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Derivatives of Hydrazine

VIII. A Study of Dithiocarbazic Acids, Thiocarbazoylsulfides and Selenium Analogues

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The preparation of aliphatic dithiocarbazic acids, diselenocarbazic acids, bis(thiocarbazoyl) mono- and disulfides, and bis(selenocarbazoyl) di- and triselenides is described. From the infrared spectra it is concluded that with the exception of trimethyldithiocarbazic acid the dithio- and diselenocarbazic acids are dipolar in the solid state. The sulfides and selenides may have one of the following structures, which have all been identified in at least one case: 1) both (thio- or selenocarbazoyl) parts of the molecule dipolar, 2) both parts nonpolar, and 3) one part dipolar, one part nonpolar. The skeletal stretching frequencies in the infrared region are discussed on the basis of the spectra of *N*- and *C*-deuterated compounds. It is concluded that the band at the highest frequencies originates mainly from CN stretching motion. The dithio- and diselenocarbazic acids display this band around 1300 cm^{-1}, the sulfides and selenides around 1500 cm^{-1}. This result is taken to indicate that the former compounds have less double bond character of the CN bond than the latter and is explained in terms of resonance structures. The asymmetric and symmetric CSS and CSeSe stretching bands have been identified in the fingerprint region and found to be moderately constant with a variety of associated structures. Some ^1H NMR characteristics useful for distinguishing nonpolar and dipolar structures are briefly discussed.

During work on *N*-isothiocyanatoamines it was observed [1] that the reaction between *N*-isothiocyanatodiisopropylamine and either hydrogen sulfide or 3,3-diisopropyldithiocarbazic acid gave a product, the structure of which was proposed to be bis[3,3-diisopropyl(thiocarbazoyl)]sulfide (VIII C, Table 1).

$$2\ Pr^i_2N{-}NCS \ + \ H_2S \longrightarrow (Pr^i_2N{-}NH{-}CS)_2S$$

$$Pr^i_2N{-}NCS + Pr^i_2N{-}NH{-}CSSH \longrightarrow (Pr^i_2N{-}NH{-}CS)_2S$$

VIII C

Table 1. Preparation and properties of dithiocarbazic acids (suffix A), diselenocarbazic acids (suffix B), bis(thiocarbazoyl) monosulfides (suffix C), bis(thiocarbazoyl) disulfides (suffix D), bis(selenocarbazoyl) diselenides (suffix E) and bis(selenocarbazoyl) triselenides (suffix F).

Compound	Label	Method	Yield %	M.p.[a] °C	Colour	Formula	Analyses (C, H, N)			
$NH_2NH-CSSH$	I A	Ref. 9								
$NH_2NH-CSeSeH$	I B	Ref. 9								
$(NH_2NH-CSS)_2$	I D	*a*	50	67—69 (decomp.)	colourless	$C_2H_6N_4S_4$	Found:	11.13;	2.85;	25.88
							Calc.:	11.20;	2.82;	26.14
$(NH_2NH-CSeSe)_2$	I E	*b*	78	Decomposes at 65—70 without melting	ochre	$C_2H_6N_4Se_4$	Found:	6.23;	1.49;	13.62
							Calc.:	5.98;	1.54;	13.94
$NH_2NMe-CSeSeH$	II B	*c*	77	sharp, but varying between 73—78 (decomp. c.t.)	yellow	$C_2H_6N_2Se_2$	Found:	10.99;	2.62;	13.01
							Calc.:	11.12;	2.80;	12.97
$(NH_2NMe-CSS)_2$	II D	*d*	73	86—87 (decomp. c.t.)	colourless	$C_4H_{10}N_4S_4$	Found:	20.08;	4.20;	23.29
							Calc.:	19.82;	4.16;	23.12
$(NH_2NMe-CSeSe)_2$	II E	*e*	*b*	146—146.5 (decomp.)	pale yellow	$C_4H_{10}N_4Se_4$	Found:	11.12;	2.25;	13.36
							Calc.:	11.17;	2.34;	13.03
$MeNHNMe-CSeSeH$	III B	*f*	68	83.5—84.5 (decomp. c.t.)	yellow	$C_3H_8N_2Se_2$	Found:	15.65;	3.48;	12.24
							Calc.:	15.66;	3.52;	12.18
$(MeNHNMe-CSS)_2$	III D	*d*	70	103.5—104 (decomp. c.t.)	colourless	$C_6H_{14}N_4S_4$	Found:	26.85;	5.27;	20.59
							Calc.:	26.67;	5.22;	20.74
$(MeNHNMe-CSeSe)_2$	III E	*e*	*b*	160—161 (decomp. c.t.)	pale yellow	$C_6H_{14}N_4Se_4$	Found:	15.52;	3.28;	12.43
							Calc.:	15.73;	3.08;	12.23
$Me_2NNH-CSSH$	IV A	Ref. 5								
$Me_2NNH-CSeSeH$	IV B	Ref. 5								
$(Me_2N-NH-CS)_2S$	IV C	*g*	20	140—142	colourless	$C_6H_{14}N_4S_3$	Found:	30.36;	5.96;	23.52
							Calc.:	30.25;	5.92;	23.52
$(Me_2NNH-CSS)_2$	IV D	*h*	25	132—133	colourless	$C_6H_{14}N_4S_4$	Found:	26.38;	5.29;	20.49
							Calc.:	26.67;	5.22;	20.74
$(Me_2NNH-CSeSe)_2$	IV E	*i*	40	70—71 (decomp.)	yellow	$C_6H_{14}N_4Se_4$	Found:	15.72;	3.09;	11.95
							Calc.:	15.73;	3.08;	12.23
»		*j*	54	*ca.* 70 (decomp.)	ochre-yellow	$C_6H_{14}N_4Se_4$	Found:	15.56;	3.10;	12.09

$(Me_2NNH-CSeSe)_2Se$	IV F	*k*	55	Decomposes at *ca.* 69 without melting	orange-red	$C_6H_{14}N_4Se_5$	Found:	13.61;	2.69;	10.16
							Calc.:	13.42;	2.63;	10.44
$Me_2NNMe-CSSH$	V A	*l*	54	41–42	colourless	$C_4H_{10}N_2S_2$	Found:	31.87;	6.76;	18.65
							Calc.:	32.00;	6.71;	18.66
$Me_2NNMe-CSeSeH$	V B	*f*	82	86–87 (decomp. c.t.)	pale yellow	$C_4H_{10}N_2Se_2$	Found:	19.63;	4.10;	11.45
							Calc.:	19.68;	4.13;	11.48
$(Me_2NNMe-CSS)_2$	V D	*d*	55	164–166 (c.t.)	colourless	$C_8H_{18}N_4S_4$	Found:	32.18;	6.01;	18.50
							Calc.:	32.20;	6.07;	18.77
$(Me_2NNMe-CSeSe)_2$	V E	*e*	[b]	217–218 (decomp.)	yellow	$C_8H_{18}N_4Se_4$	Found:	19.59;	3.69;	11.54
							Calc.:	19.77;	3.73;	11.53
$Et_2NNH-CSSH$	VI A	Ref. 5								
$(Et_2NNH-CS)_2S$	VI C	*g*	10	127–128	colourless	$C_{10}H_{22}N_4S_3$	Found:	40.26;	7.32;	19.28
							Calc.:	40.81;	7.53;	19.04
$(Et_2NNH-CSS)_2$	VI D	*h*	35	143–144	colourless	$C_{10}H_{22}N_4S_4$	Found:	36.76;	6.69;	16.91
							Calc.:	36.78;	6.79;	17.17
$(Pr_2NNH-CSS)_2$	VII D	*h*	30	122–123	colourless	$C_{14}H_{30}N_4S_4$	Found:	43.81;	7.91;	14.35
							Calc.:	43.97;	7.85;	14.66
$Pr^i_2NNH-CSSH$	VIII A	Ref. 10								
$(Pr^i_2NNH-CS)_2S$	VIII C	*g*	5	150–151	colourless	$C_{14}H_{30}N_4S_3$	Found:	48.10;	8.85;	15.75
							Calc.:	47.96;	8.63;	15.98
$(Pr^i_2NNH-CSS)_2$	VIII D	*h*	20	132–133	colourless	$C_{14}H_{30}N_4S_4$	Found:	43.88;	7.83;	14.44
							Calc.:	43.97;	7.85;	14.66
$(Bu_2NNH-CSS)_2$	IX D	*m*	10	89–90	colourless	$C_{18}H_{38}N_4S_4$	Found:	49.12;	8.62;	12.52
							Calc.:	49.27;	8.73;	12.77
$(Bu^i_2NNH-CSS)_2$	X D	*m*	5	108–109	colourless	$C_{18}H_{38}N_4S_4$	Found:	49.23;	8.75;	12.56
							Calc.:	49.30;	8.73;	12.77

[a] c.t. = melting point determined in a closed tube.
[b] The yield varied according to the time used for the oxidation.

In order to synthesize VIII C in an unambiguous manner it was hypothesized that the following general reaction sequence would be convenient.

$$2\,R^1R^2N{-}NHR^3 + CS_2 \longrightarrow R^1R^2N{-}NR^3{-}CSS^{\ominus}\,R^1R^2\overset{\oplus}{N}H{-}NHR^3$$

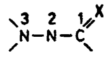
$$\xrightarrow{I_2} (R^1R^2N{-}NR^3{-}CSS)_2 \xrightarrow[-SCN^{\ominus}]{+CN^{\ominus}} (R^1R^2N{-}NR^3{-}CS)_2S$$

The first step involves the preparation of the dithiocarbazate from the parent hydrazine and carbon disulfide. The hydrazinium salts (or, in some instances, the potassium salts) were available through methods developed in connection with work [2] on metal complex compounds with dithio- and diselenocarbazic acids. The oxidation of the dithiocarbazates to disulfides was performed in a manner analogous to that used in the preparation of thiuram disulfides [3] by treatment with an ethanolic solution of iodine or an aqueous I_2/KI solution. The disulfides prepared in this way using variously substituted mono-, di-, and trialkylhydrazines are presented in Table 1. Although in all cases the reaction gave the desired product the yields were low in the case of 3,3-dialkydithiocarbazates,* diminishing with increasing size of the alkyl groups. From Table 1 it is also seen that small yields were obtained in the final step of the synthesis, which involved the use of cyanide ions to remove one of the sulfur atoms as a thiocyanate ion. This method is analogous to that described by v. Braun and Stechele [4] for the preparation of thiuram monosulfides from thiuram disulfides. The identity of each of the mono- and disulfides was verified by analysis (Table 1) and by recording the infrared (IR) and the ^{1}H NMR spectra discussed below. It was confirmed that VIII C prepared in this way was identical with the compound previously obtained from *N*-isothiocyanatodiisopropylamine showing the structure proposed above to be correct. Similarly, VI C prepared from *N*-isothiocyanatodiethylamine and hydrogen sulfide was identical with VI C prepared *via* the disulfide.

It has been shown by Jensen *et al.*[6] that tetraalkylthiuram monosulfides behave like thioanhydrides of dithiocarbamic acids, forming thiosemicarbazides on treatment with hydrazines. By analogy it was attempted to prepare thiosemicarbazides by treatment of bis(thiocarbazoyl) monosulfides with amines. Great differences in reactivity were encountered which are not at present understood. For example, IV C was unreactive towards aniline, while VIII C gave an 85 % yield of 1,1-diisopropyl-4-phenylthiosemicarbazide.

$$\underset{\text{VIII C}}{(Pr^i_2N{-}NH{-}CS)_2S} + H_2N{-}C_6H_5 \longrightarrow Pr^i_2N{-}NH{-}CS{-}NH{-}C_6H_5$$

* The IUPAC numbering has been used throughout this work.



Dithiocarbazic acids (Table 1) could in most instances be prepared from the dithiocarbazates by addition of dil. hydrochloric acid as described previously [5] for 3,3-dimethyl- (IV A) and 3,3-diethyldithiocarbazic acid (VI A).

$$R^1R^2N-NR^3-CSS^{\ominus} \xrightarrow{H^{\oplus}} R^1R^2N-NR^3-CSSH$$

I A–VIII A

This method failed in the case of 2-methyldithiocarbazic acid (II A) and 2,3-dimethyldithiocarbazic acid (III A) which were both too unstable to isolate. The former synthesis afforded an oil, identified by IR-spectroscopy as carbon disulfide, and an aqueous phase, identified in the same way after acidification and removal of the solvent as methylhydrazinium chloride. Accordingly, the acid on liberation is decomposed into the hydrazine and carbon disulfide.

Attempts to prepare III A gave instead 3,4-dimethyl-1,3,4-thiadiazolidine-2,5-dithione.

Diselenocarbazic acids (Table 1) could be prepared in good yields by acidifying solutions of dieselenocarbazates. It is an as yet unexplained fact, that 2-methyldiselenocarbazic acid (II B) and 2,3-dimethyldiselenocarbazic acid (III B) were stable in contrast to the analogous sulfur compounds II A and III A.

$$R^1R^2N-NR^3-CSeSe^{\ominus} \xrightarrow{H^{\oplus}} R^1R^2N-NR^3-CSeSeH$$

I B–V B

Rosenbaum *et al.*[7] have investigated oxidation of diselenocarbamates and shown that a mixture of bis(selenocarbamoyl) mono- and triselenides is formed instead of the bis(selenocarbamoyl) diselenide expected by analogy with the sulfur compounds. This result is of considerable interest with regard to an understanding of the chemistry of selenium and a parallel investigation of the oxidation products of different diselenocarbazates was therefore made. If a filtered aqueous solution of the hydrazinium diselenocarbazate was oxidised slowly with atmospheric oxygen only the diselenide was obtained (with reproducible elemental analyses and IR spectra).

$$2\ R^1R^2N-NHR^3 + CSe_2 \longrightarrow R^1R^2N-NR^3-CSeSe^{\ominus}\ R^1R^2\overset{\oplus}{N}H-NHR^3$$

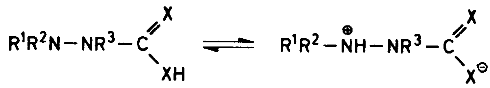
$$\xrightarrow{O_2} (R^1R^2N-NR^3-CSeSe)_2$$

II E, III E, V E

In the case of I E and IV E this method furnished only impure products. However, I E and IV E could instead be obtained by first liberating the diselenocarbazic acids and subsequently oxidize these with dimethylsulfoxide

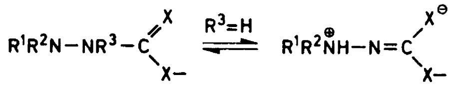
Table 2. Structures of the thio- and selenocarbazoyl compounds listed in Table 1.

Nonpolar and dipolar forms of acids



form 1 X=S,Se form 2

Nonpolar and dipolar forms of sulphides and selenides



form 1 X=S, Se form 3

Compound	Form	Infrared spectra [a] in KBr-discs (cm^{-1}) except where otherwise indicated
I A	2	ν(NH^+): 2500−3200 s br, with submaxima at 2600 and 2900. ν(ND^+): 1900−2300 s br, with submaxima at 1980 and 2210. ν(NH)/ν(ND): 3240vs/2410vs.
I B	2	ν(NH^+) and ν(NH): 2400−3250 vs br, with submaxima at 2600, 2880 and 3220. ν(ND^+) and ν(ND): 1900−2450 vs br, with submaxima at 1980, 2180 and 2410.
I D	3	ν(NH^+): 2500−3200 vs br, with submaxima at 2640 and *ca.* 2900, probably ν(NH) at 3245 vs.
I E	3	ν(NH^+): 2500−3200 s br, with submaxima at 2520, 2620, 3030. ν(ND^+): 2000−2400 s br, with submaxima at 2060, 2400. probably ν(NH)/ν(ND): 3200vs/2400vs.
II B	2	ν(NH^+): 2300−3000 vs, with submaxima at 2500 and 2760. ν(ND^+): 1800−2200 vs, with submaxima at 1930 and 2060. ν(CH): Too weak to be located even on *C*-deuteration.
II D	1	ν(NH)/ν(ND): 3180s, 3253m sh, 3268s br, 3300s/2340m, 2445m, 2468m. ν(CH)/ν(CD): 2918w,/2050vw, 2090vw. δ(NH_2)/δ(ND_2): 1613s/1150m.
II E	1	ν(NH)/ν(ND): 3152s, 3195m, 3230m, 3252m, 3310s/2315m, 2434m, 2474m ν(CH)ν(CD): 2910w/2046vw, 2095vw, 2163vw. δ(NH_2)/δ(ND_2): 1590s/1142m.
III B	2	ν(NH^+): 2300−2800 vs br, with submaxima at 2340 and 2520. ν(ND^+): 1800−2200 vs br, with submaxima at 1835 and 1965.
III D	1	ν(NH)/ν(ND): 3238s, 3252s/2391m sh, 2410s. ν(CH): 2791w, 2844w sh, 2870m, 2921s, 2959m, 2992m.
III E	1	ν(NH)/ν(ND): 3228s/2400s. ν(CH): 2785w sh, 2832w sh, 2867m, 2919m, 2959m, 2987m.
IV A	2	ν(NH^+): 2600−3000 vs, with submaxima at 2700 and 2880. ν(ND^+): 2000−2300 vs, with submaxima at 2060, 2120 and 2210. ν(NH)/ν(ND): 3080s/2270s sh. ν(CD): 2045m, 2190w. The corresponding ν(CH) could not be located.

Table 2. Continued.

IV B	2	$\nu(NH^+)$: 2600−2950 vs, with submaxima at 2640 and 2870. $\nu(ND^+)$: 2000−2250 vs, with submaxima at 2120 and 2210. $\nu(NH)/\nu(ND)$: 3040vs/2280s sh. $\nu(CH)/\nu(CD)$: 2930m/2050w, 2260w.
IV C	1+3	$\nu(NH^+)$: 2750s and 2910vs br. $\nu(NH)$: 3120s. $\nu(CH)$: 2793m, 2834m, 2865m, 2956m, 2994w, 3022w.
IV D	3	$\nu(NH^+)$: 2733s br, 2900m br and 2950.
IV E	1	$\nu(NH)/\nu(ND)$: 3062vs/2260s. $\nu(CH)$: 2779m, 2802m, 2818m, 2859m, 2881m, 2915m sh, 2947s, 2992m.
IV E	3	$\nu(NH^+)/\nu(ND^+)$: 2720m br and 2900m br/2080m br and 2140m. $\nu(CD)$: 2047m and 2260m. The corresponding $\nu(CH)$ could not be located.
IV F	3	$\nu(NH^+)$: 2720s br and 2890s br.
V A	1	$\nu(CH)$: 2791m, 2800m, 2833m, 2868m, 2887m, 2915m, 2931m, 2955m, 2988m. $\nu(SH)$: 2543w. In CCl_4 nearly the same frequencies were observed.
V B	2	$\nu(NH^+)$: 2000−2500 m br, with submaxima at 2220, 2300, 2450 and 2500. 2920m br. $\nu(ND^+)$: 1700−1900 m br, with submaxima at 1780, 1840 and 1890. $\nu(CH)$: 3002m and 3020m, unchanged by *N*-deuteration.
	1	In CCl_4, $CHCl_3$ and CS_2 the nonpolar form was obtained. In CCl_4, for example, the following absorptions are significant: $\nu(CH)$: 2785m, 2795m sh, 2833m. 2868m, 2887m, 2915m, 2933m, 2965m, 3001m. $\nu(SeH)$: 2286w, sharp.
V D	1	$\nu(CH)$: 2780m, 2792m, 2827m, 2860m, 2880m, 2905m, 2920m sh, 2953m, 2992m.
V E	1	$\nu(CH)$: 2781m, 2792m, 2826m, 2861m, 2878m sh, 2909m, 2921msh, 2954m, 2989m.
VI A	2	$\nu(NH^+)$: 2600−3000 vs, with submaxima at 2770 and 2930. $\nu(NH)$: 3090s.
VI C	1+3	$\nu(NH^+)$: 2600−2900 s br with submaxima at 2740 and 2840. $\nu(NH)$: 3120m br.
VI D	3	$\nu(NH^+)$: 2670m, 2730m, 2770m.
VII D	1	$\nu(NH)$: 3102vs.
VIII A	2	$\nu(NH^+)$: 2500−3000 s, with submaximum at 2770. $\nu(NH)$: 3070s.
VIII C	1+3	$\nu(NH^+)$: 2600−2900 s br with submaxima at 2660 and 2760. $\nu(NH)$: 3120m br.
VIII D	1+3	$\nu(NH^+)$: 2600−2800 m br with submaxima at 2650 and 2750. $\nu(NH)$: 3100s.
IX D	1	$\nu(NH)$: 3120vs.
X D	1	$\nu(NH)$: 3090s br.

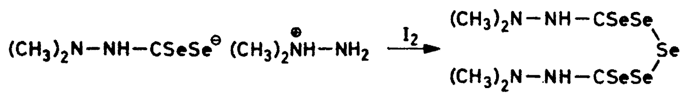
[a] As abbreviation for a stretching vibration, or a band occurring in the region in question and behaving like a stretching vibration *e.g.* on deuteration, ν has been used. $\delta(NH_2)$ = the symmetric deformation (scissoring) vibration of the amino group. In many cases the absorption maxima are ill-defined, and rounded values are quoted in the table.

(DMSO) as reported for thiols.[8] By adding water to the filtered DMSO solutions, I E and IV E, were precipitated. In the case of IV E an adduct with DMSO could also be isolated.

$$2\ R^1R^2N{-}NR^3{-}CSeSeH \xrightarrow[-(CH_3)_2S,\ -H_2O]{DMSO} (R^1R^2N{-}NR^3{-}CSeSe)_2$$

I E, IV E

In one instance a triselenide was obtained by oxidation. If crude 1,1-dimethylhydrazinium 3,3-dimethyldiselenocarbazate was oxidised with iodine in ethanol a clear solution was obtained from which a moderate yield of triselenide precipitated on addition of water:



IV F

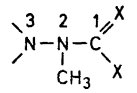
Since the normal diselenide IV E could be prepared by the oxidation of the analytically pure 3,3-dimethyldiselenocarbazic acid with DMSO this unusual result is attributed to a content of selenium or triselenocarbazate in the crude diselenocarbazate.[7]

DISCUSSION OF THE STRUCTURE

3,3-Dialkyldithio- and diselenocarbazic acids have previously been investigated by one of us [5] and found to possess a considerable thermal stability in the solid state. From IR evidence it was concluded that the solid compounds existed mainly or exclusively on a dipolar form (form 2, Table 2). Furthermore, both unsubstituted dithiocarbamic acid and hydrochlorides of the 3,3-dialkyl dithiocarbazic acids, which have in common the $>N{-}CSSH$ group, were known to be unstable substances. It was therefore argued that the unexpected stability of 3,3-dialkyldithio- and diselenocarbazic acids originated in the achievement of a dipolar structure. The implicit premise, that all dithiocarbamic acids are also unstable, has, however, turned out to be wrong since an investigation of these compounds [11] has shown *e.g.* 2-phenyl-2-isopropyldithiocarbamic acid to be stable both in the solid state and in solution. The present work provides examples which definitely prove that nonpolar dithio- and diselenocarbazic acids may have a stability comparable to that of the dipolar acids.

Before entering into a discussion of the results it should be pointed out, that statements concerning the dipolar *vs.* nonpolar structure based on IR analysis are founded only on observations made when the diagnostic absorption bands were clearly visible in the spectra. Therefore, small amounts of by-forms may in many instances have been overlooked, or impossible to detect unambiguously. The results obtained for the dithio- and diselenocarbazic acids in the solid state are listed in Table 2. Most of these compounds (I A, I B, II B, III B, IV A, IV B, V B, VI A, and VIII A) are characterized as the dipolar forms (form 2, Table 2) by the positions and the shapes of the absorptions due to the NH stretching vibration [10,12] and CH stretching vibration.[12] No sensible explanation could be found for the anomalous behaviour of trimethyldithiocarbazic acid (VA) having equally unambiguously a nonpolar structure judged by the presence of the SH stretching band at 2543 cm^{-1} and the usual CH stretching pattern [13] consisting of a series of sharp bands. Only six of these dithio- and diselenocarbazic acids (III B, IV A, IV B, V A, V B, and VIII A) could be dissolved in solvents applicable to IR and ^1H NMR spectroscopy, and only these compounds therefore were investigated in solution. A saturated solution of III B in $CDCl_3$ showed ^1H NMR absorption at τ=7.26, 7.02, and 6.28 ppm in the proportions 3:3:2 indicating a dipolar structure (form 2, Table 2) with the peaks corresponding to the two methyl groups and the NH_2^+ protons. The compounds IV A and IV B decomposed rapidly in $CHCl_3$ ($CDCl_3$) and unambiguous results were not obtained. The IR spectra of V A and V B (Table 2) showed these compounds to be nonpolar in solution; the same conclusion was drawn from the chemical shifts of the methyl protons in the ^1H NMR spectra (Table 3) being identical to those found for the (necessarily) nonpolar disulfides and diselenides listed in Table 3. Finally, VIII A in $CDCl_3$ was proved from the ^1H NMR spectrum to consist

Table 3. ^1H NMR spectra (τ, ppm) of 5–7 % solutions of nonpolar methyl substituted dithio- and diselenocarbazic acids, sulfides and selenides, containing the structure.



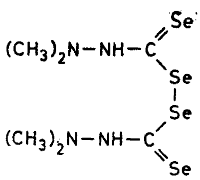
X=S, Se

Compound	Solvent	^1H NMR-signals (multiplicity)			
		N^2-CH_3	N^3-H	N^3-CH_3	$X-H$
II D	$(CD_3)_2SO$	6.40(1)	4.12(1)		
II E	$(CD_3)_2SO$	6.48(1)	3.86(1)		
III D	$(CD_3)_2SO$	6.48(1)	3.90(4)[a]	7.35(2)[a]	
III E	$(CD_3)_2SO$	6.55(1)	3.60(4)[b]	7.35(2)[b]	
V A	$CDCl_3$	6.75(1)		7.45(1)	6.23(1)
V B	$CDCl_3$	6.59(1)		7.38(1)	6.18(1)
»	CCl_4	6.61(1)		7.31(1)	6.39(1)
»	CS_2	6.66(1)		7.35(1)	6.45(1), broad
V D	$CDCl_3$	6.59(1)		7.28(1)	
V E	$CDCl_3$	6.63(1)		7.29(1)	

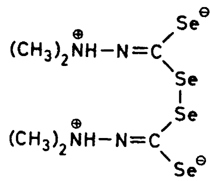
[a] J_{CHNH}=6.0 Hz. [b] J_{CHNH}=6.3 Hz.

of *ca.* 90 % nonpolar form (CH_3: two doublets at $\tau = 8.80$ and 8.85 ppm, CH: one septuplet at $\tau = 6.68$ ppm) and 10 % dipolar form (CH_3: two doublets at $\tau = 8.55$ and 8.58 ppm, CH: not observed) by using the criteria put forward in a previous paper.[14] The latter result is particularly interesting in definitely showing the existence of dipolar dithiocarbazic acids in solution. All these things considered, the stability of dithio- and diselenocarbazic acids bears no obvious relation to their structure being nonpolar or dipolar.

Sulfides and selenides of the type indicated at the top of Table 3 must necessarily exist in a non-amphoionic (nonpolar) form (form 1 of Table 2). This is also reflected in the IR data quoted in Table 2. The results obtained with sulfides and selenides which can be both nonpolar and dipolar are given in Table 2 (IR spectra in KBr). Of special interest are the observations made during the preparation of bis[3,3-dimethyl(selenocarbazoyl)]-diselenide (IV E), which formed an adduct containing two moles of dimethyl sulfoxide. If this adduct was treated several times with water it decomposed with liberation of a nonpolar form of IV E (form 1 of Table 2), but if it was instead kept in solution in dimethyl sulfoxide and water added to the filtered solution a dipolar form (form 3 of Table 2) precipitated:



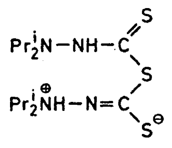
IV E, form 1



IV E, form 3

Proof for this proposal is provided in Table 2. However, it should be mentioned that before realizing the importance of the amount of solvent used materials were obtained showing IR spectra with characteristics corresponding both to that of the dipolar form 3 and to that of the nonpolar form 1. The relative amounts of the two forms appeared to vary independently of each other indicating mixtures to be present. Owing to the low solubilities of both forms of IV E ^1H NMR investigations did not clarify this point. The triselenide IV F had an IR spectrum almost indistinguishable from the dipolar form of IV E. The ^1H NMR spectrum of the disulfide IV D (dipolar in KBr) dissolved in DMSO-d_6 indicated two forms to be present in a ratio different from 1:1, while the spectrum of the ethyl homologue VI D in DMSO-d_6 indicated the presence of three forms. In the case of the isopropyl homologue (VIII D) in DMSO-d_6 the methyl protons were nonequivalent [14] and the signals partly overlapping. In $CDCl_3$, however, VIII D showed a ^1H NMR spectrum corresponding to *ca.* 50 % nonpolar form (CH_3: two doublets at $\tau = 8.77$ and 8.88 ppm, CH: one septuplet at $\tau = 6.70$ ppm) and *ca.* 50 % of a mixture of at least two dipolar forms (CH_3: absorption centred around $\tau = 8.50$ ppm, CH: absorption centred around $\tau = 6.25$ ppm). Of course, this might arise not only from the presence of another dipolar form, but also from a content of different amounts of *cis-trans* isomers.[14]

The IR spectra of the three monosulfides investigated (IV C, VI C and VIII C) showed that these compounds in the crystalline state all consisted of mixtures of dipolar and nonpolar forms. Of these compounds, VIII C gave ^{1}H NMR signals in $CDCl_3$ and DMSO-d_6 which were fairly well resolved. The signals in $CDCl_3$ corresponded to 50 % nonpolar form (CH_3: a doublet at τ=8.84 ppm without signs of nonequivalence, CH: a septuplet at τ=6.66 ppm) and 50 % dipolar form (CH_3: two doublets at τ=8.50 and 8.56 ppm, CH: two septuplets centred at *ca.* τ=6.28 and 6.18 ppm because of coupling with the NH proton [12]). It is interesting that the ^{1}H NMR spectrum in DMSO-d_6 also corresponded to 50 % nonpolar form (CH_3: a doublet at τ=8.96 ppm, CH: a septuplet at τ=6.76 ppm) and 50 % dipolar form (CH_3: two doublets at τ=8.73 and 8.65 ppm, CH: two septuplets at τ=6.20 and 6.27 ppm) since these two solvents are very different in solvating properties. The only reasonable conclusion which can be drawn is that VIII C (and probably the other monosulfides as well) in solution exists preponderantly as a mixed dipolar-nonpolar form, *viz.*



VIII C, form 1+3

INFRARED SPECTRA OF METHYLHYDRAZINIUM SALTS

The interpretation of the IR spectra of the nonpolar and the dipolar derivatives of dithio- and diselenocarbazic acids described above depends upon a correct assignment for the substituted hydrazines and hydrazinium salts from which they may be considered derived by extension of the skeleton with the CXX grouping (X=S, Se). Recently we have revised the assignment of the fundamentals of methylhydrazine, 1,1-dimethylhydrazine, and 1,2-dimethylhydrazine by comparison of the IR spectra with those of *N*- and *C*-deuterated compounds.[13] Investigations of the IR spectra of hydrazinium salts are limited to the hydrazinium mono- and dihalides [15,16] (IR region 400—3500 cm^{-1}), alkyl- and arylhydrazinium salts [17] (IR region 2000—3500 cm^{-1}, *i.e.* the NH stretching region), and 1,1,1-triethylhydrazinium chloride [18] (identification of the two stretching vibrations and the symmetric deformation vibration of the amino group). The IR spectra of related 2,2-dialkyltriazanium salts [19] have also been recorded and absorption characteristics of the amino groups identified by *N*-deuteration. To extend the basis for the interpretation of IR spectra of compounds containing hydrazinium groupings, the spectra of methylhydrazinium chloride, 1,1-dimethylhydrazinium iodide and 1,1,1-trimethylhydrazinium iodide have been recorded and compared with those of *C*- and *N*-deuterated compounds. The investigation was mainly limited to the solid state, but a few results obtained with saturated methanol solutions are given. In this way a consistent picture of group frequencies has been derived, which is presented partly in Table 4.

Table 4. Infrared spectra (600–1700 cm^{-1}) in KBr and proposed group frequency assignments iodide and some *C*- and

Assignment	$CH_3\overset{+}{N}H_2NH_2$	$CH_3\overset{+}{N}D_2ND_2$	$CD_3\overset{+}{N}H_2NH_2$	$CD_3\overset{+}{N}D_2ND_2$	$(CH_3)_2\overset{+}{N}HNH_2$	$(CH_3)_2\overset{+}{N}DND_2$ [b]
$\delta(NH_2)/\delta(ND_2)$	1608s	1206vs	1608s	1210vs	1610s	1219vs
$\delta(\overset{+}{N}H_2)/\delta(\overset{+}{N}D_2)$	1593m	1177s	1595s	1188s	—	—
$\omega(\overset{+}{N}H_2)/\omega(\overset{+}{N}D_2)$	1489s	1123m	1475m	1125w	—	—
$\delta(CH_3)/\delta(CD_3)$	1457m 1449m 1422w 1404m	1453m 1443m 1422w 1402m	1171w 1082m	1169m 1082m	1467s 1460s sh 1423m 1398m	
$\delta(\overset{+}{N}H)/\delta(\overset{+}{N}D)$	—	—	—	—	1411m sh	1049m
$\omega(NH_2)/\omega(ND_2)$	1342m 1334m	1051m	1318w 1306w	1050m	1361m br	1027m
$\tau(\overset{+}{N}H_2)/\tau(\overset{+}{N}D_2)$	1247m	931m 918w	1224m	916w	—	—
$\varrho(CH_3)/\varrho(CD_3)$	1247m 1149w 1133w	1240m 1141m	952m 944m	950m 865m 843m 839m	1244m 1193m 1111w	
skeletal stretching	1113s 892m 888m	967s 869s	1044m 790s	994m 789m	1083s 988s 801m	942s 904m 802m
$\delta(\overset{+}{N}H)/\delta(\overset{+}{N}D)$	—	—	—	—	1051m	862m
$\varrho(\overset{+}{N}H_2)/\varrho(\overset{+}{N}D_2)$	1010s	783m	990m sh	726w	—	—
$\varrho(NH_2)/\varrho(ND_2)$	946s sh 933s	739s	1009vs	682m	930s	790vs

[a] The following abbreviations have been used: δ=deformation, ω=wagging, τ=twisting, and ϱ=rocking motion. The absorptions are designated vs=very strong, s=strong, m=medium, w=weak, vw=very weak, br= broad, sh=shoulder. [b] Data incomplete owing to incomplete deuteration.

The bands in the region between 2000 cm^{-1} and 3500 cm^{-1} have been omitted from Table 4 since this region is expected to exhibit considerable absorption due to combination modes *etc.* For purposes of identification some useful features can be summarized as follows. The stretching vibrations of an amino group attached to a positively charged nitrogen atom ($>\overset{+}{N}-NH_2$)

of methylhydrazinium chloride, 1,1-dimethylhydrazinium iodide, and 1,1,1-trimethylhydrazinium *N*-deuterated derivatives.[a]

$(CD_3)_2\overset{+}{N}HNH_2$	$(CD_3)_2\overset{+}{N}DND_2$[b]	$(CH_3)_3\overset{+}{N}NH_2$	$(CH_3)_3\overset{+}{N}ND_2$	$(CD_3)_3\overset{+}{N}NH_2$	$(CD_3)_3\overset{+}{N}ND_2$
1610s	1227s	1610s	1175m	1606s	1226m
—	—	—	—	—	—
—	—	—	—	—	—
1160s 1101m 1086m 1068m		1474s 1465m 1431w 1400m	1469s 1430m 1398s	1210m 1152m 1096m 1057m	1206m sh 1148m 1129m 1057m
1426m 1409m	1053s	—	—	—	—
1338m	1030m	1391m	1075w	1380m	1031w
—	—	—	—	—	—
946m 805m		1282m 1252w 1142m	1288w 1260w 1143w 1126w 1006m	882m 876m 824m 795m	881m 877m 834m 795m
1044vs 843s 740m	980s 926m 920m 730m	1054s 897s 746m	960m 894m 739w	1003vs 802m 687w	914m 803m 681w
1055s sh	843m	—	—	—	—
—	—	—	—	—	—
990vs	775s	942s	793s	1003vs	775m

give rise to two or three strong bands in the range between 3120 and 3290 cm^{-1} (and between 2290 and 2470 cm^{-1} in the corresponding *N*-deuterated compounds). The stretching vibrations of hydrogen atoms bonded as in NH^+ or NH_2^+ groups, on the contrary, give rise to absorption located exclusively below 3000 cm^{-1}. The CH stretching vibrations of methyl groups attached to the positively charged nitrogen atom ($\rangle\overset{+}{N}-CH_3$) lead only to two bands of medium strength in the vicinity of 3000 cm^{-1}. The simplification of the normal pattern obtained for the CH_3-N grouping on protonation of the nitrogen atom has been discussed in a previous work [12] and used for identification in the foregoing section of this paper.

In the IR region between 2000 cm^{-1} and 600 cm^{-1} the amino group in the hydrazinium salts (*i.e.* $\rangle\overset{+}{N}-NH_2$) was expected to give bands with the following origin: one $\delta(NH_2)$ deformation vibration (1600—1620 cm^{-1}), one $\omega(NH_2)$ wagging motion (1300—1320 cm^{-1}), and one $\varrho(NH_2)$ rocking motion (930—950 cm^{-1}). Absorption due to torsional oscillation was expected to be below this range. The absorption ranges quoted in parentheses are those found for methylhydrazines [13] and therefore only to a certain extent normative. In methylhydrazinium chloride the corresponding group (*i.e.* $-N^+H_2-$) should give rise to four absorptions with the same origins, however, the force constant associated with the torsional motion is much higher, and the corresponding band shifted towards higher frequencies. The positions of the bands must be close to those for dimethylammonium chloride, reported [20] to be $\delta(NH_2^+)$ 1582 cm^{-1}, $\omega(NH_2^+)$ 1421 cm^{-1}, and $\varrho(NH_2^+)$ 878 cm^{-1}. In this compound the torsional oscillation is infrared inactive, but other evidence [21] points to a position of the $\tau(NH_2^+)$ torsional band near 1200 cm^{-1}. The assignments for dimethylammonium chloride were confirmed by Ebsworth and Sheppard [20] by *N*-deuteration. We have supplemented the investigation with the IR spectrum of the *C*-deuterated compound, which confirms the position of the $\delta(NH_2^+)$ and $\omega(NH_2^+)$ bands (at 1588 and 1433 cm^{-1}, respectively), but shows the $\varrho(NH_2^+)$ band to be coupled, probably with a $\varrho(CH_3)$ rocking band.

The bands originating from the amino groups in 2,2-dimethyltriazanium chloride (of the $-N^+-NH_2$ type) were identified by Utvary [19] as $\delta(NH_2)/\delta(ND_2)$ at 1620/1180 cm^{-1} and rocking or wagging at 1095/820 cm^{-1}. The first of these assignments is undoubtedly correct, but the second assignment fails to account for the disappearance of a band of medium strength at 1455 cm^{-1} and the appearance of a band of medium strength at 625 cm^{-1} on *N*-deuteration of 2,2-dimethyltriazanium chloride. The following revised assignment is therefore proposed: $\omega(NH_2)/\omega(ND_2)$ at 1455/1100 cm^{-1} and $\varrho(NH_2)/\varrho(ND_2)$ at 860/625 cm^{-1}. The band at 1095 cm^{-1} is assigned to a skeletal stretching motion (found at 1025 cm^{-1} in the deuterated compound) and it is proposed that the band at 820 cm^{-1} in the deuterated compound is also due to skeletal stretching and has its counterpart at 860 cm^{-1} in the undeuterated compound.

The assignments of the bands originating from the NH_2 and the NH_2^+ groups of the hydrazinium salts in Table 4 are chosen so as to correspond to the IR regions discussed above while being internally consistent. The deformation and wagging bands require no further comments. The assignment of the $\tau(NH_2^+)$ mode at 1247 cm^{-1} in methylhydrazinium chloride is open to discussion. The principal reason is that only a weak band was expected because the molecule approximates to that of dimethylammonium chloride in which the corresponding fundamental is IR-inactive. However, it was chosen because it was displaced to 1210 cm^{-1} (believed to be a result of a change of hydrogen bonding) when the IR spectrum was recorded using a saturated methanol solution.

The assignments of the NH_2 and NH_2^+ rocking modes are also problematic. The starting point was, that they were identified in the IR spectrum of the perdeuterated methylhydrazinium chloride as the two bands at 682 and 726 cm^{-1}. The rocking modes in the undeuterated material may now be associated with the two bands at 933 and 1010 cm^{-1}, giving isotopic shift ratios of 1.37 and 1.39, respectively. The lower of these bands must be $\varrho(NH_2)$ since only this band is also observed in the IR spectra of di- and trimethylhydrazinium iodide. As will be explained, the band at 1113 cm^{-1} in methylhydrazinium chloride, displaced to 967 cm^{-1} on *N*-deuteration, cannot be considered an alternative to the $\varrho(NH_2)$ mode, but rather is a skeletal stretching band. A similar band is found in the IR spectra of di- and trimethylhydrazinium iodide, but in these cases also both explanations are possible. The explanation is, that this alternative assignment rendered it impossible to account for the bands at 682 and 726 cm^{-1} in perdeuterated methylhydrazinium chloride. Furthermore, the isotopic shift ratios are much too small (1.10—1.15) and should instead be explained by coupling with other vibrations of the correct symmetry. In the methylhydrazinium ion, for example, the isotopic shift ratios of the wagging and deformation bands of the amino groups are too small by an order of magnitude corresponding to a coupling with the skeletal stretching band at 1113 cm^{-1} (assuming the molecule to have C_s symmetry and the vibrations in question to be of species a′).

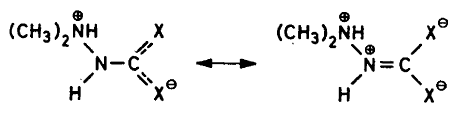
In 1,1-dimethylhydrazinium iodide two NH^+ bending modes will occur. In trimethylammonium salts the corresponding mode was identified [20] with a band near 1420 cm^{-1}, close to the position of one of the bands in Table 4 (1411 cm^{-1}). No counterpart of the other bending band at low frequency (1051 cm^{-1}) seems to have been reported before.

The remaining bands exhibited by the hydrazinium salts given in Table 4 have not been assigned in detail. Indeed, it must be pointed out that in several cases more absorptions have been assigned than allowed by the relevant number of normal vibrations of the hydrazinium ions, but there is at the present stage of approximation no safe way of deleting the superfluous bands. Three types of group frequencies have been distinguished in the Table: $\delta(CH_3)$ deformation bands, $\varrho(CH_3)$ rocking bands, and skeletal stretching bands. The skeletal deformation bands and various torsional modes have not been identified.

The assignments were performed by starting with 1,1,1-trimethylhydrazinium iodide and then transferring the assignments to the other hydrazinium salts, taking symmetry and number of normal vibrations expected for each compound into consideration. In the case of 1,1,1-trimethylhydrazinium iodide much help in the assignment was obtained from the recent normal co-ordinate analysis of trimethylamine oxide within the framework of the Urey-Bradley force field.[22] The following bands were observed from the $(CH_3)_3N^+$ group of this compound (*i.e.* in the C_{3v} approximation): $\delta(CH_3)$: 1482, 1472, 1457, and 1398 cm^{-1}, $\varrho(CH_3)$: 1240 and 1124 cm^{-1}, and finally the antisymmetrical and the symmetrical stretching vibrations of the NC_3 skeleton at 946 and 756 cm^{-1}, respectively. Assuming the deviation of the 1,1,1-trimethylhydrazinium ion from C_{3v} symmetry to be too small to be significant in this respect, it appeared possible to transfer all these assignments as listed in Table 4. An extra skeletal stretching vibration was added at 1054 cm^{-1}, which, within the usual limits of the group frequency concept, approximates to an N—N stretching motion. This value is quite comparable with those of the corresponding bands at 973 cm^{-1} in hydrazinium monochloride [15] and 1027 cm^{-1} in hydrazinium dichloride.[16]

INFRARED SPECTRA OF DITHIO- AND DISELENOCARBAZIC ACID DERIVATIVES

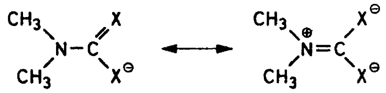
The IR characteristics of the dipolar 3,3-dimethyldithiocarbazic acid (IV A) have been discussed in a previous paper [5] by one of the present authors; the basis was the changes induced in the spectrum on deuteration and comparison with the IR spectrum of the dipolar selenium analogue, 3,3-dimethyldiselenocarbazic acid (IV B). The skeletal stretching bands situated at the highest frequencies in IV A and IV B were identified at 1282 cm^{-1} and 1291 cm^{-1}, respectively, *i.e.* as essentially ν(C—N) and not ν(C=N) stretching bands. Accordingly it was concluded that resonance stabilization



of the following type played only a minor role in both acids. Two strong absorption bands at 1035 cm^{-1} and 680 cm^{-1} in IV A had their counterparts at 927 cm^{-1} and 581 cm^{-1}, respectively, in IV B. They were unaffected by deuteration and therefore assigned to the ν_{as}(CXX) asymmetric skeletal stretching and the ν_s(CXX) symmetric skeletal stretching vibration, respectively.

Considerable material has been presented from this laboratory to substantiate that the position of the ν_{as}(CSS) IR absorption is in the range 950—1090 cm^{-1} in quite different surroundings, *e.g.* attached to phosphorus,[23] carbon or nitrogen.[24] From the evidence discussed below it appears that this range should be widened to 910—1090 cm^{-1} to cover the bulk of the results; in one instance ($ND_3^+NDCSS^-$) the band has been found exceptionally low (873 cm^{-1}). The corresponding ν_{as} (CSeSe) band has been found from 100 cm^{-1} [25] to 200 cm^{-1} [26] towards lower frequencies and supplemented with the material obtained in this investigation a range of 850—990 cm^{-1} can be quoted. However, the band is observed at 828 cm^{-1} in $ND_3^+NDCSeSe^-$.[9]

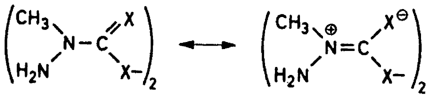
The papers dealing with the IR spectra of dithio- and diselenocarbamates have recently been reviewed [27] by Durgaprasad *et al.* and the results supplemented with a normal co-ordinate analysis of nickel(II) 2,2-dimethyldithiocarbamate and nickel(II) 2,2-dimethylselenocarbamate. The following skeletal stretching frequencies were calculated:



X=S, Se

X=S		X=Se	
ν(C=N):	1551 cm^{-1}	ν(C=N):	1547 cm^{-1}
ν_{as}(CNC):	1269 cm^{-1}	ν_{as}(CNC):	1278 cm^{-1}
ν_s(CNC):	990 cm^{-1}	ν_s(CNC):	977 cm^{-1}
ν_{as}(CSS):	980 cm^{-1}	ν_{as}(CSeSe):	946 cm^{-1}
ν_s(CSS):	605 cm^{-1}	ν_s(CSeSe):	574+348 cm^{-1}

The results of these calculations proved very valuable in assigning the corresponding bands in the IR spectra of bis 2-methyl(thiocarbazoyl) disulfide (II D) and the analogous selenium compound (II E). Both these compounds are nonpolar and stabilized by electron delocalisation:



X=S, Se

II D and II E

It is seen that the structure of II D and II E bears a close resemblance to the structure of the dithio- and diselenocarbamates depicted above. Accordingly, the positions and the origins of the skeletal stretching bands should be similar provided: 1) the modes are not significantly altered by the diminished symmetry of II D and II E relative to the carbamates, 2) the force constants of the C—N and N—N bonds do not differ essentially and 3) the polar resonance structures of II D and II E are of similar importance to those of the carbamates.

These conditions seem to be fulfilled to the necessary extent as shown by the results listed in Table 5. The ν(CN) stretching frequency varies between 1430 cm^{-1} and 1495 cm^{-1}. It is only weakly coupled to the CXX part of the molecules but somewhat more strongly both to the $\delta(NH_2)$ and $\delta(CH_3)$ deformation vibrations. The position of the band suggests that the resonance structures with a double bond between C and N have a similar weight (condition 3 above). The ν_{as}(NNC) absorption band is remarkably constant to both deuteration and selenation (*i.e.* substitution of selenium for sulfur). The lowering in frequency relative to the calculated position is some

Table 5. **Infrared spectra (KBr, 600–2000 cm^{-1}) of bis[2-methyl(thiocarbazoyl)] disulfide (II D), bis[2-methyl(selenocarbazoyl)] diselenide (II E) and the corresponding *N*- (N-d_4), *C*- (C-d_6), and perdeuterated (d_{10}) compounds.**[a]

Assignment	II D	II D–N–d_4	II D–C–d_6	II D–d_{10}	II E	II E–N–d_4	II E–C–d_6	II E–d_{10}
$\delta(NH_2)/\delta(ND_2)$	1613s	1150m	1610s	1148m	1590s	1142m	1586s	1133m
$\nu(C{=}N)$	1468s	1495s	1435s	1465s	1460m	1495s	1448s sh 1430s	1460s
$\delta(CH_3)/\delta(CD_3)$	1428m sh 1378s	1432m 1380s	1234w sh 1095m	1216m sh 1097w	1435m sh 1378m	1435m 1382m	1173w sh 1079w	1206m sh 1069w
$\omega(NH_2)/\omega(ND_2)$	1294w	945w	1294w	947w	1279w	—	1278w	—
$\nu_{as}(NNC)$	1207s	1211s	1199s	1200s	1204s	1209m	1198s	1196s
$\varrho(CH_3)/\varrho(CD_3)$	1105s	1101s	787vw	788w	1089m	1083s	779w	776m
$\nu_{as}(CSS)$ and $\nu_{as}(CSeSe)$	1050m 1037m	1007s	1047s	1035s sh 1021s	981m	944s 936s	987m br	963s sh 954s
$\varrho(NH_2)/\varrho(ND_2)$	944s 929s	741w	945s	735w	892s	731m	886s	726m
$\nu_s(NNC)$	887m	853m	899s 874m sh	902s	859s	829s	860s sh	885s
$\nu_s(CSS)$ and $\nu_s(CSeSe)$	562m 530w	549w 531m	544m 527w	542w 533m	504m	474m	473m	445m

[a] The following abbreviations have been used in addition to those listed in Table 4: ν_{as}=asymmetrical stretching, ν_s=symmetrical stretching. The *N*- and the *C*-deuterated compounds are indicated by the suffixes N-d_x and C-d_x, respectively, x indicating the number of hydrogen atoms substituted with deuterium.

50 cm^{-1} which is a reasonable deviation. As expected, the ν_{as} (CSS) frequency in II D situated in the range 1007—1050 cm^{-1} is changed to the lower ν_{as}(CSeSe) frequency in II E between 936 and 987 cm^{-1}. The ν_s(CSS)/ν_s(CSeSe) bands do not only couple with the NH/ND and CH/CD motions but also to a small extent mutually. Nevertheless they are sufficiently close to the calculated positions to be identified. The assignment of the $\delta(NH_2)$, $\omega(NH_2)$, and $\varrho(NH_2)$ modes in II D and II E to bands near 1600, 1300, and 900 cm^{-1} is based on the shifts induced on deuteration and the location of the corresponding bands in methylhydrazine [13] at 1615, 1305, and *ca.* 930 cm^{-1}, respectively. The assignments of the $\delta(CH_3)$ and $\varrho(CH_3)$ modes are then straightforward.

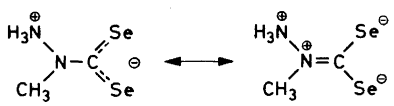
To evaluate the influence of polarity on the skeletal stretching frequencies, comparison was made with a dipolar compound with the same heavy-atom skeleton. Since II A could not be prepared Table 6 lists only the IR data for 2-methyldiselenocarbazic acid (II B) and its differently deuterated derivatives. The figures of Table 5 and Table 6 compare well, except that

Table 6. Skeletal stretching bands in the IR spectra (KBr, cm^{-1}) of 2-methyldiselenocarbazic acid (II B) and its deuterated derivatives.[a]

Compound	Assignment				
	ν(CN)	ν_{as}(NNC)	ν_{as}(CSeSe)	ν_s(NNC)	ν_s(CSeSe)
II B	1359m	1218s	924s	838m	486w
II B—N—d_3	1348m	1215s	906s	806m	489w
II B—C—d_3	1369m	1203s	922s	878m sh	489w
II B—d_6	1360s	1193s	909s	886m sh	485w

[a] See footnotes to Tables 4 and 5.

the ν(CN) stretching bands are lowered by *ca.* 100 cm^{-1} and the ν_{as}(CSeSe) bands by *ca.* 50 cm^{-1}. The former shift reflects a diminished double bond character of the CN band in question and clearly indicates that the electron delocalisation described for II D and II E is here insignificant:



II B

This was expected, since displacement of an electronpair to form the N^+=C—Se^- structure must work against the electrostatic field already present in the dipolar acid. This argument also explains the importance of this resonance structure in the nonpolar compounds II D and II E discussed above, where no such field is present to hinder resonance stabilization.

In the IR spectra of unsubstituted dithiocarbazic acid (I A), diselenocarbazic acid (I B), the disulfide (I D), and the diselenide (I E) only four types of skeletal stretching frequencies are expected: ν(CN), ν(N—N), ν_{as}(CXX), and ν_s(CXX). These bands were assigned by comparison with the *N*-deuterated compounds (I A—N—d_4, I B—N—d_4, and I E—N—d_6) as stated in Table 7. From the deuteration results it is clear that the vibrations of the NH/ND and NH_3/ND_3 groups couple rather heavily with the skeletal stretching vibrations in the cases of I A and I B, rendering the assignments open to criticism. In spite of this coupling, the positions of the ν(CN),

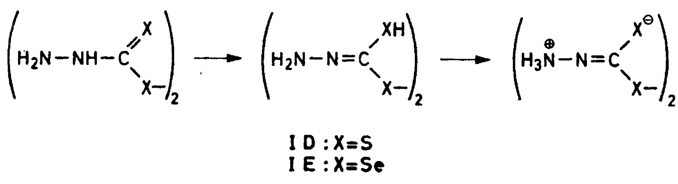
Table 7. Skeletal stretching bands in the IR spectra (KBr, cm^{-1}) of dithiocarbazic acid (I A), diselenocarbazic acid (I B), bis(thiocarbazoyl) disulfide (I D), and bis(selenocarbazoyl) diselenide (I E) and the perdeuterated species.[a]

Compound	Assignment			
	ν(CN)	ν(N—N)	ν_{as}(CXX)	ν_s(CXX)
I A	1269vs	1064vs	986vs	653m
I A—N—d_4	1336vs	—	873s	620m
I B	1268vs	1022s	896vs	529m 489m
I B—N—d_4	1334vs	—	828s	495m 484m
I D	1513vs	1018s	970vs	692s
I E	1498s	973vs	858vs	537m
I E—N—d_6	1463vs	970m	851vs	—

[a] See footnotes to Tables 4 and 5.

ν_{as}(CSeSe), and ν_s(CSeSe) bands in the spectrum of I B are satisfactorily close to those of the corresponding bands in II B (Table 6).

Bis(thiocarbazoyl) disulfide (I D) and the analogous diselenide (I E) are both dipolar. In contrast to the acids I A and I B, which are dipolar by virtue of the possibility of transfer of the SH or SeH proton to the basic nitrogen atom, the dipolar forms of I D and I E can be visualized as derived from the nonpolar forms *via* the enethiol, or eneselenol forms, resp.:



I D : X=S
I E : X=Se

In accordance with the presence of a C=N bond in such dipolar forms, the IR spectra displayed a strong absorption band in the neighbourhood of 1500 cm^{-1} (Table 7). Again, the $\nu_{as}(CXX)$ and the $\nu_s(CXX)$ frequencies are transferred with only minor changes from the corresponding acids I A and I B. The position of the ν(N—N) stretching band near 1000 cm^{-1} corresponds to that found for the hydrazines (*cf.* the foregoing part of this paper).

Since II B, II D, and II E have identical structures to III B, III D, and III E, respectively, (Table 2) the IR spectra should be comparable apart from 1) an extra skeletal stretching band in the latter compounds, 2) the effect of changing an amino group to a methylamino group and 3) the resulting coupling changes. The skeletal stretching vibrations of 2,3-dimethyldiselenocarbazic acid (III B, Table 8) can therefore be approximated by a ν(CN), a $\nu_{as}(CXX)$, and a $\nu_s(CXX)$ mode; in addition three modes will arise from the dimethylhydrazine part of the molecule, and from lack of more precise knowledge they are termed $\nu^1(C_2N_2)$, $\nu^2(C_2N_2)$, and $\nu^3(C_2N_2)$. The disulfide (III D) and diselenide (III E) will display the same bands as long as the identical halves do not couple measurably with each other. The $\nu_{as}(CXX)$ and the $\nu_s(CXX)$ bands are double in III D and III E, which might be explained in this way. Apart from this new feature, the assignments of Table 8 need only few comments. It should be noted that the position of the ν(CN) band confirms III B to be dipolar and only insignificantly resonance stabilized. By comparing the figures of Table 8 with those of Table 5—6 it is possible to identify the extra skeletal stretching band around 1000 cm^{-1} as $\nu^2(C_2N_2)$. This is, as expected, in the region of CC and CN stretching vibrations.

Table 8. Skeletal stretching bands in the IR spectra (KBr, cm^{-1}) of 2,3-dimethyldiselenocarbazic acid (III B), bis[2,3-dimethyl(thiocarbazoyl)] disulfide (III D), and bis[2,3-dimethyl(selenocarbazoyl)] diselenide (III E), and the *N*-deuterated compounds.[a]

Compound	Assignments					
	ν(CN)	$\nu^1(C_2N_2)$	$\nu^2(C_2N_2)$	$\nu_{as}(CXX)$	$\nu^3(C_2N_2)$	$\nu_s(CXX)$
III B	1386m	1212s	1049m	878vs	806w	540w 490w
III B—N—d_2	1338s	1212s	—	867vs	800w	529w 487w
III D	1527s	1213s	1059s	966m sh 957s	810m 797s	588m 581m
III D—N—d_2	1486s	1225s	1017s	927s 922s	843m 833m	585m 579m
III E	1508s	1213m	1050s	899s 873w	776m	554m 484m
III E—N—d_2	1480s	1222m	982m	873s 867vs	828m	554w 477w

[a] See footnotes to Tables 4 and 5.

The same comments apply, *mutatis mutandis*, to the 3,3-dimethyl-substituted derivatives given in Table 9, except that the dipolar forms of IV D and IV E should also be compared to I D and I E. As before, the deviation

Table 9. Skeletal stretching bands in the IR spectra (KBr, cm^{-1}) of 3,3-dimethyldithiocarbazic acid (IV A), 3,3-dimethyldiselenocarbazic acid (IV B), the dipolar bis[3,3-dimethyl(thiocarbazoyl)] disulfide (IV D) and the dipolar and nonpolar forms of bis-[3,3-dimethyl(selenocarbazoyl)] diselenide (IV E).[a]

Compound	Assignments				
	ν(CN)	$\nu^1(C_2N_2)$	$\nu^2(C_2N_2)$ ν_{as}(CXX)	$\nu^3(C_2N_2)$	ν_s(CXX)
IV A	1286s	—	1037s +970s	843s	683s
IV A—N—d_2	1303m	—	1013vs+968s	808s	660s
IV A—C—d_6	1307s	1173m	953vs	740s	664s
IV A—d_8	1297s	1145m	942vs	740s	650s
IV B	1293s	—	977s +929s	819s 809s	583s
IV B—N—d_2	1320s	—	1003vs+863s	793s	562s
IV B—C—d_6	1269s	1202m	900vs	742s	562s
IV B—d_8	1267s	1140m	948vs	727s	545s
IV D	1485s	—	970vs+917s	812s	700s
IV E— dipolar	1488s	—	926s +878s	779s	596s 593s 591s
IV E—N—d_2	1487s	—	1018s +880vs	780s	587s 578s
IV E—C—d_{12}	1480vs	—	871vs	730m	573s 566s
IV E-d_{14}	1477vs	—	868s +852s	726m	571s
IV E— nonpolar	1500s	—	1003s +939vs	818vs	595m
IV E—N—d_2	1487m	—	1019s +879vs	779s	592m

[a] See footnotes to Tables 4 and 5.

from the C_{2v} symmetry of the reference compound (2,2-dimethyldithiocarbamic acid) and the increased number of normal vibrations present, causes a coupling of the ν_{as}(CXX) and the ν_s(CXX) modes with the NH/ND and CH/CD modes. However, the coupling with the other skeletal stretching vibrations has gained significance in the 3,3-dimethylsubstituted compounds. This is indicated in Table 9 by placing the figures in a common column. It should also be mentioned that the identification of the $\nu^1(C_2N_2)$ band was in most cases impossible because of the strong coupling with the $\varrho(CH_3)$ or the $\delta(CD_3)$ internal modes. Apart from these features, the previously published results are verified.

Finally the IR spectra of the trimethylsubstituted derivatives of dithiocarbazic acid and diselenocarbazic acid (V A—V E) were investigated. Since

C-deuterated 1,1,2-trimethylhydrazine was not available only *N*-deuteration was used in the analysis of the spectra. It can be mentioned that the ν(CN) band was found in the range 1472—1513 cm^{-1} in the nonpolar compounds and around 1350 cm^{-1} in the dipolar form of V B in accordance with the previous findings. In support of the structures proposed on the basis of the results given in Table 2, the spectra in the region 500—1600 cm^{-1} of the nonpolar V A and V D are nearly identical, as are the spectra of the nonpolar V B and V E.

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of this laboratory. The melting points (uncorrected) were determined using a Büchi melting point apparatus. In the cases where definite melting points could not be determined directly they were instead recorded using material in a closed tube (marked as c.t. in Table 1). The infrared spectra (400—4000 cm^{-1}) were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer by the potassium bromide pellet technique or in solution. The nuclear magnetic resonance spectra were obtained on a Varian A—60 A instrument equipped with a Varian variable temperature controller. Tetramethylsilane was used as an internal reference. Some of these spectra were recorded using a Varian Time Averaging Computer Model C 1024. The following directions refer to entry 'Method' of Table 1.

Method a. The hydrazinium dithiocarbazate was prepared [2] from carbon disulfide and anhydrous hydrazine. A solution of iodine (2×10^{-3} mol) in absolute ethanol (25 ml) was dropped into a vigorously stirred and ice-cooled solution of hydrazinium dithiocarbazate (4×10^{-3} mol) in water (10 ml) during 2 h. The iodine colour disappeared immediately and very shortly after the addition had started the crystalline disulfide began to precipitate. At the end of the reaction the product was filtered off, washed with water, and dried *in vacuo*. An elemental analysis performed directly on the crude material showed the purity to be satisfactory.

Method b. Hydrazinium diselenocarbazate was prepared in 70—80 % yield from carbon diselenide and anhydrous hydrazine.[9] Diselenocarbazic acid was then liberated immediately before use in 60—70 % yield with hydrochloric acid. Diselenocarbazic acid (1 g) was dissolved in dimethyl sulfoxide (10 ml); a process which was strongly exothermic. The dark red brown suspension was filtered to remove precipitated selenium and polymeric material. Water (80 ml) was added to the filtered orange solution to precipitate the diselenide. This was filtered off, washed four times with water, and dried *in vacuo* to give the pure diselenide. Repeated washing with carbon disulfide resulted in partial removal of selenium, and the resulting material gave an elemental analysis corresponding to a mixture of mono- and diselenide.

Method c. A solution of methylhydrazinium 2-methyldiselenocarbazate (2×10^{-3} mol prepared from carbon diselenide and methylhydrazine [2]) in water (8 ml) was filtered and cooled in an icebath. During a period of 15 min 1 N HCl (2 ml) was added dropwise to the stirred solution, and the crystalline precipitate filtered off, washed with small amounts of cold water, and finally dried *in vacuo* at room temperature.

Method d. A solution of iodine in aqueous potassium iodide was added dropwise to a filtered aqueous solution of alkylhydrazinium or potassium alkyldithiocarbazate [2] with vigorous stirring. The precipitated crystalline product was filtered off or isolated by centrifugation, washed with water, and dried *in vacuo*. It was recrystallized from 96 % ethanol (II D with 63 % recovery, III D with 65 % recovery) or an ethanol-water mixture (V D with 70 % recovery). Both III D and V D were also isolated in varying amounts as water-insoluble by-products in the synthesis of the potassium or alkylhydrazinium salts used as starting materials.[2]

Method e. A slow stream of oxygen was passed through a filtered, aqueous solution of alkylhydrazinium alkyldiselenocarbazate [2] at 20°C. The crystalline material which separated from the solution was filtered off, washed with water and dried *in vacuo* at room temperature. The crude product was generally analytically pure diselenide. The yield was very variable, depending primarily on the length of time the solution was aerated with oxygen and the tendency of the salt for oxidation. Thus, II E after several hours only furnished from 25 to 50 % yield, while III E and V E were formed more easily from the respective diselenocarbazates. For this reason they could also be isolated as water-insoluble by-products in the synthesis [3] of the diselenocarbazates, and if thoroughly washed with water and sometimes polar organic solvents they were analytically pure.

Method f. As for method c, but with careful exclusion of oxygen to avoid formation of diselenides. The solvents were boiled for some time, saturated with nitrogen, and the synthesis performed in a nitrogen atmosphere.

Method g. The bis[3,3-dialkyl(thiocarbazoyl)] disulfide (0.05 mol) was dissolved in the minimum amount of 96 % ethanol at room temperature and the saturated solution filtered. After addition of potassium cyanide (0.05 mol) dissolved in water (5 ml) the solution turned yellow. After ½ h a crystalline precipitate started to settle; after a further 1½ h it was filtered off and washed with small amounts of water. Usually, the crude products were analytically pure.

Method h. A solution of carbon disulfide (0.1 mol) in absolute ethanol (25 ml) was added dropwise to a cooled solution of the hydrazine (0.2 mol) in absolute ethanol (50 ml). The temperature was kept near 0°C during the addition, and afterwards the reaction mixture was allowed to stand for 1 h at room temperature to complete the formation of the hydrazinium salt. The temperature was again held near 0°C during the addition of a concentrated solution of iodine (0.1 mol) in absolute ethanol. The iodine colour disappeared immediately and the disulfide started to precipitate a few minutes after the addition of the iodine solution had started. The addition was complete in 5 min and the precipitate was then filtered off. The collected material was washed with four 10 ml portions of water and dried *in vacuo*. The crude products were analytically pure.

Method i. When IV B (2×10^{-4} mol) was treated with dimethyl sulfoxide (0.1 ml) it dissolved after a short time with formation of a brown solution. The acid was still not completely dissolved when a yellow crystalline precipitate appeared. This was isolated by centrifugation, washed several times with dry ether and dried *in vacuo*. The m.p. was 76.5–77°C and according to elemental analysis it was composed of the diselenide IV E and dimethyl sulfoxide in the mole proportion 1:2. (Found: C 19.35; H 4.20; N 9.20. Calc. for $C_{10}H_{26}N_4O_2S_2Se_4$: C 19.55; H 4.27; N 9.12). If this adduct was treated several times with water it decomposed with formation of another yellow crystalline compound. This was isolated, dried *in vacuo* and characterized by infrared spectroscopy to be a crystalline, nonpolar form of IV E. The crude product was analytically pure.

Method j. If IV B (2×10^{-4} mol) was instead treated with a greater amount of dimethyl sulfoxide (1–1½ ml) the adduct (see method *i* above) did not precipitate. The solution was filtered, and water (6–8 ml) added. The precipitate was filtered off, washed several times with water and dried *in vacuo*. To secure the formation of an analytically pure material all operations must be performed under a nitrogen atmosphere. The crystalline product was characterized by its infrared spectrum as a dipolar form of IV E.

Method k. Crude dimethylhydrazinium 3,3-dimethyldiselenocarbazate [5] (1 g) was suspended in ethanol (25 ml) and oxidized by the addition of the equivalent amount of iodine dissolved in ethanol. After a few minutes the suspension had changed to a clear solution. Addition of water gave a precipitate which was filtered off, washed with water and dried. The crude product was analytically pure, but gave off elementary selenium on standing or on prolonged boiling with carbon disulfide.

Method l. With stirring, 1.0 N HCl (1.5 ml) was added dropwise over a period of 15 min to a filtered and cooled solution of potassium trimethyldithiocarbazate (1.5×10^{-3} mol) in water (9 ml). The colourless precipitate was isolated by centrifugation, washed with water and dried *in vacuo* at room temperature. The acid may be prepared from the trimethylhydrazinium salt in nearly the same yield.

Method m. The method was essentially the same as method *h*, but no product could be induced to precipitate after the iodine oxidation, even after prolonged scratching with a spatula and cooling to –80°C. However, if water was added to the reaction mixture an oil separated. This was dissolved in ether (50 ml) and the solution extracted once with water (20 ml). The ethereal extract was dried over magnesium sulfate and the solvent evaporated. Finally, the crystalline residue was recrystallized from petroleum ether.

Potassium trimethyldithiocarbazate. (Potassium salt of V A). A suspension of finely pulverized potassium hydroxide (2×10^{-2} mol) in a mixture of trimethylhydrazine (2×10^{-2} mol) and dioxan (40 ml) was stirred vigorously while a solution of carbon disulfide (2×10^{-2} mol) in dioxan (25 ml) was added over a period of 1 h. A colourless precipitate was formed which was filtered off, washed successively with dioxan and dry ether and finally dried *in vacuo*. The yield of crude product was 66 %. The potassium salt could be purified by dissolution in absolute ethanol and reprecipitation with dry ether as creamy, leafy crystals.

Potassium 2,3-dimethyldithiocarbazate. (Potassium salt of III A). By a synthesis identical with the foregoing, but using 1,2-dimethylhydrazine instead of trimethylhydrazine, an 80—86 % yield of colourless salt was obtained. The reaction was performed in a nitrogen atmosphere.

Attempted preparation of III A. To an aqueous, filtered solution of the potassium salt of III A (see above) was added 1 N HCl with stirring until the pH had reached *ca.* 4. The resulting oily suspension liberated hydrogen sulfide and after some time colourless needles precipitated from the stirred mixture. The compound was filtered off, washed with water and dried *in vacuo*. The yield of colourless compound was very dependent on the reaction time and the amount of HCl added. The sharp m.p. of 163—165°C suggested it to be pure and it was submitted to elemental analysis. (Found: C 26.91; H 3.46; N 15.92. Calc. for $C_4H_6N_2S_3$: C 26.97; H 3.40; N 15.73). Since this compound was obviously not be desired III A it was investigated by ^{1}H NMR and IR spectroscopy. In the ^{1}H NMR spectrum ($CDCl_3$) only one signal was observed at $\tau=6.08$ ppm showing a symmetrically substituted $-NCH_3-NCH_3-$ grouping to be present. In support of this conclusion the IR region between 2500 and 3500 cm^{-1} showed absorption only in the CH stretching region near 3000 cm^{-1}, and both in KBr and in $CHCl_3$ solution it was devoid of bands which could be attributed to NH stretching. The compound was recognized as *3,4-dimethyl-1,3,4-thiadiazolidine-2,5-dithione* by the identity of its IR spectrum with that of an authentic compound, as prepared by Thorn [28] by heating dimethylhydrazine and carbon disulfide under reflux for 9 h in ethanol and reported to have a m.p. of 168—169°C.

1,1-Diisopropyl-4-phenylthiosemicarbazide. Equimolar amounts of VIII C and aniline dissolved in ethanol were boiled for 10 min. A crystalline precipitate obtained by adding small amounts of water was filtered off, washed with aqueous ethanol and dried. It was identified as the title compound by the melting point (99—100°C), the mixed melting point (98—100°C) and the identity of the IR spectrum with that of an authentic specimen.[29]

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