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Density functional theory study of the photosensitization mechanisms of indigo

Research Article

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Abstract: The triplet excited state properties and photosensitization mechanisms of indigo were investigated based on density functional theory calculations. The solvent effects on the photosensitization mechanisms of indigo have also been considered. The thermodynamic feasibility of the possible $^1O_2$ and O_2·⁻-photogeneration pathways by triplet excited state indigo in different solvents was explored, in order to gain some deeper insights into the photosensitization characters of the dye.

Keywords: *Indigo • Triplet excited state • Photosensitization mechanisms • Singlet oxygen • Density functional theory*

1. Introduction

Indigo (Fig. 1) is a naturally occurring dye that comes from several species of plants [1]. It exhibits a distinctive blue color and has been widely used as an important dyestuff with a long history. Moreover, a recent study indicated that indigo possesses photosensitive properties and can photogenerate singlet oxygen ($^1O_2$) [2]. As we know, photosensitizers are initially raised form the ground (S_0) state to the singlet excited (S_1) state upon irradiation and then may intersystem cross to the triplet excited (T_1) state, which is mainly responsible for the photosensitizing reactions owing to its relatively long lifetime. Therefore, the T_1 state properties of a photosensitizer, *e.g.* triplet excitation energy (E_{T1}), electron affinity and ionization potential, are crucial to understanding its photosensitization mechanisms.

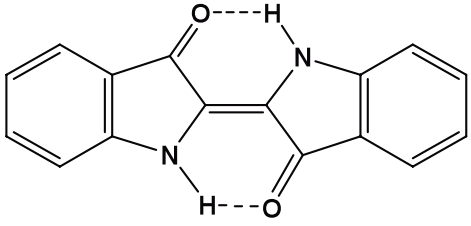

Figure 1. Chemical structure of indigo.

In view of the importance of indigo as one of the most employed organic pigments, the photosensitization mechanisms of indigo were explored on the basis of its T_1 state properties estimated using density functional theory (DFT) calculations, which have been widely employed to investigate the photo-physicochemical characters of various photosensitive compounds [3-6].

2. Experimental Procedures

All calculations were completed with Gaussian 03 package [7]. Molecular structure of indigo was fully optimized by the B3LYP/6-31+G(d,p) method in solvents (benzene and DMSO). The E_{T1} of indigo was obtained by the TD-DFT formalism with the same functional and basis set in solvents [8-10], whose accuracy in estimating the E_{T1} of various photosensitizers has been verified [3-6]. Then, the total electronic energies of the anion and cation radicals were also calculated by using the optimized geometry of the parent molecule to estimate the ground state vertical electron affinity (VEA) and vertical ionization potential (VIP) of indigo. The VEA and VIP in T_1 state (VEA_{T1} and VIP_{T1}) were estimated according to the following equations: $VEA_{T1} = VEA_{S0} - E_{T1}$; $VIP_{T1} = VIP_{S0} - E_{T1}$. The solvent

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(benzene and DMSO) effects were considered by employing the self-consistent reaction field (SCRF) method with polarizable continuum model (PCM) of Tomasi and coworkers during the calculations [11-13].

3. Results and discussion

3.1. Triplet excited state properties

As the E_{T1} of a photosensitizer is crucial to understanding its photosensitization mechanisms, the E_{T1} of indigo was estimated firstly by employing TD-DFT method and shown in Table 1. The theoretical E_{T1} of indigo is about 1.02 eV in benzene and 0.99 eV in DMSO, which is close to the experimental value (1.04 ± 0.10 eV) [14]. The effectiveness of TD-DFT method in estimating the E_{T1} of various photosensitizers has also been verified by previous studies [3-6].

Moreover, as shown in Table 1, the solvents influence significantly on the VEA and VIP of indigo. The VEA of indigo in benzene is much higher than that in DMSO, implying that indigo in benzene exhibits relatively lower electron-attracting ability. Similar analysis indicates that indigo in benzene possesses relatively weaker electron-donating potential in comparison with that in DMSO because of the higher VIP in benzene. The observed solvent effect on the electronic parameters of indigo may arise from the more significant stabilization effect of polar solvent on the anion/cation radicals generated through one electron-attracting or -donating process from the parent indigo.

3.2. Photosensitization mechanisms

Residing in the long-lived triplet excited state, indigo may react with $^3O_2$ to give birth to reactive oxygen species theoretically through the following possible pathways.

The first photosensitization pathway involves the $^1O_2$ generation through the energy transfer from the T_1 state indigo (IN) to $^3O_2$ as represented in Eq. 1.

$$IN(T_1) + {}^3O_2 \rightarrow IN(S_0) + {}^1O_2 \quad (1)$$

As the TD-DFT estimated E_{T1} of indigo (Table 1) is a little larger than the energy needed to bring $^3O_2$ to the singlet excited state (0.98 eV) [15], indigo can in principle photogenerate $^1O_2$ through direct energy transfer pathway. This is in agreement with the experimental report that indigo is an efficient $^1O_2$ sensitizer upon irradiation [2].

The second photosensitization pathway may result in the formation of superoxide anion radical ($O_2^{\cdot -}$) through electron transfer from the T_1 state indigo to $^3O_2$ (Eq. 2).

$$IN(T_1) + {}^3O_2 \rightarrow IN^{\cdot +} + O_2^{\cdot -} \quad (2)$$

The thermodynamic feasibilities of this pathway in benzene and DMSO are explored. In benzene, the summation of VIP_{T1} of indigo and electron affinity of $^3O_2$ is positive (2.78 eV), suggesting that $O_2^{\cdot -}$ can not be generated through this pathway. Similar analysis shows that the direct electron transfer pathway is also thermodynamically unfavorable in DMSO because of the positive reaction energy.

Moreover, the T_1 state indigo may be reduced by their neighboring S_0 state or T_1 state (Eqs. 3 and 4) termed autoionization reactions, which leads to the formation of the corresponding anion-cation radical couples. Subsequently, the anion radical of the indigo may pass one electron to $^3O_2$ to give birth to $O_2^{\cdot -}$ (Eq. 5).

$$IN(T_1) + IN \rightarrow IN^{\cdot +} + IN^{\cdot -} \quad (3)$$

$$IN(T_1) + IN(T_1) \rightarrow IN^{\cdot +} + IN^{\cdot -} \quad (4)$$

$$IN^{\cdot -} + {}^3O_2 \rightarrow IN + O_2^{\cdot -} \quad (5)$$

The feasibilities of reactions (3) and (4) rely on VEA_{T1} + VIP and VEA_{T1} + VIP_{T1} of indigo, respectively. The present results indicate that reaction (3) and (4) are unfavorable on thermodynamic grounds in benzene owing to their respective positive values of the reaction energy (Table 1). Therefore, the anion radical of indigo cannot be formed in benzene, which makes the subsequent $O_2^{\cdot -}$-generation (Eq. 5) impossible. In DMSO, the reaction (3) is also thermodynamically unfavorable, because of the small reaction energy (0.02 eV), while the occurrence of a reaction (4) remains probable to form an anion radical of indigo. Moreover, the generation of the anion radical of indigo will be enhanced especially in the case of suitable electron donors (D) exist in solution (Eq. 6). Subsequently, $O_2^{\cdot -}$ can be formed through

Table 1. Lowest triplet excitation energy (E_{T1}, in eV), vertical electron affinity (VEA, in eV) and vertical ionization potential (VIP, in eV) of indigo in benzene and DMSO.

	E_{T1}	VEA_{S0}	VEA_{T1} [a]	VIP_{S0}	VIP_{T1} [b]
in benzene	1.02	–2.62	–3.64	6.13	5.11
in DMSO	0.99	–3.39	–4.38	5.39	4.40

[a] $VEA_{T1} = VEA_{S0} - E_{T1}$;
[b] $VIP_{T1} = VIP_{S0} - E_{T1}$.

reaction (5), which is feasible from a thermodynamic point of view in DMSO. Previous studies proposed that $^1O_2$ and $O_2^{\cdot -}$ are involved in the oxidative cleaveage of indigo and its derivatives [2,16].

$$IN(T_1) + D \rightarrow IN^{\cdot -} + D^{\cdot +} \quad (6)$$

4. Conclusion

The photosensitization mechanisms of indigo have been studied in the present work employing DFT approach, taking into account the solvent effects. According to the theoretically estimated parameters, including E_{T1}, VEA and VIP, the $^1O_2$ and $O_2^{\cdot -}$-photogeneration mechanisms by indigo have been proposed on thermodynamic grounds.

Acknowledgments

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