Thermochemistry of Adducts of Arsenic Trihalides with Saturated Heterocyclic Bases

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The adducts $AsX_3 \cdot nL$ (where L is piperazine (Pipz), morpholine (Morph), or piperidine (Pipd); X is Cl, Br, or I; and *n* is 1, $^3/_2$, or 2) have been synthesized and characterized by melting points, elemental analysis, thermal studies, and infrared spectroscopy. By means of calorimetric measurements in solution, the mean standard enthalpies of the arsenic−nitrogen bonds were determined as well as the values of other thermochemical parameters of the adducts.

Introduction

In a previous article (Dunstan and Airoldi, 1988), we have described the synthesis, characterization, and thermochemistry of arsenic trihalide complexes with heterocyclic amines, in which the mean arsenic−nitrogen coordinated bond energies were determined. Few adducts of arsenic trihalides with saturated heterocyclic amines are reported in the literature (Montignie, 1935). No information about the enthalpy of the arsenic−nitrogen bond in these adducts is available.

In this work adducts of arsenic trihalides with piperazine, morpholine, and piperidine were synthezied and characterized. The thermochemical study of these adducts is made with the purpose of obtaining the enthalpies involved in the formation of the adducts. The coordination ability of the saturated heterocyclic bases was also investigated.

Experimental Section

All preparations and manipulations were carried out in polyethylene glovebags under a nitrogen atmosphere.

Chemicals. Arsenic trihalides were prepared as described in a previous paper (Dunstan and Airoldi, 1988). Piperazine (99% Aldrich Chemical Co., Inc.) was purified by recrystallization from methanol. Morphine (ACS., Aldrich Chemical Co., Inc.) and piperidine (RPE, Analyticals, Carlo Erba) were purified by distillation.

Solvents used in the synthesis of adducts were purified by distillation and stored over Linde 4A molecular sieves. Ethanolamine (99% (p/v), Casa Americana de Artigos para Laboratórios Ltda.) was used without purification for preparing the calorimetric solvent.

Analytical Section. Carbon, hydrogen, and nitrogen contents were determined by microanalytical procedures. Halogen analysis was obtained by gravimetry using a standard 0.1 mol L^{-1} $AgNO_3$ solution, after the adducts were dissolved in water (Kolthoff, 1956). Arsenic content was determined by redox titration of the aqueous solution of adduct samples, with standard 0.025 mol L^{-1} iodine solution, to the appearance of the blue color of starch used as an indicator (Kolthoff, 1956).

Adduct Synthesis. The adducts were prepared by the reaction of arsenic trihalides and the ligands in solution. A typical procedure is given below.

$AsCl_3 \cdot 2Morph$. To a solution of 2.00 mL of $AsCl_3$ (23.9 mmol) in 20 mL of ethanol was added 1.45 mL of morpholine (23.9 mmol) in 20 mL of ethanol slowly and dropwise with stirring. The stirring was maintained for at least 3 h. After filtration, the white crystals formed were washed with three portions of 20 mL of petroleum ether, and dried for several hours in vacuo. The compound obtained was stored in a desiccator over calcium chloride. All the adducts are prepared with a molar ratio donor/acceptor of 1/1. In all cases petroleum ether was used as a solvent for washing. Dichloromethane was used for dissolving arsenic tribromide. Carbon disulfide was used for dissolved arsenic triiodide.

Infrared Spectra. These were obtained with samples in a KBr matrix for adducts and piperazine and a film of ligand sandwiched between KBr plates for piperidine and morpholine. A Perkin-Elmer 1600 series FTIR spectrophotometer was used in the region (4000 to 400) cm^{-1}.

Thermal Studies. These were made in an argon atmosphere in a DuPont 951 TG analyzer and DuPont 910 DSC equipment, with samples varying in mass from 12 mg to 19 mg (TG) and from 10 mg to 13 mg (DSC) and a heating rate of 10 K min^{-1}.

Calorimetric Measurements. All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described before (Dunstan, 1992).

The solution calorimetry measurements were performed by dissolving samples of (5 to 100) mg of adduct or AsX_3 in 100 mL of calorimetric solvent and the ligand in the AsX_3 solution, maintaining a molar relation equal to the stoichiometry of the adduct.

Results and Discussion

All the complexes prepared were solids. The yields range from 18% to 89%. The yields, melting points, colors, appearance, and analytical data are summarized in Table 1.

Infrared Data. The more important IR bands are reported in Table 2. The pattern of the infrared spectra of the adducts is similar to that of the free ligands, although dislocation and splitting of some bands is observed. Considerable shifts to lower frequencies of the ν_{N-H} of coordinated ligands with respect to the uncoordinated ligands are observed. This shows that the ligands are coordinated to the arsenic atom by means of the nitrogen atom of their N−H group (Ahuja, 1969; Ahuja and Garg, 1971; Pellacani et al., 1973; Soriego and Costamagna, 1971). In morpholine adducts the positive shift of the C−O−C stretching vibration, that is found at 1097 cm^{-1} in the free ligand, excludes

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Table 1. Melting Points, Yields, Appearance, and Analytical Data of the Adducts

				% C		% H		% N		% halogen		% As	
compd	yield (%)	MP/K	appearance[a]	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$AsCl_3$·Pipz	52	581−583	wh cr							39.77	40.12	28.02	28.16
$AsCl_3$·2Morph	18	468	wh cr							29.92	29.86	20.67	20.94
$AsCl_3$·2Pipd	20	515−517	wh cr							30.25	29.94	21.31	21.10
$AsBr_3$·Pipz	48	587[b]	pa ye pw	11.99	12.38	2.51	2.78	6.99	7.37	59.81	60.10	18.69	18.34
$AsBr_3$·Morph	51	395−397	pa ye pw	11.95	11.85	2.26	2.36	3.49	3.33	59.67	59.97	18.65	19.03
$AsBr_3$·Pipd	60	446−448	wh pw	15.02	16.28	2.77	2.66	3.50	3.61	59.96	60.20	18.74	18.57
AsI_3·$^3/_2$Pipz	54	495−497	pa or pw	12.32	12.52	2.59	2.68	7.18	6.98	65.10	65.41	12.81	13.05
AsI_3·2Morph	89	463−465	ye pw	15.26	15.36	2.88	2.90	4.45	4.34	60.44	60.08	11.89	11.75
AsI_3·Pipd	46	403−405	or pw	11.11	10.95	2.05	2.03	2.59	2.43				

[a] Key: wh, white; pa, pale; ye, yellow; or, orange; cr, crystals; pw, powder. [b] Key: not melting at 587 K.

Table 2. More Important IR Bands (cm^{-1})

compd	γ_{N-H}	γ_{C-O-C}	δ_{H-N-C}
Pipz	3328 (m)[a]		861 (m), 815 (s)
$AsCl_3$·Pipz	3241 (m)		932 (s), 869 (m)
$AsBr_3$·Pipz	3246 (m)		865 (m), 844 (w)
AsI_3·$^3/_2$Pipz	3264 (s)		863 (m), 802 (w)
Morph	3320 (m)	1097 (s)	889 (m), 835 (s)
$AsCl_3$·2Morph	3282 (m)	1104 (s)	899 (vs), 871 (vs), 824 (w)
$AsBr_3$·Morph	3078 (sh)	1102 (s)	883 (w), 868 (m)
AsI_3·2Morph	3092 (s)	1108 (s)	868 (s)
Pipd	3276 (m)		860 (s), 824 (m)
$AsCl_3$·2Pipd	3196 (m)		874 (w), 862 (m)
$AsBr_3$·Pipd	3144 (s)		861 (m), 800 (m)
AsI_3·Pipd	3133 (m)		880 (w), 844 (w)

[a] In CCl_4. Intensity of bands: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder

the possibility of oxygen-to-arsenic coordination (Ahuja and Garg, 1971). In the H−N−C deformation region a great change is observed that affords evidence of the coordination of the N atom of the ligands (Soriego and Costamagna, 1971; Greenwood and Wade, 1960; Birnbaum, 1969).

Thermal Studies. The thermogravimetry (TG-DTG) of the adducts shows the loss of ligands and trihalides in several steps. The adducts of piperazine lose part of the trihalide (or nearly all the ligand in the case of AsI_3·$^3/_2$Pipz) in the first step of loss of mass. They lose the rest of the trihalide (or all the trihalide in the case of AsI_3·$^3/_2$Pipz) and all or part of the piperazine in the second step. Only in the case of $AsCl_3$·Pipz is a third step observed with the loss of $AsCl_3$ and piperazine together but with a mass relation different from that of the second step. The capillary melting points of the adducts showed their decompositon on melting. They are unstable in the liquid phase. The DSC curves of the piperazine adducts, that are consistent with the TG data, showed several peaks. An exothermic peak is observed at 563 K. As it is inside a

Table 3. Thermoanalytical Data of the Compounds

	mass lost/%					
compd	calcd	obs	temp range/K	species lost	DSC peak *T*/K	enthalpy/kJ mol^{-1}
$AsCl_3$·Pipz	5.42	5.30	336−358	−0.08 $AsCl_3$	388	53.60
	35.69	36.20	433−573	−0.29 ($AsCl_3$· 2Pipz)	563	−12.01
	58.85	58.05	573−621	−0.64 ($AsCl_3$· 0.75 Pipz)	588	−30.70
					608	−6.24
					638	−31.57
$AsCl_3$·2Morph	24.51	32.00	423−523	−Morph	448	91.90
	75.49	67.22	523−550	−$AsCl_3$· Morph	481	−107.37
					535	−43.38
$AsCl_3$·2Pipd	24.22	24.00	438−527	−Pipd	521	2.61
	75.78	75.84	527−576	−$AsCl_3$·Pipd	532	−30.42
					539	−7.62
					553	−3.81
$AsBr_3$·Pipz	3.93	3.69	345−387	−0.05 $AsBr_3$	412	40.72
	96.07	93.39	523−660	−0.95 $AsBr_3$· Pipz	522	13.07
		2.90[a]			605	−35.06
					633	−22.62
$AsBr_3$·Morph	19.51	19.47	350−389	−0.9 Morph	388	28.95
	47.60	47.46	389−549	−0.58 $AsBr_3$· 0.1 Morph	553	−2.99
	32.89	32.29	549−589	−0.42 $AsBr_3$	563	−33.96
$AsBr_3$·Pipd	10.65	10.88	347−376	−0.5 Pipd	368	17.72
	45.01	44.52	392−525	−0.45 ($AsBr_3$· Pipd)	430	23.63
	43.29	44.08	527−611	−0.05 ($AsBr_3$· Pipd)	559	−35.24
					586	−13.21
AsI_3·$^3/_2$Pipz	22.09	21.40	448−541	−$^3/_2$Pipz	329	15.49
	77.91	74.76	541−800	−AsI_3	595	10.33
		4.17[a]			628	125.57
AsI_3·2Morph	17.29	17.60	431−511	−1.25 Morph	458	122.70
	82.71	76.44	511−580	−AsI_3· 0.75 Morph	587	148.71
		5.96[a]				
AsI_3·Pipd	18.10	16.80	433−510	−0.14 (AsI_3· 2.86 Pipd)	409	26.43
	72.45	72.86	510−638	−0.86 AsI_3	488	14.62
	5.51	5.50	650−688	−0.35 Pipd	533	−4.97
	3.94	3.80	719−758	−0.25 Pipd	575	−72.47
					633	−13.70
					729	−11.20

[a] Key: residue at 1073 K.

Table 4. Enthalpies of Dissolution at 298.15 K

m/mg	$n \times 10^6$/mol	Q_r/J	m/mg	$n \times 10^6$/mol	Q_r/J
$AsCl_3$(l) + 10% EA−H_2O[a]					
18.06	99.62	−27.08	32.31	178.23	−45.50
109.97	606.63	−162.08	27.69	152.75	−36.02
38.17	210.56	−54.97	41.52	229.04	−57.79
57.27	315.92	−83.21	29.74	164.06	−37.86
40.28	222.20	−55.71	29.50	162.73	−40.56
23.37	128.92	−32.26	31.41	173.27	−41.59
32.31	189.93	−47.36			
$\Delta_1H°$/kJ mol^{-1} = −259.21 ± 2.98					
Pipz(s) + $AsCl_3$−10% EA−H_2O					
8.58	99.61	−0.35	27.21	315.89	−1.19
13.47	156.38	−0.70	32.12	372.89	−1.37
$\Delta_2H°$/kJ mol^{-1} = −3.77 ± 0.13					
$AsCl_3$·Pipz(s) + 10% EA−H_2O					
7.10	26.55	−0.23	7.55	28.23	−0.26
15.82	59.16	−0.65	13.75	51.42	−0.53
24.10	90.12	−1.05			
$\Delta_3H°$/kJ mol^{-1} = −11.07 ± 0.41					
2Morph(l) + $AsCl_3$−10% EA−H_2O					
25.62	294.07	−6.71	22.46	257.80	−6.65
33.09	379.25	−10.06	11.38	130.62	−2.54
29.18	334.93	−7.47			
$\Delta_2H°$/kJ mol^{-1} = −48.49 ± 2.09					
$AsCl_3$·2Morph(s) + 10% EA−H_2O					
9.68	27.23	−0.21	15.97	44.92	−0.33
10.62	29.87	−0.23	30.87	86.83	−0.61
16.26	45.74	−0.35	27.82	78.25	−0.54
$\Delta_3H°$/kJ mol^{-1} = −7.17 ± 0.15					
2Pipd(l) + $AsCl_3$−10% EA−H_2O					
63.06	740.57	−17.66	36.66	430.53	−10.45
35.93	421.96	−9.38	42.20	495.60	−11.77
38.10	447.45	−10.72	39.50	346.53	−7.69
$\Delta_2H°$/kJ mol^{-1} = −47.14 ± 0.62					
$AsCl_3$·2Pipd(s) + 10% EA−H_2O					
23.17	65.90	+1.34	24.22	68.89	+1.39
23.39	66.53	+1.34	21.56	61.32	+1.23
5.63	16.01	+0.34	46.25	131.55	+2.70
$\Delta_3H°$/kJ mol^{-1} = −20.34 ± 0.08					
$AsBr_3$(s) + 10% EA−Methanol[a]					
59.63	189.51	−48.10	99.69	316.80	−80.16
58.99	187.48	−51.47	117.94	373.83	−99.85
26.39	83.87	−20.60	44.17	140.38	−35.46
29.05	92.33	−21.84	73.30	232.96	−60.60
94.66	300.84	−79.57	68.80	218.66	−59.52
$\Delta_1H°$/kJ mol^{-1} = −261.91 ± 2.63					
Pipz(s) + $AsBr_3$−10% EA−Methanol					
18.83	218.60	+ 2.77	15.29	177.51	+1.96
11.67	135.55	+1.87	19.48	226.15	+2.70
$\Delta_2H°$/kJ mol^{-1} = +12.22 ± 0.48					
$AsBr_3$Pipz(s) + 10% EA−Methanol					
19.93	49.73	−0.15	27.70	69.11	−0.33
36.00	89.82	−0.48	57.81	144.24	−0.96
$\Delta_3H°$/kJ mol^{-1} = −5.86 ± 0.62					
Morph(l) + $AsBr_3$−10% EA−Methanol					
24.35	279.49	−2.10	26.68	306.24	−2.21
25.78	295.91	−2.10	30.02	344.57	−2.55
$\Delta_2H°$/kJ mol^{-1} = −7.39 ± 0.06					

m/mg	$n \times 10^6$/mol	Q_r/J	m/mg	$n \times 10^6$/mol	Q_r/J
$AsBr_3$·Morph(s) + 10% EA−Methanol					
18.41	45.82	−8.10	78.65	195.76	−34.95
29.68	73.87	−12.84	54.38	135.35	−24.50
41.78	104.01	−17.88			
$\Delta_3H°$/kJ mol^{-1} = −177.82 ± 1.50					
Pipd(l) + $AsBr_3$−10% EA−Methanol					
20.40	239.58	−2.65	33.00	387.55	−4.51
26.93	316.26	−3.58	19.38	227.60	−2.35
36.83	432.53	−5.08			
$\Delta_2H°$/kJ mol^{-1} = −11.43 ± 0.21					
$AsBr_3$·Pipd(s) + 10% EA−Methanol					
8.77	21.94	−3.12	15.07	37.69	−4.79
8.10	20.26	−2.42	12.55	31.39	−4.10
14.44	36.12	−4.77			
$\Delta_3H°$/kJ mol^{-1} = −130.17 ± 2.72					
AsI_3(s) + 10% EA−Methanol					
54.41	119.42	−57.76	83.89	184.12	−35.71
113.75	249.65	−50.43	46.55	102.17	−23.29
38.84	85.24	−20.06	42.01	92.20	−21.15
77.21	169.46	−33.78	80.87	177.49	−39.24
91.53	200.88	−41.77	102.55	225.07	−49.13
102.97	225.99	−54.21	144.02	316.09	−67.95
113.82	249.81	−49.34			
$\Delta_1H°$/kJ mol^{-1} = −212.42 ± 3.66					
$^3/_2$Pipz(s) + AsI_3−10% EA−Methanol					
18.34	212.94	1.46	12.22	141.87	0.89
9.72	112.84	0.76	31.21	362.33	2.62
19.73	229.05	1.46			
$\Delta_2H°$/kJ mol^{-1} = +10.36 ± 0.47					
AsI_3·$^3/_2$Pipz(s) + 10% EA−Methanol					
13.91	23.78	−1.11	14.83	25.36	−1.10
22.77	38.93	−1.90	12.04	20.59	−0.85
24.33	41.60	−1.99			
$\Delta_3H°$/kJ mol^{-1} = −48.24 ± 1.38					
2Morph(l) + AsI_3−10% EA−Methanol					
52.97	607.99	−4.69	39.65	455.11	−3.22
8.04	92.33	−1.45	21.76	249.81	−3.93
24.69	283.39	−4.34			
$\Delta_2H°$/kJ mol^{-1} = −15.25 ± 0.27					
AsI_3·2Morph(s) + 10% EA−Methanol					
38.81	61.61	−5.28	20.03	31.80	−2.36
4.35	6.90	−0.29	23.80	37.78	−3.19
9.50	15.08	−1.10			
$\Delta_3H°$/kJ mol^{-1} = −82.86 ± 2.87					
Pipd(l) + AsI_3−10% EA−Methanol					
8.70	102.17	−0.98	20.50	240.75	−2.62
6.15	72.23	−0.73	24.86	291.95	−3.59
15.11	177.49	−2.21			
$\Delta_2H°$/kJ mol^{-1} = −11.68 ± 0.44					
AsI_3.Pipd(s) + 10% EA−Methanol					
4.01	7.42	−1.00	34.61	64.00	−9.53
13.67	25.28	−3.75	52.66	97.38	−15.60
25.78	47.67	−7.78	15.63	28.90	−4.06
$\Delta_3H°$/kJ mol^{-1} = −156.46 ± 2.93					

[a] Calorimetric solvent: 100 mL of 10% (v/v) of ethanolamine (EA) in water or 100 mL of 10% (v/v) of ethanolamine in methanol.

region of mass loss of the adduct $AsCl_3$·Pipz, it is attributed to decompositon and elimination of part of $AsCl_3$ and part of piperazine. The other endothermic peaks observed are due to elimination of part of the trihalide or part of the trihalide together with part of the ligand. In the case of AsI_3·$^3/_2$ Pipz, a residue is observed, probably carbon (Dunstan, 1994a,b), as the product of the redox degradation of the ligand. The DSC curve of this adduct shows an endothermic peak at 595 K consistent with this behavior. The endothermic peak at 329 K is attributed to elimination of nearly all the ligand. The endothermic peak at 628 K is due to elimination of the AsI_3, as it is near the temperature of vaporization of AsI_3. The adducts of morpholine lose mass in two or three steps. The first step

Table 5. Summary of the Thermochemical Results (kJ mol^{-1})

compd	$\Delta_r H^\circ$	$\Delta_f H^\circ$	Δ_s^9H° or Δ_l^gH°	$\Delta_m H^\circ$	$\Delta_D H^\circ$	$\Delta_r H^\circ$(g)	$\bar{D}_{As-N}$
$\mathrm{AsCl_3(l)}$		−305.0[a]	43.5[a]				
$\mathrm{AsBr_3(s)}$		−197.5[a]	67.5[a]				
$\mathrm{AsI_3(s)}$		−58.2[a]	95.0[b]				
Piperazine(s)		−45.6 ± 1.6[c]	84.2[d]				
Morpholine(l)		−170.2[d]	42.3[c]				
Piperidine(l)		−88.0 ± 1.0[c]	39.1 ± 1.8[c]				
$\mathrm{AsCl_3 \cdot Pipz(s)}$	−251.91 ± 3.01	−602.5 ± 3.6		−397.6 ± 3.3	336.1 ± 3.2	−295.4 ± 3.5	147.7 ± 1.8
$\mathrm{AsCl_3 \cdot 2Morph(s)}$	−300.53 ± 3.64	−945.9 ± 4.3		−428.6 ± 4.3	385.1 ± 4.2	−386.3 ± 4.4	193.2 ± 2.2
$\mathrm{AsCl_3 \cdot 2Pipd(s)}$	−326.69 ± 3.04	−807.7 ± 3.8		−448.4 ± 3.7	404.9 ± 5.9	−409.3 ± 6.0	204.6 ± 3.0
$\mathrm{AsBr_3 \cdot Pipz(s)}$	−243.83 ± 2.74	−486.9 ± 3.3		−295.5 ± 3.1	328.0 ± 2.9	−311.3 ± 3.2	155.7 ± 1.6
$\mathrm{AsBr_3 \cdot Morph(s)}$	−91.48 ± 3.03	−459.2 ± 3.3		−201.3 ± 3.3	133.8 ± 3.2	−159.0 ± 3.5	159.0 ± 3.5
$\mathrm{AsBr_3 \cdot Pipd(s)}$	−143.17 ± 3.79	−428.7 ± 4.0		−249.8 ± 4.3	182.3 ± 4.2	−210.7 ± 4.7	210.7 ± 4.7
$\mathrm{AsI_3 \cdot {}^3/2Pipz(s)}$	−153.82 ± 3.94	−280.4 ± 4.7		−375.1 ± 4.3	280.1 ± 4.2	−290.9 ± 4.4	97.0 ± 1.5
$\mathrm{AsI_3 \cdot 2Morph(s)}$	−144.81 ± 4.66	−543.4 ± 5.2		−324.4 ± 5.2	229.4 ± 5.1	−282.1 ± 5.3	141.1 ± 2.7
$\mathrm{AsI_3 \cdot Pipd(s)}$	−67.64 ± 4.71	−213.8 ± 4.9		−201.7 ± 5.1	106.7 ± 5.0	−162.6 ± 5.4	162.6 ± 2.7

[a] Wagman *et al*. 1982. [b] Karapet'Yants and Karapet'Yants, 1970. [c] Pedley and Rylance, 1970. [d] See text.

with elimination of all or part of the ligand. The second step with elimination of the trihalide or part of it and the rest of the ligand. Only in the case of $\mathrm{AsBr_3 \cdot Morph}$ was a third step observed with elimination of the rest of $\mathrm{AsBr_3}$. Only in the case of $\mathrm{AsI_3 \cdot 2Morph}$ was a residue, probably carbon, observed (Dunstan, 1995). The DSC curves of the morpholine adducts that are consistent with the TG data showed several peaks. Endothermic peaks at (448, 388, and 458) K are due to the melting and decomposition of the adducts. Other exothermic peaks are due to decomposion and elimination of part of the trihalide together with part of the ligand or part of $\mathrm{AsBr_3}$. The redox degradation of morpholine leaves a residue of carbon only in the case of $\mathrm{AsI_3 \cdot 2Morph}$ (Dunstan, 1996). The adducts of piperidine lose mass in two, three, or four steps. In the first step they lose the ligand or part of it. Only in the case of $\mathrm{AsI_3 \cdot Pipd}$ are part of $\mathrm{AsI_3}$ and part of piperidine lost together. In the second step the trihalide or part of it and part of the ligand are eliminated. Only in the case of $\mathrm{AsI_3 \cdot Pipd}$ is the rest of $\mathrm{AsI_3}$ eliminated. In the third step part of $\mathrm{AsBr_3}$ and part of piperidine together are eliminated as well as part of piperidine for the other adduct. The fourth step eliminates the rest of piperidine. The DSC curves of the piperidine adducts that are consistent with the TG data show several peaks. Endothermic peaks at (521, 430, and 409) K are due to melting and decomposition of the adducts. Endothermic peaks due to decompositon and elimination of part of trihalide and part of ligand together are also observed. Exothermic peaks due to the redox degradation of the ligand are also observed (Dunstan, 1994a,b, 1995, 1996). Table 3 presents the thermoanalytical data of the adducts.

Calorimetric Measurements. The standard enthalpies of dissolution of arsenic trihalides, ligands, and complexes ($\Delta_\iota H^\circ$) were obtained as previously reported (Dunstan and Airoldi, 1988). Table 4 gives these standard thermochemical values, Uncertainty intervals given in this table are twice the standard deviations of about five replicate measurements on each compound. Combined errors were calculated from the square root on the sum of the square of the component errors. From the standard enthalpies of dissolution, the standard enthalpies of the acid/base reactions ($\Delta_r H^\circ$), the standard enthalpies of formation ($\Delta_f H^\circ$), the standard enthalpies of decomposition ($\Delta_D H^\circ$), the lattice standard enthalpies ($\Delta_M H^\circ$), and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\circ$(g)) can be obtained by using the appropriate thermochemical cycles (Dunstan and Airoldi, 1988; Dunstan and dos Santos, 1989). The $\Delta_r H^\circ$(g) values can be used to calculated the standard enthalpies of the As−N bonds (Dunstan and dos Santos, 1989). Table 5 lists the values obtained for all these thermochemical parameters for the adducts. For the determination of $\Delta_r H^\circ$(g) it was necessary to assume that the molar standard enthalpy of sublimation of each adduct was equal to the enthalpy of sublimation of 1 mol of ligand (Dunstan and Airoldi, 1988; Dunstan and dos Santos, 1989; Dunstan, 1994a,b; Chagas and Airoldi, 1989), as melting points and thermal studies showed that the adducts decompose on heating and were not found in the liquid phase and probably not in the gaseous phase. From the $\bar{D}_{As-N}$ values for a series of adducts with the same stoichiometry and the same trihalide and not considering that Pipz is a bidentate ligand, the basicity order Pipd > Morph > Pipz can be obtained. Considering that Pipz is a bidentate ligand and comparing with adducts of stoichiometry 1/2, the same order is obtained. The expected order would be Pipd > Morph due to an inductive effect of substitution of one carbon atom in the ring of the Pipd by the more electronegative oxygen atom. Pipz substitutes one carbon atom in the ring by one nitrogen atom that is more electronegative than the carbon atom but less electronegative than an oxygen atom. It would be expected to be a better acid than Morph but the substitution leaves the Pipz as a bidentate ligand and competition between the two nitrogen atoms causes it to be a worse base than Morph. Considering adducts with the same stoichiometry and the same ligand, from $\bar{D}_{As-N}$ values, the acidity order is $\mathrm{AsBr_3} > \mathrm{AsCl_3}$ (for Pipz), $\mathrm{AsCl_3} > \mathrm{AsI_3}$ (for Morph), and $\mathrm{AsBr_3} > \mathrm{AsI_3}$ (for Pipd). The expected order from the electronegativety values of halogen atoms would be $\mathrm{AsCl_3} > \mathrm{AsBr_3} > \mathrm{AsI_3}$. The $\bar{D}_{As-N}$ values show that $\mathrm{AsBr_3}$, is a better acid to Pipz than $\mathrm{AsCl_3}$ as the stronger bond is formed with the stronger acid. The inversion in the expected order would be due to the nature of the bond formed between the donor and acceptor atoms (Dunstan and Airoldi, 1988; Srivastava et al., 1976; Ochiai, 1953; Zackrisson, 1961).

In synthesis, the $\bar{D}_{As-N}$ and other thermochemical parameters data indicate that the As−N bond is stronger as we go in the sequence Pipz < Morph < Pipd. The substitution of one carbon atom in the saturated ring of the Pipd by the more electronegative atoms oxygen or nitrogen causes the decrease of the electronic density on the nitrogen atom by an inductive effect. For a given ligand, the stronger bond is formed with the stronger acid, as is also shown by the $\bar{D}_{As-N}$ data and other thermochemical parameters data.

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