

FINAL TECHNICAL REPORT

Introduction

Understanding energy and charge transfers in electronically excited molecules are of fundamental importance to photochemistry and photobiology. Traditionally, the excited-state dynamics of organic molecules are described in terms of $\pi\pi^*$ and $n\pi^*$ states that are thought to be the only low-lying electronic states of pertinence. Our recent work on fluorinated benzenes,¹ coumarins,² nucleobases,³⁻⁸ and substituted benzonitriles⁹⁻¹¹ and benzethynes,¹²⁻¹⁵ however, indicates that in a number of molecular systems a biradical state (including $\pi\sigma^*$ state) lies near or below the conventional excited state. Because of the greatly different equilibrium geometry of a biradical state relative to $\pi\pi^*$ (and $n\pi^*$) states, the potential energy profile of the biradical state commonly crosses that of the initially prepared excited state (of $\pi\pi^*$ or $n\pi^*$ character) as well as the ground state, leading to an ultrafast radiationless decay (including CT) of the photoexcited molecules. During the past three years, our major research efforts have been directed toward the understanding of the origin of the ultrafast internal conversion in photoexcited nucleic acid bases, and photoinduced intramolecular charge transfer (ICT) in dialkylaminobenzonitriles and related electron donor-acceptor (EDA) molecules, which have been topics of great interest during the past four decades. For this purpose, we have adopted a three-pronged approach that involves synthesis of tailor-made molecules, quantum chemistry calculations, and time-resolved electronic spectroscopy. The results of this study reveal evidence for the active involvement of a biradical state in the internal conversion of nucleobases and in the ICT of dialkylaminobenzonitriles.

I. DNA/RNA Bases

Because of their biological importance, the DNA/RNA bases have been the subjects of many spectroscopic and photophysical studies over the past four decades.¹⁶ The most striking photophysical property of the natural nucleobases is the ultrafast (sub-picosecond) internal conversion that rapidly returns the photoexcited molecule to the ground state before chemical reaction in the excited state can cause significant UV photodamage. Equally intriguing is the effect of simple chemical modifications on internal conversion. In cytosine, for example, the ~ 720 fs excited-state lifetime of the unmodified base in water increases to ~ 88 ps by replacement of the C5 hydrogen by fluorine,¹⁷ and to ~ 280 ps by acetylation of the amino group attached to the C4 carbon atom¹⁷ (see Scheme 1 for structures). In adenine (6-aminopurine), the excited-state lifetime in water is about one ps, whereas 2-aminopurine has a nanosecond lifetime.¹⁸ Clearly, these are important observations that a successful model must be able to account for.

Another remarkable photophysical property of DNA/RNA bases is the dramatic temperature and excitation energy dependence of their excited-state lifetimes. The subpicosecond excited-state lifetimes of most bases in solution at room temperature increase to nanoseconds in glassy matrices at or below 77 K.¹⁹ In the gas phase under supersonic free expansion, the fluorescence lifetimes of adenine and guanine, which are in the range of nanoseconds for excitation into the very low-lying vibronic levels of the lowest-energy $\pi\pi^*$ state, decreases to subpicoseconds for excitation into the higher-lying vibronic levels.^{20,21} This leads to an abrupt break-off of fluorescence, which in adenine occurs about 200 cm^{-1} above the electronic origin of the $^1\pi\pi^*$ state, Fig. 1. Both the anomalously strong temperature dependence of fluorescence in solution and the fluorescence break-off in supersonic free jet could be rationalized if a dark electronic state crosses the $\pi\pi^*$ state at energies slightly above the electronic origin of the $\pi\pi^*$ state. To probe the possible existence of a dark state, we have carried out CIS and CR-EOM-CCSD(T) calculations of the potential energy profiles of cytosine, uracil, and their derivatives at optimized CIS geometries.³ The results indicate that the $S_1 \rightarrow S_0$ internal conversion occurs through a barrierless state switch from the initially excited $^1\pi\pi^*$ to a biradical state, which intersects the ground state at lower

energy, Fig. 2 (left). In the biradical state, the C5 and C6 hydrogen atoms are almost perpendicular to the average ring plane and are displaced in opposite directions (see inset of Fig. 2). As a result, the p_z orbitals of the C5 and C6 carbon atoms are decoupled from the π -electron system and are singly occupied, giving the state a biradical character. Replacement of the C5 hydrogen of cytosine by fluorine stabilizes the $\pi\pi^*$ state and introduces an energy barrier for the $\pi\pi^* \rightarrow$ biradical state switch,⁴ whereas replacement of the C6 hydrogen by fluorine does not,⁴ Fig. 3. The excited-state lifetimes of the two-fluorinated cytosines are therefore expected to be vastly different. These predictions are borne out by experiment (~ 88 ps for 5-fluorocytosine and < 1 ps for 6-fluorocytosine⁴). Replacement of one of the amino hydrogen atoms by an acetyl group (to yield *N*⁴-acetylcytosine)³ increases the energy barrier for the $^1\pi\pi^* \rightarrow$ biradical state switch even more (through the formation of an intramolecular C–H:O hydrogen bond), consistent with the greatly increased lifetime (~ 240 ps) of the molecule.¹⁷ Extension of these computational methodologies to uracil and thymine shows that the same biradical-mediated internal conversion applies to all of the pyrimidine bases. Interestingly, the calculations predict that the barrier height for the $\pi\pi^* \rightarrow$ biradical state switch is significantly smaller in uracil than in cytosine, Figs. 4 and 5, in accordance with the much shorter excited-state lifetime of the former (~ 100 fs)²² relative to the latter (~ 700 fs).²² A similar, dramatic, lifetime difference also exists between 5-fluorouracil (~ 0.7 ps)²² and 5-fluorocytosine (~ 90 ps).¹⁷

More recently, we have performed CC2, EOM-CCSD and CR-EOM-CCSD(T) calculations of the potential energy profiles of the purine bases, adenine,⁵ and guanine,⁵ at optimized CIS geometries using the cc-pVDZ basis set. The results of this study indicate that the internal conversion of purine bases is also mediated by a biradical state, which crosses both the $\pi\pi^*$ and the ground states, Fig. 2. The electronic structure of the biradical state of the purine bases is dominated by an electronic configuration in which one unpaired electron occupies a π^* orbital localized on the five-membered ring and the other occupies an orbital localized very strongly on a p -type C2 atomic orbital of the six-membered ring.⁵ The biradical state, arising from the twist of the N3-C2 bond (Scheme 1), has a strongly puckered six-membered ring and the C2-H bond of adenine, or the C2-N bond of guanine, which is nearly perpendicular to the average ring plane,⁵ Fig. 2. Consistent with the biradical-mediated radiationless

decay, the measured $\pi\pi^*$ -state lifetime in supersonic jet is extremely short (sub-picoseconds) in adenine and 9-methyladenine²³ for which the calculation⁵ places the biradical state below the initially excited $\pi\pi^*$ state, slightly longer in *N,N*-dimethyladenine (~ 3 ps),²³ which is predicted to have a small energy barrier for the $\pi\pi^* \rightarrow$ biradical state switch,⁵ and very long (nanoseconds)^{21,23} in 2-aminopurine, which has the biradical state substantially above the $\pi\pi^*$ state.⁵

Interestingly, for both the pyrimidines²⁴⁻²⁷ and purines,²⁸⁻³¹ the biradical structures obtained from the geometry optimization with the simple CIS method³⁻⁵ are similar to the geometries at the $\pi\pi^*/S_0$ conical intersections (CI) located by using high-level multi-reference *ab initio* methods. This similarity suggests that the out-of-plane deformation leading to the $\pi\pi^*/S_0$ CI is closely related to the reaction pathway for isomerization of the planar $\pi\pi^*$ -state geometry into the biradical geometry. Independent of the question of whether the CI with the ground state is accessed directly from the initially excited state or through an intermediate biradical state, it is expected that covalent modification of nucleobase leading to hindrance of the C5-C6 twist in the pyrimidines and N3-C2 twist in the purines would lead to a dramatic retardation of the internal conversion rate. The predicted, critical role of the out-of-plane deformations could be tested experimentally by making use of tailor-made derivatives of nucleobases in which the nonpolar deformation cannot easily occur for steric reasons. To this end, we have recently synthesized and characterized the photophysical properties of trimethylenecytosine (TMC),⁷ trimethyleneturacil (TMU),⁷ and propanodeoxyguanosine (PdG).⁸ The results of fluorescence decay measurements, based on the picosecond time-correlated single-photon counting (TCSPC), demonstrate that the fluorescence lifetime is about 1.2 ns for TMC, Fig. 4 about 29 ps for TMU, Fig. 5 and about 12 ns for the slow-decaying component (assigned to a planar conformer⁸) of PdG in aqueous solution of pH7 at room temperature, Fig. 6. Consistent with these observations, CC calculations indicate that the $^1\pi\pi^*$ state of TMC, TMU, and the planar conformer of PdG all have $^1\pi\pi^*$ states that are very stable against the out-of-plane deformation (leading to biradical geometries), Figs. 4–6. The computed energetics also suggest that the dramatically shorter fluorescence lifetime of TMU relative to TMC can be attributed to the presence in TMU of an

efficient, secondary nonradiative decay channel of the $\pi\pi^*$ state involving a close-lying $n\pi^*$ state (as opposed to the TMC in which the $\pi\pi^*$ state is significantly below the $n\pi^*$ state).⁷

II. Dialkylaminobenzonitriles and Related EDA Molecules

Spectroscopy and photophysics of 4-(dimethylamino)benzonitrile (4-DMABN) and related electron donor–acceptor (EDA) molecules, scheme 3, have been subject of intense experimental and theoretical studies for over four decades.³² This interest stems from the discovery by Lippert and co-workers that, upon excitation in the near ultraviolet, 4-DMABN exhibits dual fluorescence in polar solvents,³³ Fig. 8. The shorter-wavelength fluorescence band with small Stokes shift was identified as emission for the S_1 (L_b or locally excited (LE)) state, whereas the longer-wavelength fluorescence was assigned to the emission from the L_a -like state of high polarity, commonly referred to as intramolecular charge transfer (ICT) state.³³ The lack of ICT fluorescence in the gas phase or in solvents of low polarities has been attributed to the higher energy of the ICT state relative to the L_b state. Consistent with the large dipole moment of the ICT state, the picosecond transient absorption spectra of 4-DMABN in polar solvent display 410 nm transient that closely mimic the absorption spectra of benzonitrile anion.^{14,34,35} The transient absorption spectra of 4-DMABN and *p*-dimethylamino-*p*'-cyano-diphenylacetylene (DACN-DPA) measured at 100 ps delay³⁴ are given in Fig. 9. Similar behavior has been reported for many related compounds.³²

Despite the long lists of experimental and theoretical studies of the ICT state,³² the nature of the geometrical distortion that leads to the ICT state is not properly understood. More specifically, the question of whether the ICT state of 4-DMABN has a twisted amino group (TICT for twisted), a planar amino group (PICT for planar), or other geometries remains unsettled. Experimental support for the TICT model, which is due to Grabowski *et al.*,^{36,37} comes from the observation that aminobenzonitriles with pre-twisted amino group (3,5-dimethyl-DMABN, for example) exhibit only the (anomalous) lower-energy fluorescence characteristic of the emission from the ICT state. On the other hand, the observation of dual fluorescence from “planarized aminobenzonitriles”, such as 1-tert-butyl-6-cyano-1,2,3,4-tetrahydroquinoline (NTC6), in which the torsion of the amino group is sterically hindered, provides support for the PICT model of Zachariasse *et al.*^{38,39} The $(CH_3)_2N$ -phenyl bond has a single-bond

character in the TICT model, whereas it has a double bond character in the PICT model due to the planarization of the amino group.

A majority of theoretical studies indicates the amino group twists as the reaction coordinate along which the LE \rightarrow ICT reaction occurs. For example, a recent correlated CC2 calculation of Köhn and Hättig⁴⁰ finds no indication of a PICT-like stationary point on the ICT potential energy hypersurface, and shows that the twisting of the dimethylamino group is the dominant reaction coordinate. Sobolewski *et al.*⁴¹ also conclude that stabilization of the L_a state along the TICT reaction path is responsible for the appearance of the ICT emission, based on energy profiles calculated with CIS, CASSCF, and CASPT2 methods. However, a more recent CASSCF calculation of Robb and co-workers⁴² indicates the PICT model cannot be excluded. Experimentally, picosecond infrared (IR) and Raman measurements have shown that the *N*-phenyl bond has a single-bond character in the ICT state of 4-DMABN, consistent with the TICT model.⁴³

Apart from the question of the ICT-state geometry, there is also the question of the nature of the excited electronic states that are actively involved in the ICT reaction. Based on the analyses of the biexponential LE and ICT fluorescence, it has been concluded that the ICT state of 4-DMABN is formed from the LE ($\pi\pi^*$) state.⁴⁴ The recent studies of Sobolewski and Domcke,^{45,46} and Zgierski and Lim,^{9,10} however, have shown that the excited state of $\pi\sigma^*$ configuration, which arises from the promotion of an electron from the aromatic π orbital to the σ^* orbital localized on the cyano group, can be low lying and it may play an important role in the photophysics of aminonitriles, including the ICT reaction. Thus, for 4-DMABN and 4-aminobenzonitrile (4-ABN), our TDDFT/cc-pVDZ and CIS/cc-pVDZ calculations have shown that the lowest-energy $\pi\sigma^*$ state (or RICT state^{45,46} for “rehybridized ICT”) of bent geometry, with CCN angle of about 120°, is of lower energy than the lowest-energy $\pi\pi^*$ state of L_b type, at the respective optimized geometries,⁹ Fig. 10. Because the vertical transition from the ground state of linear geometry to the bent $\pi\sigma^*$ state is Franck–Condon forbidden, direct excitation of the ground-state molecule to the $\pi\sigma^*$ state is not allowed, and the radiative transition from the $\pi\sigma^*$ state to the ground state is essentially dipole forbidden. Thus, the $\pi\sigma^*$ (RICT) state is a dark state that is formed and decays by radiationless

transitions.⁹ At the optimized ground-state geometry, the vertical excitation energy of the dark $\pi\sigma^*$ state of 4-DMABN or 4-ABN is greater than that of the $\pi\pi^*$ state, and the two states cross at CCN angle of ~ 150 degrees,⁹ Fig. 10. The energy barrier for the state crossing from the potential energy minimum of $\pi\pi^*$ state (L_b or L_a) to the dark $\pi\sigma^*$ state is less than ~ 0.2 eV.⁹ The predicted state switch from the bright $\pi\pi^*$ state to the dark $\pi\sigma^*$ state can account for the abrupt break-off (loss) of the LE fluorescence following higher-energy excitation of aminobenzonitriles in the gas phase,⁴⁷ Fig. 11, and the thermally activated $S_1(L_b) \rightarrow S_0$ internal conversion in alkane solvents,⁴⁸ where no ICT occurs. The observed threshold energy for fluorescence break-off, and the activation energy for internal conversion, are similar to the calculated energy barriers for the $\pi\pi^* \rightarrow \pi\sigma^*$ state switch.⁴⁷ We consider these observations strong evidence for the occurrence of the $\pi\pi^* \rightarrow \pi\sigma^*$ state switch from the higher vibronic levels of S_1 or S_2 .

In the spectral range of 400–800 nm, our calculation on 4-DMABN predicts only one intense excited-state absorption at about 700 nm, which is due to a $\pi\sigma^* \leftarrow \pi\sigma^*$ transition,¹⁰ Fig. 12. The excited-state absorptions from the $\pi\pi^*$ state (L_b or L_a) are much weaker, Table I. The calculations also indicate that the $\pi\sigma^*$ state can be identified by its anomalously low frequency (~ 1460 cm^{-1}) of the CN stretch, relative to the corresponding vibrational frequencies (~ 2200 cm^{-1}) in the $\pi\pi^*$ and ground states.¹⁰ The greatly reduced CN stretch frequency of the $\pi\sigma^*$ state is due to the decrease in CN bond order (from three to about two) that accompanies the $\pi \rightarrow \sigma^*$ excitation. Consistent with these predictions, 4-DMABN, 4-ABN, and 4-(diisopropylamino)benzonitrile (4-DIABN) all display picosecond transient absorption at ~ 700 nm in non-polar and polar solvents following the 267 nm, 305 nm, or 325 nm excitation of the L_a state.¹⁴ Moreover, in 4-DMABN, the Raman active 1467 cm^{-1} CN stretch exhibits a large resonance enhancement when the probe (Raman excitation) wavelength is set to 600 nm⁴⁹ (which is close to the $\pi\sigma^* \leftarrow \pi\sigma^*$ absorption¹⁰) and a decrease in intensity when the probe wavelength is set to 460 nm,⁴⁹ where the $\pi\pi^* \leftarrow \pi\pi^*$ absorption occurs, Fig. 13. These results further support the existence of a low-lying $\pi\sigma^*$ state and the occurrence of an ultrafast (< 1 ps) state switch from the initially excited $\pi\pi^*$ state (L_b or L_a) to the $\pi\sigma^*$ state¹⁰, Table II.

We have proposed^{9,10} that the highly polar $\pi\sigma^*$ state, which has the greatest dipole moments of all low-lying excited states of 4-DMABN¹⁰ is the intermediate state of the sequential ICT reaction that takes the initially excited $\pi\pi^*$ state to the fully charge-separated ICT state of the molecule in polar solvents, Scheme 4.^{9,10} Consistent with this proposal, we have found that 4 ps rise time of the ICT-state absorption at 410 nm is identical to the decay time of the $\pi\sigma^*$ -state picosecond transient at 700 nm for 4-DMABN in acetonitrile,¹¹ Fig. 14. This has very recently been confirmed by Drughinin *et al.*,³⁵ who however assign the 700 nm transient (4.1 ps) to the LE (L_b)-state absorption.

To probe the validity of the $\pi\sigma^*$ -mediated ICT mechanism, we have recently undertaken a systematic experimental and computational study of the excited-state absorption and dynamics of various dialkylaminobenzonitriles and 4-dimethylaminobenzethyne (4-DMABE) by time-resolved transient absorption and TDDFT potential-energy profile calculations.¹⁴ The results indicate that 2-DMABN and 3-DMABN, which do not exhibit ICT fluorescence in any solvent,⁵⁰ have $\pi\sigma^*$ state that lies high above the $\pi\pi^*$ (L_b and L_a) states.¹⁴ The $\pi\pi^* \rightarrow \pi\sigma^*$ state switch, required for the $\pi\sigma^*$ -mediated ICT, cannot therefore occur in 3-DMABN and 2-DMABN. On the other hand, 4-diisopropylaminobenzonitrile (4-DIABN)⁵¹ and 3,5-dimethyl-4-DMABN,⁵² which exhibit ICT emission even in non-polar solvent, have a $\pi\sigma^*$ state that lies below the lowest-energy $\pi\pi^*$ (L_b) state.¹⁴

In acetonitrile, the rate of ICT process, as measured by the decay time of the $\pi\sigma^*$ -state transient at 700 nm or by the rise time of the ICT-state absorption at 410 nm, is much faster for 4-DIABN than for 4-DMABN, Fig. 14. Interestingly, 4-DMABE with a low-lying $\pi\sigma^*$ state does not exhibit an ICT reaction,^{11,53} Fig. 15, in sharp contrast to the closely related 4-DMABN. The lack of the ICT reaction in 4-DMABE can be attributed to the highly endothermic $\pi\sigma^* \rightarrow$ ICT transition that prevents the formation of fully charge transferred ICT state from the intermediate $\pi\sigma^*$ state (*vide infra*). These results suggest that the necessary condition for the occurrence of the ICT reaction is the presence of a $\pi\sigma^*$ state that lies below the lowest-energy $\pi\pi^*$ state, but above the ICT state.¹¹

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