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

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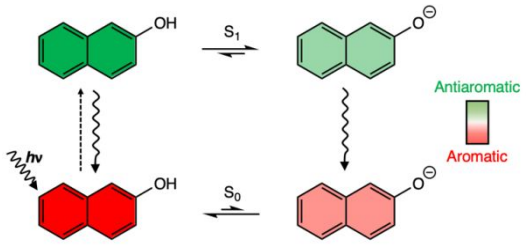
Photoacids like substituted naphthalenes (X = OH, NH_3^+, COOH) are aromatic in the S_0 state and antiaromatic in the S_1 state. Nucleus independent chemical shifts analyses reveal that deprotonation relieves antiaromaticity in the excited conjugate base, and that the degree of "antiaromaticity relief" explains why some photoacids are stronger than others.

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, [4*n*+2] π-rings are antiaromatic and [4*n*] π-rings are aromatic in the first ππ* state. These predictions were later extended to the first singlet ππ* states (S_1), and explained the reactivities of many Baird-type antiaromatic [4*n*+2] π-systems.[2-7] Benzene, in the S_1 state, is reactive and readily isomerizes to fulvene.[7,8] Among other [4*n*+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.

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 ammonium 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, ΔpK_a = –6.7), and can deprotonate to the solvent producing an electronically excited conjugate base.[15] A Stokes' shift in the fluorescence spectrum of 2-naphthol in water was interpreted by Förster as radiative decay emitting from the excited conjugate base (see depiction of "Förster cycle" in Scheme 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. 2-Naphthylammonium displays increased acidity in the S_1 state (pK_a = 4.1, pK_a* = –0.8, ΔpK_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, ΔpK_a = +7.3).[29]



Scheme 1. The Förster cycle of 2-naphthol. As indicated by the color scheme above, 2-naphthol is [4*n*+2] π-aromatic in the ground state (red) but becomes [4*n*+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.

Table 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 [4*n*+2] π-electrons are aromatic, and those with [4*n*] π-electrons are antiaromatic.[30] But this electron-counting rule reverses in the first ππ* state following Baird's rule.[1-7] 2-Naphthol is [4*n*+2] Hückel aromatic (ten π-electrons in naphthalene) in the ground state, but becomes [4*n*+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

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Electronic Supplementary Information (ESI) available: Cartesian coordinates for all structures, computed ground state NICS data, HOMA analyses, and bond alternation analysis for the ^1L_a and ^1L_b states of naphthalene. See DOI: 10.1039/x0xx00000x

resonance structure with breached cyclic [4*n*+2] π-electron delocalization—this alleviates antiaromaticity in the S_1 state of the acid (see Scheme 1 and resonance structure for the excited conjugate base in Figure 1a, 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.[6] 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]

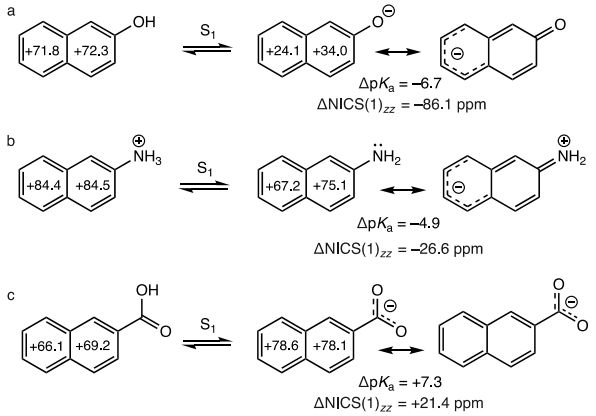


Figure 1. Computed NICS(1)$_{zz}$ and ΔNICS(1)$_{zz}$ (sum of NICS(1)$_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S_1 states of the acid and conjugate base at CASSCF(12,12)/6-311+G(d,p), for a) 2-naphthol, b) 2-naphthylammonium, and c) 2-naphthoic acid. Negative 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 S_1 states of the aromatic acids;[13-15] notably, these ideas were published roughly ten years prior to Dewar[33] and Zimmerman's[34] independent works and Baird's[1] proposal (60's-70's) of a reversed Hückel π-electron-counting rule for aromaticity and antiaromaticity in the first ππ* states of transition states[33,34] and of π-conjugated rings.[1] Weller reasoned that when 2-naphthol is electronically excited to the S_1 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 [4*n*+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 1b, 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-naphthol[37] undergo proton transfer from NH_3^+ in the ground state (i.e., to retain aromaticity of the π-ring), but deprotonate from the OH group in the S_1 state (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 1c).

We performed dissected nucleus independent chemical shifts,[38,39] NICS(1)$_{zz}$, to quantify excited-state antiaromaticity in the S_1 states[40] of the acids and conjugate bases of 2-naphthol, 2-naphthylammonium, and 2-naphthoic acid (Figure 1). The computed ring NICS(1)$_{zz}$ values of excited 2-naphthol are large and positive (+71.8, +72.3 ppm, strongly antiaromatic) but become much less so in the excited conjugate base (+24.1, +34.0 ppm, weakly antiaromatic), suggesting decreased antiaromaticity upon deprotonation of the excited acid (ΔNICS(1)$_{zz}$ = –86.1 ppm, Figure 1a). 2-Naphthylammonium reveals a lesser degree of antiaromaticity relief upon deprotonation (ΔNICS(1)$_{zz}$ = –26.6 ppm, Figure 1b). 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 S_1 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 optimized geometries in the Supporting Information, SI).

In contrast, computed ring NICS(1)$_{zz}$ values for 2-naphthoic acid in the S_1 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 (ΔNICS(1)$_{zz}$ = +21.4 ppm, Figure 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. In the excited conjugate base, the exocyclic C–C bond lengthens to 1.534 Å (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 SI). In the ground state, deprotonation has less effect on the 10 π-electron aromatic character of the naphthalene ring, in 2-naphthol (ΔNICS(1)$_{zz}$ = +8.5 ppm), 2-naphthylammonium (ΔNICS(1)$_{zz}$ = +2.2 ppm), and 2-naphthoic acid (ΔNICS(1)$_{zz}$ = –1.2 ppm); positive/negative values indicate aromaticity loss/gain (see full data in the SI).

Naphthols with cyano (CN) substituents at the C5 and C8 positions are very strong photoacids: 8-cyano-2-naphthol (pK_a = 8.4, pK_a* = –0.8, ΔpK_a = –9.2) and 5,8-dicyano-2-naphthol (pK_a = 7.8, pK_a* = –4.5, ΔpK_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 (ΔNICS(1)$_{zz}$ = –137.2 ppm, Figure 2a) show significant excited-state antiaromaticity relief upon deprotonation, and the effect in 5,8-dicyano-2-naphthol (ΔNICS(1)$_{zz}$ = –167.3 ppm, Figure 2b) is even greater (cf. ΔNICS(1)$_{zz}$ = –86.1 ppm, for 2-naphthol). As suggested by the resonance forms in Figure 2, 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., sulfonyls, also have π-systems on the substituents capable of delocalizing negative charge of the excited conjugate base.

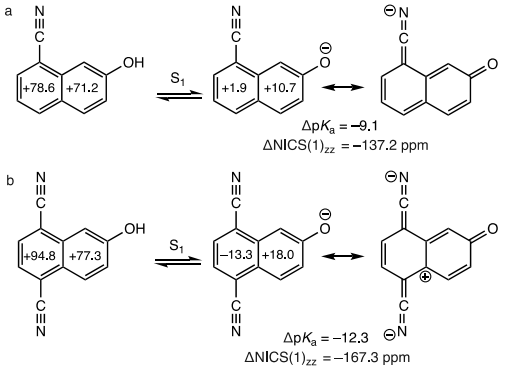


Figure 2. Computed NICS(1)$_{zz}$ and ΔNICS(1)$_{zz}$ (sum of NICS(1)$_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S_1 states of the acid and conjugate base at CASSCF(12,12)/6-311+G(d,p), for a) 8-cyano-2-naphthol and b) 5,8-dicyano-2-naphthol. Negative ΔNICS(1)$_{zz}$ values indicate antiaromaticity relief upon formation of the excited conjugate base. Experimental ΔpK_a values are included for reference. Note resonance form showing delocalization of the negative charge into the CN groups.

Computed deprotonation reaction energies (ΔE) based on the equation: ArOH + $H_2O \rightarrow ArO^- + H_3O^+$, document the energetic effects of (anti)aromaticity loss in the S_0 and S_1 states upon deprotonation, and agree with the conclusions based on NICS analyses. Compared to computed ΔE values in the S_0 state, deprotonation is *less* endothermic for the S_1 states of 2-naphthol ($\Delta\Delta E$ = –17.99 kcal/mol, $\Delta\Delta E = \Delta E(S_1) - \Delta E(S_0)$), 2-naphthylammonium (–2.77 kcal/mol), 8-cyano-2-naphthol (–28.85 kcal/mol), and 5,8-dicyano-2-naphthol (–29.28 kcal/mol), but *more* endothermic for the S_1 states of 2-naphthoic acid (+1.39 kcal/mol) (see full data in the SI).

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 (ΔNICS(1)$_{zz}$ = +0.1 ppm) (Figure 3, 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 (ΔNICS(1)$_{zz}$ = –44.4 ppm) (Figure 3, 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.

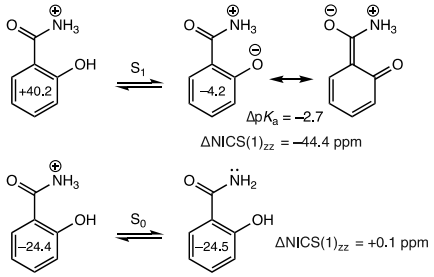
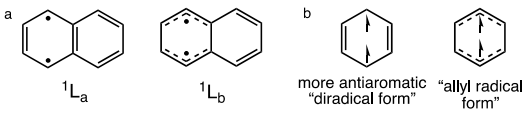


Figure 3. Computed NICS(1)$_{zz}$ and ΔNICS(1)$_{zz}$ (sum of NICS(1)$_{zz}$ values of the conjugate base minus that of the acid) (in ppm) values for the S_0 and S_1 states of protonated salicylamide an its conjugate base at CASSCF(12,12)/6-311+G(d,p). Negative ΔNICS(1)$_{zz}$ values indicate antiaromaticity relief upon formation of the excited conjugate base. Positive ΔNICS(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, ΔpK_a = –9.7) compared to its structurally similar 2-naphthol isomer (pK_a = 9.5, pK_a^* = 2.8, ΔpK_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_1^*) 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-napththol 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 the SI). 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") (Scheme 2). We note that Baird's original paper on the effects of triplet (anti)aromaticity also recognized a more antiaromatic "diradical form" for triplet benzene.[1]



Scheme 2. 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.

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.

Computational 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 S_0 and S_1 states[40] 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. $\Delta NICS(1)_{zz}$ values were calculated based on the sum of ring $NICS(1)_{zz}$ values of the conjugate base minus that of the acid.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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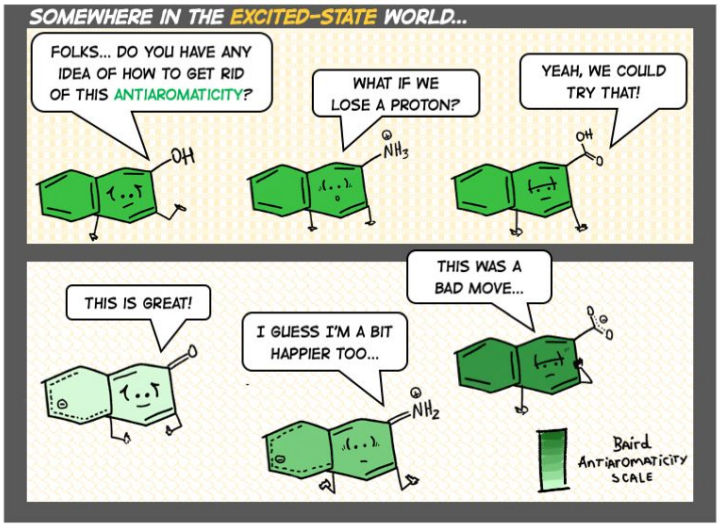
TOC Figure


SOMEWHERE IN THE EXCITED-STATE WORLD...
FOLKS... DO YOU HAVE ANY IDEA OF HOW TO GET RID OF THIS ANTIAROMATICITY?
WHAT IF WE LOSE A PROTON?
YEAH, WE COULD TRY THAT!
THIS IS GREAT!
I GUESS I'M A BIT HAPPIER TOO...
THIS WAS A BAD MOVE...
Baird Antiaromaticity Scale