

## Tentative Assignments of Fundamental Vibrations of Thio- and Selenoamides. VII. 1,2-Dimethyl-3-pyrazolidinethione, a Cyclic Thiohydrazide

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In order to develop a basis for future interpretation of vibrational spectra of thiohydrazides, 1,2-dimethyl-3-pyrazolidinethione (DMPT) was investigated. This compound was chosen as a model for thiohydrazides, because it is stable, simple, and does not give rise to complications due to conformational isomerism of the thiohydrazide group. The IR and Raman spectra of DMPT and five deuterium labelled analogs have been recorded below 4000  $\text{cm}^{-1}$ . A tentative assignment of the fundamentals is proposed, based on a normal coordinate analysis fitting 50 valence force constants to *ca.* 275 observed frequencies. The bands characteristic of the thiohydrazide group are discussed in some detail.

Metal complexes of hydrazine, hydrazides and thiohydrazides are a subject of considerable interest and their vibrational spectra have been extensively investigated. However, a reliable assignment of the fundamental modes of the free ligands have only recently received some interest. Thus, normal coordinate analyses (NCA) based upon IR and (partly) Raman data are now available for hydrazine,<sup>1</sup> semicarbazide,<sup>2</sup> thio- and selenosemicarbazide,<sup>3</sup> carbonylhydrazide,<sup>4</sup> thio- and selenocarbonylhydrazide,<sup>5</sup> and metal complexes of thiosemicarbazide<sup>6</sup> and thiocarbonylhydrazide.<sup>7</sup> Metal-isotope data combined with *N*-deuteration were also used in the study of bis(dithiocarbazato)nickel(II)<sup>8</sup> and the nickel(II) complex of *O*-ethylmonothiocarbamate.<sup>9</sup>

To our knowledge no similar work has been reported for simple thiohydrazides, though it would

be interesting to compare the spectrum of *e.g.* thioformhydrazide with those of thiosemicarbazide and thiocarbonylhydrazide. The main problem is, that simple thiohydrazides are rather unstable compounds. Furthermore, they exist as a mixture of *E* and *Z* isomers due to hindered rotation around the thioamide CN bond. The simplest thiohydrazide without these disadvantages is 2-methyl-3-pyrazolidinethione. However, as much better spectra were obtained for 1,2-dimethyl-3-pyrazolidinethione (DMPT) the latter compound was selected for investigation.

We shall report our spectral investigations of DMPT in the liquid and solid phases and discuss the results of an NCA with special reference to the identification of bands characteristic of the thiohydrazide group. Since DMPT contains no elements of symmetry, extensive deuterium labelling was used in order to obtain the necessary amount of data for the NCA. The spectra of 1-trideuteriomethyl-2-methyl-3-pyrazolidinethione (DMPT-1-*d*<sub>3</sub>), 1-methyl-2-trideuteriomethyl-3-pyrazolidinethione (DMPT-2-*d*<sub>3</sub>), and 1,2-bis(trideuteriomethyl)-3-pyrazolidinethione (DMPT-*d*<sub>6</sub>) gave information for determining the force field referring to each of the two methyl groups.

The spectra of 4,4,5,5-tetradeuterio-DMPT (DMPT-*d*<sub>4</sub>) and perdeuterio-DMPT (DMPT-*d*<sub>10</sub>) provided data to determine the large force field of the methylene groups. For economical reasons, isotopic substitution of the NNCS groups was not possible. However, comparison with the spectrum of the corresponding selenium compound, 1,2-

dimethyl-3-pyrazolidineselone (DMPS), proved a useful method ("selenation") in identifying the bands involving vibrations of the NCS group. Raman polarisation data were included since it was assumed (and confirmed) that the Raman depolarisation ratio for a certain band will show only small changes when DMPT is deuterated. Accordingly not only the overall form and intensity but also the depolarisation ratios were used for selection of corresponding bands in DMPT and its deuterated derivatives.

## STRUCTURE

Several X-ray determinations of thiosemicarbazides and thiocarbohydrazides have been carried out. However, crystal structures for simple thiohydrazides have not hitherto been reported. Therefore, two crystalline DMPT derivatives, 5-(*p*-methoxyphenyl)-DMPT and 5-(*p*-chlorophenyl)-DMPT, were prepared and subjected to preliminary X-ray measurements. The latter was found suitable, and was shown to be of space group  $C_{2h}^6$  ( $C2/c$ ) with 8 molecules in the unit cell. The bond lengths of the thiohydrazide group were: N–N 1.45; C–N 1.31; C–S 1.67 Å, and the C–C–S and the N–C–S angles were both 126°. The details of the investigation will be reported elsewhere.<sup>10</sup> The structural parameters used for DMPT in the calculations were unaltered, with the minor exception of changing all C–H distances to 1.09 Å and using tetrahedral arrangement around the carbon atoms of the two methyl groups. Also, the *p*-chlorophenyl group was substituted with a hydrogen atom placed in the same direction. The final coordinates may be obtained from the authors on request.

## EXPERIMENTAL

**Chemicals.** DMPT was prepared (36% overall yield) by reacting 1,2-dimethylhydrazine with ethyl acrylate<sup>11</sup> to give 1,2-dimethyl-3-pyrazolidinone, followed by reflux (3.5 h) with  $P_4S_{10}$  in dry pyridine (1.4 g/10 ml) analogous to the preparation of thioureas.<sup>12</sup> The almost colourless oil, b.p. 59–60 °C/0.3 mm, was stored in the cold and purified by distillation prior to recording the vibrational spectra. (Found: C 46.2; H 7.2; N 21.5; S 24.4. Calc. for  $C_5H_{10}N_2S$ : C 46.1; H 7.7; N 21.5; S 24.6).

Similarly, (4,4,5,5- $D_4$ )DMPT was prepared from 1,2-dimethyl(*N,N*- $D_2$ )hydrazine and ethyl ( $D_3$ )-acrylate in methan( $D$ )ol. (Found: C 44.6; H/D 7.5;

N 20.9; S 23.5. Calc. for  $C_5H_6D_4N_2S$ : C 44.7; H/D 7.4; N 21.0; S 23.9). Also, ( $D_{10}$ )DMPT was obtained from ( $D_8$ )-1,2-dimethylhydrazine and ethyl ( $D_3$ )-acrylate (Anal.  $C_5D_{10}N_2S$ : C, D, N, S). The ethyl ( $D_3$ )acrylated was prepared in 15% yield by a Reppe synthesis<sup>13</sup> using ethan( $D$ )ol (30 ml), 20%  $DCl$  (50 ml),  $Ni(CO)_4$  (17.1 g) and an excess of ( $D_2$ )-ethyne generated from calcium carbide and deuterium oxide.

In the synthesis of the DMPT's labelled on the methyl groups only, 1-benzoyl-3-pyrazolidinone was used as starting material. Equimolar amounts of hydrazine and acrylonitrile, condensed according to the method described by Dorn and Zubek<sup>14</sup> gave 3-amino- $\Delta^3$ -pyrazoline sulfate (89%, m.p. 139–140 °C). Hydrolysis<sup>15</sup> afforded 3-pyrazolidone hydrochloride (65%) which was treated with benzoyl chloride<sup>15</sup> to give 1-benzoyl-3-pyrazolidone (80%, m.p. 176–178 °C). Methylation by ( $D_6$ )dimethylsulfate followed by hydrolysis<sup>16</sup> gave 2-( $D_3$ )methyl-3-pyrazolidinone. Stirring this with methyl iodide in aqueous ethanol for 17 h gave after basification (solid KOH), extraction ( $CHCl_3$ ), drying, evaporation of the solvent and distillation 1-methyl-2-( $D_3$ )-methyl-3-pyrazolidinone (30%). This was converted into the corresponding thione 2-( $D_3$ )DMPT with  $P_4S_{10}$  as before. Repeating the above procedure using instead dimethyl sulfate followed by ( $D_3$ )-methyl iodide gave 1-( $D_3$ )methyl-2-methyl-3-pyrazolidinone, converted with  $P_4S_{10}$  to 1-( $D_3$ )DMPT. 2-( $D_3$ )methyl-3-pyrazolidinone was stirred with ( $D_6$ )dimethylsulfate for 2 h at 20 °C. Basification with NaOH, extraction ( $CHCl_3$ ), drying ( $MgSO_4$ ), evaporation of the solvent and distillation gave 1,2-( $D_6$ )dimethyl-3-pyrazolidinone, converted with  $P_4S_{10}$  to the corresponding thione, ( $D_6$ )DMPT. All these compounds gave satisfactory elemental analyses and were pure by TLC. The isotopic purity of the DMPT derivatives were 99% or better.

Slow addition of 1,2-dimethylhydrazine (100% excess) to ethyl *p*-chlorocinnamate in abs. ethanol at reflux followed by boiling for 44 h gave 1,2-dimethyl-5-(*p*-chlorophenyl)-3-pyrazolidinone. The crude product, on subsequent treatment with  $P_4S_{10}$  in dry pyridine at the boiling point for 2 h, gave 1,2-dimethyl-5-(*p*-chlorophenyl)-3-pyrazolidinethione, m.p. 73–74 °C, needed for the X-ray investigation. (Found: C 54.8; H 5.6; N 11.4; S 13.2; Cl 14.9. Calc. for  $C_{11}H_{13}N_2SCl$ : C 54.9; H 5.4; N 11.6; S 13.3. Cl 14.7). Using instead ethyl *p*-methoxycinnamate, a similar procedure gave 1,2-dimethyl-5-(*p*-methoxyphenyl)-3-pyrazolidinethione, m.p. 116–119 °C. (Found: 60.9; H 7.1; N 11.6; S 13.9. Calc. for  $C_{12}H_{16}N_2OS$ : C 61.0; H 6.8; N 11.9; S 13.6). The latter compound had a pronounced tendency for twin crystal formation and had to be rejected for X-ray investigation.

**Spectra.** The technique and equipment used for

Table 1. Final valence force constants for DMPT.

Type and symbol <sup>a</sup>	Value <sup>b</sup>	Type and symbol <sup>a</sup>	Value <sup>b</sup>	Type and symbol <sup>a</sup>	Value <sup>b</sup>
CH <sub>3</sub>		CH <sub>2</sub> (-CS)		Ring stretch	
H <sub>τ1</sub> = H <sub>τ2</sub> (torsion)	0.0526	H <sub>δ2</sub> (bend)	0.470	Ring stretch-stretch	
CH <sub>3</sub> (-N <sup>1</sup> )		H <sub>γ3</sub> = H <sub>γ4</sub> (bend)	0.592	F <sub>DL2</sub> = F <sub>DB2</sub>	0.570 <sup>e</sup>
K <sub>r</sub> (stretch)	4.722	H <sub>γ3</sub> = H <sub>γ4</sub> (bend)	0.693	Ring stretch-bend	
F <sub>rr</sub> (stretch-stretch)	0.008	F <sub>γ3γ4</sub> (bend-bend)	-0.321	F <sub>Dμ1</sub> = F <sub>Dμ2</sub>	0.422
H <sub>α</sub> (bend)	0.515	F <sub>γ3γ4</sub> (bend-bend)	0.077	F <sub>L2μ3</sub> = F <sub>Aε3</sub>	0.485
H <sub>β</sub> (bend)	0.763	CH <sub>2</sub> (-N)		F <sub>L1γ1</sub> = F <sub>L1γ2</sub> = F <sub>L1γ3</sub> = F <sub>L1γ4</sub>	0.353
F <sub>ββ</sub> (bend-bend)	-0.037	H <sub>δ1</sub> (bend)	0.432	F <sub>B2μ2</sub>	0.90 <sup>e</sup>
CH <sub>3</sub> (-N <sup>2</sup> )		H <sub>γ1</sub> = H <sub>γ2</sub> (bend)	0.780	F <sub>B2μ3</sub>	0.63 <sup>e</sup>
K <sub>r</sub> ' (stretch)	4.802	H <sub>γ1</sub> = H <sub>γ2</sub> (bend)	0.657	F <sub>L2ω2</sub> = F <sub>L1ω1</sub> = F <sub>L1ω2</sub> = F <sub>B1θ2</sub> = F <sub>B1θ3</sub> = F <sub>Aθ1</sub> = F <sub>Aθ3</sub> = F <sub>P1θ1</sub> = F <sub>P1θ2</sub> = F <sub>P2ε2</sub> = F <sub>P2ε1</sub>	0.738
F <sub>rr</sub> ' (stretch-stretch)	-0.134	F <sub>γ1γ2</sub> (bend-bend)	-0.136	F <sub>P1β</sub> = F <sub>P2β</sub>	0.660
H <sub>α</sub> ' (bend)	0.512	F <sub>γ1γ2</sub> (bend-bend)	0.086	Ring bend-bend	
H <sub>β</sub> ' (bend)	0.723			F <sub>ω</sub>	0.720
F <sub>ββ</sub> ' (bend-bend)	-0.031				
CH <sub>2</sub>					
K <sub>d</sub> (stretch)	4.722				
F <sub>dd</sub> ' (stretch-stretch)	0.035				
F <sub>γγ</sub> ' (bend-bend <sup>c</sup> )	0.058				
F <sub>γγ</sub> ' (bend-bend <sup>d</sup> )	0.081				

<sup>a</sup> For meaning of symbols, see Fig. 1. <sup>b</sup> In units of mdyn/Å (stretch constants), mdyn/rad (stretch-bend interactions) and mdyn Å/(rad)<sup>2</sup> (bending and torsion constants). <sup>c</sup> HCC-CCH interaction of CH<sub>2</sub>CH<sub>2</sub> with C-C common to interacting coordinates. <sup>d</sup> HCC-OCH interaction of CH<sub>2</sub> with C-H common to interaction coordinates. <sup>e</sup> Transferred from tetramethylthiourea and held fixed.

recording the IR and Raman spectra have previously been reported.<sup>17,18</sup> A liquid nitrogen cryostat was used for obtaining the IR spectra of polycrystalline DMPT at 85 K. The window used was CsI and the DMPT was allowed to evaporate and be collected directly on the window for *ca.* 2½ h. Each film was annealed to a temperature just below the m.p. of DMPT, however, spectra of annealed and unannealed films were hardly distinguishable.

## NORMAL COORDINATE ANALYSIS

Since DMPT contains no elements of symmetry, most of the symmetry coordinates were identical with the internal coordinates shown in Fig. 1. Local symmetry coordinates of the conventional type were used in describing the internal vibrations of the CH<sub>3</sub> and CH<sub>2</sub> groups. All calculations were performed using the method described by Schachtschneider and Snyder<sup>19</sup> as in the previous papers of this series. The part of the force field relating to the CH<sub>3</sub> and CH<sub>2</sub> groups approximate a true GVFF (general valence force field) because a rapid convergence to physically acceptable values was observed during the calculations. The force constants of each of the methyl groups are determined by using DMPT-1-*d*<sub>3</sub> and DMPT-2-*d*<sub>3</sub> in connection with DMPT-*d*<sub>6</sub> and DMPT-*d*<sub>10</sub>. Since it was not feasible to deuterate selectively each of the CH<sub>2</sub> groups the force constants for the methylene groups

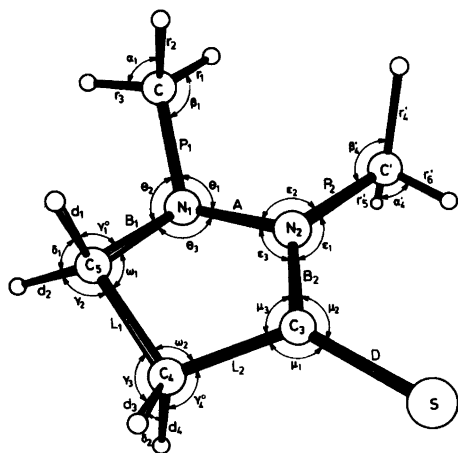


Fig. 1. Internal coordinates for DMPT. The following coordinates are not shown on the figure:  $\tau_1$ , N<sup>1</sup>-CH<sub>3</sub> torsion;  $\tau_2$ , N<sup>2</sup>-CH<sub>3</sub> torsion;  $\Delta$ , CS out-of-plane bend.

obtained by the use of DMPT-*d*<sub>4</sub> and DMPT-*d*<sub>10</sub> are less accurate. We wish to stress this point because it was necessary to use different force fields for the CH<sub>2</sub>CS and the CH<sub>2</sub>N methylene groups, and since one of the interaction constants ( $F_{\gamma_3\gamma_4}$ ) finally required a physically unrealistic value (Table 1).

The problems encountered in using potential functions of the GVFF type for cyclic compounds have been discussed by several authors.<sup>20-27</sup> We tried first to use the overlay technique for the remaining part of the DMPT molecule. A total of 8 stretching and 12 deformation force constants necessary to describe the motions of the heavy atoms were transferred from molecules having similar structures. Some 40 interaction force constants (stretch-stretch, stretch-bend, bend-bend) which were estimated *a priori* to be significant were similarly transferred. By allowing only the 20 diagonal (stretching and bending) force constants to vary, it was possible to obtain a satisfactory fit between observed and calculated frequencies (maximum error below 1% for each of the isotopic species). This overlay force field (OFF) was used for calculating the spectrum of DMPS with the result that the majority of the fundamentals were predicted within 10 cm<sup>-1</sup>. However, inspection of the force constant correlation matrix showed that many of the interaction force constants were so highly coupled that the OFF was in no way unique. We therefore preferred to reduce the number of force constants, but imposed the requirement that the potential energy distribution (PED) should be retained in gross features.

The methods described by other authors<sup>20-27</sup> for reducing the number of force constants were now tried in succession. In each case the success of the approach was estimated by comparison of the PED with that from the OFF (both for DMPT and DMPS) and considering the physical significance of the resulting value of each force constant. Three force constants ( $F_{B_2D}$ ,  $F_{B_2\mu_2}$  and  $F_{B_2\mu_3}$ ) were too highly correlated to be included in the iteration but were nevertheless necessary to obtain a good fit, and they were therefore transferred from tetramethylthiourea.<sup>17</sup> The ring bending force constants were difficult to determine because the lowest fundamentals of DMPT (below 100 cm<sup>-1</sup>) could not be assigned with certainty. Their number was therefore reduced by setting  $H_{\epsilon_1} = H_{\epsilon_2}$ ,  $H_{\theta_1} = H_{\theta_2}$ ,  $H_{\epsilon_3} = H_{\theta_3}$ , and  $H_{\omega_1} = H_{\omega_2}$ . The stretch-stretch interactions gave smaller and smaller contributions

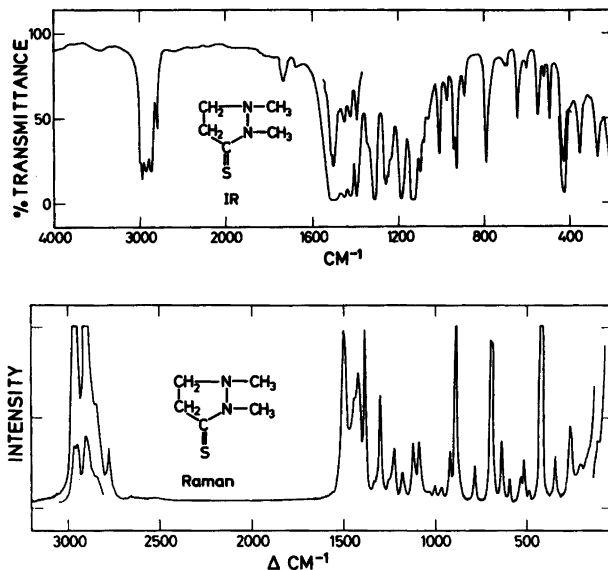


Fig. 2. The infrared spectrum (top) and the Raman spectrum (bottom) of 1,2-dimethyl-3-pyrazolidinethione (DMPT) in the liquid state.

to the PED as the calculations proceeded and were finally omitted. The stretch-bend interactions were very poorly determined and it proved necessary to introduce the drastic assumption that all interactions between single bonds and neighbouring bond angles were identical. The remaining force field listed in Table 1 was obtained by a conventional least squares refinement and converged rapidly to give a very good fit (below 0.76 % for each species of DMPT and prediction of most of the spectrum of DMPS within *ca.*  $10 \text{ cm}^{-1}$ ). Almost all force constants have physically reasonable values. The force constant for NN stretching found here ( $5.35 \text{ m dyn}/\text{\AA}$ ) is in agreement with that recently published for hydrazine<sup>1</sup> ( $5.60 \text{ m dyn}/\text{\AA}$ ). This supports our present assignment of the band near  $1340 \text{ cm}^{-1}$  having the highest NN stretching character (*cf.* Tables 2 and 3).

## RESULTS AND DISCUSSION

The IR and Raman survey spectra of DMPT recorded in the liquid phase are shown in Fig. 2. In Table 2 the available information of the vibrational spectra of DMPT is summarised. The band positions of the IR and Raman spectra are in most

cases almost coincident and only small changes are observed in the IR spectrum on dissolution in  $\text{CCl}_4$  or on solidification on cooling. The frequencies calculated for the 48 normal modes of DMPT are listed for comparison and an assignment of the spectra and approximate description of the fundamentals is given. Special care has been taken to list all but very small contributions from the NNCS group in order to locate vibrations originating in the thiohydrazide group. In Table 3, the best values (mean values in most instances) of the observed IR and Raman frequencies associated with the fundamental vibrations of the five isotopically substituted molecules are compared with the corresponding calculated frequencies. Also in this case the fundamentals are described with emphasis on contributions from the NNCS group. In analysing the spectra of DMPT and its deuterated derivatives valuable information was also obtained from the spectra of the hydrochlorides, the *S*-methyl iodides, the metal complexes (*e.g.*  $2 \text{ DMPT} \cdot \text{HgCl}_2$ ), and the corresponding selenium compound (DMPS), some of which will be treated separately in later papers.

*The region of CH and CD stretching vibrations.* A general feature of the IR spectra is the intensity differences between the stretching vibrations of

Table 2. Observed and calculated vibrational frequencies ( $\text{cm}^{-1}$ ) of 1,2-dimethylpyrazolidine-3-thione, tentative assignment of the spectra, and description of the fundamentals.<sup>a</sup>

Observed		Infrared liquid		CCl <sub>4</sub>	Raman liquid <sup>c</sup>	Calc. <sup>d</sup>	Assignment and description (PED, %) <sup>e</sup>
solid <sup>b</sup>	liquid	liquid					
2985m,sh	2985w,sh		2993w		2985s(0.5)	2988	$\nu_{\text{as}}\text{CH}_3(99)$
2961m	2962m		2965m		2967s(0.4)	2985	$\nu_{\text{as}}\text{CH}_3(99)$
	2930w,sh		2926w		2928m,sh	2972	$\nu_{\text{as}}\text{CH}_2(98)$
2915w	2920w		2916w,sh		2921s(0.2)	2967	$\nu_{\text{as}}\text{CH}_3(99)$
2852w	2860w		2860w		2867m(0.2)	2964	$\nu_{\text{as}}\text{CH}_3(99)$
2791w	2792w		2792w		2792m(0.3)	2958	$\nu_{\text{as}}\text{CH}_2(99)$
1500vs	1501vs		1493vs		1503s(0.5)	2930	$\nu_{\text{as}}\text{CH}_2(98)$
1460m,sh	1464w,sh		1466w,sh		1466m,sh	2929	$\nu_{\text{s}}\text{CH}_2(99)$
1449m	1451m		1454m		1450m,sh	2918	$\nu_{\text{s}}\text{CH}_2(99)$
			1448m		1450m,sh	2862	$2 \cdot \nu_{1,9}$
1440m			1435vw		1438w,sh	1498	$\nu_{1,1}\nu\text{C}^3\text{N}(53), \delta_{\text{as}}\text{CH}_3(27)$
1421m	1424m		1425m		1426s(0.6)	1464	$\nu_{1,2}\nu\text{C}^2\text{N}(13), \delta_{\text{as}}\text{CH}_3(54), \delta\text{CH}_2(21)$
	1416w,sh		1412m		1459	1459	$\delta_{\text{as}}\text{CH}_3(90)$
1389s	1391m		1391s		1455	1455	$\delta_{\text{as}}\text{CH}_3(99)$
1340w	1340w		1344w,sh		1395s(0.35)	1443	$\nu_{1,5}\nu\text{C}^3\text{N}(4), \delta_{\text{as}}\text{CH}_3(82)$
1313s,sh	1312m,sh		1313m,sh		1344vw(0.5)	1431	$\delta_{\text{as}}\text{CH}_3(14), \delta\text{CH}_2(71)$
1307s	1306s		1306s		1314m,sh(0.2)	1421	$\delta\text{CH}_2(75)$
1258m	1259m		1258m		1257w(0.4)	1415	$\delta_{\text{s}}\text{CH}_3(97)$
1249m	1248m		1247w		1245w,sh(0.6)	1391	$\nu_{1,8}\delta_{\text{s}}\text{C}^3\text{N}(5), \delta_{\text{s}}\text{CH}_3(95)$
1231m	1232w		1233w,sh		1232m(0.5)	1347	$\nu_{1,9}\nu\text{N}(33), \nu, \delta\text{ring}(61)$
1187s	1186s		1185m		1188m(0.5)	1317	$\nu_{2,1}\text{tCH}_2(46), \omega\text{CH}_2(26), \text{vring}(15)$
1176m,sh	1174m,sh		1174m,sh		1175w,sh	1309	$\omega\text{CH}_2(51), \text{tCH}_2(20), \text{vring}(23)$
1130vs	1131vs		1133s		1132m(0.3)	$\nu_{3,3} + \nu_{4,1}$	
	1118s,sh		1121m,sh(0.3)		1121m,sh(0.3)	$\nu_{3,5} + \nu_{3,7}$	
1094s	1095m		1096m(0.45)		1096m(0.45)	$\nu_{2,3}\nu\text{tCH}_2(35), \nu, \delta\text{ring}(45), \rho\text{CH}_3(25)$	
1076m	1076m		1076w,sh		1084m,sh	1233	$\text{tCH}_2(41), \omega\text{CH}_2(20), \rho\text{CH}_3(26)$
1059w	1059w		1060w,sh		1064w,sh	1196	$\text{vring}(40), \omega\text{tCH}_2(35), \rho\text{CH}_3(24)$
1045w,sh	1043vw,sh		1043vw,sh		1042w(0.5)	1168	$\rho\text{CH}_3(61), \text{vring}(22)$
						1137	$\nu_{3,6} + \nu_{3,8}$
						1100	$\nu_{2,7}\rho\text{CH}_3(95)$
						1088	$\nu_{2,8}\nu_{\text{as}}\text{NCS}(11), \rho\text{CH}_3(38), \delta/\text{vring}(33)$
						1060	$\nu_{2,9}\nu\text{CC}(46), \rho\text{CH}_2(27)$
						1046	$\nu_{3,0}\nu_{\text{as}}\text{NCS}(7), \rho\text{CH}_3(29), \text{vring}(48)$

Table 2. Continued.

1006m	1005m	1007w(0.6)	996	$\nu_{31}$	$\rho\text{CH}_2(67), \nu\text{CC}(15)$
970w	971w	974w(0.5)		$2 \cdot \nu_{38}$	
942m	939m	939w	949	$\nu_{32}$	$\nu\text{NN}(8), \rho\text{CH}_2(43), \text{vring}(25)$
928m	926m	926m(0.3)	904	$\nu_{38} + \nu_{39}$	
893m	891w	893s(0.35)	800	$\nu_{33}$	$\nu\text{NN}(14), \nu\text{CS}(7), \text{vring}(30), \rho\text{CH}_2$
789m	786m	787m(0.45)		$\nu_{34}$	$\nu\text{CS}(31), \nu\text{NN}(6), \nu/\delta\text{ring}(76)$
702vw	702w	703s(0.2)		$2 \cdot \nu_{42}$	
690w	689w	693s(0.2)	691	$\nu_{35}$	$\nu\text{C}^3\text{N}(10), \text{vring}(33), \delta\text{ring}(42)$
640m	639m	641m(0.2)	638	$\nu_{36}$	$\nu\text{NN}(13), \text{vring}(58), \delta\text{ring}(43)$
598mw	596w	598w(0.8)		$\nu_{39} + \nu_{45}$	
548m	544m	544w,sh	553	$\nu_{37}$	$\Delta\text{CH}_3 - \text{N} < \zeta(53), \text{vring}(24)$
537m	536m,sh	538w(0.4)		$2 \cdot \nu_{43}$	
522w	518w	521m(0.3)		$\nu_{42} + \nu_{45}$	
491m	488m	491w(0.5)	490	$\nu_{38}$	$\Delta\text{CS}(28), \Delta\text{CH}_3 - \text{N} < \zeta(29), \text{vring}(18)$
448m,sh	452w,sh	450vw,sh		$\nu_{42} + \nu_{46}$	
430vs	431s,sh	434m,sh(0.4)	429	$\nu_{39}$	$\nu\text{CS}(32), \nu\text{NN}(13), \Delta\text{CS}(4), \delta\text{ring}(36)$
422vs	422s	424s(0.3)	421	$\nu_{40}$	$\Delta\text{CS}(44), \Delta\text{CH}_3 - \text{N} < \zeta(37), \text{vring}(21)$
376vw	375vw	370vw,sh	378	$\nu_{41}$	$\nu/\delta\text{ring}(53), \rho\text{CH}_2(44)$
350m	349m	350m(0.3)	338	$\nu_{42}$	$\delta\text{CH}_3 - \text{N} < \zeta(\text{CH}_3' - \text{N} < (47), \nu/\delta\text{ring}(65)$
270m	267m	268m(0.65)	268	$\nu_{43}$	$\delta\text{CS}(63), \delta\text{CH}_3' - \text{N} < (18)$
216m	214m,sh	212w(0.5)		$\nu_{46} + \nu_{47}$	
206m,sh	202m	203w,sh	202	$\nu_{44}$	$\tau\text{CH}_3'(68)$
		170vw	171	$\nu_{45}$	$\tau\text{CH}_3(92)$
		118w(0.5)	118	$\nu_{46}$	$\delta\text{ring}(91)$
			67	$\nu_{47}$	$\delta\text{ring}(98)$
			22	$\nu_{48}$	$\delta\text{ring}(101)$

<sup>a</sup> The following abbreviations have been used: s, strong; m, medium; w, weak; br, broad; sh, shoulder. Weak and very weak bands not assigned to fundamentals have been omitted from the Table. <sup>b</sup> At liquid N<sub>2</sub>-temperature, annealed at -90 °C. <sup>c</sup> The depolarisation ratio is given in parenthesis ( $\rho = 0.75$  corresponds to a fully depolarised band). <sup>d</sup> Iteration based upon all isotopic species. <sup>e</sup> Abbreviations:  $\nu$  = stretch;  $\delta$  = deformation;  $\Delta$  = out-of-plane deformation;  $\rho$  = rock;  $\omega$  = wag;  $t$  = twist;  $\tau$  = torsion;  $s$  = symmetric;  $as$  = antisymmetric. Vibrations of the pyrazolidine ring and the attached heavy atoms are designated 'ring' or using the following nomenclature: N<sup>1</sup>-CH<sub>3</sub>, N<sup>2</sup>-CH<sub>3</sub>, C<sup>3</sup>S. The potential energy distribution (PED,  $x_{ik} = 100F_{ik}^2/\lambda_i$ ) is stated only for significant contributions. The PED referring to the thiohydrazide group is underlined.

Table 3. Observed and calculated fundamentals ( $\text{cm}^{-1}$ ) for isotopically substituted DMPT compounds with approximate description of the fundamentals.<sup>a</sup>

No.	DMPT-1- $d_3$		DMPT-2- $d_3$		DMPT-4- $d_6$		DMPT- $d_{10}$	
	obs. <sup>b</sup>	calc. description <sup>c</sup>	obs. <sup>b</sup>	calc. description <sup>c</sup>	obs. <sup>b</sup>	calc. description <sup>c</sup>	obs. <sup>b</sup>	calc. description <sup>c</sup>
1	2981	2972 $\nu_{\text{as}}\text{CH}_2$	2985	2988 $\nu_{\text{as}}\text{CH}_3$	2981	2972 $\nu_{\text{as}}\text{CH}_2$	2989	2988 $\nu_{\text{as}}\text{CH}_3$
2	2967	2967 $\nu_{\text{as}}\text{CH}_3$	2985	2985 $\nu_{\text{as}}\text{CH}_3$	2954	2959 $\nu_{\text{as}}\text{CH}_2$	2989	2985 $\nu_{\text{as}}\text{CH}_3$
3	2963	2964 $\nu_{\text{as}}\text{CH}_3$	2985	2972 $\nu_{\text{as}}\text{CH}_2$	2928	2930 $\nu_{\text{as}}\text{CH}_2$	2965	2967 $\nu_{\text{as}}\text{CH}_3$
4	2963	2958 $\nu_{\text{as}}\text{CH}_2$	2966	2959 $\nu_{\text{as}}\text{CH}_2$	2916	2918 $\nu_{\text{as}}\text{CH}_2$	2965	2964 $\nu_{\text{as}}\text{CH}_3$
5	2932	2930 $\nu_{\text{as}}\text{CH}_2$	2925	2930 $\nu_{\text{as}}\text{CH}_2$	2243	2238 $\nu_{\text{as}}\text{CD}_3$	2928	2929 $\nu_{\text{as}}\text{CH}_3$
6	2924	2929 $\nu_{\text{as}}\text{CH}_3$	2915	2918 $\nu_{\text{as}}\text{CH}_2$	2214	2231 $\nu_{\text{as}}\text{CD}_3$	2868	2862 $\nu_{\text{as}}\text{CH}_3$
7	2924	2918 $\nu_{\text{as}}\text{CH}_3$	2861	2862 $\nu_{\text{as}}\text{CH}_3$	2232	2220 $\nu_{\text{as}}\text{CD}_3$	2237	2220 $\nu_{\text{as}}\text{CD}_2$
8	2246	2238 $\nu_{\text{as}}\text{CD}_3$	2232	2220 $\nu_{\text{as}}\text{CD}_3$	2112	2211 $\nu_{\text{as}}\text{CD}_3$	2196	2200 $\nu_{\text{as}}\text{CD}_2$
9	2214	2231 $\nu_{\text{as}}\text{CD}_3$	2113	2211 $\nu_{\text{as}}\text{CD}_3$	2111	2111 $\nu_{\text{as}}\text{CD}_3$	2157	2158 $\nu_{\text{as}}\text{CD}_2$
10	2056	2062 $\nu_{\text{as}}\text{CD}_3$	2059	2062 $\nu_{\text{as}}\text{CD}_3$	2059	2062 $\nu_{\text{as}}\text{CD}_3$	2137	2136 $\nu_{\text{as}}\text{CD}_2$
11	1505	1497 $\nu_{\text{C}^3}\text{N}(53)$ , $\delta_{\text{as}}\text{CH}_3$	1476	1480 $\nu_{\text{C}^3}\text{N}(73)$	1474	1478 $\nu_{\text{C}^3}\text{N}(78)$	1500	1495 $\nu_{\text{C}^3}\text{N}(55)$ , $\delta_{\text{as}}\text{CH}_3$
12	1467	1464 $\nu_{\text{C}^3}\text{N}(14)$ , $\delta_{\text{as}}\text{CH}_3$	1455	1458 $\delta_{\text{as}}\text{CH}_3$	1438	1438 $\delta\text{CH}_2$	1459	1458 $\delta_{\text{as}}\text{CH}_3$
13	1448	1443 $\nu_{\text{C}^3}\text{N}(5)$ , $\delta_{\text{as}}\text{CH}_3$	1455	1455 $\delta_{\text{as}}\text{CH}_3$	1425	1425 $\delta\text{CH}_2$	1459	1455 $\delta_{\text{as}}\text{CH}_3$
14	1425	1430 $\delta\text{CH}_2$	1437	1438 $\delta\text{CH}_2$	1341	1338 $\nu_{\text{N}}(47)$ , $\nu/\delta\text{ring}$	1451	1450 $\nu_{\text{C}^3}\text{N}(6)$ , $\delta_{\text{as}}\text{CH}_3$
15	1419	1422 $\delta\text{CH}_2$	1424	1424 $\delta\text{CH}_2$	1327	1323 $\text{tCH}_2$	1434	1440 $\nu_{\text{C}^3}\text{N}(11)$ , $\delta_{\text{as}}\text{CH}_3$
16	1393	1392 $\nu_{\text{C}^3}\text{N}(5)$ , $\delta_{\text{as}}\text{CH}_3$	1412	1414 $\delta_{\text{as}}\text{CH}_3$	1308	1303 $\omega\text{CH}_3$ , $\nu\text{ring}$	1415	1414 $\delta_{\text{as}}\text{CH}_3$
17	1344	1346 $\nu_{\text{N}}(32)$ , $\nu/\delta\text{ring}$	1342	1343 $\nu_{\text{N}}(44)$ , $\nu/\delta\text{ring}$	1211	1211 $\nu_{\text{N}}\text{NCS}(7)$ , $\omega/\text{tCH}_2$	1392	1391 $\nu_{\text{C}^3}\text{N}(6)$ , $\delta_{\text{as}}\text{CH}_3$
18	1311	1315 $\omega/\text{tCH}_2$	1324	1223 $\text{tCH}_2$	1173	1172 $\nu_{\text{N}}\text{NCS}(8)$ , $\text{tCH}_2$	1345	1352 $\nu_{\text{N}}\text{NCS}(33)$ , $\nu/\delta\text{ring}$
19	1304	1304 $\omega/\text{tCH}_2$ , $\nu\text{ring}$	1309	1306 $\omega/\text{tCH}_3$ , $\nu/\delta\text{ring}$	1127	1132 $\nu_{\text{N}}\text{NCS}(8)$ , $\text{tCH}_2$	1283	1293 $\nu_{\text{N}}\text{NCS}(12)$ , $\nu\text{ring}$
20	1223	1216 $\omega/\text{tCH}_3$ , $\nu/\delta\text{ring}$	1227	1227 $\rho\text{CH}_3$ , $\nu/\delta\text{ring}$	1091	1091 $\delta\text{CD}_3/\text{CD}_3$ , $\nu\text{ring}$	1200	1204 $\rho\text{CH}_3$ , $\nu/\delta\text{ring}$
21	1170	1172 $\omega/\text{tCH}_2$ , $\nu/\delta\text{ring}$	1188	1196 $\rho\text{CH}_3$ , $\text{tCH}_2$	1071	1070 $\delta\text{CD}_3$ , $\nu\text{ring}$	1182	1176 $\rho\text{CH}_3$ , $\nu/\delta\text{ring}$
22	1132	1137 $\nu\text{CS}(5)$ , $\nu/\delta\text{ring}$	1174	1171 $\nu_{\text{N}}\text{NCS}(7)$ , $\nu\text{ring}$ , $\rho\text{CH}_3$ , $\text{tCH}_2$	1050	1056 $\nu_{\text{N}}\text{NCS}(6)$ , $\delta\text{CD}_3$ , $\nu\text{ring}$ , $\nu/\rho\text{CH}_3$	1141	1149 $\rho\text{CH}_3$ , $\nu\text{ring}$
23	1114	1100 $\rho\text{CH}_3$	1132	1139 $\rho\text{CH}_3$ , $\nu\text{ring}$	1047	1042 $\delta\text{CD}_3/\text{CD}_3$	1097	1103 $\rho\text{CH}_3$ , $\nu\text{ring}$
24	1092	1088 $\delta\text{CD}_3$ , $\nu\text{ring}$	1079	1077 $\delta\text{CD}_3$ , $\nu\text{ring}$	1034	1038 $\delta\text{CD}_3$	1095	1098 $\rho\text{CH}_3$ , $\nu\text{ring}$
25	1066	1060 $\nu\text{CS}(11)$ , $\nu\text{ring}$ , $\rho\text{CH}_3/\rho\text{CH}_2$	1058	1062 $\rho\text{CH}_3$ , $\nu\text{ring}$	1034	1036 $\delta\text{CD}_3/\text{CD}_3$	1071	1073 $\nu_{\text{N}}\text{NCS}(18)$ , $\rho\text{CH}_3$
26	1055	1051 $\nu\text{ring}$ , $\rho\text{CH}_3$ , $\delta\text{CD}_3$	1052	1055 $\delta\text{CD}_3$ , $\rho\text{CH}_3$ , $\nu\text{ring}$	1034	1033 $\delta\text{CD}_3$	1042	1043 $\nu\text{CS}(5)$ , $\delta\text{CD}_2$
27	1044	1042 $\delta\text{CD}_3$	1040	1036 $\delta\text{CD}_3$	1001	1006 $\rho\text{CH}_3$ , $\nu/\delta\text{ring}$	1023	1011 $\delta\text{CD}_2$ , $\nu/\delta\text{ring}$
28	1032	1039 $\delta\text{CD}_3$	1034	1033 $\delta\text{CD}_3$	985	986 $\rho\text{CH}_2/\text{CD}_3$ , $\nu\text{ring}$	995	996 $\delta/\omega/\text{tCD}_2$
29	1025	1014 $\nu_{\text{N}}\text{N}(7)$ , $\delta\text{CD}_3$ , $\nu/\delta\text{ring}$	982	994 $\rho\text{CH}_2$ , $\nu\text{ring}$	963	960 $\rho\text{CH}_2/\text{CD}_3$ , $\nu\text{ring}$	925	923 $\nu_{\text{N}}\text{N}(11)$ , $\nu\text{ring}$ , $\text{tCD}_2$
30	1003	995 $\rho\text{CH}_2$ , $\nu\text{ring}$	932	941 $\rho\text{CH}_2$ , $\nu\text{ring}$	907	901 $\nu_{\text{CS}}(27)$ , $\rho\text{CD}_3$ , $\nu\text{ring}$	902	900 $\nu_{\text{N}}\text{N}(9)$ , $\nu\text{CS}(6)$ , $\nu/\delta\text{ring}$ , $\omega/\text{tCD}_2$
31	961	963 $\rho\text{CH}_2/\text{CD}_3$	920	914 $\nu_{\text{CS}}(28)$ , $\nu_{\text{N}}\text{N}(7)$ , $\nu\text{ring}$ , $\rho\text{CD}_3$	886	884 $\rho\text{CH}_2/\text{CD}_3$	823	823 $\omega/\text{tCD}_2$ , $\nu\text{ring}$
32	899	885 $\rho\text{CH}_2/\text{CD}_3$	883	879 $\rho\text{CD}_3$ , $\nu/\text{ring}$	863	856 $\rho\text{CD}_3$	807	804 $\nu_{\text{CS}}(20)$ , $\nu_{\text{N}}\text{N}(5)$ , $\rho\text{CD}_2$ , $\nu/\delta\text{ring}$
33	833	832 $\nu_{\text{CS}}(25)$ , $\nu_{\text{N}}\text{N}(17)$ , $\rho\text{CD}_3$ , $\nu/\delta\text{ring}$	838	858 $\rho\text{CD}_3$	806	801 $\nu_{\text{N}}\text{N}(12)$ , $\nu\text{ring}$ , $\rho\text{CD}_3/\text{CD}_3$	772	764 $\nu_{\text{CS}}(10)$ , $\rho\text{CD}_2$
34	760	768 $\nu_{\text{CS}}(12)$ , $\nu_{\text{C}^3}\text{N}(6)$ , $\nu/\delta\text{ring}$ , $\rho\text{CD}_3$	757	757 $\nu_{\text{N}}\text{NCS}(30)$ , $\rho\text{CD}_3$ , $\nu/\delta\text{ring}$	743	748 $\nu_{\text{N}}\text{NCS}(24)$ , $\rho\text{CD}_3$ , $\nu/\delta\text{ring}$	733	726 $\rho\text{CD}_3$ , $\nu/\delta\text{ring}$
							695	699 $\nu_{\text{CS}}(7)$ , $\nu/\delta\text{ring}$ , $\rho\text{CD}_2/\text{CD}_3$
							800	795 $\nu_{\text{N}}\text{N}(13)$ , $\nu_{\text{CS}}(4)$ , $\rho\text{CD}_3/\text{CD}_3$ , $\nu\text{ring}$
							858	858 $\rho\text{CD}_3$
							811	822 $\omega/\text{tCD}_2$
							933	935 $\rho\text{CD}_3$ , $\text{tCD}_2$
							920	915 $\nu_{\text{CS}}(12)$ , $\rho\text{CD}_3/\text{CD}_3$
							885	885 $\nu_{\text{CS}}(16)$ , $\rho\text{CD}_3$ , $\text{tCD}_2$
							1017	1026 $\delta\text{CD}_3/\text{CD}_3/\text{CD}_2$
							996	992 $\delta/\omega/\text{tCD}_2$
							974	975 $\nu/\delta\text{ring}$ , $\delta\text{CD}_2$



35	688	675	$\nu\text{NCS}(12), \nu/\delta\text{ring}$	669	666	$\nu\text{NCS}(9), \nu/\delta\text{ring}$	656	649	$\nu\text{NCS}(12), \nu/\delta\text{ring}$	638	654	$\nu\text{C}^3\text{N}(10), \rho\text{CD}_3, \nu/\delta\text{ring}$	610	624	$\nu\text{C}^3\text{N}(8), \nu/\delta\text{ring}$
36	625	614	$\nu\text{NN}(12), \rho\text{CD}_3, \nu/\delta\text{ring}$	614	619	$\nu\text{NN}(11), \nu/\delta\text{ring}$	604	593	$\nu\text{NN}(11), \rho\text{CD}_3, \nu/\delta\text{ring}$	616	602	$\nu\text{NN}(11), \nu/\delta\text{ring}$	572	570	$\nu\text{NN}(11), \nu/\delta\text{ring}$
37	519	518	$\Delta/\delta\text{CD}_3 - \text{N} < \text{N}(\delta(40)), \nu/\delta\text{ring}$	532	546	$\Delta\text{CH}_3 - \text{N} < \text{N}(\delta(54)), \nu/\delta\text{ring}$	506	513	$\Delta/\delta\text{CD}_3 - \text{N} < \text{N}(\delta(36)), \nu/\delta\text{ring}$	522	513	$\delta/\Delta\text{CH}_3 - \text{N} < \text{N}(\delta(34)), \nu/\delta\text{ring}$	502	478	$\delta/\Delta\text{CD}_3 - \text{N} < \text{N}(\delta(29)), \nu/\delta\text{ring}$
38	485	480	$\Delta\text{CS}(38), \nu/\delta\text{ring}$	487	484	$\Delta\text{CS}(29), \nu/\delta\text{ring}$	480	475	$\Delta\text{CS}(37), \nu/\delta\text{ring}$	446	454	$\Delta\text{CS}(31), \nu/\delta\text{ring}$	439	437	$\Delta\text{CS}(31), \nu/\delta\text{ring}$
39	422	418	$\nu\text{CS}(30), \nu\text{NN}(10), \nu/\delta\text{ring}$	426	427	$\nu\text{CS}(33), \nu\text{NN}(12), \nu/\delta\text{ring}$	409	417	$\nu\text{CS}(30), \nu\text{NN}(9), \nu/\delta\text{ring}$	418	419	$\Delta\text{CH}_3 - \text{N} < \text{N}(\delta(24)), \nu/\delta\text{ring}$	398	405	$\Delta\text{CD}_3 - \text{N} < \text{N}(\delta(16)), \nu/\delta\text{ring}$
40	406	408	$\Delta\text{CS}(33), \nu/\delta\text{ring}$	419	418	$\Delta\text{CS}(6), \nu/\delta\text{ring}$	401	405	$\Delta\text{CS}(8), \nu/\delta\text{ring}$	398	402	$\Delta\text{CS}(2), \nu/\delta\text{ring}$	382	389	$\Delta\text{CS}(6), \nu/\delta\text{ring}$
41	374	371	$\nu/\delta\text{ring}, \rho\text{CH}_2, \nu/\delta\text{ring}$	370	369	$\Delta\text{CH}_3 - \text{N} < \text{N}(\delta(39)), \nu/\delta\text{ring}$	370	365	$\nu/\delta\text{ring}, \rho\text{CH}_2, \nu/\delta\text{ring}$	340	344	$\Delta\text{CH}_3 - \text{N} < \text{N}(\delta(25)), \nu/\delta\text{ring}$	312	312	$\Delta\text{CD}_3 - \text{N} < \text{N}(\delta(41)), \nu/\delta\text{ring}$
42	331	329	$\delta\text{CD}_3 - \text{N} < \text{N}(\delta(49)), \nu/\delta\text{ring}$	331	320	$\delta\text{CD}_3 - \text{N} < \text{N}(\delta(39)), \nu/\delta\text{ring}$	305	308	$\delta\text{CD}_3 - \text{N} < \text{N}(\delta(50)), \nu/\delta\text{ring}$	292	292	$\delta\text{CD}_3 - \text{N} < \text{N}(\delta(25)), \nu/\delta\text{ring}$	285	282	$\delta\text{CD}_3 - \text{N} < \text{N}(\delta(41)), \nu/\delta\text{ring}$
43	267	265	$\delta\text{CS}(63), \delta\text{CH}_3 - \text{N} < \text{N}(\delta(49)), \nu/\delta\text{ring}$	250	256	$\delta\text{CS}(58), \delta\text{CD}_3 - \text{N} < \text{N}(\delta(39)), \nu/\delta\text{ring}$	250	255	$\delta\text{CS}(59), \delta\text{CD}_3 - \text{N} < \text{N}(\delta(39)), \nu/\delta\text{ring}$	264	260	$\delta\text{CS}(55), \delta\text{CH}_3 - \text{N} < \text{N}(\delta(39)), \nu/\delta\text{ring}$	250	250	$\delta\text{CS}(57), \delta\text{CD}_3 - \text{N} < \text{N}(\delta(39)), \nu/\delta\text{ring}$
44	201	201	$\tau\text{CH}_3, \delta\text{ring}$	170	171	$\tau\text{CH}_3, \delta\text{ring}$	155	157	$\tau\text{CD}_3, \delta\text{ring}$	202	195	$\tau\text{CH}_3, \delta\text{ring}$	155	152	$\tau\text{CD}_3, \delta\text{ring}$
45	132	132	$\tau\text{CD}_3, \delta\text{ring}$	155	158	$\tau\text{CD}_3, \delta\text{ring}$	130	131	$\tau\text{CD}_3, \delta\text{ring}$	168	169	$\tau\text{CH}_3, \delta\text{ring}$	123	124	$\tau\text{CD}_3, \delta\text{ring}$
46	110	109	$\tau\text{CD}_3, \delta\text{ring}$	115	115	$\delta\text{ring}$	107	106	$\delta\text{ring}$	104	102	$\delta\text{ring}$	95	96	$\delta\text{ring}$
47	65	65	$\delta\text{ring}$	60	60	$\delta\text{ring}$	59	59	$\delta\text{ring}$	66	66	$\delta\text{ring}$	61	58	$\delta\text{ring}$
48	21	21	$\delta\text{ring}$	21	21	$\delta\text{ring}$	20	20	$\delta\text{ring}$	21	21	$\delta\text{ring}$	20	20	$\delta\text{ring}$

<sup>a</sup> See a, Table 2. <sup>b</sup> Best value from IR and Raman spectra. <sup>c</sup> See e, Table 2.

of  $\text{N}^1\text{-CH}_3/\text{CD}_3$  (strongest),  $\text{CH}_2/\text{CD}_2$  (medium strong) and  $\text{N}^2\text{-CH}_3'/\text{CD}_3'$  (weak). A positive identification of the latter bands would not have been possible if the spectra of the deuterated compounds DMPT-1- $d_3$  and DMPT-2- $d_3$  had not been available. Similar intensity variations are observed in the Raman spectra, but since these are in general characterised by much larger intensity variations the feature is much less conspicuous here. The typical frequencies for the vibrations are the following ( $\text{cm}^{-1}$ ):  $\nu_{\text{as}}\text{CH}_3$  2985;  $\nu_{\text{as}}\text{CH}_3'$  2965;  $\nu_{\text{as}}\text{CH}_2$  2985+2965;  $\nu_{\text{s}}\text{CH}_3$  2860;  $\nu_{\text{s}}\text{CH}_3'$  2930;  $\nu_{\text{s}}\text{CH}_2$  2920-30. The corresponding deuterated groups absorb as follows ( $\text{cm}^{-1}$ ):  $\nu_{\text{as}}\text{CD}_3$  2245+2215;  $\nu_{\text{as}}\text{CD}_3'$  2235+2215;  $\nu_{\text{as}}\text{CD}_2$  2235+2195;  $\nu_{\text{s}}\text{CD}_3$  2055;  $\nu_{\text{s}}\text{CD}_3'$  2110;  $\nu_{\text{s}}\text{CD}_2$  2135+2155. From the results listed in Tables 2 and 3 it appears that many of the bands are coincident as expected from the typical ranges stated. Furthermore, this region is complicated by the appearance of overtones and combination modes of the deformation fundamentals (several weak bands have been omitted from Table 2).

The fundamental  $\nu_{11}$  near  $1500\text{ cm}^{-1}$  in DMPT. In the IR spectra of DMPT and its deuterated derivatives this band occurs strong and broad, usually as the strongest band in the spectrum. In the Raman spectra it is less prominent (*cf.* Fig. 2) but nevertheless easy to identify. The PED indicates that in the spectra of DMPT, DMPT-1- $d_3$  and DMPT- $d_4$  the band originates primarily in  $\text{C}^3\text{N}$  stretching (*ca.* 50%) coupled to deformation of the adjacent  $\text{CH}_3'$  group (*ca.* 25%). An alternative representation can be obtained from the form of the normal mode estimated from the elements of the  $L$ -matrix. Apart from deformation of the  $\text{CH}_3'$  group the normal mode is characterised entirely by displacements of the  $\text{C}^3\text{N} < \text{N} < \text{N}^1$  group. This thiohydrazide group vibration can be described as a stretching of the central  $\text{C}-\text{N}$  bond followed by a shortening of the four other bonds and an opening of the opposite  $\text{CCS}$  and  $\text{NNC}'$  angles. The strong tendency for this vibration to couple with  $\delta_{\text{as}}\text{CH}_3'$  and  $\delta_{\text{s}}\text{CH}_3'$  is also apparent from the contributions to the fundamentals in the  $1435-1470\text{ cm}^{-1}$  and  $1390\text{ cm}^{-1}$  regions of DMPT, DMPT-1- $d_3$ , and DMPT- $d_4$  predominantly of this origin. If the  $\text{CH}_3'$  group is deuterated (DMPT-2- $d_3$ , DMPT- $d_6$ , and DMPT- $d_{10}$ ), the fundamental  $\nu_{11}$  is displaced to the region  $1470-1475\text{ cm}^{-1}$  following removal of the contribution from methyl deformation. As expected, in these cases the NCA indicates a sole

origin of this fundamental in the same thiohydrazide vibration as before. The characteristic shift of this band towards higher frequencies on *e.g.* *S*-methylation or metal complex formation ('B band'<sup>28</sup>) will be discussed in a later paper.

*Internal deformational modes of CH<sub>3</sub>/CH<sub>2</sub> and CD<sub>3</sub>/CD<sub>2</sub> groups.* The bands due to  $\delta\text{CH}_3$ ,  $\delta\text{CH}'_3$ , and  $\delta\text{CH}_2$  are superimposed in the region 1390–1470  $\text{cm}^{-1}$ , but a study of the deuterated DMPT isomers has disclosed the position of the 'pure' bands as follows (*cf.* Tables 2 and 3, approximate values in  $\text{cm}^{-1}$ ):  $\delta_{\text{as}}\text{CH}_3$  1455;  $\delta_{\text{as}}\text{CH}'_3$  1435–1460;  $\delta_{\text{s}}\text{CH}_3$  1415;  $\delta_{\text{s}}\text{CH}'_3$  1390;  $\delta\text{CH}_2$  1420–1440. The corresponding vibrations of the deuterated groups fall in the range 1015–1090  $\text{cm}^{-1}$  with the following typical frequencies ( $\text{cm}^{-1}$ ):  $\delta_{\text{as}}\text{CD}_3$  1040;  $\delta_{\text{as}}\text{CD}'_3$  1035;  $\delta_{\text{s}}\text{CD}_3$  1090;  $\delta_{\text{s}}\text{CD}'_3$  1050–1080;  $\delta\text{CD}_2$  1020–1045. However, strong mutual coupling is often observed between  $\delta\text{CH}_3$ ,  $\delta\text{CH}'_3$  and  $\delta\text{CH}_2$ , and the deuterated compounds show additional coupling to skeletal stretching modes. These facts strongly restrict the diagnostic use of these bands, which may otherwise be strong with a characteristic appearance. The vibrations due to  $\omega\text{CH}_2$  and  $\text{tCH}_2$  couple to a high degree, and are typically observed as two bands in the 1300–1330  $\text{cm}^{-1}$  range and two bands between 1170 and 1235  $\text{cm}^{-1}$ . The rocking modes are in most cases found as follows ( $\text{cm}^{-1}$ ):  $\rho\text{CH}_3$  1130–1235;  $\rho\text{CH}'_3$  1040–1115;  $\rho\text{CH}_2$  940–1010.

*Vibrations of the thiohydrazide group.* In the IR and Raman spectra of DMPT a weak to very weak band is observed near 1340  $\text{cm}^{-1}$  which is easy to overlook and would certainly not be expected to originate in the thiohydrazide group. However, the band is observed with almost unchanged position and intensity in all the deuterated derivatives of DMPT. Furthermore, on conversion of DMPT to the hydrochloride by protonisation of the basic  $\text{N}^1$  atom the intensity of the band rises sharply and it becomes one of the strongest bands in the IR spectrum. This effect is also observed on conversion of *e.g.* DMPT-*d*<sub>10</sub> to the hydrochloride.

No other fundamentals occur in the range 1300–1400  $\text{cm}^{-1}$  in this compound (*cf.* Table 3) and since the band is almost unchanged on *N*-deuteration of the hydrochloride, errors in the assignment appear to be excluded. In DMPT the NCA indicates that in addition to a small contribution from internal deformations of the  $\text{CH}_3$  group, the main component (94 % by PED) arises from a vibration of the  $\text{C}_s^>\text{C}-\text{N}<\text{N}^<$  grouping, as

is the case for  $\nu_{11}$ . The thiohydrazide group vibration in this case occurs mainly at right angles to the central C–N bond and consists of asymmetric stretching of the CCS and NNC' groups coupled to asymmetric deformation (increase of the angles CCN and CNN simultaneously with a decrease of the angles SCN and CNC'). According to the PED the band is best characterised as NN stretching (33 %) or  $\nu_{\text{as}}\text{NNC}'$  (51 %). The composition of the band is almost unchanged on deuteration, except that the contributions from the  $\text{CH}_3$  group are removed.

From Tables 2 and 3 it can be seen that several other bands in the region between 1000 and 1300  $\text{cm}^{-1}$  have small contributions from the stretching vibrations of the thiohydrazide group. The fundamentals situated in the range 500–1000  $\text{cm}^{-1}$  also share a considerable amount of thiohydrazide stretching character (30–40 %  $\nu\text{CS}$ , 10–20 %  $\nu\text{C}^3\text{N}$ , 15–30 %  $\nu\text{NN}$ ). The two most prominent bands of this type are  $\nu_{33}$  at 893  $\text{cm}^{-1}$  and  $\nu_{34}$  at 787–789  $\text{cm}^{-1}$  in the solid state Raman and IR spectra. In the corresponding deuterated DMPT compounds, however, the PED between  $\nu\text{CS}$ ,  $\nu\text{NN}$ , and  $\nu\text{C}^3\text{N}$  vary in a quite irregular way and the position is strongly influenced by coupling to other vibrations. On conversion of DMPT to the methiodide or mercury(II) chloride complex, or by selenation, both bands apparently show a shift by 10–20  $\text{cm}^{-1}$  towards lower frequencies. Again, NCA's on the three latter compounds (to be published) indicate that the PED's between the thiohydrazide stretching vibrations are subject to considerable changes. Therefore, we conclude that the contributions of  $\nu\text{CS}$ ,  $\nu\text{NN}$  and  $\nu\text{C}^3\text{N}$  vibrations to bands in this region are very variable, *i.e.* that characteristic thiohydrazide bands do not occur here.

In the low-frequency region we expect the CS stretching ( $\nu\text{CS}$ ), the in-plane bending ( $\delta\text{CS}$ ), and the out-of-plane bending ( $\Delta\text{CS}$ ) vibrations. These bands have only been identified with reasonable certainty in a few other compounds containing the thioamide group. In the spectra of *N,N*-dimethylthioformamide,<sup>29</sup> its metal complex compounds<sup>30</sup> and *N,N*-dimethylselenoformamide,<sup>31</sup> we expect  $\Delta\text{CS}$  at 500–600  $\text{cm}^{-1}$ ,  $\nu\text{CS}$  in the range 400–525  $\text{cm}^{-1}$ , and  $\delta\text{CS}$  near 225  $\text{cm}^{-1}$ . Thioacetamide is also fairly well investigated by isotopic substitution,<sup>32</sup> complex formation<sup>33</sup> and by selenation.<sup>34</sup> The  $\Delta\text{CS}$  vibration is found near 515  $\text{cm}^{-1}$ , weak in the infrared but of medium intensity in the

Raman spectrum; it is almost unchanged in frequency by complex formation but shifted by  $30\text{ cm}^{-1}$  towards lower frequencies on selenation. A strong IR and Raman band near  $470\text{ cm}^{-1}$ , also unaffected by complex formation but shifted to  $ca. 400\text{ cm}^{-1}$  on selenation, arises mainly from  $\delta\text{CS}$ . These vibrations are often highly coupled and only suggest the appropriate ranges for the similar bands in DMPT. The  $\Delta\text{CS}$  vibration, for example, may be subject to great variations, and has been assigned to the range  $100\text{--}200\text{ cm}^{-1}$  in thiovalerolactam.<sup>35</sup> In some instances it may even shift towards higher frequencies on selenation, *e.g.* from thiourea ( $\Delta\text{CS} = 410\text{ cm}^{-1}$ ) to selenourea ( $\Delta\text{CSe} = 475\text{ cm}^{-1}$ ).<sup>36</sup> In a recent<sup>37</sup> survey for five-membered heterocyclic compounds, the ranges  $\Delta\text{CS}$   $200\text{--}500\text{ cm}^{-1}$ ,  $\delta\text{CS}$   $250\text{--}350\text{ cm}^{-1}$ , and  $\nu\text{CS}$   $450\text{--}520\text{ cm}^{-1}$  seem typical. However, in six-membered rings<sup>38</sup>  $\delta\text{CS}$  has been assigned to bands in the  $450\text{--}500\text{ cm}^{-1}$  range. It is therefore of utmost importance for assigning these bands in DMPT to have some independent evidence of their origin.

Inspection of the low-frequency region of DMPT revealed, that the band of medium strength in both Raman and IR near  $350\text{ cm}^{-1}$  was almost unaffected by deuteration of the methylene groups, but displayed a downward shift on deuteration of both the  $\text{N}^1\text{-CH}_3$  and  $\text{N}^2\text{-CH}_3$  groups. Since it occurred also in the spectrum of DMPS, the band was assigned in accordance with the NCA's to deformation of the methyl groups approximately in the plane of the ring coupled to stretching and deformation of the ring. The corresponding  $\text{N}^1\text{-CH}_3$  out-of-plane deformation vibration is the main component of  $\nu_{37}$ , which is found with the Fermi enhanced overtone  $2 \cdot \nu_{43}$  and a combination mode (probably  $\nu_{42} + \nu_{45}$ ) as three bands in the range  $510\text{--}550\text{ cm}^{-1}$  of opposite intensities in the IR and Raman spectra. This fundamental is also observed in the same range in DMPS.

This leaves four bands in the region  $200\text{--}500\text{ cm}^{-1}$  (at *ca.*  $270, 420, 430,$  and  $490\text{ cm}^{-1}$ ) to be assigned to the CS stretching and deformation modes. The in-plane  $\delta\text{CS}$  vibration was now identified with the medium intensity band near  $270\text{ cm}^{-1}$  in both the IR and Raman spectra by the following distinguishing features. (i) According to the NCA it should be weakly coupled to the in-plane deformation vibration of the neighbouring  $\text{N}^2\text{-CH}_3$  group. This means that the band should shift towards lower frequencies in all DMPT derivatives where this group is deuterated (DMPT-

$2\text{-d}_3$ , DMPT- $d_6$ , and DMPT- $d_{10}$ ), as is confirmed by the results in Table 3. (ii) On selenation it is shifted by *ca.*  $50\text{ cm}^{-1}$  towards lower frequencies in accordance with NCA results on DMPS (to be published). (iii) On complex formation it is also shifted towards lower frequencies in accordance with NCA results (to be published). (iv) On *S*-methylation,  $\delta\text{CS}$  couples with the deformation vibration of the  $\text{C-S-CH}_3$  group and with  $\nu\text{CS}$  to give two new bands at *ca.*  $240$  and  $300\text{ cm}^{-1}$  in accordance with NCA results (to be published). The latter behaviour seems to be specific for the  $\delta\text{CS}$  band and allows a safe identification in the IR spectrum. A similar effect has been observed in the case of 2-methyl-3-pyrazolidinethione, where the  $\delta\text{CS}$  band at  $270\text{ cm}^{-1}$  is split into two bands at  $225$  and  $285\text{ cm}^{-1}$  on *S*-methylation. This effect has apparently not been noted before, probably because it occurs in a less accessible region of the IR spectrum. (v) In the hydrochloride of DMPT  $\delta\text{CS}$  is found with almost unchanged frequency and intensity, supporting that protonisation occurs on the basic  $\text{N}^1$  atom.

The NCA reveals that one of the three remaining bands is due to the CS stretching mode coupled to other ring stretching and deformation modes. It is further calculated that this band will be shifted *ca.*  $100\text{ cm}^{-1}$  towards lower frequencies in DMPS due to the mass effect of substituting sulfur with selenium. In DMPS the strongest band in the low-frequency region both in the IR and the Raman spectra is observed near  $320\text{ cm}^{-1}$ , and undoubtedly has a substantial contribution from CSe stretching. Therefore, in DMPT the corresponding mode must be assigned to one of the two very strong bands in the  $420\text{--}430\text{ cm}^{-1}$  region. In accordance with the NCA it was attributed to  $\nu_{39}$ , *i.e.* the assignment is really based upon the observed isotopic DMPT shifts of the band. In the  $\text{HgCl}_2$  complex of DMPT it is observed at almost identical frequency, though with a somewhat different composition. In the methiodide the CS stretching couples with the deformation vibration of the  $\text{C-S-CH}_3$  group and has no single counterpart.

According to the NCA the two remaining bands at  $491\text{ cm}^{-1}$  and  $422\text{--}424\text{ cm}^{-1}$  originate in the  $\Delta\text{CS}$  mode coupled to an out-of-plane  $\text{N}^1\text{-CH}_3$  deformational mode. The isotopic shifts calculated by the NCA follow closely the observed shifts (Table 3). In DMPS,  $\Delta\text{CSe}$  contributes to bands at  $365$  and  $419\text{ cm}^{-1}$  but coupled to different modes. The bands are hardly displaced in the  $\text{HgCl}_2$

complex of DMPT (489 and 413  $\text{cm}^{-1}$  in the IR), but in the methiodide of DMPT counterparts are observed at 434 and 397  $\text{cm}^{-1}$ .

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