

1,2,5-噻重氮和 1,4-二正戊氧基苯环化的自由四氮杂卟啉及其金属镁配合物的结构和性质:密度泛函理论计算

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摘要: 用 DFT 方法计算分析了 1,2,5-噻重氮和 1,4-二正戊氧基苯环化的自由四氮杂卟啉及其金属镁配合物的分子和电子结构,理论计算的键参数和单晶结构测定结果一致。进一步对 1,2,5-噻重氮和 1,4-二正戊氧基苯环化的自由四氮杂卟啉的红外光谱进行了正则坐标分析和光谱模拟,以及用 TD-DFT 方法对 1,2,5-噻重氮和 1,4-二正戊氧基苯环化的四氮杂卟啉金属镁配合物的电子吸收光谱进行了分析和谱峰归属,比较了四氮杂卟啉环上取代基的电子性质对四氮杂卟啉衍生物光谱性质的影响。

关键词: 四氮杂卟啉; 光谱; 密度泛函理论计算

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Structures and Properties of Porphyrazine with Annulated 1,2,5-thiadiazole and 1,4-diamyloxybenzene and Its Magnesium Complex: Density Functional Theory Calculations

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Abstract: Density functional theory (DFT) calculations were carried out to describe the molecular structure, atomic charges, molecular orbital energy gaps, HOMO orbital map, and infrared (IR) spectrum of metal-free porphyrazine with annulated 1,2,5-thiadiazole and 1,4-diamyloxybenzene groups (*cis*-S₂A₂)PzH₂ (A=the annulated 1,4-diamyloxybenzene ring, S=the 1,2,5-thiadiazole ring) in the peripheral position of the porphyrazine macrocycle. The calculated structure and IR spectrum of (S₂A₂)PzH₂ are in good consistency with the experimental results. It has been found that the electron-withdrawing 1,2,5-thiadiazole groups and the electron-donating 1,4-diamyloxybenzene groups at the peripheral positions of porphyrazine ring add obviously different effect to different pyrrole and pyrrolenine rings. In addition, time dependent-DFT (TD-DFT) calculations were also performed on the electronic absorption spectrum of (S₂A₂Pz)Mg, the nature of the main transitions have been assigned accordingly. With the assistance of animated pictures produced on the basis of the normal coordinates, the vibration modes in the IR spectrum of (S₂A₂)PzH₂ have also been identified.

Key words: porphyrazine; spectroscopy; density functional theory calculations

0 Introduction

Phthalocyanine compounds have been important industrial dyes and pigments since their early synthe-

sis at the beginning of last century^[1-3]. Many potential applications, such as in energy conversion^[4], gas sensor^[5], and nonlinear optical limiting device^[6-8], are expected for these molecular materials with high thermal

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and chemical stability.

Various chemical modifications have been carried out, mainly on the benzene ring in phthalocyanine, to tune their physical properties^[9]. Recent efforts have led to the synthesis of a new series of porphyrazines that bear peripheral annulated 1,2,5-thiadiazole (or 1,2,5-selenodiazole) groups^[10-14]. Low-symmetry porphyrazines that bear peripheral annulated 1,2,5-thiadiazole (or 1,2,5-selenodiazole) and 1,4-diamyloxybenzene rings (abbr. as $(S_2A_2)PzH_2$) are promising materials for second-order nonlinear optics^[15,16]. However, there seems no theoretical study on the $(S_2A_2)PzH_2$ and $(S_2A_2)PzMg$ compounds. It is possible that the calculation and simulation of large molecules such as phthalocyanine complexes along with the development of computer capacity and calculation method^[17-25]. DFT methods have proved to be suitable for the energy-minimized structure calculations and spectroscopic property calculation of phthalocyanine derivatives, and particularly the time dependent density functional theory (TD-DFT) method can give good results for calculating electronic absorption spectra^[17,18,24,25].

The molecular structure and IR spectrum of $(S_2A_2)PzH_2$ are theoretically studied, which are in good agreement with that determined with X-ray crystal diffraction and the experimental absorption spectrum^[26]. To get insight into the electronic and optical properties of the $(S_2A_2)PzMg$, we further performed time dependent-DFT (TD-DFT) calculations on its electronic

absorption spectrum.

1 Computational details

The primal input structures of free-base porphyrazine were obtained from the results of our previous calculations, and the molecular structures were optimized using a small basis set and a cheap method. For compound $(S_2A_2)PzH_2$, 1,2,5-thiadiazole rings and four pentyloxy groups were introduced to the porphyrazine as the primal inputs, respectively. Using the energy-minimized structures generated in the previous step, normal coordinate analyses were carried out. Charge distribution is carried out using a full natural bond orbital analysis (NBO) population method^[27] based on the minimized structure with Gaussian NBO 3.1 in the Gaussian 03 program^[28]. For all case, B3LYP method and 6-31G(d) basis set were used. The calculated vibrational frequencies were scaled by the factor 0.961 4^[29]. All calculations were carried out using the Gaussian03 program^[28] in the IBM P690 system in Shandong Province High Performance Computing Centre.

2 Results and discussion

2.1 Molecular structure

The structure of $(S_2A_2)PzH_2$ with the atom labeling, calculated at B3LYP/6-31G(d) level with C_1 symmetry, is shown in Fig.1. It is worth pointing out that no imaginary vibration is predicted in the following

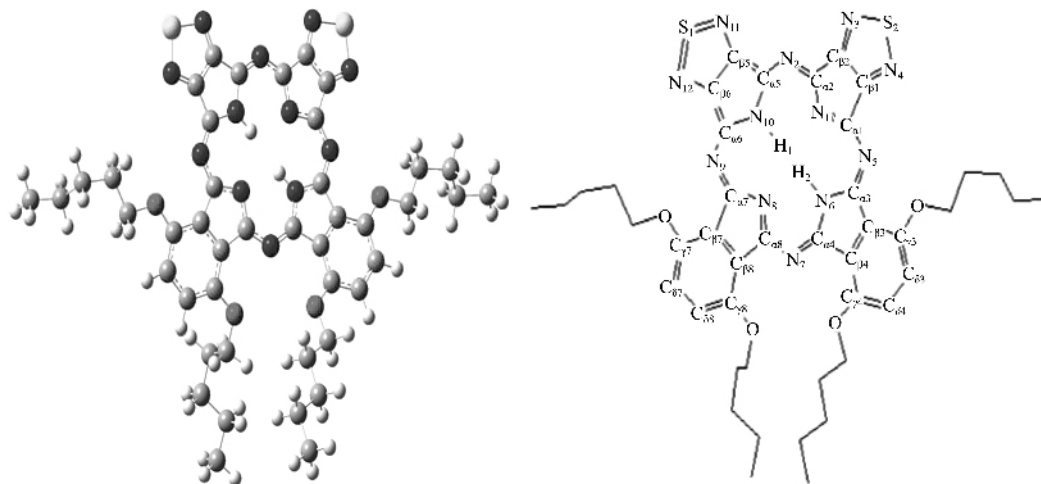


Fig.1 Optimized structure and Atom labeling of $(S_2A_2)PzH_2$

frequency calculation of the IR vibration spectroscopy, confirming that the energy minimized structure for this compound is true energy minimum.

Table 1 compares our calculated structure parameters of $(S_2A_2)PzH_2$ with the X-ray crystallography

data^[26]. As can be seen, the calculated structural data correspond well with the experimental results. The $(S_2A_2)PzH_2$ offers a good opportunity for comparing the obvious effects of the same externally annulated rings on the geometry of each individual internal pyrrole

Table 1 Calculated and Experimental Main Structural Parameters of $(S_2A_2)PzH_2$

Parameter ^a	Calculated ^b	Experimental ^c	Parameter ^a	Calculated ^b	Experimental ^c
R C _{α1} -N ₁	0.136 9	0.136 9	R C _{α7} -C _{β7}	0.146 4	0.144 6
R C _{α2} -N ₁	0.137 0	0.137 6	R C _{α8} -C _{β8}	0.147 1	0.146 4
R C _{α1} -C _{β1}	0.146 8	0.144 1	R C _{β7} -C _{γ7}	0.140 4	0.139 9
R C _{α2} -C _{β2}	0.146 6	0.146 0	R C _{β8} -C _{γ8}	0.140 5	0.138 4
R C _{β1} -N ₄	0.131 6	0.132 8	R C _{γ7} -C _{δ7}	0.140 3	0.139 1
R C _{β2} -N ₃	0.131 6	0.132 9	R C _{γ8} -C _{δ8}	0.140 5	0.139 8
R N ₄ -S	0.167 8	0.162 1	R C _{δ7} -C _{ε8}	0.139 9	0.136 8
R N ₃ -S	0.167 8	0.164 1	R C _{γ7} -O	0.135 3	0.135 3
R C _{α2} -N ₂	0.133 1	0.131 5	R C _{γ8} -O	0.135 9	0.134 4
R C _{α1} -N ₅	0.132 9	0.132 4	R C _{α8} -N ₇	0.133 6	0.135 9
R C _{α3} -N ₅	0.131 6	0.131 7	R N ₁₀ -N ₁	0.284 3	0.280 1
R C _{α3} -N ₆	0.137 9	0.137 8	R N ₁ -N ₆	0.286 4	0.288 5
R C _{α4} -N ₆	0.137 9	0.136 3	R N ₆ -N ₈	0.281 4	0.276 2
R C _{α3} -C _{β3}	0.145 1	0.143 4	R N ₈ -N ₁₀	0.285 6	0.284 4
R C _{α4} -C _{β4}	0.145 6	0.145 2	R N ₆ -N ₁₀	0.408 9	0.404 3
R C _{β3} -C _{γ3}	0.141 0	0.139 4	R N ₁ -N ₈	0.395 4	0.392 0
R C _{β4} -C _{γ4}	0.141 0	0.139 0	∠ N ₃ SN ₄	99.7	100.6
R C _{γ3} -C _{δ3}	0.139 8	0.139 7	∠ C _{β2} N ₃ S	104.6	103.8
R C _{γ4} -C _{δ4}	0.139 9	0.141 7	∠ C _{β1} N ₄ S	104.6	105.9
R C _{δ3} -C _{ε4}	0.140 4	0.138 7	∠ C _{α1} N ₁ C _{α2}	109.6	109.7
R C _{γ3} -O	0.135 1	0.135 8	∠ N ₂ C _{α2} N ₁	128.0	128.4
R C _{γ4} -O	0.135 5	0.135 4	∠ C _{α5} N ₂ C _{α2}	124.3	121.9
R N ₆ -H	0.101 3	0.949	∠ N ₁₀ C _{α5} N ₂	128.8	130.8
R C _{α4} -N ₇	0.131 8	0.133 1	∠ C _{α5} N ₁₀ C _{α6}	115.1	114.4
R C _{α6} -N ₁₀	0.138 5	0.137 3	∠ C _{β6} N ₁₂ S	104.7	103.8
R C _{α5} -N ₁₀	0.138 9	0.136 3	∠ N ₁₂ SN ₁₁	100.2	101.9
R C _{α6} -C _{β6}	0.145 8	0.144 4	∠ SN ₁₁ C _{β5}	104.8	103.5
R C _{α5} -C _{β5}	0.145 4	0.147 1	∠ N ₁₀ C _{α6} N ₉	129.4	129.3
R C _{β6} -N ₁₂	0.132 0	0.133 8	∠ C _{α6} N ₉ C _{α7}	124.6	125.0
R C _{β5} -N ₁₁	0.132 0	0.132 9	∠ N ₉ C _{α7} N ₈	127.2	127.7
R N ₁₂ -S	0.166 8	0.163 0	∠ C _{α7} N ₈ C _{α8}	107.0	107.5
R N ₁₁ -S	0.166 7	0.163 6	∠ N ₈ C _{α8} N ₇	127.1	127.8
R C _{α5} -N ₂	0.131 1	0.131 6	∠ C _{α8} N ₇ C _{α4}	124.2	123.1
R N ₁₀ -H	0.101 6	0.100 1	∠ N ₇ C _{α4} N ₆	127.5	126.0
R C _{α6} -N ₉	0.131 0	0.130 2	∠ C _{α4} N ₆ C _{α3}	112.6	109.9
R C _{α7} -N ₉	0.133 7	0.131 2	∠ N ₆ C _{α3} N ₅	128.0	128.0
R C _{α7} -N ₈	0.136 3	0.139 1	∠ C _{α3} N ₅ C _{α1}	124.9	124.5
R C _{α8} -N ₈	0.136 7	0.134 0	∠ N ₅ C _{α1} N ₁	128.7	129.1

^a Bond lengths in nm, angles in degree; ^b Present result; ^c Quoted from ref.^[26].

and pyrrolenine ring. The pyrrolenine ring has shorter $C_{\alpha 1}-N_1$ and $C_{\alpha 2}-N_1$ bond length, with the data of 0.136 9 nm and 0.137 0 nm with respect to $C_{\alpha 6}-N_{10}$ and $C_{\alpha 5}-N_{10}$ bond length of the pyrrole ring with the same annulation, of 0.138 5 nm and 0.138 9 nm. The pyrrolenine ring also has smaller $\angle C_{\alpha 1}N_1C_{\alpha 2}$ than that of pyrrole rings. We can also get some information of the effects of different externally annulated rings. The $C_{\alpha 2}-N_1$ bond length, of 0.137 0 nm, is longer than $C_{\alpha 8}-N_8$ bond length, of 0.136 7 nm, because of the presence of electron-donating 1,4-diamyloxybenzene rings at the peripheral positions. The distance from N_{10} atom to H atom is 0.100 1 nm, whereas the bond length of N_6H is 0.094 9 nm, indicating the stronger bond strength due to the electron-donating groups. The angle of $\angle C_{\alpha 1}N_1C_{\alpha 2}$, of 109.6° , is also bigger than $\angle C_{\alpha 7}N_8C_{\alpha 8}$, of 107.0° . The largest difference for bond angle, between the present calculated data and experiment result is found for $\angle C_{\alpha 4}N_6C_{\alpha 3}$, which is only 2.7° . Significant differences are found for the separation between two pairs of opposing inner N atoms (0.408 9 nm for N_6 and N_{10} , 0.395 4 nm for N_1 and N_8), indicating that the two central hydrogen atoms are directly localized on the N_6 and N_{10} .

2.2 Atomic charges

Table 2 gives the calculated atomic charges (in e) of $(S_2A_2)PzH_2$ with NBO population method. The electron-donating amyloxy groups make the charge on N_6 (-0.567 e) and N_8 (-0.614 e) atoms more negative. By comparison, the charge of N_6 atom is more positive than that on N_8 atom due to the N_6 atom is directly connected with H atom. The charge on N_1 and N_{10} atoms, -0.580 and -0.555 e, is more positive than that on N_8 and N_6 , because of the electron-withdrawing properties of the annulated 1,2,5-thiadiazole rings. The N_7 atom locates at the middle of the two pyrrole rings that bear electron-donating 1,4-diamyloxybenzene groups at the peripheral positions; as a result the charge on N_7 atom, -0.461 e is more negative than that on N_2 , -0.450 e. The N_5 and N_9 atoms are locating in the same environment, therefore the charges on N_5 and N_9 are just same, about -0.458 e. The charge on the S atom of the 1,2,5-thiadiazole ring connected

with the pyrrole ring is more positive than with the pyrrolenine ring.

Table 2 Atomic Charges (in e) of $(S_2A_2)PzH_2$

Atom	$(S_2A_2)PzH_2$	Atom	$(S_2A_2)PzH_2$
N_1	-0.580	S_1	0.867
N_2	-0.450	S_2	0.820
N_3	-0.568	H_1	0.470
N_4	-0.571	H_2	0.466
N_5	-0.458	$C_{\alpha 1}$	0.387
N_6	-0.567	$C_{\alpha 2}$	0.378
N_7	-0.461	$C_{\alpha 3}$	0.442
N_8	-0.614	$C_{\alpha 4}$	0.451
N_9	-0.459	$C_{\alpha 5}$	0.393
N_{10}	-0.555	$C_{\alpha 6}$	0.406
N_{11}	-0.569	$C_{\alpha 7}$	0.433
N_{12}	-0.572	$C_{\alpha 8}$	0.439

2.3 Molecular orbital

The calculated energies of the molecular orbital from LUMO+2 to HOMO-2 for $(S_2A_2)PzH_2$ and $(S_2A_2)PzMg$ are listed in Table 3, and the orbital map of HOMO for $(S_2A_2)PzH_2$ is shown in Fig.2 (its atomic compositions are summarized in Table S1, and see Supporting Information), which revealed that the HOMO of $(S_2A_2)PzH_2$ is mainly composed of 2Pz and 3Pz orbital of C_{α} , C_{β} , C_{γ} , O, N_3 , N_4 , N_{11} , N_{12} atoms with no composition from the S atoms. This indicates that the extended π -electron for $(S_2A_2)PzH_2$ is delocalized permeating the entire molecular units except for the peripheral amyloxy groups. The gap between the HOMO and LUMO of $(S_2A_2)PzH_2$ and $(S_2A_2)PzMg$ is important for getting information about their electron absorption spectra and correlates with the lowest energy optical transition in the electronic absorption spectrum^[24]. On

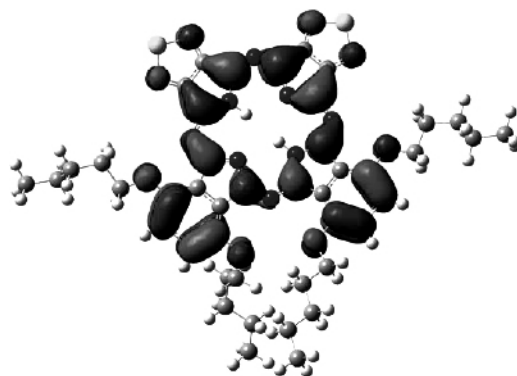


Fig.2 HOMO Molecular orbital map of $(S_2A_2)PzH_2$

Table 3 Energy levels (in eV) of some occupied and unoccupied molecular orbital for $(S_2A_2)PzH_2$ and $(S_2A_2)PzMg$

	LUMO+2	LUMO+1	LUMO	Gap	HOMO	HOMO-1	HOMO-2
$(S_2A_2)PzH_2$	-1.923 2	-2.807 3	-2.979 8	1.883 2	-4.863 0	-5.655 9	-6.096 9
$(S_2A_2)PzMg$	-1.789 3	-2.843 4	-2.861 1	1.958 3	-4.819 4	-5.628 2	-6.044 1

the basis of our calculation result, the Q band of $(S_2A_2)PzH_2$ is anticipated at the longer wavelength side than that of $(S_2A_2)PzMg$.

2.4 UV-spectrum

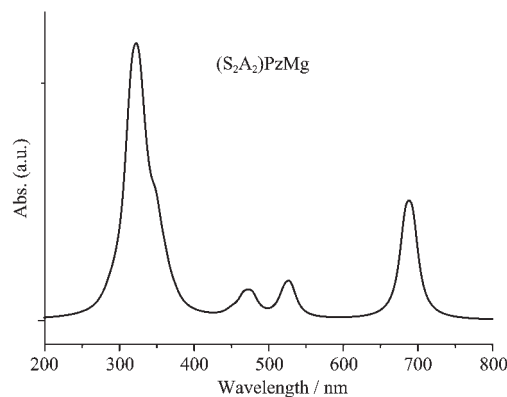
Table 4 summarizes the calculated wavelength, oscillator strength, and molecular orbital excitations for the most relevant transitions of electronic absorption spectrum of $(S_2A_2)PzMg$, obtained in vacuum system using TD-DFT method, and Fig.3 shows the simulated spectrum of $(S_2A_2)PzMg$. In the region of 300~400 (Soret band) and 600~700 (Q band) nm, compound $(S_2A_2)PzMg$ displays very intense absorptions in the simulated electronic absorption spectrum. The calculated peaks at 693 and 683 nm are mainly due to electronic transition from HOMO to LUMO+1 and HOMO to LUMO, respectively. Note that the Soret band of $(S_2A_2)PzMg$ calculated at 317 nm is assigned

Table 4 Calculated TD-DFT wavelength (λ / nm), oscillator strength (f) and composition in terms of molecular orbital excitations for the most relevant transitions

$(S_2A_2)PzMg$	
Wavelength ^a	Transition ^b
693 nm ($f=0.312$)	(0.61) 236 HOMO \rightarrow 238
683 nm ($f=0.312$)	(0.61) 236 HOMO \rightarrow 237 LUMO
530 nm ($f=0.106$)	(0.68) 235 \rightarrow 237 LUMO
350 nm ($f=0.102$)	(0.40) 230 \rightarrow 237 LUMO
	(0.23) 230 \rightarrow 238
347 nm ($f=0.107$)	(0.47) 235 \rightarrow 240
337 nm ($f=0.119$)	(0.42) 229 \rightarrow 237 LUMO
329 nm ($f=0.274$)	(0.35) 234 \rightarrow 239
	(0.35) 231 \rightarrow 238
	(0.34) 229 \rightarrow 237 LUMO
325 nm ($f=0.412$)	(0.40) 231 \rightarrow 237 LUMO
	(0.35) 234 \rightarrow 240
317 nm ($f=0.448$)	(0.52) 234 \rightarrow 239
311 nm ($f=0.233$)	(0.59) 234 \rightarrow 240

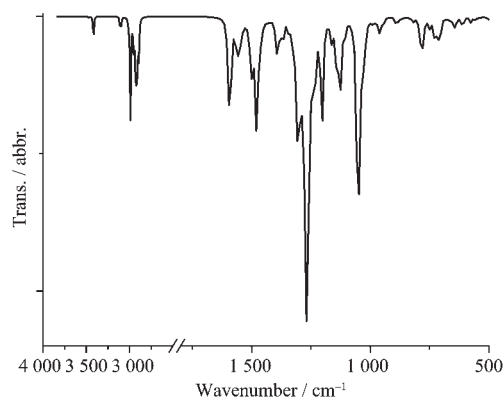
^a Calculated TD-DFT wavelength (λ /nm), the corresponding oscillator strength (f) is given in parentheses; ^b The nature of the electronic transition and contribution of each transition are shown in parentheses.

to electron transition from orbital 234 to orbital 239.

Fig.3 Simulated UV-Vis spectrum of $(S_2A_2)PzMg$ in vacuum system

2.5 Infrared spectrum

Normal coordinate analyses have been performed based on the minimum-energy geometries of $(S_2A_2)PzH_2$. The molecule of $(S_2A_2)PzH_2$ contains 12 nitrogen atoms, 44 carbon atoms, 50 hydrogen atoms, 2 sulfur atoms, 4 oxygen atoms, and therefore has 330 normal vibration modes. Fig.4 displayed the simulated IR spectrum of $(S_2A_2)PzH_2$, which is in agreement with the experimental absorption spectrum^[26]. With the assistance of animated pictures produced on the basis of the normal coordinates, the vibration modes in the $(S_2A_2)PzH_2$ IR spectrum have been identified in Table 5. According to the calculations, the two peaks at 2990 and 3417 cm^{-1} in the spectrum are N-H stretching vibrations. The peaks at 483 and 503 cm^{-1} composed of

Fig.4 Simulated IR spectrum of $(S_2A_2)PzH_2$

C_{β} -N, C-S, N-H, C_{β} - C_{β} , C_{δ} - C_{δ} , and C_{δ} -H out plane bending, which correspond well with the experimental bands at 498 cm^{-1} and 512 cm^{-1} ^[26], are due to the tor-

sion vibration of 1,2,5-thiadiazole rings. The calculated peak at $1\ 046\text{ cm}^{-1}$ is revealed to be due to the mixture of N-H, C_{δ} -H, C-H swing and C_{α} - N_1 - C_{α} , C_{γ} -O

Table 5 Calculated IR spectrum of $(S_2A_2)PzH_2$

#	Wav.	In.	Assignment ^a
1	483.09	9.931	C_{β} N, NS, N_1 H, C_{β} C_{β} , C_{δ} C_{δ} , C_{δ} H OPB
2	502.96	12.55	C_{β} N, NS, N_1 H, C_{β} C_{β} , C_{δ} C_{δ} , C_{δ} H OPB
3	575.77	14.55	macrocycles def.
4	610.90	43.23	macrocycles def., NH sw.
5	701.82	38.49	SN symstr., C_{α} N_1 C_{α} IPB, C_{α} C_{β} str.,CH sw.
6	710.47	30.45	SN str.,CH sw., C_{α} N_1 C_{α} symstr. C_{γ} C_{δ} str.
7	778.7	102.13	NH, C_{δ} H OPB,CH sw.
8	1 041.85	1 115.91	Benbre., NH sw., CC, C_{γ} O str.
9	1 045.65	261.13	NH, C_{δ} H, CH sw., C_{α} N_1 C_{α} symstr, C_{γ} O str.
10	1 050.37	265.02	Benbre, NH, C_{δ} H,CH sw., C_{α} N_1 C_{α} symstr, C_{γ} O str.
11	1 055.58	399.43	Benbre, C_{γ} O, C_{α} C_{β} str. NH, C_{δ} H, CH sw.
12	1 107.41	35.77	NH, C_{δ} H,CH sw.
13	1 123.77	232.48	NH, C_{δ} H,CH sw., C_{α} N_1 C_{α} symstr, C_{α} C_{β} , C_{β} N str.
14	1 138.04	194.47	NH, C_{δ} H,CH sw., C_{α} N_1 C_{α} symstr, C_{β} N str.
15	1 159.99	71.57	NH, C_{δ} H sw.
16	1 201.54	273.03	NH, C_{δ} H, CH sw., C_{α} C_{β} , C_{β} C_{β} str., C_{α} N_1 C_{α} symstr.
17	1 207.54	72.70	NH, C_{δ} H, CH sw., C_{β} C_{β} , C_{β} N str. C_{α} N_1 C_{α} symstr.
18	1 232.95	181.39	NH, C_{δ} H, CH sw., C_{β} C_{β} , C_{β} N str. C_{α} N_1 C_{α} symstr.
19	1 239.72	75.39	CH sw., CC str.
20	1 250.73	81.42	NH, C_{δ} H, CH sw., C_{α} N_1 C_{α} symstr. C_{α} C_{β} , C_{δ} C_{γ} str.
21	1 262.41	566.67	NH, C_{δ} H, CH sw., C_{α} N_1 C_{α} IPB, C_{α} C_{β} , C_{δ} C_{γ} , C_{γ} O str.
22	1 267.33	395.47	NH, C_{δ} H, CH sw., C_{γ} O str., benbre.
23	1 272.60	404.93	NH, C_{δ} H, CH sw., benbre., C_{γ} O str., C_{α} N_1 C_{α} symstr.
24	1 273.65	425.27	NH, C_{δ} H, CH sw., C_{γ} O, C_{α} C_{β} str., C_{α} N_1 C_{α} symstr.
25	1 292.99	210.95	NH,CH sw., C_{α} N_1 C_{α} symstr., C_{α} C_{β} , C_{δ} C_{γ} , C_{β} C_{β} str.,
26	1 297.89	133.13	NH, C_{δ} H, CH sw., C_{α} N_1 C_{α} symstr., C_{β} C_{β} , C_{δ} C_{γ} , C_{δ} C_{δ} , C_{β} C_{γ} str.,
27	1 309.22	393.85	C_{α} N_1 C_{α} symstr., C_{δ} C_{γ} , C_{β} C_{γ} str., NH, CH sw.,
28	1 342.03	53.31	CH sw., C_{α} N_1 C_{α} symstr., C_{α} C_{β} , C_{β} C_{γ} , C_{β} C_{β} , C_{δ} C_{γ} , C_{β} N str.,
29	1 378.30	50.47	C_{β} C_{β} , C_{δ} C_{δ} , C_{β} N str., NH, C_{δ} H,CH sw.
30	1 393.61	50.19	CC,CH sw.
31	1 398.06	51.57	NH, C_{δ} H,CH sw., C_{α} N_1 C_{α} symstr., C_{α} C_{β} , C_{β} C_{β} , C_{β} C_{γ} , C_{δ} C_{γ} , C_{β} N str.
32	1 477.27	205.85	CH sw. C_{γ} O str.
33	1 478.58	174.34	CH sw., C_{γ} O str.
34	1 497.82	120.91	CH sw, C_{γ} O, C_{δ} C_{γ} str.
35	1 504.48	107.24	C_{α} N_1 C_{α} IPO,CN, C_{α} C_{β} str., CH sw.
36	1 552.74	169.81	NH str., C_{α} N_1 C_{α} IPB
37	1 588.54	222.70	C_{β} C_{β} , C_{δ} C_{δ} , C_{γ} O str.
38	1 597.38	271.78	C_{β} C_{β} , C_{δ} C_{δ} , C_{γ} O str., NH str.
39	2 990.44	92.09	NH str.
40	3 416.90	107.4	NH str.

^a OPB, out-of-plane bending; IPB, in-plane bending; def. deformation; str., stretching; bre., breathing; sw., swing; symstr., symmetry stretching.

stretching. Similarly, the strongest simulated peak appearing at $1\ 262\ \text{cm}^{-1}$ is contributed by the N-H, C₈-H, C-H swing, and C_α-C_β, C₈-C_γ, C_γ-O stretching together with the C_α-N₁-C_α in-plane bending. In addition, our calculations also revealed that the peak locating at $1\ 479\ \text{cm}^{-1}$ is due to C-H swing and C_γ-O stretching, whereas the band at $1\ 597\ \text{cm}^{-1}$ due to the C_β-C_β, C₈-C₈, C_γ-O, N-H stretching.

3 Conclusion

The molecular structure, atomic charges, molecular orbital, and IR spectrum of (S₂A₂)PzH₂ have been studied by DFT calculations. It has been found that the electron-withdrawing 1,2,5-thiadiazole groups and electron-donating 1,4-diamyloxybenzene groups at the peripheral positions of porphyrazine ring add obviously different effect to each individual internal pyrrole and pyrrolenine rings. The calculated structural data and the simulated IR spectrum of (S₂A₂)PzH₂ are in good agreement with the experimental findings^[26]. The natures of the main transitions in electronic absorption spectrum of (S₂A₂)PzMg and the vibration modes in the IR spectrum of (S₂A₂)PzH₂ have been assigned.

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