Evaluation of planarity and aromaticity in sapphyrin and inverted sapphyrin using a bidirectional NICS (Nucleus-Independent Chemical Shift) scan method†

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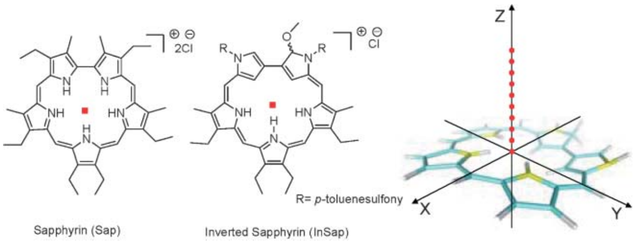
Using the bidirectional NICS scan method in conjunction with two-photon absorption (TPA) measurements, it has proved possible to determine the relationship between π-conjugation and aromaticity in two structurally related expanded porphyrin systems, sapphyrin and inverted sapphyrin, and establish that differences in these defining factors depend on the presence or absence of a key sp^3 hybrid molecular orbital within the macrocyclic periphery.

Various expanded porphyrins containing more than four pyrrole rings have been synthesized in recent years. Much of this effort has been inspired by the interesting optical properties of these systems, including those associated with the presence of more extensive π-conjugation pathways relative to those present in porphyrins and other tetrapyrrole systems.[1] However, not all expanded porphyrins contain enhanced π-conjugation pathways. Among these latter is inverted sapphyrin (InSap), a pentapyrrolic "porphyrin-like" macrocycle that was recently obtained using a novel synthetic approach. This derivative, in contrast with its parent system, sapphyrin (Sap), displays weak aromatic features as the result of what is a substantially modified electronic configuration.[2] The weak aromatic property of inverted sapphyrin was briefly introduced in the original synthetic report; however, detailed spectroscopic and theoretical analyses were not included and, indeed, were postponed for further study. Now, as part of an ongoing effort to explore in detail the aromatic properties of various expanded porphyrins, we have carried out a detailed spectroscopic study of both Sap and InSap, using *inter alia* time-resolved fluorescence, femtosecond transient absorption, femtosecond Z-scan, and *ab initio* calculation methods. Taken together, these techniques have allowed us to detail the striking progression from aromaticity in Sap to weak aromaticity or near-antiaromaticity in InSap in terms of a specific difference in molecular structure, namely a partial disruption in the π-conjugation pathway that arises from a change in an sp^2 hybridized carbon center to an sp^3 hybridized carbon atom in InSap (Scheme 1).



Scheme 1 Molecular structure of sapphyrin (Sap) and inverted sapphyrin (InSap). The unweighted geometric centers (red dots) were used for the NICS calculation in the case of each molecule.

Fig. 1 exhibits the steady-state absorption spectra of Sap and InSap in CH_2Cl_2 and the estimated oscillator strengths from an *ab initio* B3LYP/6-311 + G* TD (nstate = 20) basis set, based on the optimized geometry calculated using the same basis set. In analogy to what is seen for most common tetrapyrrolic systems, as represented by, *e.g.*, typical porphyrins, the absorption spectra of Sap and InSap show two distinct B- and Q-like optical transitions in the 400–500 and 600–800 nm spectral regions, respectively.[3] The experimentally observable oscillator strengths for the B-like bands were greater than the Q-like bands in the case of both pentapyrrolic systems. However, the Q-like band was far more intense in the case of InSap, making the Q- to B-like oscillator strength ratio much larger in the case of InSap than Sap. Presumably as the result of solvation by CH_2Cl_2, the absorption spectra recorded in this latter solvent show a bathochromic shift

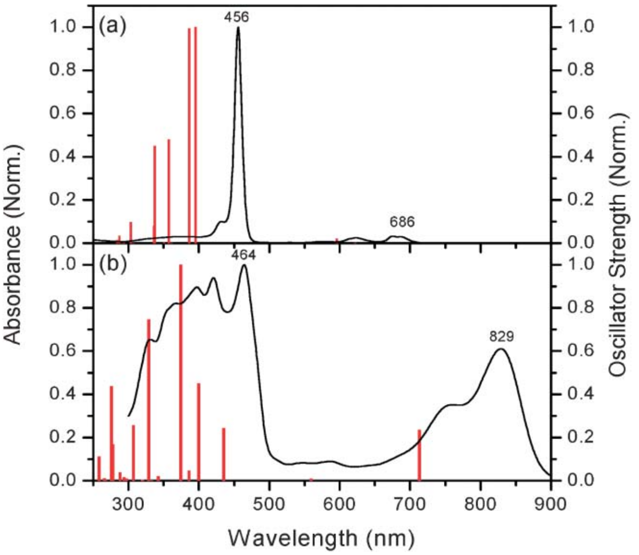


Fig. 1 Steady-state absorption spectra in CH_2Cl_2 (solid lines) and calculated oscillator strength (bars) of (a) Sap and (b) InSap.

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compared to the calculated oscillator strengths. Among the oscillator strengths calculated for the 20 major states of InSap, it is noteworthy that a relatively broader spectral distribution of oscillator strengths is predicted in the B-like band region compared to Sap, along with a strong feature at 713 nm that is not predicted in the case of Sap. These differences in calculated spectral characteristics are considered to reflect changes in the molecular symmetry of InSap (compared to Sap) that arise from the presence of an sp^3 hybridized carbon atom within one of the pyrrole rings of InSap.[4]

In order to analyze the above differences in structure, specifically π-electron delocalization pathway, and steady-state absorption spectral features in a more quantitative manner, NICS (Nucleus-Independent Chemical Shift) calculations were performed for both Sap and InSap using optimized geometries calculated from the B3LYP/6-311 + G* basis set.[5] This was done because both the signs (+ or −) and the absolute NICS values have been regarded as quantitative measures of aromaticity/antiaromaticity, at least within a readily comparable set of related structures. The NICS(0) values at the centers of Sap and InSap were calculated to be −14.9 and −2.0 ppm, indicating that Sap is more aromatic than InSap, and that this latter species is weakly aromatic.

To gain further insights into the electronic and molecular structure of Sap and InSap, we have developed a "bidirectional" (±Z) NICS scan method that extends Stanger's unidirectional (+Z) NICS scan method to one that provides a quantitative measure of aromaticity from in-plane and out-of-plane components.[6,7] With this new bidirectional NICS scan method, we could obtain quantitative information on the aromaticity by relating the ring current effect to molecular geometry as shown in Fig. 2. Due to the "smooth" ring current produced by the planar geometry of Sap, the shape of the ±Z NICS scan curve is symmetric around the Z-axis. In InSap, however, it is asymmetric due to its distorted geometry, something that is reflected in the observed geometry-dependent ring current effects. It is particularly noteworthy that the shape of the scanned curves derived from the calculated isotropic chemical shifts and their in-plane and out-of-plane contributions are representative of aromatic (a) and weakly aromatic (b) systems for Sap and InSap, respectively. In other words, while the NICS values of Sap mainly depend on out-of-plane components, those of InSap are almost equally controlled by in-plane and out-of-plane contributions.[6] One interesting feature in (b) is a crossing point at ~0.9 Å, which is thought to reflect the spatial distribution range of the out-of-plane sp^3 hybrid orbital in InSap, an effect that is not seen in Sap. In the event, this difference is consistent with the minimum (in-plane) and maximum (out-of-plane) chemical shifts influenced by the sp^3 hybrid orbital, which gives rise to the slightly distorted dome-like structure. Thus, the bidirectional NICS scan results provide support for the conclusion that it is the partial, but nonetheless significant, disruption of the π-electron delocalization pathway in InSap caused by the sp^3 hybrid orbital that constitutes the dominant factor leading to weak aromaticity. This disruption also gives rise to a distorted geometry, as confirmed by the previously reported single crystal structural analysis and NMR spectroscopic data.[2]

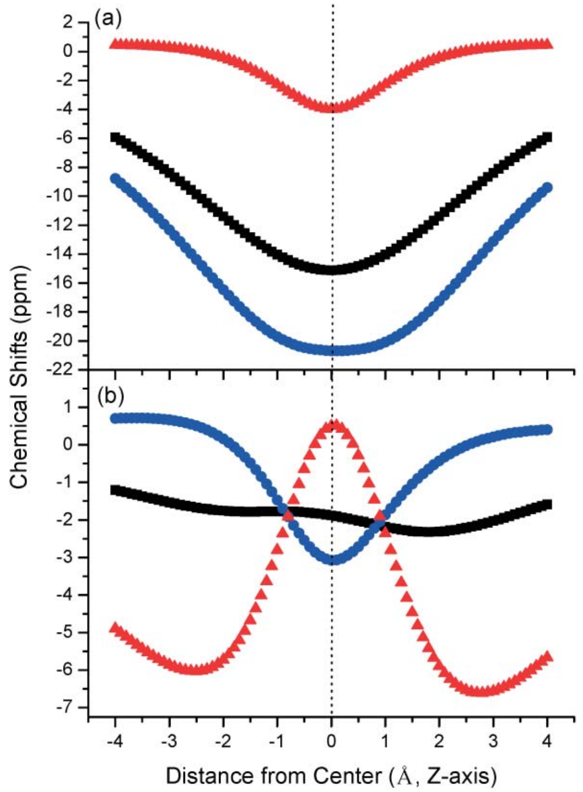

Fig. 2 NICS scan curve for (a) Sap and (b) InSap calculated with 0.1 Å spacing. ■ isotropic chemical shift; ● in-plane (XY plane) component; ▲ out-of-plane (±Z axis; *i.e.*, "bidirectional") component.

In previous work not involving InSap, it was found that the elongation of π-conjugation pathways and their correlation with molecular planarity could be inferred from TPA measurements.[8] In addition, the electronic characteristics of molecules, including transition dipole moment and polarizability, could be correlated with the TPA values. In the present study, the maximum TPA values of Sap and InSap were measured to be ~2900 and <100 GM, respectively, indicating more efficient π-electron delocalization within Sap as compared to InSap (Fig. 3 and ESI†). In the TPA spectrum of Sap, the maximum TPA value was observed at 640 nm (λ_{ex} = 1280 nm), higher than the absorption peak in the one-photon absorption (OPA) spectrum (λ_{max} = 675 nm). When considered in conjunction with the steady state absorption spectral features, the differences in the TPA values

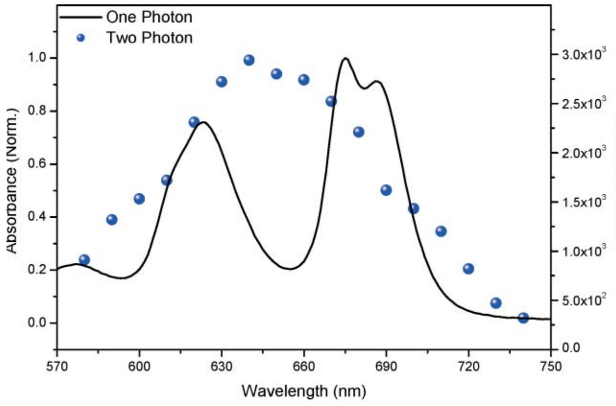

Fig. 3 Two-photon absorption (TPA) spectrum (dots) and one-photon absorption spectrum (solid line) of Sap in CH_2Cl_2 in the Q-like spectral region. The maximum TPA value was 2900 GM, which was seen upon excitation at 1280 nm.

observed for Sap and InSap can be explained in terms of the disparities in their respective π-electron delocalization pathways, fully conjugated and partially disrupted, respectively. The partial disruption of the π-conjugation pathway in InSap, a feature noted at the time of the original synthetic report,[2] is a direct consequence of the unique sp^3 hybridized carbon center contained within its periphery. It is thus the critical molecular-level change that serves to weaken the aromaticity of this particular sapphyrin analogue.

In an effort to correlate the differences in the π-electron delocalization characteristics of Sap and InSap with their corresponding excited-state dynamics, the singlet excited state lifetimes were measured in CH_2Cl_2 using femtosecond transient absorption and time-resolved fluorescence (TCSPC) spectroscopy (*cf.* ESI†). Deconvolution and fitting of the resulting decay data revealed that the singlet excited state lifetime of Sap (2.43 ns) is much longer than that of InSap (105 ps). Assuming that only a "pure" π–π* transition is involved in the excited state dynamics of both Sap and InSap, the large difference in the decay rate seen for the respective S_1 (π, π*) states leads to the conclusion that the distorted structure of InSap provides access to more nonradiative decay channels than is true in the case of the relatively flat system, Sap.[9] Thus, as in the case of the other analyses noted above, these time-resolved measurements serve to underscore the fact that a single change in the conjugation pathway within an otherwise similar pair of compounds can have a huge effect on the optical and electronic properties of the system.

In summary, comparative analyses of the photophysical and aromatic properties of Sap and InSap have been carried out using various steady-state and time-resolved spectroscopies, as well as *via ab inito* calculations. The results obtained in this way support the conclusion that Sap is strongly aromatic, whereas InSap is not. The observed TPA values, which display a strong correlation between the aromaticity features (or lack thereof) and the NLO properties of these two molecular systems, are fully consistent with this assessment. We rationalize this difference in terms of a key change in the structure and electronic configuration of these two ostensibly similar heteroannulene systems. In particular InSap contains a sp^3 hybridized carbon that serves to disrupt in part the dominant π-electron delocalization pathway present in Sap. To the extent that the present findings can be generalized, they thus serve to illustrate how the inherent electronic properties of porphyrin analogues may be perturbed to produce new chromophores with unusual optical and electronic properties.

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