



Theoretical mechanistic study of self-sensitized photo-oxygenation and singlet oxygen thermal release in a dimethyldihydropyrene derivative



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ABSTRACT

The self-sensitized photo-oxygenation and singlet oxygen thermal release mechanisms in a pyridinium-substituted dimethyldihydropyrene (DHP) derivative have been investigated using quantum chemical calculations. First, the main photophysical pathway for intersystem crossing was identified, allowing the production of a DHP triplet state. Second, the energy transfer pathway between this triplet state and the oxygen triplet ground state was computed revealing a very efficient route for the photosensitized generation of singlet oxygen. Finally, the thermal pathway for the formation of a metacyclophanedien endoperoxide and the singlet oxygen release was characterized. A concerted and a stepwise mechanism were identified, the first one being lower in energy. All these results are consistent with recent experimental results and confirm that this type of system could be attractive oxygen carriers and singlet oxygen delivery agents.

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1. Introduction

Singlet oxygen ($^1\text{O}_2$) is one of the most important reactive oxygen species. Due to its remarkable reactivity and oxidizing property, it can be exploited in various applications ranging from chemical synthesis, waste water treatment, atmospheric chemistry, materials science, optical imaging and therapy [1–14]. Not surprisingly then, the control of trapping and releasing $^1\text{O}_2$ has become a very important topic of research in the past decades.

$^1\text{O}_2$ is the first electronic excited state of molecular oxygen and the direct transition from its triplet ground state $^3\text{O}_2$ is spin forbidden. To facilitate this transition, an indirect mechanism can be achieved using photosensitizers, which are light-absorbing molecules capable of transferring a part of the photonic energy to another molecule (e.g., $^3\text{O}_2$) to induce an electronic transition (e.g., $^3\text{O}_2 \rightarrow ^1\text{O}_2$). As schematized in Fig. 1, in the present context, the photosensitizer in its ground electronic state S_0 absorbs light to produce a singlet excited state S_1 , which can decay non-radiatively by intersystem crossing (ISC) to a triplet state T_1 . Provided that this triplet state is sufficiently high in energy and that the photosensitizer is physically close enough to $^3\text{O}_2$, an energy transfer process

can occur producing $^1\text{O}_2$ and regenerating the photosensitizer in its original ground state.

One way to control the release of $^1\text{O}_2$ is to produce chemical species incorporating molecular oxygen and capable of releasing $^1\text{O}_2$ in a controlled way. This aim can be achieved by the use of specific aromatic organic compounds [8,9,15–24] that can chemically trap $^1\text{O}_2$ in the form of endoperoxides (EPO) following a cycloaddition reaction. These EPOs exhibit the exceptional feature of releasing oxygen, often in its singlet excited state $^1\text{O}_2$, under heating or UV irradiation.

The properties of molecular switches can also be used to regulate the production of $^1\text{O}_2$ [25,26]. Supramolecular species and solid materials based on spiropyran [27] and dithienylethene [11,28,29] photochromic compounds associated with an external $^1\text{O}_2$ photosensitizer (e.g., a metal complex or a porphyrin) were used for the reversible control of $^1\text{O}_2$ generation. In these systems, the production of $^1\text{O}_2$ is governed by the state ("on" or "off") of the photochromic unit. Very recently, photochromic dimethyldihydropyrene [30–35] (DHP) derivatives were also found to be efficient singlet oxygen carriers and releasing agents [36,37]. The main advantages of these DHPs over the spiropyran and dithienylethene compounds is that they do not need an external $^1\text{O}_2$ photosensitizer, as they photosensitize oxygen themselves, and they work using low energy (red) light. As illustrated in Scheme 1, a pyridinium-appended DHP **1** can be switched to its

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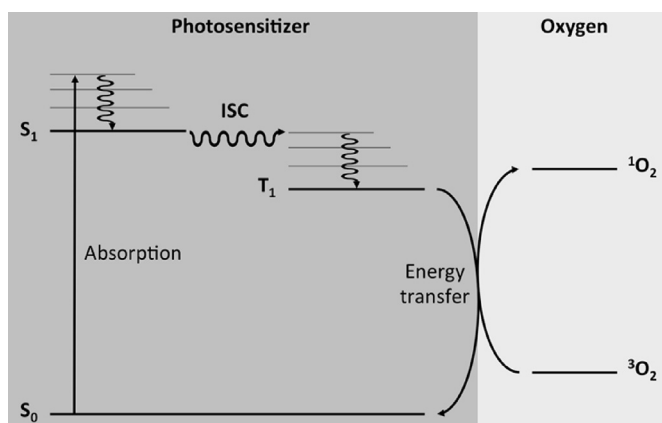
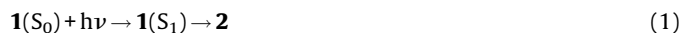


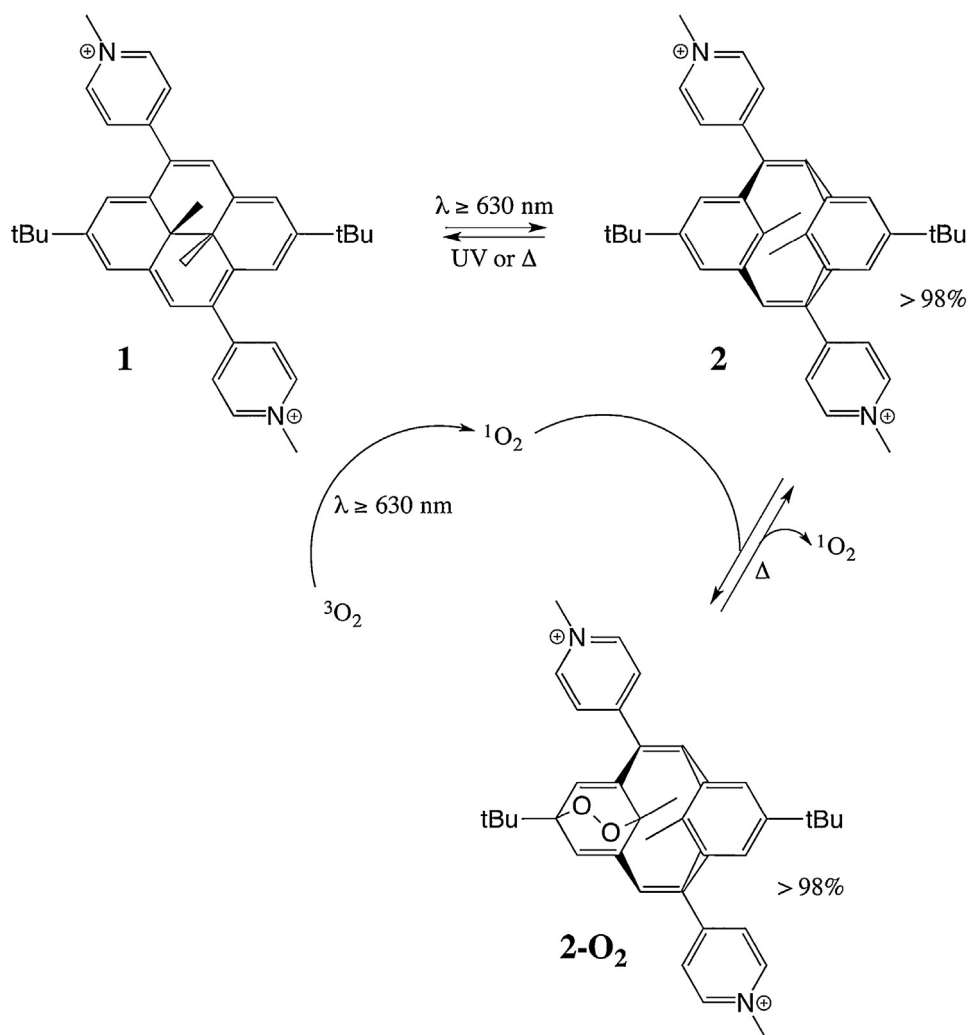
Fig. 1. Schematic diagram depicting the photosensitized excitation of oxygen in its ground triplet state ($^3\text{O}_2$) to its lowest singlet excited state ($^1\text{O}_2$).

open-ring cyclophanediene (CPD) isomer **2** by irradiation at $\lambda \geq 630$ nm [38]. The reverse conversion can be achieved either by irradiation in the UV range or thermally. A solution of **1** in the absence or presence of air and exposed to such an irradiation produces compounds **2** and **2-O₂** quantitatively. Upon heating at 35 °C the thermal release of $^1\text{O}_2$ was observed from **2-O₂**.

These experimental observations were interpreted with the mechanism proposed in Eqs. (1)–(4). Red visible irradiation of the closed isomer **1** in its ground state S_0 produces its singlet excited state $1(S_1)$, which isomerizes to **2** (Eq. (1)). However, the excited state $1(S_1)$ can also non-radiatively decay by ISC to produce the triplet $1(T_1)$ (Eq. (2)). The DHP in its lowest triplet state can then undergo an energy transfer process with molecular oxygen $\text{O}_2(T_0)$ producing singlet oxygen $\text{O}_2(S_1)$. Thus, **1** also plays the role of O_2 photosensitizer (Eq. (3)). The photogenerated $^1\text{O}_2$ rapidly reacts with **2** to form the corresponding EPO **2-O₂**, which can release singlet oxygen upon warming (Eq. (4)).



The purpose of the present study is to bring some mechanistic information on this mechanism using theoretical chemistry. While



Scheme 1. Conversion processes between **1**, **2** and **2-O₂**. Adapted from Ref. [36].

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