Tentative Assignments of Fundamental Vibrations of Thio- and Selenoamides. X. The Influence of S-Methylation on the Characteristic Thioamide Bands in 1,2-Dimethyl-3-pyrazolidine-thione

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Recent efforts to extract information on the molecular vibrations of a cyclic thiohydrazide, 1,2-dimethyl-3-pyrazolidinethione (DMPT), have involved donor–acceptor reactions with group IIb metals and substitution of sulfur with selenium. The present investigation deals with S-methylation. The IR spectra of DMPT-S-CH$_3$I and eight differently deuterated derivatives have been recorded in the range 180–4000 cm^{-1}. Based on a normal coordinate analysis tentative assignments of the fundamental vibrations of these compounds are given. In agreement with results obtained from CNDO/2 calculations, indicating an increased weight of the π-resonance structure $N^+ = C - S^-$ on S-methylation it is inferred that the force constant for CN stretching of the thiohydrazide group increases while that for CS stretching decreases. The use of S-methylation as a method for empirical classification of vibrations of the thioamide cannot be recommended.

A useful clue to the selection of IR bands originating in the thioamide group is provided [1] by comparison with the spectra of S-methiodides, metal complex compounds, and the corresponding selenoamides. The present status of the two latter methods has been summarized in the preceeding papers.[2,3] In this paper we describe the origin and significance of the IR shifts following conversion of the thioamide group into the S-methiodide.

It was originally proposed [1] (and is still assumed a suitable model [4]) that S-methylation is followed by an increased CN bond order and a decreased

CS bond order of the thioamide group. As a result, the force constants for CN and SC stretching will increase and decrease, respectively. In the vibrational spectra an increase in frequency is observed for bands assigned mainly to CN stretching and a downward shift for bands originating from the CS stretching. In some instances (e.g. 1,3-dimethyl-thiourea [5]) upwards frequency shifts have also been reported for the CS in-plane and out-of-plane deformation bands, but rationalizations do not seem to have been attempted. In studies of thio-amides, thioureas, and thiocarbamates, it was noted by Devillanova and Verani [4] and by Sathyanarayana et al. [5] that in some cases the shifts of the thioamide bands on S-methylation were much smaller than expected. In addition, frequency shifts sometimes occur in bands without contributions from vibrations of the thioamide group. These anomalies can either arise from changes in the composition of the potential energy distribution (PED) of the thioamide bands or from electronic displacements influencing the bond orders of the thioamide group. The absence of any full normal coordinate analyses (NCA) on S-methylated thioamides precludes definite conclusions to be made regarding this interesting point. A perturbational NCA treatment [6] of the changes in the spectrum of tetramethylthiourea on S-methylation not only suggests that the question may be settled in this way, but also that the changes in force constants can be correlated to the charge redistribution of the thioamide group as calculated by the CNDO/2 method.

As an extension of our study of the vibrational spectra of 1,2-dimethyl-3-pyrazolidinethione (DMPT) [7] and its derivatives, we have measured the IR spectra in the range $180-4000$ cm^{-1} of the methiodide, DMPT-S-CH$_3$I, and the trideutero-methiodide, DMPT-S-CD$_3$I. In order to obtain the amount of data necessary to carry out a full NCA, the IR spectra of the following deuterated compounds were recorded (cf. Ref. 7): DMPT-1-D$_3$-S-CH$_3$I, DMPT-1-D$_3$-S-CD$_3$I, DMPT-D$_4$-S-CH$_3$I, DMPT-D$_4$-S-CD$_3$I, DMPT-D$_6$-S-CH$_3$I, DMPT-DMPT-D$_{10}$-S-CH$_3$I and DMPT-D$_{10}$-S-CD$_3$I. An attempt is made to correlate the change in force field on S-methylation with the corresponding bond orders or change densities calculated by the CNDO/2 method.

EXPERIMENTAL

The methiodides were prepared in almost quantitative yield by addition of excess of methyl iodide (or CD$_3$I) to an alcoholic solution of DMPT (parent or deuterated). The precipitate was isolated by filtration or centrifugation and washed with small
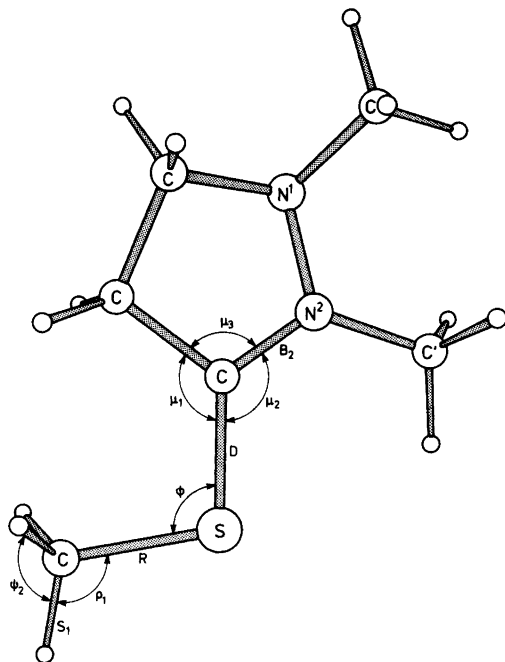

Fig. 1. Internal coordinates in the neighbourhood of the CH$_3$–S group of DMPT·CH$_3$S. Other coordinates are not shown on the figure: τ_3, $\overset{C}{\underset{N}{>}}$C –S torsion, τ_4, S–CH$_3$ torsion.

amounts of ice cold solvent. All compounds gave correct elemental analyses and had an isotopic purity exceeding 95%. The spectra were recorded on a Perkin-Elmer model 580 spectrometer in KBr and/or CsI discs. No signs of halide vibrations were observed in the spectra.

NORMAL COORDINATE ANALYSIS

Crystal data on the S-methylisothiuronium ion [8] and the S-methyl isothiocarbonohydrazidium cation [9] suggest that the structure of DMPT is hardly altered on S-methylation except for a small elongation of the CS bond of the thioamide group. The available data also suggest that the S-methyl carbon atom is located approximately in the plane of the thioamide group. For these reasons we used a model with the S-methyl group situated trans to the N^2 – CH$_3$ group in the N^{2}CS plane (see Fig. 1). The bond angles and distances for the CH$_3$ – S – C group were taken from S-methylated thiocarbono-hydrazide.[9] The secular equation was set up for the S-methyl-1,2-dimethyl-3-pyrazolidinethionium cation taking all 22 atoms into account and the calculations carried out using internal coordinates (or simple linear combinations) as symmetry coordinates in a manner identical to that used previously for DMPT.[7] The internal coordinates necessary for describing the vibrations of the CH$_3$ – S – C group are chosen as shown in Fig. 1.

The final force constants, which are listed in Table 1, have been determined as follows. An initial set of valence force constants was taken from previous studies of DMPT,[7] methanethiol [10] and alkane-thiols and thioalkanes.[11] Attempts to adjust the force constants by taking into account the values of the Jacobian matrix gave discrepancies (of some of the low-frequency vibrations related to CS in-plane deformation) which could not be removed despite various adjustments of the force constants. Therefore an interaction force constant between the C – C – S and C – S – CH$_3$ deformations of the CH$_2$ – C – S – CH$_3$ chain was introduced to obtain a satisfactory fit. As stated in the footnote of Table 1, several interaction force constants were also fixed to the values found for DMPT to ensure convergence to physically reasonable values. From this point a simultaneous least-squares adjustment was made for all the compounds by fitting 50 force constants to approximately 450 observed frequencies. The vibrational frequencies calculated by the final force field had an average standard error below 1% for

Table 1. Final valence force constants for DMPT·CH$_3$I compared with DMPT.[a]

Symbol	Value		Symbol	Value	
	DMPT·CH$_3$I	DMPT		DMPT·CH$_3$I	DMPT
CH$_3$/CH$_3'$			Ring		
K_r	4.732	4.722	K_D	3.384	3.758
F_{rr}	0.003	0.008	K_{L_2}	3.829	3.883
H_α	0.518	0.515	K_{L_1}	4.555	4.590
H_β	0.805	0.763	K_{B_1}	3.924	3.974
F_β	−0.041	−0.037	K_A	5.367	5.354
K_r'	4.748	4.802	K_{B_2}	8.727	7.507
F_{rr}'	−0.086	−0.134	K_{P_1}	4.639	4.642
H_α'	0.506	0.512	K_{P_2}	4.900	5.070
H_β'	0.754	0.723	H_{μ_1}	1.799	0.585
F_β'	−0.034	−0.031	H_{μ_2}	2.209	1.766
CH$_2$			H_{μ_3}	0.603	0.820
			$H_{\varepsilon_1}=H_{\varepsilon_2}$	1.265	1.270
K_d	4.716	4.722	$H_{\theta_1}=H_{\theta_2}$	2.474	2.422
F_{dd}	0.030	0.035	$H_{\varepsilon_3}=H_{\theta_3}$	0.748	0.754
f_γ	0.055	0.058	H_Δ	0.267	0.351
F_γ'	0.072	0.081	$F_{L_1\gamma_1}$ etc.	0.344	0.353
H_{δ_2}	0.472	0.470	$F_{L_2\omega_2}$ etc.	0.860	0.738
$H_{\gamma_3}=H_{\gamma_4}$	0.588	0.592	$F_{P_1\beta}=F_{P_2\beta}$	0.639	0.660
$H_{\gamma_3}'=H_{\gamma_4}'$	0.663	0.693	CH$_3$−S		
$F_{\gamma_3}=F_{\gamma_4}$	−0.346	−0.321			
$F_{\gamma_3\gamma_4}$	0.030	0.077			
H_{δ_1}	0.446	0.432			
$H_{\gamma_1}=H_{\gamma_2}$	0.803	0.780			
$H_{\gamma_1^\circ}=H_{\gamma_2^\circ}$	0.645	0.657			
$F_{\gamma_1\gamma_2}$	−0.105	−0.136			
$F_{\gamma_1^\circ\gamma_2^\circ}$	0.092	0.086			

CH$_3$−S

$K_R = 3.158$, $H_\phi = 2.282$, $K_S = 4.843$, $F_{SS} = 0.054$,
$H_\rho = 0.554$, $F_\rho = -0.069$, $H_\psi = 0.519$, $H_{\tau_3} = H_{\tau_4} = 0.03$,
$F_{\mu_1\phi} = 0.684$

[a] For interpretation of symbols, units, and force field for DMPT, see Ref. 7. The values of H_r, $F_{DL_2}=F_{DB_2}$, $F_{B_2\mu_2}$, $F_{B_2\mu_3}$, $F_{L_2\mu_3}=F_{A_{\varepsilon_3}}$, $F_{D_{\mu_1}}=F_{D_{\mu_2}}$, H_ω, and F_ω were transferred and held fixed.

each of the 9 isotopic species of DMPT$-S-$CH$_3$ included in the NCA.

The resulting force field is listed in Table 1. The differences between the force constants found for DMPT and DMPT·CH$_3$I are, in most instances, small and demonstrate convincingly that *S*-methylation indeed leaves most of the molecule largely unchanged. In accordance with simple resonance theory we observe the force constant for CS stretching, K_D, to decrease from 3.76 to 3.38 mdyn/Å and that for CN stretching, K_{B_2}, to increase from 7.51 to 8.73 mdyn/Å on *S*-methylation. The increase in the force constants related to NCS in-plane deformation, H_{μ_1} and H_{μ_2}, and the decrease in the force constant of the corresponding out-of-plane deformation, H_Δ, suggest an increased electron density in the plane of the NCS group at the expense of the π-density. The results pertaining the CH$_3$S group are remarkable in that an interaction constant $F_{\mu_1\phi}$ of 0.684 mdyn Å/(rad)^2 is necessary to account for the position of the fundamentals v_{52} and v_{53} (see Table 2). A similar interaction force constant (with opposite sign) has been found necessary to describe the spectrum of methanethiol.[10]

CNDO/2 CALCULATIONS

More information of the nature and the extent of the electron densities of DMPT and DMPT$-S$ $-$CH$_3$ was obtained from CNDO/2 calculations. The electronic density changes in the plane of the NCS group (σ-plane) and in a parallel plane 0.85 Å

Table 2. Observed and calculated frequencies (cm^{-1}) of the methiodide (DMPT·CH_3I) and trideuteromethiodide (DMPT·CD_3I) of 1,2-dimethyl-3-pyrazolidinethione (DMPT). Tentative assignment of the IR spectrum of DMPT·CH_3I, description of the fundamentals and frequency shift relative to DMPT.[a]

Observed, IR		Calculated[b]		DMPT-shift[c]		DMPT·CH_3I Assignment and description (PED, %)[d]
DMPT·CH_3I	DMPT·CD_3I	DMPT·CH_3I	DMPT·CD_3I	Obs.	Calc.	
2998w,sh	2247m	3002	2240	—	—	ν_1, $\nu_{as}CH_3(S)$ (99)
		3000	2235	—	—	ν_2, $\nu_{as}CH_3(S)$ (100)
2983m	2987m	2988	2988	-2	0	ν_3, $\nu_{as}CH_3$ (99)
		2985	2985	-2	0	ν_4, $\nu_{as}CH_3$ (99)
2968m,sh	2870m,sh	2971	2971	(-17)	-1	ν_5, $\nu_{as}CH_2$ (99)
		2966	2966	-1	-2	ν_6, ν_sCH_3 (99)
2960m	2962m	2962	2962	-1	-2	ν_7, ν_sCH_3 (99)
		2958	2958	-1	0	ν_8, ν_sCH_2 (98)
	2122w	2932	2112	—	—	ν_9, $\nu_sCH_3(S)$ (100)
2925w,sh	2930w,sh	2928	2928	-3	-2	ν_{10}, ν_sCH_2 (98)
		2924	2924	-3	-5	ν_{11}, ν_sCH_3 (99)
2918m	2920m	2914	2914	+3	-4	ν_{12}, ν_sCH_2 (99)
2872m	2878m	2869	2869	+20	+7	ν_{13}, ν_sCH_3 (100)
1606vs	1608vs	1606	1606	+106	+103	ν_{14}, νC^3N (78)
1466m,sh	1467m,sh	1464	1464	(+17)	+5	ν_{15}, $\delta_{as}CH_3$ (90)
1455m	1458m	1460	1460	-5	-4	ν_{16}, $\delta_{as}CH_3$(42), $\delta_{as}CH_3$(37)
		1459	1459	+6	+4	ν_{17}, $\delta_{as}CH_3$(62), $\delta_{as}CH_3$(26)
	1446w,sh	1441	1441	-3	-2	ν_{18}, $\delta_{as}CH_3$(54), δCH_2(20)
1437m,sh	1038m,sh	1437	1036	—	—	ν_{19}, $\delta_{as}CH_3(S)$ (97)
		1436	1033	—	—	ν_{20}, $\delta_{as}CH_3(S)$ (100)
1424m	1439w,sh	1435	1435	-3	+4	ν_{21}, $\delta_{as}CH_3$(54), δCH_2(28)
1405m	1426m	1419	1419	+3	+4	ν_{22}, δ_sCH_3 (99)
	1412m	1411	1411	-16	-10	ν_{23}, δCH_2 (77)
1388m,sh	1387m,sh	1387	1387	-1	-4	ν_{24}, δ_sCH_3 (98)
1350mw	1351mw	1353	1352	+10	+6	ν_{25}, νNN(25), ν/δ ring(58)
1320s	1320s	1320	1319	+7	+2	ν_{26}, ωCH_2(58), tCH_2(19), vring(16)
1310s	1068w,sh	1312	1072	—	—	ν_{27}, $\delta_sCH_3(S)$ (86)
1308m,sh	1305vw,sh	1309	1309	+1	0	ν_{28}, ωCH_2(18), tCH_2(33), ring(22)
1249mw	1251w,sh			0		
1236mw	1238mw	1237	1237	+6	+4	ν_{29}, ω/tCH_2(45), ν/δring(38), ρCH_3(23) and $\nu_{41} + \nu_{50}$
1200ms	1204m	1206	1206	+13	+10	ν_{30}, ω/tCH_2(66), ρCH_3(20)
1175w,sh	1175w,sh	1171	1171	-1	+3	ν_{31}, vring(35), ω/tCH_2(30), ρCH_3(36)
1129vs	1133vs	1141	1141	-1	+4	ν_{32}, ρCH_3(59), vring(24)

Obs. I	Obs. II	Calc. I	Calc. II	Shift I	Shift II	Assignment (PED)
1099m	1100mw	1101	1101	+5	+1	ν_{33}, $\rho CH_3(96)$
1076m	1080mw	1092	1092	0	+4	ν_{34}, $\nu_{as}NCS(6)$, $\rho CH_3'(41)$, $\nu/\text{ring}(41)$
1060w,sh	1068w,sh	1063	1061	+1	+3	ν_{35}, $\nu CS(4)$, $\nu CC(35)$, $\rho CH_2(37)$
1041w	1043w	1043	1042	-4	-3	ν_{36}, $\nu_{as}NCS(4)$, $\rho CH_3'(24)$, $\nu\text{ring}(61)$
993m	1000m	995	995	-13	-1	ν_{37}, $\rho CH_2(54)$, $\nu CC(21)$ and $\nu_{46} + \nu_{48}$
975w,sh	980w,sh	968	732	—	—	ν_{38}, $\rho CH_3(S)(90)$
956m	{730w, 723w,sh}	952	718	—	—	ν_{39}, $\rho CH_3(S)(100)$
940m	943m	939	940	-2	-10	ν_{40}, $\nu NN(9)$, $\rho CH_2(52)$, $\nu\text{ring}(24)$ and $\nu_{47} + \nu_{48}$
920w,sh	880ms	895	898	-17	-9	ν_{41}, $\nu NN(16)$, $\nu CS(8)$, $\nu\text{ring}(33)$, $\rho CH_2(22)$
876ms	788m	788	806	-8	-12	ν_{42}, $\nu CS(27)$, $\nu/\delta\text{ring}(76)$ and $\nu_{49} + \nu_{50}$
781m	776m	738	709	—	—	ν_{43}, $\nu CH_3 - S(46)$, $\nu/\delta\text{ring}(40)$
760w,sh	688w	685	638	—	—	ν_{44}, $\nu CH_3 - S(36)$, $\nu/\delta\text{ring}(45)$ and $\nu_{50} + \nu_{52}$
706w	670w	625	615	(-8), (-3)	-13	ν_{45}, $\nu NN(10)$, $\nu\text{ring}(62)$, $\delta\text{ring}(37)$ and $\nu_{48} + \nu_{55}$
689mw	637w	563	561	(0)	+10	ν_{46}, $\Delta CH_3 - N{<}^{N}_{C}(58)$, $\nu\text{ring}(30)$ and $\nu_{52} + \nu_{53}$
662w,sh	638vw	470	467	-14	-20	ν_{47}, $\nu CS(11)$, $\Delta CS(10)$, $\delta CSC(5)$, $\nu/\delta\text{ring}(55)$
632vw	596mw	438	429	+4	+9	ν_{48}, $\nu CS(12)$, $\nu NN(14)$, $\Delta CS(12)$, $\delta CSC(22)$, ring(49)
595mw	548m	396	395	-26	-25	ν_{49}, $\Delta CS(33)$, $\Delta CH_3 - N{<}^{N}_{C}(37)$, $\delta\text{ring}(32)$
548m	536w,sh	373	372	-9	-5	ν_{50}, $\Delta CS(12)$, $\nu/\delta\text{ring}(60)$, $\rho CH_2(26)$
525w,sh	479w	341	339	+5	+3	ν_{51}, $\delta CS(16)$, $\delta CSC(9)$, $\nu/\delta\text{ring}(90)$
477w	432m	302	292	—	—	ν_{52}, $\delta CS(17)$, $\delta CSC(29)$, $\nu CS(17)$, $\delta\text{ring}(31)$
434m	400m	245	227	(-4)	—	ν_{53}, $\delta CS(33)$, $\delta CSC(25)$, $\nu/\delta\text{ring}(22)$
396m	370m	200	199	—	-2	ν_{54}, $\tau CH_3(66)$
367m	350w,sh	171	171	—	0	ν_{55}, $\tau CH_3(92)$
355w,sh	300m	123	89	—	—	ν_{56}, $\tau S - CH_3(88)$
302m	230m	110	112	—	-8	ν_{57}, δring
240m	197mw	72	70	—	+5	ν_{58}, δring
202w		38	36	—	—	ν_{59}, $\tau C - SCH_3$
		20	19	—	-2	ν_{60}, δring

Fig. 2. Difference map (DMPT·CH$_3$I – DMPT) of the total molecular density in the NCS plane (left) and in a parallel plane 0.85 Å above this plane (right) as calculated by the CNDO/2 method. Solid, dashed and dotted lines represent positive, zero and negative difference densities, respectively, plotted linearly with a spacing of 0.001 electron/Å^3.

apart (π-plane) are illustrated in Fig. 2. The difference-density maps are calculated by substracting the density of DMPT from that of DMPT·CH$_3$I.

The density of the sulfur p-orbital directed towards the methyl group decreases from 1.98 to 1.05 on S-methylation. This means that bonding between sulfur and methyl takes place essentially by sharing of the electrons of one of the sulfur lone-pairs. This leaves the sulfur atom with a fractional positive charge which may be compensated by different displacements of the σ- and π-electrons of the thiohydrazide group. The π-changes are mainly confined to the NCS group, and may be described by the classical resonance structure $N^+ = C - S^-$. Thus, the π-density of the nitrogen atoms decreases from 1.58 to 1.38, while the π-bond order of the neighbouring CN bond increases from 0.66 to 0.80 on S-methylation. At the same time the π-bond order of the CS bond decreases from 0.57 to 0.35 and the π-density of the sulfur atom increases from 1.69 to 1.88. In addition a small increase from 0.70 to 0.75 in the π-density of the carbon atoms is calculated, but this hardly invalidates the main conclusion. In total, the π-density changes tend to increase the

force constant for CN stretching and decrease that for CS stretching.

The changes in the σ-density are illustrated on the left-hand side of Fig. 2. An increase in the electron-attracting properties of sulfur on S-methylation is clearly revealed by the polarization induced in the $S - C^3 - C^4 - C^5$ chain. Thus, the sulfur atom polarizes the $S - C^3$ bond, which in turn polarizes the $C^3 - C^4$ bond and so on. The polarization diminishes with the distance from the sulfur atom. However, proceeding in the same way along the $S - C^3 - N^2 - N^1$ chain seems to indicate a similar increase in the electron-attracting properties of the N^2-atom on S-methylation. The C^3N bond in the thioamide group is under both influences and the result is very weak polarization. (The increased electron attraction by N^2 may be due to the fact that nitrogen is not sp^2-hybridized but slightly pyramidal. The orthogonality of σ- and π-electrons of the NCS group therefore breaks down, and the decreased π-density of the N^2 atom is transmitted to the σ-core.) Though the σ-core is strongly polarized the changes in σ-densities and σ-bond orders on S-methylation are only small. They can be summarized as a slight increase in the total σ-
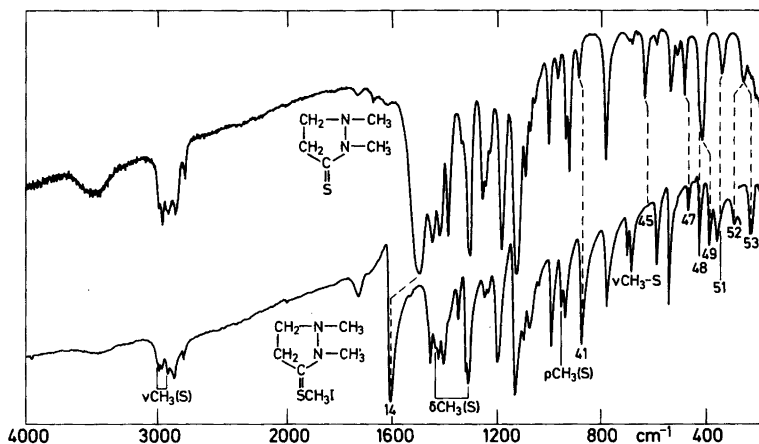
Fig. 3. The IR spectra of 1,2-dimethyl-3-pyrazolidinethione in the liquid state (top) and the *S*-methiodide in the solid state (bottom). Corresponding bands (see text) are indicated by dotted lines. The bands originating mainly from the *S*-methyl group are indicated separately in the figure.

density of the CS bond polarized in the direction C^+S^-. In total the σ-density changes therefore result in a small increase of the force constant for CS stretching.

The changes described here on *S*-methylation of DMPT are almost the same as those described previously for complex formation with metal halides.[3] In both cases, attack on the sulfur atom is followed by a π-change rationalized as $N^+ = C - S^-$ and a polarization of the σ-electrons of the CS bond corresponding to $C^+ - S^-$. Nevertheless an important difference should be noted. When DMPT is *S*-methylated, the force constant for CS stretching will decrease because the changes in π-density exceed those in the σ-core. However, on conversion to metal complex compounds the polarization of the σ-electrons of the CS bond exceeds the changes in the π-density with the result that the force constant for CS stretching increases slightly.

DISCUSSION OF THE S-METHYLATION EFFECTS ON THE SPECTRUM OF DMPT

Survey spectra of DMPT and DMPT·CH_3I at room temperature are shown in Fig. 3. The IR spectrum of DMPT refers to the liquid state, but is virtually unchanged from that of crystalline DMPT. To facilitate comparison of the bands, dotted lines are added on the figure. If the bands originating from the $CH_3 - S$ group are disregarded there is a fair, but not striking, similarity of the spectra, and several

shifts would indeed be difficult to establish without the results of the NCA. In Table 2 the observed frequencies of DMPT are tabulated, together with those of DMPT·CD_3I, as an example of the changes arising from deuteration of the *S*-methyl group. The table includes an assignment of the spectrum based upon the calculated frequencies of the fundamentals. The fundamentals are described in terms of the PED of the internal coordinates. Finally, the frequencies shifts of corresponding bands in DMPT and DMPT·CH_3I(DMPT-shift) are tabulated. Since it is precisely these shifts which form the basis of the diagnostic use of *S*-methylation for revealing bands with contributions from vibrations of the thioamide group, they will be the main subject of the following discussion.

Firstly, it should be noted that in spite of the close similarity between DMPT and DMPT·CH_3I it is not possible to establish a one-to-one correspondence visually, *i.e.* merely by comparing the position, form, and intensity of the bands. Three of the reasons (intensity changes, intensity reversal and changes in PED) have been discussed in some detail in the preceeding papers[2,3] and examples documenting their operation on *S*-methylation are easily found from Table 2. A fourth reason is the occurrence of coupling between the vibrations of DMPT and the attached *S*-methyl group. From Table 2 it is seen that the stretching, deformation and rocking vibrations of the $S - CH_3$ group do not couple significantly with the vibrations of DMPT.

On the other hand, the CH_3-S stretching vibrations couple strongly with the fundamental v_{35} of DMPT near 690 cm^{-1} to give the doublet v_{43} and v_{44} around 700 cm^{-1} in DMPT·CH$_3$I. The CS in-plane deformation vibration which is the main component of the fundamental v_{43} near 270 cm^{-1} in DMPT also couples strongly with the $C-S-CH_3$ deformation vibration to give two new bands (v_{52} and v_{53}) in DMPT·CH$_3$I near 240 and 300 cm^{-1}. Since similar couplings probably arise on S-methylation of other thioamides the latter results may have general significance and may be useful in qualitative work.

Secondly, our results demonstrate that it is not possible to distinguish between bands with and without contributions from the thiohydrazide group by the shifts obtained on S-methylation even in cases where the one-to-one correspondence can be proved. The fundamentals v_{23} and v_{30} are examples of bands which display a definite shift in frequency relative to the corresponding bands in DMPT. However, the origins of the shifts are to be found in changes in PED, not in contributions from vibrations of the thiohydrazide group. On the contrary, v_{48} and v_{51} are examples of bands which have significant contributions from vibrations of the thiohydrazide grouping, but nevertheless hardly shift on S-methylation. A quite similar conclusion for heterocyclic thioamides was reached empirically by Devillanova and Verani.[4] For these reasons, S-methylation cannot be recommended as a tool for assignment of bands due to the NCS group.

However, in the light of the results of the NCA it is possible to comment briefly on the shifts on the bands of DMPT as a result of S-methylation. The very strong fundamental v_{16} near 1500 cm^{-1} in DMPT mostly due to CN stretching of the thiohydrazide group is shifted *ca.* 100 cm^{-1} towards higher frequencies in DMPT·CH$_3$I (v_{14}) mainly as a result of an increase in the force constant for CN stretching, K_{B_2}. The weak fundamental v_{20} near 1340 cm^{-1} in DMPT has a substantial contribution from NN stretching. On S-methylation the polarity and transition moment of the NN bond will increase (due to the structure $N-N^+=C-S-CH_3$) and the corresponding fundamental v_{25} near 1350 cm^{-1} in DMPT·CH$_3$I consequently increases in intensity.

The two prominent bands, v_{33} and v_{34} near 890 and 790 cm^{-1} in DMPT, have considerable CS stretching character and are both displaced towards lower frequencies in DMPT·CH$_3$I (v_{41} and v_{42}) partly as a result of the lower force constant for CS

stretching. A third band, v_{39} at 430 cm^{-1} in DMPT with 32% CS stretching character, has no close counterpart in DMPT·CH$_3$I since the bands v_{47} and v_{48} now share this contribution. The fundamental v_{40} in DMPT near 420 cm^{-1} has a 44% contribution from CS out-of-plane defor-mation. As a result of a decrease in the corresponding force constant, H_{A}, the counterpart v_{49} in DMPT·CH$_3$I is found at 26 cm^{-1} lower frequencies, and some of the CS out-of-plane character is even transferred to the next lower fundamental v_{50}.

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