mobility in hydrogen-bonded assemblies of quinacridone and epindolidione. We also found that many organic acids that are Hückel aromatic in the ground state can convert to Baird antiaromatic in the excited state, triggering facile proton transfer. Stronger photoacids show enhanced “antiaromaticity relief” upon releasing a proton. Together this series of works highlight examples of the underlying effects of (anti)aromaticity in organic chemistry and increase chemical understanding.

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Chapter 1

Introduction

1.1 Overview

Shortly following Michael Faraday's (1825) isolation of benzene,¹ August Hofmann (1855) first coined the term "aromaticity" to describe this family of fragrant molecules.² At the time, it was difficult to imagine that the concept of aromaticity would have such significant impact on organic chemistry today. My PhD dissertation focuses on demonstrating modern applications of aromaticity and antiaromaticity in organic chemistry, covering the following topics: 1) understanding molecular designs of antiaromatic compounds as potential organic electronics materials, 2) recognizing Clar sextet effects on the electronic properties of organic pigments, and 3) explaining the structural origins of photoacidity.

Polycyclic aromatic compounds, for example, have attracted attention as components of organic electronics, for applications such as organic field-effect transistors (OFET).³⁻⁸ These compounds have extended π -conjugated frameworks, and their electronic properties can be modulated by substituent effects and self-assembly in the solid state.³⁻⁵ Candidates with promising charge transport properties typically display low LUMO energy levels and narrow HOMO-LUMO gaps.^{7,8} In this dissertation, we highlight two instances of how hydrogen bonding self-assembly can boost charge transport in the solid states of representative organic pigments, by modulating aromaticity and antiaromaticity of the self-assembled monomers.

Organic pigments containing N-H and C=O groups were long avoided in the designs of organic electronics because of an assumed "poor" π -conjugation. However, recent works, especially from the group of Głowacki,⁹⁻¹² have shown that popular pigments like the indigos

and acridones can show good charge transport potential rivaling those of acenes. In Chapter 2, we present a detailed computational study on a series of indigo compounds, showing that hydrogen bonding in the solid state could increase antiaromatic character of these compounds, thereby lowering the LUMO energy and narrowing the HOMO-LUMO gap. In Chapter 3, we investigate the effects of hydrogen bonding on Clar sextet patterns in acridone compounds. A Clar sextet describes a fully benzenoid ring where all π -electrons of a six membered ring belong to a single sextet.^{13,14} Isomers of polycyclic aromatic compounds with a greater number of Clar sextet typically show increased aromatic character, while those with fewer Clar sextets have lower aromaticity.¹⁵⁻¹⁹ For example, the HOMO-LUMO gap of an acene becomes narrower as the length of the acene increases, due both to extended π -conjugation as well as a reduced ratio of Clar sextets.¹⁴ Based on computed magnetic criteria of aromaticity, we suggest that hydrogen bonding interactions can strongly polarize the π -system of acridones to reduce the numbers of Clar sextets, resulting in narrower HOMO-LUMO gaps in the solid state.

Substituted polycyclic aromatic hydrocarbons such as 2-naphthol and the 2-naphthylammonium are photoacids, which can have useful biomedical applications as pH switches.²⁰ These compounds show a significant drop in pK_a value upon photoexcitation.^{21,22} In Chapter 4, we reason that the phenomena of photoacidity can be attributed to a reversal of aromaticity and antiaromaticity in the excited state. We recognize that acids like 2-naphthol and the 2-naphthylammonium can be considered as “aromatic” in the ground state, i.e., having $[4n+2]$ π -electrons (i.e., Hückel rule),²³ but convert to “antiaromatic” in the lowest $\pi\pi^*$ states

(i.e., Baird’s rule).²⁴ In this work, we connect Baird’s rule—a reversal of the Hückel rule in the excited state—to explain why photoacidity occurs. We show that relief of excited-state antiaromaticity drives proton transfer.

Despite having a “non-measurable” nature, the concept of aromaticity has been associated with many observable traits, such as enhanced thermochemical stability, as well as spectroscopic and geometric features suggestive of extensive electron delocalization.^{25,26} Following advancements in computational quantum chemistry, sophisticated computational tools were designed and employed to quantify (anti)aromaticity. The nucleus-independent chemical shifts (NICS) method,^{27,28} for example, is a very popular computational approach for quantifying magnetic (anti)aromaticity. NICS measures the magnetic shielding effect of an induced ring current. A NICS probe can be placed anywhere in the vicinity of the molecule of interest, and the signs and magnitude of the computed NICS values reveal whether a system is aromatic (large negative NICS values) or antiaromatic (large positive NICS values). The harmonic oscillator model of aromaticity (HOMA) method is a geometric index that evaluates bond length equalization in ring systems.²⁹ Gauge-including magnetically induced current (GIMIC) provides visualization on aromaticity by evaluating the ring current densities of systems.³⁰ Developments of these approaches have made it possible to study the effects of aromaticity in many areas of chemistry, and these approaches are applied in the works collected in this dissertation.

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Chapter 2

Antiaromaticity Gain Increases Potential for *n*-Type Charge Transport in Hydrogen-Bonded π -Conjugated Cores

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2.1 Introduction

Antiaromatic compounds are gaining traction as promising candidates for the design of *n*-type organic field effect transistors (OFET), because of their potential to have low LUMO energy levels, narrow HOMO-LUMO gaps, and high conductivity.¹⁻⁴ But formally antiaromatic—cyclic $[4n]$ π -conjugated—cores can sometimes be too reactive (e.g., pentalene cores easily dimerize) to be useful unless stabilized by fused benzenoid rings. Some successful examples of $[4n]$ π -conjugated *n*-type OFET candidates include expanded pentalenes, indacenes, and indenofluorenes.⁵⁻⁸ In this paper, we consider a class of non-aromatic organic dyes, including: indigo, isoindigo, diketopyrrolopyrrole (DPP), and naphthodipyrrolidone (NDP) (Figure 2.1), which show *n*-type behavior.⁹⁻¹¹ We show that when these compounds self-assemble through hydrogen bonding interactions, they show increased antiaromaticity and lower LUMO energy levels.

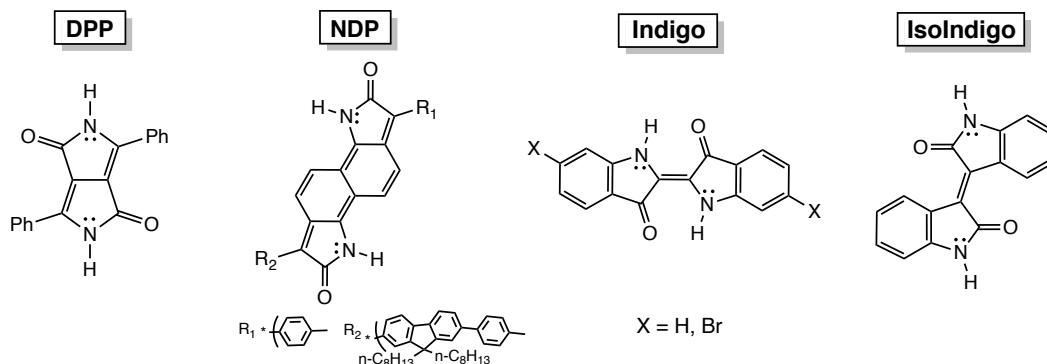


Figure 2.1 Formally non-aromatic π -conjugated cores.

Organic dyes like indigo, isoindigo, DPP, and NDP are traditionally thought to be poor candidates for applications as organic electronics, as the N–H and C=O groups were

considered to disrupt π -conjugation thereby lowering electron or hole mobility. But recent works from Głowacki and others have shown that N–H and C=O containing pigments like acridones and indigos can exhibit high charge mobilities, rivaling those of traditional acene-based OFETs.¹²⁻¹⁵ Zhu and co-workers reported that hydrogen bonding increases the hole mobilities of indigo (4.06×10^{-6} to 3.24×10^{-5} cm²/Vs), isoindigo (1.91×10^{-5} to 9.05×10^{-5} cm²/Vs),⁹ and DPP (1.30×10^{-4} to 7.89×10^{-4} cm²/Vs), compared to their analogs of hydrogen bonding sites.¹⁰ NDP displayed significant increase in electron mobility (from 2.40×10^{-4} to 0.01 cm²/Vs) upon removal.¹¹

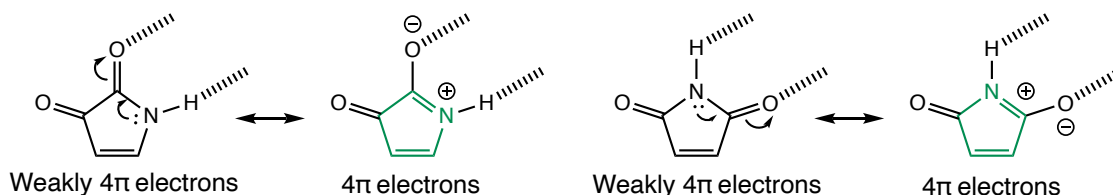


Figure 2.2 Hydrogen bonding interactions increase antiaromaticity (i.e., $[4n]$ π -electron delocalization) in diketopyrroles.

Here we show that the high charge mobility of these organic dyes from increased antiaromatic character in the π -conjugated cores upon forming hydrogen bonding interactions. Indigo, isoindigo, DPP, and NDP are formally non-aromatic. But hydrogen bonding interactions at the N–H and C=O sites can polarize the ring π -electrons to increase $[4n]$ π -antiaromatic character. Consider the two isomers of diketopyrrole shown in Figure 2.2. Both rings have four ring π -electrons and two exocyclic carbonyl groups that breach cyclic π -electron delocalization. Upon hydrogen bonding, the ring π -electrons are polarized, resulting

in increased resonance contribution from a formally $[4n]$ cyclic delocalized structure (see Figure 2.2, structure in green). Hydrogen bonded indigo, isoindigo, DPP, and NDP exhibit similar antiaromaticity gain.

2.2 Methods

Geometries of all monomers, hydrogen-bonded trimers, and tautomers were optimized with C_s constraint, except for the hydrogen-bonded trimer of isoindigo (optimized with C_1 symmetry). All geometries were optimized in the gas-phase at the B3LYP-D3¹⁶/6-311+G(d,p) level, employing Gaussian16.¹⁷ HOMO and LUMO energies were calculated at TD- ω B97X-D¹⁸/6-311+G(d,p). HOMO-LUMO gaps were derived from HOMO to LUMO excitation energies.¹⁹ NICS(1)_{zz} values were computed at PW91PW91/IGLOIII.^{20,21} Magnetically induced current density plots were computed using the GIMIC method.²²

2.3 Results and Discussion

Three computational models were considered: 1) the monomer of the π -conjugated core, 2) the central unit of a hydrogen bonded trimer of the π -conjugated core, and 3) a $[4n]$ π -electron tautomer of the π -conjugated core (approximating the upper bound electronic effect of a highly polarized monomer). Computed nucleus-independent chemical shifts (NICS) quantified the aromaticity and antiaromaticity of the individual rings,^{20,21} and time-dependent density functional theory (TD-DFT) computations were performed to estimate the HOMO and LUMO levels of each model system.¹⁹ As shown in Figure 2.3, hydrogen bonding interactions

lower the LUMO levels of all π -conjugated cores, and the $[4n]$ antiaromatic tautomers display even lower LUMO levels. Details of the HOMO and LUMO levels are included in Table A2.1-A2.4.

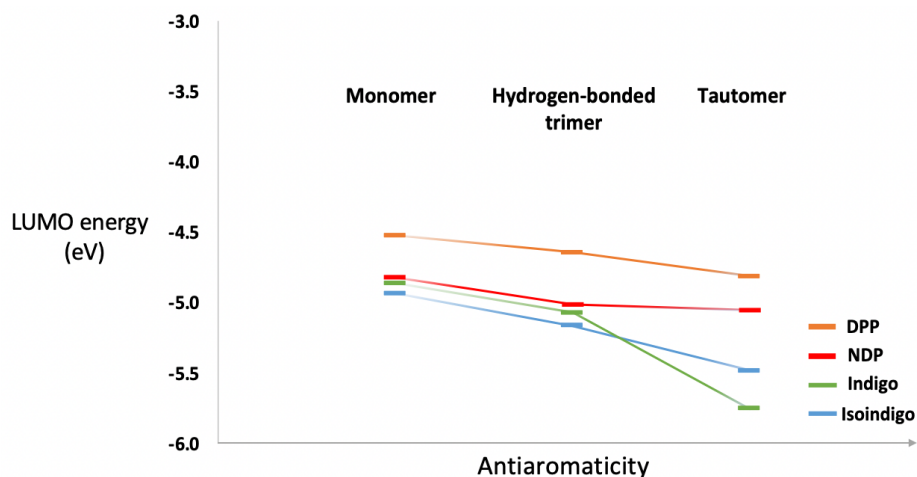


Figure 2.3 Computed LUMO energy levels for the monomers, central units of hydrogen bonded trimers, and $[4n]$ tautomers of DPP (orange), NDP (red), indigo (green), and isoindigo (blue).

According to computed nucleus-independent chemical shifts (NICS), all of the non-aromatic π -conjugated cores become more antiaromatic upon hydrogen bonding, and even more so upon tautomerizing to the $[4n]$ isomer. NICS(1)_{zz} values were computed at 1 Å above each of the ring centers and include only shielding tensor components from the out-of-plane “zz” direction. Negative NICS(1)_{zz} values indicate aromaticity, positive NICS(1)_{zz} values indicate antiaromaticity. NICS(1)_{zz} values close to zero suggest a non-aromatic ring. According to computed NICS(1)_{zz}, the five and six membered ring moieties of DPP and NDP are non-aromatic in the monomer form (NICS(1)_{zz} values between -1 and +1 ppm), and

become weakly antiaromatic upon hydrogen bonding (+3 to +5 ppm). NICS(1)_{zz} values for the five and six membered ring moieties in the [4*n*] π -tautomers are even more positive (+15 to +20 ppm) (see Figure 2.4).

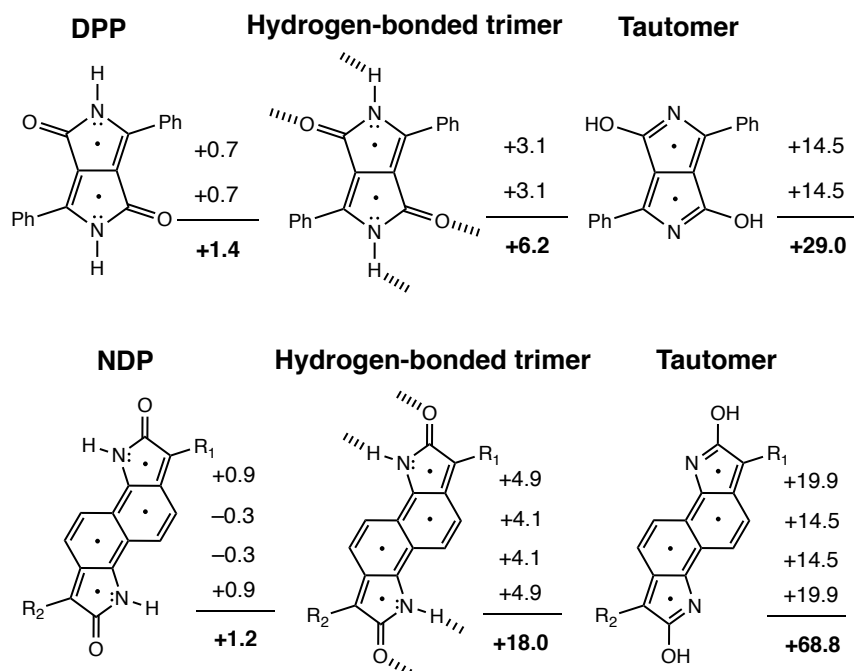


Figure 2.4 Computed NICS(1)_{zz} values and sum of NICS(1)_{zz} values (in ppm) for the five and six membered rings of DPP and NDP, in the monomer, hydrogen bonded, and tautomeric forms.

Indigo and isoindigo also show increased antiaromatic character upon hydrogen bonding and tautomerization to the [4*n*] isomers (Figure 2.5). For both systems, the six membered rings are six π -electron aromatic (i.e., two Clar sextets each), and the five membered rings are weak to non-aromatic. Hydrogen bonding reduces the aromatic character of the six membered rings, and increases the antiaromatic character of the five membered

rings (NICS(1)_{zz} values between +3 and +7 ppm). The [4*n*] tautomers of indigo and isoindigo lose even more aromatic character, as the five membered rings become more antiaromatic (NICS(1)_{zz} values between +12 and +19 ppm).

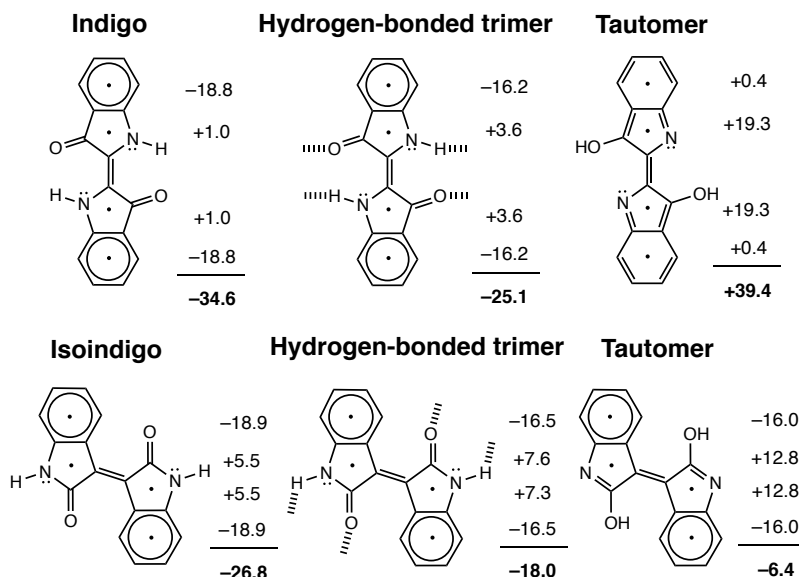


Figure 2.5 Computed NICS(1)_{zz} values of indigo and isoindigo systems (the Clar sextet were noted by black circles).

Note the significant gain in antiaromaticity in the [4*n*] tautomer of indigo. As shown in Figure 2.5, both indigo and isoindigo have two Clar sextets (i.e., a cyclic delocalization of six π -electrons that resist disruption). But the [4*n*] tautomer of indigo loses both Clar sextets (see Lewis structure in Figure 2.5), while the [4*n*] tautomer of isoindigo retains both. This difference also is reflected in the especially low LUMO energy for [4*n*] indigo (-5.75 eV, Figure 2.3). Previous works have shown that Clar sextet patterns can influence the HOMO

and LUMO energy levels of π -conjugated compounds; lower numbers of Clar sextet are often associated with smaller HOMO-LUMO gaps and lower LUMO energy levels.²³⁻²⁵

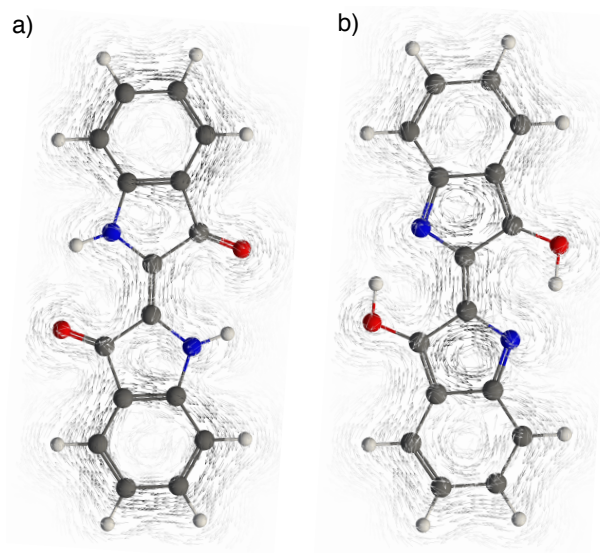


Figure 2.6 GIMIC plots for a) indigo and its b) $[4n]$ tautomer.

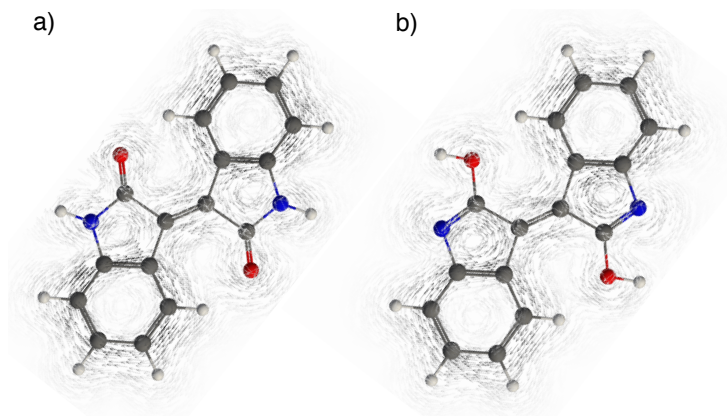


Figure 2.7 GIMIC plots for a) isoindigo and its b) $[4n]$ tautomer.

Gauge-including magnetically induced current (GIMIC)²² plots of indigo and isoindigo were computed to visualize the effects of arrangements of benzofusion on the numbers of possible Clar sextets in the $[4n]$ tautomers. Indigo displays strong diatropic (clockwise) rings currents around the six membered rings (i.e., two Clar sextets) and weak paratropic (anti-clockwise) ring currents around the five membered rings (Figure 2.6a). In the $[4n]$ tautomer, the diatropic ring currents weaken significantly (in line with a disappearing Clar sextet) and the paratropic currents at the five membered rings become stronger (Figure 2.6b). GIMIC plots for isoindigo and its $[4n]$ tautomer looks more similar. Both show notable diatropic (clockwise) rings currents around the six membered rings (i.e., two Clar sextets) and weak paratropic (anti-clockwise) ring currents around the five membered rings (Figure 2.7).

We also performed same calculations on some potential *n*-type OFETs compounds A and B, without experimental data reported before. According to computed NICS(1)_{zz} values, the systems of A and B both gradually become less aromatic or more antiaromatic as the polarization effect enhances from monomer to hydrogen-bonded trimer, to their tautomers (See Figure 2.8). Noticeably, the dramatical antiaromaticity gain from hydrogen-bonded trimer to tautomer in A system from the Clar sextet number loss (from 1 to 0), the calculated HOMO-LUMO gaps of compound A are accordingly change from 3.40 eV (monomer) to 3.04 eV (hydrogen-bonded trimer), to 1.26 eV (tautomer). As contrast, the calculated HOMO-LUMO gap of compound B, from 4.22 eV (monomer) to 4.17 eV (hydrogen-bonded trimer), to 4.11 eV (tautomer).

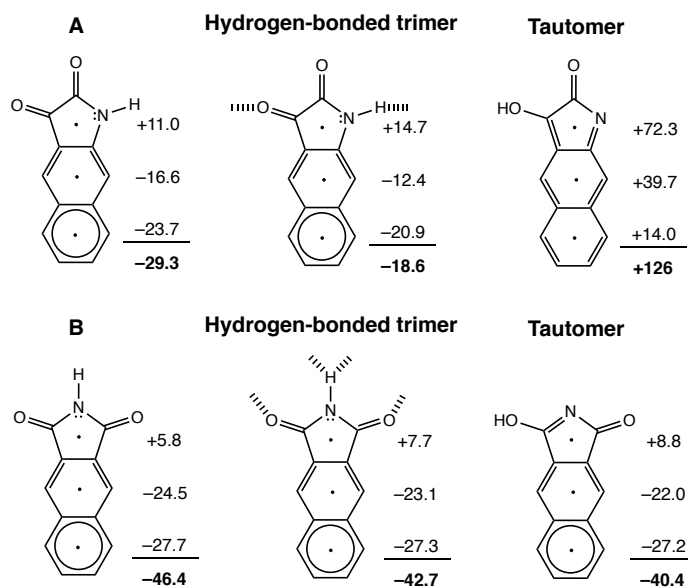


Figure 2.8 Computed NICS(1)_{zz} values and sum of NICS(1)_{zz} values (in ppm) of potential OFET compounds A and B, in the monomer, hydrogen bonded, and tautomeric forms.

Substituents effect also can influence the antiaromaticity and potential *n*-type behavior of [4*n*] π -conjugated cores. For example, tyrian purple (6,6'-dibromoindigo, see Figure 2.1) is known to exhibit a 40 times higher electron mobility than that of unsubstituted-indigo in OFET devices.^{14,26} Our calculations suggest that the lower LUMO level of tyrian purple (−5.17 eV) vs. indigo (−4.86 eV), may be explained by reduced aromaticity (sum of NICS(1)_{zz} = −31.9 ppm, compared to −34.6 ppm for indigo). Orbital energies and NICS(1)_{zz} results for tyrian purple are included in Table A2.5 and Figure A2.1.

2.4 Conclusions

Hydrogen bonding interactions can be used to introduce [4*n*] antiaromatic character into formally non-aromatic π -conjugated cores, to improve orbital energy levels for *n*-type

charge transport behavior. We show that this relationship provides understanding to factors relevant to the molecular design of *n*-type OFET compounds and expands the library of potential candidates to non-aromatic cores with “near $[4n]$ π -conjugated” topologies.

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2.6 Appendix

Table A2.1 Computed orbital energies and HOMO-LUMO gap (in eV) for DPP monomer, hydrogen-bonded trimer, and tautomer at TD- ω B97X-D/6-311+G(d,p)

DPP	Monomer	Hydrogen-bonded trimer	Tautomer
HOMO	-7.38	-7.48	-7.54
LUMO	-4.52	-4.64	-4.81
HOMO-LUMO Gap	2.89	2.84	2.73

Table A2.2 Computed orbital energies and HOMO-LUMO gap (in eV) for NDP monomer, hydrogen-bonded trimer, and tautomer at TD- ω B97X-D/6-311+G(d,p)

NDP	Monomer	Hydrogen-bonded trimer	Tautomer
HOMO	-6.94	-7.01	-7.14
LUMO	-4.82	-5.01	-5.05
HOMO-LUMO Gap	2.12	2.00	2.09

Table A2.3 Computed orbital energies and HOMO-LUMO gap (in eV) for indigo monomer, hydrogen-bonded trimer, and tautomer at TD- ω B97X-D/6-311+G(d,p)

Indigo	Monomer	Hydrogen-bonded trimer	Tautomer
HOMO	-7.41	-7.38	-7.15
LUMO	-4.86	-5.07	-5.75
HOMO-LUMO Gap	2.55	2.31	1.40

Table A2.4 Computed orbital energies and HOMO-LUMO gap (in eV) for isoindigo monomer, hydrogen-bonded trimer, and tautomer at TD- ω B97X-D/6-311+G(d,p)

Isoindigo	Monomer	Hydrogen-bonded trimer	Tautomer
HOMO	-7.90	-7.93	-8.27
LUMO	-4.93	-5.16	-5.48
HOMO-LUMO Gap	2.97	2.77	2.79

Table A2.5 Computed orbital energies and HOMO-LUMO gap (in eV) for tyrian purple monomer, hydrogen-bonded trimer, and tautomer at TD- ω B97X-D/6-311+G(d,p)

Tyrian purple	Monomer	Hydrogen-bonded trimer	Tautomer
HOMO	-7.76	-7.74	-7.43
LUMO	-5.17	-5.40	-6.02
HOMO-LUMO Gap	2.59	2.34	1.41

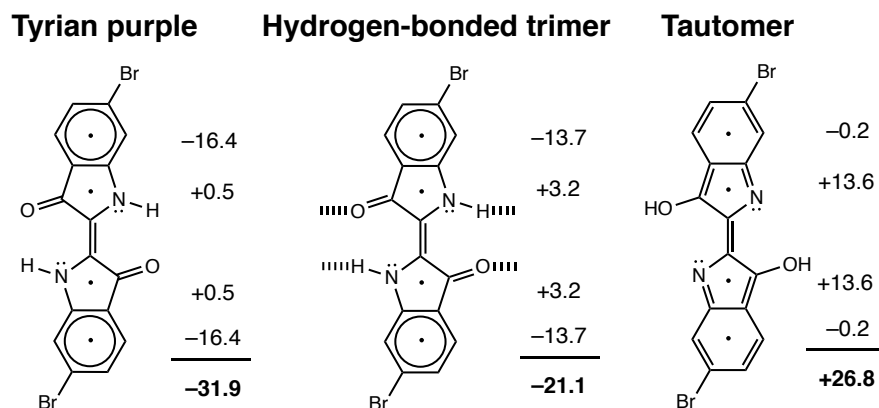


Figure A2.1 Computed NICS(1)_{zz} (in ppm) for tyrian purple monomer, hydrogen-bonded trimer, and tautomer (NICS points were added at 1 Å above the center of each ring).

Chapter 3

Decreasing Aromaticity Enhances Charge Transport Properties in Acridone Pigments with Hydrogen Bonding Functionality

3.1 Introduction

Acridone pigments like quinacridone (**1**) and epindolidione (**2**) (a structural isomer of indigo) (Figure 3.1) are low-cost, air-stable, and have use as paints, cosmetics, and printing inks, but their potential application as components of organic field-effect transistors has received little attention until the last decade.¹⁻⁵ These compounds were intentionally avoided in the designs of organic electronics, as the amine and carbonyl groups were thought to disrupt π -conjugation. Yet many solid-state pigments, containing N–H and C–O groups, have been found to exhibit high charge mobilities, rivaling those of acenes.³⁻⁶ In the solid state, **1** has a hole mobility comparable to that of pentacene (0.1 vs. 0.1 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)³ and **2** displays a hole mobility higher than that of tetracene (1.5 vs. 0.1 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$).⁴ It was suggested that hydrogen bonding can increase acene character of the monomers (see Figure 3.1, imminium-enolate resonance structures on right).

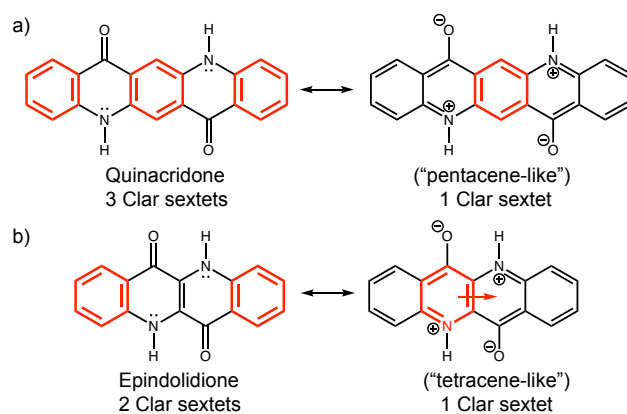


Figure 3.1 a) Quinacridone (QA), b) epindolidione (EPI), and their imminium-enolate resonance forms. Clar sextets are drawn in red. A red arrow across two rings indicates equivalent Clar structures.

Many N–H and C=O containing chromophores display large bathochromic UV-vis absorption shifts going from dilute solution to the solid state.⁵⁻⁷ Quinacridone is yellow in solution, but turns red to violet in the solid state.^{8,9} Epindolidione is blue in solution, and turns yellowish to orange in the solid state.⁴ When dissolved in sulfuric acid, the doubly protonated quinacridone displays a narrower HOMO-LUMO gap than the neutral parent, showing a UV-vis spectrum similar to that of pteridine.⁵ These changes suggest that polarization of the π -system through hydrogen bonding, can reduce the HOMO-LUMO gaps of acridone pigments giving rise to increased charge mobility.⁵ Hydrogen bonding interactions were found to improve the electronic properties of other conjugated organic systems^{10,11} and donor-acceptor pairs.¹²⁻¹⁴

Here, we relate the known effects of enhanced charge mobility in hydrogen-bonded acridones to decreased aromaticity of the π -system. First called the “aromatic sextet” in 1925,¹⁵ and then proposed by Clar to follow a selective placement in polycyclic systems,¹⁶ the “Clar sextet” describes a fully benzenoid ring where all π -electrons of a six membered ring belong to a single sextet. As shown in Figure 3.1, **1** has three Clar sextets, and **2** has two, but polarization of the N–H and C=O sites enhance the contribution of “acene-like” resonance forms which can have only one Clar sextet.¹⁷⁻¹⁹ In this way, hydrogen bonding self-assembly can reduce Clar sextet ratio of the acridone π -system, and the drop in aromaticity can be related to a decreased HOMO-LUMO gap.^{20,21} Isomers of closed-shell polyaromatic hydrocarbons (PAH) with fewer numbers of Clar sextets typically have lower ionization potentials, light absorption shifted towards the visible region, and a smaller HOMO-LUMO

separation.²²⁻²⁶ We previously reported that formally non-aromatic organic dyes, like diketopyrrolopyrrole, naphthodipyrrolidone, indigo, and isoindigo, can show increased antiaromaticity upon hydrogen bonding.²⁷ The effects of intermolecular hydrogen bonding on aromaticity also can be seen in contrasting examples of the 2-pyridone dimer (aromaticity gain upon hydrogen bonding) and the 2-hydroxypyridine dimer (aromaticity loss upon hydrogen bonding) (see also supplementary data in the Figure A3.1-A3.3).²⁸

In this work, the Clar sextet patterns of **1** and **2** are compared to those of a doubly protonated form (**-prot**) and an acene-like tautomeric form (**-taut**), to model the highly polarized π -system of the monomers in the solid state. Crystal structures of the α , β , and γ polymorphs of quinacridone²⁹⁻³² have C=O bond distances (α : 1.373 Å, β : 1.266 Å, γ : 1.299 Å) longer than the typical carbonyl C=O length (ca. 1.23 Å), indicative of strong π -polarization of the monomers in the solid state. Comparing this data to the computed C=O lengths for **1** (1.227 Å), **1-prot** (1.321 Å), and **1-taut** (1.352 Å) suggests that the π -systems of self-assembled quinacridone monomers may be appropriately modeled by the π -systems of **1-prot** and **1-taut**.

3.2 Methods

All geometries were optimized at B3LYP/6-311+G(d,p)³³ with constrained C_{2h} symmetry for **1**, **2**, **1-prot**, **2-prot**, **1-taut**, and **2-taut** employing the Gaussian16 program.³⁴ Nucleus-independent chemical shifts (NICS) computed at the PW91PW91/IGLOIII level quantified aromaticity of the individual rings. NICS(1)_{zz} values were computed at 1 Å above

the ring centers and include only shielding tensor components from the out-of-plane “*zz*” direction.^{35,36} Clar sextets are identified by a more negative NICS(1)_{*zz*} in a ring compared to all of its neighboring rings. Isotropic magnetic shielding (IMS) plots were computed at the same level at 1 Å above the molecular plane using regular grids of points with an interval of 0.1 Å. These plots were previously shown by Lampkin, Karadakov, and VanVeller to provide feature-rich descriptions of aromaticity in PAHs.³⁷ Gauge-including magnetically induced current (GIMIC) plots computed at B3LYP/6-311+G(d,p) provided a visualization of the numbers and positions of Clar sextet(s) in the π -system.³⁸ Diatropic ring currents are indicated by a clockwise current intensify at the positions of the Clar sextet locations.²⁴ Time-dependent (TD) density functional theory computations were performed at TD- ω B97X-D/6-311+G(d,p) to estimate the HOMO and LUMO levels of each model system. HOMO-LUMO gaps were derived by the HOMO to LUMO excitation energies.³⁹

3.3 Results and Discussion

Figure 3.2 compares the computed NICS(1)_{*zz*} values of **1** and **2**, to their **-prot** and **-taut** forms, and acene reference. In **1**, the three arene rings show large negative NICS(1)_{*zz*} values indicating three Clar sextets that are separated by two weak to non-aromatic pyridone rings, which have small negative NICS(1)_{*zz*} values. In **1-prot**, the two pyridone rings gain significant aromatic character, but the three arene rings still display more negative NICS(1)_{*zz*} values, and the NICS patterns of the individual rings indicate the presence of three Clar sextets. In **1-taut**, the two pyridone rings become more aromatic than the terminal rings, and

now only the central ring can be recognized as a Clar sextet. NICS patterns of the individual rings of **1-taut** follow that of pentacene.

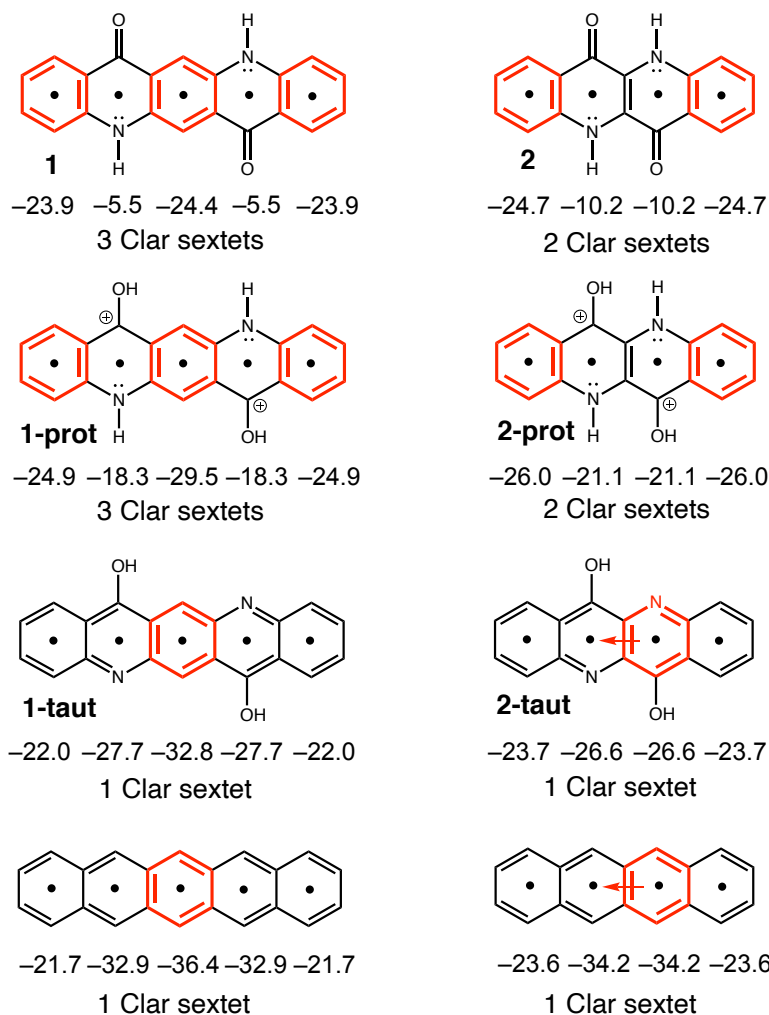


Figure 3.2 Computed NICS(1)_{zz} values for **1**, **1-prot**, and **1-taut**, compared to pentacene, and for **2**, **2-prot**, and **2-taut**, compared to tetracene. Clar sextets are drawn in red. A red arrow across two rings indicates equivalent Clar structures.

Like **1**, computed NICS(1)_{zz} for **2**, **2-prot**, and **2-taut**, show increased diatropicity of the pyridone rings as the π -system becomes more polarized. NICS patterns of the individual

rings of **2-taut** resemble those of tetracene, indicating one Clar sextet. In **2-taut** and in tetracene, the two central rings are equivalent Clar structures (indicated by a red arrow in Figure 3.2) like that in naphthalene (cf. data for iso-epindolidione in the SI, where polarization of the π -system *increases* the number of Clar sextet rings). Remarkably, hydrogen bonding can reduce aromaticity in **1** and **2** by lowering the numbers of Clar sextets in the π -system. Consistent with experimental findings, the computed HOMO-LUMO gaps of both **1**, 3.23 eV (cf. 2.95 eV for a hydrogen-bonded trimer) and **2**, 3.52 eV (cf. 3.30 eV for a hydrogen-bonded trimer) become narrower upon hydrogen bonding at the N–H and C=O sites.

Plots of isotropic magnetic shielding (IMS) (Figure 3.3) were computed to visualize the Clar sextet patterns of **1**, **2** and their π -polarized analogs. The IMS plot of **1** shows three particularly shielded regions ($> +12$ ppm) at the positions of the arene rings, indicative of three Clar sextets. In **1-prot**, the central ring becomes even more shielded (see dark purple region, $> +15$ ppm), suggesting enhanced aromaticity, and the shielded areas of the terminal arene rings move towards the pyridone rings. In **1-taut**, the central ring is the most strongly shielded region (note cyclic dark purple region, indicating a Clar sextet, $> +15$ ppm), followed by the pyridone rings, and then the terminal arene rings (cf. IMS plot for pentacene). IMS plots for **2**, **2-prot**, and **2-taut**, show the same trends, suggesting a migration of the Clar sextets from the outer rings to the central rings (cf. IMS plot for tetracene).

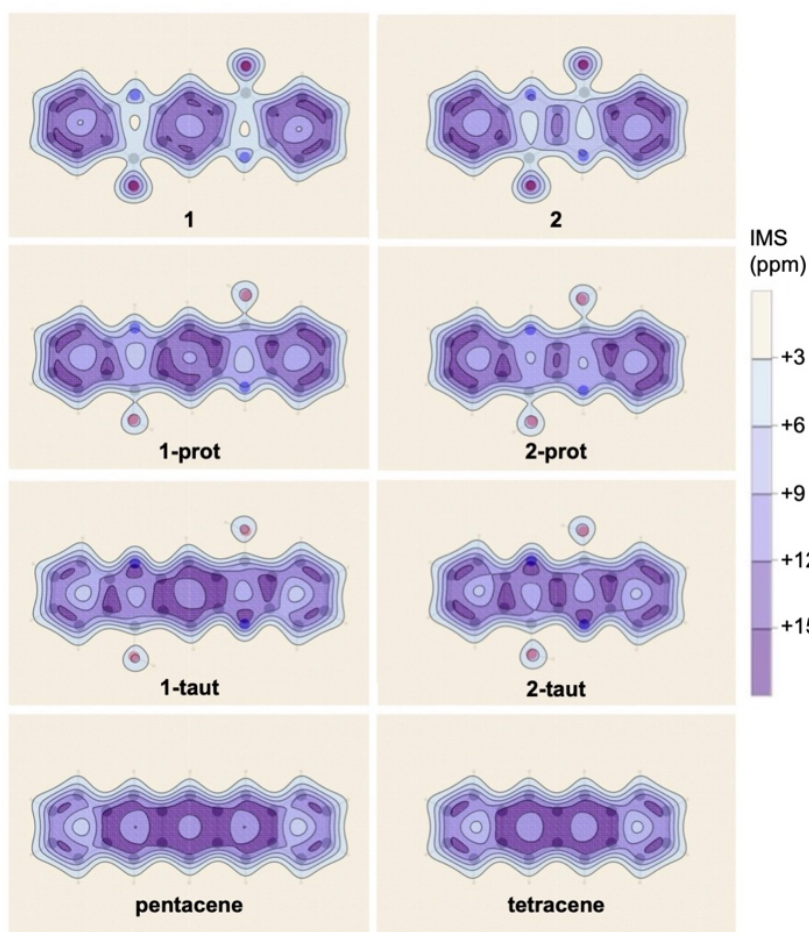


Figure 3.3 Computed IMS plots for **1**, **1-prot**, and **1-taut**, compared to pentacene, and for **2**, **2-prot**, and **2-taut**, compared to tetracene.

Details of the induced ring currents of **1**, **2**, and their π -polarized analogs are shown in Figure 3.4 by the gauge-including magnetically induced current (GIMIC) plots. **1** displays three localized diatropic ring currents, located at the positions of the arene rings. A weakly diatropic current encompasses the periphery of the five fused rings. **1-prot** shows a pronounced macrocyclic diatropic ring current around the periphery of the molecule which intensifies at the central ring and terminal rings. Note that only the central ring shows a

complete localized diatropic ring current, while the terminal rings show a breached local ring current. In **1-taut**, the macrocyclic diatropic current becomes dominant, and is strongest at the central ring and weakest at the terminal rings. These features agree with the findings of NICS and IMS, showing a reduced Clar sextet ratio going from **1** (three Clar sextets) **1-prot**, to **1-taut** (one Clar sextet). GIMIC plots for **2**, **2-prot**, and **2-taut**, also shown an increasingly delocalized diatropic ring current. In **2**, there are two localized diatropic ring currents, located at the positions of the arene rings, indicating the presence of two Clar sextets. But as the π -system becomes increasingly polarized, a macrocyclic diatropic ring current dominates, and the GIMIC plots of **2-prot** and **2-taut**, become more tetracene-like.

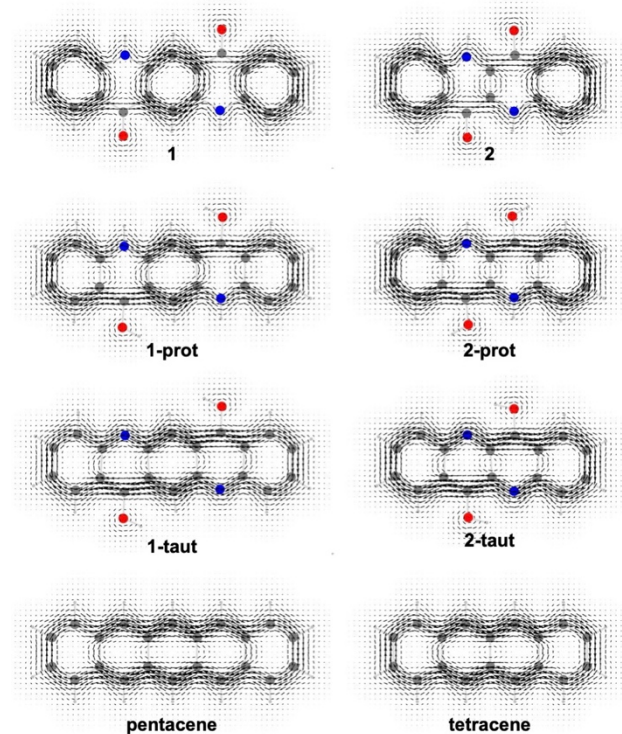


Figure 3.4 Computed GIMIC plots for **1**, **1-prot**, and **1-taut**, compared to pentacene, and for **2**, **2-prot**, and **2-taut**, compared to tetracene.

3.4 Conclusions

Hydrogen bonding interactions can play an important role in the molecular design of organic semiconductors. Besides controlling solid state structure, hydrogen-bonding interactions can be used to perturb aromatic character of conjugated organic molecules to modulate electronic property. Here, we show that reducing the ratios of Clar rings can be considered as a design strategy to enhance charge transport property in popular organic dyes.

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3.6 Appendix

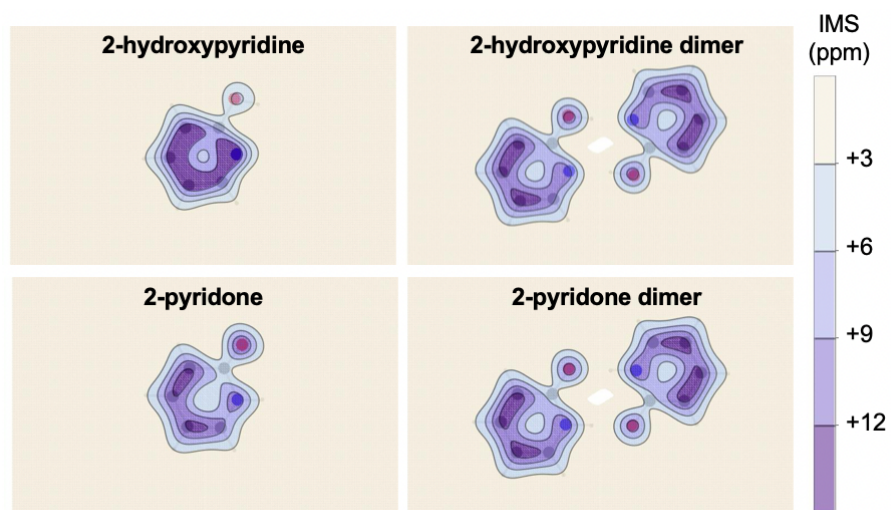


Figure A3.1 Computed IMS plots of 2-hydroxypyridine and 2-pyridone and their dimers.

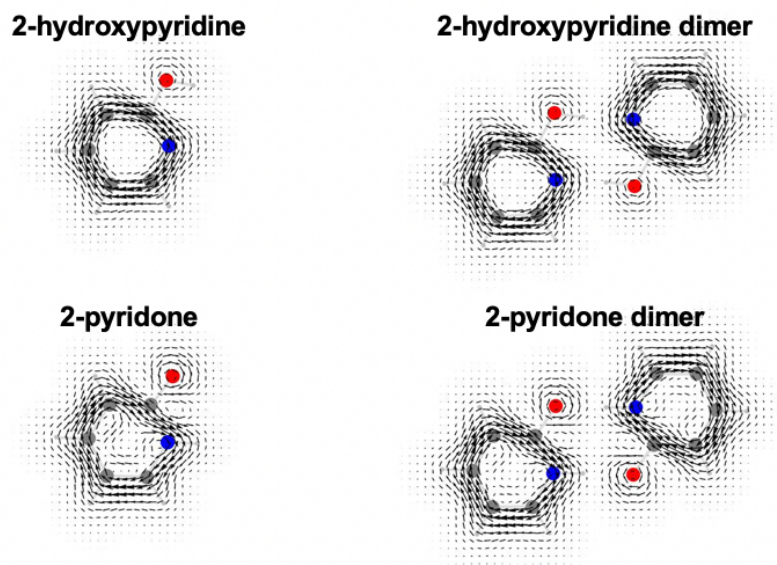


Figure A3.2 Computed GIMIC plots of 2-hydroxypyridine and 2-pyridone and their dimers.

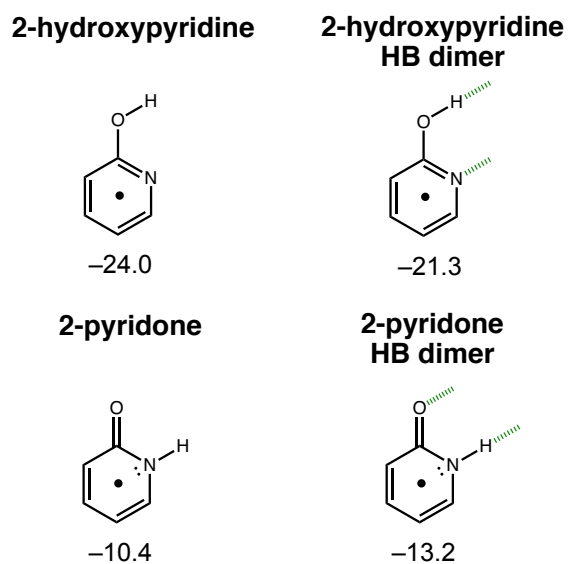


Figure A3.3 Computed NICS(1)_{zz} values (in ppm) of 2-hydroxypyridine and 2-pyridone and their dimers.

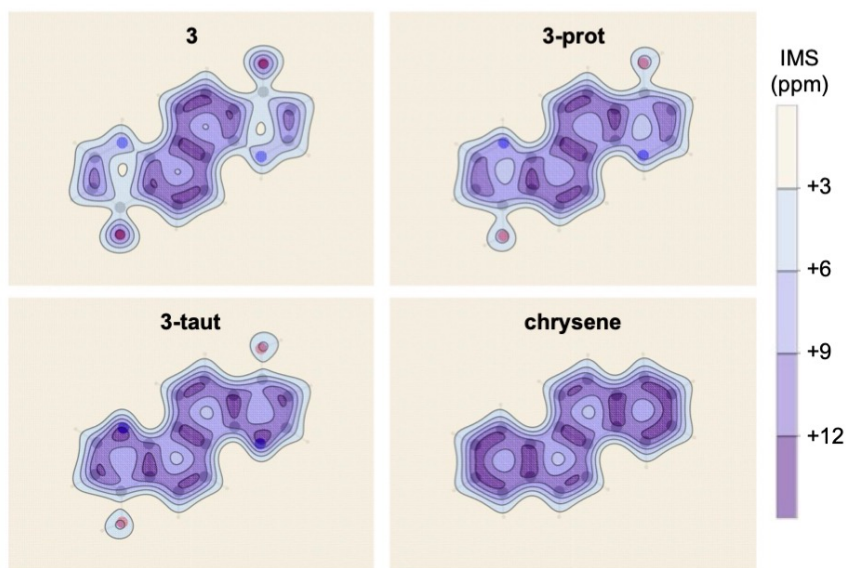


Figure A3.4 Computed IMS plots of **3**, **3-pro**, **3-taut**, and **chrysene**.

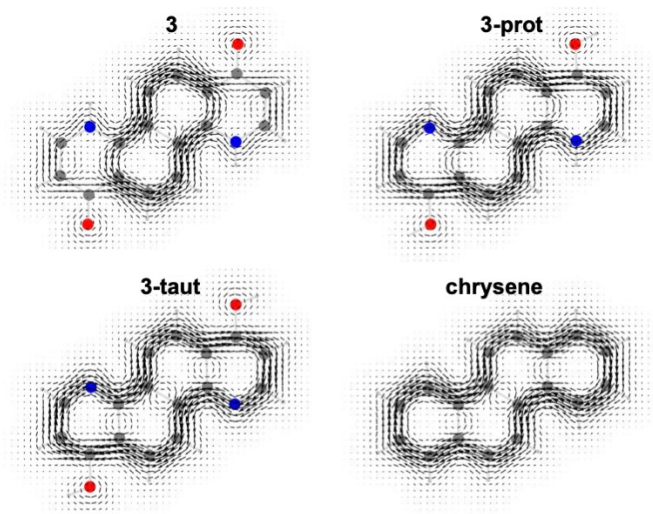


Figure A3.5 Computed GIMIC plots of **3**, **3-prot**, **3-taut**, and **chrysene**.

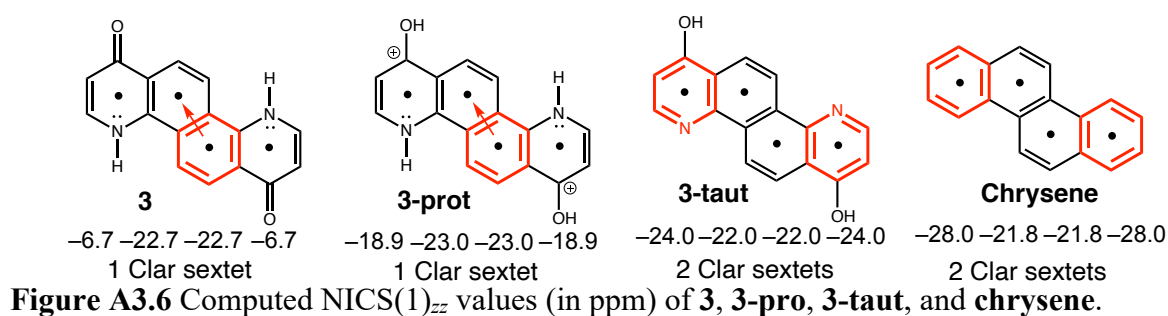


Figure A3.6 Computed NICS(1)_{zz} values (in ppm) of **3**, **3-prot**, **3-taut**, and **chrysene**.

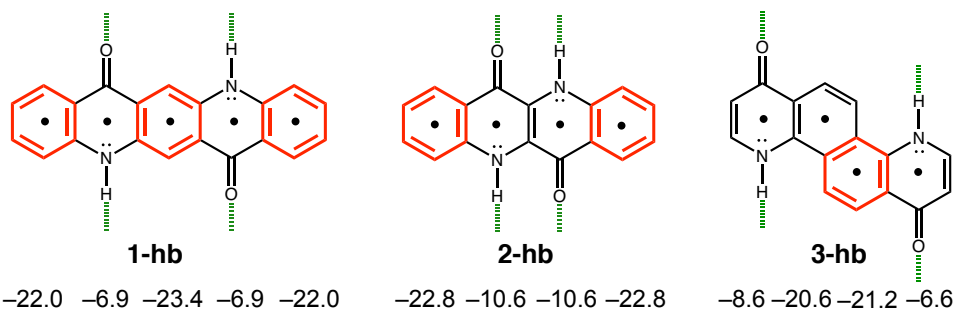


Figure A3.7 Computed NICS(1)_{zz} values (in ppm) of **1-hb**, **2-hb**, and **3-hb**.

Chapter 4

How Does Excited-State Antiaromaticity Affect the Acidity Strengths of Photoacidity?

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4.1 Introduction

Baird first proposed a set of rules suggesting that the electron-counting rules of aromaticity and antiaromaticity reverse in the lowest triplet states of π -conjugated cycles.¹ Based on this set of rules, $[4n+2]$ π -rings are antiaromatic and $[4n]$ π -rings are aromatic in the first $\pi\pi^*$ state. These predictions were later extended to the first singlet $\pi\pi^*$ states (S_1), and explained the reactivities of many Baird-type antiaromatic $[4n+2]$ π -systems.²⁻⁷ Benzene, in the S_1 state, is reactive and readily isomerizes to fulvene.^{7,8} Among other $[4n+2]$ π -ring systems, salicylic acid, in the S_1 state, undergoes intramolecular proton transfer.^{9,10} Here we show that, in the S_1 state, differences in the acidity strengths of photoacids might be rationalized by the effects of “antiaromaticity relief” upon deprotonation, followed by a redistribution of electrons in the excited conjugate base.

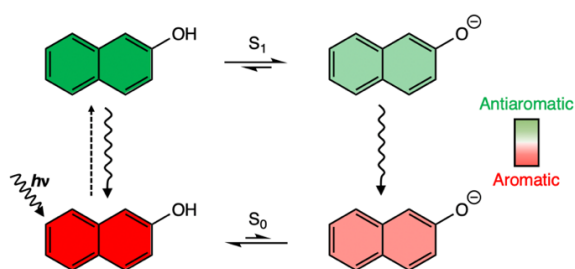


Figure 4.1 The Förster cycle of 2-naphthol. As indicated by the color scheme above, 2-naphthol is $[4n+2]$ π -aromatic in the ground state (red) but becomes $[4n+2]$ π -antiaromatic in the S_1 state (green). Deprotonation relieves excited-state antiaromaticity, stabilizing the excited conjugate base (light green). In the S_0 state, the conjugate base (light red) is only moderately less aromatic than the acid.

Following the early independent works of Förster^{11,12} and Weller,¹³⁻¹⁵ it was recognized that some aromatic acids (e.g., with hydroxyl or amine groups) can turn into

stronger Brønsted acids in their first excited (S_1) states.¹¹⁻¹⁶ 2-Naphthol, a prototypical organic “photoacid,” is a weak acid in the ground state, but shows enhanced acidity in the S_1 state ($pK_a = 9.5$, $pK_a^* = 2.8$, $\Delta pK_a = -6.7$), and can deprotonate to the solvent producing an electronically excited conjugate base.¹⁴ A Stokes’ shift in the fluorescence spectrum of 2-naphthol in water was interpreted in the early works of Förster as radiative decay emitting from the excited conjugate base (see depiction of “Förster cycle” in Figure 4.1).¹¹ Yet, despite a large body of theoretical and experimental efforts towards understanding excited-state proton transfer reactions in aromatic acids,¹⁷⁻²⁷ reasons underlying the occurrence of photoacidity remain unclear. The disparate effects of substituents on photoacidity are even more puzzling (see Table 4.1). 2-Naphthylammonium displays increased acidity in the S_1 state ($pK_a = 4.1$, $pK_a^* = -0.8$, $\Delta pK_a = -4.9$), deprotonating from an NH_3^+ group, but the change in acidity, ΔpK_a , is two-folds less than that of 2-naphthol.²⁸ Aromatic acids, like the 2-naphthoic acid, show the opposite effect and exhibit decreased acidity in the S_1 state ($pK_a = 4.2$, $pK_a^* = 11.5$, $\Delta pK_a = +7.3$).²⁹

Table 4.1 Experimental pK_a , pK_a^* , and ΔpK_a values

Compound	pK_a	pK_a^*	ΔpK_a	Reference
2-Naphthol	9.5	2.8	-6.7	15
2-Naphthylammonium	4.1	-0.8	-4.9	28
2-Naphthoic acid	4.2	11.5	+7.3	29
8-Cyano-2-naphthol	8.4	-0.8	-9.2	19
5,8-Dicyano-2-naphthol	7.8	-4.5	-12.3	19
Salicylamide	-2.6	-5.3	-2.7	35

Why do substituents have such disparate effects on the photoacidities of aromatic acids? Here, we relate the effects of photoacidity to a switch in the ground and excited-state (anti)aromatic character of aromatic acids. According to the Hückel rule, cyclic π -conjugated rings with $[4n+2]$ π -electrons are aromatic, and those with $[4n]$ π -electrons are antiaromatic.³⁰ But this electron-counting rule reverses in the first $\pi\pi^*$ state following Baird's rule.¹⁻⁷ 2-Naphthol is $[4n+2]$ Hückel aromatic (ten π -electrons in naphthalene) in the ground state, but becomes $[4n+2]$ antiaromatic in the S_1 state. Upon deprotonation, an excited conjugate base forms, and negative charge on the O^- delocalizes into the ring, giving rise to a resonance structure with breached cyclic $[4n+2]$ π -electron delocalization—this alleviates antiaromaticity in the S_1 state of the acid (see Figure 4.1 and resonance structure for the excited conjugate base in Figure 4.2a, note delocalization of the negative charge into the ring). In this way, photoacidity might be considered as a consequence of antiaromaticity relief in the S_1 states of aromatic acids. Based on a more bond equalized S_1 vs. S_0 state of 2-naphtholate, Agmon et al. pointed out similarly that the excited conjugate base of 2-naphthol might be stabilized by increased aromatic character.^{19,20} The effects of ground and excited-state (anti)aromaticity also have been recognized in other excited-state proton transfer processes.^{31,32}

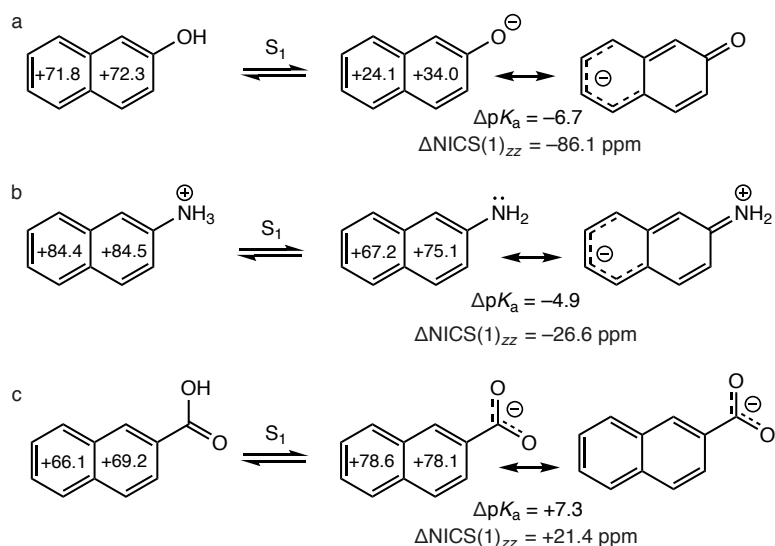


Figure 4.2 Computed NICS(1)_{zz} and ΔNICS(1)_{zz} (sum of NICS(1)_{zz} values of the conjugate base minus that of the acid) (in ppm) values for the S₁ states of the acid and conjugate base at CASSCF(12,12)/6-311+G(d,p), for a) 2-naphthol, b) 2-naphthylammonium, and c) 2-naphthoic acid. Negative ΔNICS(1)_{zz} values indicate antiaromaticity relief, and positive values indicate antiaromaticity gain, upon formation of the excited conjugate base. Experimental ΔpK_a values are included for reference.

Even though not realized at the time, the possible effects of excited-state antiaromaticity relief were implied in Weller's original explanation (1950's) of photoacidity—argued based on a redistribution of ring π -electrons in the S₁ states of the aromatic acids;¹³⁻¹⁵ notably, these ideas were published roughly ten years prior to Dewar³³ and Zimmerman's³⁴ independent works and Baird's¹ proposal (60's-70's) of a reversed Hückel π -electron-counting rule for aromaticity and antiaromaticity in the first $\pi\pi^*$ states of transition states^{33,34} and of π -conjugated rings.¹ Weller reasoned that when 2-naphthol is electronically excited to the S₁ state, intramolecular charge transfer from the hydroxyl oxygen to the aromatic ring increases acidity of the OH group. Later, it was suggested that even more

pronounced charge redistribution happens upon deprotonation (as indicated by shortened C–O bond lengths and changes in dipole moments),²¹ stabilizing the excited conjugate base. We now relate the effects of “charge redistribution” in the excited conjugate base to “relief of excited-state antiaromaticity.” This rationale also may explain why photoacidity only is observed for aromatic acids (i.e., with $[4n+2]$ ring π -electrons), but not for other hydroxyl, amine, or ammonium compounds.

Compared to 2-naphthol, the effect of charge redistribution for alleviating antiaromaticity in the excited conjugate base of 2-naphthylammonium is much weaker, since delocalization of a neutral nitrogen lone pair into the naphthalene ring is less effective (see Figure 4.2b, note charge separated resonance form). In the S_1 state of 2-naphthylammonium, deprotonation produces a neutral amine (NH_2); proton transfer alleviates antiaromaticity of the excited naphthalene ring, but to a lesser degree compared to that of 2-naphthol. Notably, compounds with competing deprotonation sites like salicylamide^{35,36} and 3-ammonium-2-naphthol³⁷ undergo proton transfer from NH_3^+ in the ground state (i.e., to retain aromaticity of the π -ring), (i.e., to alleviate excited-state antiaromaticity of the π -ring) when solvated in water. In the S_1 state of 2-naphthoic acid, deprotonation of the carboxylic group gives a carboxylate (COO^-). But negative charge is mostly delocalized between the two oxygen atoms, and does not help lessen excited-state antiaromaticity in the naphthalene ring (Figure 4.2c).

4.2 Results and Discussion

We performed dissected nucleus independent chemical shifts,^{38,39} NICS(1)_{zz}, to quantify excited-state antiaromaticity in the S₁ states⁴⁰ of the acids and conjugate bases of 2-naphthol, 2-naphthylammonium, and 2-naphthoic acid (Figure 4.2). The computed ring NICS(1)_{zz} values of excited 2-naphthol are large and positive (+71.8, +72.3 ppm, strongly antiaromatic) but are much less positive in the excited conjugate base (+24.1, +34.0 ppm, weakly antiaromatic), suggesting decreased antiaromaticity upon deprotonation of the excited acid ($\Delta\text{NICS}(1)_{zz} = -86.1$ ppm, Figure 4.2a). 2-Naphthylammonium reveals a lesser degree of antiaromaticity relief upon deprotonation ($\Delta\text{NICS}(1)_{zz} = -26.6$ ppm, Figure 4.2b). Accordingly, the computed exocyclic CO and CN bond distances of 2-naphthol (1.350 Å) and 2-naphthylammonium (1.476 Å), are longer in the S₁ state acid, and shorter in the excited conjugate base (1.247 Å and 1.373 Å, respectively), indicative of electron delocalization from the deprotonated site into the excited naphthalene ring (see data in Figure A4.1)

In contrast, computed ring NICS(1)_{zz} values for 2-naphthoic acid in the S₁ state are positive for the acid (+66.1, +69.2 ppm, strongly antiaromatic) but become even more so in the excited conjugate base (+78.6, +78.1 ppm, strongly antiaromatic), suggesting increased antiaromaticity upon deprotonation of the excited acid ($\Delta\text{NICS}(1)_{zz} = +21.4$ ppm, Figure 4.1c). The exocyclic C–C bond of the excited acid is 1.471 Å (cf. 1.40 Å CC length of benzene), indicating modest π -conjugation between the carboxylic group and the naphthalene ring, but lengthens to 1.534 Å in the excited conjugate base (cf. 1.53 Å CC length of ethane), suggesting little resonance between the exocyclic carboxylate group and the excited

(antiaromatic) naphthalene (see geometries in the A4.1). In the ground state, deprotonation has less effect on the 10 π -electron aromatic character of the naphthalene ring, in 2-naphthol ($\Delta\text{NICS}(1)_{zz} = +8.5$ ppm), 2-naphthylammonium ($\Delta\text{NICS}(1)_{zz} = +2.2$ ppm), and 2-naphthoic acid ($\Delta\text{NICS}(1)_{zz} = -1.2$ ppm); positive/negative values indicate aromaticity loss/gain (see full data in Figure A4.2, A4.3).

Naphthols with cyano (CN) substituents at the C5 and C8 positions are very strong photoacids: 8-cyano-2-naphthol ($\text{p}K_a = 8.4$, $\text{p}K_a^* = -0.8$, $\Delta\text{p}K_a = -9.2$) and 5,8-dicyano-2-naphthol ($\text{p}K_a = 7.8$, $\text{p}K_a^* = -4.5$, $\Delta\text{p}K_a = -12.3$) show increased acidities of up to 12 units in the S_1 state.^{17,18,41,42} These strong photoacids can undergo excited-state proton transfer reactions in methanol, methylsulfonyl, and other organic solvents in the absence of water, first expanding the possibility of studying proton transfer kinetics in non-aqueous solvents.⁴¹ Computed ring NICS(1)_{zz} values for the S_1 state of 8-cyano-2-naphthol and its excited conjugate base ($\Delta\text{NICS}(1)_{zz} = -137.2$ ppm, Figure 4.3a) show significant excited-state antiaromaticity relief upon deprotonation, and the effect in 5,8-dicyano-2-naphthol ($\Delta\text{NICS}(1)_{zz} = -163.5$ ppm, Figure 4.3b) is even greater (cf. $\Delta\text{NICS}(1)_{zz} = -86.1$ ppm, for 2-naphthol). As suggested by the resonance forms in Figure 4.3, the electron-withdrawing CN groups help increase charge redistribution in the excited conjugate base, by inductive effects, but also by resonance stabilization (see resonance contributors with negative charges delocalized to the nitrogen atoms). We note that other known strong photoacids with electron-withdrawing groups, e.g., sulfonyl groups, also have π -systems on the substituents capable of delocalizing negative charge of the excited conjugate base.

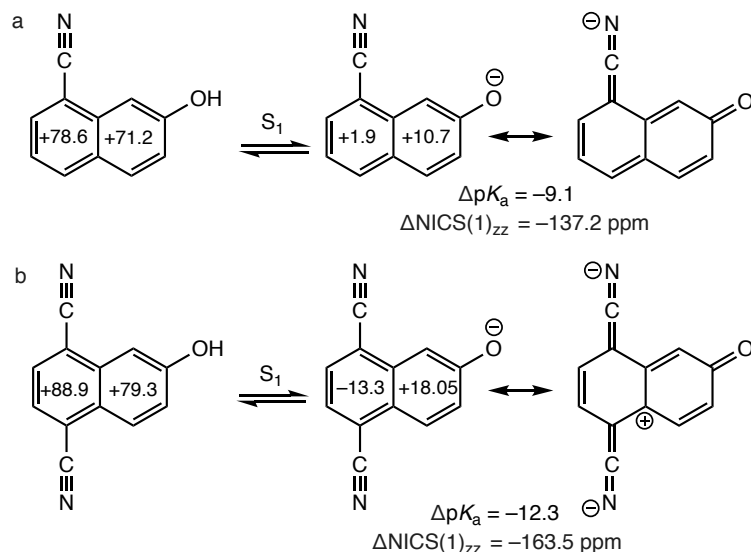


Figure 4.3 Computed NICS(1)_{zz} and Δ NICS(1)_{zz} (sum of NICS(1)_{zz} values of the conjugate base minus that of the acid) (in ppm) values for the S_1 states of the acid and conjugate base at CASSCF(12,12)/6-311+G(d,p), for a) 8-cyano-2-naphthol and b) 5,8-dicyano-2-naphthol.

Aromatic acids with competing deprotonation sites like salicylamide undergo proton transfer from NH_3^+ in the S_0 state, but deprotonate from the OH group in the S_1 state.^{35,36} In the S_0 state, computed NICS(1)_{zz} for the acid (-24.4 ppm) and conjugate base (-24.5 ppm, deprotonated at NH_3^+) give nearly the same values (Δ NICS(1)_{zz} = +0.1 ppm) (Figure 4.4, bottom). But in the S_1 state, the ring NICS(1)_{zz} value for protonated salicylamide is large and positive (+40.2 ppm) while that for the excited conjugate base is modestly negative (-4.2 ppm, deprotonated at OH), documenting the effects of excited-state antiaromaticity relief (Δ NICS(1)_{zz} = -44.4 ppm) (Figure 4.4, top). Notably, when a proton is removed from the NH_3^+ site of the electronically excited acid, computed NICS(1)_{zz} for the excited conjugate base (+65.8 ppm) show increased excited-state antiaromaticity in the benzene ring.

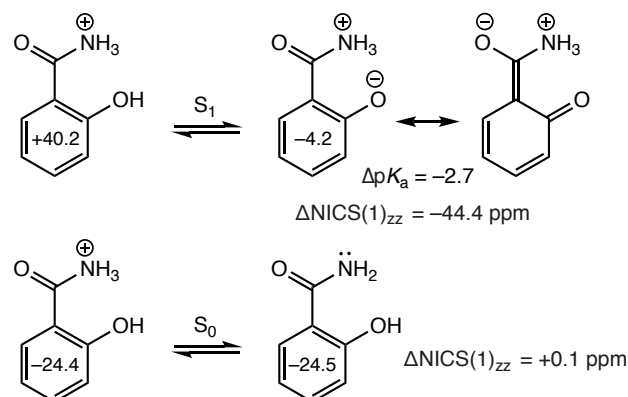


Figure 4.4 Computed $\text{NICS}(1)_{zz}$ and $\Delta \text{NICS}(1)_{zz}$ (sum of $\text{NICS}(1)_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S₀ and S₁ states of protonated salicylamide and its conjugate base at CASSCF(12,12)/6-311+G(d,p). Negative $\Delta \text{NICS}(1)_{zz}$ values indicate antiaromaticity relief upon formation of the excited conjugate base. Positive $\Delta \text{NICS}(1)_{zz}$ values in the ground state indicate aromaticity loss upon formation of the conjugate base. An experimental ΔpK_a value is included for reference.

A long-standing and much debated anomaly is the stronger photoacidity of 1-naphthol ($pK_a = 9.2$, $pK_a^* = -0.5$, $\Delta pK_a = -9.7$) compared to the structurally similar 2-naphthol isomer ($pK_a = 9.5$, $pK_a^* = 2.8$, $\Delta pK_a = -6.7$); note 3-fold ΔpK_a difference!⁴³⁻⁴⁵ Based on time-resolved emission spectroscopy and steady state spectrofluorometry experiments, 1-naphthol displayed a rate of deprotonation (k_I^*) greater than 2-naphthol by 280 times.⁴⁴ It was proposed that the stronger photoacidity of 1-naphthol was a consequence of populating and emitting from the ¹L_a state, while 2-naphthol shows near degenerate ¹L_a and ¹L_b states, emitting from the ¹L_b state.^{17,46,47} We speculate that naphthols promoted to the ¹L_a state deprotonate more readily because of pronounced antiaromatic character in the ¹L_a state of naphthalene. Computed geometric indices of aromaticity for excited naphthalene show a more bond alternated ¹L_a state and a more bond equalized ¹L_b state (see data in Figure A4.4). See also resonance

structures of naphthalene in the 1L_a (B_{2u}) state (“diradical form,” note “antiaromatic” Clar sextet structure in the 1L_a) and 1L_b (B_{3u}) state (“allyl radical form”) (Figure 4.5). Notably, Baird’s original paper on the effects of triplet (anti)aromaticity also recognized a more antiaromatic “diradical form” for triplet benzene.¹

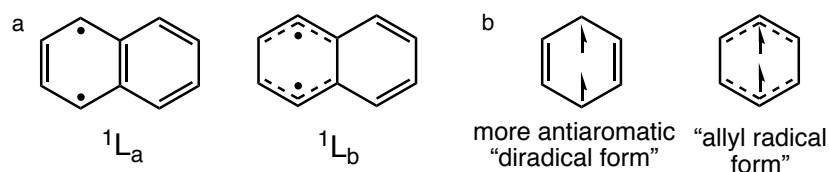


Figure 4.5 a) Resonance structures for the 1L_a and 1L_b states of excited state naphthalene, and b) the “diradical” (B_{1u}) and “allyl radical” (B_{2u}) forms of triplet benzene.

4.3 Conclusions

Although substituents are typically considered to have negligible effects on aromaticity (unless charged or in the presence of other push/pull substituents),^{48,49} they can easily perturb the excited-state antiaromaticity of organic compounds,⁵⁰ having tremendous effects on reactions such as the excited-state proton transfer of photoacids. These findings are another manifestation of the increasingly recognized effects of excited-state (anti)aromaticity on the photochemical reactivity of organic compounds.

4.4 Methods

Geometry optimization for the ground (S_0) and excited (S_1 , $^1\pi\pi^*$) states of all acid and conjugate base structures were performed at CASSCF(12,12)/6-311+G(d,p) with C_s symmetry, employing Molpro2012.1.⁵¹ The S_0 and S_1 geometries of 5,8-dicyano-2-naphthol

and its conjugate base were computed at CASSCF(10,10)/6-311+G(d,p) with C_s symmetry. Computed dissected nucleus-independent chemical shifts, NICS(1)_{zz},^{38,39} were performed at CASSCF(12,12)/6-31G(d,p), employing the Dalton2016 program,⁵² to quantify the magnetic effects of aromaticity and antiaromaticity in the S₀ and S₁ states⁴⁰ of the acids and conjugate bases. NICS(1)_{zz} values were computed at 1 Å above each of the six membered ring centers and include only contributions from the “out-of-plane” (zz) tensor component perpendicular to the ring plane. ΔNICS(1)_{zz} values were calculated based on the sum of ring NICS(1)_{zz} values of the conjugate base minus that of the acid.

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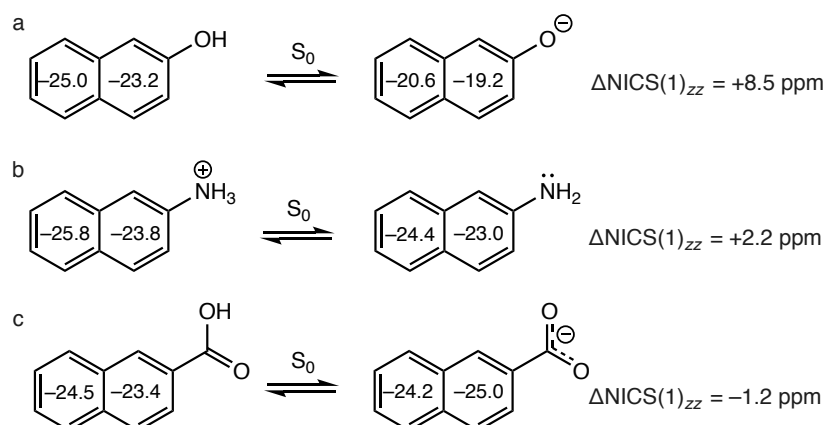


Figure A4.2 Computed $\text{NICS}(1)_{zz}$ and $\Delta\text{NICS}(1)_{zz}$ (sum of $\text{NICS}(1)_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S_0 states of the acid and conjugated base at CASSCF(12,12)/6-311+G(d,p), for a) 2-naphthol, b) 2-naphthylammonium, and c) 2-naphthoic acid. Negative $\Delta\text{NICS}(1)_{zz}$ values indicate aromaticity gain, and positive values indicate aromaticity loss, upon formation of the conjugate base.

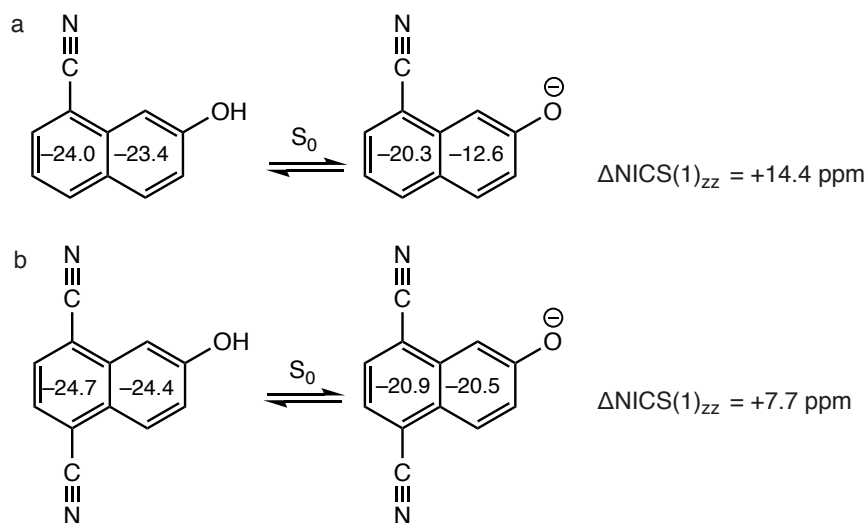


Figure A4.3 Computed $\text{NICS}(1)_{zz}$ and $\Delta\text{NICS}(1)_{zz}$ (sum of $\text{NICS}(1)_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S_0 states of the acid and conjugate base at CASSCF(12,12)/6-311+G(d,p), for a) 8-cyano-2-naphthol and b) 5,8-dicyano-2-naphthol. Positive $\Delta\text{NICS}(1)_{zz}$ values indicate aromaticity loss upon formation of the conjugate base.

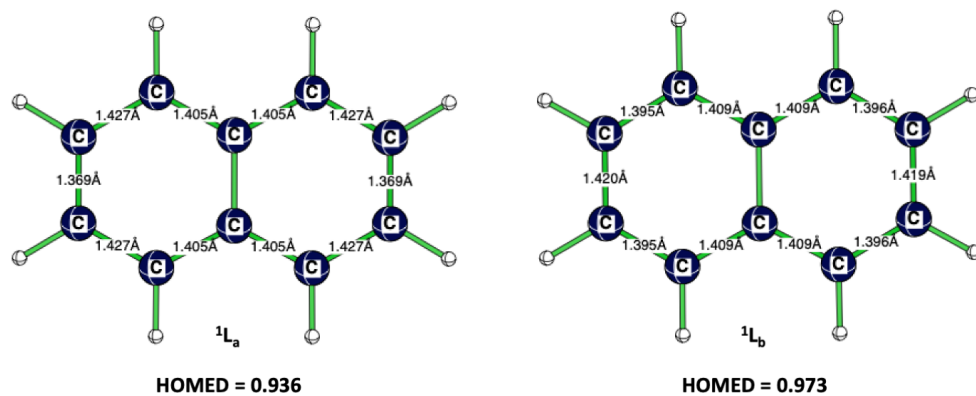


Figure A4.4 Optimized geometries and computed HOMED values for naphthalene (constrained C_{2v} symmetry) in the 1L_a (B_{2u}) and 1L_b (B_{3u}) states, at TD- ω B97X-D/6-311+G(d,p). The smaller HOMED value for the 1L_a state suggests greater excited-state antiaromatic character compared to the 1L_b state.

Chapter 5

Conclusions

Although the concept of (anti)aromaticity was long considered to have only conceptual interest, useful only for interpret existing experimental observations, a renaissance of the (anti)aromaticity concept in modern organic chemistry is happening due to the growing sophistication as well as versatility of computational tools. We have demonstrated that antiaromaticity can be introduced to formally non-aromatic π -conjugated cores through hydrogen bonding interactions, which give rise to decreased LUMO energy levels and improved n -type charge transport performance. The reciprocal relationship between (anti)aromaticity and hydrogen bonding interaction provides insight to the molecular design of organic electronics and can expand the library of potential candidates to non-aromatic cores with “near $[4n]$ π -conjugated” topologies. Hydrogen bonding interactions also can effectively modulate the numbers and positions of Clar sextets in extended π -systems with hydrogen bonding functionalities. Reducing the ratio of Clar sextets could be regarded as an efficient way to lower aromaticity and improve charge transport property in organic pigments. Besides hydrogen bonding, proton transfer reactions also can significantly perturb the aromatic and antiaromatic character of polycyclic aromatics. We recognized that excited-state antiaromaticity relief is a key driving force for the phenomenon of photoacidity; the degree of “antiaromaticity relief” explains why some photoacids are stronger than others. We also found that substituents could significantly influence the excited-state antiaromaticity of organic compounds, opening doors to the rational design of organic photoacid compounds. I hope the works presented in this dissertation will stimulate more discoveries of modern applications of the (anti)aromaticity concept.