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Tetrahedron Letters 49 (2008) 1856–1859
Tetrahedron Letters

Synthesis and electronic structures of D_{2h}-symmetry tetrabenzoporphyrins

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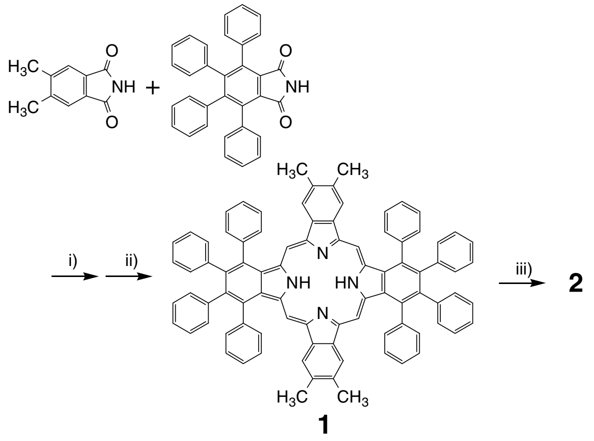
Received 25 October 2007; revised 31 December 2007; accepted 8 January 2008
Available online 11 January 2008

Abstract

A novel low-symmetry tetrabenzoporphine with D_{2h} symmetry (**1**) and its zinc complex (**2**) were prepared via mixed condensation reaction of 5,6-dimethyl phthalimide and 4,5,6,7-tetraphenyl phthalimide with sodium acetate in the presence of zinc acetate. The zinc complex **2** exhibited a split Q band at 640 and 623 nm and a single Soret band at 435 nm. The absorption spectra of **1** and **2** were calculated and analyzed using Hartree–Fock theory based on INDO/S Hamiltonian.

Keywords: Porphyrinoids; Benzoporphyrins; Magnetic circular dichroism; Density functional theory; Semiempirical calculations

Porphyrinoids with extended π-conjugation, such as tetrabenzoporphyrins (TBPs) and phthalocyanines (Pcs), have been intensively investigated due to their potential applications in many scientific areas.[1] TBPs were first synthesized by Helberger et al. in 1938,[2] and later in 1940–1950 by Linstead et al.[3] Although various types of TBP derivatives have been studied to date,[4] few studies have been reported on low-symmetry TBP derivatives,[1b] which is in great contrast to the large number of investigations concerning low-symmetry Pc derivatives. Herein, we report the synthesis, spectroscopic properties, and molecular orbital (MO) calculations of a novel, D_{2h} symmetry tetrabenzoporphine (**1**) and its zinc(II) complex (**2**) (Scheme 1). As shown below, almost perfect correspondence was found between the observed and calculated spectroscopic properties that not only the D_{2h} symmetry of **2** but also the direction of pyrrole hydrogen of **1** were determined unequivocally.



Scheme 1. Reagents and conditions: (i) AcONa/Zn(OAc)$_2$, N$_2$ gas 340–360 °C; (ii) AcOH/HCl (3:1 v/v), reflux; (iii) Zn(OAc)$_2$, EtOH/CH$_2$ClCH$_2$Cl (1:1 v/v), reflux.

Our synthetic strategy originated from the synthesis of Pcs with D_{2h} symmetry.[1b] Both ZnTBP and ZnPc can be synthesized using zinc ion as a template.[4] In particular,

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0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.01.023

when two kinds of phthalonitrile are used as starting materials, it is already well established that the use of 3,6-diphenylphthalonitrile can lead to the selective formation of D_{2h} type Pcs due to steric hindrance between phenyl groups.[5] In a similar manner, 2,3-dicyano-1,4-diphenylnaphthalene could be used to obtain D_{2h} type Pc analogues.[6] These observations indicate that D_{2h} type TBPs can be synthesized using aromatic imide containing two phenyl groups adjacent to the imide ring (note that Pcs can be prepared using aromatic ortho dinitriles, and TBPs by the corresponding imides).[4] Thus, free-base D_{2h} symmetry TBP (**1**) was obtained by the condensation of 4,5-dimethylphthalimide[7] and easily accessible tetraphenylphthalimide[8] with sodium acetate in the presence of zinc acetate at 340–360 °C.[9] The reaction mixture was refluxed in acetic-acid–HCl (=3:1 v/v) to remove the central zinc ion, since the zinc complexes were unstable during the purification process. Pure **1** was obtained in 1.1% yield by chromatographic techniques. Elemental analysis, ^{1}H NMR, and mass spectroscopy confirmed the formation of the desired macrocycle.[10] The zinc complex (**2**) was then prepared by insertion of a zinc ion into pure **1**.[11]

Figure 1a shows the electronic absorption and magnetic circular dichroism (MCD) spectra of the zinc complex (**2**) in *p*-dioxane, together with those of ZnTBP as a reference.[4c] Single Q and B (Soret) bands are observed for ZnTBP. The sharp, intense dispersion-type MCD signals in the Q and B bands of ZnTBP are Faraday *A* term arising from transitions involving degenerate final states due to the D_{4h} symmetry of the macrocycle. In contrast, the low-symmetry TBP (**2**) exhibited two resolved Q bands at 640 and 623 nm. These peak positions are very similar to the observed MCD trough (640 nm) and peak (627 nm), so that the signals are attributable to coupled Faraday *B* terms, which arise from magnetically induced mixing of nondegenerate excited states. According to studies on unsymmetrical TBPs[12] and Pcs,[13] *trans*-type D_{2h} porphyrinoids exhibit a split Q band, while *cis*-type C_{2v} porphyrinoids do not. The present observation is therefore consistent with the previous studies. In contrast to the Q region, the B band of **2** appears to be a single band. The peak position (435 nm) is longer than that of ZnTBP (425 nm) by 10 nm. The MCD signals in the B region were assigned to the pseudo *A* term, which arises as a superposition of two closely lying Faraday *B* terms of opposite sign.

Figure 1b shows the spectra of the metal-free TBP (**1**) and its deprotonated form generated by the addition of tetra-*n*-butylammonium hydroxide (TBAH).[14] Two intense absorption bands (441 and 423 nm) were observed in the B region, which are characteristic of metal-free TBPs.[4] The MCD signals corresponding to these bands can be assigned to coupled *B* terms, thus indicating a splitting of the B band. In the Q region, **1** exhibited four absorption bands (676, 660, 624, and 603 nm). The MCD signals corresponding to these bands were assigned to the *B* terms, and the signs were −, −, +, +, in ascending energy. The spectral pattern of the deprotonated form of **1** is similar to that of the zinc complex, although the Q and B peaks appear at longer wavelengths.

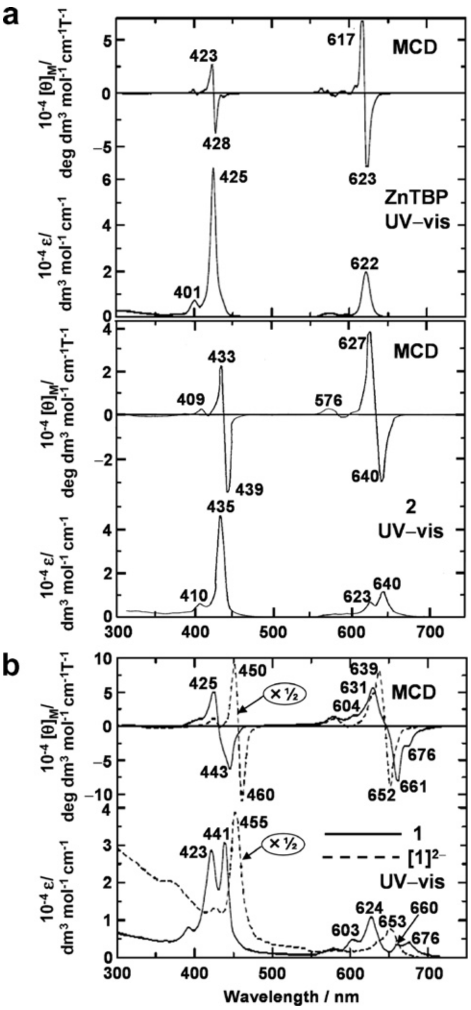

Fig. 1. Electronic absorption and MCD spectra of (a) ZnTBPs, (b) **1** (solid lines) and its deprotonated form (broken lines) in *p*-dioxane at room temperature.

To confirm our interpretation of the experimental spectra, the absorption spectra of the present TBPs were calculated and analyzed using Hartree–Fock theory based on the intermediate neglect differential overlap/spectroscopic approximation (INDO/S).[15] The ground state geometries of TBPs were calculated using Becke's three-parameter hybrid functional (B3LYP) with 6-31G(d) basis sets. The calculated spectra of ZnTBP and **2** are shown in Figure 2a. These spectral features are in good agreement with the experimental data, although the calculations underestimated the excitation energies for the Q bands. The degenerate Q transition of D_{4h} ZnTBP (770 nm) split into two bands (802 and 772 nm) for the low-symmetry TBP (**2**). These transitions are associated with the HOMO→LUMO and HOMO→LUMO + 1 transitions, respectively. Since the polarization of these bands is perpendicular to each other, these MCD signals are predicted to have different signs. Since the frontier orbitals of **2** are derived from

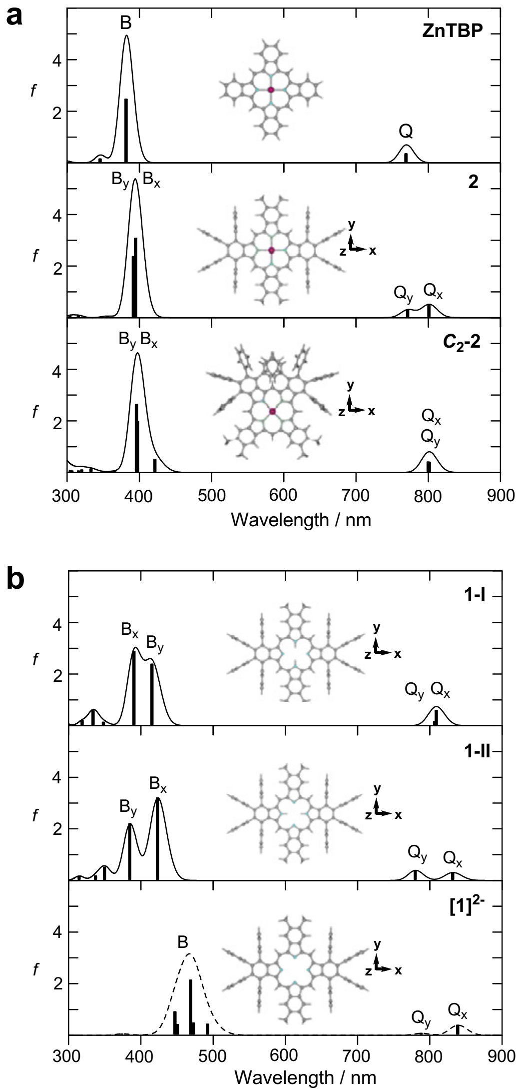

Fig. 2. Computed absorption spectra of (a) ZnTBPs and (b) H_2TBPs calculated using the INDO/S method. Gaussian bands with half-bandwidth of 400^{-1} cm (Q region) or $1500\,\mathrm{cm}^{-1}$ (B region) were used. Inset shows the B3LYP-optimized geometries.

Gouterman's orbitals, the observed absorption peaks at 640 and 623 nm can be assigned to the Q_x and Q_y transitions, respectively. The B band of **2** did not split significantly but shifted to the red by ca. 10 nm, which agrees well with the observed single absorption band and the pseudo *A* term. In contrast to the D_{2h} TBP (**2**), almost degenerate transitions were predicted for the Q and B regions of the stereoisomer of **2** (C_2-**2**), which cannot reproduce the observed spectroscopic properties.

In the case of the free-base TBP, two possible isomers (**1**–**I**, **1**–**II**) were calculated (Fig. 2b). The central protons of isomer **1**–**I** and **1**–**II** are located along the *y*- and *x*-axis, respectively. Compared to the observed spectra, the calculations for **1**–**II** give a better reproduction than those for **1**–**I**, implying that the isomer **1**–**II** (the structure shown in Scheme 1) is a major isomer under the experimental conditions. Red-shifted B transitions were predicted for the deprotonated form, [**1**]$^{2-}$, reproducing the experimental spectral pattern. The spectral pattern for the Q region of [**1**]$^{2-}$ is similar to that of the zinc complex.

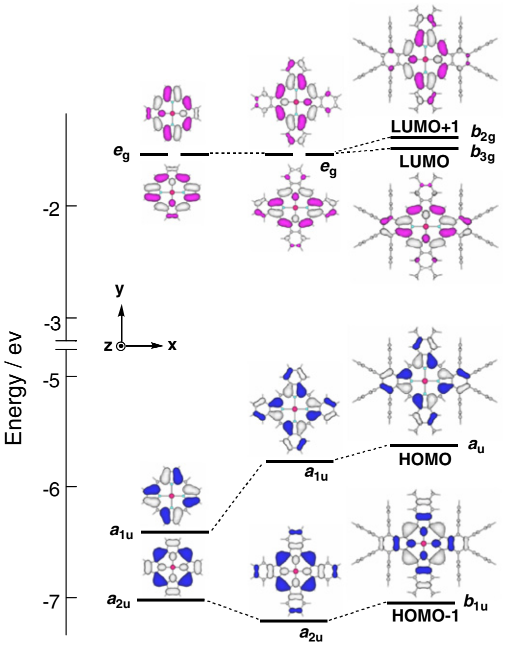

Fig. 3. Frontier molecular orbitals and the energy correlation diagram of the B3LYP-optimized structure of ZnPor (left), ZnTBP (center), and **2** (right) calculated using the INDO/S Hamiltonian.

For a detailed understanding of the electronic and MCD spectra of the TBPs in this study, MO analysis was carried out. Figure 3 shows the frontier MOs and the energy correlation diagram for zinc porphine, ZnTBP, and **2**. It is clearly seen from the figure that tetrabenzo annulations destabilize the HOMO (a_{1u}) significantly, and that perturbation of the peripheral substituents is relatively small. This results in intensification of the transition dipole moments for the Q band and red-shifted Q and B transitions. The low-symmetry perturbation lifts the degeneracy of the LUMO, leading to split Q transitions. The origin of accidentally degenerate Q transitions predicted for the isomer C_2-**2** arises from the small energy difference between the LUMO and LUMO + 1.

Finally, the origin of the MCD signals is discussed. Michl successfully interpreted the MCD signs of low-symmetry porphyrins by using the perimeter model.[16] According to the model, the absolute MCD signs of the Q bands of porphyrinoid chromophores are mainly derived from the relative size of two MO energy differences between ΔHOMO and ΔLUMO, which represent the difference between the absolute value of the energy separation of the two highest occupied MOs (i.e., HOMO and HOMO − 1) and between the two lowest unoccupied MOs (i.e., LUMO and LUMO + 1), respectively. In the case of the present TBP systems, the absolute value of ΔHOMO is always larger than that of ΔLUMO, so that a negative/positive sign sequence with increasing energy is predicted for both the Q and B transitions. These predictions agree well with the experimental results.

In summary, a combined experimental and computational study has demonstrated that a D_{2h} type, low-symmetry TBP (**1**) was synthesized as a result of a mixed condensation of two kinds of phthalimides. The zinc complex (**2**) exhibited a split Q band and a single B band. The INDO/S calculations nicely reproduced the observed spectral patterns.

Acknowledgments

A.M. is indebted to the ERYS (Tohoku University) for a research grant. Part of the computational results was obtained using supercomputing resources at the Information Synergy Center, Tohoku University. This research was partly supported by a Grant-in-Aid for Exploratory Research (No. 19655045) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and notes

1. (a) Kadish, K. M.; Smith, K. M.; Guilard, R. In *The Porphyrin Handbook*; Academic Press: New York, 2000; Vols. 1–20; (b) Kobayashi, N. In Ref. 1a, Vol. 15, Chapter 100.
2. (a) Helberger, J. H.; Reday, A. V.; Hever, D. B. *Justus Liebigs Ann. Chem.* **1938**, *533*, 197; (b) Helberger, J. H.; Hever, D. B. *Justus Liebigs Ann. Chem.* **1938**, *536*, 173.
3. (a) Barrett, P. A.; Linstead, R. P.; Rundal, F. G.; Tuey, G. A. P. *J. Chem. Soc.* **1940**, 1079; (b) Linstead, R. P.; Weiss, F. T. *J. Chem. Soc.* **1950**, 2975.
4. (a) Kobayashi, N. In *The Phthalocyanines-Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, 1993; Vol. 2, Chapter 3; (b) Lash, T. D. In Ref. 1a, Vol. 2, Chapter 10; (c) Lukyanets, E. A.; Dashkevich, S. N.; Kobayashi, N. *Russ. J. Inorg. Chem.* **1993**, *63*, 985.
5. (a) Kobayashi, N.; Ashida, T.; Osa, T. *Chem. Lett.* **1992**, 2031; (b) Fukuda, T.; Homma, S.; Kobayashi, N. *Chem. Eur. J.* **2005**, *11*, 5205; (c) Matsushita, O.; Muranaka, A.; Kobayashi, Y.; Kobayashi, N. *Heterocycles*, in press.
6. Kobayashi, N.; Ashida, T.; Osa, T.; Konami, H. *Inorg. Chem.* **1994**, *33*, 1735.
7. Godinez, C. E.; Zepada, G.; Mortko, C. J.; Garcia-Garibay, M. A. *J. Org. Chem.* **2004**, *69*, 1652. However, we have synthesized this compound by another method.
8. Harris, F. W.; Norris, S. O. *J. Heterocycl. Chem.* **1972**, *9*, 1251.
9. Kopranenkov, V. N.; Makarova, E. A.; Dashkevich, S. N.; Luk'yanets, E. A. *Chem. Heterocycl. Compd.* **1988**, 630.
10. ^{1}H NMR: (δ ppm, 500 MHz, $CDCl_3$): −2.92 (s, 2H, NH), 1.86 (s, 12H, Me), 6.42–6.71 (br m, 16H, arom), 6.9–7.2 (br m, 28H, arom), 9.72 (s, 4H, meso); Elemental Anal. Calcd for $C_{88}H_{62}N_4$: C, 89.92; H, 5.32; N, 4.77. Found: C, 89.47; H, 5.60; N, 4.58. UV–vis in *p*-dioxane, λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 676 nm (4000), 660 nm (3400), 624 nm (11,000), 603 nm (4800), 441 nm (31,000), 423 nm (29,000); FAB-MS *m/z* 1175 (M$^+$).
11. Elemental Anal. Calcd for $C_{88}H_{60}N_4Zn$: C, 85.32; H, 4.88; N, 4.52. Found: C, 84.91; H, 5.27; N, 4.34. UV–vis in *p*-dioxane, λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 640 nm (23,000), 623 nm (14,000), 435 nm (90,000), 410 nm (12,000); FAB-MS *m/z* 1238 (M$^+$).
12. Makarova, E. A.; Kopranenkov, V. N.; Shevtsov, V. K.; Luk'yanets, E. A. *Chem. Heterocycl. Compd.* **1989**, 1159.
13. (a) Kobayashi, N.; Miwa, H.; Nemykin, V. N. *J. Am. Chem. Soc.* **2002**, *124*, 8007; (b) Kobayashi, N.; Fukuda, T. *J. Am. Chem. Soc.* **2002**, *124*, 8021; (c) Kobayashi, N.; Mack, K.; Ishii, K.; Stillman, M. J. *Inorg. Chem.* **2002**, *41*, 5350; (d) Miwa, H.; Ishii, K.; Kobayashi, N. *Chem. Eur. J.* **2004**, *10*, 4422.
14. The increase in absorbance in ca. 350–440 nm is due to TBAH.
15. Mack, J.; Asano, Y.; Kobayashi, N.; Stillman, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 17697.
16. (a) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801; (b) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6812; (c) Keegan, J. D.; Stolzenberg, A. M.; Lu, Y.-C.; Linder, R. E.; Barth, G.; Moscositz, A.; Bunnenberg, E.; Djerassi, C. *J. Am. Chem. Soc.* **1982**, *104*, 4305; (d) Keegan, J. D.; Stolzenberg, A. M.; Lu, Y.-C.; Linder, R. E.; Barth, G.; Moscositz, A.; Bunnenberg, E.; Djerassi, C. *J. Am. Chem. Soc.* **1982**, *104*, 4317.