

Fourier-transform infrared spectroscopic studies of dithia tetraphenylporphine

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Abstract. We present here infrared absorption spectra of dithia tetraphenylporphine and its cation in the 450–1600 and 2900–3400 cm^{-1} regions. Most of the allowed IR bands are observed in pairs due to overall D_{2h} point group symmetry of the molecule. The observed bands have been assigned to the porphyrin skeleton and phenyl ring modes. Some weak bands, which are forbidden under D_{2h} , also appear in the spectra due to the distortion of the molecule from planarity-caused by the out-of-plane positioned N and S atoms. Increased intensity of some phenyl ring bands compared to free-base tetraphenylporphine is explained on the basis of rotation of phenyl rings towards the mean molecular plane. Contrary to the point group symmetry of cation of dithia tetraphenylporphine, certain bands are observed to be degenerate due to identical bonding arrangements in pyrrole rings of the cation.

Keywords. Infrared spectra, dithia tetraphenylporphine, dithia tetraphenylporphine cation.

1. Introduction

There is much current interest in the study of core modified porphyrins because of their interesting electronic properties and possible use as photosensitizer, catalyst and complexing agents.^{1–8} Core-modified porphyrinoid systems have been synthesized and studied to understand their electronic spectra,^{1,9} vibrational structure,¹⁰ electrochemical behaviour,¹¹ aromatic character¹² and complexing ability^{1,9} etc. Solid understanding of the structure and vibrations of the more complicated chalcogen porphyrins first requires good understanding of dithia tetraphenylporphine (S_2 TPP), which is one of the simplest core-modified tetraphenylporphine (TPP) macrocycles.

Vibrational spectroscopy provides rich and unique information about the bonding arrangement in a molecule in liquid or vapour state. Vibrations of a molecule can be probed by either Raman scattering technique or infrared (IR) absorption spectroscopy, which are complementary to each other. The Raman scattering under resonance condition has been utilized extensively in the study of vibrations of porphyrin molecules. On the other hand, IR absorption data are sparsely available on certain porphyrin molecules

because of the fact that their IR spectra are crowded with large number of vibrational bands. Therefore, it is not an easy task to decipher information from the IR spectra of a macromolecule like TPP. Irrespective of these difficulties/shortcomings, IR spectroscopy has been used in the study of some TPPs and their oxidized products,^{13–17} since this technique is quite useful in arriving at the structure and bonding arrangements in these complexes. The S_2 TPP and its dication have been studied in the past and differences between neutral and cationic species are well characterized by resonance Raman (RR) spectroscopy.^{10,18} However, for complete vibrational analysis of the molecule, study of the Raman scattering and IR absorption both would be necessary. Moreover, we have not come across any IR absorption study on S_2 TPP except a brief mention of its spectrum in a limited region 1000–1150 cm^{-1} .¹⁰ Therefore, in the present paper we report and analyse Fourier-transform infrared (FT-IR) spectra of S_2 TPP and its chemically prepared cation.

2. Experimental

Dithia tetraphenyl porphyrine was received from Professor A L Verma as a gift and used without further purification. However, its purity was checked

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with electronic absorption spectroscopy. H_2TPP was obtained from Sigma. Benzene and Br_2 from Qualigens Fine Chemicals, were also used without any purification. The cation of S_2TPP was prepared by adding trifluoroacetic acid or Br_2 to C_6H_6 solution of S_2TPP . For recording of IR spectra, few drops of solution of S_2TPP were put on a KBr window. Solvent was allowed to evaporate before taking the measurements in order to remove the IR absorption peaks of the solvent. Similar procedure was followed for IR measurements of cationic species. UV-visible spectra were recorded on a Hitachi 330 UV-Vis-NIR spectrophotometer. IR spectra were recorded on a Perkin-Elmer PE-Rx1 FTIR spectrophotometer. Spectral resolution of the IR spectrometer was 2 cm^{-1} throughout the experiment.

3. Results and discussion

Figure 1 gives the structure and atom-labeling scheme of S_2TPP . From UV-visible absorption spectroscopy, first of all the purity of S_2TPP was checked. The observed bands (figure not shown) at 435 nm (Soret) and 512, 545, 632 and 695 nm (Q bands) match well with the reported values.¹⁹ The observed pattern of electronic absorption bands can be explained on the basis of overall D_{2h} molecular symmetry and structural change caused by the rotation of phenyl rings towards the porphyrin plane. Rotation of phenyl rings increases the interaction between porphyrin macrocycle and phenyl rings accompanied by much larger overlap between their p systems.¹⁹

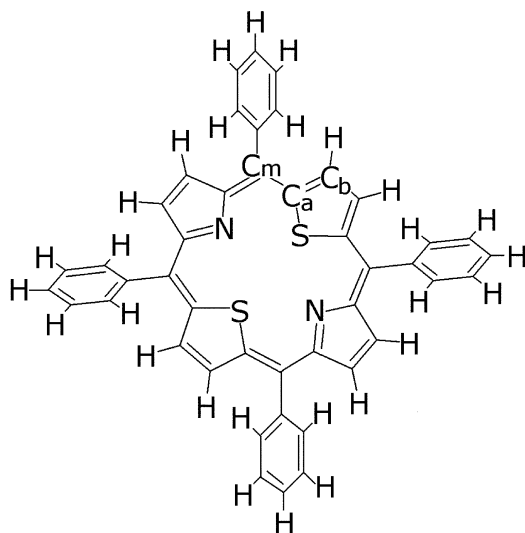


Figure 1. Structure and atom labelling scheme of dithia tetraphenylporphyrin.

IR spectra of S_2TPP and its dication in different wave number regions are shown in figures 2–4. Spectra of H_2TPP and its dication (H_4TPP^{2+}) are also included for comparison. As can be seen from the figures, the spectra of S_2TPP contain more IR absorp-

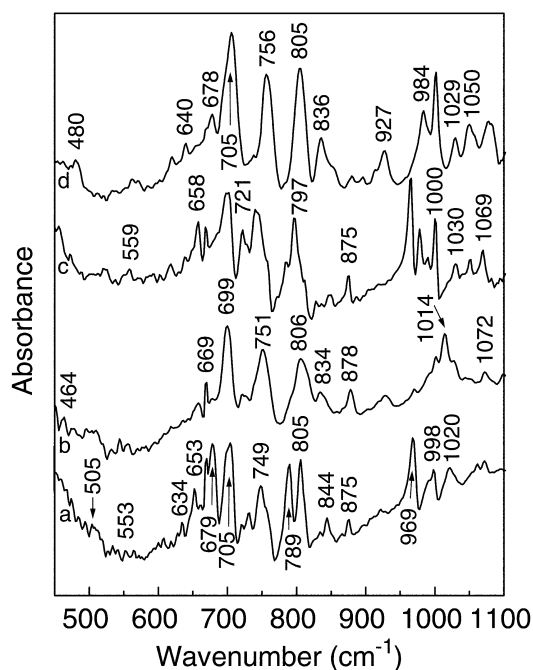


Figure 2. IR spectra of (a) S_2TPP ; (b) S_2TPP cation; (c) H_2TPP and (d) $H_4TPP^{2+} 2Br^-$ in the $450\text{--}1100\text{ cm}^{-1}$ region.

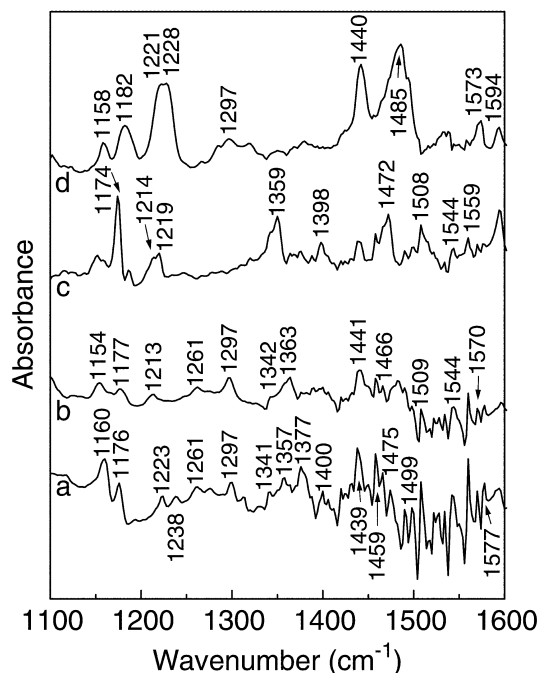


Figure 3. IR spectra of (a) S_2TPP ; (b) S_2TPP cation; (c) H_2TPP and (d) $H_4TPP^{2+} 2Br^-$ in the $1100\text{--}1600\text{ cm}^{-1}$ region.

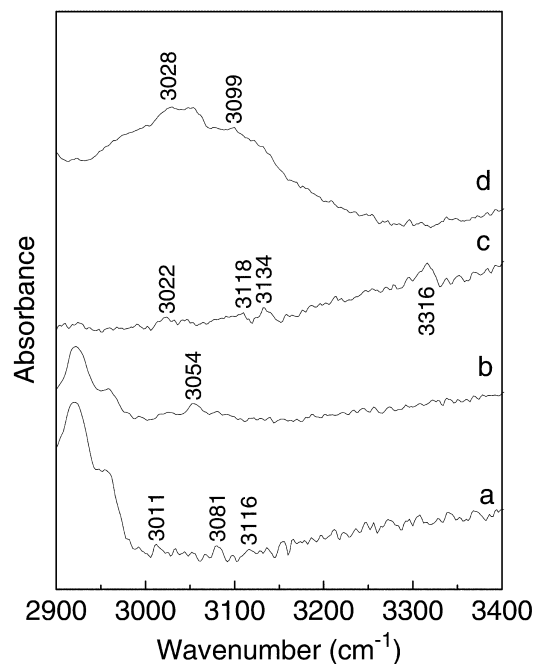


Figure 4. IR spectra of (a) S_2TPP ; (b) S_2TPP cation; (c) H_2TPP and (d) $H_4TPP^{2+} 2Br^-$ in 2900–3400 cm^{-1} region.

tion bands than the H_2TPP spectra. Moreover, intensity patterns are also different. Some bands are also shifted with respect to the corresponding bands in H_2TPP . S_2TPP has two central S atoms on diagonally opposite pyrrole rings with an overall symmetry of D_{2h} . Addition of two extra protons at two diagonally positioned N atoms results in the formation of dication of S_2TPP , which still maintains D_{2h} symmetry. Spectra of both these molecules consist of a few intense in-plane bands of B_{2u}/B_{3u} symmetry and out-of-plane bands of B_{1u} symmetry, which are allowed according to the selection rules of the D_{2h} point group. These modes carry A_{2u} (out-of-plane vibration) and E_u (in-plane vibration) symmetry label in D_{4h} point group, applicable in case of the metalloporphyrins. In S_2TPP splitting of the E_u modes into B_{2u} and B_{3u} symmetry modes can be interpreted in terms of point group symmetry of the molecule, because of the fact that there are two distinct pairs of pyrrole rings in S_2TPP . These two rings have different bond lengths and electron density. Therefore, corresponding to pyrrole ring with N atoms and S atoms, the E_u symmetry modes split into two species with different frequencies as can be seen in figures 2a and 3a. A large number of weak bands, including the symmetry forbidden ones, which become allowed due to distortions in the molecule, can also be seen in the spectra of both S_2TPP and its cation. The IR spectra contain more bands that can not be accounted for by the porphyrin

skeleton. These bands might be due to overtones and combination modes. The assignment of the observed bands in the IR spectra is difficult because of its extreme complexity due to a large number of strong phenyl contributions. We have utilized a simpler, qualitative approach to interpret the IR data of S_2TPP on the basis of mode compositions of H_2TPP and $NiTPP$. This is a reasonable approach in this case, since the data show that the modes retain the same general character in the S_2TPP molecule as in other TPPs. Although normal coordinate calculations are not available for S_2TPP , they are available for H_2TPP ,^{16,20} free-base porphine (H_2P),^{21,22} nickel tetraphenylporphyrin ($NiTPP$)¹⁵ and free-base tetraphenylbacteriochlorin.²³ These calculations along with the reported RR studies of these complexes^{10,18} and IR study of H_2TPP ^{14,17} considerably simplify the assignment of the IR bands of S_2TPP . We have made suitable allowance for the difference in modes involving the two types of pyrrole rings. Changes with respect to spectra of other TPPs are also expected due to the altered masses apart from bonding effects. We expect that the mode compositions obtained in this way are reasonably accurate and that the major contributing motions are correct. The observed IR bands and their assignments are listed in table 1. Throughout this discussion, the mode numbering from refs.^{15,21,22} is used for TPP with appropriate labeling for substituted and non-substituted pyrrole rings.

3.1 Porphine skeleton modes

3.1a Low wave number region: Figure 2 shows the IR spectra of S_2TPP , H_2TPP and their cations in the wave number region 450–1100 cm^{-1} . This region is generally dominated by bands due to ring torsion, ring rotation, and in-plane and out-of-plane bending modes of the porphyrin skeleton. We observe two well-isolated bands at 553 and 565 cm^{-1} in the spectrum of S_2TPP (figure 2a). The latter band disappears while the former shows slight upshift with concomitant increase in the width for cationic species (figure 2b). Appearance of two bands may be due to the substitution of NH atoms by S atoms. It may be mentioned here that only one band is reported for H_2TPP around this wave number, which is assigned to C_a-C_m bending motion. Disappearance of the band at 565 cm^{-1} suggests that the motion of the part of the molecule containing N atoms (with non-substituted pyrrole rings) is responsible for this band, while the

Table 1. Position and assignment of observed IR bands of S₂TPP and its cation in C₆H₆.

Band (cm ⁻¹)		Mode no. ¹	Assignment ²⁻⁴	Band (cm ⁻¹)		Mode no. ¹	Assignment ²⁻⁴
S ₂ TPP neutral	S ₂ TPP cation			S ₂ TPP neutral	S ₂ TPP cation		
453	452	n ₃₃ , B _{1g}	d (Pyr rot)	1062	–	n _{52b} , B _{3u}	d (C _b –H) _{sym}
460, 468	464	n ₄₉ , B _{2u} /B _{3u}	d (Pyr rot)	1072	1072	n _{52a} , B _{2u}	d (C _b –H) _{sym}
475	476	n ₂₅ , B _{1g}	d (Pyr rot)	1117	–		
485	–			1126	1126		
495	496		Phenyl	1136	1134		
505, 508	504		Phenyl	1151	1154	y ₇ , A _u	Phenyl
513	511	p ₅ ^{''} , B _{2u} /B _{3u}	Phenyl	1160	1154	y ₇ , B _{1u}	Phenyl
519, 527	520		Phenyl	1176, 1193	1177	f ₆ ^{''} , B _{2u} /B _{3u}	Phenyl
534	532	g ₃ , A _u	g (C _a –C _m)	1201	–		
541	544		g (C _a –C _m)	1208	–		
553	556	g ₇ , B _{1u}	g (C _a –C _m)	1223	1213	n ₅₁ , B _{2u}	d (C _b –H) _{asym}
565	–		g (C _a –C _m)	1238	–	n _{40b} , B _{2u}	n (Pyr quarter-ring)
572	570						
576, 582	576, 582	g ₄ , B _{2g} /B _{3g}	g (C _a –C _m)	–	1247	n ₂₇ , B _{1g}	n (C _m -phenyl)
607	608	n _{47b} B _{3u}	n (Pyr breath)	1261	1261	n ₃₆ , B _{2u} /B _{3u}	n (C _m -phenyl)
618	618		Phenyl	1275	1272	y ₆ ['] , B _{1u}	Phenyl
628	–		Phenyl	1290	–	y ₆ ['] , B _{2u} /B _{3u}	Phenyl
635	636	y ₉ ['] , B _{1u}	Phenyl	1297	1297	n _{40a} , B _{3u}	n (Pyr quarter-ring) _{sym}
646	644	g ₇ , B _{1u}	g (C _b –H) _{sym}				
653, 661	657	g ₅ , B _{2g} /B _{3g}	g (C _b –H) _{sym}	1313	1363	n _{41b} , B _{3u}	n (Pyr half-ring) _{sym}
669	669	f ₉ ['] , B _{2u} /B _{3u}	Phenyl				
679	677	g ₁ , A _u	(Pyr fold) _{asym}	1320	1320	y ₅ ['] , B _{1u}	Phenyl
–	686		Phenyl	1329	1328		Phenyl
699	699	p ₄ ^{''} B _{2u} /B _{3u}	Phenyl	1341	1342		Phenyl
705	699	g ₈ , B _{1u}	g (C _b –H) _{sym}	1357	1363	n _{41a} , B _{2u}	n (Pyr half-ring) _{sym}
721	722	g ₀ , B _{2g} /B _{3g}	(Pyr fold) _{asym}				
731	727	g ₁ , A _u	(Pyr fold) _{asym}	1377	1377		C _b –H bend
749, 755	751	p ₃ ^{''} , B _{2u} /B _{3u}	Phenyl	1380	1382		C _b –H bend
789	791	g ₅ , B _{1u}	(Pyr fold) _{sym}	1387	1389		C _b –H bend
805	806	g ₅ , B _{1u}	(Pyr fold) _{sym}	1400	1400		C _b –H bend
824	–	n ₂₄ , B _{1g}	(Pyr def) _{asym}	1406	1406		C _b –H bend
834	834	n _{46a} , B _{2u}	d (Pyr def) _{asym}	1421	1420		Phenyl
844	–	n _{46b} , B _{3u}	d (Pyr def) _{asym} +	1425	1424		Phenyl
			Phenyl	1431	1432	y ₄ , A _u	Phenyl
865	–	n _{48b} , B _{3u}	d (Pyr def) _{sym}	1439	1441	y ₄ , B _{1u}	Phenyl
875	878	g ₃ , A _u	d (C _b –H) _{asym}	1449	1449	y ₄ ^{''} , B _{2g} /B _{3g}	Phenyl
886	–	g ₄ , A _u	d (C _b –H) _{asym}	1459	1459	n _{39a} , B _{2u}	n (C _a –C _m) _{in-phase}
896	868	n _{48a} , B _{2u}	d (Pyr def) _{sym}	1466	1466	n ₃ , A _g	n (C _a –C _m) _{in-phase}
906	903			1475	–	n _{39b} , B _{3u}	n (C _a –C _m) _{in-phase}
912	–	p ₂ ^{''} B _{2u} /B _{3u}	Phenyl	1482	1483	n ₂₈ , B _{1g}	n (C _a –C _m) _{in-phase}
921	919		Phenyl	1491	1493	f ₅ ['] , B _{2u} /B _{3u}	Phenyl
929	928		Phenyl	1499	1500		
937	–		Phenyl	1509	1509	n _{38a} , B _{2u}	n (C _b –C _b)
945	–		Phenyl	1523	1523	n ₁₁ , A _g	n (C _b –C _b)
952	–		Phenyl	1527	1528	n ₂ , A _g	n (C _b –C _b)
969	970	n _{47a} , B _{2u} +	d (Pyr breadth)	1534	1535	n _{38b} , B _{3u}	n (C _b –C _b)
		s ₁ ['] , B _{2g} /B _{3g}	+ phenyl	1542	1544	n _{37a} , B _{2u}	n (C _a –C _m) _{out-of-phase}
991	992	n _{44a} , B _{2u}	n (Pyr half-ring) _{asym}	1550	1550	n ₁₉ , B _{1g}	n (C _a –C _m)
				1560	1560	n _{37b} , B _{3u}	n (C _a –C _m) _{out-of-phase}
998	1001	f ₈ ['] , B _{2u} /B _{3u}	Phenyl	1571	1570	y _{3a} ^{''}	Phenyl
1020	1014	n _{44b} , B _{3u}	n (Pyr half-ring) _{asym}	1577	1577	y _{3b} ^{''}	Phenyl
				1591, 1594	1591, 1597	f ₄ ['] + f ₄	Phenyl
1028	1028		Phenyl	–	–		
1053	1050	y ₈ ['] , B _{1u}	Phenyl	–	–		

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Table 1. (Continued from facing page)

Band (cm ⁻¹)				Band (cm ⁻¹)			
S ₂ TPP neutral	S ₂ TPP cation	Mode no. ¹	Assignment ²⁻⁴	S ₂ TPP neutral	S ₂ TPP cation	Mode no. ¹	Assignment ²⁻⁴
3011	3014	f''_{3a}	Phenyl	3081	3080	$n_{43}, B_{2u}/B_{3u}$	n (C _b -H) _{sym}
3022	3022	f''_{3b}	Phenyl	3116	3117	$n_{45}, B_{2u}/B_{3u}$	n (C _b -H) _{asym}
–	3054		Phenyl	–	3308		n (N-H)

¹Mode numbering and symmetry are based on ref. [22]

²Assignments are based on references [15, 21, 22]

The **n**, **d**, **g** denote stretching, in-plane bending and out-of-plane bending modes respectively. The subscript *sym* and *asym* represent the symmetric and asymmetric modes respectively

⁴**p**, **f** and **y** denote phenyl ring vibrations

former band is due to the substituted pyrrole rings, since on cation formation, H atoms are added to the pyrrole rings containing N atoms, thereby affecting the vibrations of only the ring with N atoms. In the spectra of S₂TPP and its cation, bands due to pyrrole fold motion can be seen at 679, 721 and 731 cm⁻¹. The lower wave number band is assigned to the **g**₁ mode of A_u symmetry. The band due to this mode in H₄TPP²⁺ has also been reported at the same frequency.¹⁷ Assignment of this band gets support from the fact that electrochemical data reported in the literature²⁴ also indicate similarity in properties of S₂TPP and H₄TPP²⁺. Interestingly, the band due to this mode is absent in the spectrum of H₂TPP but present in H₄TPP²⁺, however, the reverse is true for S₂TPP and its cation with the only difference that its intensity is not completely diminished for the S₂TPP cation. Since **g**₁ is a symmetry-allowed vibration under D_{4h}, D_{2h} point groups and their sub groups, it should have also been present with reasonable intensity in the spectrum of cationic S₂TPP. However, its intensity is considerably reduced on cation formation. The reduction in the intensity may be explained, if we consider mixing between this mode and other modes with the same symmetry and similar eigenvectors. The mixing leads to negligible or complete cancellation of intensity of one band while the intensity of the other band increases due to phasing. This situation is similar to metallo-TPPs in which mixing of eigenvectors of **n**₂ and **n**₃ modes is responsible for reduced intensity of the RR band assigned to **n**₃.²⁵ We feel that the **g**₁ mode, for which C_b and C_a atoms move out of phase, may mix with the C_b-H asymmetric bending mode **g**₃, which also has A_u symmetry. Due to this mixing, the intensity for the former mode is nearly cancelled due to phasing while for the latter the intensity increases. The **g**₃ mode is present at

875 cm⁻¹ in the IR spectrum of S₂TPP cation with relatively increased intensity compared to S₂TPP.

A pair of well-resolved bands with strong intensity can be seen at 789 and 805 cm⁻¹ in the spectrum of S₂TPP (figure 2a). On cation formation, the lower wave number band almost disappears while the higher wave number band remains unchanged. These bands may be assigned to symmetric pyrrole-folding modes **g**₁₅ and **g**₅ respectively with contribution from the C_b-H bending. This assignment is based on the latest DFT-based normal coordinate analysis of H₂TPP and NiTPP.^{15,16,20} The **g**₅ mode is predicted to have a large out-of-plane component of dipole moment due to large in-phase out-of-plane displacement of the C_b-H atoms. Hence, the latter intense band is assigned to **g**₅. A band at 799 cm⁻¹ in H₂TPP is assigned to N-H out-of-plane bending motion in a recent study.¹⁶ However, we observe a band at 805 cm⁻¹ even in the IR spectrum of S₂TPP. If this band is due to N-H bending, then it should not be present in the spectrum of S₂TPP until the molecule is oxidized by addition of protons. Hence, this mode does not arise due to N-H bending in S₂TPP. Therefore, assignment of this band to **g**₅ mode is justified by the above discussion and is in agreement with the IR band at 794 cm⁻¹ in NiTPP assigned to **g**₅ mode by Rush *et al*.¹⁵ A band at 824 cm⁻¹ may be assigned to asymmetric pyrrole deformation mode **n**₂₄ of B_{1g} symmetry. Similarly, a doublet at 834 and 844 cm⁻¹ may also arise due to asymmetric pyrrole deformation motion and accordingly we have assigned them to **n**_{46a} and **n**_{46b} respectively of B_{2u}/B_{3u} symmetry. On cation formation, these bands can be seen at 834 cm⁻¹ in the IR spectrum (figure 2b). Symmetric pyrrole deformation modes **n**_{48a} and **n**_{48b} give rise to IR bands at 865 and 896 cm⁻¹. Since these modes involve movement of N and/or S atoms, in the spec-

trum vibrational frequency of a band should be lower for the pyrrole rings with S atoms and, therefore, the former band is assigned to \mathbf{n}_{48} mode with contribution from the S-substituted pyrrole rings and the latter from non-substituted pyrrole rings. On cation formation, H atoms are attached to the N atoms of the pyrrole rings. It is observed for H₂TPP that the electron density on the N atoms decreases due to dication formation.²⁶ If we assume a similar situation for S₂TPP, then the latter band should shift downward for cationic S₂TPP, while the former may show either no shift or very small shift in its position. Based on this argument, we assign a band (shoulder) at 868 cm⁻¹ to symmetric pyrrole deformation mode \mathbf{n}_{48} for S₂TPP cations.

We may assign bands at 969 and 607 cm⁻¹ to pyrrole breathing modes \mathbf{n}_{47a} (B_{2u}) and \mathbf{n}_{47b} (B_{3u}) respectively. Stein *et al*⁹ have assigned a band at 630 cm⁻¹ in the RR spectra of S₂TPP to C_a-S stretching, which arises due to pyrrole breathing stretching mode \mathbf{n}_6 . Corresponding IR active band involving pyrrole breathing mode is \mathbf{n}_{47} . It is observed in X-ray structure analysis¹⁹ and molecular orbital calculations²⁷ that replacement of NH groups by S atoms drains electron density from the porphyrin ring and also S atoms are known to take part in direct bonding interactions within the porphyrin core. NMR studies also show changes in the inner and outer aromatic pathways of the core due to bonding interaction between S atoms and the ring.²⁸ Since S atoms change the inner ring aromaticity more than the outer pathway, bonding between the inner bonds is affected more than the bonds at the outer periphery of the ring. One, therefore, expects that the vibrational frequencies of the molecule involving the inner atoms such as C_a will change more than the frequencies of the vibration related to C_b atoms. We, therefore, assign 607 cm⁻¹ band to \mathbf{n}_{47b} mode involving contribution from C_a-S. Moreover, on cation formation, there should not be any apparent change in C_a-S stretching frequency as protons are attached to N atoms. In the spectrum of S₂TPP cation (figure 2b), position of 607 cm⁻¹ is changed by only 1 cm⁻¹. Therefore, small change in the wave number of the band due to cation formation also justifies the assignment of this band. As can be seen from figure 2a and b, intensity of this band decreases on cation formation, which indicates change in the molecular symmetry due to change in planarity of the molecule. The pair of bands at 991 and 1020 cm⁻¹ may be assigned to asymmetric pyrrole half-ring stretching

vibrational modes $\mathbf{n}_{44a,b}$. These bands shift to 1014 cm⁻¹ for cationic species. The doublet at 1062 and 1072 cm⁻¹ may be assigned to $\mathbf{n}_{52a,b}$ modes of B_{2u}/B_{3u} symmetry due to in-plane C_b-H symmetric bending vibration. These bands are observed at 1072 cm⁻¹ in the spectra of the cationic species.

3.2b Mid-wave number region: In the wave number region 1100–1600 cm⁻¹, generally, bands associated with the symmetric and asymmetric C_a-C_m, C_b-C_b, pyrrole quarter-ring and pyrrole symmetric and asymmetric half-ring stretching modes are observed. In the IR spectrum of S₂TPP (figure 3a), only one band is observed around 1223 cm⁻¹ in comparison with the doublet observed at 1214 and 1219 cm⁻¹ for H₂TPP (figure 3c). The 1223 cm⁻¹ band may be assigned to asymmetric in-plane C_b-H bending vibrational mode \mathbf{n}_{51} . The other band at low wave number is absent in the S₂TPP spectrum. The lower wave number band in H₂TPP is assigned to N-H bending motion. This observation is consistent with the fact that the S₂TPP molecule does not have an NH group. Accordingly, we observe only a single band at 1223 cm⁻¹, which shifts down to 1213 cm⁻¹ for cationic S₂TPP. This shift is in agreement with the shift in other C_b-H related vibrations. The downshift can be explained on the basis of reduced electron density on C_b and H atoms attached to C_b as seen in H₄TPP²⁺ from NMR spectroscopy by Inisan *et al*²⁶. The C_m-phenyl vibrational mode, \mathbf{n}_{36} , remains at its position on cation formation and is observed at 1261 cm⁻¹ in the spectra of both S₂TPP and its cation. IR bands at 1298 and 1238 cm⁻¹ may be assigned to \mathbf{n}_{40a} and \mathbf{n}_{40b} modes respectively. The local coordinate giving rise to these bands is the pyrrole quarter ring stretching vibration. The calculated position of doubly degenerate \mathbf{n}_{40} mode by Rush *et al*¹⁵ is 1312 cm⁻¹ for NiTPP using DFT technique. However, by empirical normal coordinate analysis method, its positions are calculated at 1408 cm⁻¹ (\mathbf{n}_{40a}) and 1402 cm⁻¹ (\mathbf{n}_{40b}) for free-base porphine²² and at 1382 cm⁻¹ (\mathbf{n}_{40a}) and 1227 cm⁻¹ (\mathbf{n}_{40b}) for free-base tetraphenylbacteriochlorin.²³ Porphyrin ring-related stretching vibrations in S₂TPP show downshift with respect to the corresponding bands in H₂TPP.¹⁰ We have, therefore, assigned the 1297 and 1238 cm⁻¹ bands to $\mathbf{n}_{40a,b}$ modes due to quarter-ring stretching of substituted and non-substituted pyrrole respectively. Pyrrole quarter-ring stretching motion is coupled to C_b-H bending according to DFT calculation of porphine by Kozłowski *et al*²¹. These authors have calculated

bands at 1252 cm^{-1} of B_{2u} symmetry due to $C_b\text{-H}$ deformation with $C_a\text{-N}$ and $C_a\text{-C}_b$ stretching and at 1408 cm^{-1} of B_{3u} symmetry due to $C_a\text{-N}$ and $C_a\text{-C}_b$ stretching. Also in a recent IR study of H_2TPP , a band at 1249 cm^{-1} has been assigned to $C_a\text{-N}$ stretching mode.¹⁴ This further justifies assignment of 1297 and 1238 cm^{-1} bands to $\mathbf{n}_{40a,b}$ modes. In S_2TPP cation only a single band at 1297 cm^{-1} is observed corresponding to these bands. A weak band at 1247 cm^{-1} is also assigned to forbidden IR mode \mathbf{n}_{27} . Symmetric pyrrole half-ring stretching modes \mathbf{n}_{41b} (B_{3u}) and \mathbf{n}_{41a} (B_{2u}) are observed at 1313 and 1357 cm^{-1} for non-substituted and substituted pyrrole rings respectively in the IR spectrum of neutral compound (figure 3a). These bands shift to new position at 1363 cm^{-1} in cation spectrum. However, observation of weak bands at 1357 cm^{-1} in figure 3b shows the presence of small amount, of non-oxidized S_2TPP . As can be seen from the IR spectra of oxidized S_2TPP , all the molecules are not converted to cationic form, since some bands at 1357 cm^{-1} and between 1500 and 1600 cm^{-1} can still be seen at the positions of the neutral species with non-zero intensity. It suggests that dithia porphyrins are difficult to oxidize compared to free-base porphyrins. In fact, from the electrochemical studies of S_2TPP , it was found that the oxidation potential of this molecule is more positive compared to H_2TPP .²⁴ The symmetric pyrrole half-ring stretching mode can be described by the out-of-plane $C_a\text{-N}/C_a\text{-S}$ and $C_a\text{-C}_b$ stretching in opposite pyrrole rings. The out-of-phase stretching motion of $C_a\text{-S}$ and $C_a\text{-C}_b$ also leads to marked change in the $C_a\text{-C}_m\text{-C}_a$ angle. This in turn causes rather large amplitude in the motion of the C_m -phenyl bond. Hence, the intensity of the band assigned to C_m -phenyl in S_2TPP is more than the intensity of the corresponding band in H_2TPP . Bands at 1377 , 1411 cm^{-1} and other bands within these wave number position may be assigned to C-H bending of the porphyrin ring in accordance with recently reported studies.²⁰

Bands in the wave number region beyond 1450 cm^{-1} arise mainly due to $C_a\text{-C}_m$, $C_b\text{-C}_b$ and phenyl ring stretching vibrations. Doublets at 1459 and 1475 cm^{-1} bands in S_2TPP may be assigned to $\mathbf{n}_{39a,b}$ modes having in-phase $C_a\text{-C}_m$ motion. Weak intensity bands at 1466 and 1482 cm^{-1} bands may be assigned to forbidden modes \mathbf{n}_3 (A_g) and \mathbf{n}_{28} (B_{1g}) modes respectively. These modes also involve in-phase motion of the $C_a\text{-C}_m$ vibration. Other bands, which may also be assigned to $C_a\text{-C}_m$ vibrational modes $\mathbf{n}_{37a,b}$ (B_{2u}/B_{3u})

and forbidden \mathbf{n}_{19} (B_{1g}), are observed at 1542 , 1560 and 1550 cm^{-1} respectively. In metalloporphyrins with D_{4h} symmetry, the $C_a\text{-C}_m$ modes are grouped into two categories according to whether they are symmetric or asymmetric with respect to the $C_{2'}$ axis passing through the opposite *meso* carbon atoms. In S_2TPP and its cation as well as H_2TPP , the $C_{2'}$ axis is lost due to reduction of the molecular symmetry to D_{2h} . Therefore, according to Li and Zgierski,²² it is more appropriate to use in-phase and out-of-phase combination of the two adjacent $C_a\text{-C}_m$ stretching instead of symmetric and asymmetric respectively to describe these modes. In the spectrum of S_2TPP , bands due to $C_b\text{-C}_b$ stretching have been observed at 1509 , 1534 and 1523 and 1527 cm^{-1} and assigned to $\mathbf{n}_{38a,b}$ (B_{2u}/B_{3u}), \mathbf{n}_{11} (A_g) and \mathbf{n}_2 (A_g) modes respectively. Of these modes, the latter two are forbidden under D_{2h} symmetry. As can be seen from Figures 2–4, intensity patterns and vibrational frequencies of different IR bands in the spectra of S_2TPP are quite similar to the spectra of the dication of H_2TPP . Similarity in the spectra may be due to the similarity between their structures, although they belong to different point groups. The point group symmetry of $\text{H}_4\text{TPP}^{2+}$ is S_4 . Both are known to have considerable nonplanarity.^{19,24} According to the X-ray measurements,¹⁹ the S atoms are displaced out of the porphyrin plane by 0.09 and the N atoms by 0.24 in S_2TPP . Nonplanarity is, therefore, responsible for the appearance of the bands which are otherwise forbidden under ideal D_{2h} symmetry. The effective symmetry of this molecule in reality may be taken as C_{2v} , which is less than the assumed symmetry D_{2h} .

3.1c High wave number region: The N-H stretching bands observed at 3316 and 3310 cm^{-1} in H_2TPP and its dication respectively (figure 4) are no longer seen in the spectrum of S_2TPP . This observation is in complete agreement with the structure of the molecule, which does not have an N-H bond. Dications of S_2TPP , prepared by adding trifluoroacetic acid to the solution, have shown this band at 3308 cm^{-1} with reduced intensity. Similar observations, have been made in case of H_2TPP . However, the number of N-H bonds are just half in the cation of S_2TPP compared to $\text{H}_4\text{TPP}^{2+}$. Therefore, intensity of the band in the former compound is still weaker than in the latter. Reduction of the intensity on dication formation also indicates that the derivative of the transition dipole moment with respect to N-H stretching mode also becomes very small. Other bands observed in the

higher wave number region are due to the stretching vibrational motion of C_b-H bond of the porphyrin ring and $C-H$ stretching of phenyl rings. Spectrum of S_2TPP shows bands due to C_b-H stretching modes at 3081 and 3116 cm^{-1} with shoulders and other weak bands. It seems that the above bands correspond to 3108 and 3134 cm^{-1} bands of H_2TPP (figure 4a,c). The downshift in the wave numbers of these bands for S_2TPP compared to H_2TPP indicates the weakening of C_b-H bonds of the former compound. This observation gets support from earlier reported work on this molecule.²⁴

3.2 Phenyl ring modes

A number of phenyl ring modes are observed in the IR spectra of S_2TPP , similar to H_2TPP . Modes internal to the phenyl rings are expected to occur at essentially the same frequencies as in other TPPs. Although steric hindrance between the ortho hydrogen atoms of the phenyl groups and the adjacent pyrrole rings opposes the rotation of phenyl group in the porphyrin plane in ground state, yet most phenyl ring modes are mixed with porphyrin ring modes through the phasing of their eigenvectors.

The band at 669 cm^{-1} does not show any change in its position and intensity on cation formation. Hence, this band may be assigned to the in-plane phenyl ring vibrational mode f''_9 . Other bands, which may arise due to phenyl ring stretching are observed at 749 and 755 cm^{-1} and can be assigned to $p''_{3a,b}$ modes respectively. In the spectrum of cationic species only one band is seen at 751 cm^{-1} corresponding to $p''_{3a,b}$. The 844 cm^{-1} band may have contribution from the phenyl ring according to Zhang *et al*¹⁶, therefore, this band is also assigned to phenyl ring vibration. A number of weak bands at 912, 952 cm^{-1} and between these wave number positions may also be assigned to phenyl ring vibrations. The 1151 and 1160 cm^{-1} bands are due to out-of-plane phenyl ring vibrational modes y_7 and y'_7 of A_u and B_{1u} symmetry respectively. These are seen at 1154 cm^{-1} for dication. Bands at 1431, 1439 and 1449 cm^{-1} may be assigned to phenyl ring modes y_4 (A_u), y'_4 (B_{1u}) and y''_4 (B_{2g}/B_{3g}) respectively. These bands also do not show any shift on cation formation. As can be seen, IR bands related to phenyl rings are more intense in S_2TPP spectra than in H_2TPP . This indicates orientational change of the phenyl rings with respect to the porphyrin plane in the former molecule in comparison with the latter. Orientational change is a result

of the structural change caused by the presence of the S atoms as discussed above. X-ray and electronic absorption spectroscopy¹⁹ also suggest rotation of phenyl rings in S_2TPP towards the mean porphyrin plane, which is accompanied by much larger overlap between their p systems.

As mentioned above, the E_u symmetry modes in the spectra of S_2TPP split into B_{2u} and B_{3u} species due to its point group symmetry D_{2h} similar to H_2TPP . However, contrary to its point group symmetry, certain porphyrin ring as well as phenyl ring related bands in the spectra of S_2TPP cation are degenerate as in H_4TPP^{2+} . There is one fundamental difference in the degeneracy of these bands in these molecules. In H_2TPP , the symmetry of the molecule increases from two-fold to four-fold (S_4) due to addition of protons at the N atoms of the deprotonated pyrrole rings on cation formation. Thus in case of H_4TPP^{2+} , not only is the point group symmetry of the molecule increased but the pyrrole rings are also similar to each other in every respect as far as bonding arrangements and force constants are concerned. Similar to H_4TPP^{2+} , two protons attach to N atoms of non-substituted pyrrole rings on formation of S_2TPP cation. Thus, effective point group symmetry of the molecule is still two-fold even after addition of two protons. Therefore, the degeneracy of IR bands cannot be explained only on the basis of point group symmetry. In H_4TPP^{2+} , extra protons attached to the N atoms of pyrrole rings reduce electron density on the pyrrole rings.²⁶ Addition of protons in case of S_2TPP may also have similar effect on the electron density on pyrrole rings. We can, therefore, assume that the electron density on the pyrrole rings with N atoms is reduced on oxidation (protonation). On the other hand, electron density on the substituted pyrrole rings is already reduced by the S atoms. Thus, the net effect of the protonation of the molecule is the reduction of electron density on the non-substituted pyrrole rings to an extent that it becomes nearly equal to the electron density on the substituted pyrrole rings, thereby making the two types of pyrrole ring equivalent in terms of electron density, bond order and force constants. Hence, some of the vibrations are accidentally degenerate in the spectra of S_2TPP cation, contrary to the point group symmetry.

In the high wave number region, some bands can be identified with the phenyl ring vibrations. Bands at 3011 and 3022 cm^{-1} either remain at their respective positions or change their position by a few wave numbers with reduced intensity for cations. On the

other hand, phenyl C–H stretching band at 3054 cm^{-1} , which does not have detectable intensity for neutral species, gains intensity in the cation spectrum (figure 4b). These observations indicate that the bonding arrangements in phenyl rings of S_2TPP and its cation are almost identical, but orientation is different as already mentioned above.

4. Conclusions

From the above discussion, it is clear that the observed IR bands of S_2TPP can be assigned, in general, on the basis of overall D_{2h} symmetry of the molecule. Reduction in symmetry, due to small out-of-plane displacement of N and S atoms is responsible for non-zero intensity of forbidden bands under D_{2h} point group. Further from the analysis of the spectra of S_2TPP cation, it can be concluded that two types of pyrrole rings in cationic species are identical in bonding arrangements.

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