

The [ICNI]⁺ cation: a combined experimental and theoretical study. Reaction of [ICNI]⁺[AsF₆]⁻ with CsN₃ †

Thomas M. Klapötke*

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

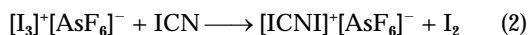
(Iodocyno)iodine hexafluoroarsenate, [ICNI]⁺[AsF₆]⁻, containing the linear 22-valence-electron [ICNI]⁺ cation was synthesized either by the reaction of iodine cyanide with [I₃]⁺[AsF₆]⁻ or directly from ICN, I₂ and AsF₅ and characterized by chemical analysis, IR, Raman and ¹⁹F NMR data. A combined vibrational (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_{∞v} symmetry, RMP4(SDQ), *d*(I–C) = 2.001, *d*(C≡N) = 1.167, *d*(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]⁺[AsF₆]⁻ with CsN₃ in SO₂ClF afforded IN₃, Cs⁺[AsF₆]⁻ and ICN.

Various neutral compounds and cations containing a direct nitrogen–iodine bond have recently been studied, *i.e.* NI₃¹ (*cf.* also [NI₃][NH₃]_{*n*}, *n* = 1, 3 or 5),² IN₃³ (*cf.* also azidoiodine derivatives),⁴ (IN₃)_∞,⁵ [I₂N₃]⁺⁶ and [I(N₃)₂]⁺⁷ {*cf.* also [I(N₃)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 NI₃ and [NI₃][NH₃] and the N–I bond energy in these (formally sp³ hybridized) compounds were determined on the basis of solution calorimetric procedures: Δ*H*_f^o[NI₃][NH₃](s) = 146 ± 6 kJ mol⁻¹, Δ*H*_f^o[NI₃](g) = 287 ± 23 kJ mol⁻¹ and b.e.(N–I, NI₃) ‡ = 169 ± 8 kJ mol⁻¹.¹² For iodine azide, IN₃, with the nitrogen next to the iodine according to a natural bond order (NBO) analysis formally also being sp³ 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: Δ*H*_f^o[IN₃](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]⁺[AsF₆]⁻ (X = Cl or Br) due to the thermodynamically favourable adduct formation XCN·AsF₅ and elimination of ClF or BrF, respectively [equation (1)],¹³



ICN does react with I⁺ donors to form compounds of the type [ICNI]⁺[AsF₆]⁻ [equation (2)].¹⁴ A preliminary account of the



experimental work related to equation (2) has been published.¹⁴ In this contribution a new synthesis (method 2, see below) for [ICNI]⁺[AsF₆]⁻, the reaction behaviour of [ICNI]⁺[AsF₆]⁻

towards CsN₃ 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_{∞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–I¹⁵ a C_{∞v}-type structure was proposed. The ν₁ and ν₃ bands in the IR spectrum of the [ICNI]⁺ cation (KBr disc) had also been assigned incorrectly due to partial decomposition into ICN·AsF₅.¹³ 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, [I₃]⁺[AsF₆]⁻, AsF₅ and CsN₃ were prepared according to literature procedures;^{14a,16} ICN was always freshly sublimed prior to use. The solvents SO₂ (BOC), SO₂ClF (Aldrich) and CFCl₃ (Merck) were dried over CaH₂ (Aldrich; SO₂, SO₂ClF) or P₄O₁₀ (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 ¹⁹F NMR spectra in SO₂ 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]⁺[AsF₆]⁻

Method 1 [original method, see ref. 14(b)]. The salt [I₃]⁺[AsF₆]⁻ (1.595 g, 2.80 mmol) was suspended in CFCl₃ (7 cm³) and treated with ICN (0.428 g, 2.80 mmol) dissolved in SO₂ (10 cm³) at 10 °C and the slurry stirred for 30 min. The reaction mixture was evaporated to dryness and the remaining solid then extracted with CFCl₃ (20 times with 10 cm³ CFCl₃ for

* E-mail: tmk@chem.gla.ac.uk.

† *Non-SI units employed*: Å = 10⁻¹⁰ m, au ≈ 4.36 × 10⁻¹⁸ J ≈ 6.275 × 10² 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 IN₃(g) → I(g) + N₂(g); NI₃(g) → NI₂(g) + I(g). b.e. = Bond enthalpy term, *e.g.* the enthalpy (*H*) for the reaction NI₃(g) → N(g) + 3I(g).

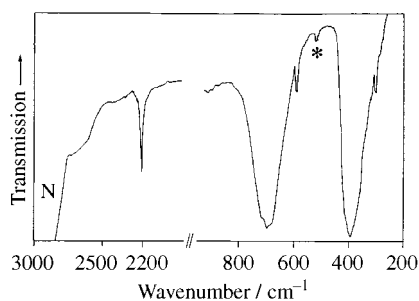


Fig. 1 Infrared spectrum of [ICNI]⁺[AsF₆]⁻ as a Nujol mull between CsI plates. N = Nujol, * = impurity

Table 1 Infrared and Raman data (cm⁻¹) for the [ICNI]⁺ cation and ICCI¹⁵

[ICNI] ⁺		ICCI		Assignment
Raman ^a	IR ^b	Raman ^a	IR ^c	
	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]⁺[AsF₆]⁻ (1.28 g, 97.5%) (Found: C, 2.4; N, 2.95. Calc. C, 2.55; N, 3.0%). ¹⁹F NMR (84.7 MHz, relative to CFCl₃): δ -55.1. IR (CsI, Nujol mull): 2200s [ν_1 (ICNI⁺)], † 590m [ν_2 (ICNI⁺)], 698vs [ν_3 (AsF₆⁻)], 400vs [ν_4 (AsF₆⁻)] and 292m cm⁻¹ [ν_3 (ICNI⁺)]. Raman (-90 °C, range 800–100 cm⁻¹): 685m [ν_1 (AsF₆⁻)], 317w (br) [ν_3 (ICNI⁺)?], 179m [ν_4 (ICNI⁺)] and 148w cm⁻¹ [ν_5 (ICNI⁺)].

Method 2. A mixture of ICN (0.61 g, 4.0 mmol) and I₂ (0.51 g, 2.0 mmol) in SO₂ (10 cm³) was treated with AsF₅ (6.0 mmol) and allowed to react for 15 min at 0 °C. The mixture was then evaporated to dryness, the by-product AsF₃ was pumped off and the remaining solid extracted with CFCl₃ (five times with 10 cm³ CFCl₃ for each step) to remove traces of iodine, leaving a nearly white solid [ICNI]⁺[AsF₆]⁻ (1.44 g, 77%). ¹⁹F NMR (188.3 MHz): δ -56.5 (q, ¹J_{AsF} = 945 Hz). IR (CsI, Nujol mull): 2200s [ν_1 (ICNI⁺)], † 590m [ν_2 (ICNI⁺)], 705vs [ν_3 (AsF₆⁻)], 395vs [ν_4 (AsF₆⁻)] and 292m [ν_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]⁺[AsF₆]⁻ in CFCl₃ and decomposition in SO₂ within a few hours.

Reaction of [ICNI]⁺[AsF₆]⁻ with CsN₃

Freshly prepared [ICNI]⁺[AsF₆]⁻ (0.45 g, 0.96 mmol) was suspended in SO₂ClF (10 cm³) and treated with CsN₃ (0.18 g, 1.0 mmol) suspended in SO₂ClF (5 cm³) and the slurry stirred for 30 min. The reaction was filtered and the insoluble product identified by its IR spectrum as Cs⁺[AsF₆]⁻ (0.286 g, 89%). IR (CsI: 698vs [ν_3 (AsF₆⁻)] and 400vs cm⁻¹ [ν_4 (AsF₆⁻)]. After carefully evaporating the remaining solution to dryness, ICN and IN₃ 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 [ν_{asym} (NNN, IN₃)].

Computational methods

The structure and vibrational spectrum of the [ICNI]⁺ cation

† An additional band sometimes occurring at 2240–2250 cm⁻¹ is due to partial decomposition into ICN·AsF₅.¹³

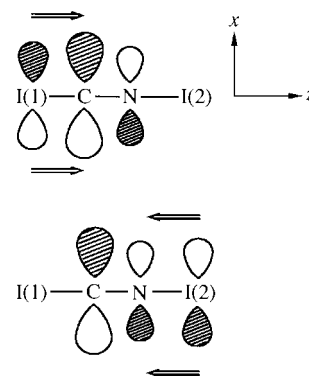


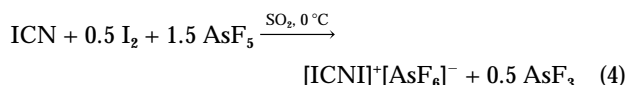
Fig. 2 Hyperconjugation in the [ICNI]⁺ cation (bond axis = z axis): top, p_x-l.p.[I(1)] → π*_x(C-N), 101.2 kJ mol⁻¹, analogue for p_y-l.p.[I(1)] → π*_y(C-N); bottom, p_x-l.p.[I(2)] → π*_x(C-N), 82.2 kJ mol⁻¹, analogue for p_y-l.p.[I(2)] → π*_y(C-N)

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 HYPERCHEM¹⁹ 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 \hat{H}^F is the Fock operator.²²

$$E_{\phi\phi^*}^{(2)} = -2\langle\phi|\hat{H}^F|\phi^*\rangle^2/(E_{\phi^*} - E_{\phi}) \quad (3)$$

Results

The new ternary [ICNI]⁺ cation ([AsF₆]⁻ 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 I₂-AsF₅ according to equation (4). The elemental



analysis (C, N) corresponds to the compound formulated ([ICNI]⁺[AsF₆]⁻) and the IR as well as the ¹⁹F NMR spectra clearly show the presence of octahedral [AsF₆]⁻ 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_{∞v} or a bent C_s structure could not be answered conclusively.

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_{∞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_{∞v} [RMP4(SDQ)] symmetry to give the linear C_{∞v}

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

Level of theory	Symmetry	<i>E</i> /au	<i>d</i> [I(1)–C]/Å	<i>d</i> (C–N)/Å	<i>d</i> [N–I(2)]/Å
AM1	<i>C_s</i> ^a	<i>b</i>	1.939	1.163	1.916
PM3	<i>C_s</i> ^a	<i>b</i>	1.896	1.165	1.892
RHF ^c	<i>C_s</i> ^a	–114.291 42	2.023	1.132	2.030
RMP2 ^c	<i>C_{∞v}</i>	–114.628 69	1.986	1.176	0.020
RMP4(SDQ) ^c	<i>C_{∞v}</i>	–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_{∞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
<i>v</i> ₁	σ, 1	2494	2438	2585 (285)	2205 (119)	2285 (167)	2200s (IR)	ν(C≡N)
<i>v</i> ₂	σ, 1	760	1032	615 (48)	624 (14)	615 (2)	590m (IR)	ν _{asym} (IC, NI) ^c
<i>v</i> ₄	π, 2	430	361	427 (11)	291 (4)	317 (6)	292m (IR)	δ _{ip,asym} (ICNI) ^c
<i>v</i> ₃	σ, 1	223	287	181 (3)	179 (3)	178 (3)	179s (Raman)	ν _{sym} (IC, NI)
<i>v</i> ₅	π, 2	134	112	110 (0.5)	103 (1)	105 (1)	148w (Raman)	δ _{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, NH₃ and NI₃^a

	Symmetry	<i>d</i> (A–B)/Å	<i>d</i> (B–C)/Å	<i>d</i> (C–D)/Å	B–A–B/ ^o
A–B–C–(D)					
[HCNH] ⁺	<i>C_{∞v}</i>	1.078	1.154	1.016	
[ICNI] ⁺	<i>C_{∞v}</i>	1.986	1.176	2.020	
HCCH	<i>D_{∞h}</i>	1.063	1.219	1.063	
HCN	<i>C_{∞v}</i>	1.065	1.178		
AB ₃					
NH ₃	<i>C_{3v}</i>	1.013			106.1
NI ₃	<i>C_{3v}</i>	2.191			109.2

^a RMP2/6-31G** for [HCNH]⁺, HCCH, HCN and NH₃, LANL2DZ for [ICNI]⁺ and NI₃.

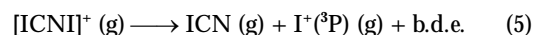
[ICNI]⁺ cation.²³ No minimum at the RMP2 level was found for a bent structure which, of course, does still not preclude that a bent minimum may be found at the fourth-order Møller–Plesset level. Frequency calculations at all levels gave zero-point vibrational energies (z.p.e.s) and a number of imaginary frequencies (Table 3). Whereas the semiempirical calculations had predicted the structure of the [ICNI]⁺ cation qualitatively correctly (*C_{∞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 (*v*₁, σ), 485 (*v*₂, σ) and 304 (*v*₃, π); HF/LANL2DZ, 2567 (*v*₁, σ), 505 (*v*₂, σ) and 371 (*v*₃, π); RMP2/LANL2DZ, 2141 (*v*₁, σ), 314 (*v*₂, σ) and 283 cm^{–1} (*v*₃, π).

The question as to why the [ICNI]⁺ cation prefers to adopt *C_{∞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 NH₃ were also calculated at the RMP2/6-31G** level and the NI₃ 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 NI₃ (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 NI₃ (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

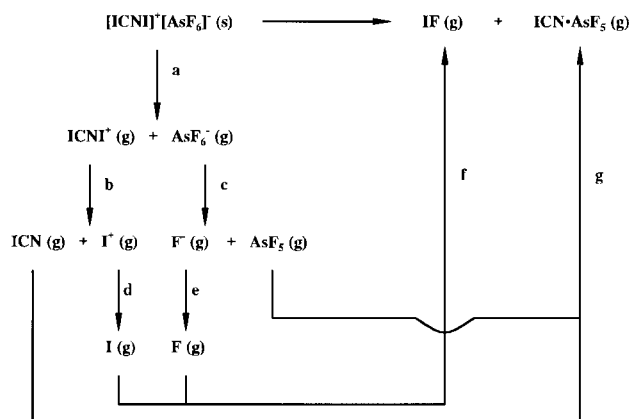


all levels of theory applied. The calculated reaction enthalpy for it reveals an N–I bond in the cation [ICNI]⁺ which is slightly stronger than that in IN₃ [*cf.* b.d.e.(N–I, IN₃) = 191.4 kJ

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

Theory	$E(\text{ICN})^{a,b}$	$E(\text{I}^+)^a$	$E([\text{ICNI}]^+)^a$	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

^aTotal energies for AM1 and PM3 in kJ mol⁻¹, for RHF and RMP2 in au. ^bZero-point energies for ICN in kJ mol⁻¹: AM1, 20.69; PM3, 22.79; RHF, 22.79; RMP2, 18.06; exptl. 19.6. ^c $E^{\text{AM1}}(\text{I}^+, ^1\text{D}) = 1072$ kJ mol⁻¹, $E^{\text{PM3}}(\text{I}^+, ^1\text{D}) = 952$ kJ mol⁻¹, $E^{\text{RHF}}(\text{I}^+, ^1\text{D}) = -10.722$ 92 au, $E^{\text{RMP2}}(\text{I}^+, ^1\text{D}) = -10.736$ 45 au. ^d6-31G(d) basis set for C and N, LANL2DZ electron core potentials for I. ^eRHF method for ICN and [ICNI]⁺, unrestricted (U)HF method for I⁺. ^fRMP2 method for ICN and [ICNI]⁺, PMP2 method for I⁺(³P), UMP2 method for I⁺(¹D).



Scheme 1 Energy cycle to estimate the reaction enthalpy according to equation (6): a, $U_L([\text{ICNI}]^+[\text{N}_3]^-)$ estimated as ≈ 557.6 kJ mol⁻¹ using the linear relationship $U_L = 556.3 V_M^{-0.33} + 26.3$,²⁶ with V_M taken to be equal to $7 \times 20 = 140 \text{ \AA}^3$ (U_L in kcal mol⁻¹, V_M in \AA^3);²⁷ b, b.d.e.([ICN-I]⁺) = 207 kJ mol⁻¹ [see text, equation (5)]; c, f.i.a.(AsF₅)⁺ = 464 kJ mol⁻¹,^{11b,28} d, $E_1(\text{I}) = 1012$ kJ mol⁻¹,²⁵ e, $E_{\text{ea}}(\text{F}) = 333$ kJ mol⁻¹,¹¹ f, b.d.e.(IF) = 276 kJ mol⁻¹,¹¹ g, b.e.(ICN·AsF₅) = 45 kJ mol⁻¹,²⁹ (f.i.a. = fluoride ion affinity)

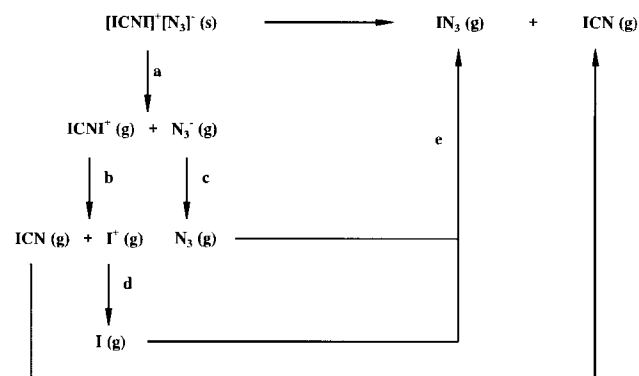
mol⁻¹.)^{9a,10b} This new calculated b.d.e.(N-I, [ICN-I]⁺) value of 207.4 kJ mol⁻¹ shows that the N-I bond strength in the cation [ICNI]⁺ is nicely in agreement with an earlier estimate predicted on the basis of hard-soft acid-base (HSAB) theory considerations (200.8 kJ mol⁻¹).[†] This excellent agreement 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(AsF₅)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]⁺[AsF₆]⁻ into IF and the adduct ICN·AsF₅. 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



confidence limits of the $\Delta H(6)$ value are difficult to ascribe it nevertheless reflects the stability of [ICNI]⁺[AsF₆]⁻ with respect to IF and the adduct ICN·AsF₅.¹³ [equation (6)].

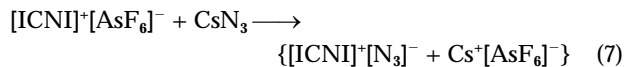
The metathetical reaction of [ICNI]⁺[AsF₆]⁻ with CsN₃ in SO₂ClF afforded Cs⁺[AsF₆]⁻, IN₃ and ICN (see Experimental section). Using a cycle shown in Scheme 2 the reaction enthalpy was estimated according to equation (8) as $\Delta H(8) = -140.4$ kJ mol⁻¹. Although the confidence limits are again difficult to ascribe this value nevertheless nicely explains the instability of [ICNI]⁺[N₃]⁻ formed as a likely intermediate in the initial

[†] 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.



Scheme 2 Energy cycle to estimate the reaction enthalpy according to equation (8). a, $U_L([\text{ICNI}]^+[\text{N}_3]^-) \approx 557.6$ kJ mol⁻¹ (see Scheme 1); b, b.d.e.([ICN-I]⁺) = 207 kJ mol⁻¹ [see text, equation (5)]; c, $E_{\text{ea}}(\text{N}_3) = 293$ kJ mol⁻¹,³⁰ d, $E_1(\text{I}) = 1012$ kJ mol⁻¹,²⁵ e, b.d.e.(N₃-I) = 191 kJ mol⁻¹,^{10b}

metathesis reaction of [ICNI]⁺[AsF₆]⁻ with CsN₃ [equation (7)].



Conclusion

From the studies presented in this paper the following conclusions can be drawn. (i) (Iodocyno)iodine hexafluoroarsenate, [ICNI]⁺[AsF₆]⁻, containing the 22-valence-electron [ICNI]⁺ cation can be synthesized either by the reaction of iodine cyanide with [I₃]⁺[AsF₆]⁻ or directly from ICN, I₂ and AsF₅. (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_{∞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 IN₃ 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]⁺[AsF₆]⁻ with CsN₃ in SO₂ClF afforded Cs⁺[AsF₆]⁻, IN₃ and ICN. The instability of the likely intermediate [ICNI]⁺[N₃]⁻ can be rationalized using a simple Born-Haber energy cycle.

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References

- 1 I. C. Tornieporth-Oetting and T. M. Klapötke, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 677.
- 2 J. Jander and U. Engelhard, in *Developments in Inorganic Nitrogen Chemistry*, ed. C. B. Colburn, Elsevier, Amsterdam, 1973, vol. 2, p. 184; H. Hartl, H. Bärnighausen and J. Jander, *Z. Anorg. Allg. Chem.*, 1968, **375**, 225; J. Jander, L. Bayersdorfer and K. Höhne, *Z. Anorg. Allg. Chem.*, 1968, **357**, 215; I. C. Tornieporth-Oetting, T. M. Klapötke and J. Passmore, *Z. Anorg. Allg. Chem.*, 1990, **586**, 93.
- 3 M. Hargittai, J. Molnar, T. M. Klapötke, I. C. Tornieporth-Oetting, M. Kolonits and I. Hargittai, *J. Phys. Chem.*, 1994, **98**, 10095.
- 4 V. V. Zhdankin, A. P. Krasutsky, C. J. Kuehl, A. J. Simonsen, J. K. Woodward, B. Mismash and J. T. Bolz, *J. Am. Chem. Soc.*, 1996, **118**, 5192.
- 5 P. Buzek, T. M. Klapötke, P. v. R. Schleyer, I. C. Tornieporth-Oetting and P. S. White, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 275.
- 6 I. C. Tornieporth-Oetting, P. Buzek, P. v. R. Schleyer and T. M. Klapötke, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1338.
- 7 I. C. Tornieporth-Oetting, T. M. Klapötke, A. Schulz, P. Buzek and P. v. R. Schleyer, *Inorg. Chem.*, 1993, **32**, 6540.
- 8 U. Müller, R. Dübgen and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1980, **463**, 7.
- 9 I. C. Tornieporth-Oetting and T. M. Klapötke, (a) *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 511; (b) in *Combustion Efficiency and Air Quality*, eds. I. Hargittai and T. Vidoczy, Plenum, New York, 1995.
- 10 (a) A. Finch and J. P. B. Sandall, *Asian J. Chem.*, 1989, **1**, 313; (b) M. Otto, S. Lotz and G. Frenking, *Inorg. Chem.*, 1992, **31**, 3647; (c) A. Schulz, I. C. Tornieporth-Oetting and T. M. Klapötke, *Inorg. Chem.*, 1995, **34**, 4343.
- 11 (a) D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, Cambridge University Press, Cambridge, 1982; (b) T. M. Klapötke and I. C. Tornieporth-Oetting, *Nichtmetallchemie*, VCH, Weinheim, 1994, p. 92.
- 12 R. H. Davies, A. Finch and P. N. Gates, *J. Chem. Soc., Chem. Commun.*, 1989, 1461.
- 13 M. Broschag and T. M. Klapötke, *Polyhedron*, 1992, **11**, 443.
- 14 (a) I. C. Tornieporth-Oetting, Dissertation (Ph.D. Thesis), TU Berlin, Berlin, 1992; (b) I. C. Tornieporth-Oetting and T. M. Klapötke, *Chem. Ber.*, 1990, **123**, 1343.
- 15 P. Klaboe, E. Klostewr-Jensen, D. H. Christensen and I. Johnsen, *Spectrochim. Acta, Part A*, 1970, **26**, 1567.
- 16 G. Brauer, *Handbuch der Präparativen und Anorganischen Chemie*, 3rd edn., F. Enke, Stuttgart, 1978; J. Passmore and P. Taylor, *J. Chem. Soc., Dalton Trans.*, 1976, 804.
- 17 M. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4499; M. J. S. Dewar, M. L. McKee and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 3607; M. J. S. Dewar, E. G. Zoebisch and E. F. Healy, *J. Am. Chem. Soc.*, 1985, **107**, 3902; M. J. S. Dewar and C. H. Reynolds, *J. Comput. Chem.*, 1986, **2**, 140.
- 18 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209, 221.
- 19 HYPERCHEM 4.0, Molecular Visualization and Simulation Program Package, Hypercube, Waterloo, Ontario, 1994.
- 20 GAUSSIAN 94, Revision B.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Pateresson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
- 21 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
- 22 A. Reed, L. A. Curtis and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899; A. Reed and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1987, **109**, 7362; *Inorg. Chem.*, 1988, **27**, 3969.
- 23 J. S. Binkley and J. A. Pople, *Int. J. Quantum Chem.*, 1975, **9**, 229 and refs. therein.
- 24 (a) T. M. Klapötke and A. Schulz, *Quantenmechanische Methoden in der Hauptgruppenchemie*, Spektrum, Heidelberg, 1996; (b) R. D. Harcourt, in *Lecture Notes in Chemistry*, eds. G. Berthier, M. J. S. Dewar, H. Fischer, K. Fukui, G. G. Hall, H. Hartmann, H. H. Jaffé, J. Jortner, W. Kutzelnigg, K. Ruedenberg and E. Scrocco, Springer, Berlin, Heidelberg, New York, 1982; (c) R. D. Harcourt, in *Valence bond theory and chemical structure*, eds. D. J. Klein and N. Trinajstić, Elsevier, Amsterdam, 1990, p. 251.
- 25 (a) I. C. Tornieporth-Oetting and T. M. Klapötke, *Chem. Ber.*, 1991, **124**, 1571; (b) R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.*, 1983, **105**, 7512; (c) R. G. Pearson, *Inorg. Chem.*, 1988, **27**, 734; (d) I. C. Tornieporth-Oetting, T. M. Klapötke, U. Behrens and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1992, 2055.
- 26 T. E. Mallouk, G. L. Rosenthal, G. Müller, R. Brusasco and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167; T. J. Richardson, F. L. Tarzella and N. Bartlett, *J. Am. Chem. Soc.*, 1986, **108**, 4937.
- 27 A. C. Larson, F. L. Lee, Y. Le Page, M. Webster, J. P. Charland, E. J. Gabe and P. S. White, *The NRCVAX Crystal Structure System*, NRC, Chemistry Division, Ottawa, 1995, tutorial appendix.
- 28 K. O. Christie, D. A. Dixon, J. C. P. Sanders, G. J. Schrobilgen and W. W. Wilson, *Inorg. Chem.*, 1994, **33**, 4911.
- 29 I. C. Tornieporth-Oetting, T. M. Klapötke, T. S. Cameron, J. Valkonen, P. Rademacher and K. Kowski, *J. Chem. Soc., Dalton Trans.*, 1992, 537.
- 30 K. Jones, in *Comprehensive Inorganic Chemistry*, eds. J. C. Bailar, H. J. Emelius, R. Nyholm and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 2, p. 287.

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