The identification and origin of N–H group overtone and combination bands in the near infrared spectra of 2-thiopyrrole-1,2-dicarboximides

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Abstract. Near infrared spectra (4000–12 000 cm^{-1}) of 2-thiopyrrole-1,2-dicarboximide (TPH) and its N-deuterated analogue were measured in polycrystalline form at different temperatures between 410 K and 273 K. Spectra in solution were recorded as a function of concentration and temperature. The prominent bands so obtained could be interpreted in terms of overtone and combination bands of the N–H(D) and C–O groups modes. The results in CHCl$_3$ and CCl$_4$ solutions allowed differentiation between hydrogen bonded and non-hydrogen bonded bands. A comparison of cubic potential constant K_3, mechanical anharmonicity $\omega_e\chi_e$ and electrical anharmonicity μ_2/μ_1 for the stretching bands indicates that these constants are not affected much by N-deuteration.

Keywords. Near IR spectra; combination modes; anharmonicity in N–H and C=O group vibrations: H-bonding in thiopyrroles.

1. Introduction

In view of the biological and medicinal uses of substituted pyrroles (Cotton *et al* 1964; Sindellari *et al* 1982) and the fact that a few of them form dimagnetic complexes with transition metals (Bosnich *et al* 1974; Saheb *et al* 1981), studies of the physical and chemical properties and their correlation with the vibrational and electronic spectra of these compounds have been of common interest. In this series we have reported the infrared vibrational analysis of the fundamental bands (200–4000 cm^{-1}) in a few thiopyrroles (Ram 1984; Ram *et al* 1984). The hydrogen bonding properties of the functional groups N–H and C=O along with the data on thermodynamic functions ΔH, ΔG and ΔS have been discussed therein. Singh and Agarwala (1979) and Saheb *et al* (1983) have reported dimagnetic complexes of similar molecules with transition metal ions in various oxidation states. Saheb *et al* (1983) and Saheb (1984) have also attempted the analysis of vibrational transitions (only fundamental modes) associated with the pyrrole ring and the *d-d* electronic transitions associated with transition metal ions.

The highly excited N–H group vibrations of pyrroles that fall in the near IR region have been shown to provide a better understanding of the hydrogen bonded molecular associations. This region of the spectrum is also important for physicochemical measurements and chemical analysis. In this paper we report the near IR

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(4000–12 000 cm^{-1}) spectra and thus the identity and origin of the characteristic bands of 2-thiopyrrole-1,2-dicarboximide (TPH) and its N-deuterated analogue (TPH-ND). Attempts have been made to clarify and evaluate the effects of the molecular associations on the character of the functional group vibrational modes.

2. Experimental

TPH was prepared by the method reported by Papadopoulos (1973) and was recrystallized in aqueous ethanol before use. The solvents CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 were of BDH reagent grade. N-deuterated TPH was obtained by refluxing a solution of TPH in D_2O for 10 hours. The process was repeated several times with fresh D_2O and the product was finally dried in a vacuum desiccator over P_2O_5.

The IR spectra (200–4000 cm^{-1}) were recorded on a Perkin-Elmer-621 spectrophotometer using NaCl cells for solutions and KBr pellets ($\approx$ 1 mg/200 mg KBr) for solid samples. Measurements in the near IR region (4000–12 000 cm^{-1}) were made on a Cary-17D spectrophotometer using quartz cells for solutions.

The temperatures at which spectra were recorded were varied and for solutions were maintained within ± 2 K by circulating water through a water-bath, while for solid samples a Specac variable temperature cell using liquid nitrogen was used as the coolant. The reported frequencies are accurate to within ± 5 cm^{-1}.

3. Results and discussion

3.1 *Fundamental absorption bands of N–H (D) and C=O groups of TPH and N-deuterated TPH*

The spectral changes induced by the solvents and by N-deuteration are taken as the bases for the present assignments of the TPH bands in the near IR region. The IR bands which are potential contributors to this region are therefore established under the same condition of measurements. The data are summarised in table 1. As expected, the studies carried out in CCl_4 solution are more effective in the identification of hydrogen bonded and non-hydrogen bonded bands than those carried out in $CHCl_3$ solution because the former solvent permits a greater degree of self-association of the molecules.

The N–H and C=O stretching modes exhibit similar band structures giving rise to two/three different band components. The results in CH_3Cl and CH_2Cl_2 solutions are similar and do not give extra information over that in $CHCl_3$ solution. The intensities of the two band-groups at $\approx$ 3200 and $\approx$ 1750 cm^{-1} are very sensitive to concentration. The band component at the highest frequency of each group is attributed to the free monomer, the middle one to intramolecular H-bonded (through O – – – H bonding between $>$C=Ö and $>$N̈–H groups) monomer, and the third one to the intermolecular self-associated dimer of TPH (Ram 1984). These bands in N-deuterated TPH shift to lower frequencies by a factor $\approx$ 1·4. The reliability of this assignment appears to be affirmed by both sets of experimental data and is further corroborated by our temperature and pressure dependence studies, wherein the intensities of the monomer bands increase, and those of the dimer band decrease as temperature increases from 77 K to 410 K. The identification of the other bands of

Table 1. Prominent fundamental bands (in cm^{-1}) observed in the IR spectra of TPH and N-deuterated TPH as solids and in solution at room temperature (298 K).

| Solid		CCl$_4$ Solution (0·05 M)		CHCl$_3$ Solution (0·50 M)		
TPH	TPH-ND	TPH	TPH-ND	TPH	TPH-ND	Assignment
476 (32)	475 (33)	—	—	—	—	ν_{25} IP C=S bend
845 (12)	840 (8)	840 (120)	835 (110)	840 (100)	840 (90)	ν_{21} IP C=O bend
1122 (38)	1120 (35)	1135 (140)	1140 (130)	1120 (95)	1120 (70)	C=S stretch
1142 (64)	1141 (65)	1145 (500)	—	1145 (290)	1145 (280)	ν_{17}
1281 (28)	965 (15)	1296 (80)	960 (40)	1295 (70)	965 (60)	ν_{13} IP N-H(D) bend
1305 (58)	970 (45)	1310 (400)	975 (260)	1315 (200)	980 (150)	
1730 (45)	1735 (30)	1760 (100)	1760 (60)	1760 (75)	1765 (50)	ν_{5c} C=O stretch
1740 (51)	1745 (40)	1782 (440)	1778 (300)	—	—	ν_{5b}
1763 (58)	1765 (50)	1793 (600)	1785 (410)	1780 (300)	1780 (250)	ν_{5a}
3100 (16)	2320 (10)	3345 (40)	2510 (20)	3340 (13)	2510 (13)	ν_{1c} N-H(D) stretch
3150 (29)	2375 (15)	3410 (83)	2560 (30)	—	—	ν_{1b}
3200 (23)	2390 (20)	3440 (135)	2570 (120)	3430 (65)	2565 (80)	ν_{1a}

ν_i (i = 1, 2, 3 etc.) refers to vibrational mode number in the Mullikan (1955 scheme; a: Free monomer, b: intrabonded monomer, c: interbonded dimer, IP: in plane; the relative peak intensities (molar absorbance in solution spectra) are written in parentheses against the frequencies.

interest, i.e., the β(NH) and ν(C=S) bands at $\approx$ 1300 and $\approx$ 1140 cm^{-1}, respectively, is consistent with the literature values (Lord and Miller 1942; Bellamy 1968).

3.2 *Near infrared absorption bands of* TPH *and N-deuterated* TPH

The near IR spectra of the two TPH comprise prominent combination and overtone bands of bonded and non-hydrogen bonded modes of N–H(D) and C=O groups. The H-bonded modes exert a greater influence on the character of the near IR spectrum than do the non-hydrogen bonded modes in any case. The band intensity and structure of a few H-bonded bands are modified drastically in going from solid to solution, and also within solutions of different concentrations in the same solvent. Figures 1 and 2 provide a comparison of these bands in TPH and N-deuterated TPH. The frequencies and relative band-intensities of the observed bands along with their proper assignment are summarized in table 2. The tentative assignments given here are based on the following: (i) the strong overtone/combination bands would arise primarily from the in plane-in plane oscillations of parent bands having appreciable intensities, whereas the weaker bands are expected to appear either from the in plane-out of plane oscillations of the >N̈–H(D) and >C=Ö groups (or of the TPH ring) or from the in plane-out of plane oscillations of the modes belonging to the cross species of these; (ii) the H-bonded bands would exhibit higher mechanical anharmonicity than the non-hydrogen bonded bands; (iii) the N–D bands in N-deuterated TPH would have relatively smaller mechanical anharmonicity than the N–H bands of TPH; (iv) while assigning an observed band to a suitable combination/overtone mode, an attempt is made to keep the mechanical anharmonicity to a minimum and of negative sign. In the following sections we will discuss briefly a few assignments that require further justification.
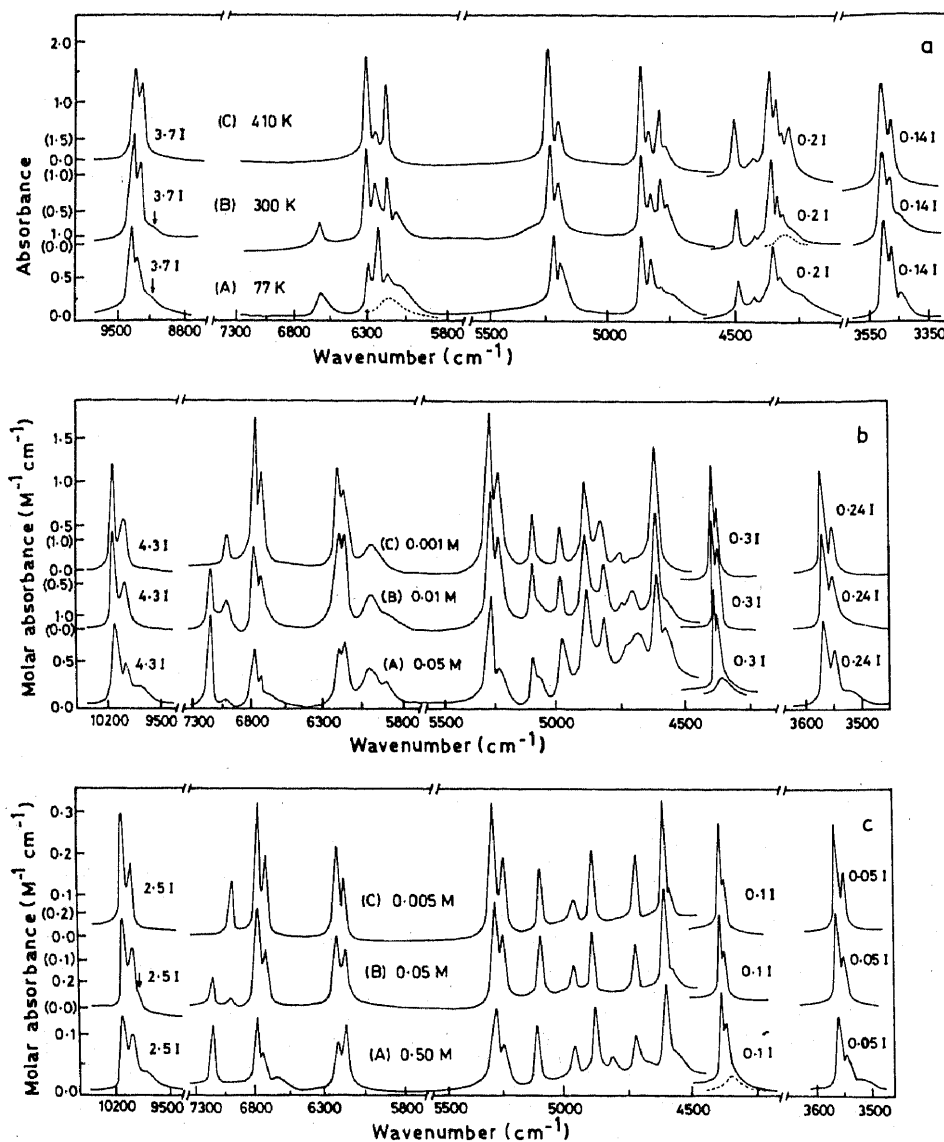
Figure 1a.   The near IR absorption spectra of TPH at three different temperatures (A) 77 K, (B) 300 K and (C) 410 K. The dotted curves are the approximate contributions of the interbonded dimer bands (for discussion see the text). 0·14 I, 0·2 I and 3·7 I represent 0·14, 0·2 and 3·7 times intensity I (absorbance) respectively, given on the vertical axis. **b.** The near IR spectra of TPH corresponding to those of figure 1a in CCl_4 solution at three different concentrations (A) 0·05 M (B) 0·01 M and (C) 0·001 M (M : mole/litre). **c.** The near IR spectra of TPH corresponding to those of figure 1b in $CHCl_3$ solution at three different concentrations (A) 0·50 M, (B) 0·05 M and (C) 0·005 M.
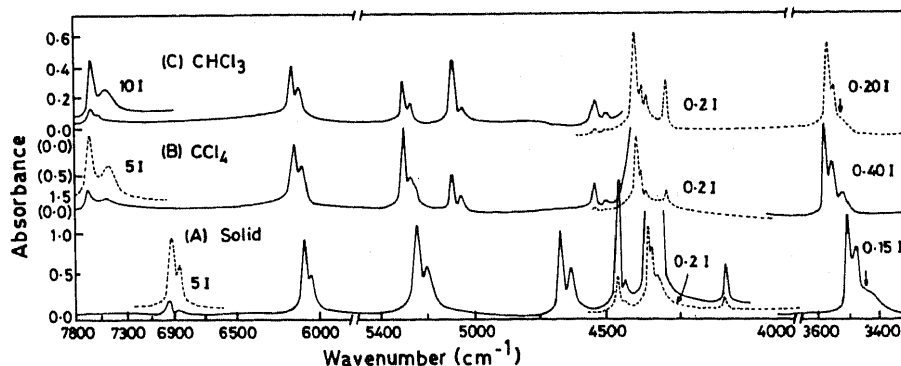
Figure 2. The near IR spectra of N-deuterated TPH in (A) solid, (B) CCl_4 solution (0·05 M) and (C) $CHCl_3$ solution (0·01 M). The solid and dotted curves represent the same spectra but at different intensity scales as is indicated.

3.2a *N-H and N-D groups stretching bands*: The N-H stretching vibrations of TPH in the fundamental mode show very little change with variations of temperature and concentration, but those in the overtone and combination bands differ drastically. The broad bands at ~ 6200 and $\sim 9200 \, cm^{-1}$ in the solid sample comprise at least three different components. An advantage of measuring the spectrum between 77 and 410 K appears clearly in the $6200 \, cm^{-1}$ band. There is an intensity changeover in its three components at 6180, 6240 and 6295 cm^{-1} (values at 77 K) in going from 77 K to 410 K (see figure 1a). This may be due partly to a change of bonded $\rightleftharpoons$ non-bonded configuration and partly to a change of bandwidths leading to changed overlap conditions. The intensity of the latter two components increases with increase in temperature. These involve the $2v_{1a}$ and $2v_{1b}$ modes of TPH respectively. The $6180 \, cm^{-1}$ band is accordingly assigned to $3v_{5a} + v_{21}$. The dimer band $2v_{1c}$ does not appear at temperatures above ≈ 300 K. However, a considerably large and asymmetric spread (6000 to 6400 cm^{-1}) of the $6200 \, cm^{-1}$ band at ≈ 77 K indicates its presence in a weak band centred at $\approx 6160 \, cm^{-1}$. The corresponding second overtone bands likewise appear in the broad absorption at 9165, 9285 and 9310 cm^{-1}, respectively.

We have also carried out these studies in different polar and nonpolar solvents to confirm the origin of these bands. Attempts are made to correlate predicted and observed changes in band positions due to IR band perturbations, or lack thereof, induced by changing the solvents. The $2v_1$ and $3v_1$ band positions remain almost the same in $CHCl_3$ and CCl_4 solutions showing a negative anharmonicity in $\omega_e \chi_e$ (a deviation from the predicted frequencies). The band intensity is modified, however, depending on the concentration of the solution and the nature of the solvent. In general, the bands are ≈ 5 times more intense in CCl_4 solution as compared to those in $CHCl_3$ solution. The molar absorbance ε ($mol^{-1} 1 \, cm^{-1}$) in either solvent increases in non-hydrogen bonded bands (*a* species) and decreases in hydrogen-bonded bands (*b* and *c* species) as the concentration of TPH decreases. The combination bands at $6150 \, cm^{-1}$ and $6185 \, cm^{-1}$ (in CCl_4 solution) shift to higher frequencies (positive $\omega_e \chi_e$) with respect to their predicted values at 6186 and $6239 \, cm^{-1}$, respectively. This has the advantage that these do not overlap with nearby $2v_1$ bands. The result is not very surprising. Lucazeau and Sandorfy (1970) have reported several cases in the near IR

Table 2. Prominent absorption bands observed in the near infrared spectra of TPH and N-deuterated TPH at room temperature (298 K).

v (cm^{-1})	Solid $\omega_e\chi_e$ (cm^{-1})	CCl$_4$ solution (0·05 M) v (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	CHCl$_3$ solution (0·5 M) v (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	Assignment
2-Thiopyrrole-1,2-dicarboximide (TPH)						
3450 (20) ⎫	−5	3520 (7) ⎫	0	3518 (4) ⎫	−1 ⎫	$2v_{5c}$
3476 (65) ⎬	−2	3548 (25) ⎬	−8	3542 (15) ⎬	— ⎬	$2v_{5b}$
3505 (90) ⎭	−11	3568 (40) ⎭	−9	3555 (25) ⎭	−3 ⎭	$2v_{5a}$
4305 (10)	+10	4366 (5)	+6	4360 (2)	−2	$2v_{5c}+v_{21}$
4317 (26)	−4	4380 (25)	−8	4378 (10)	−4	$2v_{5b}+v_{21}$
4331 (35)	−19	4395 (38)	−13	4390 (18)	−5	$2v_{5a}+v_{21}$
4280 (16) ⎫	+8	4565 (5·5) ⎫	+20	4565 (0·5) ⎫	— ⎫	$v_{1b}+v_{17}$
4351 (60) ⎭	+9	4605 (13) ⎭	+20	4510 (1·9) ⎭	+35 ⎭	$v_{1a}+v_{17}$
4425 (7·0)	−6	4700 (4·0)	−6	—	—	$v_{1b}+v_{13}$
4488 (28)	−17	4740 (5·5)	−10	4735 (0.8)	−10	$v_{1a}+v_{13}$
4758 (6·2) ⎫	−11	4810 (8·0) ⎫	−34	4810 (0·4) ⎫	−27 ⎫	$2v_{5b}+v_{13}$
4780 (9·8) ⎭	−13	4875 (11·2) ⎭	−3	4870 (1·4) ⎭	0 ⎭	$2v_{5a}+v_{13}$
—	—	4980 (6·0)	—	4955 (0·8)	—	?
4825 (7·5) ⎫	−75	5075 (3·5) ⎫	−117	—	— ⎫	$v_{1b}+v_{5b}$
4880 (13) ⎭	−83	5118 (6·0) ⎭	−115	5115 (1·2)	−95 ⎭	$v_{1a}+v_{5a}$
5170 (8·5)	−15	5260 (4·5)	−21	5265 (1·0)	−16	$3v_{5b}$
5220 (14·5)	−13	5295 (12·5)	−19	5295 (1·6)	−13	$3v_{5a}$
—	—	5895 (3·0) ⎫	—	—	— ⎫	$v_{1c}+2v_{13}$
—	—	5975 (3·8) ⎬	—	—	— ⎬	$v_{1b}+2v_{13}$
—	—	6010 (4·5) ⎭	—	—	— ⎭	$v_{1a}+2v_{13}$
6094 (4·0)	+59	6150 (7·5)	+50	6150 (1·3)	+45	$3v_{5b}+v_{21}$
6180 (10)	+115	6185 (6·8)	+50	6190 (1·0)	+55	$3v_{5a}+v_{21}$
6160* (2·0) ⎫	−20	6660 (1·8) ⎫	−15	6665 (0·3) ⎫	−8 ⎫	$2v_{1c}$
6250 (9·0) ⎬	−25	6730 (3·5) ⎬	−45	6740 (0·8) ⎬	— ⎬	$2v_{1b}$
6305 (14·3) ⎭	−48	6780 (6·8) ⎭	−50	6780 (1·4) ⎭	−40 ⎭	$2v_{1a}$
—	—	6975 (1·0)	−33	—	—	$2v_{5a}+v_{1a}$
6640 (3·0)	−85	7140 (10·5)	−70	7130 (1·3)	—	$2v_{1b}+v_{25}$
9125 (0·6) ⎫	−38	9760 (0·4) ⎫	−77	9810 (0·15) ⎫	−63 ⎫	$3v_{1c}$
9295 (3·0) ⎬	−27	9935 (1·1) ⎬	−53	9970 (0·42) ⎬	−47 ⎬	$3v_{1b}$
9380 (4·0) ⎭	−26	10105 (2·1) ⎭	−22	10105 (0·55) ⎭	−22 ⎭	$3v_{1a}$
N-deuterated TPH						
3450 (20) ⎫	−10	3516 (3) ⎫	−2	3520 (5) ⎫	−5 ⎫	$2v_{5c}$
3475 (60) ⎬	−8	3550 (20) ⎬	−3	3545 (15) ⎬	— ⎬	$2v_{5b}$
3505 (35) ⎭	−13	3578 (35) ⎭	+4	3568 (30) ⎭	+4 ⎭	$2v_{5a}$
4130 (7)	−25	4310 (15)	−45	4310 (16)	−35	$v_{1a}+v_{5a}$
4300 (22) ⎫	+10	4365 (15) ⎫	+14	4364 (13) ⎫	+4 ⎫	$2v_{5c}+v_{21}$
4318 (40) ⎬	+3	4383 (35) ⎬	+2	4380 (16) ⎬	−5 ⎬	$2v_{5b}+v_{21}$
4330 (53) ⎭	−15	4400 (56) ⎭	−13	4405 (35) ⎭	−3 ⎭	$2v_{5a}+v_{21}$
4440 (4)	+10	4500 (2)	−10	4508 (0·6)	−2	$2v_{5b}+v_{13}$
4465 (18)	−10	4540 (3·5)	−13	4538 (1·7)	−10	$2v_{5a}+v_{13}$
4630 (6·5) ⎫	−60	5065 (3) ⎫	−27	5060 (1·0) ⎫	— ⎫	$2v_{1b}$
4670 (10·5) ⎭	−55	5100 (6) ⎭	−20	5110 (4·2) ⎭	−10 ⎭	$2v_{1a}$
5210 (7)	−8	5270 (6)	−18	5275 (1·2)	−14	$3v_{5b}$
5230 (13)	−9	5290 (13)	−19	5318 (2·7)	−11	$3v_{5a}$
6065 (5) ⎫	+15	6135 (7) ⎫	+30	6150 (2·0) ⎫	+35 ⎫	$3v_{5b}+v_{21}$
6095 (9) ⎭	+25	6175 (10) ⎭	+40	6190 (3·0) ⎭	+32 ⎭	$3v_{5a}+v_{21}$
6880 (0·8)	−22	7555 (1·0)	−14	7550 (0·20)	−13	$3v_{1b}$
6956 (1·3)	−19	7620 (1·7)	−10	7642 (0·40)	−8	$3v_{1a}$

* Band position observed at $\simeq$ 77 K; v: band frequency in cm^{-1}; $\omega_e\chi_e$: mechanical anharmonicity in cm^{-1}. The figures in parentheses are relative peak intensities (10 times the molar absorbances in the case of solution spectra).

spectra of simple aldehydes where C=O combination bands exhibit positive $\omega_e\chi_e$. In this agreement the 6150 and 6185 cm^{-1} bands can be correlated easily for the binary combination of $3v_{5b}$ and $3v_{5a}$, respectively, with v_{21} (C=O bending). The features of the other bands of interest are as usual.

The spectra of N-deuterated TPH lack or show diminished intensity in most of the bands. The band groups at $\approx$ 4300, $\approx$ 5200 and $\approx$ 6100 cm^{-1} do not shift by N-deuteration. These bands therefore do not belong to N-H group modes. The observation of first and second overtone bands of N-D stretching modes in N-deuterated TPH at $\approx$ 4650 and $\approx$ 6400 cm^{-1} in doublet structure (corresponding to a and b species) is concurrent with the absence of $\approx$ 6250 and $\approx$ 9200 cm^{-1} bands in TPH upon conversion of N-H to N-D. The N-D stretching mode of interbonded dimer (c species) exhibits extremely poor intensity and hence could not be resolved in the present investigation for any combination or overtone band.

3.2b *C=O group stretching bands*: The C=O stretching modes of TPH as well N-deuterated TPH are excited upto the third quanta. Intensity decreases continuously in successive excitations. As an example, the molar absorbences of monomer bands v_{5a}, $2v_{5a}$ and $3v_{5a}$ in the CCl$_4$ solution of TPH are 600, 4·0 and 1·25, respectively. Corresponding values in the deuterated TPH are 410, 3·5 and 1·35, respectively. This shows the validity of the second order perturbation approach. Only the intensity of the second overtone band seems to be relatively higher. H-bonded bands b and c are more distinctly observed in the first overtone band at $\approx$ 3500 cm^{-1}. The spectral changes in these highly excited bands towards the effect of temperature, concentration and solvent vary in a fashion similar to the fundamental bands. A few binary and tertiary combination bands of C=O stretching modes that appear with the N-H group modes could be identified easily by N-deuteration (see table 2).

3.3 *Anharmonicity in N-H(D) and C=O groups stretching modes*

Our previous discussions reveal that the vibrational bands of N-H(D) and C=O groups of TPH may give valuable information about the involvement of these groups in the formation of hydrogen bonds. In this section we are interested in determining how the mechanical $(\omega_e\chi_e)$ and electrical (μ_2/μ_1) anharmonicity parameters associated with these groups behave in the H-bonded and non-hydrogen bonded bands. The values for $\omega_e\chi_e$ were computed using second order perturbation formulae (Lucazeau and Sandorfy 1970), i.e.,

$$(\omega_e\chi_e)_{ii} = v_{i,01} - (v_{i,02})/2, \tag{1}$$

for the first overtone,

$$(\omega_e\chi_e)_{ii} = (v_{i,02})/2 - (v_{i,03})/3, \tag{2}$$

for the second overtone, and

$$(\omega_e\chi_e)_{ij} = v_{\text{comb}} - (v_{i,01} + v_{j,01}), \tag{3}$$

for the combination tones.

The symbols i and j represent the serial numbers of normal modes in the Mullikan (1955) notation. $v_{i,01}$, $v_{i,02}$ and $v_{i,03}$ are the frequencies measured on the cm^{-1} scale in the fundamental and in the first and second overtones bands of an ith vibration.

The electrical anharmonicity μ_2/μ_1 for a vibration can be obtained using band position and intensity in its fundamental and first overtone bands. Potential function V

and electric dipole moment μ associated with a vibration of normal coordinates q are given by

$$V = \tfrac{1}{2} K q^2 + K_3 q^3 + \ldots, \tag{4}$$

$$\mu = \mu_0 + \mu_1 q + \mu_2 q^2 + \ldots . \tag{5}$$

If we neglect higher terms in (4), the cubic potential constant K_3 in terms of ω_e and $\omega_e \chi_e$ may be written as (Foldes and Sandorfy 1966).

$$K_3 = \pm \, 0.516 (\omega_e | \omega_e \chi_e |)^{1/2}. \tag{6}$$

The positive sign is used when $\omega_e \chi_e$ is negative and vice versa.

A correlation of band intensities with frequencies (Herman and Shular 1954) in the fundamental and first overtone bands leads to

$$I_2/I_1 = [(\omega_{2-0})/(\omega_{1-0})] \{\mu_1 b + \mu_2)/(\mu_1 - 5\mu_2 b)\}^2, \tag{7}$$

if

$$b = (k_3/\omega_e) \ll 1.$$

The observed intensity ratio I_2/I_1 (I_1 for the fundamental band and I_2 for its first overtone band) and calculated values of ω_e and b when substituted in the quadratic equation (7) give two different solutions of μ_2/μ_1.

The $\omega_e \chi_e$ and μ_2/μ_1 values obtained using the observed band frequencies and intensities of the first overtone bands of the ν_1 and ν_5 vibrations are summarised in table 3. These could not be calculated for every H-bonded band as some of these are not

Table 3. The anharmonic constants $\omega_e \chi_e$, K_3 and μ_2/μ_1 as determined for the ν_1 and ν_5 modes of TPH and N-deuterated TPH in the approximation of the simple harmonic oscillator.

Vibration	$\omega_e \chi_e$ (cm^{-1}) TPH	TPH-ND	K_3 (cm^{-1}) TPH	TPH-ND	$10\,\mu_2/\mu_1$ TPH	TPH-ND
Solid sample						
ν_{1a}	48	55	205.4	191.5	1.09, 2.54	0.82, −2.57
ν_{1b}	25	60	146.1	199.6	0.77, −1.75	0.65, −2.44
ν_{1c}	20	—	129.4	—	0.37, 1.22	—
ν_{5a}	11	13	72.4	78.8	2.26, −3.39	2.34, −3.60
ν_{5b}	2	8	30.5	61.2	2.29, −2.76	2.29, −3.26
ν_{5c}	5	10	40.2	68.4	1.19, −1.80	1.39, −2.30
CCl$_4$ solution						
ν_{1a}	50	20	217.3	118.0	−0.11, −1.14	−0.10, −0.92
ν_{1b}	45	27	205.0	137.1	−0.12, −1.06	0.18, −1.25
ν_{1c}	15	—	66.8	—	−0.28, −0.68	—
ν_{5a}	9	4	65.9	43.5	0.21, −0.95	0.41, −0.91
ν_{5b}	8	3	65.7	37.7	0.17, −0.91	0.36, −0.79
ν_{5c}	0	2	0	30.7	0.59, −0.59	0.64, −1.00
CHCl$_3$ solution						
ν_{1a}	40	10	139.5	82.1	−0.20, −0.89	−0.18, −0.83
ν_{1c}	8	—	84.6	—	−0.08, −0.60	—
ν_{5a}	3	4	30.8	43.5	0.47, −0.82	0.52, −1.03
ν_{5c}	1	5	37.6	48.6	0.30, −0.73	0.43, −0.99

The parameters for ν_{1b} and ν_{5b} bands could not be estimated in the CHCl$_3$ solution as these bands do not seem to appear in this solution.

well resolved in the fundamental modes or in the overtone modes. A comparison of the data in solid state as well in solution at different conditions of temperature and concentration indicates that $\omega_e\chi_e$ have lower values in the H-bonded bands. This observation seems in contrast to the general finding that H-bonding increases the magnitude of $\omega_e\chi_e$. It appears to us that the first overtone bands $2v_5$ couple strongly with the fundamental bands v_1 as both lie in the 3100–3600 cm^{-1} region and satisfy the conditions of vibrational coupling (Varsanyi 1974). As a consequence, the frequencies of either band get modified showing no regular pattern for $\omega_e\chi_e$. In N-deuterated TPH, v_1 (N-D stretching) bands shift to lower frequencies 2350–2600 cm^{-1}, so that the coupling between these two modes becomes negligibly small. A relatively larger $\omega_e\chi_e$ value observed for a H-bonded band v_{1b} in the deuterated TPH supports this fact (see table 3). The v_5 mode has also the possibility of coupling with the C=C ring stretching vibrations. Perhaps due to this, the results of $\omega_e\chi_e$ for this vibration are not consistent even in the deuterated sample. It should be noted that the higher excited vibrations, $2v_1$, $3v_1$ and $3v_5$, are relatively free from vibrational mixing and their observed frequencies are more definite. The $\omega_e\chi_e$ derived using these band frequencies exhibit higher magnitude in H-bonded bands than in non-hydrogen bonded bands.

We now come to the effect of the N-deuteration of TPH. The $\omega_e\chi_e$ usually decreases except for the $2v_1$ and $2v_5$ bands in the solid state where its magnitude is larger in the deuterated sample. In fact, the vibrational frequency and the associated mechanical anharmonicity of a band depend largely on the local field and the symmetry of the concerned vibration site. In a pure gas phase system where the effect of nearest neighbours is minimum, the $\omega_e\chi_e$ of an X-D vibration is believed to have nearly one half the magnitude of the X-H vibration (Darling and Dennison 1940). However, in the solid state and in solution there seems no strict relation regarding their magnitudes. For example, the bending mode of water in $CoCl_2\cdot2H_2O$ and $CoCl_2\cdot2D_2O$ exhibits the same $\omega_e\chi_e \simeq 5$ cm^{-1} (Srivastava *et al* 1976). These authors have also noted a few examples in which deuterated samples may have larger $\omega_e\chi_e$ than the undeuterated samples. Thus the results observed in this investigation (where $\omega_e\chi_e$ is similar in the two TPH for most of the cases) are not ambiguous. Moreover, v_{1a} exhibits to ≈ 2.5 times lower $\omega_e\chi_e$ in CCl_4 solution and up to ≈ 4 times lower $\omega_e\chi_e$ in $CHCl_3$ solution. This indicates that both solvents offer almost similar environments for the TPH and N-deuterated TPH. The slightly lower values in the latter solvent may be attributed to a 1 : 1 complex between the sample and solvent molecules that may cause a shielding effect for vibrational coupling between favourable nearby vibrations (Nikolic *et al* 1983).

As compared to mechanical anharmonicity, the electrical anharmonicity parameter μ_2/μ_1 seems to be more sensitive to H-bonding. The origin of this parameter lies in the asymmetric variation of the effective charges during mechanical vibration in the system. In the N-H bond stretching v_{1a}, the two atoms oscillate parallel to the N-H bond. Thus any change in the frequency of Δv_{1a} in going from solid to solution would be associated with the asymmetric variation of the charges on either or on both the atoms. But μ_2/μ_1 shows no correlation with Δv_{1a} (Δv_{1a} exhibits almost the same value in CCl_4 as well as $CHCl_3$ solution while μ_2/μ_1 differs appreciably for the two solutions). So we conclude that the contribution of the charges on both atoms to the charge asymmetry is comparable. The absence of any systematic effect of N-deuteration also supports the view that the charge variation on H is less effective in the contribution to μ_2/μ_1 (if charge variations on H were the major contributors to μ_2/μ_1, the effect would be less in the deuterated sample). Also, the C=O stretching vibration v_{5a} exhibits similar features

and the charges on the C and O atoms are equally responsible for μ_2/μ_1. In the case of the interbonded polymer (figure 3c) the situation is a little different. The intensity of v_{1c} (v_{5c}) bands would appear mainly to be due to an asymmetric oscillation of the N–H ... O=C bond groups (Ram *et al* 1984). The terms R and R' represent the parts of TPH excluding the N–H and the C=O groups respectively. The integer n can take values 2, 3, 4, . . . representing the dimer, trimer, tetramer etc. Thus bands of these associated polymers would be more sensitive in contributing to μ_2/μ_1 as compared to free monomer bands (totally symmetric). The values of μ_2/μ_1 listed in table 3 are also minimum for the v_{1c} and v_{5c} bands. This supports the above facts. On the other hand, for an intrabonded monomer system (figure 3b), the change in the dipole moment due to the O---H hydrogen bond during N–H/C=O oscillation would be at an angle ϕ between C=O and O---H bonds. ϕ usually takes values different from 180°. This means that the v_{1b} or v_{5b} bands would have less effect on μ_2/μ_1. But this is not the observed case. What really happens is that the lone pair electrons on $>\ddot{\text{N}}$–H and $>\text{C}=\ddot{\text{O}}$ groups are no longer localised on the parent atoms in the intrabonded system. These are shifted towards $>\ddot{\text{N}}$---H and $\ddot{\text{O}}$---H bonds causing a slight distortion in the N–H---O=C configuration so that it almost becomes a straight line. This is consistent with our present observation where v_{1b} and v_{5b} bands behave similar to the non hydrogen bonded bands v_{1a} and v_{5a} (the vibration is parallel to the bond extension).

4. Conclusion

The near IR spectra of 2-thiopyrrole-1,2-dicarboximides are dominated by the overtone and combination bands of N–H(D) and C=O stretching vibrations. The spectra in polar solvents, e.g., in $CHCl_3$ suffer a loss of intrabonded bands in fundamental modes and in a few combination bands. This indicates an intermolecular H-bonding between the solution and solvent molecules and the masking of the intra molecular H-bonded bands of the samples. The mechanical and electrical anharmonicity constants derived using the data to the first excited overtone bands have lower values in the H-bonded bands and do not show appreciable changes upon deuteration. In fact, the v_5, $2v_5$ and v_1 vibrations are coupled strongly with nearby vibrations. The band position and
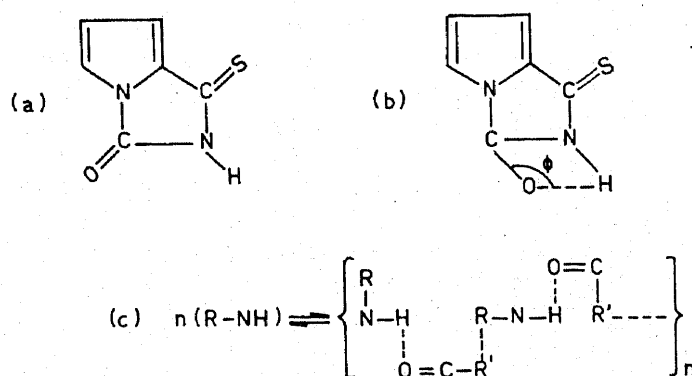

Figure 3 (a) Free TPH. **(b)** Intrabonded TPH **(c)** Interbonded TPH polymer.

intensity of these bands, as a consequence, are modified and the results of $\omega_e\chi_e$ and μ_2/μ_1 calculated using these data are no longer of consistent trend for H-bonded bands. More accurate values of these parameters can be seen in the highly excited vibrations ($3\nu_1$ and $3\nu_5$ modes) where, as expected, the $\omega_e\chi_e$ exhibit greater values for H-bonded bands. Thus, a successful elucidation of the near IR bands which can be assigned uniquely to the bonded and non-hydrogen bonded modes of the imide group would permit possible utilization of a few well isolated overtone and combination bands for quantitative H-bonding studies in molecules having this group.

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