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The $[ICNI]^+$ cation: a combined experimental and theoretical study. Reaction of $[ICNI]^+[AsF_6]^-$ with CsN_3 †

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(Iodocyano)iodine hexafluoroarsenate, $[ICNI]^+[AsF_6]^-$, containing the linear 22-valence-electron $[ICNI]^+$ cation was synthesized either by the reaction of iodine cyanide with $[I_3]^+[AsF_6]^-$ or directly from ICN, I_2 and AsF_5 and characterized by chemical analysis, IR, Raman and ^{19}F NMR data. A combined vibrational (IR, Raman) and theoretical study revealed the $[ICNI]^+$ cation to be linear. The preference of the linear over the bent structure can easily be understood in terms of hyperconjugative interactions in the cationic species [natural bond order (NBO) analysis]. The molecular structure of the $[ICNI]^+$ cation was computed semiempirically (Austin Model 1, AM1; reparameterization of AM1, PM3) and *ab initio* at the Hartree–Fock (HF/6-31G*) and correlated RMP2 (RMP, restricted Møller–Plesset) and RMP4(SDQ) levels of theory using quasi-relativistic pseudo-potentials (LANL2DZ) for the iodine atoms. The computed structural parameters at the highest level applied are: $C_{\infty v}$ symmetry, RMP4(SDQ), $d(\text{I–C}) = 2.001$, $d(\text{C≡N}) = 1.167$, $d(\text{N–I}) = 2.021$ Å. The N–I bond dissociation enthalpy for $[ICN–I]^+$ was calculated *ab initio* at the electron-correlated RMP2 level of theory as 207.4 kJ mol^{-1}. The metathetical reaction of $[ICNI]^+[AsF_6]^-$ with CsN_3 in SO_2ClF afforded IN_3, $Cs^+[AsF_6]^-$ and ICN.

Various neutral compounds and cations containing a direct nitrogen–iodine bond have recently been studied, *i.e.* NI_3[1] (*cf.* also $[NI_3][NH_3]_n$, $n = 1$, 3 or 5),[2] IN_3[3] (*cf.* also azidoiodinane derivatives),[4] $(IN_3)_\infty$,[5] $[I_2N_3]^+$[6] and $[I(N_3)_2]^+$[7] {*cf.* also $[I(N_3)_2]^-$}.[8] Owing to the instability of this bond all binary N–I species and more than a few compounds containing a direct N–I bond are very unstable and often explosive.[9] This pronounced instability of many N–I compounds has facilitated both experimental and theoretical research exploring the thermodynamics of such compounds and especially the N–I bond energy.[10] The standard enthalpy of formation of NI_3 and $[NI_3][NH_3]$ and the N–I bond energy in these (formally sp^3 hybridized) compounds were determined on the basis of solution calorimetric procedures: $\Delta H^\circ_f\{[NI_3][NH_3](s)\} = 146 \pm 6$ kJ mol^{-1}, $\Delta H^\circ_f[NI_3\,(g)] = 287 \pm 23$ kJ mol^{-1} and b.e.(N–I, NI_3)‡ = 169 ± 8 kJ mol^{-1}.[12] For iodine azide, IN_3, with the nitrogen next to the iodine according to a natural bond order (NBO) analysis formally also being sp^3 hybridized (although with some π delocalization of the lone pairs) the heat of formation and N–I bond dissociation enthalpy were calculated *ab initio* at the electron-correlated RMP2 (RMP, restricted Møller–Plesset) level of theory: $\Delta H^\circ_f[IN_3(g)] = 433.0$ kJ mol^{-1}, b.d.e.(N–I) = 191.4 kJ mol^{-1}.[9a,10b]

In contrast to BrCN and ClCN which do not form stable salts of the type $[XCNX]^+[AsF_6]^-$ (X = Cl or Br) due to the thermodynamically favourable adduct formation $XCN{\cdot}AsF_5$ and elimination of ClF or BrF, respectively [equation (1)],[13]

$$[XCNX]^+[AsF_6]^- \longrightarrow XCN{\cdot}AsF_5 + XF \qquad (1)$$

ICN does react with I^+ donors to form compounds of the type $[ICNI]^+[AsF_6]^-$ [equation (2)].[14] A preliminary account of the

$$[I_3]^+[AsF_6]^- + ICN \longrightarrow [ICNI]^+[AsF_6]^- + I_2 \qquad (2)$$

experimental work related to equation (2) has been published.[14] In this contribution a new synthesis (method 2, see below) for $[ICNI]^+[AsF_6]^-$, the reaction behaviour of $[ICNI]^+[AsF_6]^-$ towards CsN_3 as well as theoretical *ab initio* studies concerning the structure of the $[ICNI]^+$ cation are reported. In the preliminary communication the question of whether the $[ICNI]^+$ cation adopts a planar C_s or a linear $C_{\infty v}$ structure could not be answered without ambiguity, although on the basis of the obtained vibrational data in comparison with those of linear I–C≡C–I[15] a $C_{\infty v}$-type structure was proposed. The ν_1 and ν_3 bands in the IR spectrum of the $[ICNI]^+$ cation (KBr disc) had also been assigned incorrectly due to partial decomposition into $ICN{\cdot}AsF_5$.[13] The original Raman spectrum was recorded at low temperature on a sample sealed in a glass capillary and therefore no decomposition was observed.[14] In the present study a Nujol mull between CsI plates was used, see Experimental section.

Experimental

Materials

Iodine cyanide, $[I_3]^+[AsF_6]^-$, AsF_5 and CsN_3 were prepared according to literature procedures;[14a,16] ICN was always freshly sublimed prior to use. The solvents SO_2 (BOC), SO_2ClF (Aldrich) and $CFCl_3$ (Merck) were dried over CaH_2 (Aldrich; SO_2, SO_2ClF) or P_4O_{10} (Aldrich), respectively, and distilled prior to use.

Spectroscopy

Infrared spectra were recorded at 20 °C as Nujol mulls (dried over Na) between CsI plates on a Philips PU9800 FTIR spectrometer, the Raman spectrum at −90 °C on a Jobin Yvon Ramanor U 1000 instrument equipped with a Spectra Physics krypton-ion laser (647.09 nm, 20 mW) and ^{19}F NMR spectra in SO_2 solution at 20 °C using either a Bruker SXP 4-100 spectrometer operating at 84.7 MHz or a Bruker SY 200 spectrometer operating at 188.3 MHz.

Preparation of $[ICNI]^+[AsF_6]^-$

Method 1 [original method, see ref. 14(*b*)]. The salt $[I_3]^+[AsF_6]^-$ (1.595 g, 2.80 mmol) was suspended in $CFCl_3$ (7 cm^3) and treated with ICN (0.428 g, 2.80 mmol) dissolved in SO_2 (10 cm^3) at 10 °C and the slurry stirred for 30 min. The reaction mixture was evaporated to dryness and the remaining solid then extracted with $CFCl_3$ (20 times with 10 cm^3 $CFCl_3$ for

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† *Non-SI units employed:* Å = 10^{-10} m, au ≈ 4.36×10^{-18} J ≈ 6.275×10^2 kcal mol^{-1}.

‡ b.d.e. = Bond dissociation enthalpy, *e.g.* the enthalpy (H) for one of the following reactions (with $H = U + pV$, U = internal energy:[11] $IN_3\,(g) \longrightarrow I\,(g) + N_2\,(g)$; $NI_3\,(g) \longrightarrow NI_2\,(g) + I\,(g)$. b.e. = Bond enthalpy term, *e.g.* the enthalpy (H) for the reaction $NI_3\,(g) \longrightarrow N\,(g) + 3I\,(g)$.

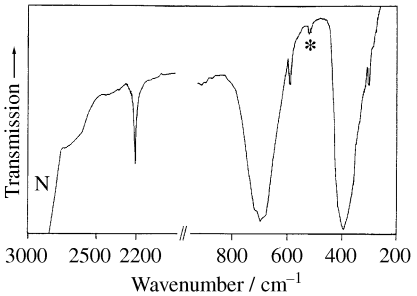

Fig. 1 Infrared spectrum of $[ICNI]^+[AsF_6]^-$ as a Nujol mull between CsI plates. N = Nujol, * = impurity

Table 1 Infrared and Raman data (cm^{-1}) for the $[ICNI]^+$ cation and ICCI[15]

$[ICNI]^+$		ICCI		
Raman[a]	IR[b]	Raman[a]	IR[c]	Assignment
	2200s	2096vs		ν_1
	590m		720vs	ν_2
317 (1, br)	292m[d]	304vs[d]		ν_4
179 (3)		190vs		ν_3
148 (1)		145m[d]	132m[d]	ν_5

[a] Solid. [b] Nujol mull. [c] Solution. [d] The assignment of this band is still questionable since the IR and the Raman wavenumbers do not agree very well.

each step) to remove the iodine, leaving a nearly white solid, $[ICNI]^+[AsF_6]^-$ (1.28 g, 97.5%) (Found: C, 2.4; N, 2.95. Calc. C, 2.55; N, 3.0%). ^{19}F NMR (84.7 MHz, relative to $CFCl_3$): δ −55.1. IR (CsI, Nujol mull): 2200s [$\nu_1(ICNI^+)$],† 590m [$\nu_2(ICNI^+)$], 698vs [$\nu_3(AsF_6^-)$], 400vs [$\nu_4(AsF_6^-)$] and 292m cm^{-1} [$\nu_3(ICNI^+)$]. Raman (−90 °C, range 800–100 cm^{-1}): 685m [$\nu_1(AsF_6^-)$], 317w (br) [$\nu_3(ICNI^+)$?], 179m [$\nu_4(ICNI^+)$] and 148w cm^{-1} [$\nu_5(ICNI^+)$].

Method 2. A mixture of ICN (0.61 g, 4.0 mmol) and I_2 (0.51 g, 2.0 mmol) in SO_2 (10 cm^3) was treated with AsF_5 (6.0 mmol) and allowed to react for 15 min at 0 °C. The mixture was then evaporated to dryness, the by-product AsF_3 was pumped off and the remaining solid extracted with $CFCl_3$ (five times with 10 cm^3 $CFCl_3$ for each step) to remove traces of iodine, leaving a nearly white solid $[ICNI]^+[AsF_6]^-$ (1.44 g, 77%). ^{19}F NMR (188.3 MHz): δ −56.5 (q, $^1J_{AsF} = 945$ Hz). IR (CsI, Nujol mull): 2200s [$\nu_1(ICNI^+)$],† 590m [$\nu_2(ICNI^+)$], 705vs [$\nu_3(AsF_6^-)$], 395vs [$\nu_4(AsF_6^-)$] and 292m [$\nu_3(ICNI^+)$].

Despite several attempts it has so far been impossible to grow crystals suitable for X-ray diffraction because of the insolubility of $[ICNI]^+[AsF_6]^-$ in $CFCl_3$ and decomposition in SO_2 within a few hours.

Reaction of $[ICNI]^+[AsF_6]^-$ with CsN_3

Freshly prepared $[ICNI]^+[AsF_6]^-$ (0.45 g, 0.96 mmol) was suspended in SO_2ClF (10 cm^3) and treated with CsN_3 (0.18 g, 1.0 mmol) suspended in SO_2ClF (5 cm^3) and the slurry stirred for 30 min. The reaction was filtered and the insoluble product identified by its IR spectrum as $Cs^+[AsF_6]^-$ (0.286 g, 89%). IR (CsI: 698vs [$\nu_3(AsF_6^-)$] and 400vs cm^{-1} [$\nu_4(AsF_6^-)$]. After carefully evaporating the remaining solution to dryness, ICN and IN_3 were identified as volatile products by gas-phase IR spectroscopy. IR [10 cm, 1 Torr (*ca.* 133 Pa, NaCl)]: 2185s [ν(CN, ICN)] and 2055vs cm^{-1} [$\nu_{asym}(NNN, IN_3)$].

Computational methods

The structure and vibrational spectrum of the $[ICNI]^+$ cation were calculated semiempirically (Austin Model 1, AM1;[17] reparameterisation of AM1, PM3)[18] and *ab initio* at the Hartree–Fock (HF) and electron-correlated RMP2 and RMP4(SDQ) levels of theory with the program packages HYPERCHEM[19] and GAUSSIAN 94,[20] respectively. For C and N a 6-31G(d) basis set was used and for I a quasi-relativistic pseudo-potential (LANL2DZ)[21] where the basis functions for the valence s and p electrons consist of the standard double-ζ basis set (notation HF/LANL2DZ or RMP2/LANAL2DZ). Calculating the *ab initio* frequencies in all cases, the second derivatives of the energy were computed numerically using analytically calculated first derivatives. An NBO analysis was carried out to account for non-Lewis contributions to the most appropriate valence structure. In the quantum-mechanical computation (NBO analysis, subjecting the HF density matrix as represented in the localized NBOs to a second-order perturbative analysis) the energy was computed according to equation (3) where h^F is the Fock operator.[22]

$$E^{(2)}_{\varphi\varphi^*} = -2\langle\varphi|h^F|\varphi^*\rangle^2/(E_{\varphi^*} - E_\varphi) \qquad (3)$$

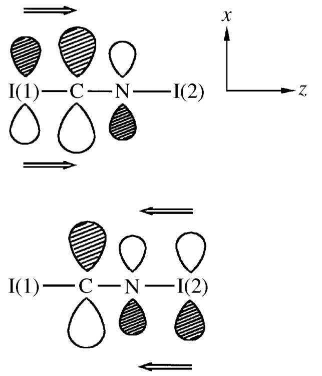

Fig. 2 Hyperconjugation in the $[ICNI]^+$ cation (bond axis = z axis): top, p_x–l.p.[I(1)] $\longrightarrow \pi^*_x$(C–N), 101.2 kJ mol^{-1}, analogue for p_y–l.p.[I(1)] $\longrightarrow \pi^*_y$(C–N); bottom, p_x–l.p.[I(2)] $\longrightarrow \pi^*_x$(C–N), 82.2 kJ mol^{-1}, analogue for p_y–l.p.[I(2)] $\longrightarrow \pi^*_y$ (C–N)

Results

The new ternary $[ICNI]^+$ cation ($[AsF_6]^-$ salt) containing a direct N–I bond was prepared according to equation (2). The same compound was also prepared from the direct reaction of ICN with I_2–AsF_5 according to equation (4). The elemental analysis (C, N) corresponds to the compound formulated ($[ICNI]^+[AsF_6]^-$) and the IR as well as the ^{19}F NMR spectra clearly show the presence of octahedral $[AsF_6]^-$ ions (Fig. 1). The cation parts of the vibrational spectra (IR, Raman) were originally assigned by comparing the observed frequencies with those obtained for the isoelectronic species ICCI (Table 1). However, the question as to whether the $[ICNI]^+$ cation really adopts a linear $C_{\infty v}$ or a bent C_s structure could not be answered conclusively.

$$ICN + 0.5\,I_2 + 1.5\,AsF_5 \xrightarrow{SO_2,\ 0\,^\circ C} [ICNI]^+[AsF_6]^- + 0.5\,AsF_3 \qquad (4)$$

The structure and vibrational frequencies of the $[ICNI]^+$ cation were calculated by semiempirical and *ab initio* methods (Tables 2 and 3). The structure was computed at the semiempirical and at the restricted (R)HF and RMP2 levels in C_s symmetry and in all cases fully optimized to $C_{\infty v}$ symmetry (no imaginary frequencies, see Table 3). Electron-correlation effects were included using Møller–Plesset (MP) perturbation theory to the second (RMP2) and fourth order [RMP4(SDQ)] and the structure of the $[ICNI]^+$ cation was fully optimized within C_s (RMP2) and $C_{\infty v}$ [RMP4(SDQ)] symmetry to give the linear $C_{\infty v}$

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† An additional band sometimes occurring at 2240–2250 cm^{-1} is due to partial decomposition into $ICN{\cdot}AsF_5$.[13]

Table 2 Fully optimized structural parameters for the cation $[ICNI]^+$ (within the constraints of the selected symmetry, see second column)

Level of theory	Symmetry	*E*/au	*d*[I(1)–C]/Å	*d*(C–N)/Å	*d*[N–I(2)]/Å
AM1	C_s[a]	*b*	1.939	1.163	1.916
PM3	C_s[a]	*b*	1.896	1.165	1.892
RHF[c]	C_s[a]	−114.291 42	2.023	1.132	2.030
RMP2[c]	$C_{\infty v}$	−114.628 69	1.986	1.176	0.020
RMP4(SDQ1)[c]	$C_{\infty v}$	−114.656 51	2.001	1.167	0.021

[a] In all cases where the computation was carried out in C_s symmetry the structure was optimized to $C_{\infty v}$ symmetry. [b] See Table 5. [c] 6-31G(d) basis set for C and N, LANL2DZ electron core potentials for I.

Table 3 Calculated (unscaled) and observed vibrational wavenumbers (cm^{-1}) for the cation $[ICNI]^+$. Calculated IR intensities in parentheses in km mol^{-1}

Mode	Symmetry, degeneracy	AM1	PM3	RHF[a]	RMP2[a]	RMP (SDQ)[a]	Exptl.	Assignment
ν_1	σ, 1	2494	2438	2585 (285)	2205 (119)	2285 (167)	2200s (IR)	ν(C≡N)
ν_2	σ, 1	760	1032	615 (48)	624 (14)	615 (2)	590m (IR)	$\nu_{\mathbf{asym}}$(IC, NI)
ν_4	π, 2	430	361	427 (11)	291 (4)	317 (6)	292m (IR)	$\delta_{\mathbf{ip,asym}}$(ICNI)[c]
ν_3	σ, 1	223	287	181 (3)	179 (3)	178 (3)	179s (Raman)	$\nu_{\mathbf{sym}}$(IC, NI)
ν_5	π, 2	134	112	110 (0.5)	103 (1)	105 (1)	148w (Raman)	$\delta_{\mathbf{ip,sym}}$(ICNI)[c]
z.p.e.[b]		27.5	28.1	26.6	22.7	23.5	23.0	

[a] 6-31G(d) basis set for C and N, LANL2DZ electron core potentials for I. [b] In kJ mol^{-1}. [c] In plane.

Table 4 Computed structural parameters for the cations $[HCNH]^+$ and $[ICNI]^+$ (for comparison) and for HCN, HCCH, NH_3 and NI_3[a]

	Symmetry	*d*(A–B)/Å	*d*(B–C)/Å	*d*(C–D)/Å	B–A–B/°
A–B–C–(D)					
$[HCNH]^+$	$C_{\infty v}$	1.078	1.154	1.016	
$[ICNI]^+$	$C_{\infty v}$	1.986	1.176	2.020	
HCCH	$D_{\infty h}$	1.063	1.219	1.063	
HCN	$C_{\infty v}$	1.065	1.178		
AB_3					
NH_3	C_{3v}	1.013			106.1
NI_3	C_{3v}	2.191			109.2

[a] RMP2/6-31G** for $[HCNH]^+$, HCCH, HCN and NH_3, LANL2DZ for $[ICNI]^+$ and NI_3.

$[ICNI]^+$ cation.[23] No minimum at the RMP2 level was found for a bent structure which, of course, does still not preclude that a bent minimum may be found at the fourth-order Møller–Plesset level. Frequency calculations at all levels gave zero-point vibrational energies (z.p.e.s) and a number of imaginary frequencies (Table 3). Whereas the semiempirical calculations had predicted the structure of the $[ICNI]^+$ cation qualitatively correctly ($C_{\infty v}$), not unexpectedly these methods seem to be unreliable for predicting vibrational frequencies.[24a] Only the electron-correlated RMP2 and RMP4 methods gave vibrational data which nicely agree with the experimental values. Moreover, the excellent agreement between the experimentally obtained ν(C≡N) stretching mode for ICN and the *ab initio* computed value at the RMP2 level gives credence to the calculated frequencies for the $[ICNI]^+$ cation: exptl.; 2188 (ν_1, σ), 485 (ν_2, σ) and 304 (ν_3, π); HF/LANL2DZ, 2567 (ν_1, σ), 505 (ν_2, σ) and 371 (ν_3, π); RMP2/LANL2DZ, 2141 (ν_1, σ), 314 (ν_2, σ) and 283 cm^{-1} (ν_3, π).

The question as to why the $[ICNI]^+$ cation prefers to adopt $C_{\infty v}$ over C_s symmetry can be rationalized in the NBO picture by two strong non-covalent contributions (donor–acceptor interaction, negative hyperconjugation): first, the donation of electron density from the p_x and the p_y lone pairs of atom I(1) into the unfilled and antibonding π_x^*(C–N) or π_y^*(C–N) orbitals, respectively (Fig. 2, top); secondly, the weaker but still pronounced donation of electron density from the p_x and the p_y lone pairs of atom I(2) also into the unfilled and antibonding π_x^*(C–N) or π_y^*(C–N) orbitals, respectively (Fig. 2, bottom). Consequently, the two iodine atoms carry most of the positive charge of the cation [RMP4(SDQ), Mulliken charges: I(1), +0.73; C, +0.17; N, −0.68; I(2), +0.78]. The linear isoelectronic ICCI molecule also shows this type of hyperconjugation. These interactions clearly strengthen the I–C and I–N bonds and weaken the CN triple bond (Fig. 2) and therefore account for a partial π-electron delocalization over the entire molecule.

To compare and contrast the bond situation in the $[ICNI]^+$ cation the species $[HCNH]^+$, HCN, HCCH and NH_3 were also calculated at the RMP2/6-31G** level and the NI_3 molecule at the RMP2/LANL2DZ level. The results are summarized in Table 4. As expected, due to strong hyperconjugation (see above) the N–I bond length in the $[ICNI]^+$ cation was calculated to be shorter (2.020 Å) than the N–I single bond in NI_3 (2.191 Å). As a consequence of the hyperconjugation in the $[ICNI]^+$ cation which is not present in the $[HCNH]^+$ cation we may deduce that the CN bond in the $[ICNI]^+$ cation should be longer than the triple bond in the $[HCNH]^+$ cation (*i.e.* 1.176 *vs.* 1.154 Å; *cf.* ref. 24*b*,*c*). Whereas the N–I bond in the $[ICNI]^+$ cation is substantially shorter than in NI_3 (see above), the N–H bond in the $[HCNH]^+$ cation (1.016 Å) has nearly the same value as the N–H single bond in ammonia (1.013 Å).

Of particular interest is also the strength of the N–I bond (*i.e.* $[ICN–I]^+$). The calculated total energies of ICN, I^+ and $[ICNI]^+$ can be used to predict theoretically the binding energy. The dissociation energy of reaction (5) was calculated (Table 5), which, after correction for the zero-point energies (Table 3), differences in rotational ($\frac{1}{2}RT$) and translational ($\frac{3}{2}RT$) degrees of freedom, and the work term (*RT*), was converted into the bond dissociation enthalpy b.d.e. at room temperature (Table 5). Table 5 shows that reaction (5) is strongly endothermic for

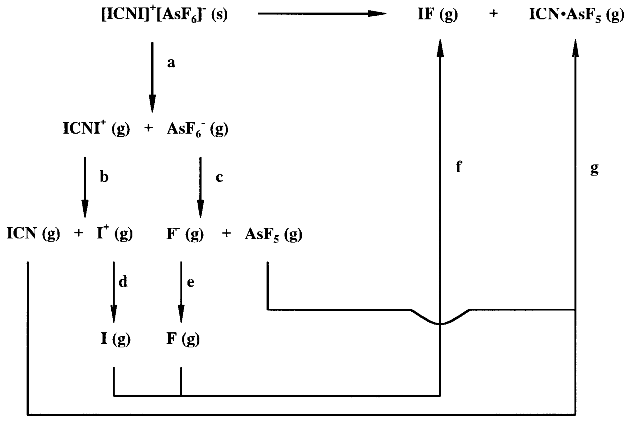
$$[ICNI]^+ (g) \longrightarrow ICN (g) + I^+(^3P) (g) + \text{b.d.e.} \qquad (5)$$

all levels of theory applied. The calculated reaction enthalpy for it reveals an N–I bond in the cation $[ICNI]^+$ which is slightly stronger than that in IN_3 [*cf.* b.d.e.(N–I, IN_3) = 191.4 kJ

Table 5 Calculated total energies of ICN, I$^+$ and [ICNI]$^+$ and reaction enthalpy D_0 for reaction (6)

Theory	E(ICN)^{a,b}	E(I$^+$)^a	E([ICNI]$^+$)^a	b.d.e.(6)/kJ mol^{-1}
AM1	−1116	+1012 (^{3}P)^c	−316	212.9
PM3	−1028	+888 (^{3}P)^c	−357	219.8
HF^{d,e}	−103.436 77	−10.801 00 (^{3}P)^c	−114.291 42	144.3
RMP2^{d,f}	−103.745 22	−10.805 46 (^{3}P)^c	−114.628 69	207.4

[a] Total energies for AM1 and PM3 in kJ mol^{-1}, for RHF and RMP2 in au. [b] Zero-point energies for ICN in kJ mol^{-1}: AM1, 20.69; PM3, 22.79; RHF, 22.79; RMP2, 18.06; exptl. 19.6. [c] $E^{\mathbf{AM1}}$(I$^+$, ^{1}D) = 1072 kJ mol^{-1}, $E^{\mathbf{PM3}}$(I$^+$, ^{1}D) = 952 kJ mol^{-1}, $E^{\mathbf{UFH}}$(I$^+$, ^{1}D) = −10.722 92 au, $E^{\mathbf{RMP2}}$(I$^+$, ^{1}D) = −10.736 45 au. [d] 6-31G(d) basis set for C and N, LANL2DZ electron core potentials for I. [e] RHF method for ICN and [ICNI]$^+$, unrestricted (U)HF method for I$^+$. [f] RMP2 method for ICN and [ICNI]$^+$, PMP2 method for I$^+$(^{3}P), UMP2 method for I$^+$(^{1}D).



Scheme 1 Energy cycle to estimate the reaction enthalpy according to equation (6): a, U_L([ICNI]$^+$[N$_3$]$^-$) estimated as ≈557.6 kJ mol^{-1} using the linear relationship $U_L = 556.3V_M{}^{-0.33} + 26.3$,[26] with V_M taken to be equal to 7 × 20 = 140 Å^3 (U_L in kcal mol^{-1}, V_M in Å^3);[27] b, b.d.e.([ICN–I]$^+$) = 207 kJ mol^{-1} [see text, equation (5)]; c, f.i.a.(AsF$_5$) = 464 kJ mol^{-1};[11b,28] d, E_i(I) = 1012 kJ mol^{-1};[25] e, E_{ea}(F) = 333 kJ mol^{-1};[11] f, b.d.e.(IF) = 276 kJ mol^{-1};[11] g, b.e.(ICN·AsF$_5$) = 45 kJ mol^{-1}[29] (f.i.a. = fluoride ion affinity)

mol^{-1}].[9a,10b] This new calculated b.d.e.(N–I, [ICN–I]$^+$) value of 207.4 kJ mol^{-1} shows that the N–I bond strength in the cation [ICNI]$^+$ is nicely in agreement with an earlier estimate predicted on the basis of hard–soft acid–base (HSAB) theory considerations (200.8 kJ mol^{-1}).[†,25a] This excellent agreement between experimentally based estimation (HSAB)[25b,c] and *ab initio* theory gives credence to those estimated b.d.e. values for which there are not yet high-level theoretical data due to the size of the system, *e.g.* for (HCN)$_3$(AsF$_5$)$_3$.[25d] Moreover, in agreement with earlier studies the N–I bond in the cation [ICNI]$^+$ seems to be strong enough to prevent the decomposition of [ICNI]$^+$[AsF$_6$]$^-$ into IF and the adduct ICN·AsF$_5$. Using a cycle shown in Scheme 1 the reaction enthalpy was estimated according to equation (6) as $\Delta H(6) = +229.9$ kJ mol^{-1}. Although

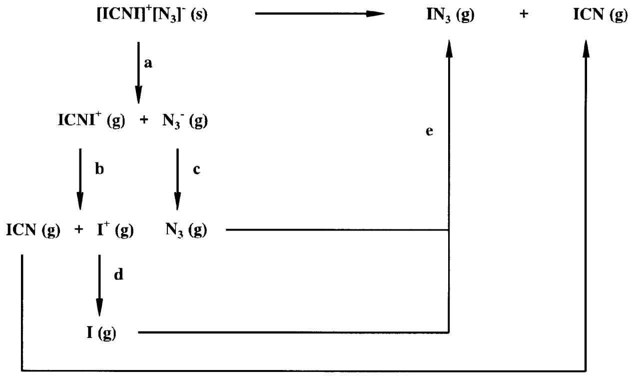
$$[\text{ICNI}]^+[\text{AsF}_6]^- \text{ (s)} \longrightarrow \text{IF (g)} + \text{ICN·AsF}_5 \text{ (g)} \qquad (6)$$

confidence limits of the $\Delta H(6)$ value are difficult to ascribe it nevertheless reflects the stability of [ICNI]$^+$[AsF$_6$]$^-$ with respect to IF and the adduct ICN·AsF$_5$[13] [equation (6)].

The metathetical reaction of [ICNI]$^+$[AsF$_6$]$^-$ with CsN$_3$ in SO$_2$ClF afforded Cs$^+$[AsF$_6$]$^-$, IN$_3$ and ICN (see Experimental section). Using a cycle shown in Scheme 2 the reaction enthalpy was estimated according to equation (8) as $\Delta H(8) = -140.4$ kJ mol^{-1}. Although the confidence limits are again difficult to ascribe this value nevertheless nicely explains the instability of [ICNI]$^+$[N$_3$]$^-$ formed as a likely intermediate in the initial metathesis reaction of [ICNI]$^+$[AsF$_6$]$^-$ with CsN$_3$ [equation (7)].

$$[\text{ICNI}]^+[\text{AsF}_6]^- + \text{CsN}_3 \longrightarrow \{[\text{ICNI}]^+[\text{N}_3]^- + \text{Cs}^+[\text{AsF}_6]^-\} \qquad (7)$$

$$[\text{ICNI}]^+[\text{N}_3]^- \text{ (s)} \longrightarrow \text{ICN (g)} + \text{IN}_3 \text{ (g)} \qquad (8)$$



Scheme 2 Energy cycle to estimate the reaction enthalpy according to equation (8). a, U_L([ICNI]$^+$[N$_3$]$^-$) ≈ 557.6 kJ mol^{-1} (see Scheme 1); b, b.d.e.([ICN–I]$^+$) = 207 kJ mol^{-1} [see text, equation (5)]; c, E_{ea}(N$_3$) = 293 kJ mol^{-1};[30] d, E_i(I) = 1012 kJ mol^{-1};[25] e, b.d.e.(N$_3$–I) = 191 kJ mol^{-1}[10b]

Conclusion

From the studies presented in this paper the following conclusions can be drawn. (*i*) (Iodocyano)iodine hexafluoroarsenate, [ICNI]$^+$[AsF$_6$]$^-$, containing the 22-valence-electron [ICNI]$^+$ cation can be synthesized either by the reaction of iodine cyanide with [I$_3$]$^+$[AsF$_6$]$^-$ or directly from ICN, I$_2$ and AsF$_5$. (*ii*) From the results of electron-correlated *ab initio* structure optimizations as well as from the very good agreement between computed and observed vibrational frequencies it can be stated beyond reasonable doubt that the [ICNI]$^+$ cation adopts a linear $C_{\infty v}$ structure and represents the first example of a compound with a direct N–I bond where the nitrogen is formally sp hybridized. (*iii*) The RMP2-computed b.d.e.(N–I, [ICN–I]$^+$) value of 207.4 kJ mol^{-1} shows that the N–I bond strength in the cation [ICNI]$^+$ is comparable to, but slightly stronger than, that in IN$_3$ and is in very good agreement with an earlier estimate predicted on the basis of HSAB considerations (200.8 kJ mol^{-1}). (*iv*) The metathetical reaction of [ICNI]$^+$[AsF$_6$]$^-$ with CsN$_3$ in SO$_2$ClF afforded Cs$^+$[AsF$_6$]$^-$, IN$_3$ and ICN. The instability of the likely intermediate [ICNI]$^+$[N$_3$]$^-$ can be rationalized using a simple Born–Haber energy cycle.

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[†] The originally reported bond energy b.e.*([ICN–I]$^-$) of 196.5 kJ mol^{-1} was converted after correction for zero-point energies (ICN, 4.70; [ICN–I]$^-$, 22.7 kJ mol^{-1}), differences in rotational and translational degrees of freedom, and the work term into the bond dissociation enthalpy at room temperature b.d.e.([ICN–I]$^+$) = 200.8 kJ mol^{-1}.

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