Proton Activated Photoisomerization of Dibenzofulvene Molecular Actuators

A dissertation submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in Chemistry

by

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Abstract

Our group has shown that dibenzofulvene rotors behave as an efficient class of light driven molecular actuators that give a range of photoisomerization quantum yields from 0.04 to 0.5 depend upon the substituents. This work shows the protonation dependence in photoisomerization quantum yields for amino and dimethylamino substituted dibenzofulvene derivatives. Both rotors were protonated with trifluoroacetic acid (TFA) and triflic acid (TfOH) and it was discovered that TfOH gives the highest quantum yield in all cases. In contrast, addition of triethlyamine (TEA) base does not significantly change quantum yields regardless of the amount added. This behavior could be due to the change in the electron densities with protonation and deprotonation, which could be explained by the electron donating/withdrawing character of each substituent. Photoisomerization was conducted at 266 and 310 nm and was monitored by gas and liquid chromatography and by $^1$H NMR. The protonation dependence is found only in amino (ATEF) and dimethylamino (DTEF) compounds. For other substituents, such as nitro and cyano, changes in protonation do not significantly affect the quantum yields. In addition, computational calculations were performed on the rotor parts of these motor prototypes.
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Dedicated to my loving mother and in memory of my father.
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Chapter 1

Introduction

1.1 Molecular Devices

The development of controllable molecular devices\(^1\text{"}^4\) is one of the most intensively sought goals in the field of nanotechnology. The large number of conceivable applications for molecules that mimic macroscopic devices has led to the synthesis of molecular wires,\(^4\text{"}^6\) switches,\(^2\text{"}^3\text{"}^7\text{"}^14\) shuttles,\(^15\text{"}^16\) gears,\(^17\text{"}^18\) and motors.\(^19\text{"}^27\) Macroscopic machines require macroscopic control and energy inputs. Similarly, useful nanoscale machines require power and control inputs. Unlike macroscopic devices, microscopic devices are always in Brownian motion at ambient temperature. In order to use these devices effectively this intrinsic random motion must be overcome. In most cases, this is done by applying an external power source to drive a motion that is not active at thermal energies. Different types of external power supplies that have been developed and implemented to control this motion, such as chemical, photochemical and thermal sources. Usually chemical energies are as-
associated with chemical reactions with another “fuel” species to generate a new molecule which can facilitate the desired motion. The fuel molecule leaves the system once the actuation process is complete. The fuel molecule can be considered as a catalyst for the actuation process. Photochemical energy requires a light source to provide photons in order to undergo a chemical process. This process could be isomerization, dissociation, addition, etc. This work is mainly focused on developing a light driven molecular actuator which is executed by light as the power source, and with chemical control of the actuation process.

1.2 Molecular Motors

The history of molecular related motors dates back to the 1970s. Various types of energy sources have been tested in recent molecular motors. Chemically driven, thermally driven and photochemically driven motors are among them. In the following sections some of the previous attempts to develop molecular motors along with different energy sources are discussed in detail.

1.2.1 Kelly’s Phosgene Fueled Motor Prototype

Kelly and coworkers were one of the first research groups to synthesize a molecular motor with the potential for unidirectionality. This is an example of a chemically driven molecular motor first reported in 1999. The Kelly motor molecule is shown in Figure 1.1. This molecule has an amine group (–NH$_2$) attached to one blade of triptycene unit and a hydroxyalkyl group (–O(CH$_2$)$_3$OH) is attached to the helicene unit.
As described below, even though this motor did not perform as intended, it was an ambitious start to the new era of molecular motors. This molecule can undergo clockwise 120° degree rotation with the unidirectional preference generated by steric interactions. The complete clockwise 120° degree rotation is shown in Figure 1.2.

Figure 1.2: Kelly’s proposed molecular motor. It completes 120° rotation driven chemically and due to the steric crowding further rotation is not possible. Taken from Ref. 19.
The process taking place during the 120° rotation can be described as follows. Molecule 1 is reacted with phosgene (Cl₂C=O) in triethylamine (Et₃N or N(CH₂CH₃)₃) to form 2 to start the process. The only functional group available for this reaction is the –NH₂ group on triptycene to form isocyante. This isocyanate group and the –O(CH₂)₃OH group attached to the base helicine unit are far apart from each other and in a low energy conformation. Therefore no urethane formation is possible at this stage. However, if 2 can rotate by 60° then the molecule is in a conformationally excited state which has the isocyanate group and the –OH group close enough for further reaction to yield 4. Due to the thermal energy in the system 4 will rotate by another 60° which makes a full 120° rotation to form 5. At this stage the urethane cleavage takes place to form 6 which is approximately in the same energetics as 1. One of the main requirements of practical molecular motor is full 360° rotation. This molecular system does not satisfy that requirement. To overcome this problem, Kelly and co-workers synthesized another version shown in Figure 1.3.

Figure 1.3: Kelly’s proposed repeatedly rotating molecular motor. This is a modification of the compound shown in Figure 1.1 and it has a different base unit as well as three –NH₂ groups attached to each triptycene blade. Taken from Ref. 20.

There are several modifications found on the new system compared to the previous attempt.
1 Three –NH₂ groups are attached to the three rotary blades.

2 The stator moiety has an additional pyridine moiety substituted with a dimethylamino group.

Actuation of this molecule is expected to follow the same sequence as for the 120° rotation explained above and that is then shown in Figure 1.4.

Figure 1.4: Modified Kelly’s molecular motor. This can undergo full 360° rotation. Taken from Ref. 20.
In this case phosgene does not directly react with amine substituents (–NH$_2$) on the rotating blades, but instead with the lone pair of the N atom on the attached pyridine moiety. The intermediate that results from the addition reaction rearranges to form the isocynate as explained above. In the presence of the 4-(dimethylamino)pyridine (DMAP) unit, phosgene can be selectively delivered to the amine in the most reactive conformation. This is followed by similar steps as in the previous motor prototype, but has the advantage that once a 120° cycle is over, there is another free amine group (–NH$_2$) waiting to undergo further 120° rotation with the help of pyridine moiety. As this can be repeated, the molecule can potentially have 360° rotation. This molecular system fulfills most of the requirements that should be satisfied by a typical molecular motor. Unfortunately, this motor system did not work as expected. Two reasons were given to explain the inability of 360° rotation.

1. The hydroxypropyl group (Figure 1.4) adopts a conformation which is different from the prototype shown and this could be due to H-bond interactions with the DMAP or the added substituents on the other two triptycene blades.

2. The constraints due to the triptycene/helicene bond rotation.

### 1.2.2 Feringa’s Light Driven Molecular Motors

Another family of molecular motors, which has a photoisomerizable elongated C=C bond acting as an axle, was synthesized and characterized by Feringa and coworkers. $^{21–27}$ This C=C bond connects the stator and the rotor as shown in Figure 1.5. The “bottom” part of these molecules is called the “stator” and the “top” part (boxed in Figure 1.5), that
undergoes isomerization, is called the “rotor”. Most of these molecular motor prototypes

Figure 1.5: Different types of molecular motors designed by Feringa and coworkers.

shown are driven by a multistep process containing both light and thermally actuated steps. Even though several modifications have been done, a purely light driven molecular motor has not been developed yet; the Feringa motors operate by a sequence of light and thermal steps. As examples, the cycles for molecule 326 and a recent development27 by the Feringa group will be discussed in detail below.

The direction of rotation of 3 is governed by the two sterogenic centers on this molecule. A full cycle involves four steps as shown in Figure 1.6. Steps 1 and 3 are controlled by light whereas the 2nd and 4th are controlled thermally. Hence this is not a pure light driven molecular motor. In step 1, the molecule is irradiated at 313 nm which favors the
Figure 1.6: Rotary cycle of a thermally powered molecular motor 3. Taken from Ref. 26.

forward reaction. This reaction can be reversed under very strict thermal control (-80°C). This isomerization step results in a conformation which has an unstable orientation of phenyl rings as well as the attached substituents. Due to the thermal energy in the system (-20°C) and the instability of the “trans” configuration, it rearranges to give the most stable configuration which is denoted in Figure 1.6 as the “stable-trans”. Increasing
the temperature of the system up to 20°C will result in another unstable conformation (“unstable-cis”) which can be reversed by irradiation at 313 nm. In order to obtain the initial conformation, the system must be warmed to 60°C. There are important features associated with each of the processes described above.

* Step 1 and 3 - Both are in equilibrium with stable and unstable conformations and can be controlled thermally as well as photochemically (313 nm).

* Step 2 and 4 - Both are irreversible forward reactions and can be driven by heating the system to 20°C and 60°C, respectively.

There are a few disadvantages of this molecule. Firstly, this system is thermally driven and controlling the temperature is really important in order to operate the motor successfully. Secondly, the molecule has to undergo a series of temperature changes which could make the molecule decompose. These thermal steps limit the rate of the reaction process.

Another version of Feringa’s molecular motor is shown in Figure 1.7, which also needs both thermal and photochemical power to operate. The full rotary cycle of that is shown in Figure 1.7. In this molecule the top half acts as the “propeller” or “rotor” and the bottom as the “stator”. The propeller rotates unidirectionally with respect to the bottom part. Upon irradiation with 366 nm light (step 1), cis/trans photoisomerization takes place which inverts the helicity and changes the conformation of the cyclopentane ring attached to the C = C bond. This rotation forces the tert-butyl to assume an unfavorable pseudoequatorial position as shown in Figure 1.7. In order to regain the favorable pseudoaxial position, the upper part of the naphthalene moiety slips past the lower part of the molecule due to the thermal
isomerization which results in the \((P) - (R) - cis\)-stable-12 configuration. Upon irradiation \((P) - (R) - cis\)-stable-12 will be converted to \((M) - (R) - trans\)-unstable-12. This can be thermally isomerized back to the original \((P) - (R) - trans\)-stable-12. The unidirectional rotation of this molecule is monitored by detecting the “reversible” chemical shift of proton (H) at the stereogenic center.

There is no simple accepted model to explain the energetics of these systems yet. But most of these results can be rationalized using generic theoretical models proposed for small molecules which have C=C bonds. This will be explained in the next section taking stilbene as an example.
1.3 Photoisomerization of Molecular Motors

A successful molecular motor undergoes continuous isomerization to yield a unidirectional rotation. Only a certain parts of the molecule can undergo isomerization. Many molecules can be isomerized if they have either a C=C bond or a N=N bond because those bonds can undergo isomerization to give the other isomer or mixture of isomers. Some of the most commonly studied examples found in literature are shown in Figure 1.8. Of these molecules, the stilbene molecular system will be considered in detail in the next section.

![Stilbene and Azobenzene](image)

Figure 1.8: Small molecules with C=C and N=N groups that can undergo isomerization.

1.3.1 Stilbene

Stilbene is a relatively simple molecule with exceptional photoisomerizability, and has distinct cis/trans isomers.\(^7\)–\(^14\) Also, stilbene has been studied by changing substituents, loca-
tion of substituents, and solvents. The basic skeletons of cis and trans stilbenes are shown in Figure 1.9. Photoisomerization of stilbene and its derivatives has been studied more

![Molecular structures of (a) trans-stilbene, (b) cis-stilbene, and a typical cis-trans photo-isomerization process.](image)

than 60 years.\textsuperscript{8,9,16} In fact, the studies on stilbene have provided a model to understand the mechanisms of more complex molecular systems which are used as molecular machines today. In addition, the condensed phase studies and gas phase studies of stilbene provided a way to understand the important role of the solvents in chemical reactions. Table 1.1 shows some of the isomerization quantum yields experimentally obtained for stilbene derivatives. It clearly shows that the quantum yield depends upon not only the substituent but also on the location of the substituent.

One of the most significant findings of the stilbene studies is the isomerization mechanism and the potential energy surfaces (PESs) associated with isomerization processes.
There are three different mechanisms proposed to explain trans $\rightarrow$ cis isomerization. They are listed below.

(I) Internal conversion from the first excited singlet state to highly excited vibrational levels of the ground state. – This has been found to be not important.

(II) Intersystem crossing to the triplet state that either crosses or nearly crosses with the ground state near the 90° twist angle.

(III) The most widely accepted mechanism is the twisting about the ethylenic double bond in the first singlet excited state which is shown in Figure 1.10.

From the two possible isomers (cis and trans), the trans isomer is energetically favorable relative to the cis isomer. For unsubstituted stilbene, the trans isomer is more stable than the cis isomer by 4.59 kcal/mol in benzene solvent. This is mainly due to less

Table 1.1: Quantum yields ($\Phi_{t\rightarrow c}$-quantum yield for trans to cis isomerization, and $\Phi_{c\rightarrow t}$-quantum yield for cis to trans isomerization) for different stilbene molecules.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$\Phi_{t\rightarrow c}$</th>
<th>$\Phi_{c\rightarrow t}$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.52</td>
<td>0.35</td>
<td>pentane</td>
</tr>
<tr>
<td>4–Cl</td>
<td>0.60</td>
<td>0.42</td>
<td>MCH-IH</td>
</tr>
<tr>
<td>4–F</td>
<td>0.50</td>
<td>0.40</td>
<td>MCH-IH</td>
</tr>
<tr>
<td>4–Br</td>
<td>0.52</td>
<td>0.35</td>
<td>pentane</td>
</tr>
<tr>
<td>3–Br</td>
<td>0.56</td>
<td>0.34</td>
<td>pentane</td>
</tr>
<tr>
<td>3–Br, 3’–Br</td>
<td>0.56</td>
<td>0.24</td>
<td>pentane</td>
</tr>
<tr>
<td>4–NO₂</td>
<td>0.50</td>
<td>0.34</td>
<td>benzene</td>
</tr>
<tr>
<td>4,4’-NO₂</td>
<td>0.47</td>
<td>0.30</td>
<td>benzene</td>
</tr>
<tr>
<td>4–NO₂, 4’–MeO</td>
<td>0.53</td>
<td>0.37</td>
<td>benzene</td>
</tr>
<tr>
<td>4–NO₂, 4’-DMA</td>
<td>0.28</td>
<td>0.40</td>
<td>MCH</td>
</tr>
<tr>
<td>4–CN</td>
<td>0.42</td>
<td>0.45</td>
<td>benzene</td>
</tr>
<tr>
<td>4–CN, 4’–CN</td>
<td>0.45</td>
<td>0.35</td>
<td>pentane</td>
</tr>
<tr>
<td>4–CN, 4’–MeO</td>
<td>0.40</td>
<td>0.40</td>
<td>benzene</td>
</tr>
</tbody>
</table>

MCH –IH: Methylcyclohexane – isohexane
Figure 1.10: A schematic representation of \textit{trans} \rightarrow \textit{cis} isomerization of stilbenes. Taken from Ref. 28,29.

Steric crowding and spatial orientation of the \textit{trans} configuration. The molecules are originally in the ground state (S\textsubscript{0}) and can be excited to higher energy levels by irradiation (h\nu).

The excited state of interest is S\textsubscript{1}. In the S\textsubscript{0} state the \textit{trans} and \textit{cis} isomers are separated by an energy barrier as shown in Figure 1.10. But in the excited state, there is no significant barrier between the \textit{cis} and \textit{trans} configurations. In order to isomerize, the \pi bond character of the C=C bond is relaxed. This allows twisting about the C-C single bond (\sigma). This process is possible in the excited state. At 90\degree the molecule has two possible path ways, either go back to the original isomer or to the new isomer as shown by the broken line. As the molecule relaxes the broken \pi bond will be formed again. The final result depends upon the solvent environment, the substitution pattern and external energy provided to the system.
1.4 Our Approach

The proposed molecular motor which is purely driven by light is shown in Figure 1.11. This molecule is assumed to have following features:

![Proposed molecular motor by Cline’s research group.](image)

Figure 1.11: Proposed molecular motor by Cline’s research group.

(1) Photon-driven: The temporal control of actuation is initiated by light.

(2) Nanoscale size: The footprint of the motor is less than 1 nm² as measured by the “stator base.”

(3) High rotary speed: Determined by the product of the rate of light absorption and the photoisomerization quantum yield. The maximum rate of absorption of light is related to the inverse of the relaxation lifetime of the rotor [by intramolecular vibrational energy relaxation (IVR), with typical lifetime < 1 ns]. To achieve full rotation, the
absorption of three photons is required, so the maximum rotary speed is on the order of 100 MHz.

(4) Potentially highly directional: Chirality of the motor potentially results in only one sense of rotation. The choice of enantiomer allows for control of clock-wise or counter-clock-wise rotation.

Due to synthesis challenges, our collaborators in the Bell research group have not yet synthesized this molecule. Instead, we test molecular motor prototypes synthesized by the Bell research group. The difference between the original proposed motor and the prototype is the unconnected phenyl rings in the trityl “stator”, making the molecule achiral. The achiral prototype is incapable of unidirectional rotation. All these prototypes are derivatives of (2,2,2-triphenylethylidene)fluorene, abbreviated as “TEF”. The generic structure of our prototype is shown in Figure 1.12.
In addition to these features, these molecular motors are stable under ambient visible light, and at room temperature. The UV-Vis absorption spectra for some of the molecules studied in our group are shown in Figure 1.13. Except for the –NO$_2$ substituted motor, none of the motors absorb at UV wavelengths longer than 350 nm. Due to that fact all our studies were performed in the UV range. Since this is a light driven molecular motor, the photoisomerization quantum yield is of interest. Table 1.2 shows the photoisomerization quantum yields obtained by our group for other substituents.
Figure 1.13: UV-Vis spectra of motor molecules studied by the Cline group. – Taken from A.I. Ismail’s dissertation (Ref. 31).

Table 1.2: The photoisomerization quantum yields, $\Phi$, of our molecular prototypes at irradiation wavelengths, $\lambda$.\textsuperscript{32,33}

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Wavelength/nm</th>
<th>$\Phi_{EZ}$</th>
<th>$\Phi_{ZE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTEF</td>
<td>266</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>CTEF</td>
<td>266</td>
<td>0.40</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.31</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>0.37</td>
<td>0.40</td>
</tr>
<tr>
<td>NTEF</td>
<td>266</td>
<td>0.25</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>0.31</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>0.21</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>ITEF</td>
<td>266</td>
<td>0.48</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0.49</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td>0.55</td>
<td>0.45</td>
</tr>
</tbody>
</table>
1.4.1 Qualitative Study of ATEF by Protonation

Experiments by Dr. Ali Ismail\textsuperscript{31} in the Cline group demonstrate that protonation protonation of ATEF increases the photoisomerization quantum yield. In these experiments ATEF is included in a thin (100 nm) film of Poly(methyl methacrylate) (PMMA), varying equivalents of TFA. Photoisomerization is revealed by reversible polarization hole-burning that results from angular-reorientation of ATEF actuators induced by polarize UV irradiation. The polarization holes are probed by polarized cavity ring down spectroscopy (CRDS).\textsuperscript{34–48} Figure 1.14(a) shows a generic pump-probe experimental setup used along with the cavity ring down technique. In these experiments the pump, or “drive” beam, creates the angular hole, and the CRDS probe beam detects the hole.
Figure 1.14: (a) Experimental setup where P is a polarization splitter and H and V are the photomultiplier tubes detecting horizontally and vertically polarized light, respectively. (b) Effects on protonation with different equivalents of TFA on ATEF. – Taken from Ref. 31.

In Figure 1.14(b) angular hole-burning is evident as a difference absorbance $\Delta A$ between the H and V polarized light. As seen in Figure 1.14(b) there was no significance effect until 10 equivalents of TFA were added. At 40 equivalents, the effect was significant and this could be due to the complete protonation of the ATEF molecules.

Similar experiments were performed in a vacuum chamber by dosing HCl onto an ATEF doped PMMA film, instead of protonating ATEF directly as explained above. Figure 1.15(a) shows the experimental setup used in the vacuum chamber. HCl was dosed from concentrated aqueous hydrochloric acid (HCl) bubbled with N$_2$ as the ATEF was being
irradiated.

Figure 1.15: (a) Experimental setup where P is the polarization splitter and H and V are the photomultiplier tubes for horizontally and vertically polarized light, respectively. (b) Effects on dosing HCl gas on ATEF. – Taken from Ref. 31.

As seen in Figure 1.15(b) once the sample was exposed to a vertically polarized drive beam, the absorbance started to change and reaches a plateau. Around 50 min, the first HCl dosing was done and that caused the ATEF molecules to get protonated to some extent. As a result of that, the difference absorbance (ΔA) increases. After the second HCl dosing at a higher rate, the effect was significant. These experiments suggests that adding acid does activate the ATEF molecules to photoisomerization.

In chapters 2 and 3 of this dissertation, photoisomerzation of 2-amino-9-(2,2,2-triphospholyl)
lethylidene)fluorene (ATEF) and 2-dimethylamino-9-(2,2,2-triphenylethylidene)fluorene (DTEF) molecules are explained, respectively. Chapter 4 discusses computational calculations performed on the rotor part of our motor molecules. Chapter 5 (Appendix) provides examples and derivations of equations used in this study.
Chapter 2

ATEF Molecular Motor Prototype.

2.1 Introduction to ATEF

The molecule 2-amino-9-(2,2,2-triphenylethylidene)fluorene (abbreviated as ATEF) is a member of TEF family, which we have studied extensively.\textsuperscript{52} Compared to other members of TEF family, this molecule has relatively low photoisomerization quantum yield. Table 1.2 suggests electron withdrawing substituents (–CN, –NO\textsubscript{2} and –I) have a tendency to give higher quantum yields. Since –NH\textsubscript{2} is an electron donating group, controlling it chemical alteration would result in a higher quantum yield. A way to do this is by adding acids or protonation.

A ball and stick structure of ATEF molecule generated by the Avogadro software\textsuperscript{49} is shown in Figure 2.1.
Figure 2.1: Ball and stick structure of the E isomer of ATEF. Color code: C - Gray, N-Blue, and H- white.

2.2 Experimental

The syntheses of Z-ATEF and E-ATEF are described in references 50 and 51, respectively. The molecule Z-ATEF is easier to prepare and was primarily studied. The photochemistry of Z-ATEF was studied in room–temperature, deoxygenated acetonitrile solutions.

2.2.1 Sample Preparation

Samples were prepared by dissolving Z-ATEF in HPLC grade CH$_3$CN purchased from Aldrich. The solubility is relatively low (0.5 mM) and was accelerated by sonication for approximately 10 min.

Figure 2.2 shows the UV absorption spectra of E-ATEF and Z-ATEF in CH$_3$CN solution. Photoisomerization of Z-ATEF in CH$_3$CN was investigated at 266 and 310 nm as a function of the number of added stoichiometric equivalents of trifluoromethanesulfonic acid (TfOH), trifluoroacetic acid (TFA), and triethylamine (TEA). The solutions were
purged with solvent-saturated N\textsubscript{2} to remove dissolved O\textsubscript{2}.

![Graph of UV-vis absorption spectra of ATEF isomers in CH\textsubscript{3}CN.](image)

**Figure 2.2**: UV-vis absorption spectra of ATEF isomers in CH\textsubscript{3}CN. Concentration of Z-ATEF is 20.2 µM and E-ATEF is 19.8 µM.

UV spectra for protonated Z-ATEF and E-ATEF with TfOH are shown in Figure 2.3 and Figure 2.4, respectively.

For comparison with previous work, photoisomerization was studied in the photoinactive solvent CH\textsubscript{3}CN. The solubility of the ATEF compound in CH\textsubscript{3}CN was estimated to be approximately 5 x 10\textsuperscript{-4} M with the E-ATEF isomer having a smaller solubility in pure CH\textsubscript{3}CN than the Z-ATEF isomer. Initially dioxane was tested as a co-solvent with CH\textsubscript{3}CN to increase the solubility but use of this co-solvent gives rise to photodecomposition of both the E and Z compounds. Interestingly, the use of a dioxane co-solvent did not promote decomposition for other substituted dibenzofulvene rotors that we have studied.\textsuperscript{33}
Figure 2.3: UV-vis absorption spectra of protonated Z-ATEF isomers with TfOH in CH$_3$CN. Concentration of Z-ATEF is 20.2 $\mu$M.

### 2.2.2 Sample Irradiation

Irradiation experiments were conducted at room temperature (24° C). The irradiation light, 266 nm, was obtained from the fourth harmonic of a pulsed Nd:YAG (Spectra Physics, Model Number: DCR–4), or the 310 nm frequency-doubled output of a Nd:YAG (Spectra
Figure 2.4: UV-vis absorption spectra of protonated E-ATEF isomers with TfOH in CH$_3$CN. Concentration of E-ATEF is 19.8 µM.

Physics GSR Qunata Ray laser, Model Number: LAB 190–10, pumped pulsed dye laser (Spectra Physics PDL–3). [4-(Dicyanomethylene)-2- methyl-6-(4-dimethylaminostyryl)-4H-pyran or DCM laser dye. The amplifier dye concentration was 0.08 mol dm$^{-3}$ and the oscillator dye concentration 0.58 mol dm$^{-3}$.] The average pulse energy was in the range of
0.4-0.6 mJ and was 5 ns in duration at a 10 Hz pulse repetition rate. Laser pulse energies were measured using an ORION-PE (Ophir Spiricon) power meter. The experimental setup used for these experiments is shown in Figure 2.5. Initial irradiation was performed on the unprotonated Z-ATEF molecule. To study the photoisomerization progress 50 µL samples were extracted from the irradiated solution at predetermined time intervals.

### 2.2.3 HPLC Studies

Photoisomerization of Z-ATEF in CH$_3$CN was investigated as a function of the number of added stoichiometric equivalents of trifluoromethanesulfonic acid (TfOH), trifluoroacetic acid (TFA), and triethylamine base (TEA) dissolved in CH$_3$CN. A detailed description of protonation of ATEF molecules can be found in section 5.1. The isomeric composition of
the samples extracted from the photoisomerized solution was measured using a HPLC (Waters 1525) with a reverse-phase column (Symmetry C18 5 µm). A flow rate of 1 mL/min of 80% acetonitrile and 20% doubly distilled water was sufficient to separate the E and Z isomers, which were detected by absorption spectroscopy at 266 nm and 290 nm. Isomer peaks were verified by comparison with chromatograms of samples of known isomeric purity. The HPLC traces for unprotonated Z-ATEF and protonated Z-ATEF with one equivalent of TfOH are shown in Figure 2.6 and Figure 2.7, respectively.
The samples (aliquots) extracted during the irradiation were used to measure the progress of photoisomerization. The integrated areas under the peaks were used to obtain the relative population of the E and Z isomers. The E isomer eluted at 10.7 min and the Z isomer at 11.7 min. Regardless of the protonation state of ATEF in the irradiated solution, the two ATEF isomers always have approximately the same elution times. Evidently this is due to deprotonation of the ATEF isomers in the column. As the irradiation time increases, two
Figure 2.7: HPLC of protonated ATEF (with one equivalent of TfOH) irradiated at 266 nm and detected at 266 nm. Corresponding irradiation times in seconds are shown on each chromatogram on the left. The peak appears between 6 and 8 min is due to impurities in the solvent. This was confirmed by injecting pure CH$_3$CN and watching the peak appears.

new peaks, which we attribute to photodecomposition products, appear at relatively short elution times (8 – 10 min range). The amplitudes of the two decomposition peaks appear to be correlated with the E and Z isomers of ATEF. This behavior was monitored with respect to the magnitudes and intensities of E and Z peaks. There are two decomposition peaks. If E has a larger peak area, then the first peak in decomposition also has a relatively large
peak compared to the second peak and vice versa. This is shown in Figure 2.8.

![HPLC peaks for E and Z isomers along with photo-decomposed peaks.](image)

As seen from Figure 2.8, the area ratios of the first and second decomposition peaks is always found to correlate with the areas of the E and Z peaks, respectively. We have observed similar type behavior in our study of CTEF photoisomerization. ³³
2.2.4 $^1$H NMR Studies

$^1$H NMR experiments were performed to measure the proton binding constant for ATEF, and to determine whether the motor molecule is fully protonated. Z-ATEF was dissolved in CD$_3$CN and the acid was used without dissolving in deuterated acetonitrile. Refer section 5.1 for details of solution preparation. A Varian 500 MHz NMR was used to record all NMR spectra. The initial $^1$H NMR spectrum, taken without adding any acid, is shown in Figure 2.9.

![Figure 2.9](image)

Figure 2.9: $^1$H NMR spectrum of unprotonated Z-ATEF. The insets are for the expansions of different regions. (1) and (3) are the peaks used in this study. Numbers represent the location of H atoms and can be found in Figure 2.10.

The peak locations in this spectrum (Figure 2.9) were used as the reference for the...
rest of the titration. Two peaks were carefully chosen for the calculation. The shifting of peaks 5.755 ppm (corresponding to a doublet due to the proton on the C1 position, in red) and at 6.485 ppm (corresponding to a doublet of doublets due to the proton on the C3 position, in blue) were carefully monitored in this study. (See Figure 2.10 for the location of protons on ATEF molecule. The –NH₂ group is on the C2 position.) A \(^1\)H NMR spectrum was recorded after each addition and the corresponding acid equivalent was recorded. All spectra were scaled by using the CH₃CN peak at 1.94 ppm as the internal reference. The peak shifts calculated from those spectra were used to determine the binding constants associated with the particular acid and Z-ATEF. The variation of \(^1\)H NMR as a function of added TfOH and TFA equivalents are shown in Figure 2.11 and Figure 2.12, respectively.

Figure 2.10: Locations of protons studied in NMR titrations. The peaks at 5.755 ppm corresponds to hydrogen on C1 and at 6.485 ppm corresponds to hydrogen on C3.
Figure 2.11: $^1$H NMR spectra of Z-ATEF as a function of added TFA equivalents. The added TFA equivalents are shown on the right side of the spectra. The ATEF concentration is $1.2 \times 10^{-3}$ M.

As seen in Figure 2.11 the two peaks of interest are initially a doublet (5.755 ppm) and a doublet of a doublet (6.485 ppm). As the TFA is added, the shape of the peak as well as the splitting change. At 0.5 equivalents of TFA and 1.0 equivalents of TFA the two peaks become a singlet and a doublet instead of a doublet and a doublet of a doublets. For 2 to 10 equivalents, the NMR time scale is not sufficient to resolve the peaks due to fast proton exchange. The peaks become clearly visible after 10 equivalents of TFA but the shifting is incomplete. After the 20 equivalents of TFA the peak shifting stops (not shown in the Figure 2.11) and the peaks are once again resolved. The resolution at the end of the
experiment is not as high as it was initially. There could be several reasons:

(1) At large equivalents of TFA, the solution properties may have changed.

(2) The TFA used for this titration was not deuterated. In addition, the acetonitrile used to prepare the TFA additions was non-deuterated. In general, deuterated solvents are used for NMR experiments. These effects are not that significant at low concentrations (or smaller equivalents) as the amount of added acid volume is not significant compared to the volume of the Z-ATEF solution. As the acid solution is added to the ATEF solution, the concentration of undeuterated acetonitrile becomes relatively large, lowering the signal-to-noise of the ATEF peaks.

Figure 2.12 shows the $^1$H NMR spectrum of ATEF as a function of added TfOH. In this case also the peaks are broadened between 0.1 – 0.9 equivalents of TfOH due to fast exchange of protons between the acid and the motor molecule. Compared with the TFA results (Figure 2.11), it can be easily concluded that ATEF molecules get protonated with small equivalents of TfOH. After 5 equivalents of TfOH some small peaks start to appear in the region between 5.8 ppm – 6.1 ppm. Theses peaks have relatively low intensity compared to the major peaks in the $^1$H NMR spectrum.

### 2.3 Results and Data Analysis

The isomerization kinetics were analyzed as a function of the average number of absorbed photons per molecule,

$$x(t) = \left( \frac{\nu_0 E_0 \lambda L}{h c} \right) \left( \frac{1}{C V N_A} \right),$$  \hspace{1cm} (2.1)
Figure 2.12: $^1$H NMR spectra of Z-ATEF as a function of added TfOH equivalents. The added TfOH equivalents are shown on the right side of the spectra. ([ATEF] = 1.2 x $10^{-3}$ M)

where $\lambda_L$ is the irradiation wavelength, $E_L$ is the average laser pulse energy, $\nu_L$ is the laser pulse repetition frequency, $h$ is Planck’s constant, $c$ is the speed of light, $C$ is the molar concentration of the solution, $N_A$ is Avogadro’s number, $V$ is the total volume of the solution, and $t$ is the irradiation time.

In this study, we did not attempt to isolate and identify photoproduct species, D, but we assumed that the mole fraction of decomposed products is given by, $f_E + f_Z + f_D = 1$, and that the molar absorptivity of decomposed product, $\varepsilon_D$, is the average of that for the E and
Z isomers. The mole fraction of each component, \( f_i \), is determined by

\[
f_i = \frac{A_i/\varepsilon_i}{A_Z/\varepsilon_Z + A_E/\varepsilon_E + A_D/\varepsilon_D},
\]

where \( A_i \) is the area under the \( i \)th peak, \( A_Z \) is the area under the peak of the Z isomer, \( A_E \) is the area under the peak of the E isomer, \( A_D \) is area under all decomposition peaks, \( \varepsilon_i \) is the molar absorptivity of \( i \)th isomer, \( \varepsilon_Z \) is the molar absorptivity of the Z-ATEF, \( \varepsilon_E \) is the molar absorptivity of the E-ATEF, and \( \varepsilon_D \) is the molar absorptivity of decomposed products.

Typical plots of Z and E mole fractions measured as a function of \( \chi(t) \) for unprotonated and protonated Z-ATEF with 1.5 equivalents of TFA and with 1.0 equivalent TfOH irradiated at 266 nm are shown in Figure 2.13.

The chemical reactions associated with the protonation of Z-ATEF with TfOH and TFA can be explained in following equations.

\[
\text{TfOH} + \text{ATEF} \rightleftharpoons \text{ATEFH}^+ + \text{TfO}^-
\]

(2.3)

\[
\text{CF}_3\text{COOH} + \text{ATEF} \rightleftharpoons \text{ATEFH}^+ + \text{CF}_3\text{COO}^-
\]

(2.4)

where \( \text{ATEFH}^+ \) is the protonated form of ATEF, \( \text{TfO}^- \) is the anion formed after the ionization of TfOH and \( \text{CF}_3\text{COO}^- \) is the anion formed after the ionization of TFA. \( K_B \) and \( K'_B \) are binding equilibrium constants. In equations 2.3 and 2.4 it is assumed that the binding constants are independent of the isomerization state of ATEF.
Figure 2.13: Mole fraction of ATEF isomers in acetonitrile as a function of the average number of 266 nm photons absorbed per molecule. The initial concentration of Z-ATEF is ca. 0.5 mM and $E$-ATEF = 0. (a) Unprotonated ATEF (b) Protonated by 1.5 equivalents of TFA (c) Protonated by 1.0 equivalents of TfOH. Dots are experimental measurements observed by HPLC peak ratios and solid curves are fits to the kinetic model explained in the text. Red traces and symbols represent the Z isomer and blue for the E isomer. Isomer fractions do not sum to unity due to photodecomposition.

The mole fraction data were analyzed assuming the following kinetic scheme, adapted from Ref. 33:

\[ Z + h\nu \xrightarrow{\Phi_{ZE}} E \]  \hspace{1cm} (2.5)

\[ E + h\nu \xrightarrow{\Phi_{EZ}} Z \]  \hspace{1cm} (2.6)

\[ Z, E + h\nu \xrightarrow{\Phi_{D}} D \]  \hspace{1cm} (2.7)
In Eqs. 2.5 – 2.7, $Z = Z$-ATEF or $Z$-ATEFH\(^+\), $E = E$-ATEF or $E$-ATEFH\(^+\), D represents photodecomposition products, $\Phi_{EZ}$ is the $E \rightarrow Z$ photoisomerization quantum yield, $\Phi_{ZE}$ is the $Z \rightarrow E$ photoisomerization quantum yield, and $\Phi_D$ is the photodecomposition quantum yield. These are “effective” quantum yields and can be considered to be population-weighted averages for the unprotonated and protonated isomers of ATEF.

The rate laws associated with the species $E$, $Z$ and $D$ were previously derived in Ref. 33 and shown to be,

$$\frac{df_E}{dx} = \frac{\Phi_{ZE} \varepsilon_Z f_Z - \Phi_{EZ} \varepsilon_E f_E - \Phi_D \varepsilon_E f_E}{\varepsilon_E f_E + \varepsilon_Z f_Z + \varepsilon_D f_D} \quad (2.8)$$

$$\frac{df_Z}{dx} = -\Phi_{ZE} \varepsilon_Z f_Z + \Phi_{EZ} \varepsilon_E f_E - \Phi_D \varepsilon_E f_E \varepsilon_E f_E + \varepsilon_Z f_Z + \varepsilon_D f_D \quad (2.9)$$

$$\frac{df_D}{dx} = \frac{2\Phi_D (\varepsilon_Z f_Z + \varepsilon_E f_E)}{\varepsilon_E f_E + \varepsilon_Z f_Z + \varepsilon_D f_D} \quad (2.10)$$

where $\varepsilon_Z$ and $\varepsilon_E$ are the molar absorptivities of $Z$ and $E$ isomers, respectively. These are obtained from Figure 2.2 for a given excitation wavelength. $\varepsilon_D$ is the molar absorptivity due to photo-decomposed products and this was assumed to be equal to the average of $\varepsilon_Z$ and $\varepsilon_E$ and $x$ is the number of absorbed photons per molecule. This is a big assumption that we made during our experiments. We made this assumption based on fact that the total peak area of a given chromatogram does not change significantly compared to the initial chromatogram ($t = 0$). The molar absorptivities of motor prototype do not change significantly with addition of TFA, but with TfOH change significant (about 30\%) with $Z$-ATEF as seen in Figure 2.3.

Equations 2.8, 2.9 and 2.10 were numerically integrated and the values of $\Phi_{EZ}$, $\Phi_{ZE}$,
and $\Phi_D$ were optimized in a fit to the experimentally measured $f_E(x)$, $f_Z(x)$, and $f_D(x)$. Fits for unprotonated and protonated (1.5 TFA equivalents and 1.0 TfOH equivalent) Z- ATEF compounds irradiated at 266 nm are also shown in Figure 2.13. The photoisomerization quantum yields obtained as a function of TfOH equivalents, TFA equivalents, and TEA equivalents irradiated at 266 nm and 310 nm and detected at 266 nm are tabulated in Tables 2.1–2.5 in the Appendix and these are plotted in Figure 2.14. These data show that the highest photoisomerization quantum yields are obtained at 1.5 equivalents of TFA and over 1 equivalent of TfOH.

### 2.3.1 Determination of Binding Constant

The binding constants associated with equations 2.3 and 2.4 were determined by using the shifts of selected $^1$H NMR peaks as described in section 2.2.4. The binding constant $K_B$ is given by

$$K_B = \frac{\Delta \delta_{obs}}{(\Delta \delta_{\infty} - \Delta \delta_{obs})([A] - \frac{\Delta \delta_{obs} \times [Z - ATEF]}{\Delta \delta_{\infty}})}$$

(2.11)

where $\Delta \delta_{obs}$ is the $^1$H NMR peak shift in ppm, $\Delta \delta_{\infty}$ is the peak shift when the system is fully protonated, and $[A]$ is the concentration of the acid.

Equation 2.11 was rearranged to yield a quadratic equation expressing $\Delta \delta_{obs}$ as a function of $[A]$, with $K_B$ and $\Delta \delta_{\infty}$ as parameters. This expression was fitted to experimental measurements of $\Delta \delta_{obs}$ with $K_B$ and $\Delta \delta_{\infty}$ optimized by a non linear least squares method. The result is shown by the solid lines in Figure 2.15. The experimental peak shifts are shown as dots in Figure 2.15. The binding constant ($K_B$) associated with Z-ATEF /TfOH
Figure 2.14: Photoisomerization quantum yields as a function of acid and base equivalents, (a) TfOH dependence at 266 nm excitation, (b) TFA dependence at 266 nm excitation. (c) TEA dependence at 310 nm excitation. The red dots represent $\Phi_{EZ}$ and the blue dots for $\Phi_{ZE}$. The fits shown in (a) and (b) were calculated by using the method explained in Appendix A.

was $4.33 \times 10^8$ L mol$^{-1}$ and $K_B'$ for the Z-ATEF/TFA system was $1.22 \times 10^3$ L mol$^{-1}$.
Figure 2.15: The $^1$H NMR peak shifts of Z-ATEF as a function of added acid equivalents (a) TfOH dependence (b) TFA dependence. The blue dots corresponding to the peak shift of H on C1 and red for the H on C3 of the motor molecule. The lines are fits to Eq. 2.11 for each titration. Also, $[\text{H}^+] = [\text{A}]$ in equation 2.11.

The measured $K_B$ value between TfOH and Z-ATEF can be used to predict the effective photoisomerization quantum yields according to,

$$\Phi_{eff} = g_{ATEF} \Phi_{ATEF} + g_{ATEFH^+} \Phi_{ATEFH^+}$$

where $\Phi_{eff}$ is the predicted effective photoisomerization quantum yield, $g_{ATEF}$ is the mole fraction of ATEF, $\Phi_{ATEF}$ is the photoisomerization quantum yield due to unprotonated
ATEF observed experimentally, $g_{ATEFH^+}$ is the mole fraction of ATEFH$^+$, and $\Phi_{ATEFH^+}$ is the average photoisomerization quantum yield due to protonated ATEF observed experimentally. The value of $g_{ATEF}$ can be calculated by,

$$g_{ATEF} = \frac{K_B[A]_0 - K_B[ATEF]_0 - 1 + \sqrt{K_B^2([ATEF]_0 - [A]_0)^2 + 2K_B([ATEF]_0 + [A]_0) + 1}}{2K_B[ATEF]_0}$$

(2.13)

Equation 2.12 can be expressed in terms of molarity units as follows.

$$\Phi_{eff} = \frac{[Z - ATEF]}{[Z - ATEF] + [Z - ATEFH^+]\Phi_{Z - ATEF} + [Z - ATEFH^+]\Phi_{Z - ATEFH^+}}$$

(2.14)

Rearranging, collecting terms, subtracting $[Z - ATEFH^+]\Phi_{Z - ATEFH^+}$ from both sides of and simplifying gives,

$$[Z - ATEFH^+] = [Z - ATEF]\frac{\Phi_{eff} - \Phi_{Z - ATEF}}{\Phi_{Z - ATEFH^+} - \Phi_{eff}}$$

(2.15)

The equilibrium constant associated with Eq. 2.3 and 2.4 can be written as following.

$$K_B = \frac{[Z - ATEFH^+]}{[Z - ATEF][A]}$$

(2.16)

where [A] is the concentration of acid. This can be rewritten by using, $[Z$-ATEF$] = ([Z-
ATEF]₀ - [Z-ATEFH⁺]) and [A] = ([A]₀ - [Z - ATEFH⁺])

\[ K = \frac{[Z - ATEFH⁺]}{([Z - ATEF]₀ - [Z - ATEFH⁺])([A]₀ - [Z - ATEFH⁺])} \] (2.17)

Substituting the value of [Z-ATEFH⁺] from Eq. 2.14 into Eq. 2.16, a quadratic equation of \( \Phi_{eff} \) can be generated which will be solved to obtained \( \Phi_{eff} \) values. The predicted \( \Phi_{eff} \) from Eq. 2.12 are shown as solid lines in Figure 2.14. The predicted \( \Phi_{eff} \) values match the measurements for TfOH but significantly overestimate the measured quantum yields for protonation by TFA at acid concentrations above 1.5 equivalents.

### 2.4 Discussion

#### 2.4.1 Theoretical Evidence

A theoretical understanding of the photoisomerization mechanism for these molecules is beyond the scope of our present studies but related calculations are discussed in chapter 4. From theoretical and experimental studies on other molecular systems by other theoretical groups, a generalization can be presented. Although the potential energy surfaces are not known for this family of molecules, we can compare to theoretical and experimental studies for stilbene and fulvene type molecules. Figure 2.16 shows the schematic representation of the potential energy surface predicted for the photoisomerization of aromatic ethylene.
Figure 2.16: The potential energy surface (PES) for stilbene type molecules. The conical intersection (CI) facilitates the nonadiabatic radiationless transition from the excited state to the ground state. The isomerization takes place once the angle of rotation completes approximately 90°. The blue dotted line shows the path of conversion of cis (E) to trans (Z) or trans (Z) to cis (E) with photoexcitation.

Bearpark et al.\textsuperscript{54} and Sumita et al.\textsuperscript{55} have proposed a singlet mechanism for the photoisomerization of fulvene. It involves excitation from the ground singlet state to the first excited singlet state, followed by twisting of the exocyclic double bond about the angle θ, crossing to the S\textsubscript{0} surface at a conical intersection, and subsequent relaxation on the S\textsubscript{0} surface, to accomplish a 180° rotation about θ. Theoretical studies suggest that substitution of the π–system can influence the location of the crossing region shown in Figure 2.16.\textsuperscript{54}

According to this singlet state mechanism, Bearpark et al. theoretically predicted a very low photoisomerization quantum yield is possible for fulvenes.\textsuperscript{54} In light of our reports on the TTEF substituted motor molecule, Sumita et al. have shown that the S\textsubscript{1} → S\textsubscript{0} crossing
will most likely occur at $80^\circ - 90^\circ$ as shown in Figure 2.16.\textsuperscript{55} They showed it could be influenced by a substituent that changes the location of the conical intersection along the $\theta$ reaction coordinate.

![Figure 2.17: The energy difference in $S_1$ and $S_0$ states. Taken from Ref. 55.](image)

With more sophisticated theory using more accurate potential surfaces Sumita \textit{et al.}\textsuperscript{55} showed that for fulvene type molecules relaxation should take place at $0^\circ < \theta < 75^\circ$. That would result in a return to the initial configuration of $\theta = 0$ with no isomerization. A complete $180^\circ$ rotation was only accessible for angles $80^\circ - 90^\circ$.\textsuperscript{55} As seen in Figure 2.17, the most likely crossing occurs at a twist angle of $63^\circ$, resulting no photoisomerization. However, the introduction of the benzene rings and other substituents would stabilize the molecule in the region $80^\circ-90^\circ$ in order to allow the $180^\circ$ rotation of the exocyclic double bond.\textsuperscript{55} According to our studies, it appears that electron withdrawing substituents move
the crossing position to increase the photoisomerization probability.

**2.4.2 ATEF Molecular System**

The origin of the $H^+$ concentration dependence of $\Phi$ for ATEF is of interest. The increase in photoisomerization quantum yields in protonated ATEF relative to unprotonated ATEF can be due to several factors.

1. The observed $H^+$ dependence of $\Phi$ could be the result in changes in the solvent environment with higher $H^+$ concentration. We have studied ATEF under two acidic environments. The results for both are explained in next sections.

2. Alternatively, changes in $\pi$ bonding character in the dibenzofulvene rotor upon substitution could also affect quantum yields.

3. It is well known that the N–lone pair of an amino substituent can behave as an electron donor in photoinduced electron transfer (PET) processes.$^{61}$ PET quenching of excited states is well-known, and protonation of the amino substituent of ATEF could result in an increase in $\Phi$ relative to other substituents.

**2.4.3 TfOH Dependence**

The ATEF shows higher photoisomerization quantum yields when it is protonated with TfOH. Figure 2.13(c) shows the kinetics at 1 equivalents of TfOH. Comparing Figure 2.13(a) and 2.13(c), it is clear that the photoisomerization is more efficient (by 33 fold) with TfOH than for its unprotonated counterpart. The photoisomerization quantum yields
of the protonated amino form with different acid equivalents of TfOH at 266 nm and 310 nm excitation wavelengths are shown in Tables 2.1 and 2.2, respectively, of the Appendix section. Photodecomposition is relatively low in the TfOH study which suggests that TfOH would be a better candidate to control the photoisomerization quantum yield of ATEF along with giving higher quantum yields. To measure the protonation of Z-ATEF by TfOH, we did a $^1$H NMR titration. It reveals that Z-ATEF molecules are completely protonated at 1 equivalents of TfOH, which is shown in Figure 2.15 (a). In addition we found that the binding constant ($K_B$) associated with this process is greater than $10^8$ L mol$^{-1}$.

### 2.4.4 TFA Dependence

As seen in Figure 2.14(b), and Tables 2.3 and 2.4, addition of 1.5 equivalents of TFA increases the photoisomerization quantum yield of ATEF by more than a factor of 10 compared to its unprotonated counterpart in 266 nm excitation. The decrease in quantum yields at higher acid equivalents could be due to changes in the solvent properties or the solvation shell around the molecular actuator. For stilbene, it is well known that photoisomerization quantum yields are solvent dependent.29

For further understanding of this effect of protonation, as in the TfOH studies, $^1$H NMR studies were done. The protonation was monitored as a function of TFA equivalent along with selected peak shifts. To understand these effects better we have plotted peak shift as a function of TFA equivalents and this is shown in Figure 2.15(b). That figure reveals that the Z-ATEF is not fully protonated even after 30 equivalents of TFA have been added whereas the amino molecules are completely protonated upon addition of one equivalent of TfOH.
From the $^1$H NMR studies, we found that the binding constant associated with Z-ATEF and TFA ($K'_{b}$) is $1.22 \times 10^3$ L mol$^{-1}$, which is approximately $10^5$ times smaller than the value between Z-ATEF and TfOH. Another possibility for this peak like behavior may be due to the decomposition of ATEF/ATEFH$^+$ at higher acid concentrations. We may need to investigate other systems to understand this trend thoroughly.

2.4.5 TEA Dependence

A possible concern is whether small H$^+$ concentrations are present even in the absence of added acid, and that this small H$^+$ concentration is responsible for the measurable, though small, photoisomerization at [TFA] = 0 or [TfOH] = 0.

To investigate this possibility we added the base triethylamine (TEA). The deprotonation of Z-ATEF by the base does not significantly change the quantum yield of Z-ATEF and the system does not achieve the photo-stationary state even after long time irradiation (8 hrs). The photoisomerization quantum yields for Z-ATEF with different base equivalents are shown in Figure 2.14(c). From these results we discovered that there is no significant TEA (base) dependence for photoisomerization quantum yields.

For other motor compounds, such as NTEF and CTEF, protonation or deprotonation does not significantly change the quantum yields. For example the TFA dependence of NTEF is shown in Figure 2.18.
2.4.6 Change in (π) Electronic Character

Changes in photoisomerization quantum yields could also be due to the changes in electron densities in phenyl rings with protonation. For example, for benzene, NH$_2$ is an electron-donating group (EDG) and a strong phenyl ring activator whereas NH$_3^+$ is an electron withdrawing group (EWG) and a strong phenyl ring deactivator.\textsuperscript{56–60} In general, EDGs activate phenyl rings toward electrophilic substitution reactions whereas EWGs deactivate phenyls
rings toward electrophilic substitution reactions compared to unsubstituted benzene. Special
unpaired electrons (in this case from the N atom) can be donated to the ring, and
stabilize the transition state. Due to this –NH₂ and –NH₃⁺ substituents are located at the
opposite end of the Figure 2.19.

![Figure 2.19: Electrophilic aromatic substitution order for substituted benzene. Adapted from Ref. 56 and 57.](image)

Changing the aromatic electron density may increase the quantum efficiencies because
we observed that both CN and NO₂ are EWGs, and both yield higher quantum efficiencies
than our prototype, as shown in Table 1.2.32,33
2.4.7 Intramolecular Charge Transfer Hypothesis

Intramolecular charge transfer (ICT) could also support the fact that the Z - ATEF has a relatively low quantum yield. The full ICT mechanism for unprotonated ATEF is shown in Figure 2.20. The motor molecules are initially in the ground state (π - HOMO). Absorption results in a π - HOMO electron being promoted to the π - LUMO. The lone pair of –
NH₂ is closer and higher in energy than the π - HOMO of the motor unit, which results in hopping of one of those electrons to the vacant π - HOMO. This process results in the deactivation of the molecule as shown in step D in Figure 2.20. The π - LUMO electron on the excited molecule in D can go back to the nitrogen lone pair (step E). This causes efficient quenching of the excited state.

For protonated ATEF molecules, intramolecular charge transfer is not possible because there is no lone pair available. This process is shown in Figure 2.21.

Figure 2.21: Photoisomerization of protonated ATEF. A– ground state electronic configuration of the molecule. B – Excitation of the molecule. C – Excited motor molecule undergoes isomerization.

This change could be supporting the fact that protonated form has a higher quantum
efficiency.

2.5 Conclusions

Chapter 2 presented a method to control photoisomerization quantum yields of the amino substituted dibenzofulvenes (ATEF) as a function of TFOH and TFA. Z- ATEF has a very low photoisomerization quantum efficiency. We found that protonation does make it more efficient and 1.5 equivalents of TFA give the highest quantum yield and one or higher equivalents of TfOH maintain approximately the same quantum yield. This could be due to the lone pair of electrons on the nitrogen atom. The effect of those electrons can be avoided by protonating –NH$_2$ substituents by adding strong acids. But deprotonation with TEA does not significantly change the quantum yields. Also we discovered that quantum yields are lowered at higher acid concentrations of TFA even though the ATEF compound was not fully protonated whereas this is not observed with TfOH. This could be mainly due to the change in the properties of the solvent such as viscosity and ionic strength. In addition we found that for other motor compounds, such as NTEF and CTEF, protonation and deprotonation does not significantly affect the quantum yields. This discovery paves in new path to control the photoisomerization quantum yields in condensed phase at different acid environments, which could ultimately be used in switching and sensing applications. In other words with all these discoveries the Z-ATEF is a good candidate for a molecular motor which has both chemical and photo control characteristics. These molecules can be potentially used as light controlled actuators, storage registers and power sources.
2.6 Appendix - Data Tables

Each data point showed in Table 2.1 – 2.4 is an average of three trials and data points in Table 2.5 is an average of three trials except the zero equivalent experiments, for which three trials were performed.52

Table 2.1: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-ATEF irradiated at 266 nm and absorbance was detected at 266 nm as a function of different TfOH equivalents.

<table>
<thead>
<tr>
<th>TfOH Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.76 ± 0.55</td>
<td>0.41 ± 0.06</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>0.33</td>
<td>12.80 ± 1.16</td>
<td>7.30 ± 0.53</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>0.67</td>
<td>16.61 ± 1.50</td>
<td>9.54 ± 0.74</td>
<td>0.05 ± 0.03</td>
</tr>
<tr>
<td>1.00</td>
<td>24.61 ± 2.28</td>
<td>14.48 ± 1.17</td>
<td>0.09 ± 0.04</td>
</tr>
<tr>
<td>1.33</td>
<td>23.59 ± 2.19</td>
<td>13.47 ± 1.09</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td>2.00</td>
<td>26.79 ± 2.49</td>
<td>16.08 ± 1.32</td>
<td>0.09 ± 0.03</td>
</tr>
<tr>
<td>3.33</td>
<td>24.7 ± 2.31</td>
<td>14.22 ± 1.17</td>
<td>0.09 ± 0.04</td>
</tr>
<tr>
<td>6.67</td>
<td>25.94 ± 2.57</td>
<td>13.64 ± 1.19</td>
<td>0.06 ± 0.04</td>
</tr>
</tbody>
</table>

Table 2.2: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-ATEF irradiated at 310 nm and absorbance was detected at 266 nm as a function of different TfOH equivalents.

<table>
<thead>
<tr>
<th>TfOH Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.60 ± 0.20</td>
<td>1.10 ± 0.20</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>0.17</td>
<td>4.24 ± 0.36</td>
<td>4.14 ± 0.22</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>0.33</td>
<td>5.78 ± 0.43</td>
<td>5.38 ± 0.29</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>0.50</td>
<td>12.93 ± 0.94</td>
<td>11.74 ± 0.70</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td>0.67</td>
<td>17.03 ± 1.32</td>
<td>14.83 ± 0.98</td>
<td>0.12 ± 0.03</td>
</tr>
<tr>
<td>0.83</td>
<td>17.88 ± 1.40</td>
<td>16.02 ± 1.09</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td>1.00</td>
<td>21.21 ± 1.72</td>
<td>18.46 ± 1.29</td>
<td>0.18 ± 0.03</td>
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<tr>
<td>1.33</td>
<td>21.49 ± 1.71</td>
<td>19.28 ± 1.34</td>
<td>0.15 ± 0.03</td>
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<tr>
<td>1.67</td>
<td>20.10 ± 1.61</td>
<td>17.22 ± 1.21</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>2.00</td>
<td>20.52 ± 1.62</td>
<td>17.95 ± 1.23</td>
<td>0.15 ± 0.03</td>
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<td>3.33</td>
<td>17.75 ± 1.45</td>
<td>14.45 ± 1.00</td>
<td>0.13 ± 0.03</td>
</tr>
<tr>
<td>6.67</td>
<td>17.78 ± 1.53</td>
<td>12.63 ± 0.92</td>
<td>0.14 ± 0.03</td>
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Table 2.3: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-ATEF irradiated at 266 nm and absorbance was detected at 266 nm as a function of different TFA equivalents.

<table>
<thead>
<tr>
<th>TFA Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.76 ± 0.63</td>
<td>0.41 ± 0.06</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>0.5</td>
<td>1.64 ± 0.27</td>
<td>1.19 ± 0.08</td>
<td>0.24 ± 0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>6.02 ± 0.45</td>
<td>3.50 ± 0.18</td>
<td>0.16 ± 0.03</td>
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<tr>
<td>1.5</td>
<td>8.94 ± 0.69</td>
<td>5.49 ± 0.30</td>
<td>0.35 ± 0.03</td>
</tr>
<tr>
<td>2.0</td>
<td>3.53 ± 0.28</td>
<td>2.09 ± 0.19</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td>3.0</td>
<td>3.49 ± 0.26</td>
<td>2.08 ± 0.02</td>
<td>0.11 ± 0.02</td>
</tr>
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</table>

Table 2.4: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-ATEF irradiated at 310 nm and absorbance was detected at 266 nm as a function of different TFA equivalents.

<table>
<thead>
<tr>
<th>TFA Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.60 ± 0.20</td>
<td>1.10 ± 0.20</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>2.90 ± 0.45</td>
<td>2.80 ± 0.40</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>1.5</td>
<td>9.80 ± 1.50</td>
<td>9.02 ± 1.30</td>
<td>0.35 ± 0.03</td>
</tr>
<tr>
<td>2.0</td>
<td>7.55 ± 0.11</td>
<td>2.61 ± 0.02</td>
<td>0.47 ± 0.01</td>
</tr>
<tr>
<td>3.0</td>
<td>6.55 ± 0.08</td>
<td>2.44 ± 0.02</td>
<td>0.29 ± 0.01</td>
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</tbody>
</table>

Table 2.5: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-ATEF irradiated at 310 nm and absorbance was detected at 266 nm as a function of different TEA equivalents.

<table>
<thead>
<tr>
<th>TEA Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.60 ± 0.20</td>
<td>1.10 ± 0.20</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>0.00 ± 0.87</td>
<td>0.39 ± 0.42</td>
<td>0.30 ± 0.28</td>
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<td>2.0</td>
<td>0.37 ± 0.60</td>
<td>0.48 ± 0.48</td>
<td>0.32 ± 0.27</td>
</tr>
<tr>
<td>3.0</td>
<td>0.44 ± 0.30</td>
<td>0.47 ± 0.39</td>
<td>0.35 ± 0.03</td>
</tr>
</tbody>
</table>
Chapter 3

DTEF Molecular Motor Prototype.

3.1 Introduction to DTEF

The molecule 2-dimethylamino-9-(2,2,2-triphenylethylidene)fluorene (abbreviated to DTEF) is a member of the TEF family with a ball and stick structure shown in Figure 3.1.  

![Figure 3.1: The ball and stick structure of the E isomer of the –N(CH₃)₂ substituted TEF molecule.](image-url)
We have previously studied the ATEF molecule, where the –NH₂ group is the substituent attached on 2 position on TEF. We observed that upon protonation, photoisomerization efficiency can be enhanced dramatically. The purpose of this study is to test whether our prediction is valid for the –N(CH₃)₂ substituted motor molecule. We hypothesized that electron donating groups have tendency to lower the quantum yield and electron withdrawing groups have tendency to increase the quantum yields. The photochemistry of this molecule was studied using methods similar to those explained in chapter 2.

3.2 Experimental

DTEF was studied in a solution prepared by dissolving it in HPLC grade CH₃CN (purity greater than 99.9%) purchased from Aldrich. The solubility of DTEF was relatively low, estimated to be around 0.2 mM, and dissolution was accelerated by sonication. The DTEF solution has a yellow color in CH₃CN. To protonate DTEF, trifluoromethanesulfonic acid, commonly known as triflic acid (TfOH), and trifluoroacetic acid (TFA) were used. The protonation was done by adding pre-calculated amounts of acid diluted in CH₃CN. After the addition of acid, the mixture becomes a colorless solution. In order to deprotonate DTEF, triethylamine (TEA) base was added.

3.2.1 Sample Irradiation

The color of the solution disappears as acid is added to the DTEF solution. UV spectra as a function of added acid equivalents for both TFA and TfOH were recorded and are shown
in Figure 3.2 and in Figure 3.3, respectively.

Figure 3.2: UV-vis absorption spectra of Z–DTEF isomer in CH$_3$CN as a function of added TFA equivalents. The DTEF concentration is 0.17 mM. Added acid equivalents are also shown in the figure.
Figure 3.3: UV-vis absorption spectra of Z–DTEF isomer in CH$_3$CN as a function of added TfOH equivalents. The DTEF concentration is 0.17 mM. Added acid equivalents are also shown in the figure.

The experimental setup used in this study is the same as explained in Chapter 2. For this study a 310 nm photoisomerization wavelength was selected. The average pulse energy was set in the range of 0.4 – 0.6 mJ in the initial experiments. Later the average power was reduced to a range of 0.2 – 0.4 mJ but changing the laser power did not affect the re-
results. Laser pulse energies were measured using an ORION-PS power meter as in previous studies.

### 3.2.2 HPLC Studies

Photoisomerization of the DTEF in CH$_3$CN was investigated as a function of the number of added equivalents of trifluoroacetic acid (TFA), triflic acid (TfOH) and triethylamine (TEA). The mixtures were purged with solvent-saturated N$_2$ to remove any dissolved O$_2$.

The progress of photoisomerization was studied by HPLC. To separate E and Z isomer peaks, a CH$_3$OH: H$_2$O = 9:1 solvent system was used with a flow rate of 1.0 mL/min and products were detected at two pre-selected wavelengths of 254 nm and 300 nm. Chromatograms for unprotonated and protonated DTEF are shown in Figure 3.4 and Figure 3.5, respectively.
Figure 3.4: The HPLC for unprotonated Z-DTEF. Corresponding irradiation times in seconds are shown on each chromatogram on the left.

Unlike in the ATEF study, we did not have the other isomer (E-DTEF) to compare relative elution times of the E and Z isomer peaks. From our previous experience and the nature of the isomerization progress we identified the peak with shorter elution time to be E-DTEF and the peak with longer elution time to be Z-DTEF respectively.
As in the ATEF study, we have observed two significant features by HPLC. (1) As the irradiation time increases, new peaks with shorter elution times (between approximately 7 – 9 min) appear in the chromatograms, which may be related to unidentified photoproducts (Figure 3.4 and 3.5), (2) At very short elution times (2 – 2.5 min), a peak with approxi-
mately constant peak area appears regardless of protonation and irradiation status. For our calculations, we ignored that peak assuming it was due to impurities in the solvent. This was confirmed by injecting pure CH$_3$CN and watching the peak appear.

### 3.2.3 $^1$H NMR Studies

In addition, $^1$H NMR studies were performed with both acids in order to determine the proton binding constants. DTEF was dissolved in CD$_3$CN and the acid was used without dissolving in deuterated acetonitrile. A Varian 500 MHz NMR was used to record all NMR spectra. In this study two proton NMR peaks were monitored as a function of added acid equivalents. Those are the doublet at 6.154 ppm (due to the H atom on C1 position) and the doublet at 7.512 ppm (due to the H atom on the C4 position) in Figure 3.6. The proton

\[
X = N(CH_3)_2 \quad DTEF
\]

\[
X = NH(CH_3)_2^+ \quad HDTEF^+
\]

Figure 3.6: Locations of protons studied in NMR titrations. The peak at 6.154 ppm corresponding to the hydrogen on C1 and the peak at 7.512 ppm due to the hydrogen on C4.
NMR of DTEF is shown in Figure 3.7.

Figure 3.7: The $^1$H NMR spectrum of unprotonated Z-DTEF. Peak number labels represent the location of H atoms and can be found in Figure 3.6.

Figure 3.8 shows the peak shifts as a function of added TFA equivalents and Figure 3.9 shows peak shifts as a function of added TfOH equivalents.
Figure 3.8: The $^1$H NMR peak shifting of Z-DTEF as a function of added TFA equivalents. The added TFA equivalents are shown on the right side of the spectrum. The DTEF concentration is $1.92 \times 10^{-4}$ M.
Figure 3.9: The $^1$H NMR peak shifting of Z-DTEF as a function of added TfOH equivalents. The added TfOH equivalents are shown on the right side of the spectrum. The DTEF concentration is $1.92 \times 10^{-4}$ M.
3.3 Results and Data Analysis

The isomerization kinetics were analyzed as a function of the average number of absorbed photons per molecule, x(t), calculated using equation 2.1. An example of the photoisomerization kinetics for Z-DTEF is shown in Figure 3.10. The isomer fraction of each component, $f_i$, is determined by dividing the peak area under the particular chromatogram peak by the total peak areas,

$$f_i = \frac{A_i}{A_Z + A_E + A_D},$$

(3.1)

where $A_i$ is the area under the $i^{th}$ peak, $A_Z$ is the area under the peak of Z isomer, $A_E$ is the area under the peak of E isomer, and $A_D$ is the area under all decomposition peaks. Fits were calculated by using equations 2.8, 2.9 and 2.10. Fits for unprotonated and protonated (2 TFA equivalents and 2 TfOH equivalents) DTEF irradiated at 310 nm are also shown in Figure 3.10 as solid lines.
Figure 3.10: Mole fraction of DTEF isomers in CH$_3$CN as a function of the average number of 310 nm photons absorbed per molecule. The initial concentration of Z-DTEF is 0.19mM and $E$-DTEF = 0. (a) Unprotonated DTEF (b) protonated by 2 equivalents of TFA (c) protonated by 2 equivalents of TfOH. Dots are experimental measurements observed by HPLC peak ratios and solid curves are fits to the kinetic model explained in the text. The dark circles represent the Z isomer whereas the dark triangles represent the E isomer.

By a data analysis similar to that explained in chapter 2, the photoisomerization quantum yield can be obtained as a function of added acid equivalent or base equivalent. The
results for irradiation at 310 nm, and detection at 254 nm, are tabulated in Tables 3.1 –3.2 (Appendix) and are plotted in Figure 3.11. This shows that photoisomerization quantum yields are approximately the same at higher acid equivalents of TFA and TfOH.

Figure 3.11: Photoisomerization quantum yields as a function of (a) TfOH equivalents, (b) TFA equivalents, and (c) TEA equivalents. All experiments were performed at 310 nm excitation. The red dots represent $\Phi_{EZ}$ and the blue dots $\Phi_{ZE}$. The fits shown in (a) and (b) were calculated by using the method explained in Chapter 2.
3.4 Determination of Binding Constant

The reactions associated with protonation of DTEF with TfOH and TFA are,

\[
\text{TfOH} + \text{DTEF} \xrightleftharpoons{K_B} \text{DTEFH}^+ + \text{TfO}^-
\]  (3.2)

\[
\text{CF}_3\text{COOH} + \text{DTEF} \xrightleftharpoons{K'_B} \text{DTEFH}^+ + \text{CF}_3\text{COO}^-
\]  (3.3)

where \(\text{DTEFH}^+\) is the protonated form of DTEF, \(\text{TfO}^-\) is the anion formed after the ionization of TfOH and \(\text{CF}_3\text{COO}^-\) is the anion formed after the ionization of TFA. \(K_B\) and \(K'_B\) are the binding constants between DTEF /TfOH and DTEF /TFA respectively. Here we have assumed that both E and Z isomers have the same binding constants. The binding constants can be determined by using equation 2.11. From this method we found that \(K_B\) is greater than \(10^8\) L mol\(^{-1}\) and \(K'_B\) is \(1.77 \times 10^3\) L mol\(^{-1}\).

3.5 Discussion

The origin of the \(H^+\) concentration dependence of \(\Phi\) is of interest in both this and in the previous study explained in chapter 2. Comparing the amino (\(-\text{NH}_2\)) group on ATEF and the dimethylamino group (\(\text{–N(CH}_3\text{)}_2\)) on DTEF, the N atom on the DTEF has higher electron density on the than the N atom on the ATEF due to the fact that two methyl groups (\(-\text{CH}_3\)) on the DTEF are electron donating. This could lead the DTEF to have higher photoisomerization quantum yields compared to ATEF, even for the unprotonated molecule. In
addition, this can also be explained in terms of PET quenching related to dimethylamino substituted molecules. The acid dependence and the base dependence of the photoisomerization quantum yields of DTEF are discussed separately in the next sections.

3.5.1 Acid Dependence
Figure 3.10 (a,b,and c) shows the photoisomerization kinetics for unprotonated, protonated with 2 equivalents of TFA, and protonated with 2 equivalents of TfOH of Z-DTEF, respectively irradiated at 310 nm and detected at 254 nm. It is clear from these three plots that the photoisomerization is more efficient with both acids than for the unprotonated Z-DTEF motor molecule. The photoisomerization quantum yields of Z-DTEF with different acid equivalents of TfOH and TFA at 310 nm excitation wavelengths are shown in Table 3.1 and 3.2 respectively (See Appendix) and the graphical representation is shown in Figure 3.11.

As seen in Figure 3.11, it is clear that a plateau in photoisomerization quantum yields with TfOH experiments is achieved very quickly compared to TFA. The protonation with TfOH increases approximately 30-fold in $\Phi_{EZ}$ and 25-fold in $\Phi_{ZE}$. The photodecomposition is relatively low at shorter irradiation times but significant after 1 h irradiation. The average photodecomposition quantum yield is 0.44% for the Z-DTEF/TfOH system and 0.27% for the Z-DTEF/TFA system. Regardless of that, the super acid, TfOH, would be a better candidate to control the photoisomerization quantum yield of Z-DTEF.

$^1$H NMR can be used to test the status of protonation of Z-DTEF with either acid. It reveals that Z-DTEF molecules are completely protonated at 1 equivalent of TfOH as is
Figure 3.12: The $^1$H NMR peak shifts of Z-DTEF as a function of added acid equivalents (a) TfOH dependence (b) TFA dependence. The blue dots corresponding to the peak shift of H on C1 and red for the H on C4 of the motor molecule. The lines are theoretical fits for each titration.

shown in Figure 3.12(a). But Z-DTEF does not get fully protonated (see Figure 3.12(b)) until considerably larger equivalents of TFA are added. From these $^1$H NMR studies, the binding constant between Z-DTEF and TfOH was found to be greater than $10^8$ L$^{-1}$ mol
and that of the DTEF / TFA system was found to be $1.77 \times 10^3 \text{ L}^{-1} \text{ mol}$.

## 3.5.2 TEA Dependence

To find out whether the photoisomerization quantum yield of Z-DTEF can be completely switched off, we did the above experiments with a relatively strong base, TEA.

Figure 3.11(c) shows the effects of TEA on photoisomerization quantum yields at 310 nm irradiation as a function of TEA equivalents. Table 3.3 (Appendix) shows the corresponding quantum yield values along with photodecomposition quantum yields. For comparison, the graph is plotted with the quantum yields for unprotonated Z-DTEF. It is clear from the data that there is no significant effect on the quantum yields even after the addition of 10 equivalents of TEA. This proves the fact that this molecule can be used under various basic environments without changing the quantum yields. Also we noticed that the system does not achieve the photo-stationary state and it has a similar kinetic behavior to unprotonated Z-DTEF. The error bars associated with $\Phi_{ZE}$ are relatively high compared to $\Phi_{EZ}$.

In the Z-ATEF study we discovered that protonation increases the photoisomerization efficiency. According to that prediction the protonation of $-\text{N(CH}_3\text{)}_2$ should also increase the photoismerization efficiency.

The theoretical explanation related to the current work is similar to what was explained in Chapter 2.\textsuperscript{52} There we predicted that the electron-withdrawing character and electron-donating character would change the quantum yield associated with each substituent on the dibenzofulvene motor prototype. That prediction was proven to be true with the results of
the current study. In addition, the intramolecular charge transfer mechanism is still valid for this study.

3.6 Conclusions

Chapter 3 shows and proves the method presented in chapter 2 by using dimethylamino substituted dibenzofulvenes (DTEF) as a function of TFA and TfOH. Protonation makes quantum yields more efficient at higher equivalents of both TFA and TfOH but TfOH maintains approximately the same quantum yields. But deprotonation with TEA does not significantly change the quantum yields. As pointed out in chapter 2, this discovery paves a new way to control photoisomerization quantum yields in the condensed phase at different acid environments, which could ultimately be used in switching and sensing applications. In other words with all these discoveries, Z-DTEF is a good candidate for a molecular motor which has both chemical and photo control characteristics.
3.7 Appendix - Data Tables

Each data point showed here is an average of three trials.\textsuperscript{62}

Table 3.1: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-DTEF irradiated at 310 nm and absorbance was detected at 254 nm as a function of different TfOH equivalents.

<table>
<thead>
<tr>
<th>TfOH Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.06 ± 0.63</td>
<td>0.79 ± 0.06</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>0.5</td>
<td>14.64 ± 1.51</td>
<td>8.01 ± 0.72</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>1.0</td>
<td>29.20 ± 3.26</td>
<td>19.26 ± 1.97</td>
<td>0.36 ± 0.02</td>
</tr>
<tr>
<td>1.5</td>
<td>33.60 ± 3.57</td>
<td>24.05 ± 2.35</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td>2.0</td>
<td>30.86 ± 3.29</td>
<td>21.54 ± 2.12</td>
<td>0.47 ± 0.02</td>
</tr>
<tr>
<td>3.0</td>
<td>29.13 ± 3.14</td>
<td>20.61 ± 2.04</td>
<td>0.46 ± 0.02</td>
</tr>
<tr>
<td>5.0</td>
<td>30.38 ± 3.17</td>
<td>22.24 ± 2.10</td>
<td>0.43 ± 0.03</td>
</tr>
<tr>
<td>10.0</td>
<td>30.14 ± 3.20</td>
<td>22.27 ± 2.15</td>
<td>0.38 ± 0.03</td>
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</tbody>
</table>

Table 3.2: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-DTEF irradiated at 310 nm and absorbance was detected at 254 nm as a function of different TFA equivalents.

<table>
<thead>
<tr>
<th>TFA Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.06 ± 0.63</td>
<td>0.79 ± 0.06</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>0.5</td>
<td>5.17 ± 0.27</td>
<td>2.49 ± 0.08</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>6.44 ± 0.69</td>
<td>3.33 ± 0.30</td>
<td>0.23 ± 0.03</td>
</tr>
<tr>
<td>1.5</td>
<td>10.00 ± 0.69</td>
<td>5.28 ± 0.30</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>2.0</td>
<td>11.19 ± 0.28</td>
<td>6.29 ± 0.19</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>3.0</td>
<td>14.18 ± 0.26</td>
<td>8.18 ± 0.02</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td>5.0</td>
<td>22.97 ± 0.26</td>
<td>14.28 ± 0.02</td>
<td>0.37 ± 0.02</td>
</tr>
<tr>
<td>10.0</td>
<td>25.00 ± 0.26</td>
<td>17.07 ± 0.02</td>
<td>0.44 ± 0.02</td>
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</table>
Table 3.3: Photoisomerization quantum yields $\Phi_{ZE}$ and $\Phi_{EZ}$ and photodecomposition quantum yield $\Phi_D$ for Z-DTEF irradiated at 310 nm and absorbance was detected at 254 nm as a function of different TEA equivalents.

<table>
<thead>
<tr>
<th>TEA Equivalents</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
<th>$\Phi_D/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.06 ± 0.63</td>
<td>0.79 ± 0.06</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>0.00 ± 2.87</td>
<td>0.39 ± 0.42</td>
<td>0.30 ± 0.28</td>
</tr>
<tr>
<td>5.0</td>
<td>0.37 ± 3.00</td>
<td>0.48 ± 0.48</td>
<td>0.32 ± 0.27</td>
</tr>
<tr>
<td>10.0</td>
<td>0.44 ± 1.30</td>
<td>0.47 ± 0.39</td>
<td>0.35 ± 0.03</td>
</tr>
</tbody>
</table>
Chapter 4

Computational Calculations of

Substituted Dibenzofulvene Molecules.

4.1 Introduction

From our studies on the family of TEF molecules, we have seen that substitution changes photoisomerization quantum yields. We can use the concept of the substituent constant, $\sigma^{65-69}$ to explain the changes in the photoisomerization quantum yield. Figure 4.1 shows the location of $X$ with respect to $C^*$ on the meta position and with respect to $C^{**}$ on the para position.
Figure 4.1: Motor molecule, where X = H for TEF, CN for CTEF, NO$_2$ for NTEF, C(CH$_3$)$_3$ for TTEF, I for ITEF, NH$_2$ for ATEF, NH$_3^+$ for ATEFH$^+$, N(CH$_3$)$_2$ for DTEF and NH(CH$_3$)$_2^+$ for DTEFH$^+$.

Table 4.1 shows experimental $\Phi_{EZ}$ values, $\Phi_{ZE}$ values along with reported $\sigma_{meta}$ and $\sigma_{para}$ values for aromatic substitution. There is no direct relationship to correlate photoisomerization quantum yields and $\sigma$ values. As far as we are aware, there are no reported $\sigma$ values for $\text{–NH}_3^+$ and $\text{–NH}(	ext{CH}_3)_2^+$ substituents available in literature. But the values for $\text{–N}(	ext{CH}_3)_3^+$ are available such that $\sigma_{meta} = 0.88$ and $\sigma_{para} = 0.82$.  

Table 4.1: Comparison of substituent constants ($\sigma_{meta}$ and $\sigma_{para}$) and photoisomerization quantum yields ($\Phi_{ZE}$ and $\Phi_{EZ}$) for the substituents studied. ATEFH$^+$ and DTEFH$^+$ represent protonated forms of ATEF and DTEF with TfOH. $\sigma$ values were taken from Ref. 65, 66, and from 67.

<table>
<thead>
<tr>
<th>Motor Molecule</th>
<th>$\sigma_{meta}$</th>
<th>$\sigma_{para}$</th>
<th>$\Phi_{ZE}/10^{-2}$</th>
<th>$\Phi_{EZ}/10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATEF</td>
<td>-0.161</td>
<td>-0.66</td>
<td>0.76</td>
<td>0.41$^{32}$</td>
</tr>
<tr>
<td>ATEFH$^+$</td>
<td>NR</td>
<td>NR</td>
<td>25.13</td>
<td>14.38</td>
</tr>
<tr>
<td>ITEF</td>
<td>+0.353</td>
<td>+0.180</td>
<td>50.00</td>
<td>46.00$^{33}$</td>
</tr>
<tr>
<td>CTEF</td>
<td>+0.856</td>
<td>+0.660</td>
<td>35.00</td>
<td>42.00$^{33}$</td>
</tr>
<tr>
<td>NTEF</td>
<td>+0.710</td>
<td>+0.778</td>
<td>25.00</td>
<td>18.00$^{33}$</td>
</tr>
<tr>
<td>DTEF</td>
<td>-0.211</td>
<td>-0.205</td>
<td>1.06</td>
<td>0.79</td>
</tr>
<tr>
<td>DTEFH$^+$</td>
<td>NR</td>
<td>NR</td>
<td>30.00</td>
<td>25.00</td>
</tr>
<tr>
<td>TTEF</td>
<td>-0.069</td>
<td>-0.170</td>
<td>7.00</td>
<td>10.00$^{32}$</td>
</tr>
</tbody>
</table>

NR - Not reported in literature.

Even though there is no quantitative relationship we can deduce some features from Table 4.1
(1) The substituents with large quantum yields always have positive $\sigma$ values.

(2) Only ATEF, DTEF and TTEF have negative $\sigma$ values.

(3) Once ATEF and DTEF are protonated, a significant change in quantum yield implies that ATEFH$^+$ and DTEFH$^+$ may have positive $\sigma$ values. In other words, negative values of $\sigma$ are associated with low photoisomerization quantum yields whereas positive values are associated with higher quantum yields.

The above statements are supported by the electron-withdrawing nature of $\text{–NH}_3^+$ and $\text{–NH(CH}_3)_2^+$ attached to phenyl groups. That shows that protonation or addition of an alkyl group to an N atom would change the electronic character dramatically. Computational chemistry can be used to understand these effects.

Computational chemistry simulates chemical structures, chemical reactions and intermediates numerically. This allows chemists to study chemical reactions, and chemical phenomena just by running a simulation using a computer. There are two areas of computational chemistry.

(1) Molecular Mechanics (MM) - Using the laws of classical physics to predict the properties and structures of molecules.

(2) Electronic Structure Theory - Using the laws of quantum mechanics by solving the Schrödinger equation.

Computational chemistry studies of fulvene by Sumita and coworkers$^{55}$ showed that there is a conical intersection (CI) between the excited $S_1$ surface and the ground $S_0$ surface.
of fulvene at a torsional angle about the exocyclic C=C bond of 63° as seen in Figure 2.17. For an efficient photoisomerization the CI must be close to 90°.

The dibenzofulvene rotor in our system has two phenyl groups fused on both sides of fulvene as in Figure 1.12. Having two phenyl rings fused to the fulvene moiety must alter the electronic properties of fulvene. Attached substituents on one of the phenyl rings could also affect the electronic density. The main goal of this study is to locate ground state and excited states of the dibenzofulvene type molecules shown in Figure 4.2. In addition, computational studies of the dibenzofulvene unit is much easier than our motor molecules crowded with phenyl rings.

Figure 4.2: Dibenzofulvene unit. This is the rotor part of the molecular motor (Figure 1.12) studied in chapters 2 and 3. X = H for Dibenzofulvene (DBF), CN for Cyano (CDBF), NO₂ for Nitro (NDBF), C(CH₃)₃ for T-Butyl (TDBF), NH₂ for Amino (ADBF) and N(CH₃)₂ for Dimethylamino (DDBF).
4.2 Computational Method

Several levels of theory have been used in these calculations. To map the ground state, \((S_0)\) of all the molecules, the B3LYP method hybrid features was used with the 6-31G basis set.\(^{70,71}\) All molecules have been optimized and torsion energies about the C=C bond have been calculated. Structural parameters such as bond lengths, bond angles and dihedral angles were obtained. In this study, two constraints were applied to make sure results are consistent and acceptable. The dihedral angles shown in Figure 4.3 were kept constant so that they would force planarity of the C atoms on the five membered ring with the C=C bond. To map the ground state potential energy surface, twisting about the C=C bond was done in 15° intervals from 0° to 90°. The 90° to 180° region was generated with an assumption of symmetry.

![Figure 4.3: Constraint applied during rotation about the C=C bond. Dihedral angles due to carbon atoms 6, 5, 1, 2 and carbon atoms 6, 5, 4, 3 were fixed at 0° or 180°.](image)

The mapping of the first excited state (\((S_1)\)) is more complicated than that of the ground
state. Initially, cartesian coordinates for a particular rotation were generated and used as the geometry optimized file for the rest of the calculation. Mainly the CIS level of theory\textsuperscript{72,73} was used. There are several possible excitations due to the high number of electrons. The CIS method provides an easy way to calculate three excitations at the same time. They will be discussed in the “Results and Discussion” section along with the resulting molecular orbitals obtained by using Avogadro software.\textsuperscript{49} In addition, the oscillator strengths for those transitions were also calculated by the CIS method in the equilibrium geometry. The oscillator strength, $f$, is a measure of the intensity of a transition, and is a dimensionless quantity.\textsuperscript{53,74} Oscillator strength can be used to compare different transitions. The value of the oscillator strengths can range from 0 to 1. A strong transition will have an $f$ value close to 1. In addition, the transitions originating from a single level will sum to 1, $\Sigma f_i = 1$.

### 4.3 Results and Discussion

It is clear from Figure 4.4, Figure 4.5 and Figure 4.6 that the HOMO –1, HOMO, LUMO and LUMO + 1 of ADBF, CDBF, and DDBF (i.e molecular orbitals shown in bottom) are very similar to the ATEF, CTEF and DTEF molecular orbitals shown in (a) of each figure. Therefore our studies were mainly focused on substituted dibenzofulvene molecules.
Figure 4.4: Comparison of molecular orbitals. (a) ATEF molecule, (b) ADBF molecule.
Figure 4.5: Comparison of molecular orbitals. (a) CTEF molecule, (b) CDBF molecule.
Figure 4.6: Comparison of molecular orbitals. (a) DTEF molecule, (b) DDBF molecule.
4.3.1 Dibenzofulvene Unit, X = H

Results obtained from this molecule can be considered as a reference for substituted molecules. The change in the C=C bond length and the pyramidalization of the HCH bond angle due to rotation about the C=C bond in the ground state are shown in Figure 4.7. The C=C bond length changes from 1.342 Å to 1.374 Å as molecule is twisted about C=C bond. In addition, the HCH bond angle changes from 116.445° to 98.823° during a 0° to 90° rotation about the C=C bond. This causes the hybridization of carbon atom on the far end of the exocyclic bond to change from sp² character to sp³ character. At 90° of twisting, the exo-cyclic carbon carbon double bond becomes a partial double bond.

The transitions from the ground state to the excited states were calculated by using the CIS method and are shown below with plots of the HOMO -1, HOMO, LUMO and LUMO+1. Inspection of the nodal structure along the photoactive exocyclic C=C bond (Figure 4.8) shows that (HOMO -1) has bonding character, the HOMO non-bonding character, and the LUMO and LUMO + 1 anti-bond character with respect to the C=C bond. The S₀ → S₁ and S₀ → S₂ transitions are relatively weak, and the overall intensity distribution is qualitatively consistent with the measured absorption spectrum in Figure 1.13, although the absorption energies calculated are blue-shifted with respect to the experimental spectra.
4.3.2 Amino Substituted Dibenzofulvene Unit, $X = \text{NH}_2$

Here, two cases are considered.

(I) Unprotonated amino substituted dibenzofulvene unit (ADB). Ground state potential energy surface was generated by a similar method explained previously.

(II) Protonated amino substituted dibenzofulvene unit (HADBF$^+\text{)}$). A proton was added to the N atom on the $-\text{NH}_2\text{ group and the geometry optimized structure was used for calculations.}$
Both these cases are discussed together for convenience. A similar trend in C=C bond lengths and HCH bond angles along with rotation about the C=C is seen in Figure 4.9 compared to Figure 4.7.

In addition, in the ground state, the C–N bond lengths are different for the protonated and unprotonated molecules. Table 4.2 shows a bond length comparison of molecules studied here along with literature values.

From these values it can be confirmed that the protonated molecule has a C–N bond similar in character to a C–N single bond found in ammonium salts. Protonation of the
amino group lowers the π–bonding character of the C–N bond so that electron donation from the N atom to the phenyl ring is lowered. This can be further observed from a molecular orbital comparison of the unprotonated (Figure 4.10) and protonated (Figure 4.11) molecules.

Several observations can be seen by comparing Figure 4.10 and Figure 4.11:

(I) The $S_0 \rightarrow S_1$ transition (HOMO $\rightarrow$ LUMO) is relatively weak in ADBF ($f = 0.0587$)
Table 4.2: The C–N bond length comparison of amino substituted dibenzofulvene (ADBF) and protonated ABDF (HADBF\(^+\))

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calculated Bond Length (Å)</th>
<th>Literature values (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADBF</td>
<td>1.392</td>
<td>1.395 - C(sp(^2)) and N in aromatics.(^75)</td>
</tr>
<tr>
<td>HADBF(^+)</td>
<td>1.493</td>
<td>1.465- C (sp(^3)) and N atom in an ammonium salt.(^75)</td>
</tr>
</tbody>
</table>

Figure 4.10: Molecular orbitals of the ADBF rotor calculated by the CIS method. Major transitions, excitation energies in eV, and oscillator strengths are also shown in the figure. The energy level spacings are not to scale.

where as it is strong in HADBF\(^+\) \((f = 0.1210)\).

(II) The \(S_0 \rightarrow S_3\) transition (HOMO - 1 \(\rightarrow\) LUMO) and is the most intense transition in ADBF whereas the \(S_0 \rightarrow S_1\) transition (HOMO \(\rightarrow\) LUMO) and \(S_0 \rightarrow S_3\) transition (HOMO \(\rightarrow\) LUMO + 1) in HADBF\(^+\) become stronger since they originated from
bonding orbitals. This could support higher photoisomerization quantum yields as the HOMO becomes bonding once it is protonated.

(III) The HOMO - 1 → LUMO and HOMO → LUMO + 1 transitions, have reversed their energetic ordering.

(IV) The HOMO has non-bonding C=C character in ADBF whereas the HOMO has bonding C=C character in HADBF+. Also, electron delocalization on the N atom in HADBF+ significantly decreased by protonation which suggests that –NH3+ group
does not communicate with adjacent phenyl rings as much as in ADBF. It is evident that electron donation from the –NH$_2$ group can be controlled by protonation which supports the intramolecular charge transfer hypothesis explained in chapter 2.

### 4.3.3 Dimethylamino Substituted Dibenzofulvene Unit, $X = N(CH_3)_2$

Here also two cases are considered.

(I) Unprotonated dimethylamino substituted dibenzofulvene unit (DDBF). The potential energy surface was generated by a method similar to those explained previously.

(II) Protonated dimethylamino substituted dibenzofulvene unit (HADBF$^+$). A proton was added to the N atom on the –N(CH$_3$)$_2$ group and the geometry optimized structure was used for calculations.

A similar trend was observed in changes in bond lengths and bond angles as in Figure 4.7. From the ground state calculations on DDBF we found that C–N bond lengths are different for the protonated and unprotonated molecules. Table 4.3 shows a bond length comparison of the molecules studied here along with literature values. The values in Table 4.3 suggest that the protonated molecule has a C–N bond similar to a character of C–N single bond found in ammonium salts. Molecular orbitals for DDBF and HADBF$^+$ are shown in Figure 4.12 and in Figure 4.13, respectively.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calculated Bond Length (Å)</th>
<th>Literature values (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDBF</td>
<td>1.399</td>
<td>1.395 - C(sp$^2$)and N in aromatics. 75</td>
</tr>
<tr>
<td>HDDBF$^+$</td>
<td>1.498</td>
<td>1.465- C(sp$^3$) and N atom in an ammonium salt. 75</td>
</tr>
</tbody>
</table>
As in the ADBF study, several observations are of interest in comparing Figure 4.12 and Figure 4.13.

(I) The $S_0 \rightarrow S_1$ transition (HOMO $\rightarrow$ LUMO) is relatively weak in DDBF ($f = 0.0875$) where as it is strong in HDDBF$^+$ ($f = 0.1175$). This is due to the fact that HDDBF$^+$ has a bonding HOMO whereas DDBF has non-bonding HOMO. In both cases, the LUMOs have anti-bonding character.

(II) The HOMO - 1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO + 1 transitions, have reversed their
Figure 4.13: Molecular orbitals of the HDDBF$^+$ rotor calculated by the CIS method. Major transitions, excitation energies in eV, and oscillator strengths are also shown in the figure. The energy level spacings are not to scale.

energetic ordering in HDDBF$^+$

(III) The change in bonding character in the HOMO also suggests that the –NH(CH$_3$)$_2^+$ group on HDDBF$^+$ acts as an independent unit similar to –NH$_3^+$ in HADBF$^+$. This means the electron donation from the –N(CH$_3$)$_2$ group can be controlled by protonation.
4.3.4 Cyano (X = CN), Nitro(X = NO$_2$), and T-Butyl (X = C(CH$_3$)$_3$) Substituted Dibenzofulvene Unit

In all these three cases a similar trend was observed in changes in bond lengths and bond angles as seen in Figure 4.7.

![Molecular orbitals of the CDBF rotor calculated by the CIS method](image)

Figure 4.14: Molecular orbitals of the CDBF rotor calculated by the CIS method. Major transitions, excitation energies in eV, and oscillator strengths are also shown in the figure. The energy level spacings are not to scale.
Figure 4.15: Molecular orbitals of the NDBF rotor calculated by the CIS method. Major transitions, excitation energies in eV, and oscillator strengths are also shown in the figure. The energy level spacings are not to scale.

Comparing Figure 4.14 and Figure 4.15, it is clear that the \( S_0 \rightarrow S_1 \), or HOMO \( \rightarrow \) LUMO, transitions for CTEF and NTEF have oscillator strengths greater than 0.2 whereas Figure 4.16 shows that the \( S_0 \rightarrow S_1 \) transition has a smaller oscillator strength for TDBF. But all three \( S_0 \rightarrow S_1 \) transitions originated from C=C non-bonding molecular orbitals. The small oscillator strength of the \( S_0 \rightarrow S_1 \) transition in TDBF supports its relatively low photoisomerization quantum yield as was the case for ADBF and DDBF.
Figure 4.16: Molecular orbitals of the TDBF rotor calculated by the CIS method. Major transitions, excitation energies in eV, and oscillator strengths are also shown in the figure. The energy level spacings are not to scale.

Table 4.4 shows oscillator strengths determined by CIS calculations for all major transitions discussed in this chapter along with the photoisomerization quantum yields for the TEF family molecules.
Table 4.4: Oscillator strengths (f) for transitions for DBF type molecules along with quantum yields (Φ) for TEF type molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( S_0 \rightarrow S_1 )</th>
<th>( S_0 \rightarrow S_2 )</th>
<th>( S_0 \rightarrow S_3 )</th>
<th>( \Phi_{EZ} )</th>
<th>( \Phi_{ZE} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBF</td>
<td>0.0511</td>
<td>0.0838</td>
<td>0.3898</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>TDBF</td>
<td>0.0751</td>
<td>0.1246</td>
<td>0.3511</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>ADBF</td>
<td>0.0587</td>
<td>0.2209</td>
<td>0.3005</td>
<td>0.0076</td>
<td>0.0041</td>
</tr>
<tr>
<td>HADBF(^+)</td>
<td>0.1210</td>
<td>0.1956</td>
<td>0.3849</td>
<td>0.25</td>
<td>0.16</td>
</tr>
<tr>
<td>DDBF</td>
<td>0.0875</td>
<td>0.2846</td>
<td>0.2682</td>
<td>0.011</td>
<td>0.0079</td>
</tr>
<tr>
<td>HDDBF(^+)</td>
<td>0.1175</td>
<td>0.2395</td>
<td>0.2912</td>
<td>0.30</td>
<td>0.21</td>
</tr>
<tr>
<td>CDBF</td>
<td>0.2310</td>
<td>0.1346</td>
<td>0.3585</td>
<td>0.40</td>
<td>0.45</td>
</tr>
<tr>
<td>NDBF</td>
<td>0.2829</td>
<td>0.2066</td>
<td>0.1816</td>
<td>0.25</td>
<td>0.17</td>
</tr>
</tbody>
</table>

As seen in Table 4.4 whenever, oscillator strengths are relatively small for the HOMO \( \rightarrow \) LUMO (\( S_0 \rightarrow S_1 \)) transition, the photoisomerization quantum yields are also low. It is clear that the \( S_0 \rightarrow S_1 \) transition is stronger when substituents are electron withdrawing groups such as –CN or –NO\(_2\). In addition, –NH\(_2\) and –N(CH\(_3\))\(_2\) are electron donating groups (see Table 4.1) and have relatively low photoisomerization quantum yields as well as smaller oscillator strengths. But once they are protonated to –NH\(_3^+\) and –NH(CH\(_3\))\(_2^+\) they become strong electron withdrawing groups and they have relatively high oscillator strengths. These transitions are of interest because they have excitation energies in the 260 nm - 270 nm region.
4.4 Conclusions

Here we have shown a method to understand possible transitions in the molecular motor prototype we have studied. We discovered that the electron densities of HOMO - 1, HOMO, LUMO and LUMO + 1 are concentrated on the rotor part of our molecules. Therefore, attention was focused on the study of the rotor part of the motor molecule. Almost all these molecules have non-bonding HOMOs and anti-bonding LUMOs. But once ADBF and DDBF are protonated, their HOMOs become bonding in character, which results in stronger HOMO $\rightarrow$ LUMO transitions. This supports higher photoisomerization quantum yields in the HATEF$^+$ and HDTEF$^+$ molecules as discussed in Chapters 2 and 3, respectively.
Chapter 5

Appendix

5.1 Solution Preparation for Acid Additions to Motor Prototype

Acid is added to acetonitrile solution of motor prototype in the form of an acid solution in acetonitrile. The recipe is the same for TFA and TfOH.

(a) The mass \( m \) if acid in acetonitrile solution is given by

\[ m = \rho \times v \]  \hspace{1cm} (5.1)

where \( \rho \) is the density of acid and \( v \) is the volume of the acid used to prepare the acid solution in 99.9% HPLC grade acetonitrile. The purity of TFA and TfOH was 99%. To
account for the acid purity, we modify Eq. 5.1 to be

\[ m = (0.99) \rho \times v \quad , \tag{5.2} \]

The number of acid moles present in that solution is given by,

\[ n = \frac{m}{M} = \frac{(0.99) \rho \times v}{M} \quad , \tag{5.3} \]

where \( M \) is the molar mass of the acid. The concentration of the acid is then

\[ [HA] = \frac{n}{V} = \frac{(0.99) \rho \times v}{M \times V} \quad , \tag{5.4} \]

where \( V \) is the volume of 99.9% HPLC grade acetonitrile solution. For TFA the concentration, \([TFA]\), in the 99.9% HPLC grade acetonitrile we prepared was 0.269 M and for TfOH the concentration was 0.349 M.

(b) 3 mL of the ATEF solution, prepared in 99.9% HPLC grade acetonitrile by dissolving ATEF ([ATEF] = 0.5 mM), was taken into a cuvette.

(c) The amount of acid needed to protonated ATEF by a 1:1 ratio was calculated. Eg:

Assume the concentration of ATEF is 0.5 mM and 3 mL of it is used for the experiment.

The volume of TFA (\( V_{\text{acid}} \)) from the above solution required to protonate ATEF at 1:
1 equivalent is given by

\[ V_{acid} = \frac{0.5 \times 10^{-3} \text{ mol L}^{-1} \times 3 \times 10^{-3} \text{L}}{0.269 \text{ mol L}^{-1}} = 5.58 \mu \text{L} \quad (5.5) \]

Using a micro-pipette we can measure 5.6 \( \mu \text{L} \).

(d) 5.6 \( \mu \text{L} \) of TFA from solution prepared in step (a) were added to the ATEF in step (b) to protonate by one equivalent. If it were two equivalents, then 11.2 \( \mu \text{L} \) were added and so on.

Similar calculations were done to protonate with TfOH and to deprotonate with TEA.

5.2 Assumptions

Several assumption have been made deriving equations 2.8 - 2.10 explained in chapter 2.

(1) Optically dense solution; all photons absorbed.

![Figure 5.1: The sample cuvett for a typical irradiation experiment. I\(_s\) denotes the intensity of incident beam and I denotes the intensity of transmitted beam.](image-url)
The Beer Lambert law\textsuperscript{26,77} for the system shown in Figure 5.1 can be written as follows:

\[
I = I_0 e^{-\varepsilon cl} \quad (5.6)
\]

where \(I\) is the intensity of transmitted beam, \(I_0\) is the intensity of incident beam, \(\varepsilon\) is the molar absorptivity of isomer, \(c\) is the concentration, and \(l\) is the path length in cm. Substituting the values for a typical experiment (\(\varepsilon = 25000 \text{ L cm}^{-1} \text{ mol}^{-1}\), \(c = 0.0005 \text{ mol L}^{-1}\), and \(l = 1 \text{ cm}\)) for an ATEF experiment irradiated at 266 nm gives,

\[
\frac{I}{I_0} = 3.73 \times 10^{-6} \quad (5.7)
\]

which is negligible.

(2) Constant photon flux

(3) Solution is stirred; all molecules have equal probability to absorb photons

### 5.3 Calculation of Number of Photons Absorbed by Molecule

This section explains and presents a sample calculation of how to determine the number of photons absorbed by motor molecules.

Assume the experiment is performed at a wavelength of 266 nm. The energy of the
photons is given by

\[ E = h\nu = \frac{hc}{\lambda}, \tag{5.8} \]

where \( h \) is the Plank constant, \( \nu \) is the frequency of laser light, \( c \) is the speed of light in vacuum, and \( \lambda \) is the wavelength of light. By substituting the values for \( h \) and \( \nu \) we get the energy, \( E = 7.44 \times 10^{-19} \) J / photon. If the average pulse energy is set to be 500 \( \mu \) J, the number of photons per pulse (\( P \)) is given by,

\[ P = \frac{500 \times 10^{-6}}{7.44 \times 10^{-19}} \tag{5.9} \]

This results in \( 6.7 \times 10^{14} \) photons/pulse. Since the laser has a repetition rate of 10 Hz, we have \( 6.7 \times 10^{15} \) photons/second.

If the concentration of motor prototype in the test solution is \( 5.00 \times 10^{-7} \) mol L\(^{-1} \), in 3 mL of solution has \( 3.11 \times 10^{17} \) molecules. The starting volume of the solution is 3 mL. Therefore, number of photons per molecule per second is given by,

\[ \frac{6.7 \times 10^{15}\text{ photons/s}}{3.11 \times 10^{17}\text{ molecules}} = 0.02514 \text{ photons/molecule.s} \tag{5.10} \]

If that solution was irradiated 100s, there would be 2.154 photons per molecule. This is the number shown in the x- axes of kinetics plots in Chapter 2 and 3 as “Photons/Molecule”.
5.4 Determination of the Binding Constant

This is an important quantity that determines how much the molecules want to bind to each other. In order to determine the binding constants for equations 2.3, 2.4, 3.3 and 3.4, the following derivation was done by using the recipe explained in reference 44. As an example, the process shown in equation 2.3 is explained in detail here. The proton NMR peak shift in equation 2.3 can be written as the following,

\[ \delta_{obs} = N_{Z-ATEF} \delta_{Z-ATEF} + N_{Z-ATEFH^+} \delta_{Z-ATEFH^+} \]  

(5.11)

where \( N_{Z-ATEF} \) is the mole fraction of unprotonated \( Z \)-ATEF, \( \delta_{Z-ATEF} \) is the proton chemical shift for unprotonated \( Z \)-ATEF, \( N_{Z-ATEFH^+} \) is the mole fraction of \( Z - ATEFH^+ \) and \( \delta_{Z-ATEFH^+} \) is the proton chemical shift for \( Z - ATEFH^+ \). This equation is valid for a system where a rapid exchange is possible and can be rewritten as the following,

\[ \delta_{obs} = \frac{[Z - ATEF]}{[Z - ATEF] + [Z - ATEFH^+]} \delta_{Z-ATEF} + \frac{[Z - ATEFH^+]}{[Z - ATEF] + [Z - ATEFH^+]} \delta_{Z-ATEFH^+} \]  

(5.12)

The binding constants (\( K_B \) values) associated with any chemical reactions mentioned above can be determined by using the following equation.

\[ K_B = \frac{\Delta \delta_{obs}}{(\Delta \delta_{\infty} - \Delta \delta_{obs})([A_c] - \frac{\Delta \delta_{obs} \times [M]}{\Delta \delta_{\infty}})} \]  

(5.13)

where \( \Delta \delta_{obs} \) is the peak shift of choice observed in ppm, \( \Delta \delta_{\infty} \) is the peak shift when the
system is fully protonated, and \([A_{o}]\) is the initial concentration of the acid and \([M]\) is the initial concentration of the motor molecule under the study.

### 5.4.1 Calculation of Fit to Experimental Quantum Yields

As the acid is added to the motor molecule, there will be both protonated and unprotonated molecules. The effective photoisomerization quantum yield in such a system, due to both protonated and unprotonated motor molecules, can be written as

\[
\Phi_{\text{eff}} = f_{\text{ATEF}}\Phi_{\text{ATEF}} + f_{\text{ATEFH}+}\Phi_{\text{ATEFH}^+},
\]

(5.14)

where \(\Phi_{\text{eff}}\) is the photoisomerization quantum yield calculated, \(f_{\text{ATEF}}\) is the mole fraction of ATEF in the NMR solution under study, \(\Phi_{\text{ATEF}}\) is the photoisomerization quantum yield due to unprotonated ATEF observed experimentally, \(f_{\text{ATEFH}^+}\) is the fraction of ATEFH\(^+\) in NMR solution under the study and \(\Phi_{\text{ATEFH}^+}\) is the average photoisomerization quantum yield due to protonated ATEF observed experimentally.

For convenience the symbols A, B and AB are used throughout the derivation, where A = ATEF, B = H and AB = ATEFH\(^+\). Using new symbols the equation 5.14 can be rewritten as

\[
\Phi_{\text{eff}} = f_A\Phi_A + f_{AB}\Phi_{AB}
\]

(5.15)

Since \(f_A\) can be expressed in terms of \([A]\), \([B]\) and \([AB]\), the equation 5.15 can be expressed in terms of molarity units as following.
\[ \Phi_{eff} = \frac{[A]}{[A] + [AB]} \Phi_A + \frac{[AB]}{[A] + [AB]} \Phi_{AB} \] (5.16)

The equilibrium constant associated with the equation 2.3 is as following.

\[ K_B = \frac{[AB]}{([A_o] - [AB])([B_o] - [AB])} \] (5.17)

Substituting the value of [AB] from equation 5.16 on 5.17, and rearranging gives an equation which can be rearranged to give a quadratic equation of \( \Phi_{eff} \) as following.

\[
0 = \Phi_{eff}^2 + \left\{ (\Phi_\infty + \Phi_A) + (\Phi_\infty - \Phi_A) \frac{[B_o]}{[A_o]} + \frac{(\Phi_\infty - \Phi_A)}{K_B[A_o]} \right\} \Phi_{eff} \\
+ \left\{ (\Phi_\infty - \Phi_A) \frac{[B_o]}{[A_o]} + \Phi_\infty \Phi_A + \Phi_A \frac{(\Phi_\infty - \Phi_A)}{K_B[A_o]} \right\} 
\] (5.18)

This is a generic quadratic equation in the form of \( 0 = aX^2 + bX + c \) where,

\[ a = 1, \]
\[ b = (\Phi_\infty + \Phi_A) + (\Phi_\infty - \Phi_A) \frac{[B_o]}{[A_o]} + \frac{(\Phi_\infty - \Phi_A)}{K_B[A_o]}, \] and
\[ c = \Phi_\infty (\Phi_\infty - \Phi_A) \frac{[B_o]}{[A_o]} + \Phi_\infty \Phi_A + \Phi_A \frac{(\Phi_\infty - \Phi_A)}{K_B[A_o]} \]

The \( \Phi_{eff} \) values obtained by solving this equation are used as fits to the experimentally observed measurements as in Figure 2.14 and in Figure 3.11. The \( K_B \) value was previously calculated through the \(^1\)H NMR peak shifts as explained in text.
Bibliography


66. [http://www.colby.edu/chemistry/NMR/sp3CH.html](http://www.colby.edu/chemistry/NMR/sp3CH.html) (accessed March 15, 2011) and references there in.


