Electronic Consequences of Nonplanar Core Conformations in Electron-Deficient Porphyrins: The Structure and Spectroscopic Properties of [5,10,15,20-Tetrakis(heptafluoropropyl)porphinato]cobalt(II)

Stephen G. DiMagno,* Alan K. Wertsching, and
Charles R. Ross, II

Department of Chemistry, University of Nebraska—Lincoln
Lincoln, Nebraska 68588-0304

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The conformational variability of tetrapyrrolic macrocycles observed in protein crystal structures is hypothesized to play a role in controlling the redox, spectroscopic, and catalytic properties of metalloenzymes.[1–4] Conformationally constrained porphyrins and metalloporphyrins have been proposed as model systems to study the electronic consequences of ring deformation.[5] Sterically demanding groups at the porphyrin periphery lead to extensive nonplanar distortions in the relatively flexible porphyrin macrocycle, and substantial alterations in the absorption spectra often accompany these structural changes.[6–11] The conclusions drawn from this work are that nonplanar core conformations cause red shifts in the electronic spectra of porphyrins by destabilizing the porphyrin HOMO. The goal of our work is to ascertain experimentally the intrinsic contribution of nonplanar ring distortions upon the electronic properties of porphyrins. Such information will impact the analysis of spectra of porphyrin-containing metallobiomolecules and will have crucial implications for the design of biomimetic oxidation catalysts.

The activity and stability of porphyrinic metal–oxo species in alkane hydroxylation and alkene epoxidation have been shown to be correlated with HOMO oxidation potential.[12,13] Metalloporphyrin catalysts bearing 12 electron-withdrawing substituents, such as those employing the 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ligand (OBTPFP), invariably adopt a nonplanar conformation as a result of steric interactions at the porphyrin periphery.[6] If nonplanar distortions of the porphyrin core destabilize the porphyrin HOMO and facilitate porphyrin radical cation formation, the practical limit of catalytic activity and stability may already have been achieved.

The recent synthesis of porphyrins bearing perfluoroalkyl groups in the meso position has enabled a number of new, extremely electron deficient metalloporphyrins to be prepared.[14] These compounds represent a new class of metalloporphyrins: they are simultaneously extremely electron-deficient and nonplanar, and they contain no substituent groups capable of π-interaction with the ring. They are therefore excellent compounds to probe the electronic consequences of porphyrin ring distortions in the absence of conjugation effects. Here we report the structure and properties of [tetrakis(heptafluoropropyl)porphinato]cobalt(II) **1**. Examination of the spectroscopic properties of **1** and of the free base, **2**, in conjunction with theoretical studies, indicates that nonplanar conformations have an extremely modest effect on the electronic properties of these ligands.

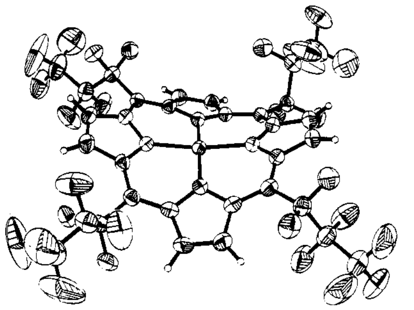

Figure 1. ORTEP view of **1** with thermal ellipsoids at 50% probability.

Compound **1** is readily prepared from the dilithium salt of **2** and anhydrous $CoCl_2$ in THF,[15] and is easily purified by recrystallization from acetonitrile at −20 °C. The associated acetonitrile is quantitatively removed from the five-coordinate complex by heating at 80 °C for several hours under vacuum.[16] Desolvated **1** was recrystallized from hexane by slow evaporation to yield crystals of the four-coordinate cobalt(II) porphyrin which were suitable for X-ray diffraction. The structure of **1** is shown in Figure 1. The perfluoropropyl groups extend from the porphyrin core in an all-trans conformation, and they are staggered with respect to one another. The pyrrole rings are essentially planar. The average Co–N bond distance (1.937 Å) is significantly shorter than that found in Co(TPP) (1.949 Å) and approaches that reported for highly nonplanar [octaethyltetraphenylporphyrinato]cobalt(II) (1.929 Å).[17] These results mirror previous observations that show a correlation between degree of core nonplanarity and metal–nitrogen distance.[18] The structure of the core is essentially a saddle incorporating some ruffling.[19] The maximum displacements of the β-pyrrole carbon atoms are in excess of 1 Å from the mean plane of the porphyrin ring. These displacements are larger than those seen in the structures of all other simple meso-tetrasubstituted cobalt derivatives, and they are only matched in crystallographic studies of extremely sterically crowded porphyrins.[17] The structure of **1** shows several very short H–F nonbonded contacts, the closest two of which are only 2.14 Å. This distance is well within the sum of the van der Waals radii. Because the H–F steric interactions are more severe in the planar structure, we hypothesize that they are principally responsible for the dramatic twisting of the porphyrin core.

A summary of the optical spectra of **1**, **2**, (TPP)Co^{II}, and TPP in hexane and in the solid state is given in Table 1. The optical spectra of the perfluoroalkyl derivatives show blue shifts both

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Table 1. Transition Wavelengths (nm) for Porphyrins in Hexane Solution and in the Solid State

compd	medium	Soret λ_{max}	Q(1,0) λ_{max}	Q(0,0) λ_{max}	spectral midpoint[a]
1	hexane	392	547	579	467
1	KBr	392		580	468
2	hexane	401.5	593.5	648	496
2	KBr	404.5	596	648	498
(TPP)$\mathrm{Co^{II}}$	hexane	406	525		470[b]
(TPP)$\mathrm{Co^{II}}$	KBr	423	537		488[b]
TPP	hexane	414	591.5	651	506
TPP	KBr	435	596	652	522

[a] Calculated from the average of the transition energies of the Soret and Q(0,0) bands as described in ref 22. [b] Estimated by using a vibrational spacing of 1300 $\mathrm{cm^{-1}}$.

in solution and in the solid state compared to the corresponding TPP derivatives. The most striking aspect of these data is that the solution and solid state absorption spectra for the perfluoroalkyl derivatives are virtually superimposable, indicating that either the solution and solid state conformations are very similar or the conformational differences are of no consequence to the optical spectra. In contrast, the data for TPP and (TPP)$\mathrm{Co^{II}}$ show that the crystalline samples have impressive red shifts in the absorption spectra compared to the solution data. These results are consonant with the observation that nonplanar porphyrin conformations adopted in the solid state are often not observed in solution.

To ascertain whether the nonplanar solid state structures of **1** and **2** are truly in potential energy wells, semiempirical molecular orbital calculations (AM1) were performed on constrained and unconstrained 5,10,15,20-tetrakis(perfluoroethyl)porphyrin, **3**, and porphine, **4**.[20,21] The perfluoroethyl groups were staggered in all of the calculations on the substituted porphyrin, as they are in the reported crystal structure. In the first set of calculations, the compounds were constrained to adopt the classic saddle distortion and the energy was calculated as a function of pyrrole ring dihedral angle with respect to the mean porphyrin plane, as summarized in Table 2. Recalculating after lifting the dihedral constraints from the nonplanar conformers gave two new minimized structures. Conformer A, obtained from table entries 1 and 2, lies 6.28 kcal/mol below the planar conformation. It contains a ruffled core structure very similar to that found in the crystal structure of **2**. Conformer B, obtained from table entries 3–6, lies 0.57 kcal/mol below A. It is an unsymmetrical saddle in which one of the pyrrole rings is twisted far from the plane. Each of the conformers has a HOMO–LUMO energy larger than that calculated for the planar structure.

Two trends are evident in Table 2: the calculated energy for porphine increases with increasing saddle distortion of the ring, while the same type of distortion lowers the energy of **3** substantially; and the energy difference between the HOMO and LUMO *increases* with increasing saddle distortion for both **3** and **4**. The hypsochromic shift results from a stabilization of the HOMO upon nonplanar bending.

The semiempirical calculations also show that the nonplanar geometry adopted by **2** in the crystalline phase is a low-energy conformation of the molecule and that the minimum energy structure is nonplanar. These results indicate that nonplanar conformations predominate in solution and that the absence of red shifts in the solution and solid phase optical spectra is consistent with nonplanar structures.

Table 2. Calculated (AM1) Orbital Energies and Transition Wavelengths of Dihedrally Constrained Saddle-Shaped Porphyrin Conformers

compd	dihedral angle (deg)	AM1[a] energy (kcal/mol)	HOMO energy (eV)	LUMO Energy (eV)	calc[b] Q(0,0) band (nm)
3	0	−702.71	−8.728	−2.824	624.5
3	5	−704.50	−8.734	−2.829	626.7
3	10	−704.61	−8.748	−2.815	623.1
3	15	−704.82	−8.790	−2.786	613.5
3	20	−703.72	−8.822	−2.772	608.9
3	25	−701.42	−8.868	−2.766	605.3
3	A (ruf)	−708.99	−8.786	−2.804	608.6
3	B (sad)	−709.56	−8.902	−2.798	565.8
4	0	242.64	−7.794	−1.409	633.5
4	5	243.15	−7.804	−1.400	625.2
4	10	244.86	−7.827	−1.405	615.3
4	15	247.88	−7.855	−1.408	607.5
4	20	253.91	−7.870	−1.402	607.2
4	25	261.04	−7.843	−1.387	617.25

[a] Enthalpy of formation. [b] Lowest energy transition calculated from AM1 CI involving eight orbitals with single and double excitations.

Previous studies have shown that aryl groups in the meso positions of highly nonplanar porphyrins cause a narrowing of the HOMO–LUMO gap which is attributed to destabilization of the HOMO. Saddle distortions allow (otherwise nearly orthogonal) aryl groups to rotate substantially into the plane of the ring and interact more strongly with the π-system.[6] We posit that the observed red shifts are not intrinsic to the ring distortion, but result from different substituent effects in planar and nonplanar conformations. This interpretation is bolstered by the observation that **1**, **2**, and dodecaalkylporphyrins, despite large nonplanar distortions, show small shifts in their absorption spectra.[9] This conclusion suggests a simple design strategy for HOMO stabilization in extremely electron-deficient porphyrins: electron-withdrawing groups that extend conjugation are to be avoided. A direct prediction from this analysis is that the incorporation of nonconjugated electron-withdrawing groups, such as halides, at the β-positions of *meso*-(perfluoroalkyl)porphyrins will greatly stabilize the porphyrin HOMO, regardless of the conformational consequences of the substitution, resulting in extremely active metalloporphyrin catalysts highly resistant to oxidative degradation. Studies directed toward these compounds are currently underway.

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Supporting Information Available: Tables of positional parameters, anisotropic temperature factors, bond distances, and bond angles and experimental procedure and full characterization data for **1** (12 pages); observed and calculated structure factors for **1** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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