

The Vibrational Spectra and Force Constants of the Tellurocyanate Ion (TeCN^-)

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The infrared spectra of crystalline samples of $(\text{C}_6\text{H}_5)_4\text{PTeCN}$ (I), $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$ (II) and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NTeCN}$ (III) including the ^{13}C isotopic species of I and II were recorded in the region $4000 - 180 \text{ cm}^{-1}$ as potassium iodide and polyethylene pellets and as Nujol mulls. Raman spectra of the crystalline compounds were obtained while III was also studied in acetonitrile and acetone solution: Spectra of the cyanide salts of the cations $(\text{C}_6\text{H}_5)_4\text{P}^+$, $(\text{C}_6\text{H}_5)_4\text{As}^+$ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}^+$ were also recorded.

The three fundamental frequencies of the TeCN^- ion were assigned. A general valence force field for I was calculated employing the ^{13}C data. The force constants are compared with those reported for the OCN^- , SCN^- and SeCN^- ions.

The vibrational spectra of the cyanate ion, NCO^- , the thiocyanate ion, NCS^- and the selenocyanate ion, NCS^- , have been the subject of considerable study in recent years.¹⁻⁵ Structural data together with spectroscopic studies on ^{13}C -enriched species have permitted the calculation of force constants for these ions.

With regard to the tellurocyanate ion, TeCN^- considerably less is known. The chemical evidence indicates that the tellurium-carbon bond is very weak and salts of this ion can only be prepared with large, non-polarizing cations.⁶

In a previous IR study on the tellurocyanate ion, tetramethylammonium, Me_4N^+ , and tetraphenylarsonium, Ph_4As^+ , salts were employed.⁷ However, difficulties arose due to the fact that Me_4NTeCN was very unstable while Ph_4AsTeCN was not sufficiently soluble to permit solution spectra to be recorded.

Recently, the bis(triphenylphosphine)-iminium tellurocyanate, $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NTeCN}$, was

prepared⁸ and this salt is quite soluble in both acetone and acetonitrile. Furthermore, the molecular structure of this salt has been solved by X-ray crystallographic methods.⁹ With the exact structural parameters on hand, together with the possibility of recording both the IR and Raman spectra of the ^{12}C - and ^{13}C -tellurocyanates, the vibrational spectra of the tellurocyanate ion could be obtained. Force constants for the last member in the XCN^- -series could thus be calculated.

EXPERIMENTAL

The syntheses of the three tellurocyanates $(\text{C}_6\text{H}_5)_4\text{PTeCN}$ (I), $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$ (II) and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NTeCN}$ (III) as well as the corresponding cyanides $(\text{C}_6\text{H}_5)_4\text{PCN}$, $(\text{C}_6\text{H}_5)_4\text{AsCN}$ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCN}$ have been described in earlier papers.^{6,8} The ^{13}C enriched samples of I and II were prepared from 90.5% ^{13}C -enriched KCN, used as received from British Oxygen Co, Ltd. All the compounds used in the present study were recrystallized from deoxygenated acetone, *p.a.*, prior to use.

Infrared spectra of the samples were recorded in the region $4000 - 180 \text{ cm}^{-1}$ on Perkin-Elmer models 225 and 180 spectrometers as Nujol mulls, KBr and polyethylene pellets. Raman spectra were obtained on a Cary 81 spectrometer excited by argon ion (CRL 52 G) and helium neon (Spectra Physics 125 A) lasers and on a Coderg model T 800 spectrometer combined with a Spectra Physics model 170-03 argon ion laser. None of the compounds I–III were stable when excited by the 5145 or 4880 Å argon ion laser beams, but decomposed slowly resulting in increased fluorescence. Reasonably good spectra were recorded with a spinning cell holder and a laser power below 40 mW. The best Raman spectra were obtained with the 6328 Å helium neon laser line. Attempts to

record the Raman spectra in saturated acetonitrile or acetone solutions were made, but only III gave reasonably successful solution spectra.

The fundamental frequencies of the counterions were determined by recording the IR and Raman spectra of the following compounds: $(C_6H_5)_4PCN$ (Ia), $(C_6H_5)_4AsCN$ (IIa) and $[(C_6H_5)_3P]_2NCN$ (IIIa) by the same procedure as the tellurocyanates I, II and III. The isotopic wave number shifts of I and II were recorded with large dispersion on the same charts using identical spectral parameter settings.

RESULTS

Because of their large size the counterions in the three present tellurocyanates all have very complicated vibrational spectra with a large number of vibrational bands. The tellurocyanate ions, on the other hand, have only three fundamental frequencies. By comparing the spectra of I, II and III with those of Ia, IIa and IIIa, respectively, we were able to determine the counterion spectra with considerable certainty, since the IR and Raman spectra were practically identical. The spectral differences were caused by the tellurocyanate ions, and the $TeCN^-$ vibrational modes could therefore be detected.

For I and II the ^{13}C isotopic species were available and the fundamentals of the tellurocyanate ion could be determined with complete certainty as the three vibrational bands which showed isotopic shifts. The complete lists of IR and Raman bands for compounds I, II and III have not been given for the sake of brevity. For II our data were essentially identical to those of our earlier paper.⁷ The IR and Raman bands assigned to

the tellurocyanate ion in compounds I, II and III as well as in the isotopic species are listed in Table 1. Our earlier assignments⁷ for the tellurocyanate fundamentals were essentially confirmed. However, for II the present data reveal that ν_2 is associated with the IR band at 353 cm^{-1} (350 cm^{-1} in Raman) rather than the neighbouring band at 359 cm^{-1} (360 cm^{-1} in Raman) assigned previously.⁷ The latter band belonged to the counterion since it was present in the spectrum of compound IIa and showed no isotopic shift.

For III we had no ^{13}C isotopic molecule available, but the tellurocyanate modes were assigned with the aid of the data from I and II. As apparent from Table 1 both ν_2 and ν_3 of III showed factor group splitting in the IR Nujol spectrum, whereas only one band for each fundamental was observed in Raman. In acetonitrile solution (Raman) the bands were slightly displaced from the solid state frequencies. Our assignments were supported by the polarization measurements in which ν_1 and ν_2 were definitely polarized while ν_3 appeared depolarized.

The bands assigned to the three fundamentals were situated at nearly the same wave numbers in the spectra of all three compounds. Also, the isotopic frequency shifts were nearly identical in I and II. Therefore, it can be concluded that the tellurocyanate ions in the three compounds have practically identical bonding energies. Moreover the crystal lattices of the compounds probably do not perturb the vibrations of the tellurocyanate ions significantly although correlation splitting was observed in the spectrum of III.

Table 1. Fundamental frequencies for the tellurocyanate ions.^a

$(C_6H_5)_4PTeCN$, I		$(C_6H_5)_4AsTeCN$, II		$[(C_6H_5)_3P]_2NTeCN$, III			Assignments
IR Nujol	Raman solid	IR Nujol	Raman solid	IR Nujol	Raman solid	Raman CH_3CN sol.	
2080 s	2079 s	2076 s	2080 s	2075 s	2078 s	2086 s,P	ν_1 ^{12}C Σ^+
2034 s	2034 s	2031 s	2033 s				ν_1 ^{13}C Σ^+
458 w	460 w	458 m	458 w	463 m } 449 m }	457 m	451 m,P	ν_2 ^{12}C Σ^+
451 w	453 w	~450 w	451 w				ν_2 ^{13}C Σ^+
349 vw	350 vw	353 m	350 w	360 w } 348 w }	365 w	365 w,D?	ν_3 ^{12}C Π
338 vw	340 vw	343 m	340 w				ν_3 ^{13}C Π

^a Abbreviations: s, strong; m, medium; w, weak; v, very; P, polarized and D, depolarized.

Table 2. Force constants (mdyn/Å) derived for the tellurocyanate ion (I).

Freq.	¹² C	¹³ C
1	2080	2034
2	458	451
3	349	338

Force const.	Set A ^a	Set B ^b
f_{11}	15.62	16.57
f_{22}	2.81	2.69
f_{12}	0	0.83
f_{33}	0.14	0.14

^a Set A, from ¹²C data, f_{12} defined as zero. ^b Set B, from ¹²C and ¹³C data.

Force constant calculations. The tellurocyanate ion is linear (as apparent from the X-ray crystallographic study⁹ of III), like the lighter homologues OCN⁻, SCN⁻ and SeCN⁻. From the two stretching modes ν_1 and ν_2 of species Σ^+ the diagonal stretching force constants f_{11} and f_{22} can easily be determined if the interaction term f_{12} is neglected. The force constant f_{33} is unequivocally determined from the bending mode ν_3 of species Π . The Te-C and C-N distances, 2.05 and 1.13 Å, respectively, determined in the X-ray study⁹ were used in the calculations. An initial set of force constants were adopted and by an iteration procedure the set A of Table 2 was determined using the assigned frequencies for the parent molecule I, chosen because the experimental data were most reliable for this compound. Adding the observed frequencies for the ¹³C

species yields just sufficient information to determine the complete valence force field, in view of the product rule. Two solutions arise, but only one, set B of Table 2, is physically reasonable.

The calculated force constants for the tellurocyanate ion agree remarkably well with the values predicted by Greenwood *et al.*¹¹ Also, the values clearly demonstrate the reduced X-C (X≡O, S, Se, Te) bond strengths in the series X-C=N¹⁻⁵ as apparent from Table 3. Comparison can also be made with the very precisely determined force constants for the halocyanides by Ruoff.¹⁰

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Table 3. Comparison between force constants (mdyn/Å) for the homologue series XCN (X=O, S, Se, Te).

Force const.	K(OCN) ^a	K(SCN) ^b	K(SeCN) ^c	(C ₄ H ₅) ₄ PTeCN ^d
f_{11}	15.42	15.95	15.97	16.57
f_{22}	11.46	5.18	3.75	2.69
f_{12}	1.15	0.9	0.88	0.83
f_{33}	0.51	0.31	0.22	0.15

^a Ref. 1. ^b Ref. 2. ^c Ref. 4. ^d This work.