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Electronic Properties of 4-Substituted Naphthalimides

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This paper describes a study of excited-state properties of naphthalimide (NI) and four 4-substituted derivatives: 4-chloronaphthalimide (Cl-NI), 4-methylthionaphthalimide (MeS-NI), 4-nitronaphthalimide (O2N-NI), and 4-(N,N-dimethylaminonaphthalimide (Me2N-NI)). Steady-state absorption and fluorescence spectra were collected in solvents of varying polarity to determine the excited-state character of NI derivatives. Furthermore, the excited-state dynamics were studied using femtosecond transient absorption spectroscopy. The experimental findings were compared to calculated data obtained using time-dependent density functional (TD-DFT) methods. We found that light absorption by all NI derivatives leads to the production of the second excited state (S2), which was found to have a n.π* character. Within ~40 ps, the S2 state undergoes internal conversion to produce the S1 state. The S1 state is relatively long-lived (~4 ns) and has charge-transfer character in NI derivatives with electron-withdrawing and electron-donating groups (MeS-NI, O2N-NI, and Me2N-NI). In the case of NI and Cl-NI, the S1 state has a π.π* character and undergoes intersystem crossing to produce the T1 state within 400 ps.

Introduction

Naphthalimides (NIs) belong to a class of chromophores for which excited-state properties can be drastically changed by the nature of a substituent present on the aromatic ring.1–3 While the nonpolar π.π* state occurs in the parent NI (i.e., without any substituents at the 4-position), the introduction of electron-donating or -withdrawing substituents (amino or nitro groups) induces a polar charge-transfer (CT) excited state.3 The compounds with CT character are especially interesting due to their strong oxidizing or reducing capacity. The oxidative nature of NIs, coupled with their ability to intercalate DNA bases, has been used in DNA photocleavage reactions.1 The oxidative cleavage of DNA has been demonstrated to be site-specific, with the damage occurring at the 5′ site of the most electron-rich GG site.5 In addition, it was found that the cleavage location can be changed from the GG to the T site by simply using nitro derivatives of NI.6 The reason for the change in the reactivity was assigned to H-atom abstraction from the methyl group of thymine by the nitro group of NI. DNA cleavage has also been accomplished indirectly, by N-hydroperoxy derivatives of NI, which produce OH radicals that in turn damage DNA.5 The capability of NIs to induce light-triggered DNA damage has been used in photodynamic therapy to destroy HIV blood viruses.8 In addition to the reactivity toward nucleic acids, NIs have been found to induce photocross-linking of proteins,6 which has been applied in light-induced tissue repair.9

The CT characteristics of NI excited states have also found use in organic materials, such as donor–acceptor systems for solar cells,3 organic light-emitting diodes (oLEDs),9 and sensors for metal ions and protons.10–12 In oLEDs, the advantage of 4-substituted NIs is in their low reduction potential and wide energy gaps, along with the high fluorescence efficiency.

Emission from intramolecular CT states contributes greatly to the electroluminescence of these devices. In the design of materials for solar cells, NIs are commonly used either as electron donors or as acceptors in D–A chemical systems designed for long-lived charge separation.8 In sensor applications, the molecular system is generally constructed from NI with an alkyl-amin substituent. The amino group is involved in photoinduced electron transfer, which diminishes the fluorescence lifetime. However, if metal ions or protons are present in the solution, the fluorescence of the NI unit is restored, leading to a “turn-on” sensing.

Because of these light-triggered applications of NI derivatives, many groups have studied their excited-state behavior.13–15 All of the compounds studied thus far contain substituents at the imide nitrogen of the NI framework. We are interested in using NIs as parts of hydrogen-bonded donor–acceptor systems that are capable of producing long-lived charge separation due to a proton-coupled electron transfer process. For this purpose, NIs offer several great advantages: (i) They absorb strongly in the UV/vis region, (ii) the oxidation and reduction potential of NIs can be readily tuned by substitution, and (iii) the imide moiety of NIs is capable of making hydrogen bonds with the acceptor. For these reasons, we sought to investigate the excited-state properties of NIs that lack any substituents in the imide position.

In this paper, we present a detailed study of the electronic properties of NI and 4-substituted derivatives shown in Scheme 1. We varied the nature of the substituents from electron-donating (MeS-NI and Me2N-NI) to electron-withdrawing (6-nitrobenzo[de]isouquinoline-1,3-dione, O2N-NI). We present the solvent-dependent steady-state absorption and fluorescence data, femtosecond optical transient absorption data, and density functional theory (DFT) calculations of NI derivatives in their ground and excited states. In contrast to previous reports,16 we find that the excitation of NI derivatives creates an n.π* excited state. In the case of NI and 4-chloro-1,8-naphthalimide (Cl-NI), the n.π* state is also responsible for their fluorescence.

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On the other hand, Me2N-NI, MeS-NI, and O2N-NI seem to have different states involved in the absorption and emission spectra. In these derivatives, the initial absorption creates an n,π* excited state, which within 40 ps undergoes an internal conversion to the polar CT π,π* state. Furthermore, we find that in polar solvents, Me2N-NI undergoes an excited-state conformational change to produce a twisted-intermolecular CT state.

Experimental Section

Materials. Dioxane (99% ACS reagent grade), acetonitrile [high-performance liquid chromatography (HPLC) grade], and dimethyl sulfoxide (DMSO, spectrophotometric grade) were purchased from Aldrich. Chloroform (HPLC grade) and dichloromethane (HPLC grade) were ordered from EMD. 2-Butanone (99% ACS reagent grade), acetonitrile (HPLC grade), and chloroform (HPLC grade) were purchased from Aldrich. Dichloromethane (HPLC grade) and chloroform (HPLC grade) were purchased from EMD. O2N-NI was obtained from ChemPacific. Cl-NI was purchased from Aldrich. Cl-NI was purchased from Aldrich. O2N-NI was obtained from ChemPacific. Cl-NI was purchased from Aldrich. Cl-NI was purchased from Aldrich.

Synthesis. Compounds were identified using 1H NMR and 13C NMR, in DMSO-d6 (Aldrich) on a Bruker 300 MHz spectrometer at room temperature. Gas chromatography—mass spectrometry (GC-MS) analysis was performed using Shimadzu QP5050A equipment. Compound II was synthesized using the published procedure.17

Compound III (6-Methylsulfanylbenzo[de]isochromene-1,3-dione). Compound I (1 g) and sodium hydroxide (0.5 g) were dissolved in 20 mL of dimethyl formamide (DMF). Methanethiol was initially condensed (~2 mL) in a trap placed in dry ice. All of the methanethiol was purged through the mixture at room temperature, and then, the temperature was elevated up to 100 °C. The mixture was heated for 7 h. After the mixture was cooled to room temperature, 30 mL of water and 1 mL of concentrated HCl were added. The precipitate was collected, washed with methanol, and dried in the oven at 60 °C for 2 h. The solid was recrystallized from a dichloromethane/hexane mixture. Yield, 0.7063 g (62%). MS-EI m/z 244 [M+], calculated for C13H8O3S. 1H NMR (DMSO-d6, 300 MHz) δ ppm: 8.58 (dd, J1 = 8.7 Hz, J2 = 7.5 Hz, 2H), 8.44 (d, J = 7.8 Hz, 1H), 7.93 (dd, J1 = 7.5 Hz, J2 = 8.7 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 3.33 (s, 3H). 13C NMR (DMSO-d6, 75 MHz) δ ppm: 161.2, 161.0, 148.3, 133.2, 132.7, 130.8, 130.1, 128.6, 127.9, 122.2, 130.1, 114.9, 14.6.

Preparation of Me2N-NI (6-dimethylaminobenzo[de]isochromene-1,3-dione). A suspension of compound III (0.2 g) in 7 mL of formamide was placed in a microwave reactor (CEM Discover). Applied were the following parameters: power, 250 W; T = 200 °C; p = 150 psig, for 10 min. The formed solution was poured into 20 mL of water. The dark brown precipitate was collected, recrystallized from ethanol, and dried in the oven. The crude MeS-NI was purified by column chromatography (silica gel 60, 190 mm × 60 mm column; eluent, a mixture of CH2Cl2/methanol in a 10/1 ratio). Yield, 0.2264 g (80%). MS-EI m/z 243 [M+], calculated for C13H9O2NS. 1H NMR (DMSO-d6, 300 MHz) δ ppm: 11.70 (s, 1H), 8.49 (dd, J1 = 8.1 Hz, J2 = 7.2 Hz, 2H), 8.34 (d, J = 7.8 Hz, 1H), 7.88 (dd, J1 = 7.5 Hz, J2 = 8.4 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 2.74 (s, 3H). 13C NMR (75 MHz DMSO-d6) δ ppm: 164.4, 164.6, 130.8, 130.3, 129.8, 129.1, 128.9, 127.5, 123.7, 121.9, 118.9, 14.6.

Preparation of MeS-NI (6-methylsulfanylbenzo[de]isochromene-1,3-dione). A suspension of compound II (0.2 g) and 7 mL of formamide was placed in a microwave reactor (CEM Discover). Applied were the following parameters: power, 250 W; T = 200 °C; p = 150 psig, for 10 min. The formed solution was poured into 20 mL of water. The dark brown precipitate was collected, recrystallized from ethanol, and dried in the oven. The crude MeS-NI was purified by column chromatography (silica gel 60, 190 mm × 60 mm column; eluent, a mixture of CH2Cl2/methanol in a 10/1 ratio). Yield, 0.2264 g (80%). MS-EI m/z 243 [M+], calculated for C13H9O2NS. 1H NMR (DMSO-d6, 300 MHz) δ ppm: 11.70 (s, 1H), 8.49 (dd, J1 = 8.1 Hz, J2 = 7.2 Hz, 2H), 8.34 (d, J = 7.8 Hz, 1H), 7.88 (dd, J1 = 7.5 Hz, J2 = 8.4 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 2.74 (s, 3H). 13C NMR (75 MHz DMSO-d6) δ ppm: 164.4, 164.6, 130.8, 130.3, 129.8, 129.1, 128.9, 127.5, 123.7, 121.9, 118.9, 14.6.
Results and Discussion

Synthesis. Scheme 2 presents the procedure for preparation of Me2N-NI and MeS-NI. The method is based on the nucleophilic aromatic substitution of a chloro-substituted naphthalene derivative with Me2N or MeS groups. It was not possible to use chloronaphthalimide as a starting material since the N-H group of NIs could react with the base used in the aromatic substitution. Instead, the starting material for reaction was the anhydride derivative I. After the Cl group was substituted by Me2N or MeS groups, the corresponding anhydrides were converted into imides using formamide in a procedure similar to the one reported for a variety of cyclic anhydrides.

UV/Vis Absorption and Fluorescence Measurements. Figure 1 presents the absorption and fluorescence spectra of five NI derivatives. The absorption maximum for NI appears at 350 nm, while its fluorescence emerges at 400 nm. Chloro substitution in the 4-position leads to minor changes in the absorption and emission spectra. A small red shift is observed in the spectra of Cl-NI relative to NI. The nature of the chloro substituent is unusual: It is an electron-donating substituent due to its lone pair of electrons, while it behaves as an electron-withdrawing substituent due to the relative electronegativity of Cl atom. Thus, the overall effect of Cl substitution is minor, and the character of the excited state is very similar to the parent NI. Substitution by \(-\text{SMe}, -\text{NO}_2,\) and \(-\text{NMe}_2\) groups leads to a more drastic change in the absorption and emission spectra: (i) A large red shift is observed relative to the spectra of NI, and (ii) the absorption and emission bands become broad and structureless. These results are consistent with the presence of the CT excited states. In the case of Me2N-NI and MeS-NI, the charge transfer occurs from the 4-substituent toward the aromatic ring. The charge transfer in O2N-NI occurs in the opposite direction: from aromatic ring toward the nitro substituent.

To further investigate the nature of the excited states in five NI derivatives, we studied the effect of solvent polarity on the absorption and emission maxima. The correlation between the solvent polarity and the absorption and emission maximum shift is described by Lippert equations:

\[
\begin{align*}
\hbar \nu_{\text{Abs}} &= \hbar \nu_{\text{Abs}}^{g} - \frac{2\mu_{e}(\mu_{e} - \mu_{g})}{a_{0}^{3}} \times f(\epsilon, n) & (1) \\
\hbar \nu_{\text{Em}} &= \hbar \nu_{\text{Em}}^{g} - \frac{2\mu_{e}(\mu_{e} - \mu_{g})}{a_{0}^{3}} \times f(\epsilon, n) & (2)
\end{align*}
\]

Here, \(\hbar \nu_{\text{Abs}}\) and \(\hbar \nu_{\text{Em}}\) are the absorption and emission energies of the molecule in a given solvent; \(\hbar \nu_{\text{Abs}}^{g}\) and \(\hbar \nu_{\text{Em}}^{g}\) are the corresponding energies in the vacuum; \(\mu_{e}\) and \(\mu_{g}\) are dipole
moments for a molecule in the ground and excited states, respectively; \( a_0 \) is the molecular Onsager radius; \( f(\varepsilon, n) \) is a function that depends on the dielectric constant \( (\varepsilon) \) and refractive index \( (n) \) of the solvent and is expressed as:

\[
f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon} - \frac{1}{2}\frac{n^2 - 1}{n^2 + 1}
\]

(3)

The Lippert equation shows that a chromophore’s sensitivity to solvent polarity arises due to the changes in the molecule’s excited-state dipole moment relative to its dipole moment in the ground state. If no net change in dipole moment occurs \( (\mu_g - \mu_x = 0) \), the absorption and emission maxima of the chromophore should not change with increased solvent polarity. If the excited-state dipole moment is larger than that of ground state \( (\mu_x > 0) \), the absorption and emission maxima should red shift with the increased solvent polarity. This situation occurs in compounds that exhibit CT and \( \pi, \pi^* \) excited states. On the other hand, if the dipole moment decreases upon excitation \( (\mu_x < 0) \), the absorption and emission maxima are expected to show a blue shift with increased polarity of solvent. This blue shift occurs in molecules with \( n, \pi^* \) excited states.

Figure 2 plots the changes in the absorption and emission maxima of five NIs as a function of the solvent’s \( f \) function. The absorption maxima show a slight blue shift (positive slope) with increased solvent polarity for all NIs except in the case of \( O_2 N-NI \). This behavior is consistent with the \( n, \pi^* \) excited state. In the computational section, we will show that the calculated \( S_1 \) state in NIs exhibits a \( \pi, \pi^* \) character, while the \( S_2 \) excited state has an \( n, \pi^* \) character. If the light absorption produced the \( S_2 \) \( (\pi, \pi^*) \) excited state, DFT calculations predict a positive Lippert slope for all NIs (Table 3). On the other hand, the excitation to \( S_2 \) state \( (n, \pi^*) \) is expected to give rise to a positive slope for all NIs except \( O_2 N-NI \), where a negative slope is calculated. It is interesting that the experimental results presented in Figure 2 correlate well with the slopes predicted for the excitation to \( S_2 \) state with \( n, \pi^* \) character except for \( O_2 N-NI \). Thus, we conclude that the absorption of light produces dominantly the \( S_2 \) excited state in these NIs.

The effect of solvent polarity on the emission maxima is not equivalent to the one observed with the absorption maxima. For example, \( MeS-NI \) exhibits a blue shift of the absorption maximum with increased solvent polarity, whereas a red shift is observed for its emission maximum (Figure 2). This result clearly demonstrates that the emissive state in \( MeS-NI \) is not the same as the one produced upon light absorption. As we described previously, the absorption of light produces the \( S_2 \) \( (n, \pi^*) \) state. From the emission data, we conclude that fast \( S_2 \) to \( S_1 \) internal conversion occurs in \( O_2 N-NI, MeS-NI, \) and \( MeN_2-NI \). The absorption decays with a lifetime of \( 0.4 \) ns and a new long-lived absorption band appears in the same spectral region. The features of this long-lived species can be observed in the spectrum at a time delay of \( t = 1200 \) ps. Here, we can see that the absorption is blue-shifted relative to the absorption of the initial \( 1(n, \pi^*) \) state. We assign this absorption band to the triplet excited state of NI. Similarly to ground-state absorption and emission spectra of NI derivatives, the CI substitution in the 4-position leads to a very small change in the transient absorption spectrum (data not shown). The absorption maximum of the \( 1(n, \pi^*) \) state of \( CI-NI \) is slightly red-shifted relative to NI. However, the \( 1(n, \pi^*) \) excited-state lifetime is the same for both NI and \( CI-NI \) (\( \tau = 0.4 \) ns). To obtain the absorption spectra of \( 1(n, \pi^*) \) and \( 1(\pi, \pi^*) \) states, we decomposed the transient absorption data using a \( 1S \rightarrow 3T \) kinetic model (global analysis). The deconvoluted spectra for NI and \( CI-NI \) are presented in Figure 4. In both cases, the \( 1(n, \pi^*) \) state absorbs at somewhat higher wavelength than the \( 1(\pi, \pi^*) \) state.

Contrary to \( CI-NI, the excited-state behavior of \( MeN_2-NI, O_2 N-NI, \) and \( MeS-NI \) are drastically different from that of NI. Figure 5 presents the transient absorption data in solutions of varying polarity. Qualitatively, all three NIs exhibit similar features: a stimulated emission peak that appears in the 500–550 nm range and an excited-state absorption in the red portion of the spectrum (600–750 nm). As expected, the increased solvent

Figure 2. Plot of the absorption (left) and emission (right) maxima of five NIs as a function of solvent’s \( f \) function (eqs 1 and 2): NI (black), Cl-NI (red), SMe-NI (cyan), NO2-NI (green), and NMe2-NI (blue).

Figure 3. Transient absorption spectrum of N in dichloromethane obtained at different probe delays: 5 (orange), 100 (blue), 400 (cyan), and 1200 ps (red). Inset: NI excited-state decay obtained at \( \lambda = 475 \) nm.
polarity gives rise to a red shift of the stimulated emission band in O2N-NI and Me2N-NI. In the case of MeS-NI, the stimulated emission peak appears to blue shift. This behavior is due to the contribution from the excited-state absorption in the stimulated emission range. With increased solvent polarity, the energy of the singlet excited state decreases, which leads to a red shift of the stimulated emission peak and a blue shift of the excited-state absorption peak. The overall effect of these two shifts gives rise to the observed blue shift of the stimulated emission signal. In accordance with the computational results presented in the next section, we assign the excited state in Me2N-NI, O2N-NI, and MeS-NI to a CT state.

In chloroform, the solvent with the lowest dielectric constant in these studies, all three NIs exhibit the same excited-state dynamics. As an example, we present the stimulated emission dynamics for O2N-NI in Figure 6. The signal exhibits a rise with the lifetime of 40 ps and a long decay with the lifetime of 3.9 ns. One possible explanation for the short-lived rise component is solvation dynamics. Because the excited state has a CT character, a large redistribution of charges upon excitation is expected to be followed by significant redistribution of the solvent dipoles. However, the solvation dynamics usually lead to a red shift in the stimulated emission peaks, which is not the case for our data. We believe that the short-lived component arises due to internal conversion from the $^1(n,\pi^*)$ to the CT excited state of NI derivatives (Scheme 3). This assignment is supported by the above-described absorption and emission experiments in solvents of varying polarity, which suggest that NI derivatives create the $^1(n,\pi^*)$ excited state ($S_2$) upon absorption, while the emission in Me2N-NI, O2N-NI, and MeS-NI...
NI occurs from the CT excited state (S\textsubscript{1}). From these data, it is obvious that the conversion between these two states must occur upon excitation. Thus, we assign the 40 ps component to the S\textsubscript{2}→S\textsubscript{1} internal conversion. The confirmation for this assignment can be best observed from transient absorption spectra of Me\textsubscript{S}-NI obtained upon excitation by a 420 nm (Figure 7). The spectrum obtained 1 ps after the excitation pulse consists of two positive signals centered at 470 and 620 nm and arises due to the absorption of the S\textsubscript{2} excited state of Me\textsubscript{S}-NI. The spectra obtained at subsequent time delays clearly show a growth of the stimulated emission signal centered at 500 nm, which is a signature of the S\textsubscript{1} CT excited state. The n,π* transitions are generally considered quasi-forbidden: They are allowed by symmetry but exhibit a small overlap between n and π* orbitals. For these reasons, the deactivation of n,π* states usually involves a thermal deactivation via conical intersection with the lower-lying states. In the case of Me\textsubscript{S}-NI, we were unable to calculate the S\textsubscript{2}→S\textsubscript{1} conical intersection using a DFT method, so we cannot discuss the exact vibrational motion that leads to the S\textsubscript{2}→S\textsubscript{1} conversion. However, it is known that n,π* excited states of simple aldehydes are pyramidalized about the C=O bond in the excited state.\textsuperscript{36} Thus, we postulate that the out-of-plane bending motions of C=O bond or in-plane distortions due to the change in bond lengths lead to a deactivation mechanism for the excited states.

An interesting effect is observed in the excited state dynamics of Me\textsubscript{N}-NI as a function of solvent polarity. While Me\textsubscript{S}-NI and O\textsubscript{2}N-NI excited-state dynamics do not change when the solvent is changed from chloroform to dichloromethane and acetonitrile, the decay of Me\textsubscript{N}-NI becomes faster (Figure 5, lower panels). The lifetime decreases from 3.9 ns in chloroform to only 360 ps in acetonitrile. We assign this lifetime shortening to the excited-state rotation of the Me\textsubscript{N} group relative to the aromatic ring. As will be discussed in the following section, the 4-substituent in Me\textsubscript{N}-NI is at a small angle relative to the aromatic ring in the ground-state optimized geometry. The situation is different in the optimized excited-state geometry, where the 4-substituent is at a 90° angle (twisted state). Thus, a rotation of the 4-substituent is expected to occur along the non potential energy surface. In nonpolar environment, the highly polar twisted excited state is not stabilized by the solvent, leading to transient absorption by the initially produced π,π* excited state. As the solvent polarity is increased, the twisted state becomes stabilized, leading to a fast deactivation of the initially produced π,π* excited state (Scheme 4). A similar effect has been observed previously with Me\textsubscript{N} derivatives of various aromatic compounds.\textsuperscript{37,38} In these reports, the authors observed dual fluorescence arising from “twisted” and “planar” excited states. The dual emission occurred only in solvents with high solvent polarity, which is consistent with our data. We did not observe any signal from the twisted state in neither fluorescence nor transient absorption spectra.

**Time-Dependent (TD)-DFT Calculations.** The calculations of the ground- and excited-state properties of NI derivatives were performed using TD-DFT\textsuperscript{26} as implemented in Turbomole software,\textsuperscript{21,22} along with the B3LYP\textsuperscript{23,39,40} functional and the 6-31+G* basis set.\textsuperscript{24} To validate the computational method, we first compared the calculated electronic absorption maxima of NI derivatives with those obtained experimentally (Table 1). While the computations were performed without corrections for solvent effects, the experiments were done in various solvents. To compensate for the disagreement in absorption maxima due to solvent effects, the “experimental” vacuum absorption maxima were obtained as \(\gamma\)-intercepts of Lippert plots (Figure 2 and eq 1).

| Table 1: Comparison of Experimental Absorption Maxima of Five NIs with Those Calculated Using TD-DFT for S\textsubscript{1} and S\textsubscript{2} Excited States\textsuperscript{a} |
|-----------------|--------|--------|--------|
| NI              | 337    | 345    | 337    |
| Cl-NI           | 356    | 348    | 348    |
| SM\textsubscript{N}-NI | 391    | 390    | 345    |
| NO\textsubscript{2}-NI | 405    | 379    | 369    |
| NMe\textsubscript{2}-NI | 416    | 404    | 342    |

\textsuperscript{a} The experimental values in vacuum were obtained as \(\gamma\)-intercepts of Lippert plots (Figure 2 and eq 1).

Figure 8 presents the difference density plots for S\textsubscript{1} and S\textsubscript{2} excited states of five NI derivatives. We have recently utilized difference density plots to elucidate several different photochemical processes,\textsuperscript{41-44} which is a strategy to visualize the changes in electron density upon vertical excitation, especially for states that are described by contributions from multiple occupied to unoccupied orbital configurations. In the case of NI, the S\textsubscript{1} excited state is characterized by electronic charge depletion from the lone electron pairs of the imide oxygen atoms and a charge accumulation on the aromatic rings. This sort of difference density plot is characteristic of an n,π* excited state, which is additionally supported by the small oscillator strength for this transition (\(f = 0.0001\)). The change in electron density for the S\textsubscript{2} excited state in NI alternates in sign on the conjugated...
system, which is characteristic of the $\pi,\pi^*$ excited state. In the case of other NI derivatives, the order of excited states is switched, with the S1 state having a $\pi,\pi^*$ character and S2 state having an $n,\pi^*$ character.

Returning to the results presented in Table 1, we can see that all of the experimental absorption maxima correlate well with the calculated absorption energies to produce $\pi,\pi^*$ states. The unusual result is observed in the case of NI, where the experimental absorption wavelength correlates better with the calculated S2 energy. To understand the reason for this behavior, we conducted a DFT calculation for NI using the PCM model for dichloromethane as implicit solvent. We found that the solvent stabilizes the $\pi,\pi^*$ excited state and destabilizes the $n,\pi^*$ state, which leads to a reversal of order of these two energy levels (Scheme 5). Given this reversal of states, it is understandable why our experimental absorption maxima correlate better with the calculated S2 energy in vacuum. Even though our experimental absorption maxima were extrapolated from Lippert plots to the vacuum values, this extrapolation is based on the assumption that the reversal of states does not occur. Thus, all NI derivatives exhibit $\pi,\pi^*$ excited state as the lowest singlet excited state.

We further calculated the optimized geometries on the excited-state potential energy surfaces, which were confirmed to be minima by calculating the second derivatives of the energy by numerical differentiation of the analytical first derivative with the NUMFORCE module in Turbomole. Comparisons of calculated emission energies with the experimental fluorescence maxima are presented in Table 2. As with the absorption values, the experimental emission maxima were obtained as $y$-intercepts in Lippert plots (Figure 2). Because of the reversal of states described previously, the value used for NI is the calculated energy of the S2 excited state. For the rest of NI derivatives, we used energies of the optimized S1 states. The agreement between experiment and theory is satisfactory for NI, CI-NI, and MeS-NI, while the calculated energies for optimized Me$_2$N-NO$_2$-NI and O$_2$N-NI excited states are significantly lower than the experimentally observed. An interesting finding is that NI derivatives in which the experimental and calculated emission energies do not correlate well are those that are expected to undergo a large change in geometry during the excited state’s relaxation. The difference between the calculated Franck-Condon and relaxed geometries of S1 states in NI, Cl-NI, and MeS-NI is only in their bond lengths. On the other hand, the relaxation of the S1 states of O$_2$N-NI and Me$_2$N-NI involves a rotation of the 4-substituent around the C-N bond (Figure 9). The ground-state geometry of O$_2$N-NI involves the NO$_2$ group at 38° out of the aromatic plane. Upon excitation, a charge transfer from aromatic rings to the NO$_2$ group drives the formation of a planar quinoidlike structure. The opposite effect occurs in the case of

**TABLE 2: Comparison of Experimental Fluorescence Maxima of Five NIs with Those Calculated Using TD-DFT for the S1 Excited State**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{exp}$ (nm)</th>
<th>$\lambda_{calc}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI</td>
<td>389</td>
<td>420$^b$</td>
</tr>
<tr>
<td>Cl-NI</td>
<td>372</td>
<td>386</td>
</tr>
<tr>
<td>SMe-NI</td>
<td>452</td>
<td>430</td>
</tr>
<tr>
<td>NO$_2$-NI</td>
<td>477</td>
<td>830</td>
</tr>
<tr>
<td>NMe$_2$-NI</td>
<td>475</td>
<td>644</td>
</tr>
</tbody>
</table>

$^a$ The experimental values in vacuum were obtained as $y$-intercepts of Lippert plots (Figure 2). $^b$ The value obtained for the S2 excited state.

**Figure 8.** Calculated difference density plots for S1 and S2 states of five NI derivatives. The red surfaces correspond to depletion of electron density from S0 state. The green surfaces correspond to the areas of accumulation of electron density.

**Scheme 5: Calculated Energies of n,$\pi^*$ and $\pi,\pi^*$ States of N in Vacuum and Dichloromethane**

**Figure 9.** Calculated geometries for Franck-Condon and relaxed S1 states of NO$_2$-NI and NMe$_2$-NI. The angle $\theta$ is a dihedral angle between the plane of the aromatic rings and the N-O/N-Me bonds of 4-substituents in NO$_2$-NI and NMe$_2$-NI, respectively.
produce the $S_1$ excited state. This state has a $\pi,\pi^*$ character in NI and Cl-NI, while it has a CT character in O$_2$N-NI, Me$_2$N-NI, and MeS-NI. In compounds with CT states, the excited state lifetimes are relatively long (3.9 ns).

We compared the experimental absorption and emission maxima for all NI derivatives with those calculated using the TD-DFT method. We find excellent agreement in all of the values, except for the fluorescence maxima of Me$_2$N-NI and O$_2$N-NI. In both of these compounds, the experimental fluorescence maxima have higher energy than the calculated maxima. An interesting finding is that this discrepancy between experiment and theory arises with the compounds that are expected to have a large structural change in the excited state.

In the case of Me$_2$N-NI, the rotation of the Me$_2$N group is expected to occur to produce a twisted excited state, while in O$_2$N-NI, the rotation of the NO$_2$ group is expected to produce a planar excited state. Thus, we believe that the discrepancy arises due to the fluorescence from the nonequilibrated excited state. A detailed computational study describing the geometrical changes in the excited state and infrared frequencies of the excited states along with the adiabatic and relaxed energetics for all five NIs will be presented in due course.

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### References and Notes
