Tentative Assignments of Fundamental Vibrations of Thio- and Selenoamides. V. Tetramethylthiouram Disulfide

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The infrared and Raman spectra of tetramethyl-thiouram disulfide (TMTD) and four ^{13}C, ^{15}N and deuterium labelled analogues have been studied in the solid state and in solution in the region below 4000 cm^{-1}. A normal coordinate analysis has been accomplished for these compounds as a 24-body problem utilizing a general valence force field. By fitting 26 force constants to reproduce ca. 300 observed frequencies, the normal modes of vibration are described in terms of the potential energy distribution between the symmetry coordinates. A tentative assignment of the fundamentals of TMTD and the perdeuterated compound is given based upon intensities, Raman depolarisation ratios, the ^{13}C/^{15}N shifts and the calculated values. The results indicate the need for revision of previous assignments for TMTD.

In the present paper, the IR and Raman spectra of tetramethylthiouram disulfide, $[(CH_3)_2NCSS]_2$ (TMTD), and the four isotopically substituted derivatives $[(CD_3)_2N-CSS]_2$ (TMTD-d_{12}), $[(CH_3)_2N-{}^{13}CSS]_2$ (TMTD-^{13}C), $[(CH_3)_2{}^{15}N-CSS]_2$ (TMTD-^{15}N), and $[(CD_3)_2N-{}^{13}CSS]_2$ (TMTD-$d_{12}-{}^{13}$C) were measured in solution and in the solid state in the region below 4000 cm^{-1}. Semiquantitative Raman depolarisation data were also obtained, but with a few exceptions vibrations of species a and b overlap completely. The assignments were supported by the results of a full normal coordinate analysis (NCA) (i.e. including treatment of the methyl groups) based upon the general valence force field (GVFF) derived for related compounds,[1,2] assuming C_2 symmetry.

The IR and Raman spectra of TMTD have previously been measured by Coleman et al.[3] in the region below 2000 cm^{-1}. A partial assignment of the fundamental vibrations was proposed from a simplified NCA treating the methyl groups as point masses. The isotopic shifts observed in our spectra were incompatible with the assignment proposed by Coleman et al. and it has been necessary to reinvestigate the spectrum of TMTD in some detail. A reproduction of the IR spectrum of TMTD in the range 4000–250 cm^{-1} has been reported[4] for use as reference spectrum in pesticide research. Contreras and Cortés[5] reported some major IR shifts of TMTD on complex formation with cobalt(II).

STRUCTURE

In a preliminary report[6] the crystal and molecular structure of TMTD has been given but has since been refined by least-squares methods to $R = 0.095$ for 426 non-zero observed reflections (personal communication from the author). TMTD consists of two planar C_2NCS_2 units with a dihedral C–S–S–C angle of 88.3°. The most important bond distances are: CH_3-N: 1.483(21) and 1.506(18) Å, C–N: 1.319(15) Å, C=S: 1.634(13) Å, C–S: 1.829(15) Å, and S–S: 2.005(7) Å. The positions of the hydrogen atoms were estimated by assuming tetrahedral configuration of the methyl group and standard C–H distances. The final Cartesian coordinates correspond to an overall C_2 symmetry and may be obtained on request.

^{1}H NMR studies of TMTD in solution indicate a restricted rotation around the C(S)–N bond with an energy barrier of ca. 15 kcal/mol.[6-10] Splittings due to the restricted rotation around the C–S and

3

S—S bonds have not been observed in these spectra. Likewise the ^{13}C NMR spectrum of TMTD (CDCl$_3$) showed only splittings due to the C—N barrier at temperatures down to −15 °C, the lowest temperature obtainable without the precipitation of TMTD. Probably the barriers around the C—S and S—S bonds do not exceed 10 kcal/mol.[11] On the NMR time scale, TMTD can therefore be considered composed by two planar dimethyldithiocarbamate units joined by the S—S bond, i.e., the C$_2$-symmetry is retained. Since new bands do not appear in the vibrational spectra of TMTD on dissolution we assume TMTD to occur in solution only as one isomer most probably of C$_2$-symmetry.

EXPERIMENTAL

The preparation of the compounds as well as the techniques and equipment used for recording the IR and Raman spectra have been given in a previous paper.[1] Infrared spectra were also run in CCl$_4$ and CS$_2$ solution but the spectra were identical within a few cm^{-1} with those recorded in CHCl$_3$ and no indication of the presence of more than one isomer was found.

Noise-decoupled ^{13}C NMR spectra were determined with a Bruker WH 90 system (22.63 MHz) operating in the Fourier transform mode. The samples were examined as saturated solutions in CDCl$_3$ and shieldings measured relative to internal TMS. The following values were obtained at room temperature: 42.0 and 47.5 ppm (CH$_3$) and 193.5 ppm (CS). The spectrum was also obtained of the ^{13}C substituted TMTD, but we were unable to discern and long-range coupling due to the ^{13}C—S—S—^{13}C grouping.

NORMAL COORDINATE ANALYSIS

The NCA was performed as a 24-body problem assuming C$_2$-symmetry of TMTD. Treatment of TMTD under point group C$_2$ reduced the normal modes of vibration to the irreducible representation $T_{vib} = 34A + 32B$, and the standard GF[12] programs[13] were employed. The potential field employed was of the general valence force field type similar to that described in previous papers.[1] Of the 66 normal modes of vibration possible, 32 are out-of-phase combinations (species B) of the two dimethyldithiocarbamate units joined by the S—S bond. The remaining 34 of species A are composed of the 32 corresponding in-phase combinations together with the S—S stretching and C—S—S—C
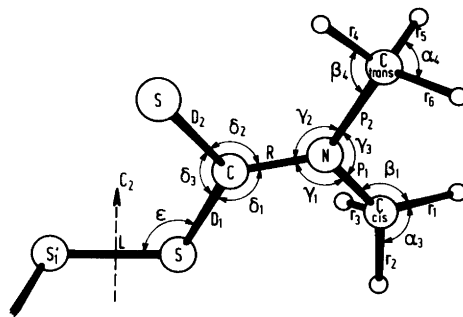

Fig. 1. Internal coordinates for TMTD (one half shown). The following coordinates are not shown on the figure: CH$_3^{cis}$—N torsion τ_1, CH$_3^{trans}$—N torsion τ_2, CH$_3^{cis}$—N—C—S torsion τ_3, CH$_3^{trans}$—N —C—S torsion τ_4, N—C—S—S torsion τ_5, S= C—S—S torsion τ_6, and S—S torsion τ_7. The twofold axis of symmetry indicated is perpendicular to the plane of the paper.

torsional modes. The internal coordinates used in setting up the F matrix are simply the changes in bond lengths and interbond angles. The symmetry coordinates are defined by the in-phase and out-of-phase combinations (Fig. 1).

The initial values for the force constants were first chosen in accordance with the NCA reported by Coleman et al.[3] but only a very poor agreement was achieved especially for the isotopic shifts. The values were then adjusted to comply with the force fields previously obtained for tetramethylthiourea [1] and dimethyldithiocarbamates.[2] This allowed assignment of more than 250 experimental frequencies by slight refinements of the diagonal elements of the F matrix using the Jacobian matrix of frequencies vs. force constants as a guide. However, attempts to refine this force field by the usual least-squares procedure failed and led only to non-converging solutions. Inspection of the correlation matrix (cf. Knoeck and Witt[14]) showed that several of the matrix elements related to the coordinates γ_1/γ_2 and P$_1$/P$_2$ were approaching 1. Accordingly, the isotopic substitution is insufficient for determining separate force fields for the cis and trans methyl groups, and the constraints $F_{R\gamma 1} = F_{R\gamma 2}$, $F_{P_1\gamma 1} = F_{P_2\gamma 2}$ and $F_{P_1\gamma 3} = F_{P_2\gamma 3}$ were introduced. Furthermore, the number of torsional force constants was reduced by setting $H_{\tau 3} = H_{\tau 4}$ and $H_{\tau 5} = H_{\tau 6}$. A new least-square adjustment of the force field to the observed frequencies revealed that several of the important interaction force constants (e.g. $F_{D_1D_2}$)

Table 1. Final valence force constants for tetramethylthiouram disulfide.

Force type	Constants symbol	Group[a]	Coordinate(s) involved	Atoms common to interacting coordinates	Value[b]
Stretch	K_r	CH_3	C-H		4.69
	K_P	CH_3-N	C-N		5.00
	K_R	N-C(S)	N-C		6.81
	K_{D_2}	C=S	C=S		3.02
	K_{D_1}	C-S	C-S		2.13
	K_L	S-S	S-S		2.58
Stretch-Stretch	F_r	CH_3	C-H,C-H	C	0.038
	F_{RD_1}	N-C-S	N-C,C-S	C	1.52
	F_{RP}	CH_3-N-C	C-N,N-C	N	0.27
	F_P	CH_3-N-CH_3	C-N,N-C	N	0.30
Bend	H_α	CH_3	<HCH		0.524
	H_β	CH_3-N	<HCN		0.773
	$H_{\gamma_1}=H_{\gamma_2}$	CH_3-N-C	<CNC		1.59
	H_{γ_3}	CH_3-N-CH_3	<CNC		2.26
	$H_{\delta_1}=H_{\delta_2}$	N-C=S/N-C-S	<NCS		0.68
	H_{δ_3}	S=C-S	<SCS		1.29
	H_ϵ	C-S-S	<CSS		0.83
Stretch-bend	$F_{R\gamma_1}=F_{R\gamma_2}$	CH_3-N-C	<CNC,N-C	N-C	0.68
	$F_{P_1\gamma_1}=F_{P_2\gamma_2}$	CH_3-N-C	<CNC,CH_3-N	CH_3-N	0.90
	$F_{P_1\gamma_3}=F_{P_2\gamma_3}$	CH_3-N-CH_3	<CNC,CH_3-N	CH_3-N	1.33
	$F_{P\beta}$	CH_3-N	<HCN,CH_3-N	CH_3-N	0.34
Bend-bend	F_β	CH_3-N	<HCN,<HCN	C-N	-0.047
Torsion	$H_{\tau_1}=H_{\tau_2}$	CH_3-N	CH_3-N		0.0314
	$H_{\tau_3}=H_{\tau_4}$	N-CS_2	N-CS_2		0.305
	$H_{\tau_5}=H_{\tau_6}$	C-S	C-S		0.177
	H_{τ_7}	S-S	S-S		0.198

[a] The force constants referring to the CH_3^{cis} and CH_3^{trans} groups have been assumed identical.

[b] In units of mdyn/Å (stretch constants), mdyn/rad (stretch-bend interaction constants) and mdyn·Å/(rad)^2 (bending and torsion constants).

were very poorly determined, and that a drastic reduction in the number of force constants was necessary. Using only the 26 force constants of Table 1 we finally obtained satisfactory convergence and good agreement between observed and calculated frequencies and $^{15}N/^{13}C$ shifts (Table 2 and 3). However, the number of independent constants of the force field has been reduced to the point where detailed considerations based upon their relative values are not clearly justified. We shall only point out that the gross features are in accordance with expectations (e.g. $K_{D_2} > K_{D_1}$, $K_R > K_P$) and that the final values are physically reasonable.

RESULTS AND DISCUSSION

The IR spectrum of TMTD in the range 250–4000 cm^{-1} is reproduced in a collection of reference spectra[4] and the region below 2000 cm^{-1}, together with the Raman spectrum, in Coleman's paper.[3] The IR spectra correspond in detail to the spectra obtained by us except for a splitting in the strong band near 1500 cm^{-1} into two branches at 1497 and 1506 cm^{-1} attributed[3] to the in-phase and out-of-phase CN stretching modes of species *a* and *b*. This splitting does not appear in any of our spectra in the solid phase nor in solution, and the calculations indicate (Table 2) that the fundamentals in question (v_7a and $v_{41}b$) are accidentally degener-

ate. The agreement of our Raman spectra with that given by Coleman *et al.* is good.

The ^{13}C and ^{15}N shifts included in Tables 2 and 3 are not in all cases definite though the quality of the spectra is excellent. For example, the IR spectrum of TMTD displays two very strong bands at

970 and 977 cm^{-1} together with a weaker band at 952 cm^{-1}. In the ^{13}C-labelled compounds we observe the corresponding three bands at 974 (medium strength), 954 (strong), and 939 cm^{-1} (very strong). Based upon the results of the NCA this is explained (Table 2) as a shift of the funda-

Table 2. Observed and calculated vibrational frequencies (cm^{-1}) of tetramethylthiouram disulfide and frequency shifts obtained by comparison with $[CH_3)_2N - {}^{13}CSS]_2$ and $[(CH_3)_2{}^{15}N - CSS]_2$.

Infrared[a]				Raman[a]				Calculated[b]			Assignment and Description[c]
solid, disc			solution	solid			solution				
parent	^{13}C-sh	^{15}N-sh	CHCl$_3$	parent	^{13}C-sh	^{15}N-sh	CHCl$_3$	parent	^{13}C-sh	^{15}N-sh	(PED,%)[d]
3010w,br	0	0		3017w	0	0					
				2980w	0	0	2988m(0.41)				
				2960w,sh	0	0					
2932m	0	0	2938m	2933s	0	0	2936s(0.14)	2954 / 2949 / 2947 / 2947	0/0/0/0	0/0/0/0	ν_1a, ν_{35}b, ν_{as}CH(99) / ν_2a, ν_{36}b, ν_{as}CH(99) / ν_3a, ν_{37}b, ν_{as}CH(99) / ν_4a, ν_{38}b, ν_{as}CH(99)
				2924m,sh	0	0					$2\cdot\nu_8$A
2895vw				2893m,sh	0	0					$\nu_8+\nu_{11}$A
2851w	0	2	2860w	2859m	0	0	2868m(0.19)	2866 / 2866	0/0	0/0	ν_5a, ν_{39}b, ν_sCH(100) / ν_6a, ν_{40}b, ν_sCH(100)
				2854w,sh			2857w,sh				$\nu_8+\nu_{12}$A
				2848w	2						$\nu_{10}+\nu_{12}$A
				2808w	−1	0	2809w(0.08)				$2\cdot\nu_{12}$A
2790vw			2800vw	2787w		2	2793vw,sh				$\nu_{12}+\nu_{13}$A
				1508w	0	0	1508w,sh				$\nu_{18}+\nu_{24}$A
1500s	18	21	1504s	1490vw			1498m,br(0.56)	1493	10	12	ν_7a, ν_{41}b, νCN(29), δCH$_3$(36), ρCH$_3$(24)
1454w,sh	0			1465m,br	6	2	ca. 1453m,br	1466 / 1462 / 1459	<0/0/0	0/0/0	ν_8a, ν_{42}b, δCH$_3$(83) / ν_9a, ν_{43}b, δCH$_3$(85) / ν_{10}a, ν_{44}b, δCH$_3$(87)
				1433w	0	−1		1442	7	7	ν_{11}a, ν_{45}b, δCH$_3$(71), νCN(18)
1400m	1	1	1409w	1400s	1	0	1408m(0.85)	1407	1	1	ν_{12}a, ν_{46}b, δCH$_3$(100)
1375s	8	9	1380s	1375s	8	9	1382s(0.67)	1385	7	5	ν_{13}a, ν_{47}b, δCH$_3$(84), νCN(17)
1335vw			1335vw	1336vw	−1		1335vw				$2\cdot\nu_{21}$A
1294vw	16	1	1297vw								$\nu_{53}+\nu_{59}$A
1235s	4	19	1245s	1239w	4	20	ca. 1245w	1248	6	18	ν_{14}a, ν_{48}b, νCH$_3$–N(51), δCH$_3$NC(33), ρCH$_3$(25)
1150s	15/4	1	1152s	1150s	13/0	0	1156(0.58)	1158 / 1155	12	2	ν_{15}a, ν_{49}b, ρCH$_3$(61), νCN(12) / ν_{16}a, ν_{50}b, ρCH$_3$(80), δCH$_3$(17)
				1134w		3	1131vw,sh				$2\cdot\nu_{22}$A
1110vw	2	3	1115w,sh	1105w	0	0					$\nu_{55}+\nu_{57}$A
1090vw	0	0	1095vw	1091w	0	4	1090vw	1091	0	0	ν_{17}a, ν_{51}b, ρCH$_3$(86), δCH$_3$(13)
1039s	1	5	1049m	1041w	0	4	1050w	1048	1	6	ν_{18}a, ν_{52}b, ρCH$_3$(57), νCH$_3$–N(39)
977vs	3	4	985s,sh	977vs	3	2					$\nu_{55}+\nu_{59}$A
970vs	31	3	976vs	977vs	30	2	986s(0.23)	982	22	3	ν_{19}a, ν_{53}b, ν_{as}CSS(37), νCN(20), νCH$_3$–N(31)
952s	−2	4	960s,sh	958m,sh	0	7	964w,sh				$\nu_{26}+\nu_{55}$B
				898vw	0	0					$2\cdot\nu_{24}$A
849s	−2/13	2	855m	852s	0/13	2	857s(0.32)	857 / 856	7/7	3/3	ν_{20}a, νCH$_3$–N(81) / ν_{54}b, νCH$_3$–N(82)
839w,sh	2	2									$\nu_{24}+\nu_{25}$A
				824vw	3						$\nu_{22}+\nu_{27}$A
790vw	1	1		795vw	2	2					$2\cdot\nu_{58}$A
				773vw	0	0					$2\cdot\nu_{25}$A
674vw				676vw	2	0		676	3	4	ν_{21}a, δ(CH$_3$)$_2$N(50), ρCH$_3$(13)
667vw				667vw				670	3	5	ν_{55}b, δ(CH$_3$)$_2$N(57), ρCH$_3$(14)

Table 2. Continued.

Infrared[a]				Raman[a]				Calculated[b]			Assignment and Description[c]
solid, disc			solution CHCl₃	solid			solution CHCl₃				(PED, %)[d]
parent	^{13}C-sh	^{15}N-sh		parent	^{13}C-sh	^{15}N-sh		parent	^{13}C-sh	^{15}N-sh	
563m/w	3	3	563m/w	561vs	2	3	565vs(0.14)	558	0	0	ν_{22}a, νS-S(75)
542w,sh	16/10	3	540w	536vw,sh		3	542vw,sh	538	13	4	ν_{23}a, tCN(65), tC-S(22)
520vw,sh	12	0						526	12	5	ν_{56}b, tCN(69), tC-s(22)
				502vw	1	0	502vw				2·ν_{27}A
				490vw	0	0	493vw				ν_{57}+ν_{66}A
			475vw	480vw	0	0					ν_{59}+ν_{61}A
441m	0	1	444m	443s	0	1	447s(0.28)	{442 / 439}	0	2	ν_{57}b, νC=S(36), δCH₃NC(40) / ν_{24}a, νC=S(38), δCH₃NC(39)
396m	0	1	396m	395s	0	1	395s(0.20)	{395 / 390}	0	0	ν_{58}b, νCSS(72), δ(CH₃)₂N(20) / ν_{25}a, νCSS(73), δ(CH₃)₂N(17)
358w	0	0		361w	0	0					2·ν_{61}A
312vw,sh	0	0		317m	1	1	314m(0.5)	312	0	1	ν_{59}b, δC-S-S(24), δS=C-S(33)
284w,sh	0	2		283w				290	1	4	ν_{26}a, tCN(54), tC-S(16)
275m	1	5		267m	0	0		266	2	3	ν_{60}b, tCN(66), tC-S(15)
268w,sh				255vw				252	1	1	ν_{27}a, δS=C-S(39), δNCS(16), νCN(12)
218vw,br											ν_{33}+ν_{61}B
				203w	0	0					2·ν_{32}A
178m				179m	0	1	175m(0.6)	175	0	0	ν_{61}b, δNCS(64), δCH₃NC(17)
151vw				158vw							ν_{32}+ν_{66}B
144vw				142vw				145	0	0	ν_{28}a, τCH₃(95)
135vw				133vw	0	0		{136 / 133 / 133 / 131}	1 / 0 / 0 / 0	0 / 0 / 0 / 0	ν_{29}a, δS-S-C(30), tCN(19), tC-S(20) / ν_{30}a, δNCS(64), δCH₃NC(15) / ν_{62}b, τCH₃(66) / ν_{63}b, τCH₃(39), δC-S-S(19), tCN(11), tC-S(14
				125vw	1	0		{125 / 124}	0 / 0	0 / 0	ν_{31}a, τCH₃(87) / ν_{64}b, τCH₃(80)
117w				116w	0	1					lattice mode
110w				110m	0	0					lattice mode
				97vw				96	0	0	ν_{32}a, tC-S(55), tCN(34)
91w,sh								93	0	0	ν_{65}b, tC-S(65), tCN(29)
84m				75s	2						lattice mode
68w				64m,sh	0	0					lattice mode
50w								51	0	0	ν_{66}b, tC-S(61), δC-S-S(25)
				44s	0			47	0	0	ν_{33}a, tC-S(60), δC-S-S(21)
38vw				37m,sh	0			39	0	0	ν_{34}a, τS-S(65)
32w											lattice mode

[a] The following abbreviations have been used: s, strong; m, medium; w, weak; br, broad; sh, shoulder. The Raman depolarisation ratio is given in parenthesis. Weak bands between 1550 and 2750 cm^{-1} have been omitted.

[b] Iteration based upon all isotopic species.

[c] Abbreviations: ν = stretching, δ, Δ = deformation, ρ = rocking, ω = wagging, t = twisting, τ = torsion, and, as subscripts, s = symmetric, as = antisymmetric.

[d] The potential energi distribution (PED) is defined as $\underline{x}_{ik}$ = 100$\underline{F}_{ii}\underline{L}^2_{ik}/\underline{\lambda}_k$. The stated PED's are only approximate and small contributions have been neglected.

mental ν_{19}a at 970 cm^{-1} by 31 cm^{-1} to 939 cm^{-1}, while the two other bands are considered combination modes which are hardly displaced on ^{13}C substitution. Though this interpretation is supported by the Raman spectra the results remain ambiguous.

Raman depolarisation measurements have been performed for both TMTD and TMTD-d_{12} in CHCl₃ solution. The fundamentals belonging to species *a* should give rise to polarised Raman lines whereas those of species *b* should appear depolarised. However, the in-phase and out-of-phase combinations in most cases superimpose to give one band which appears polarised. Therefore, only the assignments of ν_{23}a, ν_{59}b, and ν_{61}b in the

spectrum of TMTD and $v_{21}a$, $v_{22}a$, $v_{59}b$, and $v_{61}b$ in TMTD-d_{12} are supported from these measurements.

The CH$_3$ and CD$_3$ stretching modes. The four asymmetric CH stretching modes of species a are expected to fall within a narrow frequency range (7 cm^{-1} according to the NCA) coincident with the corresponding modes of species b. Furthermore, the NCA predicts the symmetric modes to coincide to one band at a lower frequency. The two strongest bands found both in the IR and the Raman spectrum of TMTD have been assigned to these overlapping fundamentals (Table 2). Some of the remaining bands are easily explained as overtones or binary

Table 3. Observed and calculated vibrational frequencies (cm^{-1}) of perdeuterotetramethylthiouram disulfide and frequency shifts obtained by comparison with $[(CD_3)_2N - {}^{13}CSS]_2$.

Infrared[a]			Raman[a]			Calculated[b]		Assignment and Description[c] (PED,%)[d]
solid, disc		solution CHCl$_3$	solid		solution CHCl$_3$			
parent	^{13}C-sh		parent	^{13}C-sh		parent	^{13}C-sh	
2262w,br		2265w,sh	2265w,br		2270w,sh			v_8+v_{11}A
		2240m,sh	2232m,sh		2240m,sh	2220	0	v_1a, v_{35}b, v_{as}CD(95)
2221w	0	2233m	2223s	2	2232s(0.50)	2204	0	v_2a, v_{36}b, v_{as}CD(97)
						2200	0	v_3a, v_{37}b, v_{as}CD(98)
						2199	0	v_4a, v_{38}b, v_{as}CD(98)
2176w	3	2190w	2177w	4	2188w			v_9+v_{11}A
2135w	3	2143m	2135s	4	2143s(0.23)			$v_{10}+v_{14}$A
2108w	0	2114w,sh	2113w,sh		2115w,sh			$2 \cdot v_{11}$A
		2107m	2102m	2	2105m(0.33)			$2 \cdot v_{12}$A
2087vw	0	2094w,sh	2090w,sh		2093w,sh			$2 \cdot v_{13}$A
2060m	0	2070s	2062m	1	2070s(0.28)	2066	0	v_5a, v_{39}b, v_sCD(98)
						2065	0	v_6a, v_{40}b, v_sCD(98)
1538vw	8		1540vw					$2 \cdot v_{20}$A
1505vw,sh			1509vw		$\sim$1500vw,br			$v_{16}+v_{21}$A
1443vs,sh	2				1447m,sh			$v_{12}+v_{24}$A
1437s	22	1437vs	1433s	21	1438s(0.79)	1434	26	v_7a, v_{41}b, vCN(70)
1419w,sh			1417vw,sh		1418vw,sh			$v_{51}+v_{56}$A
1296vw	2		1302vw					$v_{20}+v_{22}$A
1258vw,sh			1259vw					$v_{15}+v_{27}$A
1210s	4		1214w	4		1211	8	v_8a, v_{42}b, vCD$_3$-N(64), δCD$_3$NC(42)
1166vw	2		1156vw					$2 \cdot v_{21}$A
1147vw	7		1144vw	5				$v_{20}+v_{25}$A
			1124vw,sh					$2 \cdot v_{55}$A
1111m	3	1120m	1112w		1119w(0.9)	1111	1	v_9a, v_{43}b, δCD$_3$(84), vCD$_3$-N(24)
1100w,sh	0	1104w,sh	1104w,sh	3		1106	4	v_{10}a, v_{44}b, δCD$_3$(80), vCD$_3$-N(32)
			1078w	1				$v_{18}+v_{27}$A
			1074w,sh	1				$v_{54}+v_{59}$A
1057s	2		1058w	2	$\sim$1064w,br	1053	0	v_{11}a, v_{45}b, δCD$_3$(87)
1042vw,sh			1045vw			1050	0	v_{12}a, v_{46}b, δCD$_3$(83)
						1045	0	v_{13}a, v_{47}b, δCD$_3$(88)
						1043	0	v_{14}a, v_{48}b, δCD$_3$(92)
1017s	16/4	1012m	1013m	15	1021m(0.35)	1006	11	v_{15}a, v_{49}b, ρCD$_3$(37), δ(CD$_3$)$_2$N(17), vC=S(12)
946w,sh	0		942w		944w			$v_{21}+v_{25}$A
925vw,sh			928w,sh	0	928w,sh	928	0	v_{16}a, v_{50}b, ρCD$_3$(75)
910s	0/8	914s	914s	8	921s(0.60)	917	18	v_{17}a, v_{51}b, v_{as}CSS(29), vCN(18), vCD$_3$-N(17)
889m	12	899s	892m	10	899m,sh(0.81)			$v_{22}+v_{25}$A
837vw	0		834w	0	833w,sh	832	0	v_{18}a, v_{52}b, ρCD$_3$(91)
816m	2		817w	1	824w(0.7)	824	1	v_{19}a, v_{53}b, δCD$_3$(80)
770m	6		773m	5		770	3	v_{20}a, vCD$_3$-N(55), ρCD$_3$(11)
						769	3	v_{54}b, vCD$_3$-N(57), ρCD$_3$(10)
750vw	2		753vw					$2 \cdot v_{25}$A
618vw			615vw					$v_{25}+v_{27}$A
			585vw					$2 \cdot v_{59}$A
572w	1	576w	573m	1	578m(0.45)	589	0	v_{21}a, vS-S(43), ρCD$_3$(12), δ(CD$_3$)$_2$N(12)

Table 3. Continued.

Infrared[a]			Raman[a]			Calculated[b]		Assignment and Description[c] (PED, %)[d]
solid, disc		solution	solid		solution			
parent	^{13}C-sh	CHCl$_3$	parent	^{13}C-sh	CHCl$_3$	parent	^{13}C-sh	
566w,sh			566w,sh		567w,sh	559	1	ν_{55}b, $\delta(CD_3)_2N(33)$, $\rho CD_3(27)$
539w,sh		538w,sh	544w,sh					$2\cdot\nu_{26}$A
528vs	2	532s	529s	1	528vs (0.31)	528	1	ν_{22}a, νS-S(37), $\delta(CD_3)_2N(28)$
518vw	6/10		522w,sh			520	13	ν_{23}a, tCN(58), tC-S(22)
509vw	19	504vw,sh	505vw,sh		504vw,sh	506	13	ν_{56}b, tCN(64), tC-S(24)
487vw,br	0	480vw,sh	484vw,sh					$2\cdot\nu_{27}$A
396m	2		400m	2	400m	{410 / 406	0 / 0	ν_{57}b, νC=S(39), $\delta CD_3NC(35)$ / ν_{24}a, νC=S(39), $\delta CD_3NC(34)$
			387w		390m			$\nu_{26}+\nu_{62}$B
375m	1		375s	0		{379 / 377	0 / 0	ν_{58}b, $\nu_s CSS(68)$, $\delta(CD_3)_2N(25)$ / ν_{25}a, $\nu_s CSS(68)$, $\delta(CD_3)_2N(21)$
342vw	0		343m	0	340w			$2\cdot\nu_{61}$B
298m	2		300s	0	293s(0.6)	301	0	ν_{59}b, δC-S-S(21), δS=C-S(34)
271m	0		269w	0		271	1	ν_{26}a, tCN(48), tC-S(17)
			255vw			249	1	ν_{60}b, tCN(65), tC-S(17)
246m			242m	0		242	0	ν_{27}a, δS=C-S(39), δNCS(15), νCN(12)
207vw								$\nu_{30}+\nu_{63}$B
193vw			192vw	0				$\nu_{63}+\nu_{64}$A
178w			177m	0	171m(0.5)	168	0	ν_{61}b, δNCS(59), $\delta CD_3NC(18)$
158w			160w		160w(0.7)			$\nu_{34}+\nu_{62}$B
138vw			132vw	0		132	1	ν_{28}a, δS-S-C(39), tCN(17), tC-S(21)
122vw			125vw	0		{127 / 123	1 / 0	ν_{62}b, δS-S-C(31), tCN(11), tC-S(23) / ν_{29}a, δNCS(64), $\delta CD_3NC(18)$
117m			115w	0	115w	112	0	ν_{30}a, $\tau CD_3(93)$
			105m	0	102w	98	0	ν_{63}b, $\tau CD_3(66)$, tC-S(22), tCN(12)
89w,sh			93w	0		{90 / 89	0 / 0	ν_{31}a, $\tau CD_3(74)$, tC-S(14) / ν_{64}b, $\tau CD_3(90)$
83w						{87 / 82	0 / 0	ν_{32}a, $\tau CD_3(25)$, tCN(30), tC-S(41) / ν_{65}b, $\tau CD_3(33)$, tCN(21), tC-S(44)
76vw			76vw					lattice mode
67w			67s	0				lattice mode
61m			63m,sh	0				lattice mode
56m								lattice mode
43w			43s	0		{47 / 44	0 / 0	ν_{66}b, tC-S(61), δC-S-S(24) / ν_{33}a, tC-S(58), δC-S-S(17)
			37m,sh	0		38	0	ν_{34}a, τS-S(62)

[a] See footnote to Table 2 for abbreviations. Weak absorption in the range 1550 – 2000 cm^{-1} has been omitted.

[b,c,d,e] See footnotes to Table 2.

combination modes. However, the ^{13}C and ^{15}N shifts of three weak bands in the upper part of this region (2960 – 3017 cm^{-1}) are negligible and must stem from combination modes of fundamentals which also remain unchanged. Since no such fundamentals are available they probably arise through ternary combination modes.

In the spectra of TMTD-d_{12} (Table 3) the pattern is quite similar, except that one of the asymmetric CD stretching bands (ν_1a, ν_{35}b) is predicted to be shifted *ca.* 20 cm^{-1} towards higher frequency relative to the other asymmetric CD stretching

vibrations. These fundamentals have been assigned to the strong rather broad absorption near 2230 cm^{-1} with a prominent shoulder at *ca.* 2240 cm^{-1}. The NCA predicts the four symmetric CD stretching modes to be coincident at *ca.* 2065 cm^{-1} corresponding to the strongest band in the IR spectrum in this region. However, in the Raman spectrum of TMTD-d_{12} in the solid phase the strongest band in this region occurs at 2135 cm^{-1}. In CHCl$_3$ solution this band moves to 2143 cm^{-1} and becomes comparable in intensity to the band at 2070 cm^{-1}. Since the NCA strongly contradicts this to be a

fundamental it is instead assumed to be an unusually strong combination mode. Only a combination of the CD_3 deformation modes (e.g. $v_{10} + v_{14}A$) can be expected to achieve the necessary intensity enhancement by Fermi resonance with the fundamentals of this region, and the band has been assigned accordingly. The assignment of the remaining bands of TMTD-d_{12} is straightforward.

The thioureide band v_7/v_{41}. In the IR spectrum of TMTD, the prominent band near 1500 cm^{-1} (known as the thioureide band[15]) is assigned to the overlapping fundamentals v_7a and $v_{41}b$. Coleman's results showed[3] this band to consist essentially of CN stretching (81 %) weakly coupled to $C=S$ and $CH_3 - N$ stretching. The results of the present NCA (including full treatment of the CH_3 groups instead of considering them to be point masses) rather indicate this band to consist of CN stretching (29 %) strongly coupled to CH_3 deformation and rocking (total 60 %). On deuteration the coupling is removed and the corresponding band in TMTD-d_{12} near 1435 cm^{-1} consists mainly of CN stretching (70 %). Though our NCA probably overestimates the contribution of CH_3 modes to this band in TMTD (the ^{13}C and ^{15}N shifts are calculated too small) there is hardly any doubt that both CN stretching and CH_3 deformation and rocking modes contribute to this band. On complex formation with cobalt(II) chloride the frequency of this vibration is raised by 30 cm^{-1} reflecting the concomitant increase in double bond character of the CN bond.[5]

The CH_3 and CD_3 deformation and rocking vibrations. The four $\delta_{as}CH_3$ and two δ_sCH_3 modes of species a are predicted by the NCA to be coincident with the corresponding six bands of species b and to appear in the range 1380 – 1470 cm^{-1} in the spectrum of TMTD. Since only four bands are observed in this region, the broad and unresolved absorption occurring in both the Raman and IR spectrum of TMTD near 1450 – 1460 cm^{-1} has been assigned to the overlapping fundamentals $v_8 - v_{10}a/v_{42} - v_{44}b$. In the case of $v_{13}a/v_{47}b$ the observation of ^{13}C (8 cm^{-1}) and ^{15}N (9 cm^{-1}) shifts supports the occurrence of a weak coupling to CN stretching as indicated by the calculations. In the spectrum of TMTD-d_{12} (Table 3) the corresponding CD_3 deformation modes occur in the range 1040 – 1120 cm^{-1} and are easily assigned in accordance with the results of the NCA.

The ρCH_3 modes are expected from the calculations to give rise to four bands in the 1000 – 1200

cm^{-1} region each consisting of overlapping fundamentals of species a and b. On ^{13}C substitution, part of the strong band near 1150 cm^{-1} (Table 2) is displaced by 13 – 15 cm^{-1} towards lower frequencies while part of the absorption remains unchanged. The NCA indicates that the fundamentals $v_{15}a/v_{49}b$ are distinguished by a major ^{13}C shift of 12 cm^{-1} arising from coupling with the CN stretching mode while the ρCH_3 mode $v_{16}a/v_{50}b$ occurs at almost identical frequencies but is not diplaced by ^{13}C substitution. The 1150 cm^{-1} band is therefore assigned to all four fundamentals. The remaining fundamentals are assigned following the condition that $v_{17}a/v_{51}b$ is neither displaced by ^{13}C nor by ^{15}N substitution, while $v_{18}a/v_{52}b$ should shift by *ca.* 6 cm^{-1} on ^{15}N substitution as a result of coupling to the $CH_3 - N$ stretching mode. A few remaining weak bands in this region are assigned to overtones and combination modes.

Three of the ρCD_3 modes in TMTD-d_{12} should give rise to bands which are not displaced by ^{13}C substitution and, again, with complete overlap between fundamentals of species a and b. These have been identified with the weak absorption occurring near 928, 833 and 824 cm^{-1}. The overlapping fundamentals $v_{15}a/v_{49}b$, however, are calculated to exhibit a ^{13}C-shift of 11 cm^{-1} because of coupling with the $C=S$ stretching and $(CD_3)_2N$ deformation modes. These are assigned the medium to strong bands observed in both the IR and Raman spectra near 1015 cm^{-1} displaying a ^{13}C shift of 15 – 16 cm^{-1}.

The skeletal modes of TMTD in the range 800 – 1300 cm^{-1}. In the IR spectrum of TMTD a strong band occurs at 1245 cm^{-1} (CHCl$_3$) which is shifted 4 cm^{-1} on ^{13}C substitution and 19 cm^{-1} on ^{15}N substitution towards lower frequencies. The Raman counterpart is much weaker but occurs at identical frequencies and with almost identical isotopic shifts. In good agreement with the NCA this band is assigned as overlapping $v_{14}a/v_{48}b$ fundamentals due to $CH_3 - N$ stretching (51 %) weakly coupled to CH_3NC deformation and CH_3 rock. In TMTD-d_{12} the coupling with CH_3 rock is removed and the corresponding band $v_8/v_{42}b$ is found at *ca.* 30 cm^{-1} lower frequencies. Coleman *et al.*[3] assigned this band to CH_3 rocking, but this seems excluded by the isotopic shifts reported here.

One of the strongest bands in both the IR and Raman spectrum of TMTD is observed near 980 cm^{-1}. The ^{15}N shift is only *ca.* 2 cm^{-1} but on ^{13}C substitution it displays a large shift of 30 cm^{-1}.

These characteristics allow an unambiguous assignment to the overlapping fundamentals $v_{19}a/v_{53}b$ arising from an out-of-phase stretching mode of the $(CH_3)_2N-CSS$ group of TMTD involving $v_{as}CSS$-(37 %), $vCN(20 \%)$ and $vCH_3-N(31 \%)$. In TMTD-d_{12} the counterpart is calculated to appear at 917 cm^{-1} displaying a ^{13}C shift of 18 cm^{-1}. However, two strong bands occur near this position in both the IR and Raman spectra of TMTD-d_{12}, one near 915 cm^{-1} (^{13}C-shift 8 cm^{-1}) and one near 890 cm^{-1} (^{13}C shift 10$-$12 cm^{-1}). Since the *sum* of the observed ^{13}C shifts corresponds quite closely to the predicted value, an explanation could be the occurrence of an overtone or combination mode with the following features: (i) The ^{13}C shift should be negligible since the observed ^{13}C shifts of this region can be explained entirely as arising from the fundamental. (ii) At least one of the components should involve skeletal modes of the $(CH_3)_2N-CSS$ group in order that Fermi resonance with the $v_{17}a/v_{51}b$ fundamental may achieve the necessary intensity. In our opinion the assigned combination mode, $v_{22}+v_{25}A$, most closely corresponds to these demands.

The overlapping fundamentals $v_{20}a/v_{51}b$ are calculated to appear at *ca.* 855 cm^{-1} with small ^{15}N and ^{13}C shifts. Considering the PED in comparison with the elements of the *L*-matrix, it consists of more than 80 % of symmetric $(CH_3)_2N$ stretching. Except for some ambiguity in the interpretation of the experimental ^{13}C shifts these features agree with the experimental spectra. In TMTD-d_{12} weak coupling occurs to the CD$_3$ rocking mode,

The region below 700 cm^{-1} of TMTU and TMTU-d_{12}. The band observed at 565 cm^{-1} in the Raman spectrum of TMTD in CHCl$_3$ solution is the strongest band in the spectrum; furthermore, it is the band having the lowest depolarisation ratio (0.14). It must accordingly be of species *a* and originate in vibrations producing a strong Raman scattering. The counterpart in the IR spectrum is only of weak to medium strength indicating the change of dipole moment during the vibration to be small. The observed ^{13}C and ^{15}N shifts are negligible (2$-$3 cm^{-1}). These features indicate strongly (*cf.* Bellamy[16]) that this band should be assigned to $v_{22}a$, due to the S$-$S stretching mode (75 % according to our NCA). The corresponding force constant $K_L=2.58$ mdyn/Å, is intermediate between the values for aliphatic sulfides (3.10 mdyn/Å[17]) and the value proposed by Coleman *et al.* for TMTD[3] (2.30 mdyn/Å). The latter value is

obtained on the assumption, that the band with maximum S$-$S stretching character (91 % according to their NCA) is instead the strong, polarised Raman band at 447 cm^{-1} also observed with weak to medium strength in the IR at 444 cm^{-1}. Their NCA indicate the band at 565 cm^{-1} to originate in a vibration involving stretching and bending of the $CH_3-N-C-S$ part of the molecule, which, in our opinion, is not likely to be an adequate description of the strongest band in the Raman spectrum. Unfortunately, the results obtained for TMTD-d_{12} do not unambiguously support our interpretation, since the S$-$S stretching character is equiparted between the two strong Raman bands at 578 and 528 cm^{-1} (CHCl$_3$), the latter of which also appear very strong in the IR contrary to expectations. If Coleman's assignment was correct, the band originating primarily in S$-$S stretching in the spectrum of TMTD-d_{12} should be the Raman line of medium strength at 400 cm^{-1} also having an IR counterpart of similar intensity. At present a decisive interpretation cannot be given for these bands.

Torsional vibrations of the C$_2$N$-$C$-$S$-$S$-$NC$_2$ chain give rise to the fundamentals v_{23}, v_{26}, v_{32}, v_{33}, and $v_{34}a$ and v_{56}, v_{60}, v_{65}, and $v_{66}b$. These are only tentatively identified except in the case of $v_{23}a$ and $v_{56}b$, which are distinguished by displaying ^{13}C shifts calculated to *ca.* 13 cm^{-1}. In TMTU they appear as two weak bands at *ca.* 540 and 520 cm^{-1} and in TMTU-d_{12} they are displaced by *ca.* 20 cm^{-1} towards lower frequencies. In both cases the ^{13}C shifts have been difficult to establish with certainty, especially in the Raman spectrum where this region is completely dominated by the strong $v_{22}a$. Though the shifts are somewhat irregular, varying from 6 to 19 cm^{-1} according to the IR spectra, we believe these fundamentals to be correctly identified. They were not observed by Coleman *et al.*[3], likewise vibrations concerned with out-of-plane deformations and torsions were not included in their NCA. According to our NCA, some coupling occur to the τCH$_3$ bands of TMTD in the 120$-$50 cm^{-1} range and to the τCD$_3$ bands of TMTU-d_{12} between 80 and 120 cm^{-1}.

The symmetric stretching vibration of the CSS group is expected[2] to contribute significantly to strong Raman bands occurring in the 400$-$500 cm^{-1} region. In the Raman spectrum of TMTU we observe two strong, polarised bands at 447 and 395 cm^{-1} (CHCl$_3$) which might both comply with these demands. The NCA indicates the band at highest frequencies to originate in C=S stretching (36$-$

38 %) coupled to CH_3NC deformation (39−40 %), of which the former component explains the observed Raman intensity. The Raman line near 395 cm^{-1} is predominantly due to the v_sCSS mode (72−73 %) but with a weak coupling to $(CH_3)_2N$ deformation (17−20 %). This assignment is in agreement with the shifts observed on deuteration. It differs considerably from the assignments of this region by Coleman et al., however, their agreement between observed and calculated values in this range is not good.

The two skeletal deformation modes, $v_{59}b$ due to the S=C−S−S chain and $v_{27}a$ originating in the N−CS_2 group, are assigned to bands near 315 and 255 cm^{-1}, respectively, in the spectra of TMTD. In the spectra of TMTD-d_{12} both bands are shifted towards lower frequencies and are found near 300 and 245 cm^{-1}, respectively. These assignments are based exclusively upon the agreement with the results of the NCA. The in-phase and out-of-phase combinations of NCS deformation (with small contributions from CH_3NC deformation $v_{30}a$ and $v_{61}b$, are assigned to bands near 135 and 175 cm^{-1} in TMTD. The latter band has been observed in CHCl$_3$ solution as a Raman line with depolarisation ratio 0.6, not far from full depolarisation (0.75). The counterparts in the spectrum of TMTD-d_{12} are quite similar. The two bands originating from NCS deformation were calculated by Coleman et al.[3] to fall near 79 and 92 cm^{-1}, which is at much lower frequencies than our assignment for TMTD. However, their force constants for S=C−S and S=C−N bending were found to be 1.98 and 0.13 mdyn Å/(rad)^2, respectively, which seems to be a much more unrealistic result than the values found by us (Table 1). Furthermore, their calculated values for the region below 600 cm^{-1} seem to be severely hampered by the omission of torsional vibrations which, as discussed above, give rise to several bands in this region.

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