Reactivity of Lewis Acids towards Nitriles; Crystal Structure and Electron Deformation Density of $C_2N_2{\cdot}SbF_5$ and Photoelectron Spectrum of AsF_5*

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The reactivity of nitriles and dinitriles HCN, C_2N_2, $CCl_2(CN)_2$ and $CH_2(CN)_2$ towards AsF_5 and SbF_5 has been investigated. The new compounds $HCN{\cdot}AsF_5$ **1**, $HCN{\cdot}SbF_5$ **2**, $C_2N_2{\cdot}AsF_5$ **3**, $C_2N_2{\cdot}SbF_5$ **4**, $CH_2(CN)_2{\cdot}AsF_5$ **5**, $CH_2(CN)_2{\cdot}(2AsF_5)$ **6** and $CCl_2(CN)_2{\cdot}AsF_5$ **7** have been characterized by chemical analysis, IR, Raman, ^1H, ^{19}F and ^{14}N NMR spectroscopy. The crystal structure of the first example of a cyanogen adduct $C_2N_2{\cdot}SbF_5$ **4** has been determined. Compound **4** crystallizes in the orthorhombic space group $C222_1$ with cell parameters a = 6.579(1), b = 16.245(1) and c = 6.389(1) Å. The deformation density of the molecule was examined. The reactivities of HCN and C_2N_2 towards the strong Lewis acid AsF_5 are discussed on the basis of the hard–soft acid–base principle. The hitherto unknown ionization potential of AsF_5 (15.57 eV) was obtained by photoelectron spectroscopy. A semiquantitative molecular orbital scheme for AsF_5 is presented.

First attempts to synthesise the linear 22-valence-electron cation $[FCNF]^+$ in the salt $[FCNF]^+[AsF_6]^-$ by the reaction of cyanogen with F_2 and AsF_5 were unsuccessful.[1] In all cases the Raman spectra showed that the unknown adduct $C_2N_2{\cdot}AsF_5$ **3** was formed [equations (1a) and (1b)].

$$C_2N_2 + 3F_2 + 2AsF_5 \longrightarrow 2[FCNF]^+[AsF_6]^- \quad (1a)$$

$$C_2N_2 + 3F_2 + 2AsF_5 \longrightarrow C_2N_2{\cdot}AsF_5 + AsF_5 + 3F_2 \quad (1b)$$

Recently we have investigated the reaction behaviour of inorganic cyanogen compounds R–CN (R = CH_3, CF_3, CN, Br, I or H) towards $[I_3]^+[AsF_6]^-$.[2–4] We demonstrated that the substituent's electronegativity $\chi(R)$ has a great influence on the reactivity. On the basis of the hard–soft acid-base (HSAB) principle[5] we discussed the different reactivities of the Lewis bases (nitriles) towards the Lewis acid 'I^+'. We showed that the donor abilities of C_2N_2 and HCN are not high enough to co-ordinate I^+.[4]

Subsequently we became interested in the investigation of the adduct formation between AsF_5 or SbF_5 and HCN, C_2N_2, $CH_2(CN)_2$ or $CCl_2(CN)_2$, respectively. Adducts of CH_3CN with Lewis acids like BF_3,[6] AsF_5,[7] SbF_5,[8] MoF_5[9] and WF_5[9] are known and have been well characterized particularly by vibrational spectroscopy[6–9] and X-ray studies.[6,8] Whereas adducts of HCN and inorganic chlorides[10] as well as the addition compounds $NC(CH_2)_nCN{\cdot}mSbCl_5$ (n = 1–4, m = 1 or 2)[11] have been studied by elemental analysis and IR spectroscopy, the addition compounds of cyanogen and boron halides are only poorly investigated.[12] Co-ordination compounds of HCN, C_2N_2, $CH_2(CN)_2$ and $CCl_2(CN)_2$ with the pentafluorides of Group 15 elements are still unknown.

In this paper we report on the reaction behaviour of the cyanogen compounds towards AsF_5 and SbF_5. The crystal structure of $C_2N_2{\cdot}SbF_5$ **4** is presented. As far as we are aware, compound **4** represents the first example of a cyanogen–Group 15 pentafluoride adduct. All new compounds have been characterized by elemental analyses, IR, Raman, ^1H, ^{19}F and ^{14}N NMR spectroscopy. The donor abilities of HCN and C_2N_2 towards AsF_5 are discussed on the basis of the HSAB principle and compared with the donor abilities of these bases towards the cationic Lewis acid I^+.

Results and Discussion

The new compounds $HCN{\cdot}AsF_5$ **1**, $HCN{\cdot}SbF_5$ **2**, $C_2N_2{\cdot}AsF_5$ **3**, $C_2N_2{\cdot}SbF_5$ **4**, $CH_2(CN)_2{\cdot}AsF_5$ **5**, $CH_2(CN)_2{\cdot}2AsF_5$ **6** and $CCl_2(CN)_2{\cdot}AsF_5$ **7** have been formed by reaction of the nitriles or dinitriles with AsF_5 or SbF_5 in liquid sulfur dioxide at low temperatures [equations (2)–(5)]. Whereas $CH_2(CN)_2$ forms

$$HCN + EF_5 \longrightarrow HCN{\cdot}EF_5 \ (E = \text{As or Sb}) \quad (2)$$

$$C_2N_2 + EF_5 \longrightarrow C_2N_2{\cdot}EF_5 \ (E = \text{As or Sb}) \quad (3)$$

$$CH_2(CN)_2 + nAsF_5 \longrightarrow CH_2(CN)_2{\cdot}nAsF_5 \quad (n = 1 \text{ or } 2) \quad (4)$$

$$CCl_2(CN)_2 + AsF_5 \longrightarrow CCl_2(CN)_2{\cdot}AsF_5 \quad (5)$$

both 1:1 and 1:2 adducts with AsF_5, the other dinitriles C_2N_2 and $CCl_2(CN)_2$ only yield the 1:1 compounds even when treated with an excess of AsF_5 or SbF_5, respectively. Reactions

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* *Supplementary data available:* Further details concerning the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting reference CSD 55627.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 1 Vibrational data (cm^{-1}) for adducts **1–4**

HCN·AsF$_5$ **1**								
	Raman		HCN·SbF$_5$ **2**		C$_2$N$_2$·AsF$_5$ **3**	C$_2$N$_2$·SbF$_5$ **4**		
IR^a	Solution^d	Solid^c	IR^a	Raman	Raman^b	IR	Raman^c	Assignment
3205s			3158s					ν(CH)
	2330(<1)							
2192s	2181(7)	2189(7)	2178s	2175(6)^e	2386(10)^f	2382m^g	2384(8)	ν(C–N), ν_{sym}(C–N)
							2350(1)	
					2202(1)	2175mw^g	2202(1)	ν_{asym}(C–N)
					989(<1)			
	834(1)				873(1)	895mw^g		
	762(<1)							δ(HCN)
	728(1)	708(10)		663(10)^c	767(3)	695s^h	696(3)	ν(EF)$_{ax}$
	685(10)	676(7)		639(3)^c	692(9)	662vs^h	655(10)	ν(EF$_4$)$_{eq}$
	610(1)			601(2)^c	616(1)		601(2)	ν(EF$_4$)$_{eq}$
				566(1)^c		525w^g		
					511(7)	510ms^g	510(7)	δ(NC–CN)
	489(2)			416(2)^c		490mw^g		
	391(1)	390(4)			398(1)			δ(FEF$_4$)$_{wag}$
						380mw^g		
	370(1)			293(2)^c	349(<1)		290(1)	δ(EF$_4$)$_{oop}$
	312(1)							δ(AsF$_4$)$_{ip}$
	265(3)	269(8)		269(1)^c	266(<1)		266(1)	ν(E–N)
	216(<1)	170(2)		218(2)^c	193(3)		170(4)	
	132(1)	141(5)		206(2)^c	123(2)		112(1)	
				178(<1)^c				
				144(<1)^c				
				135(1)^c				
				111(<1)^c				

^{a} Fluorolube suspension. ^{b} Solid, −100 °C, 30 mW, 0.5s per point, three scans. ^{c} Solid, room temperature, 20 mW, 2s per point. ^{d} In SO$_2$, room temperature, 30 mW, 1s per point. ^{e} Solid, room temperature, 30 mW, 2s per point. ^{f} In SO$_2$ solution, room temperature, 20 mW: **3**, 2370/2378(8); C$_2$N$_2$, 2332(10) cm^{-1}. ^{g} Nujol suspension. ^{h} Pure compound between KBr plates.

of $CCl_2(CN)_2$ with other Lewis acids like PF_5, $SbCl_5$ and BiF_5 were unsuccessful. All compounds are white solids which are extremely moisture sensitive. The adduct C_2N_2·AsF_5 is the least-stable compound in this series and could not be isolated. At room temperature compounds **5–7** decompose slowly in SO_2 solution but rapidly in the solid state, and **4** decomposes slowly at room temperature. The adducts **1** and **2** are stable up to 85 or 100 °C, respectively. The decomposition products are brown solids, presumably polymerization products of the cyanogen species.

Compounds **1–4** are linear with approximate C_{4v} symmetry; the other species are non-linear with local C_{4v} symmetry at the dinitrile fragment and distorted-octahedral co-ordination at the arsenic atom.

Vibrational Spectroscopy (*IR and Raman*).—Owing to the reactivity of all compounds towards KBr plates, the IR spectra of **1**, **2** and **4–6** were measured for suspensions in Nujol or Fluorolube between KBr plates, which were coated with either Nujol or Fluorolube. The Raman spectra of **1–4** and **7** were recorded on the pure solids or if they are less stable (**1**, **7**) on dilute SO_2 solutions.

All compounds show the C≡N stretching mode at higher wavenumbers than the unco-ordinated cyanogen compounds. This is in good agreement with the increase in C≡N bond strength due to the co-ordination of the Lewis acids AsF_5 or SbF_5 and corresponds to the theory that cyanides are better σ donors rather than π acceptors.[13] The vibrational data for the linear compounds are summarized in Table 1; the non-linear species are listed in Table 2. The assignment for the nitrile or dinitrile fragment was done by comparison with the unco-ordinated compounds.[14–16] The co-ordinated pentafluorides of As and Sb are compared with other addition compounds L·AsF_5 or L·SbF_5 (L = CH_3CN, SOF_2 or COF_2).[17]

HCN *Adducts* **1** *and* **2**. The Raman spectra were taken of the solids and in the case of HCN·AsF_5 also in SO_2 solution, because of fluorescence problems in the solid state. The C≡N stretching modes are shifted 70–90 cm^{-1} to higher wavenumbers compared with unco-ordinated HCN. The CH stretching band was observed only in the IR spectra at 3205 cm^{-1} for compound **1** and 3158 cm^{-1} for **2**. The decrease in the CH stretching frequency is due to the increase in the acidity of the co-ordinated HCN. Increasing acidity was also observed in $[Ti(HCN)_2(cp)_2]^{2+}[AsF_6]^-{}_2$ (cp = η-C_5H_5) and it is more than likely that the assignments of the CH frequencies of this complex are incorrect and that the ν(CH)(cp) and (HCN) should be interchanged.[18] All values are in good agreement with the vibrational data found for HCN·BCl_3 or HCN·$SbCl_5$.[10] The pentafluoride fragment bending frequencies correspond to those of acetonitrile pentafluoride complexes of Group 15.[7]

C_2N_2 *Adducts* **3** *and* **4**. For both compounds only one band for ν_{sym}(C≡N) was observed caused by mechanical coupling of the CN groups. Both the symmetrical and asymmetrical C≡N stretching bands are shifted to higher frequencies relative to those of unco-ordinated C_2N_2. The SO_2 solution Raman spectra recorded in the region between 2300 and 2400 cm^{-1} (*cf.* Table 1) of adduct **3** shows both compound **3** and unco-ordinated C_2N_2 to be present indicative of an equilibrium in solution between **3** with C_2N_2 and AsF_5·SO_2 (see below, thermodynamic aspects). The pentafluoride moieties show absorption at higher frequencies than the pentafluorides co-ordinated to acetonitrile but have quite similar intensities and frequencies to those of some oxygen-bridged adducts of AsF_5 and SbF_5 like COF_2·AsF_5 or SOF_2·SbF_5.[17] Fig. 1 shows the Raman spectrum of the 1:1 adduct C_2N_2·SbF_5 **4**.

Non-linear adducts **5–7**. The adducts **5–7** are unstable and reactive towards KBr plates. So the spectra of **5** and **6** were recorded in the range 4000–2000 cm^{-1} for a suspension in Kel-F between KBr plates coated with Kel-F; recording of Raman spectra was not successful. The Raman spectrum of complex **7** was measured for a SO_2 solution and is shown in Fig. 2.

Table 2 Vibrational data (cm^{-1}) for adducts **5**–**7**

$CH_2(CN)_2{\cdot}AsF_5$ **5** IR[a]	$CH_2(CN)_2{\cdot}2AsF_5$ **6** IR[a]	$CCl_2(CN)_2{\cdot}AsF_5$ **7** Raman	Assignment
2960s	2945s		$\nu_{asym}(CH)$
2918s	2910s		$\nu_{sym}(CH)$
2600w			
2358vs	2327s	2334(10)[b]	$\nu(C{-}N)_{co\text{-}ord}$
2298ms (br)		2260(4)[b]	$\nu(C{-}N)_{free}$
		954(2)[c]	$\nu_{sym}(C{-}C)$
		935(1)[c]	
		798(2)[c]	$\nu_{asym}(C{-}Cl)$
		747(2)[c]	$\nu(AsF)_{ax}$
		694(10)[c]	$\nu(AsF_4)_{eq}$
		615(< 1)[c]	$\nu(AsF_4)_{eq}$
		580(< 1)[c]	$\delta(C{-}C{-}C)$
		503(8)[c]	$\nu_{sym}(C{-}Cl)$
		453(1)[c]	$\delta(C{-}C{-}Cl)$
		394(< 1)[c]	$\delta(FAsF_4)$
		356(2)[c]	$\delta(AsF_4)_{oop}$
		272(4)[c]	$\delta(Cl{-}C{-}Cl)/(As{-}N)$
		217(< 1)[c]	
		165(sh)(1)[c]	$\delta(C{-}C{-}N)$

[a] Fluorolube suspension. [b] In SO_2, room temperature, 40 mW, 2s per point, two scans. [c] In SO_2, room temperature, 40 mW, 2s per point, eight scans.

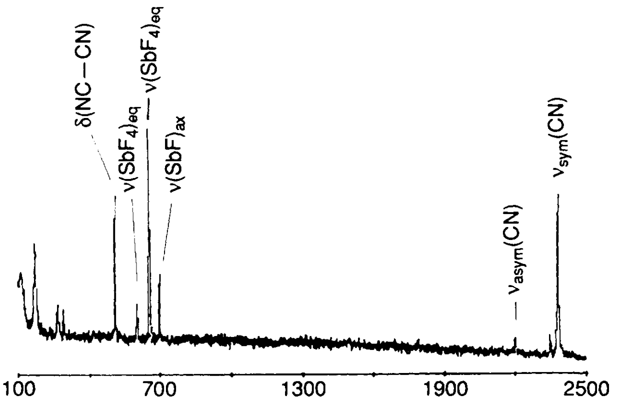

Fig. 1 Raman spectrum of $C_2N_2{\cdot}SbF_5$ **4** (*cf.* Table 1)

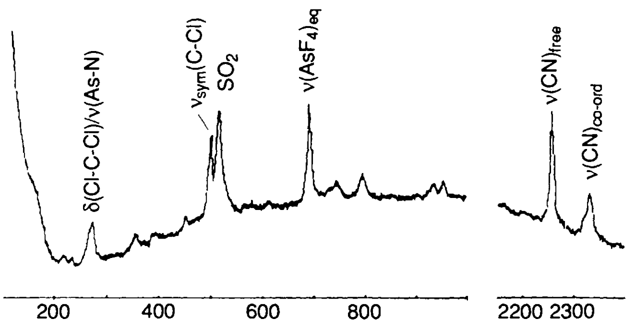

Fig. 2 Raman spectrum of $CCl_2(CN)_2{\cdot}AsF_5$ **7** (*cf.* Table 2)

Table 3 Proton, ^{19}F and ^{14}N NMR data of adducts **1**–**6**

Compound	^1H (δ_H)[a]	^{19}F (δ_F)[a]	^{14}N (δ_N)[a]
HCN	3.88 (s)		−130[b]
1 $HCN{\cdot}AsF_5$	6.07 (s)	−47.3 (s)	−187[c]
2 $HCN{\cdot}SbF_5$	6.17 (s)		
C_2N_2[d]			−113
3 $C_2N_2{\cdot}AsF_5$		−48.8 (s)	−117[c]
4 $C_2N_2{\cdot}SbF_5$		−109 (s)	
$CH_2(CN)_2$	3.36 (s)		
5 $CH_2(CN)_2{\cdot}AsF_5$	4.30 (s)		
6 $CH_2(CN)_2{\cdot}2AsF_5$	4.87 (s)		

[a] In SO_2, room temperature. [b] Neat, 36 °C. [c] *ca.* 0.5 mol dm^{-3}. [d] Ref. 21*b*.

Whereas adducts **5** and **7** show two bands for the C≡N stretching mode, **6** has only one band in this region. The higher-frequency C≡N bands were assigned to the co-ordinated CN moiety, whereas the other band is due to the free CN group. There was no mechanical coupling of the CN groups in **5** and **7** and our results are in good agreement with those for the 1 : 1 and 1 : 2 addition complexes of $NC(CH_2)_4CN$ and $SbCl_5$.[11]

Proton, ^{19}F *and* ^{14}N *NMR Spectroscopy.*—The NMR spectra of all compounds were recorded for SO_2 solutions at room temperature (high-frequency direction positive). The HCN adducts **1** (δ 6.07) and **2** (δ 6.17) show a singlet proton resonance, which is shifted significantly to lower field (high frequency) compared with the resonance of free HCN (δ 3.88). This effect is similar to that observed for the co-ordination of HCN to $Ti(cp)_2^{2+}$ in $[Ti(HCN)_2(cp)_2]^{2+}[AsF_6]^-{}_2$.[18] The proton resonance signals of **5** (δ 4.30) and **6** (δ 4.87) are shifted to lower field also. The appearance of just one broad singlet in the ^{19}F NMR spectra of **1** and **3** shifted to higher frequency relative to free AsF_5 (δ −65)[19] might very well be due to both nuclear quadrupolar broadening of the ^{14}N and ^{75}As nuclei and rapid exchange processes. Similar shifts were reported on cyanogen halide arsenic pentafluoride adducts $[XCN{\cdot}AsF_5]$ (X = F, Cl, Br, I).[20] Compound **4** shows only a very broad signal at about the same frequency as free SbF_5 (δ − 110).[19]

Compounds **1** (δ −187, $\Delta\nu_{\frac{1}{2}}$ = 95 Hz) and **3** (δ −117, $\Delta\nu_{\frac{1}{2}}$ = 173 Hz) show a singlet resonance in the ^{14}N NMR spectra. Whereas the ^{14}N NMR chemical shift of adduct **1** differs substantially from that reported for unco-ordinated HCN (δ −130)[21a] the value for species **3** is identical with that recorded for free C_2N_2 in SO_2 solution (δ −113, $\Delta\nu_{\frac{1}{2}}$ = 150 Hz)[21b] (both values are recalculated and are given relative to external (CH_3NO_2). This may be explained by the stability of **1** in solution and an equilibrium between **3** and C_2N_2 and AsF_5 which forms a loose adduct with SO_2 (*cf.* vibrational spectroscopy above and thermodynamic aspects below). The appearance of just one resonance in the ^{14}N NMR spectrum of C_2N_2 either co-ordinated to AsF_5 or unco-ordinated can be explained by rapid exchange processes between both species. All values are summarized in Table 3.

Table 4 Positional parameters of $C_2N_2{\cdot}SbF_5$ **4** and their estimated standard deviations (e.s.d.s)

Atom	x	y	z
Sb	0.000	0.130 64(2)	0.250
F(2)	0.203 6(6)	0.142 1(3)	0.060 7(7)
F(3)	0.186 9(8)	0.143 9(3)	0.465 7(7)
F(1)	0.000	0.017 6(2)	0.250
N(1)	0.000	0.266 9(3)	0.250
N(2)	0.000	0.492 5(3)	0.250
C(1)	0.000	0.336 0(3)	0.250
C(2)	0.000	0.422 2(4)	0.250

Table 5 Bond distances (Å) and angles (°) for $C_2N_2{\cdot}SbF_5$ **4** with e.s.d.s in the least significant digits in parentheses

Sb–F(2)	1.814(4)	N(1)–C(1)	1.123(7)
Sb–F(3)	1.859(5)	N(2)–C(2)	1.141(8)
Sb–F(1)	1.837(4)	C(1)–C(2)	1.400(8)
Sb–N(1)	2.213(5)		
F(2)–Sb–F(2′)	168.2(2)	F(3)–Sb–F(1)	96.7(1)
F(2)–Sb–F(3)	89.6(2)	F(3)–Sb–N(1)	83.3(1)
F(2)–Sb–F(3′)	89.0(2)	F(1)–Sb–N(1)	180.0
F(2)–Sb–F(1)	95.9(1)	Sb–N(1)–C(1)	180.0
F(2)–Sb–N(1)	84.1(1)	N(1)–C(1)–C(2)	180.0
F(3)–Sb–F(3′)	166.7(2)	N(2)–C(2)–C(1)	180.0

Primed atom related to unprimed atom by symmetry operation $-x, y, 0.5 - z$.

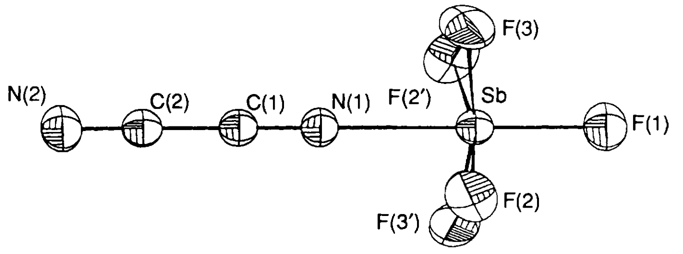

Fig. 3 Molecular structure of $C_2N_2{\cdot}SbF_5$ **4**

Crystal Structure of $C_2N_2{\cdot}SbF_5$ **4**.—Atomic parameters are given in Table 4, interatomic distances and interbond angles in Table 5. Fig. 3 shows a view of the molecule.

Compound **4** shows a linear $NCCNSbF_{ax}$ moiety with angles of exactly 180°. The C(1)–N(1) [1.123(7) Å] and the C(2)–N(2) distances [1.141(8) Å] differ from the C≡N bond distances in solid C_2N_2, which is 1.127 Å.[22] The C(1)–C(2) bond distance [1.400(8) Å] is approximately 0.03 Å longer than in C_2N_2. The antimony atom has a distorted-octahedral co-ordination. The F_{ax}–Sb–F_{eq} angles are 95.9(1) [F(2)–Sb–F(1)] and 96.7(1)° [F(3)–Sb–F(1)] and are approximately 2° greater than in the $SO_2{\cdot}SbF_5$ adduct.[23] The F_{eq}–Sb–N angles of 83.3(1) and 84.1(1)° are smaller than the F_{eq}–Sb–O angles in $SO_2{\cdot}SbF_5$. The Sb–F bond distances are shorter than in $SO_2{\cdot}SbF_5$ and this is in good agreement with the vibrational data which show different frequencies for the SbF_5 moiety.

Once the refinement had converged the deformation density[24,25] of the molecule was examined. Initially just the low-order–high-order (X-X_{HO}) maps were calculated and the map through the plane of the axial fluorine atom, two equatorial fluorine atoms (related by a two-fold axis) and the N≡C–C≡N group is shown in Fig. 4. This clearly shows the Sb–F bonding density congregating close to the fluorine atoms, the increased density in the N≡C bonds and (just) the lone-pair electrons of the terminal nitrogen atom. The vibration ellipsoids (Fig. 3) do show an increase in thermal vibration along the cyanogen group away from the antimony atom and the weaker indications of the bonding electrons down this group may well reflect this increase in vibration. The usual program for multipole analyses (MOLLY)[24] does not contain separate core- and valence-electron scattering parameters for antimony. However Coppens[25] kindly provided a set of these parameters (without the relativistic correlation) and multipole refinement is now in progress.

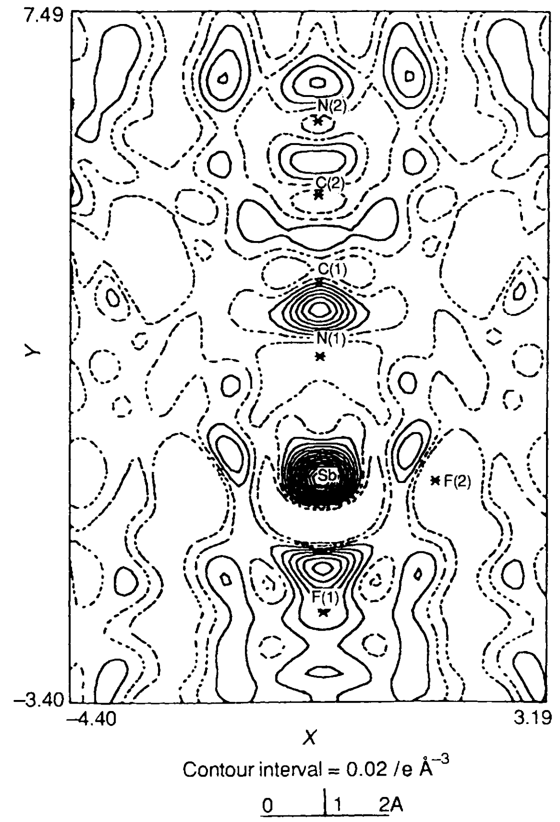

Fig. 4 Deformation density of $C_2N_2{\cdot}SbF_5$ **4**

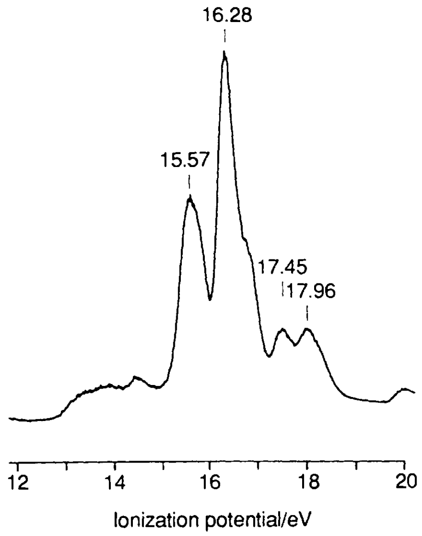

Fig. 5 Photoelectron spectrum of AsF_5 (*cf.* Experimental section)

Photoelectron Spectrum of AsF_5.—The ionization potential of AsF_5 has not been reported previously. However, for the discussion of the reaction behaviour of AsF_5 towards nitriles on the basis of the HSAB principle the value of the first ionization potential is essential. The photoelectron spectrum of AsF_5 is shown in Fig. 5. The ionization bands are marked on the

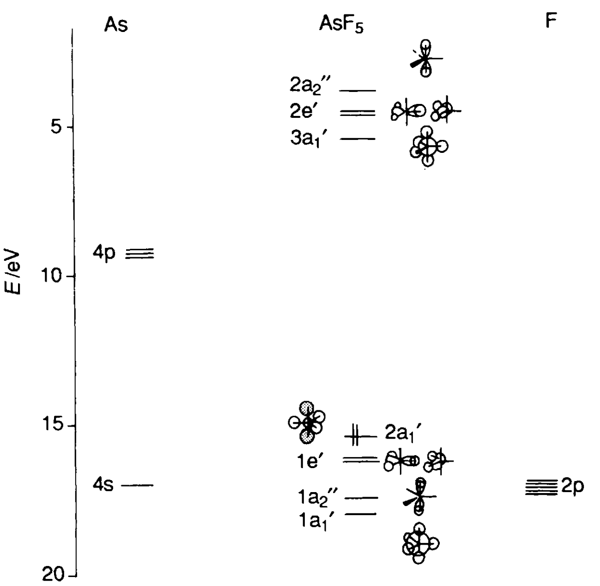

Fig. 6 Molecular orbital scheme for AsF_5

spectrum; the weaker bands are caused by unidentified impurities. A semiquantitative molecular orbital (MO) scheme using the atomic orbitals of arsenic and fluorine[26] and the qualitative MO scheme reported by Gimarc[27] are shown in Fig. 6. The ionization bands were assigned to the molecular orbitals. Using Koopmans theorem the first ionization potential of 15.57 eV was assigned to the highest occupied molecular orbital (HOMO) ($2a_1$) and the electron affinity was assigned to the lowest unoccupied molecular orbital (LUMO) ($3a_1$). The electron affinity was obtained experimentally to be 5.3 eV,[28] and the calculated value lies between 1.9 and 2.9 eV.[29] For our estimations we used the experimental value.

Thermodynamic Aspects.—Recently we have reported on the reaction behaviour of the nitriles CH_3CN, ICN and HCN towards I_3AsF_6. In these reactions I_3AsF_6 behaves as a source of 'I^+'.[2-4] We observed a decrease in stability of the adducts in the order CH_3CN > ICN > HCN; C_2N_2 did not react with I^+.[30] The different stabilities can easily be understood on the basis of the HSAB principle.[5] The number of transferred electrons (ΔN) and the gain in energy (ΔE), resulting from the reactions of the nitrile bases with I^+, decrease in the same order as that of the stability.

In this paper we report on the different stabilities of AsF_5 adducts of CH_3CN, ICN, HCN and C_2N_2. Using the values for the ionization potentials and the electron affinities we have been able to estimate the absolute electronegativities (χ) and the absolute hardness (η) of all reactants,* and hence the numbers of transferred electrons (ΔN) and the energy gain (ΔE). The stability of the AsF_5 adducts decreases in the order $CH_3CN \gg$ ICN $\gtrsim$ HCN $\gg C_2N_2$, similar to that of the corresponding nitrile iodonium compounds. The calculated values of ΔE (HSAB principle) for the reactions of the nitriles with AsF_5 are nicely in agreement with the experimental results. However, the values of ΔN and ΔE are much smaller than the values for the reactions of these bases with 'I^+'.[4] Nevertheless the AsF_5 adducts and the iodonium compounds are similar in stability. The relative lower stability of the iodonium compounds compared with the AsF_5 adducts might be caused by thermodynamically more favourable decomposition reactions. As shown by Raman and ^{14}N NMR spectroscopy, compound **3** is in equilibrium with free C_2N_2 and $SO_2{\cdot}AsF_5$ in SO_2 solution. This is in good agreement with the similar values for ΔE for adduct formation between C_2N_2 and AsF_5 or SO_2 and AsF_5, respectively. All hardness parameters are summarized in Table 6.

Experimental

The reactions were carried out in glass vessels fitted with poly(tetrafluoroethylene) valves. All manipulations were carried out in an inert-gas atmosphere (N_2, dry-box). Gaseous compounds were added volumetrically using a calibrated vacuum line.

Arsenic pentafluoride was prepared from the elements;[37] HCN[38] and C_2N_2[39] were synthesised by literature methods and purified by distillation, $CH_2(CN)_2$ (Aldrich) was purified by sublimation and dried over P_4O_{10} and $CCl_2(CN)_2$ (Aldrich), SbF_5 (Alfa) and SO_2 (Messer Griesheim, stored over CaH_2) were used after distillation.

Infrared spectra were obtained using a Perkin-Elmer 580 B instrument, Raman spectra using a Ybin Yvon Ramanor U 1000 spectrometer equipped with a Spectra Physics krypton laser (647.09 nm), ^{19}F NMR spectra using a Bruker SXP 4-100 spectrometer operating at 84.7 MHz and referenced to $CFCl_3$, ^1H NMR spectra in SO_2 solution at room temperature using a Varian EM 360 (60 MHz) and referenced to $SiMe_4$ and ^{14}N NMR spectra at 14.45 MHz on a Varian XL-200 spectrometer operating in the Fourier-transform mode using the ACOUST pulse sequence (to overcome baseline roll) with 0.03 s acquisition times and 5E-07s pulse delays. Chemical shifts are reported on the δ scale with neat nitromethane at 22 °C as an external reference.[40] Microanalyses were performed by the Technische Universität Berlin service. The photoelectron spectrum was recorded with a Leybold Haeraeus UPG 200 spectrometer equipped with a He I lamp (21.21 eV) as radiation source. The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 eV and of argon at 15.759 and 15.937 eV. The accuracy of measurement is approximately 0.02 eV for the ionization potentials.

Syntheses.—$HCN{\cdot}AsF_5$ **1**. Arsenic pentafluoride (0.884 g, 5.20 mmol) was condensed at −196 °C onto a frozen sulfur dioxide solution (10 cm^3) of HCN (0.142 g, 5.20 mmol). The reaction mixture was warmed to −50 °C, stirred for 10 min and then warmed to room temperature. The SO_2 was removed yielding adduct **1** as a white solid (0.97 g, 95%), T_{decomp} > 85 °C (Found: C, 6.0; H, 0.5; N, 7.2. $CHAsF_5N$ requires C, 6.1; H, 0.5; N, 7.1%).

$HCN{\cdot}SbF_5$ **2**. Hydrogen cyanide (0.133 g, 4.90 mmol) was added to a cooled solution of SbF_5 (1.068 g, 4.90 mmol) in SO_2 at −70 °C. After warming to room temperature and removing the SO_2 adduct **2** remained as a white solid (1.17 g, 97%), T_{decomp} > 100 °C (Found: C, 4.8; H, 0.4; N, 5.9. CHF_5NSb requires C, 4.9; H, 0.4; N, 5.7%).

$C_2N_2{\cdot}AsF_5$ **3**. Cyanogen (0.088 g, 1.70 mmol) was condensed (−196 °C) into a glass vessel, equipped with a Raman capillary. Arsenic pentafluoride (0.289 g, 1.70 mmol) was added and the reaction mixture was warmed to −20 °C. A white solid formed, which was sublimed in the Raman capillary cooled to −196 °C. This capillary was sealed off and adduct **3** was characterized by Raman spectroscopy at −100 °C. For ^{19}F, ^{14}N NMR and solution Raman spectroscopy, samples (freshly prepared in a NMR tube) in liquid SO_2 were used.

$C_2N_2{\cdot}SbF_5$ **4**. Cyanogen (0.120 g, 2.30 mmol) was condensed onto SbF_5 (0.500 g, 2.30 mmol) at −196 °C. The reaction mixture was warmed to room temperature for 30 min. A white powder formed, which was identified as compound **4** (0.57 g, 93%) (Found: C, 8.8; N, 10.7. $C_2F_5N_2Sb$ requires C, 8.9; N, 10.4%). Sublimation of the crude product under reduced pressure from room temperature to +10 °C yielded **4** as colourless crystals, suitable for X-ray diffraction study.

$CH_2(CN)_2{\cdot}AsF_5$ **5**. The compound $CH_2(CN)_2$ (0.366 g, 5.50

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* Absolute electronegativity, $\chi = 0.5\,(I + A)$,[5] absolute hardness, $\eta = 0.5\,(I - A)$,[5] number of transferred electrons, $\Delta N = (\chi_A - \chi_B)/2(\eta_A + \eta_B)$,[5] and energy gain, $\Delta E = -0.25\,(\chi_A - \chi_B)^2/(\eta_A + \eta_B)$,[5] where I = ionization potential and A = electron affinity (both adiabatic in eV).

Table 6 Hardness parameters

	I[a]/eV	A[b]/eV	χ/eV	η/eV	ΔN/eV	ΔE/kJ mol^{-1}
I^+	19.13[31]	10.45[31]	14.79[31]	4.34[31]		
AsF_5	15.57	5.3[28]	10.44	5.14		
CH_3CN	12.2[31]	−2.8[31]	4.7[31]	7.5[31]		
ICN	10.91[32]	1.4[c]	6.16	4.76		
HCN	13.6[31]	−2.3[31]	5.65	7.95		
C_2N_2	13.57[35]	−0.58[36]	6.50	7.08		
SO_2	12.3[31]	1.1[31]	6.7[31]	5.6[31]		
$CH_3CN + I^+ \longrightarrow [CH_3CNI]^+$					0.426	−207.2
$ICN + I^+ \longrightarrow [ICNI]^+$					0.474	−197.4
$HCN + I^+ \longrightarrow [HCNI]^+$					0.372	−164.0
$C_2N_2 + I^+ \longrightarrow [C_2N_2I]^+$					0.363	−145.2
$CH_3CN + AsF_5 \longrightarrow CH_3CN{\cdot}AsF_5$					0.227	−62.9
$ICN + AsF_5 \longrightarrow ICN{\cdot}AsF_5$					0.216	−44.6
$HCN + AsF_5 \longrightarrow HCN{\cdot}AsF_5$					0.183	−42.3
$C_2N_2 + AsF_5 \longrightarrow C_2N_2{\cdot}AsF_5$					0.161	−30.6
$SO_2 + AsF_5 \longrightarrow SO_2{\cdot}AsF_5$					0.174	−31.4

[a] I = Adiabatic ionization potential. [b] A = Adiabatic electron affinity. [c] A_{ad}(ICN) is estimated to be 1.4 eV by comparison with A_{vert}(ICN) = 0.9 eV,[33] A_{vert}(ICl) = 1.7 ± 0.6 eV,[34] and A_{ad}(ICl) = 2.7 ± 0.3 eV.[34]

mmol) was dissolved in SO_2 (5 cm^3) and cooled to −196 °C, when AsF_5 (0.934 g, 5.50 mmol) was added. The reaction mixture was warmed to −50 °C and SO_2 was removed under a dynamic vacuum. Adduct **5** remained as a light brown unstable solid (1.04 g, 80%) (Found: C, 15.4; H, 1.1; N, 11.8. $C_3H_2AsF_5N_2$ requires C, 15.3; H, 0.9; N, 11.9%). Freshly prepared samples were used for IR and ^{1}H NMR spectroscopy.

$CH_2(CN)_2{\cdot}2AsF_5$ **6**. The compounds $CH_2(CN)_2$ (0.158 g, 2.40 mmol) and AsF_5 (0.815 g, 4.80 mmol) were allowed to react as described above (*cf.* preparation of **5**). Adduct **6** was isolated as a light brown solid (1.60 g, 82%) (Found: C, 9.1; H, 0.5; N, 7.2. $C_3H_2As_2F_{10}N_2$ requires C, 8.9; H, 0.5; N, 6.9%).

$CCl_2(CN)_2{\cdot}AsF_5$ **7**. The compound $CCl_2(CN)_2$ (0.286 g, 2.10 mmol) and AsF_5 (0.357 g, 2.10 mmol) were allowed to react as described above (*cf.* preparation of **5**). Compound **7** is a light yellow extremely moisture-sensitive solid (0.55 g, 86%) (Found: C, 11.8; N, 9.3. $C_3AsCl_2F_5N_2$ requires C, 11.8; N, 9.2%). For Raman spectroscopy in SO_2 solution a freshly prepared sample was used.

X-Ray Crystal Structure Determination of $C_2N_2{\cdot}SbF_5$.—A colourless crystal of $C_2N_2{\cdot}SbF_5$ **4** with dimensions 0.18 × 0.20 × 0.23 mm was mounted in a dry-box in a carefully drawn Pyrex-glass capillary. Preliminary examinations and data collection were performed on a CAD4 four-circle diffractometer equipped with a graphite-crystal monochromator.

Cell constants and the orientation matrix were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $14 < \theta < 18°$. From the systematic absences (hkl, $h + k = 2n$; $00l$, $l = 2n$) and from subsequent least-squares refinement, the space group was determined to be $C222_1$ (no. 20).

Crystal data. $M = 1075.11$, orthorhombic, space group $C222_1$; $a = 6.579(1)$, $b = 16.245(1)$, $c = 6.389(1)$ Å, $U = 682.8(3)$ Å^3, $Z = 4$, $D_c = 2.61$ g cm^{-3}, $T = 178 \pm 1$ K, $\mu = 40.9$ cm^{-1}; λ(Mo-Kα1) 0.709 26 Å, $F(000) = 488$.

The data were collected at −95 °C using ω–2θ scans to $\sin(\theta_{max})/\lambda = 1.0$ ($2\theta_{max} = 90°$). A total of 2215 reflections were measured and of these 1905 were unique [1293 with $I > 3\sigma(I)$]. Lorentz, polarization[41] and absorption corrections[42] were applied. The intensities of equivalent reflections were averaged and showed an average discrepancy of 1.1%. The Sb atom was found from the Patterson function and the subsequent Fourier summation showed the positions of the remaining light atoms. The structure was refined by full-matrix least squares using CRYSTALS[43] and Dunitz and Seiler[44] weights. The refinement converged at $R = 0.031$, $R' = 0.034$ (0.048 for all reflections). The data were refined in both 'hands' and the parameters cited correspond to those giving the lowest final R value (0.048 as compared with 0.0518 for full data, or 0.031 to 0.035 for 3σ data).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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