

SAC-CI study of the excited states of free base tetrazaporphin

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Abstract

The SAC (symmetry adapted cluster)/SAC-CI method is applied to calculations of the ground and excited states of free base tetrazaporphin (FBTAP). The electronic spectrum is reproduced in fairly good agreement with experiments, and unknown absorption bands in the energy region higher than 4 eV are predicted. The effect of meso-tetraaza-substitution on the excited states of porphin macrocycle explains why the compound is colored, as in the closely related compounds, phthalocyanines, used as pigments.

1. Introduction

Free base tetrazaporphin (FBTAP) (also called porphyrazine or tetraazaporphyrin) $C_{16}N_8H_{10}$ is a tetraaza-derivative of porphin. Phthalocyanine, which is a much more popular compound, is regarded as a tetrabenzo-derivative of the molecule. Science of porphins and phthalocyanines have a rich accumulation, while tetrazaporphins have been left out of the interest for a long time. In the past, FBTAP is mainly considered as a model compound of phthalocyanine, especially in theoretical studies. A number of semi-empirical [1,2], local density model [3] and valence effective Hamiltonian [4] calculations were carried out. Recently, ab initio studies were also reported [5,6]. The present work is the first ab initio study of the excited states of FBTAP.

We study here the ground and excited states of FBTAP using the SAC [7] and SAC-CI [8] methods

[9,10]. The effect of meso-tetraaza-substitution on the excited states of porphin macrocycle is discussed through a comparison with the previous study on free base porphin (FBP) [11]. Phthalocyanines have intense absorption bands in the visible region, so that they are used as commercial pigments. Since FBTAP has similar intense bands in the visible region (so called Q bands), we discuss the reason why FBTAP has such intense Q bands.

2. Method

An optimized geometry by Ghosh et al. using a D_{2h} symmetry constraint [5] is adopted since X-ray diffraction data on FBTAP are not available in the literature.

The basis set is of double- ζ quality for the valence 2p orbitals. We used Huzinaga (63/5)/[2s2p] set [12] for carbon and nitrogen and (4)/[1s] set [13] for hydrogen. The total number of contracted GTOs is 202. The Hartree–Fock SCF orbitals, calculated

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Table 1
Dimensions of the SAC and SAC-CI calculations of FBTAP

Symmetry	After selection	Before selection	Threshold ($\pi - \pi^*$)
Ground state: SAC			
1A _g	14168	3133776	2×10^{-5} (1×10^{-5})
Excited state: SAC-CI			
1A _g	26968	3133776	1×10^{-6} (5×10^{-7})
1B _{1u}	34820	2817486	1×10^{-6} (5×10^{-7})
1B _{2u}	63746	3130319	1×10^{-6} (5×10^{-7})
1B _{3u}	61481	3130332	1×10^{-6} (5×10^{-7})

by HONDO program [14], consist of 81 occupied and 121 unoccupied MOs.

In the SAC/SAC-CI calculations, only the 1s core orbitals of carbon and nitrogen are frozen; the higher 57 occupied and 121 all unoccupied MOs are included in the active space. The total number of active orbitals is 178. The active space includes all the π -type orbitals, 13 occupied π and 35 unoccupied π^* MOs. For further details, the previous paper on FBP [11] may be referred to. The numbers of the linked configurations [10,15] are summarized in Table 1.

3. Ground state

The energies and the characters of the HF MOs in the HOMO-LUMO region are shown in Table 2, and the sketches of the four orbitals in the HOMO-LUMO region and the two lower MOs are shown in Fig. 1. The energy levels of the MOs in the HOMO-LUMO region are illustrated in Fig. 2 for FBP and FBTAP. Four lone pair orbitals on nitrogens gather in the energy region from -12.3 to -11.7 eV. The pyrrole N lone pairs predominate in 13a_g and 11b_{2u} MOs and the meso N ones in 11b_{3u} and 9b_{1g} MOs. The 11b_{2u} MO, which gives the lowest n- π^* excitation, is illustrated in Fig. 1.

Six higher occupied and eleven lower unoccupied orbitals have π character. The HOMO is 2a_u having nodes on the meso nitrogens. This is consistent with the previous semi-empirical [1] and ab initio calculations [5]. The next-HOMO is 5b_{1u}, which has large amplitudes on the meso nitrogens, so that this MO level is much lowered by the aza-substitution be-

cause of the larger electronegativity of nitrogen than that of carbon. The energy difference between HOMO and next-HOMO is 2.167 eV, while in FBP this energy difference is as small as 0.165 eV [11]. As shown in Fig. 2, this increase in the orbital energy gap in FBTAP is due to the stabilization of the 5b_{1u} MO. As we discuss in the next section, the influence of this level shift on the absorption spectrum is large. Similar lowering of the π -type MO localized on nitrogen was also seen in pyridine compared with benzene [16].

The LUMO is 4b_{3g} and the next-LUMO is 4b_{2g}. Though the ordering is different from FBP, the energy separation is so small in both molecules, and the influence on the excitation spectrum is negligible.

The HOMO, next-HOMO, LUMO, and next-LUMO constitute the so-called 'four orbitals' of Gouterman [17]. These orbitals of FBP are well

Table 2
HF orbital energies and characters of FBTAP

Symmetry	Character	Orbital energy (eV)
Higher occupied orbitals		
10b _{2u}	σ	-13.119
2b _{2g}	π	-12.477
2b _{3g}	π	-12.365
13a _g	n(pyrrole N)	-12.254
11b _{3u}	n(meso N)	-12.213
11b _{2u}	n(pyrrole N)	-11.886
9b _{1g}	n(meso N)	-11.664
3b _{1u}	π	-11.257
3b _{2g}	π	-11.160
4b _{1u}	π	-10.297
3b _{3g}	π	-10.113
5b _{1u}	π	-9.147
2a _u	π	-6.980
Lower unoccupied orbitals		
4b _{3g}	π	-0.891
4b _{2g}	π	-0.847
3a _u	π	2.153
6b _{1u}	π	4.526
5b _{2g}	π	5.136
5b _{3g}	π	5.279
4a _u	π	5.690
5a _u	π	7.040
6b _{2g}	π	7.622
7b _{1u}	π	8.018
6b _{3g}	π	8.056
12b _{3u}	σ	9.745
14ag	σ	9.823

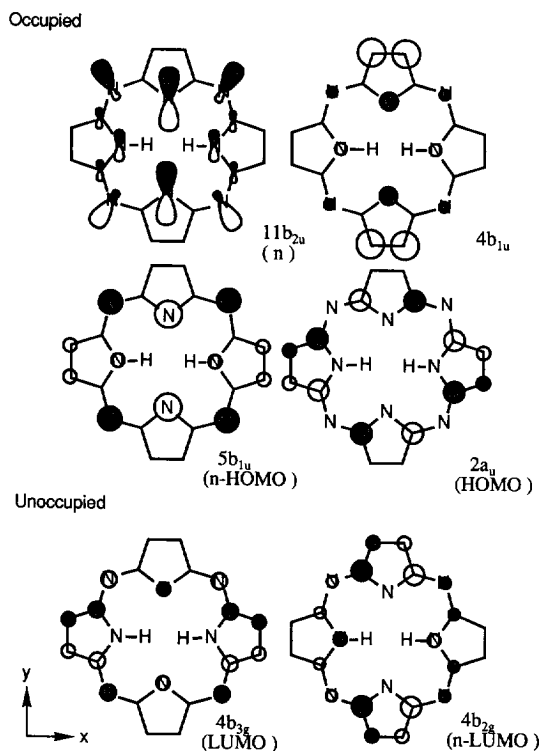


Fig. 1. Occupied ($11b_{2u}$, $4b_{1u}$, $5b_{1u}$, and $2a_u$) and unoccupied ($4b_{3g}$ and $4b_{2g}$) orbitals, which have π character except for the $11b_{2u}$ orbital.

separated from the other orbitals, giving a basis for the validity of the 'four orbital model' [17]. In FBTAP, this model is incomplete since the energy

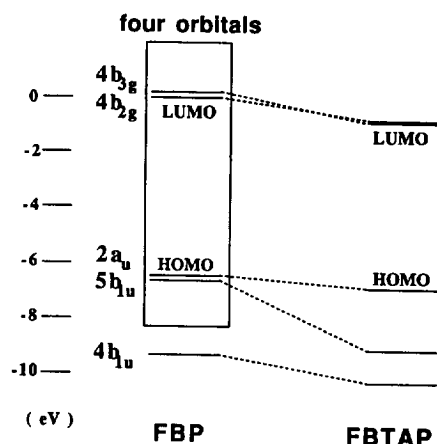


Fig. 2. Orbital energies of the four orbitals and the $4b_{1u}$ MO of FBP and FBTAP.

level of the next-HOMO ($5b_{1u}$) is closer to the lower $4b_{1u}$ MO rather than to the HOMO ($2a_u$). The $4b_{1u}$ MO strongly perturbs the four orbital model even in FBP [11], so that the $4b_{1u}$ MO should be very important to understand the excited states of FBTAP. Fig. 1 also shows the illustration of the $4b_{1u}$ MO.

The correlation energy calculated for the ground state of FBTAP is 12.5 eV.

4. Excited states

Table 3 summarizes the excited states of FBTAP calculated by the SAC-CI method. It shows the optically allowed eight $\pi-\pi^*$ and one $n-\pi^*$ excited states and the optically forbidden one $\pi-\pi^*$ state ($2A_g$).

The electronic spectra of FBTAP are shown in Fig. 3. The upper one is experimental [18], and the lower one is the SAC-CI theoretical spectrum. The most important feature of the FBTAP spectrum is that the Q bands have much larger intensities than

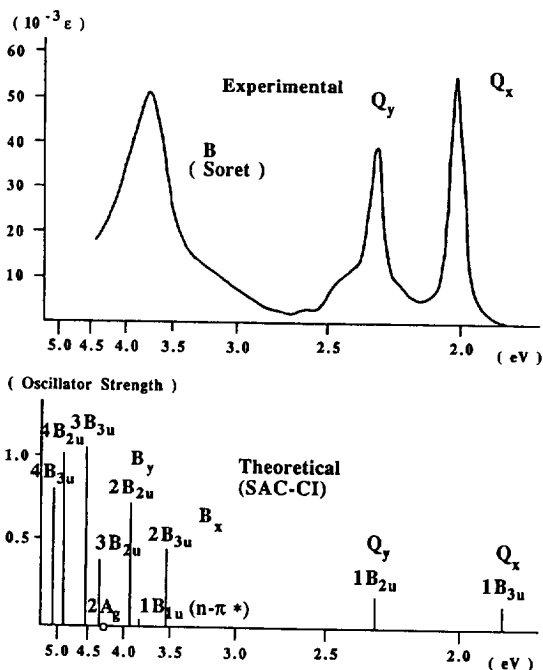


Fig. 3. Electronic excitation spectra of FBTAP observed in chlorobenzene [18] and calculated by the SAC-CI method. The optically forbidden $2A_g$ state is indicated by an open circle.

Table 3
Excited states of FBTAP calculated by the SAC/SAC-CI method

State	Main configuration ($C \geq 0.30$)	Nature	Excitation energy (eV)	Polarization	Oscillator strength	Exptl.	
						Excitation energy (eV)	
$1B_{3u}(Q_x)$	$0.79(2a_u \rightarrow 4b_{3g}) - 0.54(5b_{1u} \rightarrow 4b_{2g})$	$\pi \rightarrow \pi^*$	1.88	x	0.152	2.01	Q_x
$1B_{3u}(Q_y)$	$0.83(2a_u \rightarrow 4b_{2g}) + 0.47(5b_{1u} \rightarrow 4b_{3g})$	$\pi \rightarrow \pi^*$	2.26	y	0.220	2.27	Q_y
$2B_{3u}(B_x)$	$-0.63(4b_{1u} \rightarrow 4b_{2g}) - 0.56(5b_{1u} \rightarrow 4b_{2g})$ $-0.41(2a_u \rightarrow 4b_{3g})$	$\pi \rightarrow \pi^*$	3.56	x	0.500	3.3	
$1B_{1u}$	$-0.86(1b_{2u} \rightarrow 4b_{3g}) + 0.32(1b_{3u} \rightarrow 4b_{2g})$	$\pi \rightarrow \pi^*$	3.81	z	0.016		
$2B_{2u}(B_y)$	$-0.73(5b_{1u} \rightarrow 4b_{3g}) - 0.47(4b_{1u} \rightarrow 4b_{3g})$ $+0.37(2a_u \rightarrow 4b_{2g})$	$\pi \rightarrow \pi^*$	3.93	y	0.804	3.72	B
$2A_g$	$0.93(3b_{3g} \rightarrow 4b_{3g})$	$\pi \rightarrow \pi^*$	4.26	forbidden			
$3B_{2u}$	$-0.70(3b_{1u} \rightarrow 4b_{3g}) + 0.57(4b_{1u} \rightarrow 4b_{3g})$	$\pi \rightarrow \pi^*$	4.32	y	0.412		
$3B_{3u}$	$0.66(4a_u \rightarrow 4b_{2g}) - 0.44(3b_{1u} \rightarrow 4b_{2g})$ $-0.43(5b_{1u} \rightarrow 4b_{2g})$ $-0.31(2a_u \rightarrow 4b_{3g})$	$\pi \rightarrow \pi^*$	4.52	x	1.091		
$4B_{2u}$	$-0.61(3b_{1u} \rightarrow 4b_{3g}) - 0.59(4b_{1u} \rightarrow 4b_{3g})$ $+0.38(5b_{1u} \rightarrow 4b_{3g})$	$\pi \rightarrow \pi^*$	4.93	y	1.056		
$4B_{3u}$	$0.83(3b_{1u} \rightarrow 4b_{2g}) - 0.34(5b_{1u} \rightarrow 4b_{2g})$	$\pi \rightarrow \pi^*$	5.09	x	0.816		

those of FBP. The observed intensity ratio of the B band/ Q_x band is 50.2 for FBP in benzene [19] and 1.12 for FBTAP in chlorobenzene.

The Q band is composed of the two strong peaks Q_x and Q_y at 2.01 and 2.27 eV, respectively. By the SAC-CI calculations, Q_x and Q_y are assigned to the $1B_{3u}$ and $1B_{2u}$ states calculated at 1.88 and 2.26 eV, respectively. No other allowed excited states are found in this region. The error in the excitation energy is within 0.13 eV. The oscillator strengths of the Q_x and Q_y bands are calculated to be 0.152 and 0.220, respectively, which are quite large in comparison with those of FBP, 1.13×10^{-3} for Q_x and 5.66×10^{-3} for Q_y . The $1B_{3u}$ and $1B_{2u}$ states are polarized in the x and y directions, respectively (the x axis is along the N–H H–N bonds), in agreement with the experiment.

Now, why are the intensities of the Q bands so strong in contrast to those of FBP? This point is important since it is related with the reason why phthalocyanines are useful as pigments. Fig. 4 shows the coefficients of the main configurations and the contributions of these configurations to the transition moments in parentheses.

In both FBP and FBTAP, the Q band is written by a superposition of two configurations. For example, the $1B_{2u}$ state representing the Q_y band is written by a superposition of the two configurations, $2a_u \rightarrow 4b_{2g}$ and $5b_{1u} \rightarrow 4b_{3g}$, as shown in Table 3. In FBP, as the reflection of the validity of the four orbital model, the absolute values of the coefficients of the two main configurations are approximately equal in the individual excited state (e.g. 0.70 and 0.66 for Q_y). The transition dipole moment is expressed by a sign-reversed superposition of these two configurations, and therefore, when the weights of the configurations are equal, the moment is canceled out. This is why the Q band of FBP is weak [20]. On the other hand, in FBTAP the coefficients of the two main configurations in the Q band are unbalanced by the lowering of the $5b_{1u}$ MO. For example, the Q_y band of FBTAP consists of the superior (0.83) ($2a_u \rightarrow 4b_{2g}$) and the inferior (0.47) ($5b_{1u} \rightarrow 4b_{3g}$) configurations, because the energy difference between $2a_u$ and $4b_{2g}$ is smaller than that between $5b_{1u}$ and $4b_{3g}$. This unbalanced superposition of the configurations results in the large net transition moments as shown in the bottom of Fig. 4.

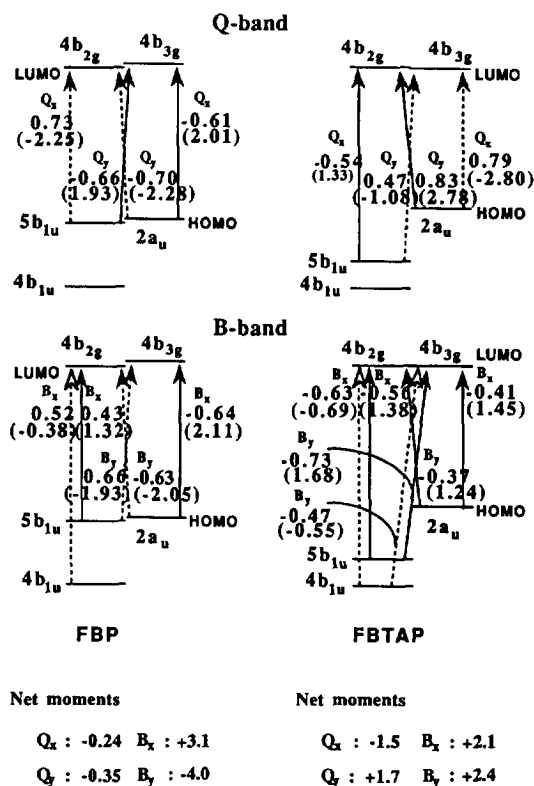


Fig. 4. Incomplete cancellations of the transition dipole moments due to an unbalanced superposition of the transitions in FBTAP in contrast to FBP. The SAC-CI coefficient and the contribution to the transition moment (in parentheses) are given. The dotted and solid arrows denote the minus and plus contributions, respectively.

The Q band is in the visible region, therefore its strong intensity colors the molecule. In fact, a solution of FBTAP is violet-blue for transmitted light. Phthalocyanines, which have a common skeleton to FBTAP, are widely used as pigments due to the intense Q band [21]. We expect that a similar unbalanced superposition of the transitions would occur in the Q bands of phthalocyanines. Thus, we conclude that a strong intensity of the Q band in the visible region is due to the breakdown of the four orbital model by the lowering of the next-HOMO which is localized on the meso nitrogens.

The B band of FBTAP is strong and broad; Dvornikov et al. suggested that the band may include some overlapping components [1]. The present SAC-CI study reveals that three allowed transitions exist in this area. The $2B_{3u}$, $1B_{1u}$, and $2B_{2u}$ states are

calculated at 3.56, 3.81, and 3.93 eV, respectively. The $2B_{3u}$ (B_x) state is polarized in the x direction, and its oscillator strength is calculated to be 0.500. It would correspond to the shoulder at around 3.3 eV on the right-hand side of the main peak. The $1B_{1u}$ state is the first $n-\pi^*$ transition and polarized in the out-of-plane z direction. This is a weak transition, whose oscillator strength is calculated to be 0.016. The $2B_{2u}$ (B_y) transition is polarized in the y direction, and its oscillator strength is the largest of the three allowed transitions in the B band, namely 0.804; it would correspond to the main peak lying at 3.72 eV. Dvornikov et al. observed the fluorescence polarization spectrum of FBTAP [1] and showed that the B band was composed of a superposition of the transitions polarized in the x and y directions. They further proposed two possibilities that the y -component is predominant in the whole region from 2.95 to 4.13 eV and that the out-of-plane z -component exists. The present study elucidates the existence of both x - and y -components, the predominance of the y -component, and the existence of the z -component, supporting the conjecture of Dvornikov et al.

Fig. 4 shows that in FBTAP the transitions from the $4b_{1u}$ MO below the four orbitals mix strongly in the B_x and B_y bands. In particular, it is the primary (-0.63) configuration of the B_x state. Similar strong perturbation of the $4b_{1u}$ MO to the four orbitals was also seen in the B (B_x) and N (B_y) bands of FBP [11], showing that the four orbital model can no longer describe the B bands of FBP and FBTAP. Furthermore, the B_x band in the lower energy side has a smaller intensity than the B_y band in the higher energy side, which is supported by the experimental spectrum shown in Fig. 3. Similar ordering of the intensities of the B_x and B_y bands was also seen for FBP [11] as shown in Fig. 4.

In the previous SAC-CI study of FBP [11] the first allowed $n-\pi^*$ transition was calculated as one component of the L bands, which lie in the higher energy region than the B band. It is noticeable that the first allowed $n-\pi^*$ transition is relatively low in FBTAP and included in the B band. This $n-\pi^*$ state consists of the major (-0.86)($1b_{2u} \rightarrow 4b_{3g}$) and the minor (0.37)($1b_{3u} \rightarrow 4b_{2g}$) configurations, the former representing the transition from the pyrrole N lone pair orbital and the latter from the meso N lone

pair orbital. It is suggested that such an interaction between the meso and pyrrole nitrogen lone pairs makes the $n-\pi^*$ state stabilized.

We calculated other four allowed transitions in the further higher energy region. The $3B_{2u}$, $3B_{3u}$, $4B_{2u}$, and $4B_{3u}$ excited states are calculated at 4.32, 4.52, 4.93, and 5.09 eV, respectively. No experimental absorption spectrum in this energy region has been reported. Since large oscillator strengths are calculated for these transitions, 0.412, 1.091, 1.056, and 0.816, respectively, we predict the corresponding intense bands in this area. Actually, for phthalocyanines the absorption spectra were observed beyond 4 eV, and the strong L and C bands were reported [21]. In FBP, we also obtained similar bands beyond the B and N bands, but the intensities were smaller there, and they were assigned to the relatively weak several L and M bands of the absorption spectrum of FBP [11].

5. Conclusion

The SAC-CI calculation reproduces the electronic absorption spectrum of FBTAP, in fairly good agreement with experiment, and reveals an important effect of the meso-tetraaza-substitution in the porphyrin macrocycle on the transition energy and the spectral intensity.

(i) The next-HOMO is much stabilized in FBTAP since it is localized on the meso nitrogens. This leads to a breakdown of the Gouterman's four orbital model.

(ii) The dissolution of the quasi-degeneracy between HOMO and next-HOMO leads to an unbalanced superposition of the transitions from these MOs in the Q bands, which results in large intensities of the Q_x and Q_y bands by an incomplete cancellation of the transition-moment components. This is why FBTAP is strongly colored and phthalocyanines are useful as commercial pigments.

(iii) The B band is composed of the weaker B_x peak in lower energy and the stronger B_y peak in higher energy. The $4b_{1u}$ MO below the four orbitals mixes strongly to the main configurations, so that the four orbital model no longer describe the B band. This result is similar to the previous result for FBP [11].

(iv) An interaction between the transition from the meso and pyrrole N lone pair orbitals stabilizes the first allowed $n-\pi^*$ state, shifting it down onto the B band.

(v) Several strong absorptions should be observed above the B bands, as actually observed in phthalocyanines.

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