Journal of Molecular Graphics and Modelling 27 (2009) 693–700

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Inner hydrogen atom transfer in benzo-fused low symmetrical metal-free tetraazaporphyrin and phthalocyanine analogues: Density functional theory studies

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ARTICLE INFO

Article history:
Received 25 August 2008
Received in revised form 13 October 2008
Accepted 27 October 2008
Available online 5 November 2008

Keywords:
Tetraazaporphyrin
Phthalocyanine
Naphthalocyanine
Inner hydrogen transfer
DFT

ABSTRACT

Density functional theory (DFT) calculations were carried out to study the inner hydrogen atom transfer in low symmetrical metal-free tetrapyrrole analogues ranging from tetraazaporphyrin H_2TAP ($A_0B_0C_0D_0$) to naphthalocyanine H_2Nc ($A_2B_2C_2D_2$) via phthalocyanine H_2Pc ($A_1B_1C_1D_1$). All the transition paths of sixteen different compounds ($A_0B_0C_0D_0$–$A_2B_2C_2D_2$ and $A_0B_0C_mD_n$, $m \leq n \leq 3$) are fully optimized at the B3LYP/6-31G(d) level and vibration analyses have been conducted to verify the optimized structures. It is revealed that the number and position of fused benzene rings onto the TAP skeleton have significant effect on the potential energy barrier of the inner hydrogen atom transfer. Introducing fused benzene rings onto the hydrogen-releasing pyrrole rings can increase the transitivity of inner hydrogen atom and thus lower the transfer barrier of this inner hydrogen atom while fusing benzene rings onto the hydrogen-accepting pyrrole rings will increase the hydrogen transfer barrier to this pyrrole ring. The transient *cis*-isomer intermediate with hydrogen atoms joined to the two adjacent pyrrole rings with less fused benzene rings is much stable than the others. It is also found that the benzene rings fused directly onto pyrrole rings have more effect on the inner hydrogen atom transfer than the outer benzene rings fused onto the periphery of isoindole rings. The present work, representing the first effort towards systematically understanding the effect of ring enlargement through asymmetrical peripheral fusion of benzene ring(s) onto the TAP skeleton on the inner hydrogen transfer of tetrapyrrole derivatives, will be helpful in clarifying the N–H tautomerization phenomenon and detecting the *cis*-porphyrin isomer in bio-systems.

1. Introduction

Tetrapyrrole compounds in particular porphyrins and phthalocyanines have been at the focus of sciences and industries for many decades due to their peculiar and unconventional chemical and physical properties [1–3]. In addition to their wide applications as dyes and pigments, tetrapyrrole derivatives have also been used as charge carriers in photocopiers and laser printers, materials for optical storage, and many other applications associated with their high thermal and chemical stability such as oxidation catalysts, solar cell functional materials, gas sensors, nonlinear optical limiting devices, photodynamic therapy agents, antimycotic materials, and corrosion inhibitors [4–6].

Due to the important roles of porphyrin derivatives in vital biological processes such as photosynthesis (chlorophyll), oxygen transport (hemoglobin), and oxygen activation (cytochrome) processes, the transfer process of the two inner hydrogen atoms in a framework of four nitrogen sites (also known as N–H tautomerization) for metal-free porphyrin has attracted considerable experimental [7–11] and theoretical [12–20] interests. It is now generally agreed that the N–H tautomerism of metal-free porphyrins occurs in a stepwise manner, proceeding via transient *cis*-porphyrin intermediates which quickly transfer into the more stable *trans*-isomers [7,9,11–15]. In contrast to the quite a large deal of interests in porphyrins, the inner hydrogen transfer for tetraazaporphyrin and phthalocyanine analogues have received negligible attention since their early synthesis despite of the great comparability between porphyrins and tetraazaporphyrins due to their isoelectronic nature. In 2004, Huang and Ma studied the mechanism and kinetics of the inner double hydrogen atom-transfer process in

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doi:10.1016/j.jmgm.2008.10.008

metal-free tetraazaporphyrin on the basis of DFT calculations and found the inner hydrogen atoms in tetraazaporphyrin can also easily transfer in a framework of four nitrogen sites [16]. In addition, it has been revealed that reducing the molecular symmetry by altering the ring size through asymmetrical peripheral fusion of aromatic rings such as benzene onto the TAP skeleton showed significant effect on the spectroscopy of the π-system [17]. However, the role of the fused benzene rings on the inner hydrogen transfer of tetraazaporphyrins is still unclear. This combined with the potential practical applications and significant importance of inner hydrogen transfer for tetrapyrrole analogues in biological systems promotes us to investigate the mechanism of the N–H tautomerization in these systems.

In this paper, we investigated the inner hydrogen transfer in low symmetrical metal-free tetrapyrrole analogues ranging from tetraazaporphyrin H_2TAP ($A_0B_0C_0D_0$) to napthalocyanine H_2Nc ($A_2B_2C_2D_2$) via H_2Pc ($A_1B_1C_1D_1$) on the basis of DFT calculations. Every possible inner hydrogen transfer path of the eleven different compounds ($A_0B_0C_0D_0$–$A_2B_2C_2D_2$) are fully optimized at the B3LYP/6-31G(d) level, and vibration analyses are carried out to verify the optimized structures. In addition, the effect of the stepwise ring enlargement through asymmetrical peripheral fusion of benzene ring(s) onto the TAP skeleton ($A_0B_0C_mD_n$, $m \leq n \leq 3$) has also been systematically investigated at the B3LYP/6-31G(d) level. The inner hydrogen transfer in benzo-fused low symmetry metal-free tetrapyrrole analogues in terms of potential energy barrier of the inner hydrogen atom transfer and transient *cis*-isomer intermediate stability is then summarized and discussed.

2. Computational details

DFT method of hybrid B3LYP functional with Becke exchange [18] and Lee–Yang–Parr correlation [19] was used throughout. In all cases, the 6-31G(d) basis set was used. The Berny algorithm using redundant internal coordinates [20] was employed in energy minimization and the default cutoffs were used throughout. The transition states were detected using QST3 method. The initial guesses for the transition states were obtained from the optimized stable or intermediate structures by moving an inner hydrogen atom to the nitrogen atom of one of the adjacent pyrrole rings. The optimized transition states were planar with C_s symmetry. The 6-31+G(d,p) basis set was also used to calculate the structures and energies of $A_0B_0C_0D_0$(S), $A_0B_0C_0D_0$(T), and $A_0B_0C_0D_0$(M) (T means transition state, M the intermediate state, and S steady state). It has been found that the difference between the calculated results with 6-31G(d) and 6-31+G(d,p) basis set is all less than 0.1 kcal/mol, indicating that the 6-31G(d) basis set used in this work is accurate enough. For the reason of time efficiency, calculations on other compounds are performed at the B3LYP/6-31G(d) level. Vibrational frequency calculations were carried out to characterize the optimized structures for S, T, and M. All calculations were carried out using the Gaussian 03 program [21] on an IBM P690 system housed at Shandong Province High Performance Computing Center.

3. Results and discussion

The molecular structures of all the steady states are shown in Fig. 1 and the inner hydrogen transfer paths for these molecules are organized in Figs. 2–7 according to different number of fused benzene rings and molecular symmetry. The four pyrrole rings are named as A, B, C, and D (Fig. 1) and the transition state, intermediate state, and steady state are contracted to T, M, and S, respectively. It is worth noting that the potential energy barrier of the concerted path is much higher than the stepwise path in energy according to the previous investigation results on the mechanism of inner hydrogen transfer in metal-free porphyrazines

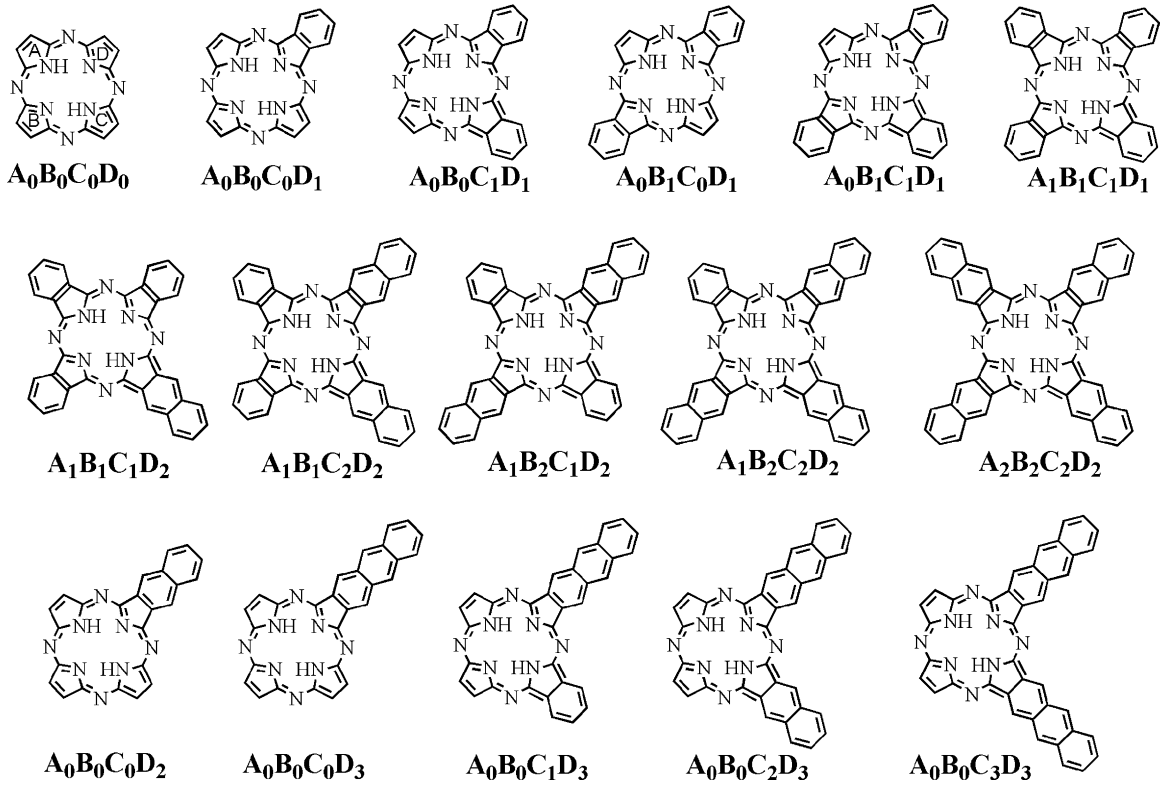

Fig. 1. Molecular structures of the benzo-fused low symmetrical metal-free tetraazaporphyrin and phthalocyanine analogues.

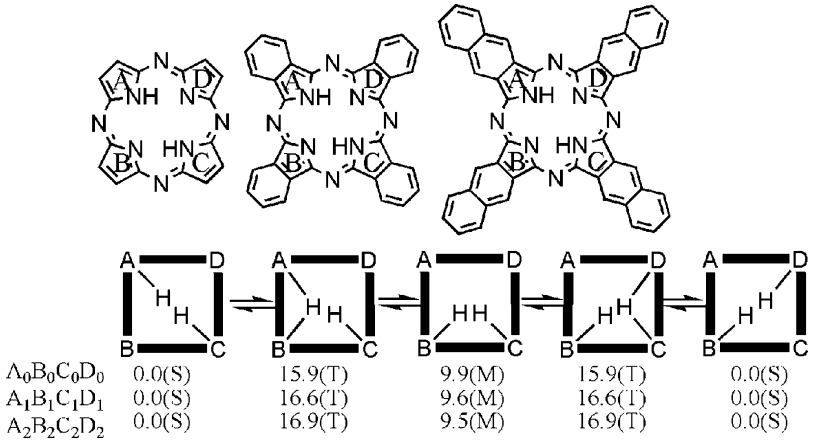

Fig. 2. Schematic diagram of the inner hydrogen transfer routes and corresponding energy (in kcal/mol) in $A_0B_0C_0D_0$, $A_1B_1C_1D_1$, and $A_2B_2C_2D_2$.

[16]. As a result, only two-stepwise pathway mechanism was taken into account in the following discussions.

It is worth noting that no basis set superposition error (BSSE) correction is carried out in this manuscript because that hydrogen transfer is occurred in the same molecule. Zero point energy (ZPE) corrections were carried out in $A_0B_0C_1D_1$ to verify if including thermal contributions can change the rule. Similar to the previous results [15], it was found that ZPE could not change the relative energy order of inner hydrogen transfer in porphyrin and its substituted derivatives, Supplementary Fig. S1. As a consequence, ZPE correction for other systems is ignored.

3.1. Hydrogen atom transfer in $A_0B_0C_0D_0$, $A_1B_1C_1D_1$, and $A_2B_2C_2D_2$

Due to the high symmetry of $A_0B_0C_0D_0$, $A_1B_1C_1D_1$, and $A_2B_2C_2D_2$ (all D_{2h}), only one possible transfer route exists which climbs over one transition state (T) and then passes through a intermediate state (the *cis*-isomer, M). As shown in Fig. 2, the *cis*-isomer of $A_0B_0C_0D_0$ [$A_0B_0C_0D_0$(M)] is about 9.9 kcal/mol higher than $A_0B_0C_0D_0$(S) with transfer barrier (the energy difference between T and S) of 15.9 kcal/mol, which corresponds well with the work of Huang and Ma [16]. When four benzene rings are fused onto the periphery of the four pyrrole rings of tetraazaporphyrin ($A_0B_0C_0D_0$), the energy difference between the *trans*- and *cis*-isomer of phthalocyanine ($A_1B_1C_1D_1$) slightly decreases to 9.6 kcal/mol while the inner hydrogen transfer barrier increase to 16.6 kcal/mol. In a similar manner, fusion of another four benzene rings onto the periphery of the four pyrrole rings of phthalocyanine ($A_1B_1C_1D_1$) leads to a further slight decreases in the energy difference between the *trans*- and *cis*-isomers of naphthalocyanine ($A_2B_2C_2D_2$) to 9.5 kcal/mol while a increase in the inner hydrogen transfer barrier to 16.9 kcal/mol. These results indicate that symmetrical fusion of four benzene rings onto the tetraazaporphyrin ring can help stabilize the *cis*-isomer intermediate with the cost of reducing the hydrogen transfer activity by increasing the transfer barrier, and the degree of such an effect decreases with the increase in the number of fused benzene rings.

This influence of the number of the fused benzene rings on the inner hydrogen transfer of tetrapyrrole derivatives can be rationalized by comparing the transfer distance (the distance from the transferred hydrogen atom to the hydrogen-accepting nitrogen atom of the adjacent pyrrole ring) and the acidity of the

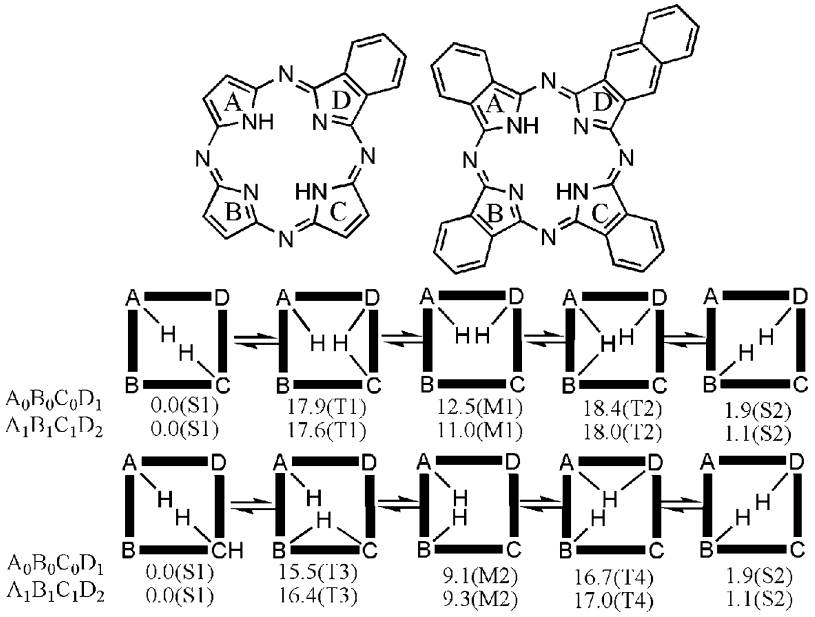

Fig. 3. Schematic diagram of the inner hydrogen transfer routes and corresponding energy (in kcal/mol) in $A_0B_0C_0D_1$ and $A_1B_1C_1D_2$.

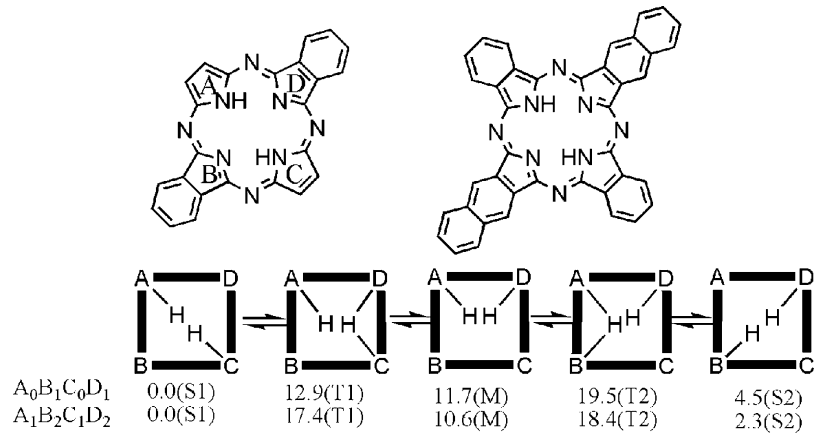

Fig. 4. Schematic diagram of the inner hydrogen transfer routes and corresponding energy (in kcal/mol) in $A_0B_1C_0D_1$ and $A_1B_2C_1D_2$.

transferred hydrogen atom. The transfer distance increases from 2.150 Å for $A_0B_0C_0D_0$(T) via 2.196 Å for $A_1B_1C_1D_1$(T) to 2.210 Å for $A_2B_2C_2D_2$(T), in line with the increase order of transfer barrier. Moreover, the weaker acidity of the transferred hydrogen atom in $A_2B_2C_2D_2$(S) in comparison with $A_1B_1C_1D_1$(S) and $A_0B_0C_0D_0$(S) also explains the higher transfer barrier in $A_2B_2C_2D_2$(S) than in $A_1B_1C_1D_1$(S) and $A_0B_0C_0D_0$(S).

3.2. Hydrogen atom transfer in $A_0B_0C_0D_1$, and $A_1B_1C_1D_2$

When one benzene ring is fused onto one of the four pyrrole rings (D for example) of $A_0B_0C_0D_0$ or the four isoindole rings of $A_1B_1C_1D_1$, two *trans*-isomer are obtained according to the relative position of the two inner hydrogen atoms. The *trans*-isomer with hydrogen atoms on the nitrogen atoms of pyrrole rings A and C (S1) is about 1.9 and 1.1 kcal/mol lower than that with hydrogen atoms on the nitrogen atoms of ring B and D (S2) for $A_0B_0C_0D_1$ and $A_1B_1C_1D_2$, respectively. As shown in Fig. 3, there are two inner hydrogen transfer routes for the two degenerate inner hydrogen atoms of $A_0B_0C_0D_1$(S1) and $A_1B_1C_1D_2$(S1): S1–T1–M1–T2–S2 and S1–T3–M2–T4–S2. Our calculation results reveal that route 1 needs to climb up much higher transfer barrier and get more instable *cis*-isomer than route 2 for both $A_0B_0C_0D_1$ and $A_1B_1C_1D_2$. For example, T1 is about 2.4 kcal/mol higher than T3 and M1 is 3.4 kcal/mol unstable in energy than M2 for $A_0B_0C_0D_1$. This might be attributed to the fact that fusion of one benzene ring onto the pyrrole of D in $A_0B_0C_0D_1$ induces a significant increase in the transfer distance [$H(N_C)$-N_D] for T1 while a decrease in the transfer

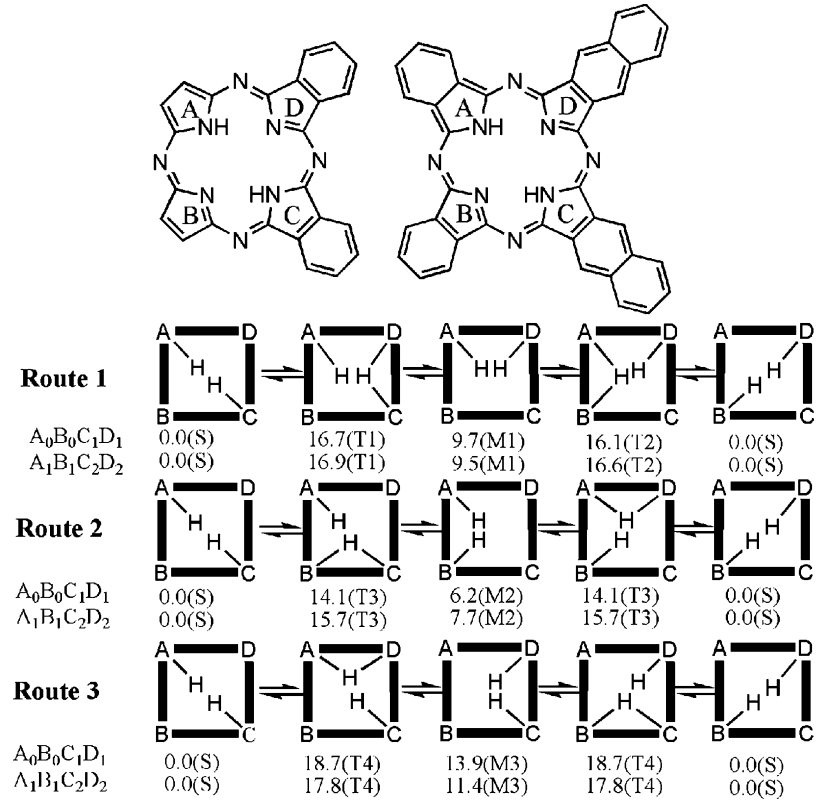

Fig. 5. Schematic diagram of the inner hydrogen transfer routes and corresponding energy (in kcal/mol) in $A_0B_0C_1D_1$ and $A_1B_1C_2D_2$.

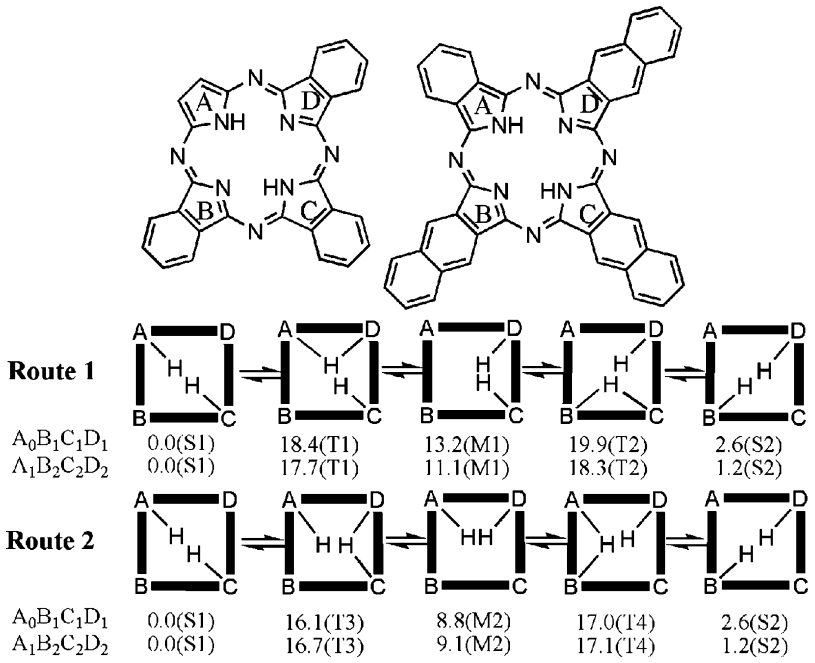

Fig. 6. Schematic diagram of the inner hydrogen transfer routes and corresponding energy (in kcal/mol) in $A_0B_1C_1D_1$ and $A_1B_2C_2D_2$.

distance [$H(N_C)$-N_B] for T3. This is disadvantageous for the inner hydrogen atom on C to transfer to D in comparison with to B though the fused benzene ring onto pyrrole D somewhat increases the basicity of N_D atom (the nitrogen atom of pyrrole ring D). T2 is 1.7 and 1.0 kcal/mol higher than T4 for $A_0B_0C_0D_1$ and $A_1B_1C_1D_2$, respectively, due to the weaker acidity and thus leads to the weaker transferability of $H(N_B)$ than $H(N_D)$ despite of the somewhat smaller $H(N_B)$-N_A distance than $H(N_D)$-N_A. As a result,

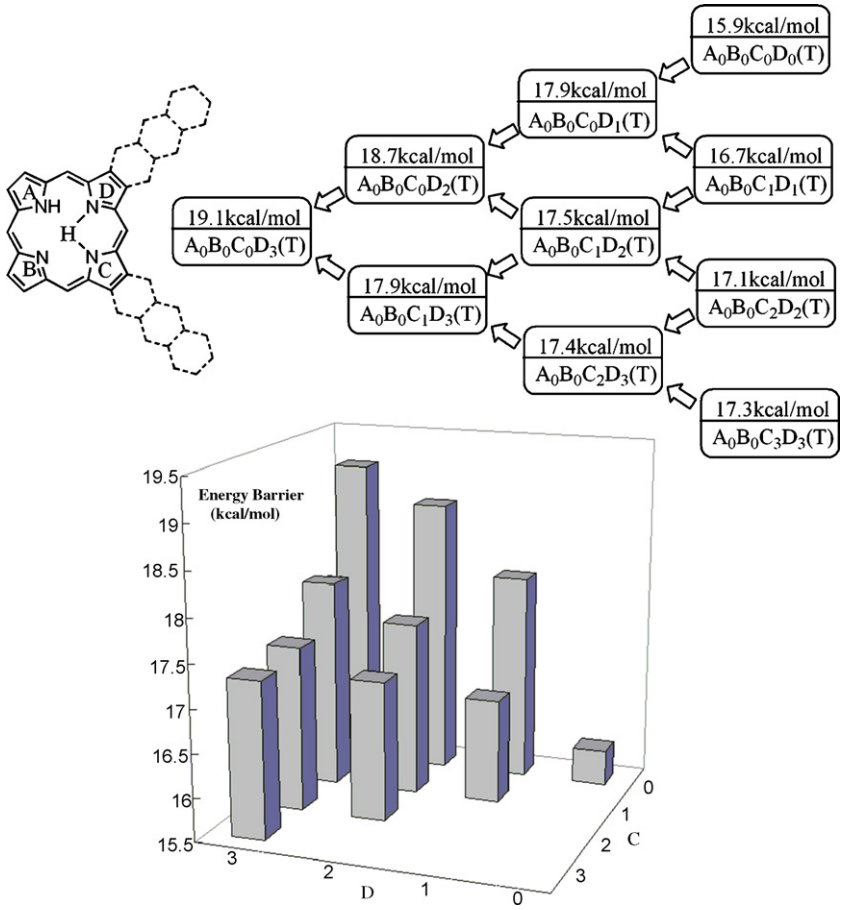

Fig. 7. Schematic diagram of one inner hydrogen transfer route and corresponding energy (in kcal/mol) in $A_0B_0C_mD_n$, $m \leq n \leq 3$.

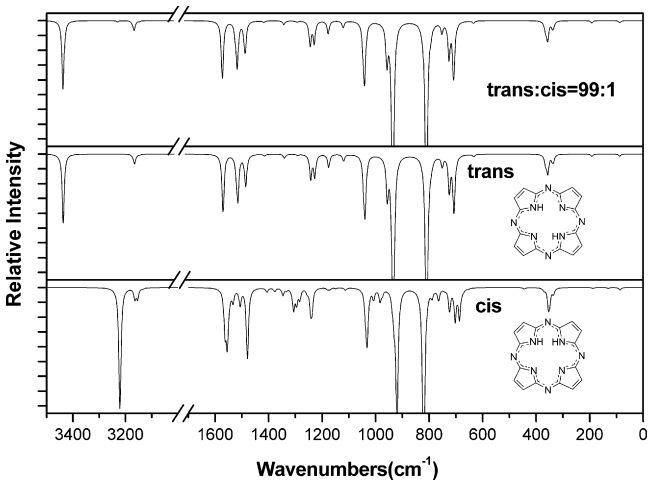

Fig. 8. The simulated IR spectra of *trans*- and *cis*-tetraazaporphyrin.

route 2 is more favorable for inner hydrogen transfer in one benzene ring fused tetraazaporphyrin and phthalocyanine analogues, i.e. $A_0B_0C_0D_1$ and $A_1B_1C_1D_2$, than route 1.

Comparison of $A_0B_0C_0D_1$ with $A_1B_1C_1D_2$ revealed that the four benzene rings in $A_1B_1C_1D_2$ induce a decrease in both the transfer barrier and energy of *cis*-isomer of route 1. In contrast, the transfer barrier and energy level of *cis*-isomer of route 2 increase for $A_1B_1C_1D_2$ in comparison with $A_0B_0C_0D_1$. As a result, the increase of four additional benzene rings in $A_1B_1C_1D_2$ than in $A_0B_0C_0D_1$ induces a decrease in the difference between the two transfer routes upon fusion of one benzene ring due to the weakened effect of the fused one benzene ring on the two transfer routes for $A_1B_1C_1D_2$ than $A_0B_0C_0D_1$, indicating that the four additional fused benzene rings are disadvantageous for the inner hydrogen transfer in one benzene ring fused tetrapyrrole compounds.

3.3. Hydrogen atom transfer in $A_0B_1C_0D_1$, $A_1B_2C_1D_2$, $A_0B_0C_1D_1$, and $A_1B_1C_2D_2$

If one more benzene ring is fused onto the pyrrole(isoindole) ring B of $A_0B_0C_0D_1$ and $A_1B_1C_1D_2$ (Fig. 4), two stable states are found according to the position of inner hydrogen atoms. Due to the C_{2v} symmetry of these two stable states, the two inner hydrogen atoms are the same and thus only one hydrogen transfer route exists. As can be seen from Fig. 4, the inner hydrogen transfer between the two stable states passes through two transition states (T1 and T2) via one *cis*-isomer (M) for both $A_0B_1C_0D_1$ and $A_1B_2C_1D_2$. Similar to the case of $A_0B_0C_0D_0$ and $A_1B_1C_1D_1$, the additional four fused benzene rings of $A_1B_2C_1D_2$ in comparison with $A_0B_1C_0D_1$ is found to increase the inner hydrogen transfer barrier but improve the stability of the *cis*-isomer due to the increase of basicity of nitrogen atoms upon introduction of electron-donating benzene group.

In good contrast, there is only one stable state when the two benzene rings are introduced onto the adjacent pyrrole rings (C and D) of tetraazaporphyrin and phthalocyanine. Due to the low symmetry (C_s) of this kind of stable state, the two inner hydrogen atoms and the two hydrogen-accepting nitrogen atoms have different environment. As a consequence, there are four transition states (T1–T4) via three intermediate states (M1–M3) (Fig. 5). T3 has the lowest transfer barrier among the four transition states. Due to the much closer distance between H(N_C) and N_B than between H(N_C) and N_D (2.120 Å vs. 2.220 Å), T1 is much higher than T3 in energy, 16.7 vs. 14.1 kcal/mol. For the same reason, T2 is much stable than T4 and T1 (Supplementary Figs. S1–S3). Despite of the longer distance between H(N_C) and N_D than between H(N_A) and N_D, T1 is about 2.0 kcal/mol more stable than T4 due to the stronger acidity of H(N_C) than H(N_A). The intermediate state M2 is about 3.5 and 7.7 kcal/mol more stable than M1 and M3, respectively. These results indicate that the most possible inner hydrogen transfer route is S–T3–M2 in $A_0B_1C_0D_1$. This is also true for $A_1B_2C_1D_2$. From $A_0B_1C_0D_1$ to $A_1B_2C_1D_2$, with the introduction of four more fused benzene rings, the transfer barrier for T1–T3 increases due to the increased transfer distance and basicity of pyrrole nitrogen atoms because of the introduction of electron-donating benzene rings. However, $A_1B_2C_1D_2$(T4) is lower in energy than $A_0B_1C_0D_1$(T4), indicating the advantage in increasing the transferability of H(N_A) by fusion of benzene ring onto A is stronger than the disadvantage by fusing benzene ring onto D.

3.4. Hydrogen atom transfers in $A_0B_1C_1D_1$ and $A_1B_2C_2D_2$

When three benzene rings are fused onto the pyrrole(isoindole) rings of $A_0B_0C_0D_0$($A_1B_1C_1D_1$), two stable isomers are formed (Supplementary Figs. S1 and S2, Fig. 6). The two inner hydrogen atoms for S1 have different environment but the hydrogen-accepting nitrogen atoms are the same due to the C_{2v} symmetry of $A_0B_1C_1D_1$ and $A_1B_2C_2D_2$. For S2, the inner hydrogen atoms are the same but the hydrogen-accepting nitrogen atoms have different environment. As a result, both S1 and S2 have two different hydrogen transfer models. As shown in Fig. 6, T3 is about 2.3 and 1 kcal/mol lower in energy than T1 for $A_0B_1C_1D_1$ and $A_1B_2C_2D_2$, respectively, due to the stronger acidity of H(N_C) than H(N_A) and basicity of N_C than N_A. T4 for $A_0B_1C_1D_1$ and $A_1B_2C_2D_2$ is also 2.9 and 1.2 kcal/mol lower in energy than T2 due to the much closer H(N_D)-N_A distance than H(N_D)-N_C. The inner hydrogen transfer in $A_0B_1C_1D_1$ and $A_1B_2C_2D_2$ therefore will pass through route 2. Similar to the case in other low symmetrical metal-free tetraazaporphyrin compounds, the four more fused benzene rings in $A_1B_2C_2D_2$ than in $A_0B_1C_1D_1$ lead to an increase in the hydrogen transfer barrier and make the *cis*-isomer less stable for route 2, while the hydrogen transfer barrier and stability of the *cis*-isomer for route 1 are decreased. This again indicates that the inner hydrogen transfer difference between different routes decreases with the increase in the number of fused benzene rings.

3.5. The rule of inner hydrogen atom transfer in low symmetry tetrapyrrole compounds

Comparison in the most favorable transfer routes in the tetraazaporphyrins fused with different number of benzene rings revealed that $A_0B_1C_0D_1$ shows the lowest inner hydrogen transfer barrier of only 12.9 kcal/mol and the most stable *cis*-isomer $A_0B_0C_1D_1$(M), which is only 6.2 kcal/mol higher in energy than $A_0B_0C_1D_1$(S). These results indicate that the inner hydrogen atoms in two benzene ring-fused tetraazaporphyrins are most active among all the benzo-fused compounds and $A_0B_0C_1D_1$ (M) is the most possible observable *cis*-isomer. The number of the fused benzene rings as well as the decrease of molecular symmetry, change of hydrogen transfer distance, change of acidity of the transferred hydrogen atoms, and increase of the basicity of the pyrrole nitrogen atoms upon the fusion of benzene rings onto the periphery of TAP ligand all have significant effect on the inner hydrogen transfer. By summarizing all the transfer routes studied, it has been found that the transferability of inner hydrogen atom increases with the increase of the number of fused benzene rings onto the pyrrole ring with transferred hydrogen. In other words, the more the number of fused benzene rings onto the pyrrole ring, the more easily the hydrogen atom transfer on this pyrrole ring. In addition, the less the number of fused benzene rings onto the pyrrole ring with hydrogen-

accepting nitrogen atom, the lower the hydrogen transfer barrier to the nitrogen atom of this pyrrole ring. As a result, the most possible inner hydrogen transfer route is that the transferred hydrogen atom which is connected to the pyrrole ring fused with most benzene rings transfers to the hydrogen-accepting nitrogen atom of the adjacent pyrrole ring which is fused with no or least number of benzene ring(s). Furthermore, it is also found that the difference between all the transfer routes upon fusion of benzene rings decreases from tetraazaporphyrin analogues to phthalocyanine analogues due to the weakened effect of the outer fused benzene rings than the inner ones on the environment of the inner hydrogen atoms. This is also true for the difference between the energy barrier of most possible transfer routes for compounds with different number of benzene rings. For example, inner hydrogen transfer barrier in phthalocyanine is 0.7 kcal/mol higher than in tetraazaporphyrin while that in naphthalocyanine is only 0.3 kcal/mol higher than in phthalocyanine.

To confirm these rules, the inner hydrogen transfer in some larger conjugated structures $A_0B_0C_mD_n$ ($m \leq n \leq 3$) are calculated, in which only the transfer route of $H(N_C)N_CN_D$ (hydrogen atom on pyrrole ring C transfers to N_D of pyrrole ring D) are examined. As can be seen from Fig. 7, the transfer barrier increases from 15.9 kcal/mol for $A_0B_0C_0D_0$ to 19.1 kcal/mol for $A_0B_0C_0D_3$ along with the increase of fused benzene rings onto the pyrrole ring D, of which the nitrogen atom accepts the transferred hydrogen atom. This is also true for the transfer barriers of $A_0B_0C_1D_1$–$A_0B_0C_1D_3$ and $A_0B_0C_2D_2$–$A_0B_0C_2D_3$. Meanwhile, the inner hydrogen transfer barrier is found to decrease from 19.1 kcal/mol for $A_0B_0C_0D_3$ to 17.3 kcal/mol for $A_0B_0C_3D_3$ along with the increase in the number of fused benzene rings on pyrrole ring C which offers the transferred hydrogen atom. For the same reason, the transfer barrier shows the order of $A_0B_0C_0D_2 > A_0B_0C_1D_2 > A_0B_0C_2D_2$ and $A_0B_0C_0D_1 > A_0B_0C_1D_1$. It is worth noting that synchronously increasing the number of fused benzene rings onto pyrrole rings of C and D from $A_0B_0C_0D_0$ to $A_0B_0C_3D_3$ induces the increase of inner hydrogen transfer barrier from 15.9 to 17.3 kcal/mol, indicating the more significant effect of benzene ring fused on the hydrogen-accepting pyrrole ring than that on the hydrogen-releasing pyrrole ring on the inner hydrogen transfer. However, the transfer barrier decreases from $A_0B_0C_0D_1$ to $A_0B_0C_2D_3$ via $A_0B_0C_1D_2$ and from $A_0B_0C_0D_2$ to $A_0B_0C_1D_3$, indicating the less influence of outer benzene rings fused onto the isoindole rings than the inner ones fused directly onto the pyrrole rings on the inner hydrogen atom transfer.

3.6. Infrared spectra predictions

Infrared spectra are most promising route to detect *cis*-porphyrin[15]. The IR spectra of $A_0B_0C_0D_0$(S,M), $A_1B_1C_1D_1$(S,M), and $A_2B_2C_2D_2$(S,M) are also calculated and the simulated spectra are shown in Fig. 8 and Supplementary Figs. S4 and S5. The calculated frequencies are scaled by the vibrational scale factor of 0.9614 [22]. Comparing the IR spectra of *trans*-tetraazaporphyrin and *cis*-tetraazaporphyrin shown in Fig. 8, one can easily observe the strong peak at 3221 cm^{-1} of *cis*-tetraazaporphyrin which is identified as N–H symmetry stretching. This peak does not exist in the spectra of *trans*-tetraazaporphyrin, and thus can be used as "fingerprints" to detect the presence of *cis*-tetraazaporphyrin. Even for the mixture of 99% *trans*-tetraazaporphyrin and 1% *cis*-tetraazaporphyrin, the peak at 3221 cm^{-1} is still visible, as is shown in Fig. 8. The same is true in the IR spectra of phthalocyanine and naphthalocyanine. As can be seen from Supplementary Figs. S4 and S5, the N–H symmetry stretching of *cis*-phthalocyanine and *cis*-naphthalocyanine occurs at 3229 and 3230 cm^{-1}, respectively. These two peaks can also be used as "fingerprints" to detect the presence of *cis*-phthalocyanine and *cis*-naphthalocyanine.

4. Conclusion

On the basis of density functional theory (B3LYP/6-31G*) calculations of the inner hydrogen transfer paths of sixteen compounds, it has been revealed that the fused benzene rings onto tetraazaporphyrin and phthalocyanine skeleton can significantly affect the inner hydrogen atom transfer by changing the transfer distance, the acidity of the transferring hydrogen, and the basicity of the hydrogen-releasing and -accepting nitrogen atoms. Nevertheless, such an effect can be tuned by controlling the number and position of the fused benzene rings onto the TAP skeleton. Introducing fused benzene rings onto the hydrogen-releasing pyrrole rings can increase the transitivity of inner hydrogen atom and thus lower the transfer barrier while fusing benzene rings onto the hydrogen-accepting pyrrole ring will increase the transfer barrier. The *cis*-isomers with hydrogen atoms joined to the two adjacent pyrrole rings with less fused benzene rings are much stable than the others. The inner benzene rings fused onto pyrrole rings are found to have more influence on the inner hydrogen transfer than the outer benzene rings fused onto the isoindole rings. The IR spectrum of *cis*-tetraazaporphyrin, *cis*-phthalocyanine, and *cis*-naphthalocyanine have significant differences from *trans*-tetraazaporphyrin, *trans*-phthalocyanine, and *trans*-naphthalocyanine, respectively, and some characteristic peaks can be used as figerpoints to detect *cis*-isomers.

Acknowledgments

Financial support from the Natural Science Foundation of China, Ministry of Education of China, and Shandong University is gratefully acknowledged. We are also grateful to the Shandong Province High Performance Computing Centre for a grant of computer time.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2008.10.008.

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