

The Infrared and Raman Spectra  
of  $(\text{CH}_3)_4\text{NSCN}$ ,  $(\text{C}_6\text{H}_5)_4\text{AsI}$   
and  $(\text{C}_6\text{H}_5)_4\text{AsNCO}\cdot 2\text{H}_2\text{O}$

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In our studies of silver pseudohalide<sup>1</sup> and tellurocyanate<sup>2</sup> anions the salts were prepared with tetramethyl ammonium and tetraphenylarsonium as counterions. Due to the large, weakly polarizable onium cations many of the salts are reasonably soluble in aprotic solvents like acetonitrile and they can therefore be studied in solution. Moreover, salts of the tellurocyanate ion with small counterions like the alkalis seem to decompose<sup>3,4</sup> in contrast to the apparently stable tellurocyanate salts with large onium cations which have been prepared.<sup>3,5</sup> In order to interpret the IR and Raman spectra of the silver pseudo-

halide<sup>1</sup> and the tellurocyanate<sup>2</sup> anions, a thorough investigation of the cation spectra was necessary. Only fragmentary data for the IR and Raman spectra of the  $(\text{CH}_3)_4\text{N}^+$  and  $(\text{C}_6\text{H}_5)_4\text{As}^+$  ions are available in the literature. In one paper, the IR spectra of the  $(\text{CH}_3)_4\text{NX}$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) salts are reported<sup>6</sup> and compared with older incomplete Raman results.<sup>7</sup> Additionally, some IR frequencies for  $(\text{C}_6\text{H}_5)_4\text{AsI}$ <sup>8</sup> and IR and Raman data for solid  $(\text{C}_6\text{H}_5)_4\text{AsCl}$ <sup>9</sup> have been published.

In the present communication we shall report the vibrational spectra of the three title compounds (one tetramethyl ammonium and two tetraphenyl arsonium salts). In addition to the Raman spectra we have recorded IR spectra from 2200 to 50  $\text{cm}^{-1}$  which was essential for the interpretation of our anion spectra.<sup>1,2</sup>

*Experimental.* The preparation of tetramethyl ammonium thiocyanate has been described previously.<sup>10</sup>

Tetraphenyl arsonium cyanate dihydrate was synthesized according to Norbury and Sinha.<sup>11</sup> Tetraphenyl arsonium iodide was made from the corresponding chloride and potassium iodide in water and recrystallized twice from acetonitrile.

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

Infrared CsI pellet	Raman solid		Infrared pellet <sup>b</sup>	Raman solid
2055 vs <sup>c</sup>	2062 vs	NCS stretch		850 vw, bd
2010 vvw			750 w	752 s
1482 s	1480 vw		744 w, sh	746 s, sh NCS stretch
	1467 m		741 w	
1445 vw, bd			485 vvw	489 vw, bd) NCS bend
1409 w	1408 m		474 w	467 m, sh
1402 w			460 w, sh	457 s
1396 vw			455 w	
1290 vw, bd	1287 w, bd			376 vw
	1178 vw, bd		320 vw, bd	
948 s, sh	947 s		195 vw, sh	
943 s			149 vw, sh	
918 vw, bd	922 vw, bd		110 w	
			95 vw, sh	

<sup>a</sup> Only bands below 2200  $\text{cm}^{-1}$  are included. <sup>b</sup> CsI pellet above 250  $\text{cm}^{-1}$ , polyethylene pellet below 400  $\text{cm}^{-1}$ . <sup>c</sup> Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder and bd, broad.

Table 2. The infrared and Raman data <sup>a</sup> for (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsI.

Infrared		Raman		Infrared		Raman	
Solid CsI pellet	Solution CH <sub>3</sub> CN	Solid	Solution CH <sub>3</sub> CN	Solid pellet <sup>b</sup>	Solution CH <sub>3</sub> CN	Solid	Solution CH <sub>3</sub> CN
1580 vw <sup>c</sup>		1580 vs	1586 s	760 w			
1481 s		1481 vw		741 vs		742 vw	
1441 s,sh		1442 vw		689 s	690 m	690 w,sh	
1438 vs				685 s			
1383 vw,bd		1380 vw,bd		670 vw,sh		673 s	675 s
				630 vw	630 vw		
1337 w		1338 w		615 w		615 m	617 m
1308 w				603 vw	603 w		
		1283 vw,bd	1285 vw	592 w			
1278 vw		1274 vw,sh				490 vw,bd	490 vw
1244 w				476 s	478 m	473 vw	
1234 w,sh	1235 w,bd			469 m	466 m		
1185 w	1187 w	1187 s	1192 w	458 s		457 vw	
1167 w		1167 s	1169 w	440 vw			
1123 vw				400 vw,bd			
1100 vw						383 w,bd	
1082 s	1082 m	1084 s	1086 m	365 w,sh			
1022 w		1027 s	1028 w	356 m			
1012 w				348 m		350 m	
		1004 vs	1005 vs,P	274 vw		276 w	
998 m	998 m	992 vw,sh		247 vw		251 m	
		932 vw				240 s	
920 vw				223 w		225 vw,sh	
915 vw				180 w		186 w	
847 vw						120 vw,sh	
834 vw		838 vw				107 w	
				79 vw		79 m	

<sup>a</sup> Only bands below 1600 cm<sup>-1</sup> are included. <sup>b</sup> CsI pellet above 250 cm<sup>-1</sup>, polyethylene pellet below 400 cm<sup>-1</sup>. <sup>c</sup> For abbreviations see footnote to Table 1.

The IR (2200–200 cm<sup>-1</sup>), far IR (400–50 cm<sup>-1</sup>) and Raman spectrometers as well as the experimental procedures have been described.<sup>1,2</sup>

**Results.** The IR and Raman frequencies of (CH<sub>3</sub>)<sub>4</sub>NSCN are listed in Table 1. Only solid state frequencies are included because of the low solubility of (CH<sub>3</sub>)<sub>4</sub>NSCN in CH<sub>3</sub>CN. A close resemblance between the frequencies of this compound and those of (CH<sub>3</sub>)<sub>4</sub>NX,<sup>6</sup> (CH<sub>3</sub>)<sub>4</sub>TeCN,<sup>2</sup> (CH<sub>3</sub>)<sub>4</sub>NAg(CN)<sub>2</sub>, (CH<sub>3</sub>)<sub>4</sub>NAg(NCO)<sub>2</sub> and (CH<sub>3</sub>)<sub>4</sub>NAg(SCN)<sub>2</sub><sup>1</sup> was observed when taking into account the expected anion frequencies. Hence the solid state spectra are to a high degree of approximation a superposition of the cation and the anion frequencies, with little evidence of crystal splitting. The three

fundamentals of the SCN<sup>-</sup> ion can be assigned to the bands around 2060 cm<sup>-1</sup> ( $\nu_1$  SCN asym. stretch), 745 cm<sup>-1</sup> ( $\nu_2$  SCN sym. stretch) and the doublet around 480 cm<sup>-1</sup> ( $\nu_3$  SCN bending) in perfect agreement with reported values for the potassium salt.<sup>12</sup> The remaining bands can be assigned to the (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> cation with approximately tetrahedral symmetry, although the IR bands below 200 cm<sup>-1</sup> are probably due to lattice vibrations.

Our observed frequencies for (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsI as a solid and in solution (Table 2) are in good agreement with previous (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As<sup>+</sup> ion spectra<sup>3,9</sup> and again no site group or factor group splitting was observed. For the sake of brevity no detailed interpretation of the (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As<sup>+</sup> ion spectra has been made. However, the approach of local C<sub>2v</sub>

Table 3. The infrared and Raman data <sup>a</sup> for (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsNCO.2H<sub>2</sub>O.

Infrared		Raman		Infrared		Raman	
Solid CsI Pellet	Solution CH <sub>3</sub> CN	Solid	Solution CH <sub>3</sub> CN	Solid Pellet <sup>b</sup>	Solution CH <sub>3</sub> CN	Solid CH <sub>3</sub> CN	Solution CH <sub>3</sub> CN
2160 m) <sup>c</sup>	2152 s	2156 w,bd	2155 w,bd*	845 vw	850 vw,bd	857 vw	
2139 vs)					740 s	745 s	755 vw
	2109 w			688 s	689 s	697 vw	
2080 vw				682 m			
1579 vw		1582 s	1584 s,D			673 m	675 s,D
1480 m	1484 m	1482 vw,bd		629 s	635 m	631 m	632 m*
1438 s	1441 s	1442 vw,bd	1445 vw,bd	622 m	625 m		
1384 vw				613 vw	612 vw	617 m	617 m
1336 w	1340 vw	1341 vw,bd		474 m	477 m	478 vw	
1307 w,bd	1315 w	1315 vw,bd		457 m	464 m	450 vw	
1282 m	1299 m	1285 w, bd	}			367 vw	
1202 vw		1201 w,sh			353 m		352 w
				345 m	345 w		
1196 m	1205 m					264 w	
1184 vw	1188 vw	1190 w	1192 w			241 s	
1165 vw	1163 vw	1170 w	1168 w	246 vvw			
1081 m	1082 m	1085 m	1087 m,D				
1022 w	1022 w	1027 s	1027 s,P	222 vw			
		1003 vs	1005 vs,P	183 vw		190 w	
997 m	997 m			114 w			
		931 vw		85 vw,sh		90 vw,sh	
918 vw,bd				63 vs			

<sup>a</sup> Only bands below 2200 cm<sup>-1</sup> are included. <sup>b</sup> CsI pellet above 250 cm<sup>-1</sup>, polyethylene pellet below 400 cm<sup>-1</sup>. <sup>c</sup> For abbreviations see footnote to Table 1. \* Bands marked with an asterisk are assigned as (NCO)<sup>-</sup> fundamentals.

symmetry of the monosubstituted benzene rings, including certain "mass sensitive" vibrations<sup>13</sup> can be successfully employed for the present cation as done for the group IVa tetraphenyl compounds.<sup>14</sup>

The IR and Raman frequencies for (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsNCO.2H<sub>2</sub>O are listed in Table 3. The cation frequencies are in good agreement with those of (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsI. The three NCO fundamentals are marked with an asterisk and appear at 2155 cm<sup>-1</sup> ( $\nu_1$  NCO asym. stretch), 1282 and 1202 cm<sup>-1</sup> for the Fermi resonance doublet ( $\nu_2$  NCO sym. stretch) and 630 cm<sup>-1</sup> ( $\nu_3$  NCO bending). These fundamentals were also observed in CH<sub>3</sub>CN solution, and are in good agreement with the corresponding KNCO values.<sup>14</sup>

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