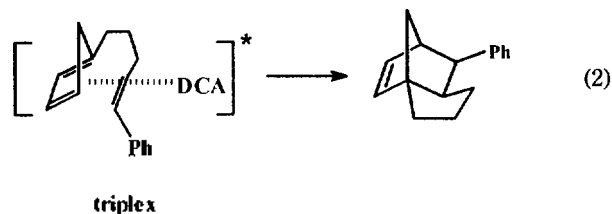


Scheme 2.

to 1 in these trienes, diene or dienophile might quench the emission of exciplex forming the triplex (eq. 2).



In a thermal intramolecular [2+4] cyclization of 1-alkenylcyclopentadienes, three carbon chain length between diene and dienophile leads specifically to structure of type A (Scheme 1 and eq. 1). On extending the results of thermal [2+4] cyclization to the triene 1 and 2, we hoped that the cycloadduct obtained from the triplex Diels-Alder reaction could be different from the thermal adduct. Our results, however, shows that the triplex condition does not change the product distribution of [2+4] cyclization. Presumably the starting triene 2 exists in equilibrium with 2' in favor of 2, which leads to type A adduct, 5 (Scheme 2).

Since the triplex cyclization of 1 and 2 did not produce the product of type B (Scheme 1), the triplex effect of two carbon chain length between diene and dienophile on [4+2] cyclizations is under investigation.

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- Spectral data for 2:  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.6-1.8 (m, 2H), 2.4 (m, 4H), 2.8-2.9 (dd, 2H), 5.8-6.2 (m, 3H), 6.4 (m, 2H), 7.1-7.3 (m, 5H); IR (neat) 3060, 3020, 2930, 1590, 1490, 1440, 1360  $\text{cm}^{-1}$ ; MS  $m/e$  210, 181, 167, 144,

130, 115, 91, 77, 65; Anal. Calcd. for  $\text{C}_{15}\text{H}_{18}$ : C, 91.37; H, 8.63. Found: C, 91.18; H, 8.82.

Spectral data for 5:  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.5-0.8 (m, 1H), 1.3-1.5 (m, 2H), 1.65-2.15 (m, 6H), 2.9 (d, 1H), 3.12 (br s, 1H), 6.23 (d, 2H), 7.1-7.3 (m, 5H);  $^{13}\text{C NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  26.517, 27.092, 28.650, 46.492, 47.773, 49.637, 50.983, 63.118, 125.103, 127.913, 127.932, 137.652, 142.566, 144.379;  $^{13}\text{C DEPT}$   $\delta$  26.517 ( $\text{CH}_2$ ), 27.092 ( $\text{CH}_2$ ), 28.650 ( $\text{CH}_2$ ), 49.637 ( $\text{CH}_2$ ), 46.492 (CH), 47.773 (CH), 50.983 (CH), 125.103 (CH), 127.913 (CH), 127.932 (CH), 137.652 (CH), 142.566 (CH), 63.118 (C), 144.379 (C); IR (neat) 3050, 3010, 2950, 2850, 1600, 1490, 1450  $\text{cm}^{-1}$ ; MS  $m/e$  210, 181, 167, 149, 130, 119, 91, 65, 39; Anal. Calcd. for  $\text{C}_{16}\text{H}_{18}$ : C, 91.37; H, 8.63. Found: C, 91.18; H, 8.66. Spectral data for 3: reference No. 3.

## Syntheses and Spectroscopic Characterization of Octabromotetrakis(2,6-difluorophenyl)-21-thiaporphyrin and Tetrabromotetrakis(2,6-difluorophenyl)-21,23-dithiaporphyrin

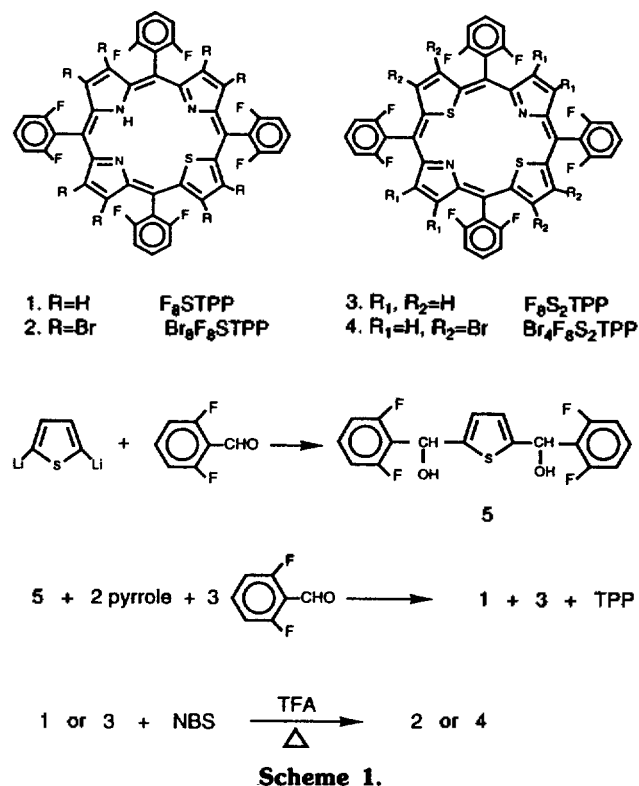
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Non-planar porphyrin compounds are of current interest, because conformational distortion influences electronic and redox properties of the porphyrin ligand in a protein. Domed and ruffled porphyrin conformation has been observed in the X-ray crystal structure of nickel-containing cofactor F430, bacterochlorophylls, chlorins and many other hemoproteins.<sup>1</sup> Porphyrin model compounds with distorted structures have been recently synthesized and their structures are determined by X-ray and NMR spectroscopic techniques.<sup>2,3</sup> The peripherally crowded porphyrin such as octaphenyl-, octaalkyl-, tetracycloalkenyl-substituted meso-tetraphenylporphyrin are severely nonplanar.<sup>4-6</sup> Also  $\beta$ -pyrrole bromination of tetraphenylporphyrin (TPP), tetrakis(2,6-dichlorophenyl)porphyrin, tetramethylporphyrin and tetrakis(pentafluorophenyl)porphyrin causes severe distortion of the porphyrin to a saddle shape.<sup>7</sup>  $^1\text{H NMR}$  study confirms that the conformational distortion is maintained in solution.<sup>3</sup> Herein we report syntheses and spectroscopic characterization of  $\beta$ -carbon brominated compounds of tetrakis(2,6-difluorophenyl)-21-thiaporphyrin ( $\text{F}_8\text{STPP}$ ) and tetrakis(2,6-difluorophenyl)-21,23-dithiaporphyrin ( $\text{F}_8\text{S}_2\text{TPP}$ ).

Halogenated thia- and dithiaporphyrin derivatives were synthesized as shown in Scheme 1. Reaction of dithiophene and 2,6-difluorobenzaldehyde in THF solution produced 2,5-bis[(2,6-difluorophenyl)hydroxymethyl]thiophene (BDHT).<sup>8</sup> Condensation of BDHT with 2 mol of 2,6-difluorobenzaldehyde and 3 mol of pyrrole in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$ , followed by oxidation with *p*-chloranil gives a mixture

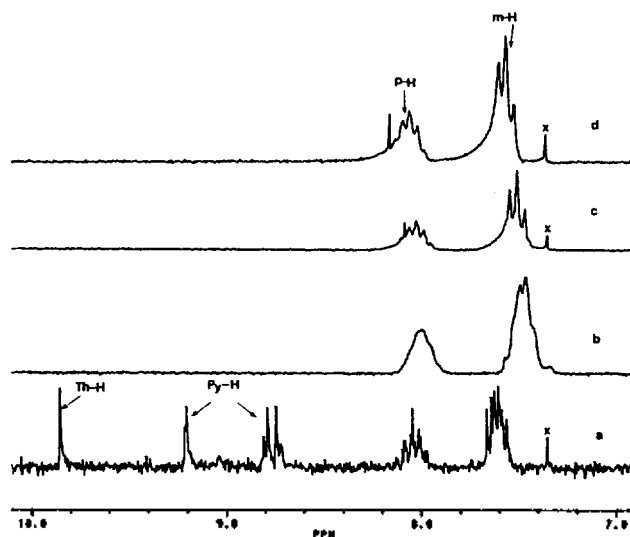


of tetrakis(2,6-difluorophenyl)porphyrin ( $F_8$ TPP),  $F_8$ STPP and  $F_8S_2$ TPP.<sup>9</sup> The mixture was purified by silica gel chromatography with chloroform-carbon tetrachloride (2:1) as an eluant. The second and third bands on elution give 2.3% yield of  $F_8$ STPP and traces of  $F_8S_2$ TPP, respectively. Yield of  $F_8$ STPP was increased from 2.3% to 4.4% when the reaction temperature was raised from room temperature to 40 °C. The reaction of BDHT with one equiv of pyrrole gives a sole product  $F_8S_2$ TPP.

Treatment of  $F_8$ STPP with 50 equiv of NBS in the presence of trifluoroacetic acid afforded the 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-difluoro-phenyl)-21-thiaporphyrin ( $Br_8F_8S_2$ TPP).<sup>10</sup> As shown in Figure 1, the complete absence of proton resonance at 9.65, 8.98, 8.65 ppm in the <sup>1</sup>H NMR spectrum of  $Br_8F_8S_2$ TPP indicates that all the protons of the pyrrole and the thiophene carbons are substituted with bromine.

$Br_8F_8S_2$ TPP is soluble in most organic solvent and stable in solution for several days. In electronic absorption spectrum the bands at 422, 506, 612, 666 nm for  $F_8$ STPP in  $CHCl_3$  were shifted to bands at 460, 554, 630, 720 nm for  $Br_8F_8S_2$ TPP. This large red shift was observed in the previously known nonplanar porphyrins.<sup>4-7</sup> Theoretical calculations revealed that severe distortion of porphyrin destabilized the HOMO more than the LUMO, and resulted in a large red-shift of the first visible absorption.<sup>11</sup> Theoretical calculations are in agreement with the observed electronic absorption spectrum.

Variable temperature NMR experiment supports that the structure of  $Br_8F_8S_2$ TPP is nonplanar in solution. Two meta-protons in the phenyl which is orthogonal to the porphyrin plane are not equivalent because the non-planar porphyrin does not possess a plane of symmetry. However, two broad



**Figure 1.** a) <sup>1</sup>H NMR spectrum of  $F_8$ STPP in  $CD_3COCD_3$ , b), c) and d) <sup>1</sup>H NMR spectra of  $Br_4F_8S_2$ TPP in  $CD_3COCD_3$  at 298 K, 273 K and 240 K, respectively. Th-H, Py-H, m-H, p-H and x represent proton resonances of thiophene β-carbon, pyrrole β-carbon, meta-phenyl, para-phenyl and impurity, respectively.

resonances for meta- and para-protons at room temperature are observed at 7.40 and 8.00 ppm due to the fast porphyrin inversion on the NMR timescale. Upon lowering temperature to 0 and -37 °C, slow inversion of non-planar  $Br_4F_8S_2$ TPP on the NMR timescale splits the meta- and para-proton resonances to the multiplet. The resonance of the para-protons which is little affected by porphyrin inversion is shifted less than that of the meta-protons.

Similar treatment of  $F_8S_2$ TPP with NBS in the presence of trifluoroacetic acid afforded 2,3,12,13-tetrabromo-5,10,15,20-tetrakis(2,6-difluorophenyl)-21,23-dithiaporphyrin ( $Br_4F_8S_2$ TPP)<sup>12</sup> in which only two β-pyrrole carbons at the trans position to each other are brominated. Attempts to synthesize  $Br_8F_8S_2$ TPP in which all the β-carbons are brominated by changing the amount of NBS and acid did not succeed. Unlike  $Br_8F_8S_2$ TPP, a large red shift in the electronic spectrum of  $Br_4F_8S_2$ TPP was not observed. This result probably indicates that bromination of all β-carbons is necessary for distorting the porphyrin ring. It is proposed that the mechanism for bromination reaction by NBS in presence of acid proceed not by free radical pathway but by electrophilic reaction of  $Br^+$  ion.<sup>13</sup> Formation of  $Br_4F_8S_2$ TPP indicates that 18-π electrons delocalize through the thiophene, and consequently imposes a full double bond character on the pyrrole β-carbon.

In summary, bromination of  $F_8$ STPP causes distortion of the porphyrin and its structure is maintained in solution like TPP derivatives. Structure determination in solid state and electrochemical studies for  $Br_8F_8S_2$ TPP are in progress.

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  - BDHT**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.30 (m, 2H, *p*-phenyl), 6.93 (m, 4H, *m*-phenyl), 6.66 (d, 2H, thiophene), 6.42 (d, 2H, methylene), 3.05 (d, 2H, hydroxyl) EIMS:  $m/e$  368 ( $\text{M}^+$ ), 351 ( $\text{M-OH}^+$ ) Anal. Calcd. for  $\text{C}_{18}\text{H}_{12}\text{F}_4\text{O}_2$ : S: C, 58.71; H, 3.26. Found: C, 58.67; H, 3.24.
  - F<sub>8</sub>STPP**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 200 MHz):  $\delta$  9.84 (s, 2H, thiophene), 9.19 (s, 2H, pyrrole), 8.75 (q, 4H, pyrrole), 8.03 (m, 4H, *p*-phenyl), 7.59 (m, 8H, *m*-phenyl), -2.63 (s, 1H, NH) UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 422 (5.53), 506 (4.61), 612 (3.73), 666 (2.67) Anal. Calcd. for  $\text{C}_{44}\text{H}_{21}\text{F}_8\text{N}_3\text{S}$ : C, 68.14; H, 2.71; N, 5.42 Found: C, 68.19; H, 2.69; N, 5.40 **F<sub>8</sub>S<sub>2</sub>TTP**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  9.56 (s, 4H, thiophene), 7.37 (m, 8H, *m*-phenyl) UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 430 (5.28), 508 (4.68), 628 (3.09), 692 (3.81) Anal. Calcd. for  $\text{C}_{44}\text{H}_{20}\text{F}_8\text{N}_2\text{S}_2$ : C, 66.68; H, 2.52; N, 3.53 Found: C, 66.72; H, 2.49; N, 3.56.
  - Br<sub>3</sub>F<sub>8</sub>STPP**: UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 460 (5.01), 554 (4.01), 630 (3.53), 720 (3.42)  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 200 MHz):  $\delta$  7.94 (m, 4H, *p*-phenyl), 7.52 (m, 8H, *m*-phenyl) Anal. Calcd. for  $\text{Br}_3\text{C}_{44}\text{H}_{13}\text{F}_8\text{N}_3\text{S}$ : C, 37.56; H, 0.92; N, 2.99 Found: C, 38.01; H, 0.95; N, 2.91.
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  - Br<sub>4</sub>F<sub>8</sub>S<sub>2</sub>TTP**: UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 434 (5.24), 520 (4.44), 628 (3.66), 688 (3.61)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  9.35 (s, 4H, thiophene), 7.34 (m, 12H, *m*, *p*-phenyl) Anal. Calcd. for  $\text{Br}_4\text{C}_{44}\text{H}_{16}\text{F}_8\text{N}_2\text{S}_2$ : C, 47.68; H, 1.44; N, 2.53 Found: C, 47.81; H, 1.40; N, 2.49.
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## Rovibronic Spectrum of Cold Benzyl Radical

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In high resolution electronic molecular spectroscopy, one of the most difficult works is to determine the structure of large molecules accurately, since large molecules have large principal moments of inertia  $I_A$ ,  $I_B$ , and  $I_C$  and consequently small rotational constants A, B, and C.<sup>1</sup> The typical values of the rotational constants are of the order of 0.1  $\text{cm}^{-1}$  in large molecules such as benzene derivatives. This means that the rotational energy levels are very closely spaced, leading to appreciable population of levels with  $J$  and  $K_a$  or  $K_c$  of the order of 100 at room temperature. As a result, something like 30,000 rotational transitions accompany any electronic or vibronic transition. The rotational transitions usually lie within *ca.* 30  $\text{cm}^{-1}$  so, on average, there is one transition for each 0.001  $\text{cm}^{-1}$ . Since the Doppler width of the transition in the gas phase is *ca.* 0.02  $\text{cm}^{-1}$  there may be about 20 transitions within the Doppler width. Thus, even with the highest resolution (*ca.* 0.02  $\text{cm}^{-1}$ ), there is little hope of resolving individual transitions.

What is observed is a rotational intensity contour with a characteristic shape. The shape of the contour strongly depends on the same parameters as one would obtain from a completely resolved spectrum, that is, the rotational selection rules (type A, B, and C or hybrid), the rotational temperature, and the rotational constants at both the ground and the excited electronic states. Also, it has been well known that the rotational contours are much more sensitive to the changes of rotational constants ( $\Delta A$ ,  $\Delta B$ , and  $\Delta C$ ) during the transition rather than to the absolute values of the constants.

The benzyl radical is a prototypical aromatic radical with seven delocalized  $\pi$  electrons and has been subjected to many spectroscopic studies. The first spectrum of benzyl radical was obtained in emission near 450 nm by Schüler *et al.*<sup>2</sup> A few years later, Porter and coworkers observed not only 450 nm band<sup>3</sup> but also 305 nm band<sup>4</sup> from the electronic absorption spectra employing the flash photolysis technique. Cossart-Magos and Leach<sup>5,6</sup> succeeded in determining the symmetry of the excited state at 450 nm from the analysis of rotational contour of the spectra. In addition, Cossart-Magos group has continued to analyze the rotational contours of the vibronic bands of the room temperature emission spectra of the methyl substituted benzyl radicals.<sup>7,8</sup> Recently, Carrick and Selco<sup>9</sup> have recently obtained a high resolution emission spectra of the benzyl radical. Also, laser induced fluorescence (LIF) method has been applied by many groups<sup>10-16</sup> to study the vibronic coupling of two lowest excited electronic states and to measure the lifetime of the benzyl radical.

As far as I am concerned, however, no one has so far succeeded in obtaining a reliable geometry data of the benzyl radical even in the ground state due to a limited resolution and a poor ratio of signal to noise of the spectra obtained.<sup>9</sup>