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Effects of photophysical properties of 1,4-cyclohexadiene derivatives on their [2 + 2] photocycloaddition reactivities: Experimental and theoretical studies

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ARTICLE INFO	A B S T R A C T
Keywords: 1,4-cyclohexadiene derivatives [2+2] photocycloaddition reactivity Photophysical properties Theoretical calculations	To study the relationship between the $[2 + 2]$ photocycloaddition reactivities of 1,4-cyclohexadiene derivatives (1,4-CHDs) and their structures, photophysical properties of a series of 1,4-CHDs were studied experimentally and by performing theoretical calculations. Specifically, UV-vis absorption spectra of these compounds in diluted solutions were acquired and the theoretical calculations were performed at the density functional theory (DFT) level. Their UV-vis absorption maxima were found to be related to the substituents on the 1,4-cyclohexadiene ring. To describe the $[2 + 2]$ photocycloaddition reactivities of the 1,4-CHDs, time-dependent density functional theory (TDDFT) was used to optimize their ground- and excited-state structures, and their electronic excitation energies were calculated at the M062X/def-TZVP level. Frontier molecular orbitals and electron-hole distribution analyses were used to illustrate the electron transition modes of the 1,4-CHDs. The differences between the ground- and excited-state structures of the different 1,4-CHDs were characterized by carrying out a root-mean-square-deviation (RMSD) analysis. The results showed that the photophysical properties of 1,4-CHDs are meaningful for explaining their $[2 + 2]$ photocycloaddition reactivities.

1. Introduction

1,4-Cyclohexadiene derivatives (1,4-CHDs) constitute one of the most common organic structural units and are widely present in many natural products and pharmaceutical molecules with physiological activities [1–5]. They are used as raw materials or intermediates for synthesizing important pharmaceutical and chemical materials [6-12]. Carrying out [2 + 2] photocycloadditions of 1,4–CHDs has been the main approach used to synthesize tetraasteranes, which constitute an important class of cage compounds with high levels of tension energy and lipophilicity [13]. Their aza and oxa derivatives, namely 3,9-diazatetraasteranes and 3,9-dioxatetraasteranes, display anti-HIV activity and antitumor activity [14-18]. The tetraasteranes were first obtained via [2 + 2] photocycloadditions of 1,4-CHDs by Cookson and Hans-Martin [19,20]. They were at that time considered as novel tetraasterane derivatives, and found to form head-to-tail (HT) cage-dimers of 3,6-dihydrophthalic anhydride with relatively low yields (of about 10 %) and low levels of regioselectivity. In view of our studies on the [2 + 2]photocycloaddition reactivities of 1,4-dihydropyridines and 4H-pyrans [21-24], their photophysical properties such as excitation energy (E) levels, oscillator strength (*f*) levels, and geometrical and electronic structures are closely related to the properties of their photochemical reactions, and may be used to understand the process by which they undergo [2 + 2] photocycloadditions [25].

To the best of our knowledge, there has been a lack of systematic studies on the relationship between photophysical properties of 1,4-CHDs and their reactivities for [2 + 2] photocycloaddition. 1,4-CHDs were selected as the subjects of the current research, and their [2 + 2] photocycloadditions were compared with that of each other to clarify the different reactivities cause by the photophysical properties. Specifically, five 1,4-CHDs were herein selected as representative compounds for scrutinizing the effects of substituents of the 1,4-cyclohexadiene ring on the photophysical properties of the compounds and on their [2+2] photocycloaddition reactivities (Scheme 1). The ultraviolet-visible (UV-vis) absorption spectra of these compounds in solution were acquired and are discussed in detail. To shed further light on the nature of their photophysical behaviors, time-dependent density functional theory (TDDFT) was used to optimize the groundand excited-state structures of the 1,4-CHDs. Frontier molecular orbitals and electron-hole distribution analyses were used to illustrate the

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Received 11 March 2021; Received in revised form 28 April 2021; Accepted 2 May 2021 Available online 4 May 2021 1010-6030/© 2021 Elsevier B.V. All rights reserved. electron transition modes of the 1,4–CHDs. Their electronic excitation energies were calculated at the M062X/def-TZVP level; meanwhile, the differences between the ground- and excited-state structures of the different 1,4–CHDs and the intrinsic characteristic of excitations were characterized by carrying out wavefunction analyses. The results have provided comprehensive insight into the photophysical properties and [2 + 2] photocycloaddition reactivities of the 1,4–CHDs.

2. Materials and methods

2.1. General procedures

The solvents and reagents were used as received without further purification. Proton NMR spectroscopy data were recorded using a Bruker AV400 spectrometer operating at 400 MHz with TMS used as an internal standard at ambient temperature (25 °C). The UV–vis absorption spectra for the compounds, in respective 1,4-dioxane solutions, were acquired using a SHIMADZU UV-2600 spectrophotometer. All experiments were performed at 25 °C and the concentrations of 1,4–CHDs **1-4** and 1,4–CHDs **5** are 4×10^{-4} M and 4×10^{-5} M, respectively.

2.2. Synthesis of 1,4-cyclohexadiene derivatives

1,4–CHDs **1** and **2** were prepared by the synthetic protocol presented in Scheme 2 and 1,4–CHDs **3–5** were commercial compounds [26,27]. All of them were verified by ¹H NMR.

4,7-dihydroisobenzofuran-1,3-dione (1): 1,3-Butadiene (180 mmol) and acetylenedicarboxylic acid (100 mmol) were added in THF (100 mL). The reaction mixture was heated at 90 °C for 12 h in a glass pressure bottle. Then the mixture was cooled down to room temperature and removed the solvent by distillation under reduced pressure and then recrystallized from ethyl acetate. Yield: 86 %; White solid; m.p. 148 °C; ¹H NMR: (400 MHz, Chloroform-d) δ 5.90 (d, 2 H), 3.14 (d, 4 H).

2,3,5,8-tetrahydrophthalazine-1,4-dione (2): Crystals of 1,4–CHDs **1** (37.5 mmol) were crushed in a mortar, and then added to a refluxing solution of NH₂NH₂·HCl (84 mmol) in AcOH (200 mL). The resulting mixture was refluxed overnight to yield a colorless, clear solution. The reaction mixture was cooled and poured into 700 mL of water. The resulting precipitate was filtered and dried under reduced pressure to yield 1,4–CHDs **2** as a white solid. Yield: 98 %; White solid; m.p. 156 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.59 (s, 2 H), 5.81 (s, 2 H), 2.99 (s, 4 H).

Dimethyl cyclohexa-1,4-diene-1,2-dicarboxylate (3): ¹H NMR (400 MHz, Chloroform-*d*) δ 5.67 (d, 2 H), 3.75 (s, 6 H), 2.97 (d, 4 H).

Dimethyl bicyclo [2.2.1] hepta-2,5-diene-2,3-dicarboxylate (4): ¹H NMR (400 MHz, Chloroform-*d*) δ 6.93 (t, 2 H), 3.95 (p, 2 H), 3.79 (s, 6 H), 2.29 (dt, 1 H), 2.11 (dt, 1 H).

2.5-Dimethyl-1,4-benzoquinone (5): ¹H NMR (400 MHz, Chloroform-*d*) δ 6.67 (q, 1 H), 1.97 (d, 3 H).

2.3. Computational details

Molecular geometry optimizations and vibrational analyses of the ground and excited states of the compounds each in 1,4-dioxane were carried out using the M062X functional [28] associated with the def-TZVP basis set [29]. The absence of an imaginary frequency



Scheme 2. Synthesized protocol for preparing 1,4–CHDs 1-2.

confirmed attainment of local geometric minima. The solvent effects were investigated using the polarizable continuum model (PCM) [30, 31] to simulate the 1,4-dioxane environment. TDDFT [32,33], which is the most popular method for these purposes due to its desirable balance between computational efficiency and accuracy, was employed here to calculate the electronic absorption spectra on the basis of the optimized geometries of the 1,4–CHDs. All wavefunction analyses were conducted using the Multiwfn 3.8 program [34] and the isosurface maps of electron-hole distribution were rendered with VMD 1.9.3 software [35]. All calculations were finished using the Gaussian 09 packages [36].

3. Results and discussion

Five 1,4-CHDs, with different substituents on the 1,4-cyclohexadiene ring, were selected as representative compounds for scrutinizing the effect of photophysical properties on [2 + 2] photocycloaddition reactivity. The 1,4-CHDs 1, having a dicarboxylic anhydride substituent on the 1,4-cyclohexadiene ring, has been shown to be able to undergo an intermolecular [2 + 2] photocycloaddition to form the novel tetraasterane derivative tetraasterantetracarbonacidanhydride [19]. The 1,4-CHDs 2 was designed by us as an aza derivative of the 1, 4-CHDs 1, with the idea of enhancing the conjugation between the carbonyl groups and the C=C double bonds in the 1,4-cyclohexadiene ring [37,38]. 1,4-CHDs 3 and 4 were each made by carrying out a ring opening of the substituent of the 1.4–CHDs 1. To date, there have been no reports on the [2 + 2] photocycloadditions of 1,4-CHDs 2 and **3.** When attempts at carrying out [2 + 2] photocycloadditions of 1, 4-CHDs 2 and 3 were made based on the reaction conditions used for 1, 4-CHDs 1 and 5 (see below), no cycloaddition products except for their aromatization products were obtained. The 1,4-CHDs 4 can undergo an intramolecular [2 + 2] cycloaddition [39]. And the 1,4-CHDs 5 has been shown to easily undergo intermolecular [2 + 2] photocycloaddition form the 1,4,5,8-tetramethylpentacyclo to [6.4.0.0^{2.7}.0^{4.11}.0^{5.10}] dodecane [20]. These experimental results (Scheme 3) revealed very different [2 + 2] photocycloaddition reactivities for the 1,4-CHDs with different substituents.



Scheme 1. Structures of the examined 1,4-CHDs.



Scheme 3. [2 + 2] photocycloadditions of 1,4–CHDs.

3.1. UV-vis absorption spectra of 1,4-CHDs 1-5

For wavelengths of 225–400 nm, UV–vis absorption spectra of 1,4–CHDs 1-5 each in 1,4-dioxane were acquired. All experiments were performed at 25 °C and the concentrations of 1,4–CHDs 1-4 and 1,4–CHDs 5 are 4×10^{-4} M and 4×10^{-5} M, respectively. The spectra



are displayed in Fig. 1 with the relevant data in Table 1, and with λ_{abs} denoting wavelength of maximum absorption (nm), E denoting excitation energy (eV), calculated using the equation $E=1240/\lambda_{abs}$, and ϵ denoting molar extinction coefficient.

As shown in Fig. 1, the absorption maxima of 1,4–CHDs 1–5 were located in the range 245-301 nm with molar extinction coefficient (ϵ) values of about 10^{3} M⁻¹ cm⁻¹. These results indicated the lowest-energy excited states of 1.4–CHDs 1–5 to be influenced mainly by π - π * transitions. The five 1,4–CHDs tested showed five different λ_{abs} values as shown in Table 1, indicating the effects of the substituents on λ_{abs} . The λ_{abs} values of the 1,4–CHDs 1 (289 nm) and 2 (301 nm) were observed to be similar and the differences between the λ_{abs} values of 1,4–CHDs 1-2 and those of 3-4 were large, namely above 30 nm, indicating a bathochromic effect of cyclizing the substituent. These results suggested the occurrence of an enhancement of the conjugation between the carbonyl groups of the substituents and the C=C double bonds in the main 1,4-cyclohexadiene ring as a result of the cyclization of the substituents. The carbonyl groups in 1,4-CHDs 1-2 were also indicated from our current results to be engaged. The aza analogue of the dicarboxylic anhydride in the 1,4-cyclohexadiene ring would reduce the excitation energies of 1,4–CHDs, and the λ_{abs} value of 1,4–CHDs 2 was observed to be higher than that of 1,4–CHDs 1, which may have been due to the particularly good conjugation of the lone-pair electrons of the nitrogen atoms with the carbonyls. The λ_{abs} value of 1,4–CHDs 5 (262 nm) was observed to be higher than those of 1,4-CHDs 3-4 and lower than those of 1,4–CHDs 1-2. The carbonyls at positions 3 and 6 of the 1,4-cyclohexadiene ring may be the main reason for the red shift (about 20 nm) of the absorbance of 1.4–CHDs 5. Comparison of the ε value of 1,4-CHDs 5 (13000 M^{-1} cm⁻¹) and those of 1-4 indicated that the inclusion of carbonyls attached to positions 3 and 6 of the 1,4-cyclohexadiene ring would bring about a higher ε . This observation was found to be in good agreement with experimental results that showed that the [2 + 2] photocycloaddition of the 1,4–CHDs 5 could occur in sunlight with high yield [20].

3.2. Theoretical calculations

Time-dependent density functional theory (TDDFT) was used to optimize the ground- and excited-state structures of 1,4-CHDs 1-5. Their electronic excitation energies at the M062X/def-TZVP level were calculated so as to gain further insight into their optical and electronic properties in their ground and excited states. First the effects of substituents of the 1,4-CHDs on their geometrical and electronic structures in the ground states were investigated, based on the optimized geometrical structures in 1,4-dioxane. Then the frontier molecular orbitals and electron-hole distribution analyses were carried out to shed light on the intrinsic characteristics of their electron excitation properties. Finally, the structures of the excited state and ground state minima of the different 1,4-CHDs were compared in order to predict the [2 + 2] photocycloaddition reactivities of 1,4-CHDs.

3.2.1. Geometrical and electronic structures of the ground states

The optimized ground-state geometrical structures of 1,4–CHDs each in 1,4-dioxane are presented in Fig. 2. Their bond length (BL) values are presented in Table 2. Apart from the bond lengths, the Laplacian bond order (LBO) values were also calculated, due to the excellent

Table 1	
Summary of UV-vis absorption spectroscopy data of 1,4-CHDs 1-5.	

1,4-CHDs	λ_{abs}/nm	E/eV	$\epsilon/ \mathrm{M}^{-1} \mathrm{cm}^{-1}$
1	289	4.29	1664
2	301	4.12	2720
3	250	4.96	1445
4	245	5.06	4516
5	262	4.73	13000



Fig. 2. Optimized ground-state geometrical structures at the M062X/def-TZVP level.

Table 2
Values for bond length (BL, Å) and Laplacian bond order (LBO, Å) of 1,4–CHDs
in the ground states in 1,4-dioxane at the M062X/def-TZVP level.

Index	1	2	3	4	5	1,4-cyclohexadiene
BL1(C ₁ -C ₂)	1.340	1.352	1.344	1.335	1.347	1.327
BL2(C2-C3)	1.490	1.504	1.511	1.534	1.479	1.502
BL3(C3-C4)	1.513	1.504	1.502	1.538	1.499	1.502
BL4(C ₄ -C ₅)	1.337	1.334	1.333	1.328	1.347	1.327
BL5(C5-C6)	1.513	1.504	1.502	1.537	1.479	1.502
BL6(C ₆ -C ₁)	1.490	1.504	1.511	1.538	1.499	1.502
LBO1	1.801	1.721	1.746	1.712	1.798	1.855
LBO2	1.057	1.023	0.991	0.848	1.193	1.049
LBO3	1.015	1.053	1.053	0.868	1.109	1.049
LBO4	1.844	1.860	1.860	1.850	1.798	1.855
LBO5	1.015	1.053	1.053	0.873	1.193	1.049
LBO6	1.057	1.023	0.992	0.829	1.109	1.049

quantitative relationship between LBO and chemical bond strength [40], and are presented in Table 2. Inspired by previous works [25,41], relative deviation of bond length (RD_{BL}) and Laplacian bond order (RD_{LBO}) were defined and calculated to investigate the effects of the substituents on geometrical and electronic structures. The results are presented in Fig. 3 with 1,4-cyclohexadiene as a reference compound.

As shown in Fig. 3, the substituents were indicated to have an obvious influence on the bond length (BL) and bond order (LBO) values of 1,4–CHDs. To be specific, the lengths of the 1,4–CHDs CC= double bonds BL1 (C1-C2) and BL4 (C4-C5) were calculated to have been increased upon introduction of the substituents by about 1.2 % and 0.8 %, respectively, with this increase attributed to the conjugation between the carbonyl groups and the C=C double bonds. As a result, LBO1 and LBO4 were weakened by about 5.0 % and 2.0 %, respectively. In particular, the RD_{BL} of BL1 (1.9%) of the 1,4-CHDs 2 was the largest for the aza ring substituent and was attributed to the low ring tension. The BL2, BL3, BL5 and BL6 values of the 1,4-CHDs 4 were clearly increased relative to those of 1,4–CHDs (by about 2.0 % of RD_{BL}) due to the inclusion of the carbon bridge while the BL1 and BL4 values were almost unchanged (with a change of only about 0.3 % of RD_{BL}). The results showed the carbon bridge and ring substituents providing the greatest contributions to the conjugation in the 1,4-CHDs. Those 1,4-CHDs having the CC= double bonds with the lowest bond orders were found to have the lowest excitation energies and to most easily undergo photochemical reactions. The results showed the carbon bridge and ring substituents providing the greatest contributions to the reducing of



Fig. 3. Bond length (BL) and Laplacian bond order (LBO) values of the 1,4-CHDs in their ground states.

excitation energies. The presence of the carbonyls in the 1,4–CHDs **5** was indicated to lead to moderate increases in BL1 and BL4 (by about 1.6 % of RD_{BL}), while BL3 and BL6 (C_1 - C_6) showed lower sensitivity to the presence of the carbonyl (RD_{BL} values of about 0.1 %). These observations were in good agreement with experimental results showing that [2 + 2] photocycloaddition of the 1,4–CHDs **1** could occur in light of longer wavelengths, and the carbon bridge reducing the distance between the two C=C double bonds of the 1,4–CHDs **4** was indicated to allow **4** to easily undergo the intramolecular [2 + 2] photocycloaddition [19,39].

3.2.2. Theoretical calculations for electron excitation

To shed light on the intrinsic characteristics of electron excitation processes, molecular orbitals (MOs) were used to illustrate the electron transition modes of these compounds, due to the overwhelming contributions of the $S_0 \rightarrow S_1$ transitions; depictions of the HOMOs and LUMOs of 1,4–CHDs 1-5 are shown in Fig. 4.

All of the frontier orbitals of these compounds were indicated to be mainly of the π -type and to be predominately located on the both sides of the 1,4-cyclohexadiene ring, hence showing a considerable separation in space. That indicated the lowest-energy transition of the 1,4-CHDs 1-3 to principally be a charge transfer (CT) excitation (Fig. 4). While the distribution of the frontier orbitals was indicated to be affected by the carbonyl groups at positions 3 and 6 of the 1,4–CHDs 5, the excitation showed an apparent local excitation (LE) mode. Besides, apparent changes of the LUMO distribution brought about by the carbon bridge of the 1,4-CHDs 4 were noticed as well, and apparently led to delocalization of LUMO and hence its spread to the other C=C double bond in our calculations. Comparing the distributions of the frontier orbitals of 1,4-CHDs 1-2 and 1,4-CHDs 3-5 showed some characteristics of their HOMOs and LUMOs having spread to the introduced dicarboxylic anhydride substitutes and aza derivative. In addition, to reveal the characteristics of the electron excitations more intuitively, the calculations of the electron-hole distributions of 1,4-CHDs 1-5 after excitation were carried out (Fig. 5).

Inspection of these plots showed the lowest-energy transitions of 1,4–CHDs **1–3** mainly being charge transfer excitation (CT), and those of 1,4–CHDs **4–5** mainly being local excitation (LE). Apparently, apart from the π - π * transition induced by electron excitation of C=C double bonds, the **n**- π * transition from the lone-pair electrons of the oxygen atom was also incorporated in the S₀→S₁ transition. Furthermore, for 1,4–CHDs **1–5**, an additional σ - π * excitation was found from the C–H single bond, and this finding explained the relatively high excitation energies of **1–5**. These observations were in good agreement with experimental results showing the excitation energies levels of 1,4–CHDs to be high (UV range) and the results showing that the ε value of the 1,4–CHDs **5** was higher than those of 1,4–CHDs **1–4** because of the local excitation mode.

3.2.3. Geometrical and electronic structures of the excited states

The bond length (BL) and Laplacian bond order (LBO) values for the 1,4-cyclohexadiene rings in their relaxed excited states are displayed in

Table 3. To evaluate the structural distinctions between the excited state (ES) and ground state (GS) minima of 1,4-CHDs 1-5, here we compared the relative deviation values for bond length (RD_{BL}) and Laplacian bond order (RD_{LBO}) calculated using a method similar to the method used in the above section, and the results are displayed in Fig. 6. Both the variations of bond length and Laplacian bond order of 1,4-CHDs 2-4 showed similar trends. The BL1 and BL4 values were calculated to be increased by 4.0 %; while in contrast, the BL3 and BL5 values were shortened by 3.0 %. For 1,4-CHDs 1 and 5, BL1 and BL4 were calculated to be just slightly changed with the relative deviation values within 5.0 % accompanied by fluctuation of bond strength of about 1.0 %, indicative of their being insensitive to excitation. According to the relative deviation values presented in Fig. 6, the RD_{LBO} of LBO3 and LBO5 were both increased by the same amount, namely 25.0 %, together with a contraction of BL1 and BL4 by 25.0 % and 15.0 %, respectively. In contrast, the strengths of the C=C double bonds in the 1,4-cyclohexadiene ring were indicated to be weakened significantly after excitation, and thus resulting in enhancements of their chemical reactivities; these double bonds have been shown to spatially coincide well with the locations of the reactive sites of their photoreactions, especially the [2 +2] photocycloaddition.

Additionally, superpositions of the ES- and GS-minima structures and their RMSD values (Å) for each of the 1,4–CHDs 1–5 are shown in Fig. 7. In particular, the structures of the first triplet states were also included; they have an important influence on the photochemical reactions of 1,4-CHDs. For the 1,4-CHDs 1 as well as for the 1,4-CHDs 2, these RMSDs were quite small and the structures were quite planar regardless of the state, attributed to restraints imposed by the dicarboxylic anhydride and aza substituents; thus each of them was expected to be able to attack another molecule without steric hindrance and undergo intermolecular [2 + 2] photocycloaddition. Nevertheless, for the 1,4–CHDs 2, no [2 + 2] photocycloaddition product has yet been produced, the reasons for which need still to be determined. A larger RMSD value was calculated for the 1,4-CHDs 3 than for the other 1,4-CHDs, illustrating an obvious distinctive feature in the structure of 3 and in accord with its considerable steric hindrance, the main reason for the lack of any observed [2+2] photocycloaddition of **3**. In addition, the carbon bridge of the 1,4-CHDs 4 also apparently prevented any considerable change in its structure, and the distance between the two C=C bonds was shortened. This analysis confirmed the experimental results showing the occurrence of only an intramolecular [2 + 2] photocycloaddition of 4. For the 1.4–CHDs 5, the presence of the conjugated carbonyls effectively maintained the planarity of the 1,4-cyclohexadiene ring structure, consistent with 5 having been observed to readily undergo an intermolecular [2 + 2] photocycloaddition.

4. Conclusions

In summary, an experimental and theoretical study of five 1,4-cyclohexadiene derivatives (1,4–CHDs) was carried out for the purpose of investigating their photophysical properties with regards to their [2 + 2]photocycloaddition reactivities. The 1,4-cyclohexadiene ring of



Fig. 4. Plots of HOMOs and LUMOs (isosurface = 0.05 a.u.) of 1,4-CHDs 1-5.



Fig. 5. Electron-hole distributions (isosurface = 0.002 a.u.) of 1,4–CHDs 1-5 after excitation. The green regions represent increases in electron density as a result of excitation and the blue regions represent depletions of electron density.

Table 3	
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Bond length (**BL**, Å) and Laplacian bond order (**LBO**, Å) values for the 1,4-cyclohexadiene ring in their relaxed excited states in 1,4-dioxane as calculated at the M062X/def-TZVP level.

Index	1	2	3	4	5
BL1	1.366	1.410	1.411	1.425	1.340
BL2	1.491	1.476	1.504	1.554	1.462
BL3	1.507	1.451	1.454	1.486	1.475
BL4	1.328	1.390	1.390	1.407	1.340
BL5	1.507	1.451	1.454	1.485	1.462
BL6	1.491	1.476	1.504	1.558	1.475
LBO1	1.544	1.287	1.297	1.249	1.742
LBO2	1.009	1.086	1.008	0.734	1.091
LBO3	1.019	1.261	1.261	1.082	1.043
LBO4	1.848	1.606	1.620	1.513	1.742
LBO5	1.019	1.261	1.261	1.093	1.091
LBO6	1.009	1.087	1.008	0.722	1.043

1,4–CHDs **1** included a dicarboxylic anhydride substituent. The 1,4–CHDs **2** was designed as an aza derivative of 1,4–CHDs **1**, 1,4–CHDs **3** and **4** as ring-opened derivatives of 1,4–CHDs **1**, and 1,4–CHDs **5** as a *p*-benzoquinone derivative.

Inspection of the UV–vis absorption spectra of the 1,4–CHDs showed significant effects of the substituents on λ_{abs} . The λ_{abs} values of the 1,4–CHDs 1 (289 nm) and 2 (301 nm) were observed to be similar, and those of 1,4–CHDs 3 (250 nm) and 4 (245 nm) were also found to be close to each other. These results suggested the occurrence of an enhancement of the conjugation between the carbonyl groups of the substituents and the C=C double bonds in the main 1,4-cyclohexadiene ring as a result of the cyclizations of the substituents. The λ_{abs} value of 1,4–CHDs 5 (262 nm) was found to be longer than those of 1,4–CHDs 3–4 and shorter than those of 1,4–CHDs 1–2. The carbonyls at positions 3 and 6 on the 1,4-cyclohexadiene ring may be the main reason for the red shift (of about 20 nm) of 1,4–CHDs 5.

Theoretical calculations of geometrical and electronic structures in the ground states revealed the carbon bridge and ring substituents providing the greatest contributions to the reducing of excitation energy of the 1,4–CHDs. A frontier molecular orbital and electron-hole distribution analysis revealed the lowest-energy transition of 1,4–CHDs **1–4** to be principally a charge transfer excitation and the distribution of the frontier orbitals to be affected by the presence of carbonyls at positions 3 and 6 of 1,4–CHDs **5**, indicated to have an apparent local excitation



Fig. 6. Bond length (BL) and Laplacian bond order (LBO) values of the relaxed excited states (ES-minima) and ground states (GS-minima) of the five 1,4–CHDs each in 1,4-dioxane. Calculations were performed at the M062X/def-TZVP level.



Fig. 7. Superpositions of the ES- and GS-minima structures and their RMSD values (Å) for each of the 1,4–CHDs 1-5.

mode. Geometrical and electronic structures of the excited states were analyzed by calculating root-mean-square-deviations (RMSDs). The substituents were shown from these calculations to have a significant influence on the variations of the structures of the excited states. Restraints provided by the dicarboxylic anhydride and aza derivative substituents were concluded to maintain the planarities of the 1,4-CHDs 1-2, so that they can each attack another molecule without steric hindrance and undergo intermolecular [2 + 2] photocycloaddition. The calculated RMSD value of 1,4-CHDs 3 was larger than those of other 1,4-CHDs, illustrating an obvious distinctive feature in the structure of 1,4–CHDs 3 and in accord with its considerable steric hindrance, the main reason for the lack of any observed [2 + 2] photocycloaddition of 1,4–CHDs 3. Also, the carbon bridge in 1,4–CHDs 4 was concluded to impede the ability of 4 to undergo considerable conformational changes and to yield a shortened distance between its two C=C bonds, features consistent with the experimental results showing 1,4-CHDs 4 undergoing intramolecular [2 + 2] photocycloaddition. For the 1,4-CHDs 5, the presence of a conjugated carbonyl was concluded to maintain the planarity of the structure of the 1,4-cyclohexadiene ring effectively, and hence allow 1,4-CHDs 5 to readily undergo intermolecular [2 + 2] photocycloaddition.

The photophysical properties of 1,4–CHDs were mainly related to their different substituents. These substituents were concluded to influence whether the 1,4–CHDs undergo an intramolecular or intermolecular [2 + 2] photocycloaddition and to also affect the choice of reaction conditions and regioselectivity.

Author statement

Xiaokun Zhang and Jingrui Cui performed the experiments. Xiaokun Zhang supervised the study. Xiaokun Zhang and Hong Yan conceived and designed the study. Xiaokun Zhang, Jingrui Cui, and Hong Yan interpreted the results, and wrote the paper. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors report no declarations of interest.

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