

## Resonance Raman Spectrum of Distorted Porphyrin Radical Cation Reveals Orbital Mixing

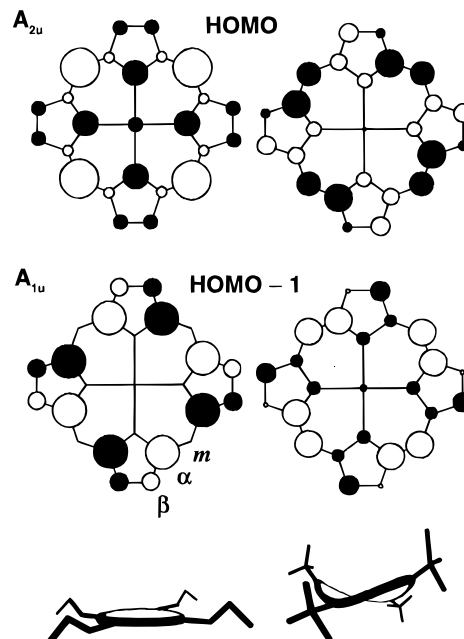
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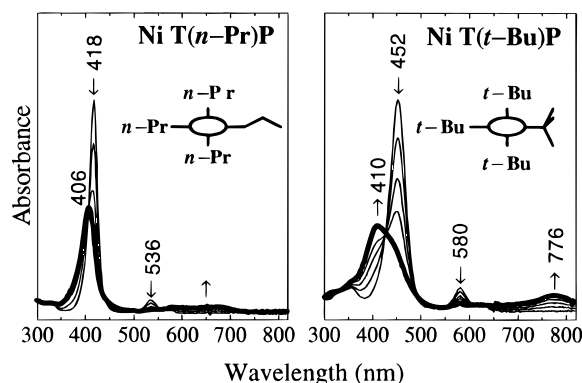
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We report striking reversals of vibrational frequency shifts in radical cations of Ni(II) porphyrins bearing *n*-propyl or *tert*-butyl substituents on the *meso*-carbon atoms (Figure 1). These reversals are evidence that the two highest occupied molecular orbitals (HOMO) are mixed by out-of-plane distortions of the porphyrin. The *n*-propyl molecule is known to be planar,<sup>1</sup> while the *tert*-butyl molecule is severely distorted by the steric clashes between the substituents and the adjacent pyrrole rings.<sup>2,3</sup> Such distortions are known to destabilize the HOMO,<sup>3</sup> as evidenced by diminution of the porphyrin oxidation potential<sup>4</sup> and of the energies of the  $\pi$ - $\pi^*$  electronic transitions.<sup>4,5</sup> However, the present results call attention to the electronic reorganization which accompanies the distortion. Such reorganization may play a role in modulating electron transfer to or from tetrapyrrolic centers in biology, which are subject to distortion by the surrounding protein.<sup>6</sup>

The two Ni(II) porphyrins undergo clean one-electron oxidations, as evidenced by isosbestic visible absorption spectra (Figure 2). The B and Q absorption energies are substantially lower for NiT(*t*-Bu)P than for NiT(*n*-Pr)P, as is the oxidation potential (0.65 and 0.85 V *vs* SCE, determined by CV). In both cases, however, oxidation leads to blue-shifted B bands and to broad low-energy absorptions, characteristic of porphyrin radical cations.<sup>7</sup> Resonance Raman (RR) spectra (Figure 3) in the 1300–1600-cm<sup>-1</sup> region are assigned to porphyrin skeletal vibrations *via* the polarization characteristics of the bands, and with reference to the previous RR study of the neutral molecules by Jentzen *et al.*<sup>3</sup> As expected for B-band excitation,<sup>8</sup> the spectra are dominated by totally symmetric skeletal modes,  $\nu_{2-4}$ . The mode frequencies are substantially lower for NiT(*t*-Bu)P than for NiT(*n*-Pr)P, an effect of the porphyrin distortion.<sup>3</sup> The same three totally symmetric modes can readily be identified



**Figure 1.** The two frontier orbitals for NiT(*n*-Pr)P (left) and NiT(*t*-Bu)P (right), calculated *via* INDO.<sup>11</sup> Filled and open circles represent oppositely oriented  $p_z$  orbitals, and the sizes are proportional to the orbital coefficients.



**Figure 2.** Absorption spectral changes of NiT(*n*-Pr)P (left) and NiT(*t*-Bu)P (right) upon one-electron oxidation. The bold lines indicate the traces of the cation radicals. Experimental conditions: OTTL cell<sup>17</sup> with sample in CH<sub>2</sub>Cl<sub>2</sub>/tetrabutylammonium perchlorate; applied potential, 0.90 and 0.75 V *vs* SCE for NiT(*n*-Pr)P and NiT(*t*-Bu)P, respectively.

in the radical cation spectra, and are shifted very differently in the two molecules. Most striking is the reversal in the  $\nu_3$  shift: down 41 cm<sup>-1</sup> in NiT(*n*-Pr)P but up 50 cm<sup>-1</sup> in NiT(*t*-Bu)P.  $\nu_2$  shifts oppositely, but by much smaller amounts: up 8 cm<sup>-1</sup> in NiT(*n*-Pr)P and down 5 cm<sup>-1</sup> in NiT(*t*-Bu)P. Meanwhile  $\nu_4$  is nearly unshifted in NiT(*n*-Pr)P but undergoes a large downshift, 37 cm<sup>-1</sup>, in NiT(*t*-Bu)P. To investigate the origin of these differences, we carried out INDO calculations<sup>9–11</sup> on the two porphyrins, focusing on the two frontier orbitals. In the planar NiT(*n*-Pr)P, these are the standard  $a_{1u}$  and  $a_{2u}$  orbitals (Figure 1).<sup>12</sup> The latter lies highest, consistent with the expected

(9) INDO calculations of the molecular orbitals was performed with the program ARGUS,<sup>10</sup> which employs the INDO/S semiempirical Hamiltonian, parametrized for first-row transition metal ions.<sup>11</sup> Structure parameters were taken from ref 1 for NiT(*n*-Pr)P, while for NiT(*t*-Bu)P, a 4° tilt of the pyrrole rings was added to the molecular-mechanics-derived ruffled structure<sup>3</sup> (see text).

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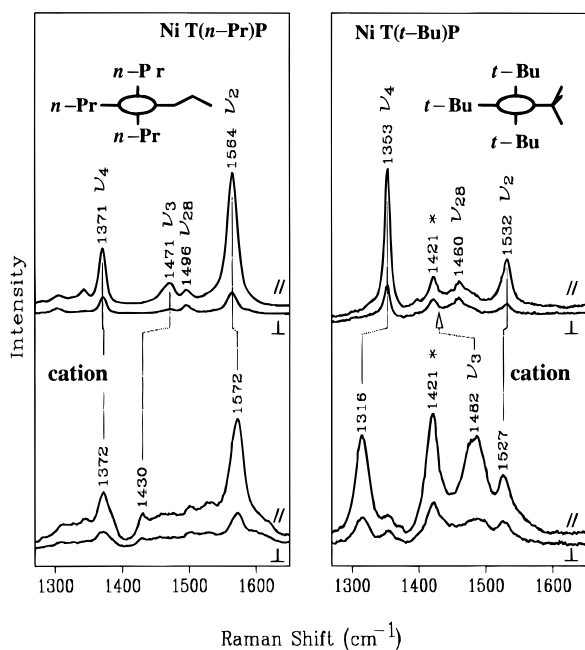
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**Figure 3.** Soret-excited RR spectra of neutral and cation radical forms of NiT(*n*-Pr)P (left, 406.7 nm) and NiT(*t*-Bu)P (right, 413.1 nm), recorded in parallel and perpendicular polarization. The 1421-cm<sup>-1</sup> solvent (CH<sub>2</sub>Cl<sub>2</sub>) peak is marked with an asterisk; its variable intensity reflects differences in self-absorption. This peak obscures the  $\nu_3$  mode of neutral NiT(*t*-Bu)P, but its position (arrow) is well established from the spectra reported in ref 3. The spectra were obtained *via* back-scattering from a spectroelectrochemical cell.<sup>18</sup>

destabilizing effect of electron-donating *meso* substituents. However, the distortion in NiT(*t*-Bu)P can mix these orbitals. If the distorted structure is  $D_{2d}$ , as a result of ruffling or saddling, then the  $a_{1u}$  and  $a_{2u}$  orbitals retain different symmetries and do not mix; the effect of either distortion is to further raise the energy of the  $a_{2u}$  HOMO, and no change in the vibrational shift pattern is expected. However, both distortions are commonly observed in sterically crowded porphyrins,<sup>2-5</sup> and we found that adding a small amount of saddling (4° of pyrrole tilting) to the ruffled structure obtained *via* molecular mechanics<sup>3</sup> induces substantial mixing<sup>13</sup> (Figure 1). The two frontier orbitals are now superpositions of the original  $a_{1u}$  and  $a_{2u}$  orbitals, with opposite phases.

The RR band shifts reflect these altered orbital patterns. The  $\nu_4$  mode is a "half-ring" pyrrole breathing mode,<sup>14a</sup> in which the  $C_\alpha C_\beta$  and  $C_\alpha N$  bonds stretch in opposite phase. The negligible frequency shift of the  $\nu_4$  mode in NiT(*n*-Pr)P can be attributed to the small electron population at the pyrrole- $C_\alpha$  atoms in the  $a_{2u}$  HOMO, and also to the orbital phasing, which cancels the effect of pyrrole bond order changes upon oxidation

because of the alternating signs of the  $p_z$  orbitals. In contrast, the HOMO orbital pattern in NiT(*t*-Bu)P results in a large  $\nu_4$  downshift because of the bonding interaction for the  $C_\alpha C_\beta$  bonds (while for the  $C_\alpha N$  bonds, the bonding and antibonding interactions mutually cancel).

On the other hand, the  $\nu_2$  and  $\nu_3$  modes are mixtures of  $C_\beta C_\beta$  and  $C_\alpha C_m$  bond stretches.<sup>14a</sup> Both of these bonds have constructive  $p_z$  overlaps in the  $a_{2u}$  orbital and should be weakened upon porphyrin oxidation. The large  $\nu_3$  downshift in NiT(*n*-Pr)P can be understood on this basis, while the small upshift in  $\nu_2$  probably results from alteration in the normal mode composition in the radical cations. We note that  $\nu_2$  has until now been considered the marker for  $C_\beta C_\beta$  and  $C_\alpha C_m$  bonding changes, since it shifts up for radical cations of metalloctaethylporphyrins ( $a_{1u}$ ) and down for metallotetraphenylporphyrins ( $a_{2u}$ ).<sup>15</sup>  $\nu_3$  shifts little in the former cations, and is not detected in the latter (perhaps because of intensity cancellation due to coordinate phasing<sup>16</sup>). However, the bond contributions to  $\nu_2$  and  $\nu_3$  vary substantially for porphyrins with different substituents, and it is likely that *meso*-alkyl substituents shift  $C_\beta C_\beta$  character to  $\nu_3$ .<sup>14</sup> It is also possible that the  $C_\alpha C_\beta$  contribution to  $\nu_2$  (it is 11% in NiOEP<sup>14b</sup>) is increased. This could help to account for the  $\nu_2$  upshift since the  $a_{2u}$  orbital is antibonding with respect to the  $C_\alpha C_\beta$  bonds (Figure 1).

The lowered symmetry in NiT(*t*-Bu)P divides the  $C_\beta C_\beta$  and  $C_\alpha C_m$  bonds into three classes:  $C_\beta C_\beta$ , for which the HOMO is slightly antibonding, and pairs of adjacent  $C_\alpha C_m$  bonds, for which the HOMO is alternately bonding and antibonding. Three totally symmetric combinations are therefore expected:  $\nu_2$ ,  $\nu_3$ , and  $\nu_{19}$ . This last mode, which has  $a_{2g}$  symmetry in the  $D_{4h}$  point group, is not normally enhanced with B-band excitation, and it may escape detection even though the porphyrin distortion renders it totally symmetric in NiT(*t*-Bu)P.  $\nu_{19}$  is expected to lie higher than  $\nu_3$ ,<sup>14a</sup> but its frequency should decrease upon radical formation because its bond-alternate phasing<sup>15</sup> exactly matches the NiT(*t*-Bu)P HOMO. The  $\nu_3$  upshift might then result from a mode crossover by  $\nu_{19}$ , and the resulting reorganization of the  $C_\alpha C_m$  coordinates. The small downshift in  $\nu_2$ , which involves in-phase  $C_\alpha C_m$  stretching, may reflect the preponderance of bonding interactions among the  $C_\alpha C_m$  bonds.

We suggest that porphyrin out-of-plane distortions, as exemplified by NiT(*t*-Bu)P, lead to a significant electronic reorganization as a result of orbital mixing. The resulting changes in bond order and in normal mode composition produce profound alterations of the vibrational spectrum in both the neutral porphyrin and its radical cation.

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