Tentative Assignments of Fundamental Vibrations of Thio- and Selenoamides. VIII. 1,2-Dimethyl-3-pyrazolidineselone, a Cyclic Selenohydrazide. Selenation of the Thioamide Group in Theory and Practice

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As a continuation of our investigation on the molecular vibrations of a cyclic thiohydrazide, 1,2-dimethyl-3-pyrazolidinethione, the IR and Raman spectra of the corresponding selenium analogue, 1,2-dimethyl-3-pyrazolidineselone, have been recorded from $40-4000$ cm^{-1}. The vibrational assignment was assisted by a normal coordinate analysis with a force field partly transferred from the sulfur compound. The scope and limitations of the methods of selenation, *i.e.* comparison of the spectra of compounds containing a thioamide grouping with the corresponding selenium analogoues, are evaluated. On the basis of CNDO/2 calculations it is concluded that the electronic structures are subject to considerable changes on selenation contrary to what is commonly assumed.

An empirical classification of the IR bands in spectra of compounds containing a thioamide group, *e.g.* thioamides, thioureas and thiosemicarbazides, may often be obtained by a comparison with the spectra of the corresponding selenium analogues. Most of the bands appear almost unchanged in intensity, shape, and frequency and would as a first approximation be expected to originate in vibrations other than the CS bond. Some bands appear to have retained their intensity and shape, but are displaced towards lower frequencies as expected for vibrations due mainly to the CS group. It is often observed that the spectra are virtually superimposable in many regions, and that only a few bands show major shifts towards lower frequencies.

On this basis we proposed[1] the term 'selenation' as a method for identification of bands characteristic for the thioamide grouping by comparison with the spectra of the corresponding selenium compound and stated that the method 'almost works like an isotopic substitution'. In this paper we want to investigate the foundation and limitations of the method.

The method was rapidly adopted by other authors.[2] Normal coordinate analyses (NCA) on dithio- and diselenocarbamates[3,4] served to clarify the relative importance of changes in geometry, mass and force field induced in the molecule on selenation. The NCA also showed that borderline cases with small selenation shifts were found whenever strong coupling occurs between vibrations of the thioamide group and the remaining molecule. Recently, in a paper dealing with the IR spectra of tetramethylthiourea and tetramethylselenourea[5] we have summarised the deficiencies of the selenation method as follows. (i) Selenation shifts may be missed because bands of different origin interfere. (ii) Bands displaying selenation shifts with unaltered shape and intensity may nevertheless originate in different vibrations. (iii) Selenation shifts may be caused not only by electronic but also by steric changes following substitution of sulfur by selenium. However, many of the above-mentioned problems are eliminated by considering selenation shifts of a large number of compounds containing the same thioamide group-

ing which was done in the original work[1] and in a study of dithiocarbamates.[6] Selenation of only a few compounds of a given type unassisted by NCA may be quite insufficient for an ample classification of the relevant bands (see e.g. a recent paper[7] on benzimidazole-, benzoxazole- and benzothiazole-2-thiones). Some authors[8-15] have extended the concept of selenation to imply (i) that the electronic structure of analogous sulfur and selenium compounds are very similar and (ii) that only slight modifications are needed in transferring the force field for a given sulfur compound to the analogous selenium compound. Both statements will be discussed below.

In the previous communication[16] the vibrational spectrum of a cyclic thiohydrazide, 1,2-dimethyl-3-pyrazolidinethione (DMPT), was discussed in some detail. In the present paper the investigation is extended to the selenium analogue, 1,2-dimethyl-3-pyrazolidineselone (DMPS). These results provide a firm basis for an evaluation of the selenation method applied to thiohydrazides. To illustrate the electronic and steric effects of selenation we have carried out CNDO/2 calculations on DMPT and DMPS. An attempt is made to correlate the changes in force field from DMPT to DMPS with the calculated changes in electronic density of the two compounds.

STRUCTURE

Experimental data on the structure of selenoamides or -hydrazides have to our knowledge not been reported. Though most of the geometrical parameters needed for this study could be transferred from similar molecules (DMPT, selenoureas) we still do not know with certainty how the CN bond length in compounds containing the thioamide grouping is influenced by substituting selenium for sulfur. For example, the CN bond length increases in selenourea[17] (1.34 − 1.45 Å) relative to thiourea[18-20] (1.33 − 1.34 Å) but decreases in selenourea solvates[21] (1.31 − 1.32 Å). Varying changes are also observed when complex compounds of ethylenethiourea and ethyleneselenourea[22,23] are compared. X-Ray analyses of closely related thio- and selenosemicarbazones[24,25] indicate an increased CN bond length in the CSe − NH$_2$ group (1.37 Å) relative to CS − NH$_2$ (1.33 Å) while the other thioureide CN bond is almost unchanged. The CN bond lengths in tetramethylthiourea[26] (1.37 Å) and tetramethylselenourea[5]

(1.347 Å) are not influenced by hydrogen bonding as in the above-mentioned examples but in these cases sterical hindrance prevents the planarity of the thio- and selenoureide groups. The trends observed for the CN bond lengths in diselenocarbamates relative to dithiocarbamates[27-29] also seem difficult to generalise.

Since the crystal structure for 5-(p-chlorophenyl)-DMPT is known[16] a sample of the corresponding selenium compound, 5-(p-chlorophenyl)-DMPS, was prepared and turned out to be isostructural with the sulfur compound. The details of this investigation will be published elsewhere, but the most important results of the X-ray structure determination will be summarised here. The CSe bond length was found to be 1.824(4) Å not far from the mean value in selenourea[17] (1.86 Å), selenourea solvate21 (1.867 Å) and selenosemicarbazones[25] (1.83(2) Å). Rather unexpectedly all other bond lengths and interbond angles were found to be identical within the experimental error. The thiohydrazide CN bond length, in particular, is 1.314(3) Å in 5-(p-chlorophenyl)-DMPT and 1.306(6) Å in the corresponding selenium compound. The fact that the geometrical structures of 5-(p-chlorophenyl)-DMPT and -DMPS are identical apart from the CS/CSe bonds does not necessarily mean that the electronic structures are also identical. Thus, the CNDO/2 calculations indicate that selenation of the thiohydrazide group introduces both electronic and steric effects. However, the effects can be mutually compensating or too small to influence the CN bond lengths significantly.

EXPERIMENTAL

Perkin-Elmer spectrometers 180, 225 and 580 were used to study the IR spectrum in the 180 − 4000 cm^{-1} range. The pure liquids were supported between KBr and CsI plates. Solutions in CCl$_4$ and CS$_2$ were run in standard cells of different thicknesses. The far IR spectra were recorded with a fast scan Fourier transform interferometer (model 114c) from Bruker using 1 mm PET cells. Beam splitters of Mylar of 3.5 and 12 nm thickness were employed to cover the region 600 − 50 cm^{-1}. The Raman spectra were recorded with a Cary model 81 spectrometer equipped with an Argon ion laser source using blue and green lines in both 180 and 90° illumination modes. The preparation and properties of DMPS and 5-(p-chlorophenyl)-DMPS will be reported elsewhere. All samples used for the spectroscopical measurements were carefully fractionated and show satisfactory elemental analyses.

NORMAL COORDINATE ANALYSIS

The normal vibrations were calculated for DMPS using the same method as for DMPT.[16] Initially a calculation was performed with the force field of DMPT but with the mass and geometry found for DMPS. The shifts calculated by this method are reproduced in Table 1. It allows a provisional assignment since most of the fundamentals in the range $100-3000 \text{ cm}^{-1}$ are predicted within 10 cm^{-1} and only eight deviated up to 30 cm^{-1} from the experimental values. The result indicated that the force fields of DMPT and DMPS were indeed, very similar, but not quite identical. To avoid a laborious isotopic substitution of DMPS we now decided to vary only the force constants pertaining to the selenohydrazide group and transfer the remaining force field from DMPT. This approach was justified by the following considerations: (i) The CNDO/2 calculation showed that changes in electron density on selenation are restricted to the selenohydrazide group. (ii) The PED (potential energy distribution) of the eight fundamentals not correctly predicted indicated significant contributions also from this part of the molecule. (iii) It proved possible to obtain a good fit in this way and the force field obtained was compatible with the CNDO/2 results.

The force constants included in the iterative procedure were primarily the five stretching, the six in-plane bending (with $H_{\varepsilon_1} = H_{\varepsilon_2}$ as in DMPT) and the ΔCSe out-of-plane bending force constants of the $N-N(CH_3')-CSe-C$ chain. Since the CNDO/2 calculation indicated small changes in electron density around the $CH_2(-CSe)$ group the relevant force constants were also included, however, almost without effect as expected. Unfortunately the force constants for $CH_3'-N-N$ and $N-N-CS$ deformation (H_{ε_2} and H_{ε_3}) depend heavily upon the location of the fundamentals below 200 cm^{-1} which is subject to considerable uncertainty. In order to secure a well-conditioned and physically significant convergence of the least-square iterative process, these force constants were fixed to the values found for DMPT, while H_{ε_1} was still allowed to vary. The iteration was designed to obtain the best possible fit between the observed and calculated selenation shifts (see Table 1) rather than to obtain agreement between observed and calculated frequencies. Furthermore the shifts were introduced in the iteration with weights reflecting their trustworthiness, as estimated from a consideration of their IR and Raman spectra. For

example, some of the fundamentals couple rather heavily with overtones and/or combination modes occurring in the same region and cannot be attributed to definite selenation shifts.

The final force field is not unique, though experience from 30 calculations with different approximations indicate that the direction and magnitude of all the major shifts are correct. The final values are the following (designation and units as in Ref. 16): K_D 3.0; K_{L_2} 3.6; K_A 5.1; K_{B_2} 7.6; K_{P_2} 4.7; H_{μ_1} 0.7; H_{μ_2} 2.9; H_{μ_3} 1.6; H_{ε_1} 0.4; H_{ω_1} 1.6; H_{δ_2} 0.49; H_Λ 0.33; $H_{\gamma_3^o} = H_{\gamma_4^o}$ 0.66; $F_{\gamma_3^o\gamma_4^o}$ 0.05. All other values were transferred from DMPT. The agreement between the calculated and the observed shifts (Table 1) are considered satisfactory with two exceptions. The downwards shifts of ca. 10 cm^{-1} of v_{21} and v_{22} are difficult to reproduce by the NCA. Explorative calculations show that agreement can only be reached if the force constant for NN stretching, K_A, is lowered considerably. This seems improbable, since almost all the NN stretching character at the same time is transferred from v_{20} to v_{22}. The calculation reproduced in Table 1 is a likely compromise. The calculated shift is also much too small for v_{33}, and again a better fit seems to be dependent upon a lowered value for K_A. The exact value found for K_{B_2}, the force constant for C^3N stretching, depends heavily upon the calculated shift for v_{11}, and the slight increase found here is probably not significant.

RESULTS AND DISCUSSION

IR spectra of DMPS and DMPT as liquids in the spectral region $180-4000 \text{ cm}^{-1}$ are given in Fig. 1. The spectra clearly show the great similarity which is the basis for the use of the selenation technique. Some important selenation shifts have been indicated on the figure to facilitate comparison in the low-frequency range where the correlation is not obvious. The numerical material is collected in Table 1, which lists all pertinent results in a manner similar to that used for DMPT in the previous paper.[16] Since the spectra of DMPS and DMPT are very similar, it is unnecessary to give a detailed account of the results obtained here for DMPS. Instead we shall concentrate on the concept of selenation, i.e. whether comparison of the IR spectra of DMPT and DMPS can be used profitably in identifying the vibrations originating in the thio- and selenohydrazide groupings.

Table 1. Observed and calculated vibrational frequencies (cm^{-1}) of 1,2-dimethylpyrazolidine-3-selone, tentative assignments of the spectra, and description of the fundamentals.[a]

Frequency					Selenation shifts[d]				Assignment and description (PED, %)[f]
IR, obs.		Raman, obs.		Calc.[c]	Obs.			Calc.[e]	
liquid	CCl$_4$/CS$_2$ solution	liquid	pol.[b]		IR liq.	IR sol.	Raman liq.		
2989m	2986m	2986m,sh	0.7	2988	+4	+3	−1	0(0)	ν_1, $\nu_{as}CH_3$ (99)
				2985				0(0)	ν_2, $\nu_{as}CH_3$ (99)
				2972				0(0)	ν_3, $\nu_{as}CH_2$ (98)
				2967				0(0)	ν_4, $\nu_{as}CH_3'$ (99)
2964m	2968m	2969m	0.5	2964	+2	+3	+2	0(0)	ν_5, $\nu_{as}CH_3'$ (99)
				2958				0(0)	ν_6, $\nu_{as}CH_2$ (98)
2926m,sh	2930m	2926m,sh	0.3	2930	−4	+4	−2	0(0)	ν_7, ν_sCH_2 (98)
				2929				0(0)	ν_8, ν_sCH_3 (99)
2910m	2910m	2909m	0.3	2918	−10	−6	−11	0(0)	ν_9, ν_sCH_3 (99)
2860m	2861m	2861w,sh	0.3	2862	0	+1	−6	0(0)	ν_{10}, ν_sCH_3 (100)
2791mw	2792mw	2792w			−1	0	0		$2 \cdot \nu_{19}$
1516vs,br	1505vs,br	1513vs	0.5	1510	+15	+12	+10	+12(0)	ν_{11}, $\nu C^3N(61)$, $\delta_{as}CH_3'$ (15)
1471m	1472m,sh	1463w,sh		1462	+7	+6	−3	−2(0)	ν_{12}, $\nu C^3N(6)$, $\delta_{as}CH_3'$ (60), δCH_2 (24)
	1457s			1458		+3		−1(0)	ν_{13}, $\delta_{as}CH_3$ (77)
1450s	1450s	1448m,sh	0.7	1455	−1	+2	−2	0(0)	ν_{14}, $\delta_{as}CH_3$ (99)
1436vw	1436vw	1435m,sh		1446		+1	−3	+3(0)	ν_{15}, $\delta_{as}CH_3'$ (83)
				1432				+1(0)	ν_{16}, δCH_2 (88)
1424s	1425s	1424m	0.6	1418	0	0	−2	−3(−2)	ν_{17}, δCH_2 (80)
1416s,sh	1414s			1415	0	+2		0(0)	ν_{18}, δ_sCH_3 (98)
1392s	1392s	1390s	0.4	1388	+1	+1	−5	−3(0)	ν_{19}, $\nu C^3N(7)$, δ_sCH_3' (95)
1385s,sh									
1340w	1344w	1339vw		1344	0	0	−5	−3(−2)	ν_{20}, $\nu NN(16)$, $\nu CSe(5)$, $\nu C^3N(5)$, $\nu/\delta ring(64)$
1300s	1303m	1297m	0.3	1310	−12	−10	−9	−7(0)	ν_{21}, $t/\omega CH_2$ (74)
	1296s			1309		−10	−2	0(−3)	ν_{22}, $\nu NN(18)$, $t/\omega CH_2$ (41), $\nu/\delta ring(29)$
1255m	1255s	1255vw	0.2		−4	−3	−9		
1239m	1240m	1236vw,sh			−9	−7			
1224m	1224m	1224w	0.6	1226	−8	−9	−8	−7(−3)	ν_{23}, ω/tCH_2 (35), $\nu/\delta ring(40)$, ρCH_3 (28)
1187s	1188s	1184w	0.5	1191	+1	+3	−4	−5(0)	ν_{24}, ω/tCH_2 (70), ρCH_3 (23)
1174m,sh	1174m,sh	1174m,sh		1165	0	0	−1	−3(−2)	ν_{25}, $\nu NNCSe(6)$, vring(31), ρCH_3 (38), ω/tCH_2 (21)
1130m,sh	1130m,sh	1127vw,sh			−1	−3	−5		
1113s	1114s	1111w,sh		1128	−5		−10	−9(−1)	ν_{26}, $\nu NNCSe(7)$, ρCH_3 (43), vring(29) *and* $\nu_{34}+\nu_{41}$

ν	DMPS	DMPS (pol)	DMPT	ρ[b]	Δ (obs)[d]	Δ	Δ	ν(calc)	Δ (calc)[e]	Assignment (PED)[f]
ν_{27}	1095m,sh	1095w,sh	—	0.5	−1	+13	0	1102	+20	$\rho CH_3'$ (56), ν/δring (19)
ν_{28}	1089s	1087w	1089s	0.7	+3	+6	+13	1099	+11(−1)	$\rho CH_3'$ (90)
ν_{29}	1064s	1062w	1066s	—	−2	−3	+5	1058	−2(−1)	νCC (45), ρCH_2 (34)
ν_{30}	1054m,sh (1038m,sh)	1054vw,sh (1039vw,sh)	1054m,sh (1040w,sh)	—	−3	−3	−5	1042	−4(−4)	$\nu NCSe$ (6), $\rho CH_3'$ (21), νring (52)
ν_{31}	1001m (1005m,sh)	1002vw	1001m (1006m)	0.7	−6	−1	−4	992	−4(0)	ρCH_2 (70), νring (17)
ν_{32}	938m (968w)	933vw,sh (966vw)	939m (967w)	0.7	−19	−1	−3	943	−6(−1)	νNN (5), ρCH_2 (58), νring (24)
ν_{33}	924m	921vw	925m	0.3	−14	−16	−1	901	−3(−3)	νNN (18), νCSe (4), νring (40), ρCH_2 (22)
ν_{34}	874m, 773m	874s, 773s	875m, 772m	0.4	−13	−5	−2	783	−17(−18)	νCSe (14), νNN (10), $\nu C^3 N$ (5), νring (25), δring (51)
ν_{35}	683w (695vw,sh)	685m (690m,sh)	687w	0.2	−4	−4	−17	686	−5(−4)	νCSe (5), νNN (5), $\nu C^3 N$ (6), νring (45), δring (21)
ν_{36}	635m	635m	635m	0.2	+4	−2	−13	630	−8(−2)	νNN (11), νring (53), δring (45)
ν_{37}	526m	525mw (540vw,sh)	524m (540w,sh)	0.6	−23	+7	−7	549	−4(−1)	$\Delta CH_3-N{<}^N_C$ (60), νring(27) *and $\nu_{42}+\nu_{43}$*
ν_{38}	468w	468w	470w	0.5	+8	−17	−6	476	−14(−7)	$\Delta CH_3-N{<}^N_C$ (25), ρCH_2 (53) *and $\nu_{41}+\nu_{46}$*
ν_{39}	458w	458w	457w	0.6	−5	+5	−4	408	−13(−7)	ΔCSe (43), $\Delta CH_3-N{<}^C_N$ (24), δring (36), νring (23)
ν_{40}	418w	419w	421w	0.5	−5	−2	+8	375	−3(−1)	ΔCSe (13), ρCH_2 (43), ν/δring (26)
ν_{41}	354w (365vw,sh)	352w (365vw,sh)	352m (365vw,sh)	0.5	+2	+3	+5	346	+8(+39)	νCSe (22), νNN (8), $\delta CH_3-N</CH_3'-N<$ (36), ν/δring(32)
ν_{42}	321ms	320s	325s	0.3	−114	−107	−110	305	−124(−129)	νCSe (36), δCSe (22), ν/δring (37)
ν_{43}	216m	221w,sh	222m	—	−47		−51	225	−43(−45)	δCSe (41), νCSe (7), νNN (6), $\delta CH_3'-N<$ (39)
ν_{44}	204m,sh	209m	207m	0.6	+6		+2	200	−2(−2)	τCH_3 (66)
ν_{45}	174w	170vw	—	—	0			170	0(0)	τCH_3 (92)
ν_{46}	—	110w	110w	—				120	+2(−1)	δring
ν_{47}	55m	—	55m	—	−8			48	−19(−1)	δring
ν_{48}	—	—	—	—				19	−3(−2)	δring

[a] The following abbreviations have been used: s, strong; m, medium; w, weak; br, broad; sh, shoulder. Weak and very weak bands not assigned to fundamentals have in most instances been omitted. [b] Approximate depolarisation ratio ($\rho=0.75$ corresponds to a fully depolarised band). [c] Using the final converged force field partly transferred from DMPT. [d] Shifts (cm^{-1}) of corresponding bands (i.e. with similar PED) in DMPS and DMPT ($\nu_{DMPS}-\nu_{DMPT}$). Values in italics are believed to be significant trends. [e] Calculated selenation shifts using the force field mentioned in note c. The part of the shift originating only in changes of mass and geometry is given in parenthesis (calculated using the geometry and mass of DMPS but the force field of DMPT). [f] Abbreviations: ν=stretch; δ=deformation; Δ=out-of-plane deformation; ρ=rock; ω=wag; t=twist; τ=torsion; s=symmetric, and as=antisymmetric. Vibrations of the pyrazolidine ring and the attached heavy atoms are designated 'ring' or using the following nomenclature: N^1-CH_3, N^2-CH_3', C^3Se. The potential energy distribution (PED, $x_{ik}=100F_{ii}L^2_{ik}/\lambda_k$) is stated only for significant contributions. The PED corresponding to the selenohydrazide group is underlined.
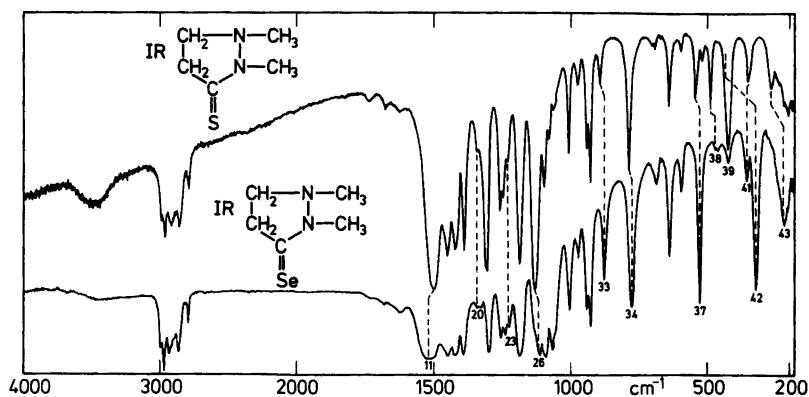
Fig. 1. IR spectra of DMPT (top) and DMPS (bottom) in the liquid state. The numbering refers to the assigned fundamentals of DMPS; the corresponding bands in DMPT are indicated with a hatched line.

To avoid possible misunderstandings the terms used below will be briefly defined. Selenation of DMPT involves: (i) A mass change from (mainly) ^{32}S to a mixture of selenium isotopes mostly in the range ^{76}Se to ^{82}Se, (ii) a geometry change, according to the X-ray results confined to the length of the CS/CSe bond and (iii) a change in force field due to the electronic and steric effects of selenium relative to sulfur. The results of selenation are the following: (i) A change in position of bands described by the selenation shift, $v_{DMPS} - v_{DMPT}$. (ii) A change in PED of the normal vibrations. As long as the changes are small we talk about corresponding bands in DMPT and DMPS, in other words, the concept of group frequencies is valid. (iii) Changes in intensity, form and depolarisation ratio may occur, especially as a result of different Fermi interactions with overtones and combination modes. In this case a visual identification of corresponding bands in DMPT is difficult or impossible.

Visual identification of corresponding bands in DMPS and DMPT. A necessary prerequisite for using the selenation method is the establishment of a one-to-one correspondence between the bands of DMPS and DMPT *e.g.* by superposition of the spectra. Moreover, at this stage we try to identify the fundamentals from eventual overtones and combination modes by intensity considerations. The number of accidentally degenerate fundamentals $(v_1 - v_3, v_4 - v_6, v_7 - v_8$ and $v_{15} - v_{16})$ is identical in DMPS and DMPT and presents no problem. The occurrence of Fermi resonance with near-lying overtones and combination modes makes the identification of v_{23}, v_{26}, v_{37} and v_{38} difficult

(see Table 1). In the case of *e.g.* v_{23}, this does not invalidate the selenation method since the form and intensity of the triad of bands between 1220 and 1260 cm^{-1} are very similar in the IR spectra of DMPT and DMPS (see Fig. 1).

The v_{37} of DMPS is different. In the spectrum of DMPT it is observed at 548 cm^{-1} with medium intensity followed by a weak Fermi enhanced combination mode at 522 cm^{-1}. In the IR spectrum of DMPS the intensity distribution is exactly opposite, and v_{37} is observed as a medium strong band at 526 cm^{-1} with a very weak shoulder at 540 cm^{-1}. The obvious conclusion is that v_{37} is displaced from 548 cm^{-1} in DMPT to 526 cm^{-1} in DMPS, *i.e.* displays a selenation shift of 22 cm^{-1} as indicated on Fig. 1. Comparison with Raman data reveals that this is probably not correct. In the Raman spectrum of DMPT, v_{37} is found at 521 cm^{-1} with medium intensity accompanied by two weak satellites at 538 and 544 cm^{-1}, while in DMPS it is a medium weak band at 525 cm^{-1} followed by a weak combination mode at 540 cm^{-1}. In our opinion this example demonstrates convincingly that a visual identification of corresponding bands by the selenation method cannot be regarded as definite without supporting data from either Raman spectra or *e.g.* spectra of deuterium substituted compounds. In the present case the results of the NCA also identifies v_{37} as originating in a vibration unperturbed by selenation, supporting the interpretation given here.

Apparently corresponding bands in DMPS and DMPT. Even when the fundamentals are correctly identified and have similar characteristics (form,

intensity, depolarisation ratio *etc.*) in DMPT and DMPS they may nevertheless have quite different PED's and thus are only apparently corresponding. The fundamentals $v_{38} - v_{43}$ in DMPS (and DMPT) with significant contributions from CSe stretching, in-plane and out-of-plane bending are obvious examples of this complication as can be verified by comparing the PED's of Table 1 with those for DMPT reported previously.[16] As an outstanding example we want to point out that v_{41} in DMPS, although containing a 25 % contribution from CSe stretching, only displays a very small shift (2 − 5 cm^{-1}) relative to a band with almost the same strength, intensity and form in DMPT (v_{42}) which has no contribution at all from vibrations of the thiohydrazide group. This demonstrates that selenation shifts may be absent even in bands with high contribution from the thiohydrazide group provided that the PED changes in a suitably way.

Measurement of the selenation shifts. From the results in Table 1 it can be concluded that the selenation shifts are subjected to small variations when calculated from the IR and from the Raman spectra, and the shifts may even go in opposite directions (*e.g.* v_{12}, v_{24} and v_{29}). In the case of Fermi resonance with neighbouring overtones and/or combination modes (v_{26}, v_{37} and v_{38}) definite shifts cannot be calculated from the data. Even the direction of the selenation shift may be difficult to assess with certainty unless the shift is prominent (v_{38}). In Table 1 significant trends are given in italics and have also been attributed increased weight in the NCA.

Mass and geometry effects in selenation. In Table 1 the calculated selenation shifts are listed together with the part of the shift originating solely from changes in mass and geometry, 'the mass-geometry shift.' We shall briefly discuss some major selenation shifts mainly of this origin. The fundamentals v_{34} and v_{35} found at 786 − 789 and 689 − 693 cm^{-1}, respectively, in DMPT are displaced on selenation to 772 − 773 and 683 − 687 cm^{-1}, respectively. Since the calculated mass-geometry shifts are of similar magnitude the obvious conclusion is that the observed selenation shifts have this origin. However, a closer inspection reveals that the change in force field by change reproduces the same selenation shifts, but with a quite different PED on the fundamentals. In our opinion this example demonstrates that a coincidence between experimental selenation shifts and calculated mass-geometry shifts may very well be fortuitous. Similar remarks
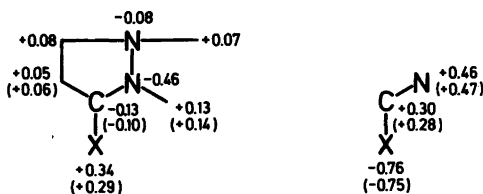
Fig. 2. The CNDO/2 charge density for DMPT (X = S) and, in parenthesis, for DMPS (X = Se). If only one figure is given, the charge densities are identical. The σ-densities are shown to the left while the π-densities of the NCX group are shown to the right.

apply to the fundamentals $v_{38} - v_{43}$ of DMPS relative to the corresponding bands in DMPT. An interesting example is v_{41} in which a major shift predicted by change in mass and geometry (+ 39 cm^{-1}) is almost compensated by the accompanying changes in force field. The 25 % contribution from CSe stretching to this fundamental would never have been suspected from experimental results alone, but is understandable from the NCA results.

Force field changes on selenation. From *ab initio* calculations[30] it is known that substitution of sulfur with selenium introduces a steric effect, the size increasing from S to Se, and a polarisability effect, the Se atom being more polarisable than the S atom. Both in S and Se compounds the lowest empty *d*-orbitals serve to polarise the basis set while the $(3d)^{10}$ orbitals of Se are essentially core orbitals. In order to explore whether similar differences are operative for DMPT and DMPS, CNDO/2 calculations were performed. The charge densities (Fig. 2) show that the π-distribution of the thioamide group in DMPT corresponds to a superposition of the familiar structures N$^+$ = C − S$^-$ and C$^+$ − S$^-$ while the σ-electrons are displaced in the opposite direction. The densities in the remaining part of the molecule are identical in DMPS and DMPT and need no further discussion. On selenation of the thioamide group, however, small but characteristic changes occur in the electron density.

Due to the increased size of Se relative to S a rehybridisation occurs. Electron density (0.06e) is transferred to the *p*- and *d*-orbitals directed towards carbon to increase the overlap density of the lengthened bond. The decrease in density of the hardly overlapping 2s-orbitals of carbon (0.03e) simultaneously with an increased p_π-density (0.02e) also adds to a better stabilisation of the CSe bond in DMPS.
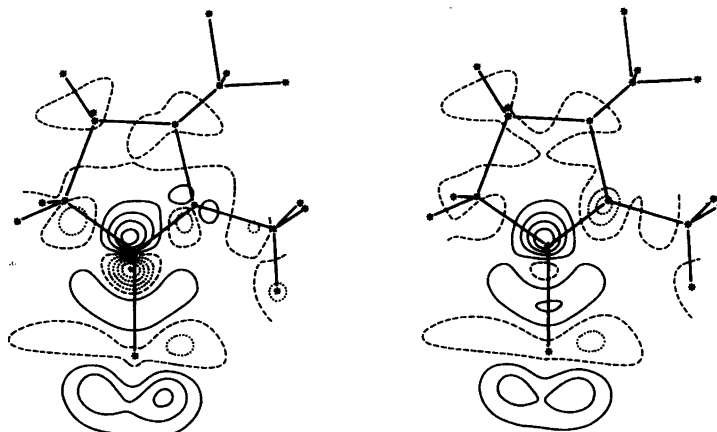
Fig. 3. Difference map (DMPS – DMPT) of the total molecular density in the NCS/NCSe plane (left) and in a plane 0.62 Å above this plane (right) as calculated by the CNDO/2 method. Solid, dashed and dotted lines represent positive, zero and negative difference densities, respectively, plotted linearly with a spacing of 0.001 electron/$Å^3$. The molecules have been arranged with coincident atoms of the rings and the methyl groups, *i.e.* the sulfur atom of DMPT is located on the C – Se bond drawn on the difference maps.

Some of the electron density necessary for stabilisation of the CSe bond (0.03e) is removed from the neighbouring CH_2, N and CH_3' groups. These changes in steric demands and *d*-orbital stabilisation compare well to those expected from *ab initio* results (*cf.* also thiophene[31]). The polarisability effect is documented by the difference density contours in Fig. 3, displaying the changes in electron density of DMPT on selenation. The changes in a plane through the NCSe group show how the large selenium atom polarises the electrons along the $-CH_2-C-N-CH_3'$ chain. The regions near Se display a consistent decrease, those further removed a corresponding increase in density. The sterically proximate CH_3' group induces a counter-polarisation of Se relative to S as expected. The changes in a plane corresponding to the π-electrons of the NCSe group also show the polarisation of Se from the CH_3' group, but otherwise only reflect the increased electron density of carbon at the expense of N and Se already noted above.

The gross features of the changes in force field and electron density on selenation seem consistent. The NCA indicates that all stretching force constants of the $C-CX-N(CH_3')-N$ (X = S, Se) chain decrease except that of the central CN bond which perhaps increases slightly. The decrease in the force constant for CX stretching from DMPT to DMPS is mainly a consequence of the diminished overlap of the longer CSe bond, which cannot be fully compensated for even from the flow of electrons from the contiguous parts of the molecule and the rehybridisation of C and Se. The diminished electron density is responsible for the decrease in the force constants for $C-C$, $N-CH_3'$, and $N-N$ stretching. The slight increase in the force constant for stretching of the central CN bond is either not significant or arises from an increased density due to polarisation, not incompatible with the curves of Fig. 3. The latter density contours also support the NCA results that the force constants for in-plane bending around the central $\underset{N}{\overset{C}{>}}C=X$ atom increase while that for $CH_3'NC$ deformation decreases. The remaining changes in force constants on selenation are small as are the changes in electron density.

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