

The Vibrational Spectra of  
 $(\text{CH}_3)_4\text{NTeCN}$  and  
 $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$

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Although the first elements of the 6th  
 A group form stable complex ions with  
 cyanide to make cyanate, thiocyanate, and  
 selenocyanate, the corresponding telluro-  
 cyanate ion has not been isolated in the  
 form of stable salts until recently.<sup>1,2</sup> Thus,  
 salts of tellurocyanate with small, polariz-  
 ing cations (like the alkali cations) appear  
 to be unstable.<sup>1,3</sup> With large, weakly  
 polarizing counterions stable tellurocyanate  
 salts which are soluble in aprotic solvents  
 have been prepared. Whereas  $(\text{C}_6\text{H}_5)_4\text{NTeCN}$   
 was first prepared by Downs,<sup>1</sup>  $(\text{C}_6\text{H}_5)_4\text{-}$   
 $\text{AsTeCN}$  and  $(\text{CH}_3)_4\text{NTeCN}$  were recently  
 synthesized by Austad *et al.*<sup>2</sup> An IR band  
 assigned to the CN stretching mode was  
 observed<sup>2</sup> at  $2081\text{ cm}^{-1}$  when  $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$   
 was dissolved in acetonitrile.

Since the cyanate, thiocyanate, and  
 selenocyanate anions have been studied  
 in considerable detail by IR spectroscopy  
 we decided to make a spectral study of  
 the two tellurocyanate salts. The IR, far  
 IR (for  $(\text{CH}_3)_4\text{NTeCN}$ ) and Raman spectra  
 of the solids were obtained and these  
 results are given in the present communica-  
 tion.

*Experimental.* The synthesis of  $(\text{CH}_3)_4\text{NTeCN}$   
 and  $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$  has been described in the  
 earlier paper.<sup>2</sup> Infrared spectra of the samples  
 were recorded in the region  $4000\text{--}200\text{ cm}^{-1}$   
 on a Perkin-Elmer model 225 spectrometer as  
 Nujol mulls and CsI pellets. Far IR spectra  
 of  $(\text{CH}_3)_4\text{NTeCN}$  ( $400\text{--}50\text{ cm}^{-1}$ ) were obtained  
 with the aid of a Perkin-Elmer Hitachi FIS-3  
 spectrometer (as polyethylene pellets). Raman  
 spectra of the solids were recorded on a Cary 81  
 Raman spectrometer equipped with a Spectra  
 Physics 125 A helium-neon laser.

Attempts were made to record the IR and  
 Raman spectra of the tellurocyanates in  
 acetonitrile. However, the solubility of  
 $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$  was too low to obtain any  
 Raman spectra, but the strong IR bands  
 were recorded. In spite of careful anhydrous

Table 1. The infrared<sup>a</sup> and Raman spectral  
 data for  $(\text{CH}_3)_4\text{N TeCN}$ .

Infrared Nujol	Raman Solid	Infrared Nujol	Raman Solid
2073 vs <sup>b</sup>	2077 vs	836 vw	
2043 vw,sh		767 vw <sup>c</sup>	
2030 vw			750 m
		698 vw	705 vw
		667 vw	685 vw
1488 s,sh		617 vw	
1483 vs	1480 w	460 w	490 w
1460 s <sup>c</sup>	1456 w		460 w
1448 s <sup>c</sup>			
1409 m	1407 w	450 w	453 s
1403 m,sh			
		366 vw <sup>d</sup>	
		350 w <sup>d</sup>	
1326 w <sup>c</sup>		305 m <sup>d</sup>	~ 310 vw
1285 w	1285 w		
1176 vw	1173 w	283 vw <sup>d</sup>	
1070 vw			
		~ 250 w <sup>d</sup>	
958 w			
948 vs		117 m,bd <sup>d</sup>	
943 m	943 m		
918 w		105 m,bd <sup>d</sup>	
858 w <sup>c</sup>			

<sup>a</sup> For the sake of brevity bands above  
 $2200\text{ cm}^{-1}$  and very weak bands in the region  
 $2000\text{--}1500\text{ cm}^{-1}$  are omitted. <sup>b</sup> Abbreviations:  
 s, strong; m, medium; w, weak; v, very; sh,  
 shoulder and bd, broad. <sup>c</sup> CsI pellets. <sup>d</sup> Poly-  
 ethylene (Rigidex) pellets.

conditions and removal of dissolved oxygen  
 in the solvent, the more soluble  $(\text{CH}_3)_4\text{NTeCN}$   
 was not sufficiently stable in acetonitrile  
 solution to permit the recording of reproducible  
 spectra of this compound. A darkening of the  
 solid  $(\text{CH}_3)_4\text{NTeCN}$  due to the formation of  
 tellurium was experienced upon irradiation  
 by the  $6328\text{ \AA}$  laser light. Furthermore, a  
 darkening of the CsI and polyethylene pellets  
 was observed, and whenever applicable the  
 Nujol mull technique appeared to be the  
 most reliable.

*Results.* The IR and Raman spectra of  
 $(\text{CH}_3)_4\text{NTeCN}$  and  $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$  are  
 listed in Tables 1 and 2, respectively.

As a first approximation we can assume that even in the crystalline state the observed spectra consist of a superposition of the cation and anion spectra with ion interaction, crystal splitting and lattice modes playing a minor role. This assumption is supported by the close resemblance of the IR and Raman spectra of the onium

counterions  $(\text{CH}_3)_4\text{N}^+$  and  $(\text{C}_6\text{H}_5)_4\text{As}^+$  in various crystals.<sup>4-6</sup> Obviously, the large majority of IR and Raman bands in Tables 1 and 2 will be due to the large cations. The tellurocyanate ion will have only two stretching and one bending fundamental and possibly some overtones or combinations. Since  $\text{TeCN}^-$  undoubtedly is linear ( $C_{\infty v}$ ) the two stretching fundamentals of species  $\Sigma^+$  should be polarized in Raman with the bending mode ( $\Pi$ ) being depolarized. The  $\text{TeCN}^-$  bands were assigned among the observed frequencies of Tables 1 and 2 which did not appear in the spectra of  $(\text{CH}_3)_4\text{N}^+$  or  $(\text{C}_6\text{H}_5)_4\text{As}^+$ .<sup>4-6</sup> Moreover, our fundamental frequencies for  $\text{TeCN}^-$  are supported by extrapolating those of  $\text{OCN}^-$ ,  $\text{SCN}^-$ , and  $\text{SeCN}^-$ ,<sup>2</sup> as well as from the isoelectronic series  $\text{FCN}$ ,  $\text{ClCN}$ ,  $\text{BrCN}$  and  $\text{ICN}$ .<sup>7</sup> A simple force constant calculation for  $\text{TeCN}^-$  gave the values: CN stretch  $\approx 2083$ , TeC stretch  $\approx 456$  whereas the  $\text{TeCN}$  bending mode was estimated to  $400 \text{ cm}^{-1}$  from a simple extrapolation.<sup>8</sup>

The assigned fundamentals for the  $\text{TeCN}^-$  ion are listed in Table 3. No uncertainty is attached to the CN stretching mode ( $\nu_1$ ) situated around  $2075 \text{ cm}^{-1}$  in the solid for both compounds. We also feel reasonably confident that the TeC stretching modes ( $\nu_2$ ) should be assigned to the prominent IR and Raman bands around  $455 \text{ cm}^{-1}$  very near a band in  $\text{Te}(\text{CN})_2$  detected<sup>8</sup> at  $459 \text{ cm}^{-1}$ . The  $\text{TeCN}$  bending mode ( $\nu_3$ ) is very uncertain since nearly all the IR and Raman bands in the expected region seem to be cation bands.<sup>4-6</sup> A weak IR band at  $366 \text{ cm}^{-1}$  for which no Raman counterpart was observed (the Raman spectrum of  $(\text{CH}_3)_4\text{NTeCN}$  was incomplete because of background

Table 2. The infrared<sup>a</sup> and Raman spectral data for  $(\text{C}_6\text{H}_5)_4\text{AsTeCN}$ .

Infrared Nujol	Raman Solid	Infrared Nujol	Raman Solid
2149 vw <sup>b</sup>			926 vw, bd
2075 m	2080 vs	919 vw	
1576 vw	1577 s	850 w	843 vw
1478 m, sh		765 w, sh <sup>b</sup>	
1437 s	1440 vw	742 s	740 vw
1390 w <sup>b</sup>		722 vw, sh	
1337 w	1337 vw	688 s	689 vw
1307 w		683 m, sh	
1279 vw	1282 vw		673 m
1183 w	1185 m	613 vw	613 m
1163 w	1163 m	476 m	
1089 w <sup>b</sup>		458 m	458 w
1079 m	1083 m	395 vw	395 vw
1068 w, sh	1067 vw	359 vw	360 w
	1025 s	353 m	350 w
1019 w		274 vw	275 w
	1001 vs	246 w	246 s
997 m			234 s
985 vw		224 w	225 w, sh
974 vw			181 m

<sup>a</sup> For the sake of brevity bands above  $2200 \text{ cm}^{-1}$  and very weak bands in the region  $2000-1600 \text{ cm}^{-1}$  are omitted. For abbreviations see Table 1. <sup>b</sup> CsI pellets.

Table 3. Tentative fundamental frequencies for the  $\text{TeCN}^-$  ion.

$(\text{CH}_3)_4\text{N TeCN}$		$(\text{C}_6\text{H}_5)_4\text{As TeCN}$			Interpretation
IR	Solid Raman	IR	Solid Raman	Solution <sup>a</sup> IR	
2073	2077	2075	2080	2081	$\Sigma^+ \nu_1$ CN stretch
450	453	458	458	466	$\nu_2$ TeC stretch
366	—	359	360	—	$\Pi \nu_3$ TeCN bend

<sup>a</sup> Acetonitrile solution.

fluorescence) is assigned to  $\nu_3$  in this compound. Although  $(C_6H_5)_4AsCl$ <sup>5</sup> and  $(C_6H_5)_4AsI$ <sup>6</sup> have various IR and Raman bands between 400 and 350  $cm^{-1}$  we have tentatively attributed the bands around 360  $cm^{-1}$  to  $\nu_3$ . No other neighboring bands in the two compounds which definitely were not cation bands were observed in this region.

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## Nuclear Magnetic Resonance of Aromatic Heterocyclics. VI. The Correlation of PMR-shifts of Monosubstituted Selenophenes with Reactivity Parameters

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A recent publication by Morel *et al.*<sup>1</sup> on the PMR spectra of some substituted selenophenes has prompted us to publish

the results we have hitherto obtained on the correlation of the NMR spectral data of selenophenes with the reactivity constants  $F'$  and  $R$  of Swain and Lupton.<sup>2</sup> We have recently shown in an extensive study of the NMR parameters of fluorothiophenes, thiophenes, and fluorobenzenes, that the chemical shifts and coupling constants could be correlated with a linear combination of the substituent parameters  $F$  and  $R$ .<sup>3</sup> The regression equations

$$z_k = i_k + f_k F + r_k R$$

where  $z_k$  is the NMR parameter,  $i_k$  is the intercept and  $f_k$ ,  $r_k$  are the regression constants, were calculated by a linear least-squares multiple correlation computer program. In this way an estimate of the relative inductive and mesomeric contributions to the shifts and coupling constants could be obtained. The chemical shifts of the substituted selenophenes given in Table 1 were taken from Ref. 1 except those of 2-fluoro- and 2-iodoselenophene which were prepared and measured at this institute.<sup>4</sup> The regression equations which were obtained are given in Table 2. It is evident that in spite of the relatively few substituents hitherto studied, and in spite of the fact that concentration dependence of the chemical shifts was not eliminated, good correlations were obtained for some of the shifts, especially those of the 2-substituted derivatives. The values of  $f$  and  $r$  are very similar to those in thiophenes.<sup>3</sup> Morel *et al.*<sup>1</sup> stated that they could not obtain any simple relation between the chemical shifts and Hammett-Taft constants or electronegativity. We have, however, found that with the halogen substituents good linear relations with electronegativity are obtained.<sup>4</sup> The success obtained thus far with the limited material available makes further investigations attractive. It is hoped that in this way information about the transmittance of inductive and mesomeric effects in aromatic heterocyclics can be obtained.

*Experimental.* NMR spectra were obtained with a Varian XL-100 spectrometer.

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