

Vibrational Spectra and Force Fields of Benzylthiocyanate, Benzylselenocyanate and Benzyltellurocyanate

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Infrared and Raman spectra of benzylthiocyanate, benzylselenocyanate and benzyltellurocyanate in the solid phase were recorded and tentative assignments, based upon force fields transferred from similar molecules, were proposed.

A number of organic thio- and selenocyanates have been studied by means of vibrational spectroscopy,¹⁻⁶ but so far very little spectroscopic work exists on organic tellurocyanates. Microwave spectroscopic studies of the ethylthio⁷ and ethylselenocyanate⁸ indicate that the preferred conformation of the linear XCN group is *syn*-clinal (*gauche*) to the methyl group. An X-ray study⁹ of 4-nitrobenzylthiocyanate, 4-nitrobenzylselenocyanate, 4-nitrobenzyltellurocyanate and benzylselenocyanate (BSeCN) shows that the *syn*-clinal conformer is also preferred in the crystalline state, and the same trend is expected for benzylthiocyanate (BSCN) and benzyltellurocyanate (BTeCN). The first indication, to our knowledge, that the *anti* conformer also exists, is a recent X-ray study of phenacylthiocyanate and phenacylselenocyanate,¹⁰ PhCOCH₂XCN.

Force fields have been developed for the methyl¹¹ and ethylthiocyanates¹² and the latter has served as a starting point for the calculations presented here. The aim of this work has been to ascertain whether reliable force fields for the title compounds could be compiled from the force fields of similar, but simpler, molecules. If so, these transferred force fields could be used as an aid in the interpretation of the complex vibrational spectra of BSCN, BSeCN and BTeCN.

EXPERIMENTAL

The preparation and purification of the title compounds together with some of their physical data, have been described previously.^{13,14}

Infrared spectra of BSCN, BSeCN and BTeCN in the solid phase were recorded on a Perkin-Elmer model 225 grating spectrometer (4000-400 cm⁻¹, KBr pellet) and a Bruker IFS 114 C evacuable Fourier Transform spectrometer (700-40 cm⁻¹, polyethylene pellet). Due to their low solubility solution spectra of BSCN, BSeCN and BTeCN were not obtained. The Fourier Transform spectrometer was equipped with a standard DTGS detector and Mylar film beam-splitters of 3.5 and 12 μm thickness were used.

Raman spectra of the pure BSCN and BSeCN solids were recorded with a Dilor RT 30 spectrometer using the 488.0 nm line of an argon ion laser for excitation (CRL model 52 G). Due to its low stability with respect to the formation of elemental tellurium, the Raman spectrum of BTeCN could not be recorded.

RESULTS AND DISCUSSION

Because of their large size, the title compounds have very complex vibrational spectra with a large number of bands. Table 1 shows the observed wavenumbers together with calculated fundamental frequencies. Parts of the infrared spectra are shown in Figs. 1 to 3 and corresponding Raman spectra are given in Figs. 4 and 5. Bands, not assigned as fundamentals, can readily be ascribed to combination frequencies, as indicated in Table 1.

The majority of the bands coincide in the spectra of the three compounds and these have

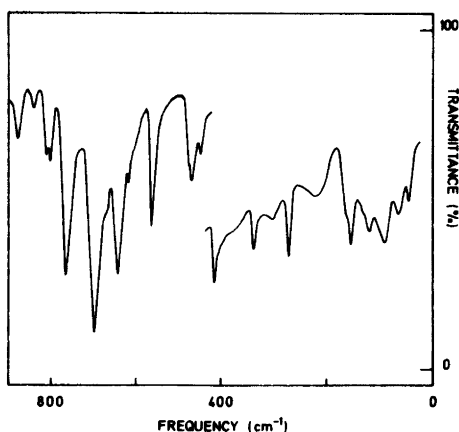


Fig. 1. Infrared spectrum of benzylthiocyanate. 900–400 cm^{-1} , KBr pellet; 400–50 cm^{-1} , polyethylene pellet.

been assigned to modes belonging to the common benzyl group. Weak bands in the region 2920–2950 cm^{-1} were interpreted as the $-\text{CH}_2$ stretching modes, and the corresponding $-\text{CH}_2$ bendings were assigned to bands at 1422–1425 cm^{-1} , 1208–1241 cm^{-1} , 1191–1202 cm^{-1} and 850–886 cm^{-1} for scissor, twist, wag and rocking modes respectively. A very strong absorption at 2145 ± 1 cm^{-1} , present in all spectra of BSCN, BSeCN and BTeCN, was attributed to the CN stretching mode.

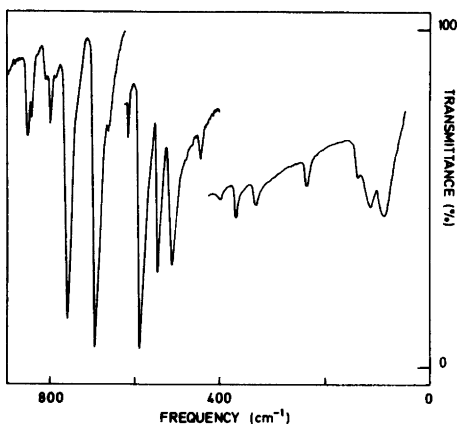


Fig. 2. Infrared spectrum of benzylselenocyanate. 900–400 cm^{-1} , KBr pellet; 400–50 cm^{-1} , polyethylene pellet.

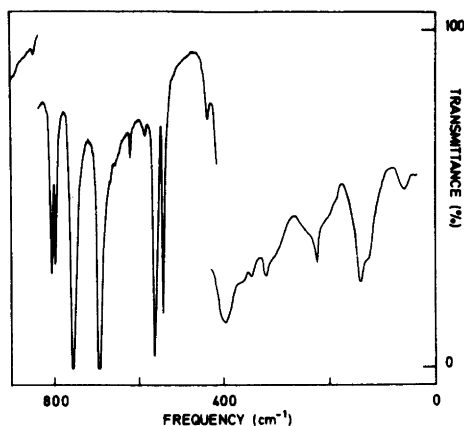


Fig. 3. Infrared spectrum of benzyltellurocyanate. 900–400 cm^{-1} , KBr pellet; 400–50 cm^{-1} , polyethylene pellet.

The region above 800 cm^{-1} could thus be assigned fairly easily by comparing the spectra of the three compounds and by comparing the present normal coordinate calculations, and in particular potential energy distributions and L-matrices, with corresponding calculations on benzene¹⁵ and *p*-fluorobenzonitrile.¹⁶

The interpretation of the spectral region below 800 cm^{-1} proved more difficult. Two stretching fundamentals are expected in this region, the XC stretching mode of the XCN group and the stretching of the C_αX bond linking the benzyl and XCN fragments. Force constant calculations immediately showed that whereas the XC vibration can be regarded as a group frequency, showing little or no mixing with other vibrations, the C_αX stretching, on the other hand, contributes significantly to several fundamentals of the molecules studied here.

A previous study of a series of alkylselenocyanates⁶ including phenylselenocyanate,^{5,17} with SeC stretching frequencies ranging from 512 cm^{-1} to 522 cm^{-1} , confirms the interpretation of a BSeCN band at 516 cm^{-1} as the SeC stretching fundamental. Likewise, spectra of the tellurocyanate ion¹⁸ confirm the assignment of a BTeCN band at 438 cm^{-1} to the corresponding TeC stretching mode. Some ambiguities still remain in the case of the thiocyanates, whether the SC stretching fundamental is to be assigned to the higher of the lower of two bands observed in the 600–700 cm^{-1} range.^{6,14} This question does

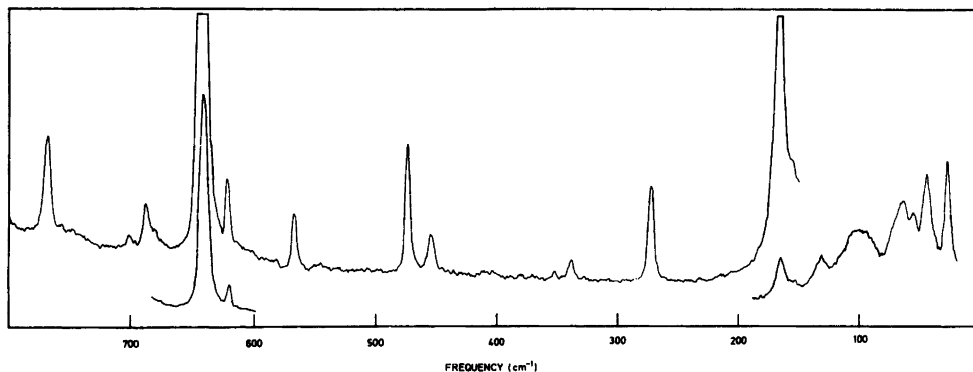


Fig. 4. Raman spectrum of solid benzylthiocyanate.

not arise in the case of BSCN since, for reasons outlined above, the very intense band at 642 cm^{-1} can only be interpreted as the SC stretching mode. As shown by the calculation, the $C_{\alpha}S$ bond stretching vibration mixes into fundamentals both at lower and higher wavenumbers than the SC mode.

The XCN linear bending vibrations have been assigned at higher wavenumbers than the CCC_{α} and $CC_{\alpha}X$ bendings, in accordance with previous normal coordinate calculations on methyl-¹¹ and ethylthiocyanate.¹²

The bending modes below 350 cm^{-1} have all been calculated at consistently lower wavenumbers than the observations, indicating that the corresponding force constants should be increased. Due to the appearance of interfering lattice modes, the CC_{α} and $C_{\alpha}X$ torsional modes have not been assigned.

FORCE CONSTANT CALCULATIONS

A force field for *p*-fluorobenzonitrile¹⁶ based upon an *ab initio* calculated force field for benzene¹⁵ was chosen as a basis for the present normal coordinate analysis. Standard bond lengths¹⁹ ($r_{CC}=139.7\text{ pm}$ and $r_{CH}=108.4\text{ pm}$) were chosen for the phenyl group, thus allowing direct comparison with previously calculated benzene fundamentals. A tetrahedral configuration around the benzyl (C_{α}) carbon was assumed with a CH bond length of 109.4 pm . The remaining geometrical parameters were taken from X-ray data.⁹ In the case of BSCN and BTeCN, structure data were transferred from the corresponding 4-nitro compound.⁹

Force fields for *p*-fluorobenzonitrile,¹⁶ including the $CC(\text{ring})C_{\alpha}$ bend force constant, toluene²⁰ and ethylthiocyanate¹² were transferred to

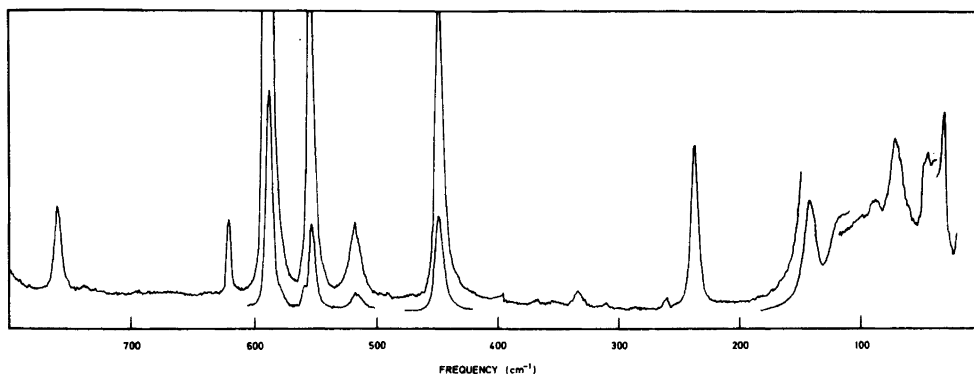


Fig. 5. Raman spectrum of solid benzylselenocyanate.

Table 1. Infrared and Raman spectral data^a and calculated fundamental frequencies (cm⁻¹) of BSCN, BSeCN and BTeCN.

BSCN			BSeCN			BTeCN			Assignment
Obs.	R/IR ^b	Calc.	Obs.	R/IR	Calc.	Obs.	IR	Calc.	
3106	-/vw ^c	3092	3094	-/vw	3092	3096	vw	3092	i.p. ^d
3087	-/w	3081	3080	-/vw	3081	3077	w	3081	i.p.
3064	w/w	3072	3066	w/vw	3072			3072	i.p.
3058	vs/-	3064	3059	m/vw	3064	3056	w	3064	i.p.
3045	w/-	3055	3040	w/-	3055			3055	i.p.
3032	-/m		3026	-/w		3025	m		comb.
3008	-/vw		3000	w/w		2998	w		comb.
2991	m/vw					2993	w		comb.
			2978	vw/vw sh		2962	vw		comb.
2948	s/w	2949	2952	s/vw	2948	2944	vw	2948	-CH ₂ asym. stretch
2925	-/vw sh	2919	2924	-/vw	2919	2922	vw	2919	-CH ₂ sym. stretch
2145	vs/vs	2170	2146	vs/vs	2161	2146	vs	2143	CN stretch
1602	s/w	1625	1598	vs/w	1625	1597	s	1625	i.p.
1585	w/w	1618	1582	w/w	1618	1581	vw	1618	i.p.
1548	-/vw		1540	-/vw		1558-1495 ^e			comb.
1491	-/s	1500	1492	w/s	1500	1491	s	1500	i.p.
1452	-/s	1437	1454	w/vs	1437	1453	s	1437	i.p.
1425	m/s	1426	1424	w/s	1424	1422	w	1427	CH ₂ scissor
1393	-/vw		1389	-/w		1387	vw		comb.
			1362	-/w					comb.
1336	-/vw	1329	1335	-/w	1330	1333	w	1327	i.p.
1323	-/vw					1318	vw		comb.
1288	vw/w	1296	1281	vw/vw	1296	1301	vw	1293	i.p.
1255	sh/-	1255	1252	w/-	1250			1250	CC _α stretch
1241	s/s	1224	1217	s/s	1222	1208	w	1218	CH ₂ twist
1202	s/m	1200	1191	w/vs	1202			1199	CH ₂ wag
1183	m/vw	1174	1176	m/m	1174	1176	vw	1174	i.p.
1173	w/-		1169	-/vw sh					comb.
1158	m/w	1162	1156	m/m	1162	1155	vw	1162	i.p.
1147	-/w		1150	-/vw sh					comb.
			1131	w/w		1139	s		comb.
						1114	vw		comb.
1109	-/w		1104	-/w		1103	vw		comb.
						1084	vw		comb.
1072	-/m	1088	1069	vw/s	1088	1059	s	1088	i.p.
1025	m/w	1022	1027	m/m	1022	1028	m	1022	i.p.
						1020	vw sh		comb.
1003	vs/vw	990	1002	vs/m	990	1001	vw	990	i.p.
990	vw/vw	982	990	vw/-	982	996	vw	982	o.o.p.
						983	vw		comb.
965	-/vw	964	966	-/w	964	963	w	964	o.o.p.
			916	vw/m }					
918	-/m	906	912	-/m }	905	912	m	904	o.o.p.
886	vw/m	840	855	vw/m	819	850	vw	829	CH ₂ rock
850	vw/vw	839	846	vw/w	839			839	o.o.p.
814	w/m }	814	814	w/vw }	809	806	m }	808	i.p.
803	m/m }	814	802	w/w }		798	m }		
767	m/s	783(37) ^f	759	m/vs	744 (3)	756	vs	741 (1)	o.o.p./C _α X stretch
695	w/vs	688 (5)	694	vw/vs	690	694	vs	690	o.o.p.
			664	-/w		654	vw sh		comb.
642	vs/vs	641	516	m/m	518 (7)	438	w	433	XC stretch

Table 1. Continued.

622	m/vw	619	620	m/w	619	620	w	619	i.p.
						585	w		comb.
688	m/vw sh	702 (22)	592	vs/vs	614 (28)	564	s	591 (19)	o.o.p./C _α X stretch
			560	vw sh/-					comb.
565	m/s	554 (6)	550	s/m	540 (7)	542	m	520 (14)	i.p./C _α X stretch
447	-/vw		481	-/vw					comb.
473	s/s	444	448	s/w	420			391	XCN linear bend
454	m/m	427 (6)	436	vw sh/-	411 (17)	397	vs	400 (20)	o.o.p./C _α X stretch
411	-/s	401	398	-/w	401			401	o.o.p.
376	-/w	399	368	-/m	378	366	m sh	367	XCN linear bend
352	vw/-					348	m		comb.
338	vw/m	285	332	w/w	285	320	m	287	CCC _α bend
303	-/vw		311	vw/-		303	vw sh		comb.
273	m/s	256 (19)	236	s/w	204 (45)	225	s	186 (51)	CC _α X bend/C _α X stretch
219	-/w b		261	w/-					comb.
165	s/w sh	143	138	m/s	127	128	s	115	C _α XC bend
155	sh/s					143	s		lattice mode
122	s/m		116	-/m					lattice mode
92	b/s	101	89	w b/m	84	57	m	76	CC _α out of plane
67	s/m		73	m/-					lattice mode
56	m/-		46	m/-					lattice mode
46	s/m		38	m/-					lattice mode
28	vs/-		32	m/-					lattice mode
		38			35			31	C _α X torsion
		4			4			4	CC _α torsion

^a Bands in the regions 4000–3200, 2900–2200 and 2100–1650 cm⁻¹ were omitted. ^b Tabulated values are infrared frequencies, except for bands of very low intensity in infrared spectra. ^c Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. ^d i.p.: Benzene in plane mode, o.o.p.: Benzene out of plane mode. ^e Several very weak bands observed in this interval. ^f Numbers in italics denote fundamentals containing C_αX stretching, values in parentheses are approximate C_αX potential energy contribution.

the phenyl, CH₂ and SCN groups, giving the calculated frequencies shown in Table 1. Since normal coordinate calculations on ethylselenocyanate and ethyltellurocyanate have not been available, reasonable approximations had to be found for the XCN force fields of BSeCN and BTeCN. As a first approximation the ethylthiocyanate force constants were transferred to BSeCN and BTeCN after being scaled according to the relation: $f_{xy} \cdot r_x \cdot r_y = \text{constant}$, where f_{xy} is the force constant in N/m and r_x and r_y are bond lengths. This simple relationship has previously been successfully applied to a series of halogenated cyclohexanes.²¹ It was found that, although the scaling works fairly well for the localized XCN modes, the C_αX and XC stretching force constants had to be treated differently.

In the case of BSeCN the SeC and C_αSe the force constants were refined in a normal coordinate calculation on ethylselenocyanate, using frequencies from the literature.⁶ The rest of the

force field, including the SeC/C_αSe stretch–stretch interaction, was transferred, after appropriate scaling, from ethyl thiocyanate both in the case of ethylselenocyanate and BSeCN. The final values were somewhat different from the scaled thiocyanate force constants (refined: $f_{C_{\alpha}Se} = 156.9$ N/m, $f_{SeC} = 340.4$ N/m; scaled: $f_{C_{\alpha}Se} = 226$ N/m, $f_{SeC} = 314$ N/m).

In the case of BTeCN a similar approach was employed, the main difference being that the TeC stretching force constant could be transferred from ethylthiocyanate along with the rest of the SCN force field. The scaled $f_{TeC} = 247$ N/m can be compared with the corresponding value from the tellurocyanate ion,¹⁸ 269 N/m.

The final BTeCN force field includes a C_αTe stretching force constant transferred from BSeCN and scaled according to the relation above. The force fields for the XCN groups, in their final form, are given in Table 2.

As apparent from Table 1 the correspondence

Table 2. Force constants of the $-\text{CH}_2\text{XCN}$ group.^a

Force constant	BSCN	BSeCN	BTeCN
Stretch and stretch-stretch; Nm^{-1}			
f_{CN}	1673	1673 ^b	1673 ^b
f_{XC}	372	340.4 ^c	247
$f_{\text{C}_\alpha\text{X}}$	265	156.9 ^c	130 ^d
$f_{\text{C}_\alpha\text{H}}$	469.6 ^e	469.6 ^e	469.6 ^e
f_{CC_α}	468.13 ^e	468.13 ^e	468.13 ^e
$f_{\text{C}_\alpha\text{H}/\text{C}_\alpha\text{H}}$	7.3 ^e	7.3 ^e	7.3 ^e
$f_{\text{C}_\alpha\text{X}/\text{XC}}$	30	25	21
Bend and bend-bend; $\text{aN}\cdot\text{m}\cdot\text{rad}^{-2}$			
$f_{\text{CC}_\alpha\text{X}}$	1.16	1.16	1.16
$f_{\text{C}_\alpha\text{XC}}$	0.68	0.68	0.68
$f_{\text{HC}_\alpha\text{X}}$	0.66	0.66	0.66
f_{XCN}	0.37 ^f	0.37 ^f	0.37 ^f
$f_{\text{CC}_\alpha\text{H}}$	0.6417 ^e	0.6417 ^e	0.6417 ^e
$f_{\text{HC}_\alpha\text{H}}$	0.5351 ^e	0.5351 ^e	0.5351 ^e
$f_{\text{HC}_\alpha\text{X}/\text{HC}_\alpha\text{X}}$	-0.125	-0.125	-0.125
$f_{\text{HC}_\alpha\text{X}/\text{CC}_\alpha\text{H}}$	-0.015	-0.015	-0.015
$f_{\text{CC}_\alpha\text{H}/\text{CC}_\alpha\text{H}}$	-0.0211 ^e	-0.0211 ^e	-0.0211 ^e
Stretch-bend; $\text{nN}\cdot\text{rad}^{-1}$			
$f_{\text{C}_\alpha\text{X}/\text{HC}_\alpha\text{X}}$	3.5	3.2	2.9
$f_{\text{CC}_\alpha/\text{CC}_\alpha\text{H}}$	2.335 ^e	2.335 ^e	2.335 ^e
Torsion; $\text{aN}\cdot\text{m}\cdot\text{rad}^{-2}$			
$f_{\text{C}_\alpha\text{X}-\tau}$	0.02	0.02	0.02
$f_{\text{CC}_\alpha-\tau}$	0.0001 ^e	0.0001 ^e	0.0001 ^e

^a Transferred from $\text{CH}_3\text{CH}_2\text{SCN}$ (Ref. 12) and scaled according to $f_{xy}\cdot r_x\cdot r_y = \text{constant}$, except where noted. ^b Transferred from $\text{CH}_3\text{CH}_2\text{SCN}$ (Ref. 12) without scaling. ^c Transferred from $\text{CH}_3\text{CH}_2\text{SeCN}$, see text. ^d Transferred from BSeCN with scaling. ^e Transferred from toluene (Ref. 20). ^f Mean of two values reported for $\text{CH}_3\text{CH}_2\text{SCN}$ (Ref. 12).

between observed and calculated low frequency fundamentals leaves room for improvement. In particular, the modes involving C_αX stretch show some deviations which could possibly be removed by refining the interaction force constants coupling the XCN and benzyl vibrations.

Where little or no mixing occurs between vibrations of the benzyl and XCN fragments, the transferred force field yields an acceptable correspondence between observed and calculated fundamentals.

Acknowledgements. Thanks are due to J. Songstad, Bergen, for supplying the samples and to C. J. Nielsen for helpful discussions.

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Received March 21, 1984.