Tentative Assignments of Fundamental Vibrations of Thio- and Selenoamides. VI. Tetramethylselenourea Dibromide and Diiodide

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Infrared spectra are reported for tetramethylselenourea diiodide, the perdeuterated and the ^{15}N substituted compound in the region below 4000 cm^{-1}. Infrared and Raman spectra have been obtained for the isostructural tetramethylselenourea dibromide and the ^{15}N-substituted compound in the same region. The spectra have been tentatively assigned using infrared and Raman polarization data. The assignments have been aided by a normal coordinate analysis fitting 46 force constants to *ca.* 250 observed frequencies. The changes in force constants on conversion of tetramethylselenourea to the dibromide agree roughly with those expected from CNDO/2 calculations.

The vibrational spectra of tetramethylthiourea (TMTU)[1] and tetramethylselenourea (TMSU)[2] have been extensively studied, resulting in an almost complete assignment and description of the fundamental vibrations. Some ambiguities in the interpretation of the spectral patterns in the 1100 – 1200 cm^{-1} range were removed by studying spectra of addition compounds of TMTU with iodine, methyl iodide, and metal halides.[3] By analogy to TMTU, the reaction between TMSU and iodine was expected to give a charge transfer complex. However, the oil transiently formed readily gave a red, crystalline compound which, according to X-ray structure determination[4] is tetramethylselenourea diiodide (TMSU·I$_2$) containing covalent bonds between selenium and iodine. It was not possible to obtain Raman spectra of TMSU·I$_2$ because of the intense, red colour. The isostructural, yellow tetramethylselenourea dibromide (TMSU·Br$_2$) gave better Raman spectra and was therefore included in the investigation.

In the present study we wish to report a tentative assignment of the fundamental vibrations of TMSU·Br$_2$ and TMSU·I$_2$. The perdeuterated diiodide, $(CD_3)_2N-CSeI_2-N(CD_3)_2$ (TMSU·I$_2$-d_{12}), and the ^{15}N-substituted compounds, $(CH_3)_2{}^{15}N-CSeI_2-{}^{15}N(CH_3)_2$ and $(CH_3)_2{}^{15}N-CSeBr_2-{}^{15}N(CH_3)_2$, were included in order to obtain the necessary amount of data.

A normal coordinate analysis (NCA) has been performed fitting 46 force constants to *ca.* 250 observed frequencies. Calculations of the electron density of TMSU and TMSU·Br$_2$ using the CNDO/2 method are reported.

STRUCTURE

TMSU·I$_2$ crystallizes in two forms (see experimental part) which, according to X-ray results[4] have quite different structures. The compound is most easily obtained as red plates crystallizing orthorhombic, space group *Pbcn*, with four molecules per unit cell located at special positions of symmetry C_2. Only the vibrational spectra of this form, shown in Fig. 1, are reported in this paper. The selenium atom is coplanar with the NCN plane, while the I−Se−I axis forms an angle of *ca.* 62° with this plane. The $(CH_3)_2N$ group is twisted relative to this plane by almost the same amount as in TMSU.[2]

The yellow TMSU·Br$_2$ is isostructural with the TMSU·I$_2$ plates (*Pbcn*). The cell dimensions are $a = 13.71$, $b = 7.33$, and $c = 10.12$ Å (*cf.* the diiodide, $a = 14.21$, $b = 7.38$, and $c = 10.90$ Å). The C=Se bonds are parallel to the *b*-axis; in agreement with this *b* is almost identical in the bromide and the

iodide. The shortening of the unit cell is pronounced along a and c corresponding to the orientation of the $I-Se-I$ bonds of TMSU·I_2. Hence, similar structures can be assumed for the bromide and the iodide. Using the difference Fourier map as a guide, the hydrogen atoms were placed tetrahedrally around carbon. Standard $C-H$ distances and retention of C_2-symmetry also in solution has been assumed. The final coordinates may be obtained from the authors on request.

EXPERIMENTAL

Instrumental. The techniques and equipment used for recording the IR and Raman spectra have previously been described in some detail.[1,2] For the purpose of IR polarization measurement, single crystals of TMSU·I_2 were grown from methanol solutions and a flat specimen of about 0.5 mm thickness selected. Since the crystal is very small the spectrum was recorded using a beam condenser. It was not possible to avoid some stray light and due to the dark, red colour of the sample a rather broad slit had to be used. Accordingly the bands were quite broad and not suitable for quantitative determination of the dichroic ratios. Nevertheless, very useful qualitative information was obtained from the observed dichroism.

Chemicals. TMSU and TMSU-d_{12} were prepared as described previously[2] while the ^{15}N-labelled compound was obtained by a new method[5] especially convenient for synthesis on a small scale. The dimethylamine-^{15}N hydrochloride used as starting material in the latter preparation was of 97.0 % isotopic purity.

Equimolar portions of TMSU and iodine were dissolved separately in hexane at room temperature. When the solutions were combined a dark red oil immediately precipitated which, on prolonged scratching with a spatula, slowly transforms into a brick-red crystalline compound. In order to investigate the oil initially formed, a Raman spectrum was recorded in the region below 200 cm^{-1} in CH_2Cl_2 and benzene solutions. In addition to a band near 114 cm^{-1} (I_3^-) a weak band occurred at 149 cm^{-1} which slowly disappeared. A similar band was observed in the spectrum of the charge transfer compound between tetramethylthiourea and iodine[3] and we, therefore, believe the red oil to be an analogous compound. However, since selenium is easier to oxidize than sulfur this is unstable and rearranges to the covalently bonded TMSU·I_2.

The TMSU·I_2 is conveniently recrystallized from methanol. By accident, the first experiment resulted in the formation of long, red needles, but

in all later experiments the compound was instead obtained as plates. Attempts to control the formation of these two forms by varying the rate of cooling and the interval of temperature were not successful. The two crystalline forms show virtually identical melting points and depression was not observed on mixing (m.p. 115–116°). The C, H and N analyses agree with the calculated values. The isotopically substituted compounds were prepared in an identical way. The overall yield was 80–90 %. The yellow TMSU·Br_2 was also prepared from the components, but in this case the crystalline compound precipitated directly without transient formation of an oil.

NORMAL COORDINATE ANALYSIS

The normal vibrations were calculated for TMSU·Br_2 and TMSU·I_2 assuming a 22-atom model of C_2 symmetry. The internal coordinates correspond to the changes in bond lengths and bond angles (Fig. 1). The symmetry coordinates and the secular equations were set up as described for TMTU[1] and TMSU.[2] Preliminary calculations were performed by transferring the GVFF of TMSU and using arbitrary values for the SeX$_2$ (X=Br,I) group. These indicated that with the exception of the force constants pertaining to the C-SeX$_2$ group, the spectra of TMSU·Br_2 and TMSU·I_2 could be

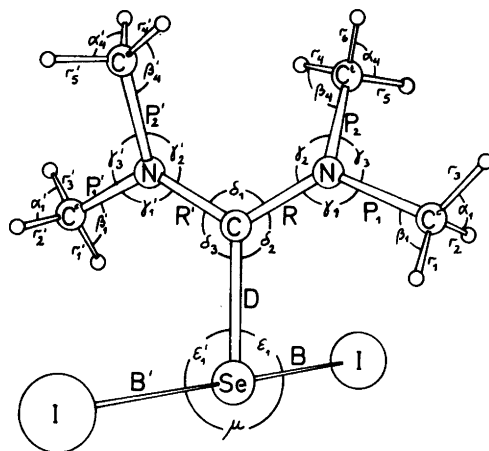*Fig. 1.* Internal coordinates for tetramethylselenourea diiodide. The following coordinates are not shown on the figure: CH_3-N torsion τ_1 and τ_2, $C-N$ torsion τ_3, $C-Se$ torsion τ_4, CSe out-of-plane bending Δ and $I-Se-I$ out-of-plane bending Γ.

reproduced with reasonable accuracy using identical GVFF's for the two molecules. In the final GVFF (Table 1), eight force constants which could only be poorly determined were instead transferred from TMSU. The remaining 38 force constants, including 28 common to and 5 specific for TMSU·Br₂ and TMSU·I₂, were allowed to vary until a converging set was obtained. The average error between the

Table 1. Final valence force constants for tetramethylselenourea diiodide.

Force type	Constants symbol	Group (X=Br,I)	Coordinates involved	Atoms common to interacting coordinates	Value[a] TMSU·I₂/[b] TMSU·Br₂	TMSU[c]
Stretch	K_r	CH₃ᶜ(CH₃ᵗ)	C−H		4.785	4.745
	K_{P_1}	CH₃ᶜ−N	C−N		4.737	4.789
	K_{P_2}	CH₃ᵗ−N	C−N		4.899	5.469
	K_R	N−CSe	N−C		6.624	6.148
	K_D	C−Se	C−Se		3.124/3.413	3.265
	K_B	Se−X	Se−X		0.701/0.734	
Stretch-stretch	F_r	CH₃ᶜ(CH₃ᵗ)	C−H, C−H	C	0.0798	0.0726
	$F_{P_1P_2}$	CH₃ᶜ−N−CH₃ᵗ	C−N, N−C	N	0.328[d]	0.328
	F_{RP_1}	CH₃ᶜ−N−CSe	C−N, N−C	N	0.298[d]	0.298
	F_{RP_2}	CH₃ᵗ−N−CSe	C−N, N−C	N	1.230[d]	1.230
	F_R	N−CSe−N	N−C, C−N	C	2.767	1.954
	F_{RD}	N−C−Se	N−C, C−Se	C	0.458[d]	0.458
	F_B	X−Se−X	X−Se, Se−X	Se	0.457/0.471	
Bend	H_α	CH₃ᶜ(CH₃ᵗ)	∠HCH		0.528	0.541
	H_β	CH₃ᶜ−N(CH₃ᵗ−N)	∠HCN		0.642	0.676
	H_{γ_1}	CH₃ᶜ−N−CSe	∠CNC		0.905	1.077
	H_{γ_2}	CH₃ᵗ−N−CSe	∠CNC		1.884	2.622
	H_{γ_3}	CH₃ᶜ−N−CH₃ᵗ	∠CNC		1.342	1.257
	H_{δ_1}	N−CSe−N	∠NCN		0.921	0.907
	H_{δ_2}	N−C−Se	∠NCSe		1.330	0.814
	H_Δ	N−CSe−N	∠N₂CSe		0.253[d]	0.253
	H_ϵ	C−Se−X	∠CSeX		0.169/0.385	
	$H_\mu = H_\Gamma$	X−Se−X	∠XSeX		0.249/0.281	
Stretch-bend	$F_{P_1\beta}$	CH₃ᶜ−N	C−N, ∠HCN	C−N	0.198	0.227
	$F_{P_2\beta}$	CH₃ᵗ−N	C−N, ∠HCN	C−N	0.306	0.302
	$F_{P_1\gamma_1}$	CH₃ᶜ−N−CSe	Cᶜ−N, ∠CᶜNC	Cᶜ−N	0.685	1.040
	$F_{P_1\gamma_3}$	CH₃ᶜ−N−CH₃ᵗ	Cᶜ−N, ∠CᶜNCᵗ	Cᶜ−N	0.488	0.619
	$F_{P_2\gamma_2}$	CH₃ᵗ−N−CSe	Cᵗ−N, ∠CᵗNC	Cᵗ−N	0.545	0.569
	$F_{P_2\gamma_3}$	CH₃ᵗ−N−CH₃ᶜ	Cᵗ−N, ∠CᵗNCᶜ	Cᵗ−N	0.353	0.736
	$F_{R\gamma_1}$	CH₃ᶜ−N−CSe	N−C, ∠CᶜNC	N−C	1.112	1.172
	$F_{R\gamma_2}$	CH₃ᵗ−N−CSe	N−C, ∠CᵗNC	N−C	1.791	1.960
	$F_{R\delta_1}$	N−CSe−N	N−C, ∠NCN	N−C	0.487[d]	0.487
	$F_{R\delta_2}$	N−C−Se	N−C, ∠NCSe	N−C	0.942	0.598
	$F_{R\delta_3}$	N−CSe−N'	N−C, ∠N'CSe	C	0.384	0.169
	$F_{D\delta_1}$	N−CSe−N	C−Se, ∠NCN	C	0.314[d]	0.314
	$F_{D\delta_2}$	N−C−Se	C−Se, ∠NCSe	C−Se	0.366[d]	0.366
Bend-bend	F_β	CH₃ᶜ−N(CH₃ᵗ−N)	∠HCN, ∠HCN	C−N	−0.0572	−0.0605
Torsion	H_{τ_1}	CH₃ᶜ−N	CH₃ᶜ−N		0.026	0.032
	H_{τ_2}	CH₃ᵗ−N	CH₃ᵗ−N		0.034	0.034
	H_{τ_3}	(CH₃)₂N−C'Se	N−C'		1.017	1.099
	H_{τ_4}	C−SeX₂	C−SeX₂		0.354	

[a] In units of mdyn/Å (stretch constants), mdyn/rad (stretch-bend interaction constants) and mdyn·Å/(rad)² (bending and torsion constants). [b] In cases where identical force constants were used only one figure is given. [c] Transferred from Ref. 2. [d] Transferred from TMSU and not varied.

calculated and the observed frequencies is less than 1.1 % for each species in the compounds.

A total of 4 force constants have been used for describing the motions of the $-SeX_2$ group, $i.e.$ a $Se-X$ stretching force constant (K_B), an interaction force constant between the two $Se-X$ stretching (F_B), a $C-Se-X$ deformation constant (H_ε) and an $X-Se-X$ deformation constant $(H_\mu=H_r)$. It has previously been shown [6] that the use of identical values for the in-plane (H_μ) and the out-of-plane (H_r) $X-Se-X$ deformation constants is a valid approximation. However, the evaluation of these force constants depends entirely upon a correct assignment of the spectra in the region below 200 cm^{-1}. Since the observed data are far from sufficient we have relied heavily upon assignments of analogous vibrations in tellurium,[7-9] antimonium,[10] and selenium compounds.[11] One of us has recently[6,12] reported simplified force constant calculations for some analogous tellurium compounds in which the $C-TeX_2$ group also has a T-shaped geometry. It was found that the $Te-Br$ stretching force constant was somewhat higher (0.73 mdyn/Å) than the $Te-I$ stretching force constant (0.66 mdyn/Å) assuming identical values for the interaction force constant $(Te-X/Te-X=0.29$ mdyn/Å). Similarly it was found,[6] that the bending force constant of $Br-Te-Br$ was higher [0.68 mdyn Å/(rad)^2] than that of $I-Te-I$ [0.40 mdyn Å/(rad)^2]. A hint of the value of the $C-Se-X$ bending force constants can be obtained from comparison with the reported values for $C-Sb-Br$ and $C-Sb-I$[13] of 0.30$-$0.65 mdyn Å/(rad)^2. The values obtained from TMSU·Br$_2$ and TMSU·I$_2$

(Table 1) agree with the reported trends except that the deformation force constants seem to be somewhat lower [0.17$-$0.38 mdyn Å/(rad)^2], and the interaction force constants F_B somewhat higher (0.46$-$0.47 mdyn/Å).

RESULTS AND DISCUSSION

The IR spectra of TMSU·I$_2$ and TMSU·Br$_2$ are almost identical except in the region below 200 cm^{-1}, therefore only the latter spectrum is reproduced in Fig. 2. The observed frequencies, together with the shifts found by comparison with the spectrum of ^{15}N-substituted TMSU·I$_2$, are listed in the first columns of Table 2. The corresponding calculated values with a tentative assignment and description of the normal modes are given in the last columns of the Table. If the results from Fig. 2 and Table 2 are compared with those reported for TMSU[2] it will be evident that the patterns observed, the assignments and the descriptions are quite similar. We have, therefore, felt justified in listing the TMSU-shifts (Table 2), $i.e.$ the frequency change for bands of almost similar PED on going from TMSU to TMSU·I$_2$. The results obtained for TMSU·I$_2$-d_{12} can be found in Table 3. Finally we have obtained vibrational data of TMSU·Br$_2$ which includes both IR and Raman frequencies. These are compared with the calculated values in Table 4.

The results summarized in Tables 2$-$4 are very similar to those reported previously for TMTU,[1] TMSU,[2] and addition compounds of TMTU,[3] and
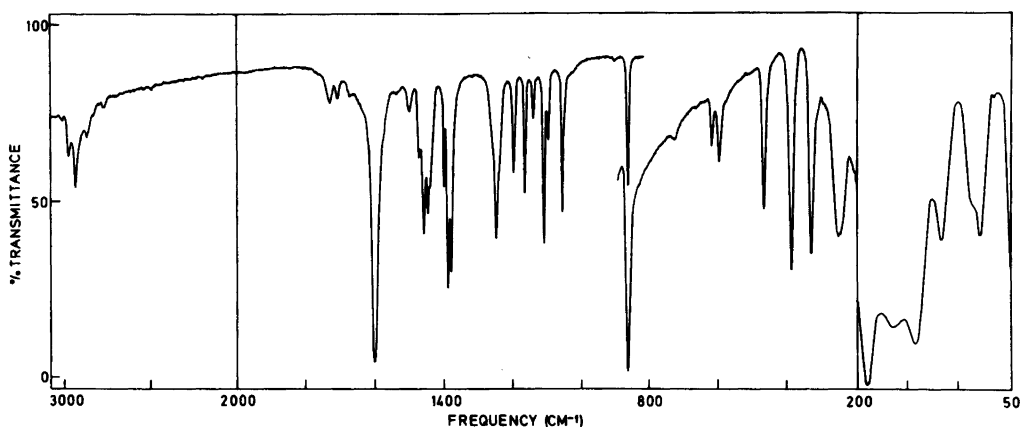

Fig. 2. Infrared spectrum of tetramethylselenourea dibromide in the solid state.

Table 2. Observed and calculated infrared frequencies (cm^{-1}) of tetramethylselenourea diiodide, frequency shifts obtained by comparison with tetramethylselenourea and $(CH_3)_2{}^{15}N-CSeI_2-{}^{15}N(CH_3)_2$, tentative assignments of the spectra, and description of the fundamentals.[a]

Observed								Calculated [e]			Assignment and description [f]
Solid			Solution [c]	TMSU-shift [d]		¹⁵N-shift		Fre-quency	TMSU-shift	¹⁵N-shift	
Disc [b]	Nujol	Polarization		Disc	Sol.	Disc	Sol.				(PED,%) [g]
3008vw				+6		0					
								2981	+13	0	ν_1a, ν_{31}b, νCH(99)
2959m			2974m	+22	+19	0	0	2977	+13	0	ν_2a, ν_{32}b, νCH(99)
								2976	+13	0	ν_3a, ν_{33}b, νCH(99)
								2975	+13	0	ν_4a, ν_{34}b, νCH(99)
2920m			2933m	+2	0	0	0	2931	+8	0	ν_5, ν_6a, ν_{35}, ν_{36}b, νCH(100)
2905m,sh			2905m,sh		+4	0	0				
2865w			2880w,sh	-2	-6	0	0				
2856w,sh			2866w,sh	+6	+3	0	0				
2825w			2838vw	+3	+5	3	2				
2795vw			2811vw	-2	+8	3	3				
2768w			2771vw			10	0				
1646w,sh											
1604s,sh	1603s,sh										
1597vs	1593vs,br		1596vs	+84	+79	20	21	1589	+83	16	ν_7a, ν_sN$_2$CSe(59), δCH$_3$NC(15), δNCN(17)
1574s,sh			1571s,sh				20				
1530vvw						10					
1493m	1492m		1493m	+3	+8	11	8				
								1465	-6	1	ν_{37}b, δ_{as}CH$_3$(93)
1465m,sh			1463s	+2	-2	0	0	1460	-9	0	ν_{38}b, δ_{as}CH$_3$(99)
								1460	-7	0	ν_8a, δ_{as}CH$_3$(100)
								1458	-7	0	ν_9a, ν_{39}b, δ_{as}CH$_3$(99)
1457s						2		1455	-7	0	ν_{10}a, ν_{40}b, δ_{as}CH$_3$(100)
1447m						1					
1438m	1438s,br		1444s	+5	+5	2	0	1453	+6	1	ν_{11}a, δ_{as}CH$_3$(94)
1417vw	1417w,sh		1413w,sh								
1410vw	1410vw		1409w		+3		0				
1400m	1403w,sh			-1		0					
1388s	1392m		1395s	+15	+17	4	3	1393	+9	5	ν_{41}b, δ_{as}CH$_3$(36), ν_{as}CN(25), νCH$_3$N(13), δNCSe(13)
								1382	+23	1	ν_{12}a, δ_sCH$_3$(98)
1377s	1385m		1380s	+17	+25	16/6	18/7	1380	+26	5	ν_{42}b, δ_sCH$_3$(86), νCH$_3$N(18)
								1343	+10	5	ν_{43}b, δ_sCH$_3$(86)
1340w,sh								1341	-2	1	ν_{13}a, δ_sCH$_3$(101)
1318vw,sh	1318vw,sh										
1254s,sh				-15							
1245s	1250s		1258s	-18	-10	25	26	1257	-9	23	ν_{14}a, νCH$_3$N(31), ρCH$_3$(40,), δCH$_3$NC(29)

[a] The following abbreviations have been used: s, strong; m, medium; w, weak; br, broad; sh, shoulder. Weak bands in the region above 1600 cm^{-1} have been omitted. [b] Mean values from KBr, KI and CsI stated. Below 500 cm^{-1} the spectra were also recorded in polyethylene. [c] Mean values from CH$_2$Cl$_2$, CD$_2$Cl$_2$ and CH$_2$Br$_2$ solutions. [d] The stated shifts are the changes in the corresponding bands of TMSU on addition of iodine to give TMSU·I$_2$. [e] Iteration based upon all isotopic species. [f] Abbreviations: ν=stretching; δ,Δ=deformation; ρ=rocking; ω=wagging; τ=torsion; and, as subscripts, s=symmetric; as=antisymmetric. [g] The potential energy distribution (PED) is defined as $x_{ik}=100F_{ii}L_{ik}^2/\lambda_k$. The stated PED's are only approximate and small contributions have been neglected.

Table 2. Continued.

1230m,sh				1228vw	−21							
1196m	1194m			1204m	−4	−5	15	15	1198	−5	12	ν_{44}b, ρCH$_3$(37), νCH$_3$N(22), τCN(15), ν_{as}CN(12)
1167m,sh												
1161s	1167s			1163s	+14		4	4	1161	+6	7	ν_{45}b, ρCH$_3$(78), νCH$_3$N(12), δCH$_3$NC(16)
1138w	1137w,br			1136w	+9		4	3	1137	+6	8	ν_{15}a, ρCH$_3$(54), νCH$_3$N(34)
1106s	1105s			1104s	−4	−1	2	1	1107	−1	4	ν_{16}a, ρCH$_3$(95)
1094s	1093s			1094s	+12	+8	2	2	1101	0	4	ν_{46}b, ρCH$_3$(89), ν_{as}CN(8)
1066w	1064m											
1055s	1053s			1058m	−1	+2	4	4	1058	−4	0	ν_{47}b, ρCH$_3$(96)
1051m,sh	1047m,sh			1055m,sh	−5	−1	7	7	1055	−2	0	ν_{17}a, ρCH$_3$(99)
									1016	−7	4	ν_{18}a, ρCH$_3$(69), νCH$_3$N(30)
1018vw				1019vw		−4		0				
									1011	−6	4	ν_{48}b, ρCH$_3$(64), νCH$_3$N(30)
974vw	974vw	965vw	B	974vw				0				
908w,sh	921vw	932vw	A		−14		4		918	−10	7	ν_{19}a, νCH$_3$N(60), ρCH$_3$(28)
902w	900m	900m	B	912m	−10		4	3	907	0	3	ν_{49}b, νCH$_3$N(39), τCN(24)
	867s,sh	870s	B									
863s	861s	860s	B	869s	−10	−10	4	5	865	−16	5	ν_{50}b, νCH$_3$N(85)
720vw,br		698m	A				12					
	615vw,sh	628w,sh		622w				2				
612w	611vw	612m	?	609w	−16	−19	0	2				
595w	595w	595m	?	598w	+1	−2	4	5	600	−9	4	ν_{20}a, ν_sCN(34), νCH$_3$N(27), δCH$_3$NC(35)
570vw	565vw,sh	566w	A	560vw			12					
465m	471w	470m	?	474w	−14	−13	3	2	476	−13	2	ν_{51}b, δCH$_3$NC(95)
	458vw,sh	452w,sh										
412vw	418vw,sh	419vw			−11				419	−5	6	ν_{52}b, δCH$_3$NC(81)
402w	400vw,sh	405w	A		−4				398	−15	2	ν_{21}a, δCH$_3$NC(66), ν_sN$_2$CSe(15)
385m	372m	375w	A	374m	−1	−7	4	4	369	−6	3	ν_{22}a, νCSe(35), δCH$_3$NC(35)
372w,sh		366w	B									
356w,sh		350vw										
330m		320w		322m	+22	+18	6	6	318	+15	6	ν_{23}a, νCSe(32), τCN(20), δNCN(12), δNCSe(9)
262m,sh		268vw					2?					
250m		238m		239m	−2		5	2				
202w,br				205vw	0			0				
190vw,sh							0					
172vw									176	−10	0	ν_{24}a, τCN(61), δCH$_3$NC(16)
163vw									166	+18	1	ν_{53}b, δNCSe(83), ν_{as}SeI(11)
									143		0	ν_{54}b, τCH$_3$(60), ν_{as}SeI(13)
137s									137		0	ν_{25}a, τCH$_3$(82)
132s,sh									132		0	ν_{55}b, τCH$_3$(45), ν_{as}SeI(15)
									125		0	ν_{26}a, ν_sSeI(100)
125m									125		0	ν_{56}b, ν_{as}SeI(13), τCH$_3$(82)
116w									117		0	ν_{27}a, τCH$_3$(93)
95vw									93		0	ν_{57}b, ν_{as}SeI(45), τCN(12)

Table 2. Continued.

86w			
66w,sh	68	0	ν_{28}a, τCSe(55), δCH$_3$NC(32)
58m			lattice mode
50m,sh	50	0	ν_{29}a, δISeI(58), δCSeI(21)
42w	41	0	ν_{58}b, δCSeI(71)
	13$-$30		ν_{30}a, ν_{59}, ν_{60}b, δCH$_3$NC, δCSeI, δISeI, ΔCSe

Table 3. Observed and calculated infrared frequencies (cm^{-1}) of perdeuterotetramethylselenourea diiodide, frequency shifts obtained by comparison with perdeuterotetramethylselenourea, tentative assignments of the spectra, and description of the fundamentals.[a]

Observed		TMSU-shift, observed[d]		Calculated[e]		Assignment and description[f] (PED,%)[g]
Solid, disc[b]	Solu-tion[c]	Disc	Solu-tion	Fre-quency	TMSU-shift	
2950m	2945m	+20				
2504w	2510w					
2385w	2396w	−35	−36			
2268w	2268w	+9				
2249w		−4				
2226m	2230m	−7	−4	2234	+9	ν_1a, νCD(96)
				2224	+10	ν_2a, νCD(97)
				2221	+11	ν_3a, νCD(98)
				2220	+12	ν_4a, νCD(98)
				2234	+10	ν_{31}b, νCD(96)
				2224	+10	ν_{32}b, νCD(97)
2217m		+8		2222	+12	ν_{32}b, νCD(98)
				2220	+12	ν_{34}b, νCD(98)
2177w		−15				
2134m	2140m	0	+7			
2106m	2111w	−2	+2	2114	0	ν_{35}b, νCD(98)
				2112	0	ν_{36}b, νCD(98)
2086w	2090w	+3	+4			
2068m	2071m	+1	−2	2114	0	ν_5a, νCD(98)
				2112	0	ν_6a, νCD(98)
1664vw	1668vw	+2	−2			
1637w	1645w	+17				
1570vs						
1565vs	1561vs	+117	+108	1575	+106	ν_7a, ν_sN$_2$CSe(67), δCD$_3$CN(15), δNCN(9)
1515m,sh	1529s					
1475vw,sh	1461vw					
1435vw	1433vw,sh					
1401s,sh						
1394s	1396s	+47	+47	1385	+30	ν_{37}b, ν_{as}CN(36), νCD$_3$N(25), δCD$_3$CN(22)
	1385s,sh					
1315w	1309w	+5	+2			
1233s,sh						

[a−g] See footnotes to Table 2.

Table 3. Continued.

1229s	1235s	−15	−13	1237	−10	ν_8a, $\nu CD_3N(72)$, $\delta CD_3CN(23)$, $\nu CN(14)$
1165m	1172m	−17	−16	1180	−9	$\nu_{38}b$, $\nu CD_3N(31)$, $\tau CN(19)$, $\nu_{as}CN(14)$, $\delta CD_3(27)$
	1133vw,br					
1112s	1113m,sh	−2	−4	1127	+11	$\nu_{39}b$, $\delta CD_3(60)$, $\nu CD_3N(38)$
1104s	1108s	−10	−9	1103	−8	ν_9a, $\delta CD_3(64)$, $\nu CD_3N(55)$
1089w,sh	1096w,sh		−2			
	1068m,sh					
1066m	1064m,sh	+3	−5	1058	−7	$\nu_{40}b$, $\delta CD_3(90)$
				1055	+1	$\nu_{10}a$, $\delta CD_3(80)$, $\nu CN(8)$
1055m	1057m	+3	+1	1049	+2	$\nu_{11}a$, $\delta CD_3(97)$
				1048	−1	$\nu_{41}b$, $\delta CD_3(97)$
				1046	−1	$\nu_{12}a$, $\delta CD_3(99)$
1043m	1046m	−4	−3	1044	−2	$\nu_{42}b$, $\delta CD_3(98)$
				1043	−2	$\nu_{13}a$, $\delta CD_3(99)$
				1040	0	$\nu_{43}b$, $\delta CD_3(97)$
1039m,sh		+1		1042	+5	$\nu_{14}a$, $\delta CD_3(96)$
				1038	+1	$\nu_{44}b$, $\delta CD_3(95)$
977m	977w,br	−15	−13	970	0	$\nu_{45}b$, $\rho CD(71)$, $\delta CD_3CN(25)$
948m	951m	−14	−13	966	+7	$\nu_{15}a$, $\rho CD(67)$, $\nu CD_3N(10)$
942m						
909m	910m	−2	+3	910	−6	$\nu_{46}b$, $\rho CD(59)$, $\nu CD_3N(21)$, $\nu_{as}CN(15)$
876vw	863vw	−7		880	−3	$\nu_{16}a$, $\rho CD_3(95)$
840m,sh						
830m	836m	−2	+2	832	−4	$\nu_{47}b$, $\rho CD_3(80)$, $\tau CN(9)$
814w	813w	+1		806	−6	$\nu_{17}a$, $\rho CD_3(97)$
808w		+4		793	−9	$\nu_{18}a$, $\rho CD_3(84)$, $\nu CD_3N(11)$
		+4		792	−11	$\nu_{48}b$, $\rho CD_3(82)$, $\nu CD_3N(14)$
777m,sh	778m	−2		782	+4	$\nu_{49}b$, $\rho CD_3(76)$, $\nu CD_3N(9)$
774m				765	−9	$\nu_{19}a$, $\rho CD_3(54)$, $\nu CD_3N(30)$
755w,sh		−5		744	−11	$\nu_{50}b$, $\rho CD_3(40)$, $\nu CD_3N(49)$
	607w					
597w	596vw	−18	−19			
539w	540w	+2	0	527	−7	$\nu_{20}a$, $\nu_s N_2CSe(40)$, $\delta CD_3NC(24)$, $\nu CD_3N(19)$
409m	410w	−9	−12	401	−16	$\nu_{51}b$, $\delta CD_3NC(75)$, $\rho CD_3(14)$
374vw				374	+2	$\nu_{52}b$, $\nu_{as}CN(53)$, $\delta CD_3NC(81)$
350w		−16		355	−17	$\nu_{21}a$, $\nu CSe(34)$, $\delta CD_3NC(43)$
333m	332w	−9	−8	331	0	$\nu_{22}a$, $\delta CD_3NC(55)$, $\nu CSe(19)$
295m		+12		301	+16	$\nu_{23}a$, $\tau CN(27)$, $\delta NCN(15)$, $\delta NCSe(11)$, $\nu CSe(13)$
265m						
233w,sh						
220m						
198w,sh						
176vw,sh						
163vw,sh				158		$\nu_{53}b$, $\delta NCSe(73)$, $\nu_{as}SeI(15)$
				155		$\nu_{24}a$, $\tau CN(58)$, $\delta CD_3NC(17)$
142s						
134s				132		$\nu_{54}b$, $\nu_{as}SeI(35)$, $\Delta CSe(17)$, $\tau CSe(13)$
124m,sh				124		$\nu_{25}a$, $\nu_s SeI(100)$
114w,sh						
101w,sh				102		$\nu_{26}a$, $\tau CD_3(74)$
				101		$\nu_{55}b$, $\tau CD_3(89)$
				96		$\nu_{56}b$, $\tau CD_3(54)$, $\nu_{as}SeI(24)$
87vw				84		$\nu_{27}a$, $\tau CD_3(93)$
79w				82		$\nu_{57}b$, $\tau CD_3(44)$, $\nu_{as}SeI(23)$
68w						
58m				60		$\nu_{28}a$, $\tau CSe(34)$, $\delta ISeI(28)$, $\delta CD_3NC(20)$
49m				48		$\nu_{29}a$, $\delta ISeI(42)$, $\tau CSe(33)$, $\delta CSeI(14)$
39vw				37		$\nu_{58}b$, $\delta CSeI(71)$
				10−26		$\nu_{30}a$, ν_{59}, $\nu_{60}b$, δCD_3NC, $\delta CSeI$, $\delta ISeI$, ΔCSe

Table 4. Observed and calculated vibrational frequencies (cm⁻¹) of tetramethylselenourea dibromide, frequency shifts obtained by comparison with tetra-methylselenourea and $(CH_3)_2{}^{15}N-CSeBr_2-{}^{15}N(CH_3)_2$, tentative assignments of the spectra, and description of the fundamentals.[a]

Infrared Disc[b]	Infrared Solution[c]	TMSU-shift[d] Disc	TMSU-shift[d] Sol.	¹⁵N-shift Disc	¹⁵N-shift Sol.	Raman Solid	Raman Solution[c]	Calc.[e] Frequency	Calc.[e] TMSU-shift	Calc.[e] ¹⁵N-shift	Assignment and Description[f] (PED, %)[g]
3004w		+2		0		3012					
2970m	2980m	+33	+25	0	2	2976m		2981	+13	0	$\nu_1 a, \nu_{31} b, \nu CH(99)$
								2977	+13	0	$\nu_2 a, \nu_{32} b, \nu CH(99)$
2947m,sh	2960m,sh							2976	+13	0	$\nu_3 a, \nu_{32} b, \nu CH(99)$
2930m	2935m	+10	+2	0	0	2941m	2939m	2975	+13	0	$\nu_4 a, \nu_{34} b, \nu CH(99)$
2908m,sh	2906vw,sh	+4	+5	0	0	2906s	2901m	2931	+8	0	$\nu_5 a, \nu_6 a, \nu_{35}, \nu_{36} b, \nu CH(100)$
2871w	2869vw,sh	+10	−17	0	1	2866m	2861m				
2860w,sh											
2828w	2813vw	+6	−20	0	3						
2797vw		0		0		2800w					
2772w	2773vw			11	0	2779vw					
2764w				6							
1664w,sh				18							
1602vs,sh											
1596vs	1601vs	+83	+84	20	22	1597m	1594w,br	1598	+92	17	$\nu_7 a, \nu_5 N_2 CSe(61), \delta CH_3 NC(14), \delta NCN(15)$
1573m,sh	1578m,sh			20							
1538w,br	1528vw			10							
1496m	1493m	+6	+8	10	9	1501w		1466	−5	1	$\nu_{37} b, \delta_{as}CH_3(93)$
								1461	−8	1	$\nu_{38} b, \delta_{as}CH_3(99)$
1472m	1463m	+9	−2	0	0	1472m	1471w,sh	1460	−7	0	$\nu_8 a, \delta_{as}CH_3(100)$
								1458	−7	0	$\nu_9 a, \nu_{39} b, \delta_{as}CH_3(99)$
1459s	1469w,sh	−4	−5	3		1455m	1458w	1455	−7	0	$\nu_{10} a, \nu_{40} b, \delta_{as}CH_3(199)$
1447m	1444m	−9		0		1451m,sh					
1440m,sh	1438m,sh	+7	−1	0	0	1435m	1443w	1453	+6	0	$\nu_{11} a, \delta_{as}CH_3(96)$
1412w,sh				0		1426vw					
1401m	1410w	−1	+4	0	0	1404m		1392	+8	7	$\nu_4 b, \delta_s CH_3(29), \nu_{as}CN(26), \nu CH_3 N(18), \delta NCSe(12)$
1389s	1397s	+16	+19	3	1			1381	+22	1	$\nu_{12} a, \delta_s CH_3(97)$
1377s	1385s	+17	+30	15	17/7	1380vs	1383s,P	1380	+26	5	$\nu_{42} b, \delta_s CH_3(93), \nu CH_3 N(17)$
1367w,sh											

[a,b,d–g] see footnotes to Table 2. [c] Mean values from $CHCl_3$, CH_2Cl_2, CD_2Cl_2, CH_2Br_2 and dimethylsulfoxide.

Table 4. Continued.

ν (IR)	Δ	ν (IR)	Δ	ν (Raman)	ν (Raman)	ν (calc)	Δ	%	Assignment
1340w,sh	+19	1340w,sh		1335w	1327w,sh	1345	+12	5	$\nu_{43}b,\ \delta_s CH_3(88)$
						1343	0	0	$\nu_{13}a,\ \delta_s CH_3(101)$
1292vw,sh		1276vw,sh	−9	1274vw	1258w,br				
1260m,sh	−14	1259m		1243w		1257	−9	23	$\nu_{14}a,\ \nu CH_3N(32),\ \rho CH_3(40),\ \delta CH_3NC(28)$
1249s	−13								
1238m,sh									
1197m	−3	1205w	−4		1202	1202	−1	11	$\nu_{44}b,\ \rho CH_3(36),\ \tau CN(18),\ \nu CH_3N(15),\ \nu_{as}CN(15)$
1166m,sh		1166m,sh							
1162m	+15	1164m		1164w	1160w,br	1161	+6	7	$\nu_{45}b,\ \rho CH_3(78),\ \nu CH_3N(10),\ \delta CH_3NC(16)$
1140w	+11	1137w		1142m	1134w,sh	1137	+6	8	$\nu_{15}a,\ \rho CH_3(60),\ \nu CH_3N(29)$
1111m,sh		1118vw,sh							
1104s	−6	1107m	+2	1107m	1102m,P	1108	0	4	$\nu_{16}a,\ \rho CH_3(96)$
1096s	+14	1097w,sh	+11	1095s	1094w	1099	−2	3	$\nu_{46}b,\ \rho CH_3(88),\ \nu_{as}CN(10)$
1075w		1075w							
1056s	0	1059m	+3	1056m	1060w	1061	−1	0	$\nu_{47}b,\ \rho CH_3(97)$
1052s,sh	−4	1054m,sh	+2			1056	−1	0	$\nu_{17}a,\ \rho CH_3(99)$
1020vw		1020vw		1018w	1018w	1016	−7	5	$\nu_{18}a,\ \rho CH_3(67),\ \nu CH_3N(32)$
						1011	−6	3	$\nu_{48}b,\ \rho CH_3(68),\ \nu CH_3N(20)$
906vw	−6	912vw	−6	906m	905m,P	921	−7	6	$\nu_{19}a,\ \nu CH_3N(63),\ \rho CH_3(25)$
875s	+1	869m	−10	866m	865w,D	909	+2	4	$\nu_{49}b,\ \nu CH_3N(56),\ \tau CN(15)$
						868	−13	5	$\nu_{50}b,\ \nu CH_3N(81)$
726vw,br		726vw,br							
620w	−8	620w	−8	620w	618w,D?	603	+6	4	$\nu_{20}a,\ \nu_s CN(35),\ \nu CH_3N(22),\ \delta CH_3NC(38)$
598w	+4	600vw	0	599s	600m,P				
578vw,br		578vw,br							
468m	−11	473w	−14		487w	477	−12	2	$\nu_{51}b,\ \delta CH_3NC(98)$
442vw,sh		442vw,sh							
406vw		406vw		402s	402m,P	418	−4	6	$\nu_{52}b,\ \delta CH_3NC(69)$
				385w,sh	390w,sh	401	−12	2	$\nu_{21}a,\ \delta CH_3NC(59),\ \nu_s N_2CSe(20)$
391s	+5	377m	−4	363s	365w	376	+1	1	$\nu_{22}a,\ \nu CSe(39),\ \delta CH_3NC(39)$
338m		337w,sh		332m,sh	340w				
333m	+25	325m	+21	322m	322w	323	+20	7	$\nu_{23}a,\ \nu CSe(16),\ \tau CN(27),\ \delta NCN(16),\ \delta NCSe(11)$
292vw,sh				295vw					
256s	+4	257w,sh		261m,br	260w,br				
242m,sh		242m,br		252m,br	250m,sh				
231w		230vw,br		236w,br	233w				
209vw		210vw,sh		210w,sh	205w,sh				
					190w,sh				

Table 4. Continued.

						Assignment
185s	178w,br	180m,sh,	$\left\{\begin{array}{l}179\\173\end{array}\right.$	-7	0	$\nu_{24}a$, $\tau CN(58)$, $\delta CH_3NC(14)$
182s					0	$\nu_{53}b$, $\delta NCSe(37)$, $\nu_{as}SeBr(23)$
163m	160vs	160s,P,	$\left\{\begin{array}{l}160\\154\end{array}\right.$		1	$\nu_{25}a$, $\nu_s SeBr(100)$
143s		142w,sh,	137		0	$\nu_{54}b$, $\nu_{as}SeBr(10)$, $\delta NCSe(37)$
	134w,sh		135		0	$\nu_{26}a$, $\tau CH_3(80)$
	129w,sh		127		0	$\nu_{55}b$, $\tau CH_3(71)$
116m	114w,sh		118		0	$\nu_{56}b$, $\tau CH_3(91)$
	108w,sh				0	$\nu_{27}a$, $\tau CH_3(93)$
	97s	95w	103		0	$\nu_{57}b$, $\nu_{as}SeBr(52)$
85m,sh	88w,br					lattice mode
78m		80vw?	80		0	$\nu_{28}a$, $\delta BrSeBr(44)$, $\delta CSeBr(30)$
ca. 63w	66s		61		0	$\nu_{29}a$, $\tau CSe(56)$, $\delta BrSeBr(12)$, $\delta CSeBr(8)$
	58m		58		0	$\nu_{58}b$, $\delta CSeBr(57)$, $\tau BrSeBr(14)$
0			13–30			$\nu_{30}a$, ν_{59}, $\nu_{60}b$, δCH_3NC, $\delta CSeBr$, $\delta BrSeBr$, ΔCSe

will not be discussed in detail. We believe that the satisfactory reproduction of most TMSU- and ^{15}N-shifts reflects the validity of the GVFF developed and the derived assignments. However, some systematic trends and points of ambiguity have emerged from these studies which deserve some comments and are dealt with below.

In the IR and Raman spectra of TMTU[1] a band of weak to medium intensity was observed at $666-668$ cm^{-1} (solution values) probably of species *b*. This was very characteristic by showing a ^{13}C-shift of *ca.* 20 cm^{-1}, which was the highest shift observed for any band in the spectra of TMTU. The results of the NCA indicated that provided this band was a fundamental it had to be $\nu_{47}b$ with a calculated ^{13}C-shift of 19 cm^{-1}, originating primarily in CH$_3$−N stretching and CN torsion. Since this assignment led to unrealistic force constants, ν_{47} was reluctantly assigned to a band at *ca.* 885 cm^{-1} displaying only a ^{13}C-shift of *ca.* 6 cm^{-1}.

It is now clear that a counterpart of the band at $666-668$ cm^{-1} in TMTU also occurs in the spectra of TMSU ($626-628$ cm^{-1}), TMSU$\cdot$Br$_2$ ($618-620$ cm^{-1}), and TMSU$\cdot$I$_2$ (622 cm^{-1}) which is definitely (polarized IR and Raman depolarization measurements) of species *b*. On deuteration it is displaced by $8-15$ cm^{-1} towards lower frequencies in the three cases investigated as expected if it was due partly to CH$_3$−N stretching. We have, therefore, reconsidered the possibility that this band should be assigned to the fundamental ν_{47} (TMTU, TMSU), respectively ν_{49} (TMTU$\cdot$Br$_2$, TMTU$\cdot$I$_2$). Calculations indicate this to be possible provided an interaction constant between torsion of the CN bonds (N−CX−N) is introduced. Unfortunately, we have not been able to reassign the other fundamentals of species *b* and simultaneously obtain an acceptable GVFF. Therefore, the question of the exact nature of this band cannot at present be definitely answered.

There are also some doubts regarding the assignment of $\nu_{24}a$, which is due mainly to CN torsion with small contributions from deformations around the dimethylamino groups. In TMTU[1] it was assigned to a polarized band of medium strength in the Raman spectrum in CHCl$_3$ at 162 cm^{-1} and this led to reasonable values for the force constants involved. However, a similar band has not been identified with certainty in any of the other compounds of this series. Instead we have left unassigned a medium to strong band at $256-261$ cm^{-1} in

TMSU·Br$_2$, 238 − 250 cm^{-1} in TMSU·I$_2$, and 219 cm^{-1} in N-d_{12}-TMSU·I$_2$, which might be attributed to v_{24}. A counterpart is also found in the spectra of TMTU/TMTU-d_{12} (269 − 277/232 − 240 cm^{-1}) and TMSU/TMSU-d_{12} (247 − 261/224 − 227 cm^{-1}) which in one instance has been definitely identified to be of species a (Raman depolarization measurements on TMSU-d_{12}).

An assignment of v_{24} to bands in the region above 200 cm^{-1} is contradicated by the values obtained for the GVFF in this case. Either the value for CN torsion should be raised to approximately 2 mdyn·Å/(rad)^2, which by all standards appears much too high, or the deformational force constants of the dimethylamino group be adjusted to higher values. However, these values are well determined by contributions to several other fundamentals the positions of which cannot be disputed. It was previously noted that the force constant for CN torsion was not raised for TMTU on S-methylation[3] even though all chemical and theoretical evidence clearly points to an increased importance of the structure $\overline{N} = C − \overline{S}$. We therefore tend to conclude that our NCA does not fare well in dealing with the CN torsional vibrations of these compounds.

Whereas the assignment of the vibrational frequencies of TMSU·Br$_2$ and TMSU·I$_2$ in the region above 200 cm^{-1} is reasonably clear, there are some doubts regarding the range between 40 and 200 cm^{-1}. A total of 12 fundamentals are calculated to fall in this region, 6 of each species. In the spectrum of TMSU 7 bands were located in this region, the essential features of which can be summarised as τCN (180 cm^{-1}), δNCSe (145 cm^{-1}), four τCH$_3$ bands (133 − 143 cm^{-1}), and out-of-plane CSe deformation (95 cm^{-1}). The 6 former bands are also observed (more or less coupled) in the spectra of TMSU·Br$_2$ and TMSU·I$_2$, but the out-of-plane CSe deformational vibration is displaced below 30 cm^{-1} due to the increase of the effective vibrating mass following halogenation of the selenium atom.

The 6 new bands of TMSU·Br$_2$ and TMSU·I$_2$ in this region include 3 of species a and 3 of species b. One of these, the symmetric Se − Br stretching mode of TMSU·Br$_2$, $v_{25}a$, was identified with certainty as the strong, polarized band at 160 cm^{-1} in the Raman spectrum. Since the NCA indicates this mode to be pure it is easy to predict the location of the corresponding Se − I stretching mode to the range 100 − 130 cm^{-1}. By analogy to TMSU·Br$_2$ it can further be predicted that the

band should be of medium strength in the IR and display no shift on deuteration. Therefore, the band at 125 cm^{-1} in the IR spectrum of TMSU·I$_2$ must be assigned to this fundamental $v_{26}a$. The asymmetric Se − Br and Se − I stretching frequencies could not be traced by a similar technique since the NCA shows heavy couplings to occur with other modes. The remaining bands of this region were, therefore, assigned by trial and error until a consistent solution was found. We wish to point out that this is by no means unique.

CNDO CALCULATIONS

We have previously reported[3] the changes in the vibrational spectra and force field of TMTU by conversion to the charge transfer complex TMTU·I$_2$. The largest change in the GVFF was a decrease in the force constant for C=S stretching of 0.48 mdyn/Å. In agreement, the IR band with the maximum amount of C=S stretching character (v_{21} at 492 cm^{-1}, 51 % C=S stretching according to the PED) was displaced $ca.$ 25 cm^{-1} towards lower frequencies. CNDO/S and CNDO/2 calculations did agree that this was due mainly to the increased positive charge on sulfur following charge transfer to iodine. These features can now be compared with the corresponding changes on conversion of TMSU to the covalent TMSU·Br$_2$ and TMSU·I$_2$. The changes in GVFF are remarkably similar with the exception of K_D, the force constant for C=Se stretching.

From Table 1 it can be seen that K_D increases by $ca.$ 0.15 mdyn/Å for TMSU·Br$_2$, but decreases by 0.14 mdyn/Å for TMSU·I$_2$. This difference arises mainly because perdeuterated TMSU·I$_2$, but not perdeuterated TMSU·Br$_2$, was included in the NCA. Since the GVFF of TMSU was based[2] upon iteration including both the parent and the perdeuterated species it is clearly K_D for TMSU·I$_2$ which is relevant for comparison. We can, therefore, conclude that the decrease in force constant for C=Se stretching on formation of a covalent halogen compound is much smaller (0.14 mdyn/Å) than the decrease in C=S stretching on charge-transfer (0.48 mdyn/Å). In agreement with this, the bands with C=Se stretching character (Tables 2 − 4) are hardly displaced towards lower frequencies, provided, of course, that they do not contain contributions from other vibrations which are affected by halogenation.

In order to account for this difference in the vibrational spectra of charge transfer and covalent compounds, we decided to extend the CNDO/2 calculations to TMSU and TMSU·Br$_2$. This necessitated an extension of the available programs to compounds containing third-row elements as described by Hase and Schweig.[14] A further small extension was made to the program. Since the CNDO eigenvectors in the SCF procedure are obtained in the ZDO approximation, they can be regarded as linear combinations of orthogonalized atomic orbitals λ derived from Slater orbitals χ by the Löwdin transformation[15]

$$\lambda = \chi S^{-\frac{1}{2}}$$

where S is the overlap matrix in the χ basis. The subroutine which performs this transformation was kindly provided by Professor Schweig.

A population analysis of the CNDO/2 wave functions for TMSU and TMSU·Br$_2$ is given in Fig. 3. The net atomic charges for (Me$_2$)N, C, and Se in TMSU are +0.13, +0.28 and −0.54, respectively, while the corresponding values for TMTU are +0.08, +0.27 and −0.44. Since the carbon charges are almost identical, the net effect of substituting selenium for sulfur is an increased charge transfer from N to the chalkogen atom. Inspection of the density matrices of TMTU and TMSU shows this to be the result of two opposite tendencies. An increased σ-polarization in the direction Se$^+$−N$^-$ is more than outweighed by transfer of π-density in the direction N$^+$−Se$^-$. The role of the d-orbitals is almost the same for S in TMTU and Se in TMSU.

By analogy with TMSU I$_2$ it has been assumed that the Br−Se−Br axis of TMSU Br$_2$ will form an angle of 62° with the N$_2$CSe plane (the XY-plane of Fig. 3). The CNDO/2 calculations indicate (Fig. 3, bottom) that the Se d-orbitals, with a strongly increased electron density (0.88) are extensively used in the formation of Se−Br bonds. On the other hand, the Se p_x- and p_z-orbitals decrease in electron density through transfer to the d-orbitals and to Br (0.19). The net result is an increased electron density (0.10) of the SeBr$_2$ group relative to Se in TMSU. This is removed from the CH$_3$ groups, since the net density changes of the N$_2$C group are close to zero.

The result of this analysis is, that the changes in the force constants of the TMSU on bromination arise through very small electronic displacements.
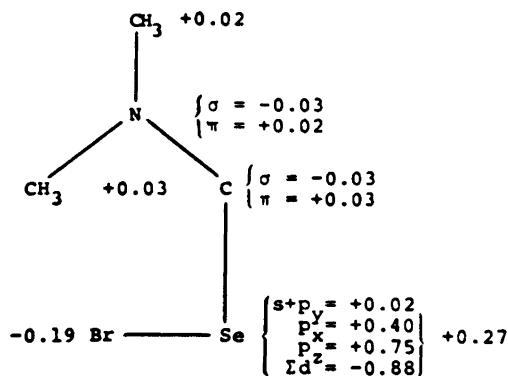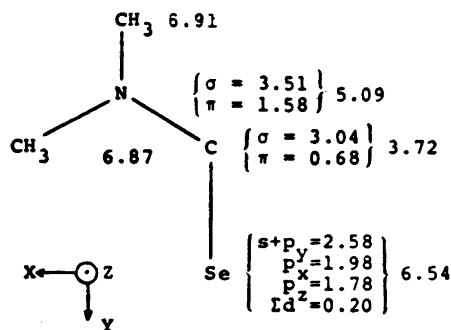
Fig. 3. The CNDO/2 electron density for TMSU and the changes on conversion to TMSU·Br$_2$. (Lower and higher densities relative to TMSU are indicated by the signs + and −, resp. The π-densities are taken at right angles (Z) to the N−CSe−N plane (X,Y). Σd indicates the sum of the electronic densities for all d-orbitals located on Se).

Let us consider first the changes in the π-density. Each of the N atoms decrease by 0.02, the central C atom by 0.03, and the Se atom by *ca.* 0.10 (dependent on how the d-orbitals are taken into account). An examination of the wave functions involved shows that these are either bonding or non-bonding for the N$_2$CSe group, while orbitals which are anti-bonding between N/C or C/Se play only a negligible role. Accordingly, the effect of a decrease in electron density of the N$_2$CSe π-electrons will be a decrease in the force constants for both stretching and bending.

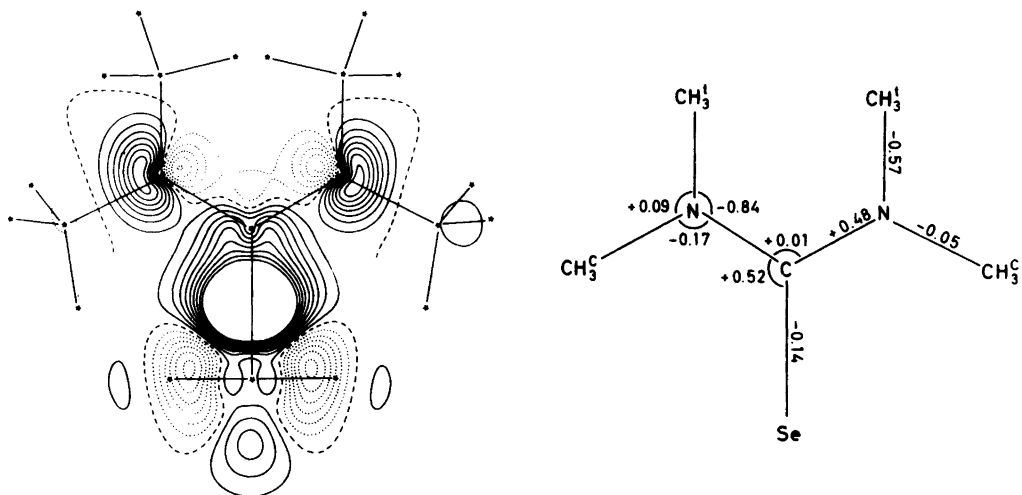The changes in the σ-density comprise a decrease in density at the Se atom (0.02) and the CH$_3$ groups

Fig. 4. (Left) Difference map (TMSU·Br$_2$ – TMSU) of the total molecular density in the C$_2$NSe plane as calculated with 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. The geometry of TMSU is used for both molecules.

(Right) Changes in deformation and stretching force constants from TMSU to TMSU·Br$_2$. Positive and negative values represent an increase and a decrease in force constants, respectively, (*cf.* Table 1).

(0.02 and 0.03), but an increase at the N atoms (0.03) and the central C atom (0.03). However, more information as to the nature and extent of the changes in these σ-densities can be obtained from a difference-density map, calculated by subtracting the electron density for TMSU from that of TMSU·Br$_2$. (In order to make this subtraction possible the atoms must be at identical places in the two compounds, and the geometry for TMSU was therefore used in this particular calculation also for TMSU·Br$_2$.) The resulting map (Fig. 4) shows the distortion in the σ-electron distribution (the N$_2$CSe plane) when TMSU is converted to TMSU·Br$_2$.

It is seen that the electron decrease is mainly found in the region limited by CH$_3^t$ – N – C – N – CH$_3^t$ and along the p_x-orbitals of selenium. The electron density increases in the remaining parts of the molecule, especially along the CSe and the N – CH$_3^c$ bonds. Although the changes in electron density are quite small, it is probably significant that regions with an increased electron density correspond to higher stretching and bending force constants and *vice versa*. Thus, the CH$_3^c$ – N stretching force constant decreases only by 0.05, while the corresponding CH$_3^t$ – N force constant decreases

by 0.57 in agreement with the increased electron density along the CH$_3^t$ – N bond. Similarly, the deformation constants around the CH$_3^c$ – N bond show only minor changes, while the CH$_3^t$ – N – C deformation constant decreases by 0.84 in complete accord with the density map. Around the central carbon atom the NCN deformation constant is unchanged while the NCSe deformation constant rises with 0.52 as expected from the density map. Only the increase in the CN stretching constant by 0.48 and the decrease in CSe stretching constant by 0.14 is at variance with the calculated changes.

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