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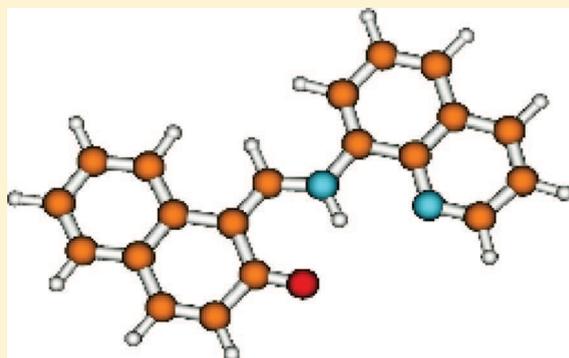
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Photochrome That Was Not: 2-Hydroxynaphthylidene-(8-aminoquinoline)

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ABSTRACT: We report the results of quantum-chemical calculations, which show that the keto form of 2-hydroxynaphthylidene-(8-aminoquinoline) (HNAQ) is slightly more stable than the enol form both in the ground and first excited $\pi\pi^*$ electronic states. The barrier for proton transfer between the enol and the ketone in the ground state is ca. 3300 cm^{-1} (HF), and 770 cm^{-1} (B3LYP), indicating a very fast (ps scale) exchange of protons between the two tautomeric forms. This barrier decreases slightly in the first excited $\pi\pi^*$ electronic state (2500 cm^{-1} - CIS), making proton exchange even faster. We show that the $\pi\pi^*$ state of the ketone tautomer is prone to radiationless transition to a state with nearly perpendicular orientation of the two ring systems, similarly to other Schiff bases that are photochromes (for instance salicydeneaniline). This state arises when an electron from the highest occupied molecular orbital (HOMO) of the ketone ring system is transferred to a LUMO localized on the CHNH group of the bridge connecting the two ring systems of the molecule. The energy minimum of this “perpendicular” state lies only ca. 0.09 eV from the ground state potential-energy surface, thus it is prone to extremely rapid radiationless decay. Further relaxation on this surface leads to a metastable conformation that lies ca. 4440 cm^{-1} above the planar, hydrogen-bonded, ketone conformation. Unfortunately, photochromism of this metastable conformation does not occur, since its absorption spectrum overlaps the spectrum of the stable species (with the predicted absorption around 438 nm vs calculated 440.6 nm in the stable ketone).



INTRODUCTION

Schiff bases that undergo internal proton transfer exist in at least two tautomeric forms, namely, enol and ketone. It occurs between the enol group attached to the aromatic system and a nearby nitrogen or oxygen atom with a lone pair of electrons. Usually the enol form is more stable in the ground state. Optical excitation into an $\pi\pi^*$ excited state produces enol prone to proton transfer to a more stable keto tautomer in which the proton is bound by a previously free lone pair of nitrogen or oxygen atoms. Many of such Schiff bases show photochromic properties, creating, following excited state intramolecular proton transfer (ESIPT), a metastable species which absorbs light usually well to the red of the absorption of the enol form.^{1–4} The model for photochromic Schiff base undergoing ESIPT is salicylidene aniline (SA). We have shown some years ago,⁵ that creation of a photochrome in this molecule follows very fast ESIPT in the doorway-state of enol and subsequent very fast internal conversion of the initial $\pi\pi^*$ state of created ketone to a “twisted” $n\pi^*$ state conformation. This twisted $n\pi^*$ state decays rapidly into a highly vibrationally excited ground state of trans-keto form. It is this trans-ketone with broken intramolecular hydrogen bond that is identified as a photochrome. A similar mechanism applies to salicydene methylamine⁶ and *N*-salicylidene- α -benzylamine.⁷ This mechanism was recently confirmed

by time-dependent density functional theory (TD/DFT), CASSCF, and CASPT2 calculations by Ortiz-Sánchez et al.⁸ We have demonstrated that whether a given Schiff base becomes a photochrome after ESIPT depends of the relative energies of the initially created $\pi\pi^*$ state and the twisted $n\pi^*$ transient. If the energy of the latter is well above that of the $\pi\pi^*$ state, then no photochrome is created, as is the case of 3,6-bis(benzoxazolyl)pyrocatechol.⁹

The stability of the enol form that is found in Schiff bases that are derivatives of salicylaldehyde, is much less pronounced in those bases that are derivatives of 2-hydroxynaphthaldehyde.^{10,11} A more extended delocalization of the π -electron system on the naphthalene ring tends to favor the keto tautomer. In particular, 2-hydroxynaphthylidene-(8-aminoquinoline) (HNAQ) (Scheme 1) shows unusual stability of the keto form, such that no enol form was detected by ¹⁵N-NMR study of HNAQ in solid phase.¹² Temperature dependence of the chemical shift of the C₂ resonance signals and of the values of the $J_{\text{NH,H}}$ coupling constants in CDCl₃ solvent, indicate thermal equilibrium between the enol and keto tautomers

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with the mole fraction of enol at room temperature estimated to be about 0.1.^{13,14} The crystal structure of HNAQ determined by X-ray crystallography shows that HNAQ molecules embedded in a crystal exist in the keto form in a very large range of temperatures (100–400 K).¹⁵ The absorption, emission, and transient absorption spectra of HNAQ were studied by Grabowska and co-workers.^{16,17} It was shown that the $S_1 \pi\pi^*$ state is very short-lived (ca. 4 ps) and the fluorescence excitation spectrum differs drastically from the absorption spectrum, which indicates that HNAQ molecules exist in the ground state as a mixture of two conformers of very similar spectral properties. Also, conflicting reports on fluorescence quantum yield exist in the literature varying dramatically from near unity¹⁶ to 3 orders of magnitude less.¹⁸

In this paper we report quantum-chemical calculations of the ground and excited states of HNAQ to deduce the structures and spectra of HNAQ in its ground and excited states. We show that the keto and enol forms in an isolated molecule are separated, in

the ground state, only by ca. 1.24 kcal/mol (B3LYP/cc-pVDZ) with the keto form being the more stable one. Similar relation of stabilities is calculated for the $S_1 \pi\pi^*$ state, namely, the keto form is more stable by 2.02 kcal/mol (CIS/cc-pVDZ) or 6.69 kcal/mol (TD/B3LYP/cc-pVDZ). Thus, like in most Schiff bases with intramolecular proton transfer, the relative stability of the keto form increases upon electronic excitation. In addition to the quasi-planar ketone S_1 minimum, we find the presence of a strongly nonplanar keto-conformer, in which the intramolecular hydrogen bond is broken. This conformer is more stable in S_1 than the planar ketone by 3.52 kcal/mol (CIS) or by 8.81 kcal/mol (TD/B3LYP). It decays via internal conversion process to nonplanar ground-state conformer, which lies ca. 11.92 kcal/mol (HF), 13.62 kcal/mol (B3LYP) above the stable planar conformation. This metastable conformer only slowly decays to the planar ketone and could form a photochrome, if only its absorption spectrum did not closely overlap the absorption spectrum of the stable molecule. From this point of view, it is a failed photochrome. On the other hand, HNAQ has two (meta) stable conformers in its ground state with overlapping absorption spectra, just as it was suggested in ref 16.

METHODS

To calculate structures and spectra of HNAQ in its ground and excited states, we use the Gaussian¹⁹ and Turbomole²⁰ programs using HF, CIS, CC2, B3LYP, and TD/B3LYP methods with the cc-pVDZ basis set.²¹ The ground and excited-state structures were optimized, and the corresponding force fields were calculated, with the HF, B3LYP, and CIS methods. The transition state geometries and frequencies for the intramolecular proton transfer process in the S_0 and $S_1 (\pi\pi^*)$ state were also calculated

Scheme 1

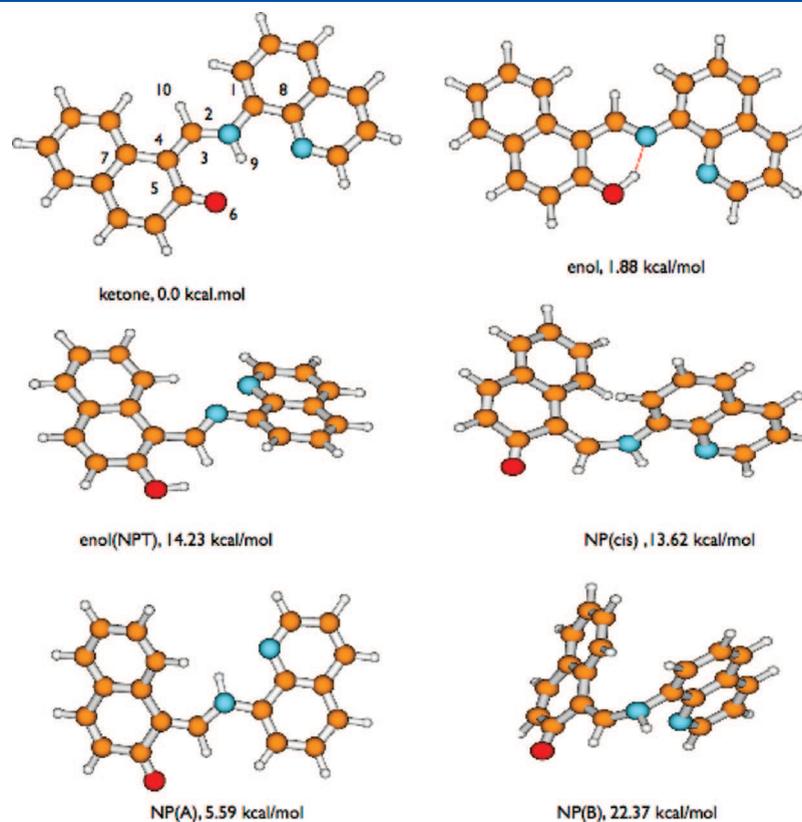
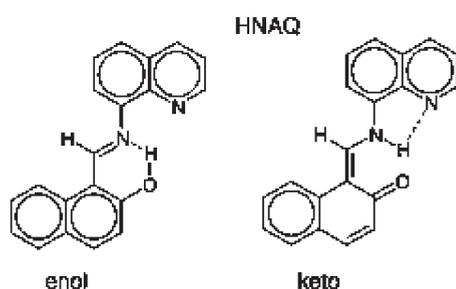


Figure 1. Structures of the ground state of HNAQ in its enol and keto tautomers. The energies relative to the most stable keto conformer are listed in kcal/mol from DFT calculations. The number of the atoms are given in the most stable keto form (top left).

Table 1. Total Energies (in a.u.) of the Optimized Structures of HNAQ in the S_0 State with the cc-pVDZ Basis Set^a

structure	HF	CC2	B3LYP	ΔE (HF)	ΔE (CC2)	ΔE (B3LYP)
ketone	−949.3721184	−952.5440436	−955.3708778	0.00	0.00	0.00
		−952.5606970 ^b			0.00	
enol	−949.3717552	−952.5453904	−955.3689073	0.23	−1.47	1.24
		−952.5621655 ^b			−0.92	
enol (pl)	−949.3689262	−952.5433430	−955.3678984	2.01	0.44	1.88
		−952.5601805 ^b			0.33	
TS	−949.3549487	−952.5437194	−955.3645642	10.82	0.20	3.98
TS (pl)	−949.3537989	−952.5432313	−955.3643858	11.55	0.51	4.09
enol (pl)	−949.3554479	−952.5269067	−955.3482941	10.51	10.80	14.23
					11.47	
NP (cis)	−949.3532116	−952.5289040	−955.3492593	11.92	9.54	13.62
		−952.5471422 ^b			8.54	
NP (A)	−949.3669404	−952.5371434	−955.3620058	3.26	4.35	5.59
		−952.5525324 ^b			5.15	
NP (B)	−949.3439189	−952.5167325	−955.3353858	17.77	17.21	22.37
		−952.5409069 ^b			12.47	

^aThe relative energies (ΔE) with respect to the keto tautomer are in kcal/mol. CC2 energies are also provided for HF geometries. ^bAt CC2 optimized geometry.

with the same methods. In addition, TD/B3LYP energies of the excited states were obtained at the calculated B3LYP and CIS geometries, for the ground and excited states, respectively. The transient absorption electronic spectra for the two excited-state minima of the ketone were obtained with the TD method.

THE GROUND STATE

The structure of HNAQ is depicted in Figure 1, which also gives the numbering of the atoms. The calculated HF and B3LYP energies of enol, ketone, and transition state energies are collected in Table 1. Here TS refers to the transition state between the ketone and enol form. At this point, the molecule possesses one imaginary frequency depicting proton movement, H_9 , from N_2 to O_6 . The calculated imaginary frequency is $1774 i \text{ cm}^{-1}$ (HF), or $1179 i \text{ cm}^{-1}$ (B3LYP). As usually is the case, the HF method gives a larger barrier and, consequently, a larger imaginary frequency than the DFT method (see ref 22). Taking the DFT value for energy difference between the two tautomers (1.24 kcal/mol), we predict that at room temperature in solution there should be about 11% of the enol tautomer, which is in good agreement with what has been concluded from NMR studies.^{13,14} Also the interconversion between the two tautomers should be very fast. Judging by the DFT value of the barrier, it should be on a picosecond scale; CC2 energies at the optimized HF geometries are also provided. It is interesting that the CC2 method, contrary to HF and DFT methods, places the enol below the ketone tautomer; CC2 optimization does not change this ordering, although it decreases the amount of stabilization of the enol.

While the keto tautomer is predicted by HF, B3LYP, and CC2 calculations to be planar, the enol tautomer, when restricted to planarity, possesses an imaginary frequency of $99 i \text{ cm}^{-1}$ (HF) or $30 i \text{ cm}^{-1}$ (B3LYP) for an out-of-plane vibration that tilts the two rings and leads to a markedly nonplanar geometry. As a result of this relaxation, the energy of the enol form decreases by 1.78 kcal/mol (HF), 0.52 kcal/mol (B3LYP), and 1.25 kcal/mol (CC2). The dihedral angles $C_7C_4C_1C_8$ are 45.4, 32.7, and 40.1° for the HF, B3LYP, and CC2 methods, respectively. A similar situation occurs for the proton-transfer transition state, which is also nonplanar;

Table 2. TD/B3LYP and CC2 Vertical Excitation Energies (eV) and Oscillator Strengths of the Transitions at the Ground State Optimized B3LYP and HF Geometries, Respectively

tautomer	state	TD/B3LYP	osc. strength	CC2	osc. strength
ketone	S_1	2.8142	0.4754	3.2505	0.7209
	S_2	3.1276	0.0000	4.1800	0.0346
	S_3	3.3919	0.0996	4.3216	0.0483
enol	S_1	3.0504	0.4663	3.8646	0.4133
	S_2	3.5707	0.0885	4.2742	0.1087
	S_3	3.7217	0.0229	4.5005	0.1285
enol (NPT)	S_1	3.2374	0.4183	4.1230	0.3460
	S_2	3.4464	0.0002	4.2162	0.0322
	S_3	3.8185	0.0091	4.5538	0.1703
NP(cis)	S_1	2.8302	0.3273	3.3041	0.3551
	S_2	2.9641	0.0025	3.4067	0.1019
	S_3	3.2959	0.0345	4.1325	0.0197
NP(A)	S_1	2.7787	0.3697	3.3156	0.5787
	S_2	3.0158	0.0136	3.4620	0.0813
	S_3	3.2575	0.0981	4.0606	0.0152
NP(B)	S_1	2.6288	0.0866	3.4665	0.0544
	S_2	3.0307	0.0013	3.6377	0.1739
	S_3	3.2823	0.1304	3.9136	0.0309

$C_7C_4C_1C_8$ angles are 40.8 and 24.3° for the HF and B3LYP methods, respectively. In crystalline conditions, the twist of rings becomes restricted, thus destabilizing the enol tautomer. This puts the ketone below the enol even for the CC2 method.

There also exists a high-energy enol form with strongly rotated aromatic rings denoted as “enol (NPT)” (the $C_7C_4C_1C_8$ angle is ca. 42°). In this conformer, the internal hydrogen bond does not exist, as the 180° rotation along the C_3C_2 bond must occur in the lowest energy enol conformer to lead to this NPT configuration.

NP(cis) denotes the energy of another ground state keto-structure, which we identify with one form of a photochrome that

was not. It is a metastable conformer, depicted in Figure 1, whose absorption spectrum overlaps with that of the stable planar keto-conformer. In this nonplanar “photochrome”, the $C_7C_4C_1C_8$ dihedral angle between the ring systems is 68.8° . At the same time, the OH and NH bonds are in a *cis* conformation ($H_9N_2C_3H_{10} = 19.2^\circ$). All dihedral angles given here and below result from B3LYP calculations. We see that a large rotation around the C_3C_4 and N_2C_1 bonds are needed to transform it into the planar stable ketone with an internal hydrogen bond.

NP(A) ketone structure is one that is obtained when the central bridge is rotated by 180° , so the OH and NH bonds are in a *trans* conformation ($H_9N_2C_3H_{10} = 164.9^\circ$), and the internal

hydrogen bond is broken. It is nearly the planar structure with $C_7C_4C_1C_8 = 160.2^\circ$. Its absorption spectrum also overlaps with the spectrum of the stable keto tautomer, and thus NP(A) can be considered as another form of a failed photochrome. In the next section, we will see that both NP(*cis*) and NP(A) conformations are easily reachable from the excited electronic state of the keto tautomer.

The highest energy ground state metastable keto-conformer NP(B), with $C_7C_4C_1C_8 = 98.7^\circ$ and $H_9N_2C_3H_{10} = 2.3^\circ$, possesses the bridge bent in a way that the two rings lie almost on top of one another (Figure 1).

EXCITED STATES

Table 2 lists TD/B3LYP/cc-pVDZ vertical electronic excitation energies at the B3LYP S_0 geometries. It also lists the CC2/cc-pVDZ excitation energies of electronic states at HF/cc-pVDZ ground state geometries. We see that the vertical excitation energy of the S_1 state is very similar in the three forms of ketone: the stable one, NP(*cis*), and NP(A). In each case, it is an intense transition to the $\pi\pi^*$ state of highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO \rightarrow LUMO) character. While the S_2 state in the enol tautomer is also of the $\pi\pi^*$ nature, the S_2 states in the three-keto tautomers are of the dominant $n_0\pi^*$ character. The calculated (TD) vertical electronic excitation energy to the S_1 state of 440.6 nm (2.814 eV) is only ca. 0.1 eV above the observed energy of the fluorescence excitation band (or the longest-wavelength absorption band) at about 458 nm¹⁶ (Figure 2). There may be eventual contribution to the structure of this band from the minor enol tautomer ca. 0.2 eV above the 0–0 transition, partially overlapping with the 0–1 transition of the ketone. This may explain in part the difference in the heights of the two peaks in the absorption and fluorescence excitation spectra¹⁶ (Figure 2).

Geometries of the S_1 state of the eight tautomers (conformers) were optimized using the CIS method. Subsequently, TD/B3LYP and CC2 energies were calculated for the optimized geometries. The results are summarized in Table 3 and in Figure 3. The calculated (TD) vertical emission energy in ketone of ca. 468 nm (2.648 eV) is ca. 0.2 eV higher than the observed one at ca. 510 nm.¹⁶ It is seen that the S_1 energy of the NP(*cis*) and NP(*trans*) ketone conformers are consistently the lowest in all three calculations. According to the TD results in Table 3, NP(*cis*) lies 0.46 eV (10.7 kcal/mol) below the ketone $\pi\pi^*$ state and only 0.09 eV above the ground state potential surface at this geometry. NP(*trans*) lies 0.69 eV (16.0 kcal/mol) below the $\pi\pi^*$ state and

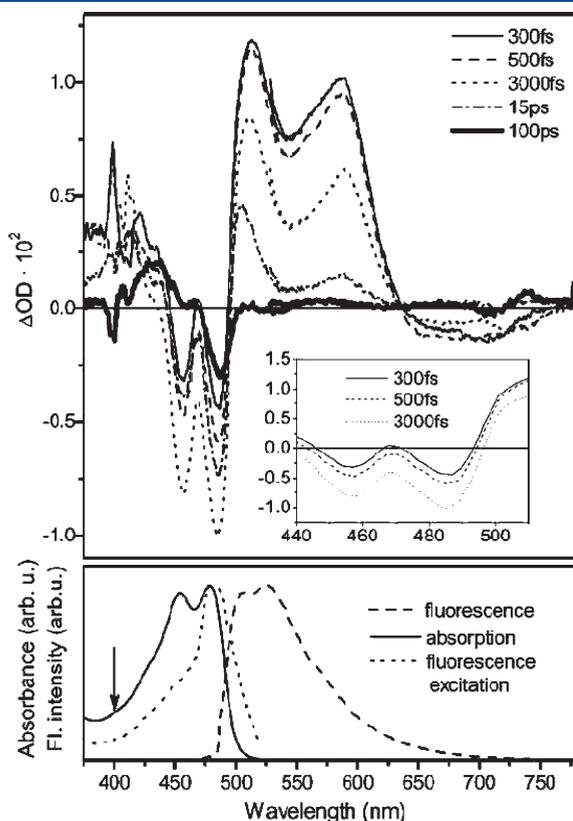


Figure 2. Transient absorption spectra (top), steady-state absorption, fluorescence, and fluorescence excitation spectra (bottom) of HNAQ in tetrahydrofuran at room temperature. Reprinted with permission from ref 16.

Table 3. The Energies of the S_1 State (a.u. +900.0) and Vertical Deexcitation Energies (eV, in Brackets) of the HNAQ State at Optimized CIS/cc-pVDZ Geometries^a

tautomer	CIS	TD/B3LYP	CC2
ketone	-49.227962 (3.663) [0.0]	-55.264384 (2.648) [0.0]	-52.439941 (2.861) [0.0]
enol	-49.224760 (3.494) [2.0]	-55.256451 (2.723) [5.0]	-52.432432 (3.016) [4.7]
TS	-49.213337 (3.568) [9.2]	-55.257811 (2.690) [4.1]	-52.440665 (2.812) [-0.5]
NP(<i>cis</i>)	-49.233463 (1.589) [-3.5]	-55.281397 (0.087) [-10.7]	-52.456939 (0.391) [-10.7]
NP(<i>trans</i>)	-49.238789 (1.410) [-6.8]	-55.289699 (-0.169) [-16.0]	-52.457660 (0.230) [-11.2]
NP(A)	-49.222926 (3.487) [3.2]	-55.256499 (2.481) [5.0]	-52.432894 (2.703) [4.4]
NP(B)	-49.217825(0.933) [6.4]	-55.256412 (-0.215) [5.0]	-52.442356 (-0.074) [-1.5]
enol(NP)	-49.230738 (1.867) [-1.8]	-55.273632 (0.781) [-5.8]	-52.452953 (1.004) [-8.2]
enol(NPT)	-49.223123 (1.670) [3.0]	-55.264301 (0.666) [0.1]	-52.442910 (0.957) [-1.9]

^aThe numbers in the square brackets are relative energies in kcal/mol.

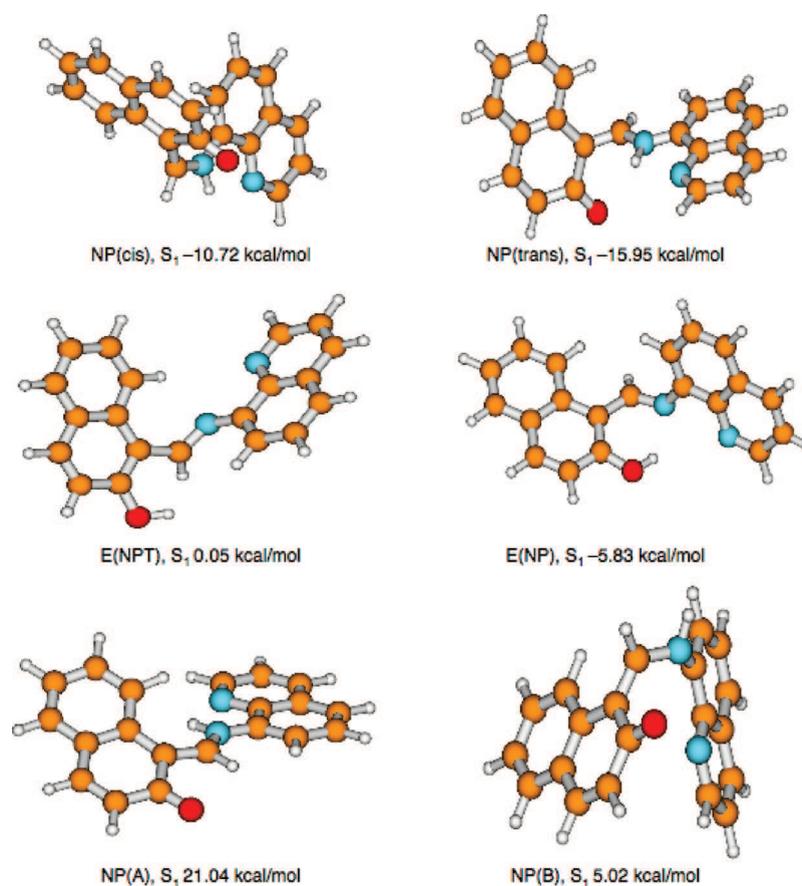


Figure 3. TD/B3LYP optimized structures of nonplanar excited states of HNAQ. The energies are relative to the most stable keto conformer.

Table 4. Computed TD Transient Absorption Spectra of the $S_1 \pi\pi^*$ Planar Ketone State (The First Line in Table 3)

transition	energy	oscillator strength
$S_1 \rightarrow S_3$	0.653 eV / 1900 nm	$f = 0.3562$
$S_1 \rightarrow S_4$	0.745 eV / 1664 nm	$f = 0.0609$
$S_1 \rightarrow S_6$	1.192 eV / 1040 nm	$f = 0.2079$
$S_1 \rightarrow S_{10}$	1.674 eV / 741 nm	$f = 0.0442$
$S_1 \rightarrow S_{13}$	2.146 eV / 578 nm	$f = 0.0643$
$S_1 \rightarrow S_{14}$	2.237 eV / 554 nm	$f = 0.1527$
$S_1 \rightarrow S_{20}$	2.584 eV / 480 nm	$f = 0.1426$
$S_1 \rightarrow S_{22}$	2.641 eV / 469 nm	$f = 0.0825$

0.17 eV below the ground state potential energy surface at the same geometry. Thus, the S_1 states of the NP(cis) and NP(trans) conformers undergo superfast radiationless decay to the ground state. NP(cis) then relaxes to NP(cis) photochromic configuration, while NP(trans) relaxes to the NP(A) configuration. In both these conformers, the intramolecular hydrogen bond is absent. Thus after the ketone $\pi\pi^*$ state decays quickly to the lower energy NP(cis) and NP(trans) conformers, they, in turn, decay even faster to the ground state owing to the very small energy gap. These two facts are the foundation for a photochrome formation. What fails in HNAQ is that both NP(cis) and NP(A) have almost the same location of the $S_0 \rightarrow S_1$ excitation as the stable ketone species. Nevertheless, the absorption spectrum, after initial excitation, should consist of two or three closely overlapping spectra

originating from two or three different ketone conformers: the stable one, NP(A), and NP(cis).

The observed difference between the absorption and fluorescence excitation spectra¹⁶ can be explained by the fact that a small excess of vibrational energy is enough to dramatically increase S_1 (ketone) $\rightarrow S_1$ (NP(cis), NP(trans)) internal conversion and wipe out most of the fluorescence. Studies of transient absorption spectra¹⁶ show two prominent absorption bands originating from the $S_1 \pi\pi^*$ state of ketone (Figure 2). They have comparable intensities and are centered at ca. 520 and 580 nm. Our calculations also locate two bands (each consisting of two closely lying electronic transitions) localized at 476 and 555 nm with the combined oscillator strengths of 0.225 and 0.217, respectively (Table 4). The temporal behavior of the transient absorption establishes the short lifetime of the initially excited $\pi\pi^*$ state (4.25 ps).¹⁶ We believe that this fast decay of the initial state proceeds via NP(trans) and NP(cis) conformers of the S_1 state. We assign the 476 (520) nm peak in the transient absorption spectrum to the $S_1 \rightarrow S_{20}$ ($f = 0.1426$, 2.584 eV) and $S_1 \rightarrow S_{22}$ ($f = 0.0825$, 2.641 eV) pair of electronic transitions, while the 555 (580) nm peak we assign to the $S_1 \rightarrow S_{13}$ ($f = 0.1527$, 2.237 eV) and $S_1 \rightarrow S_{14}$ ($f = 0.1527$, 2.237 eV) pair of electronic transitions.

As in the NP(trans) conformer, the S_1 state energy of the NP(A) conformer is higher than that of ketone by about 0.2 eV. This rules out any significant role of the NP(trans) conformer plays in the excited state dynamics of HNAQ, originating from a ketone cis-tautomer with intramolecular hydrogen bond. The same can be said about the NP(B) conformer whose S_1 energy is

also ca. 0.2 eV above that of ketone. Similarly, the TD (CIS) energy of enol is 0.216 eV (0.085 eV) above ketone, making the ketone an even more favored tautomer in the excited state than in the ground state.

The calculated CIS barrier for internal proton transfer from ketone to enol is 9.2 kcal/mol, and the imaginary frequency of the proton movement at the top of the barrier is 1713 cm^{-1} . These values are similar to those obtained for the ground state, which indicates that the TD barrier in the S_1 state should be around 4 kcal/mol, and therefore very small or nearly nonexistent on the enol side. Thus, the proton transfer from enol to ketone must be faster than 100 fs, and, consequently, the S_1 state of the enol would rather rapidly transform into the photochromic species of the ketone tautomer, than to the nonplanar conformer, E(NP), of enol.

In conclusion, our calculations indicate that the enol conformer of HNAQ is slightly less stable than ketone in the ground state. The energy of the two tautomers is closer in the crystalline state where the planarity of the enol structure is imposed. The DFT energy difference very well reproduces the conclusions drawn from NMR studies. Electronic excitation additionally stabilizes the keto tautomer. It decays within 4 ps to two nonplanar excited-state conformers of similar energies. These excited states undergo superfast radiationless decay to the photochromic species in their ground electronic state. The two transient absorption spectra, observed in experiment, are interpreted as two close pairs of electronic transitions from the excited electronic state of initially excited ketone tautomer. As the photochroms have almost the same absorption spectrum as the normal form of ketone, photochromism is not observed in NHAQ, consistent with the experiment.

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