The $I(N_3)_2^+$ Cation: Preparation, Identification by Raman Spectroscopy, and ab Initio Quantum Mechanical Studies

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Although nitrogen–iodine compounds have been known since the beginning of this century, so far only four binary species have been described, which as a result of the very labile I–N bond[1] and the associated thermodynamic instability are all explosive: IN_3,[2–4] NI_3 (or $NI_3{\cdot}NH_3$),[5,6] $I(N_3)_2^-$,[7] and $I_2N_3^+$.[8] We now report the preparation, by two methods, and identification by Raman spectroscopy of a compound containing the hitherto unknown $I(N_3)_2^+$ cation, the structure of which has been deduced by ab initio computations.

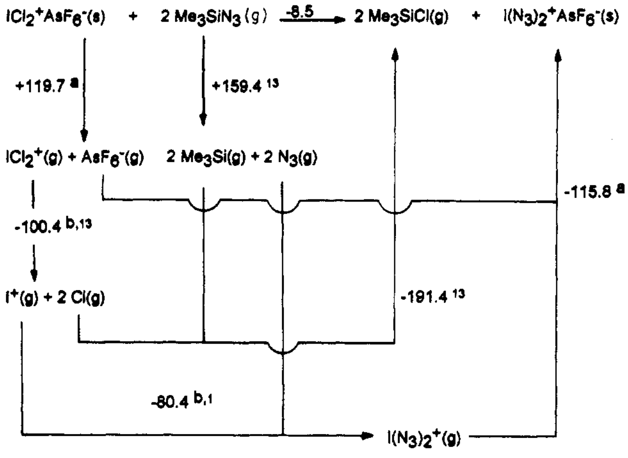
Using a similar approach as described previously,[5] we estimated that the reaction according to eq 1 should be thermodynamically

$$ICl_2^+AsF_6^-(s) + 2Me_3SiN_3(g) \rightarrow 2Me_3SiCl(g) + I(N_3)_2^+AsF_6^-(s) \quad (1)$$

favorable ($\Delta H°(1) = -8.5$ kcal/mol; Scheme I). In accordance with our work on $I_2N_3^+$,[8] we showed that the analogous reaction of $ICl_2^+AsF_6^-$ with AgN_3 leading to $I(N_3)_2^+AsF_6^-$ also is feasible (eq 2).

$$ICl_2^+AsF_6^- + 2AgN_3 \rightarrow I(N_3)_2^+AsF_6^- + 2AgCl \quad (2)$$

Scheme I. Energy Cycle for the Formation of $I(N_3)_2^+AsF_6^-$ (All Values in kcal mol^{-1})[a]



[a] U_L (kcal/mol) was calculated from $U_L = 556.3(V_M, Å^3)^{-0.33} + 26.3$.[10,11] Using $V_M(AsF_6^-) = 105$ Å^3,[12] $V_M(IC_2^+)$ was estimated from $V_M(ICl_2^+) = V_M(ICl_2^+AlCl_4^-) - V_M(AlCl_4^-) = 231 - 125$ Å^3 = 106 Å^3;[13] $V_M(I(N_3)_2^+)$ was taken to be equal to $V_M(I_3^+) = 135$ Å^3;[12] this seems to be reasonable since $V_M(I_2(s)) \approx V_M(IN_3(s))$ ($V_M(I_2(s)) = 85.4$ Å^3, $V_M(IN_3(s)) = 83.4$ Å^3)[4] and gives $U_L(ICl_2^+AsF_6^-) = 119.7$ kacl/mol and $U_L(I(N_3)_2^+AsF_6^-) = 115.8$ kcal/mol.[b] For both the I–Cl and the I–N bond energy, the values for the neutral species were used, as the stabilization due to the positive charge is likely to be similar in both cases and may very well cancel. However, we stress that the enthalpies of reaction are *estimates* and are intended for comparison of formation and decomposition reactions. The estimated values are generally in good agreement with the experimental observations.

Table I. Raman Data for $I(N_3)_2^+AsF_6^-$ (Solid; –70 °C, 10 mW, 647.09 nm) and ICl_2^+ and IN_3 for Comparison

IN_3[3]	ICl_2^+ [15]	$I(N_3)_2^+(AsF_6^-)(s)$	tentative assgnt
	147	144 (6)	δ (IX_2)
338[16a]			ν(I–X)
	364	298 (7)/311 (10)	ν_{as}(X–I–X)
	371	344 (8)/389 (5)	ν_s(X–I–X)
578/580		n.o.	$\gamma(N_3)$
648		620 (4)	$\delta(N_3)$
1240		1234 (3)	ν_s (N_3)
2045		20[illegible]3 (3)	ν_{as} (N_3)
		370 sh	$\nu_5(AsF_6^-)$[17]
		579 (<1)	$\nu_2(AsF_6^-)$
		680 (<1)	$\nu_1(AsF_6^-)$

[a] For the assignment of 338 cm^{-1}, compare ref 18.

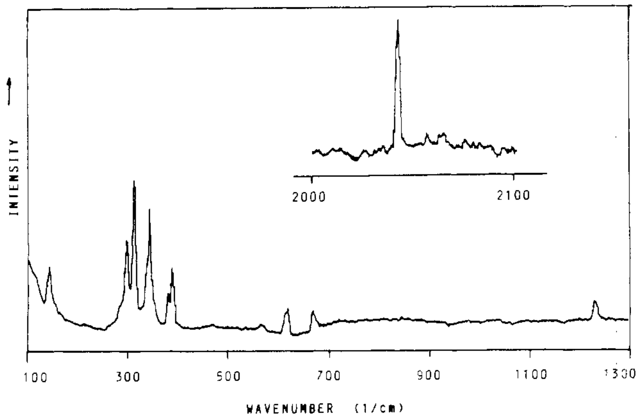


Figure 1. Raman spectrum of $I(N_3)^+AsF_6^-$ (solid, –70 °C, 10 mW, 647.09 nm).

Subsequently we identified the novel $I(N_3)_2^+$ cation from its low-temperature Raman spectrum (Table I, Figure 1) (AsF_6^- salt). The Raman data show, apart from the bands of the anions, only frequencies which can be assigned unequivocally to the $I(N_3)_2^+$ cation by comparison with ICl_2^+ and IN_3. The appearance of the ν(N–I) stretching modes at 298/311 cm^{-1} (ν_{as}) and 344/389 cm^{-1} (ν_s) is well in agreement with the spectrum of the anionic analogue $I(N_3)_2^-$ (C_2) (ν(N–I) = 269 and 285 cm^{-1}).[7] In earlier work we have shown that for N–I systems structures are often reasonably in agreement with HF/6-31+G* computations.[4] However, frequency calculations usually give only reasonable results using the very expensive correlated MP2 computations. (N.B. Whereas MP2/6-31+G* frequency calculations for NI_3 are in acceptable agreement with experiment, the uncorrelated HF calculation entirely failed.[9]) Therefore, in this paper we did not include MP2-calculated frequencies. However, we stress that structure **1** is a minimum (no imaginary frequencies at HF/6-31+G* level, although the numbers actually do not mean anything and are therefore not included). Thus we have prepared a salt

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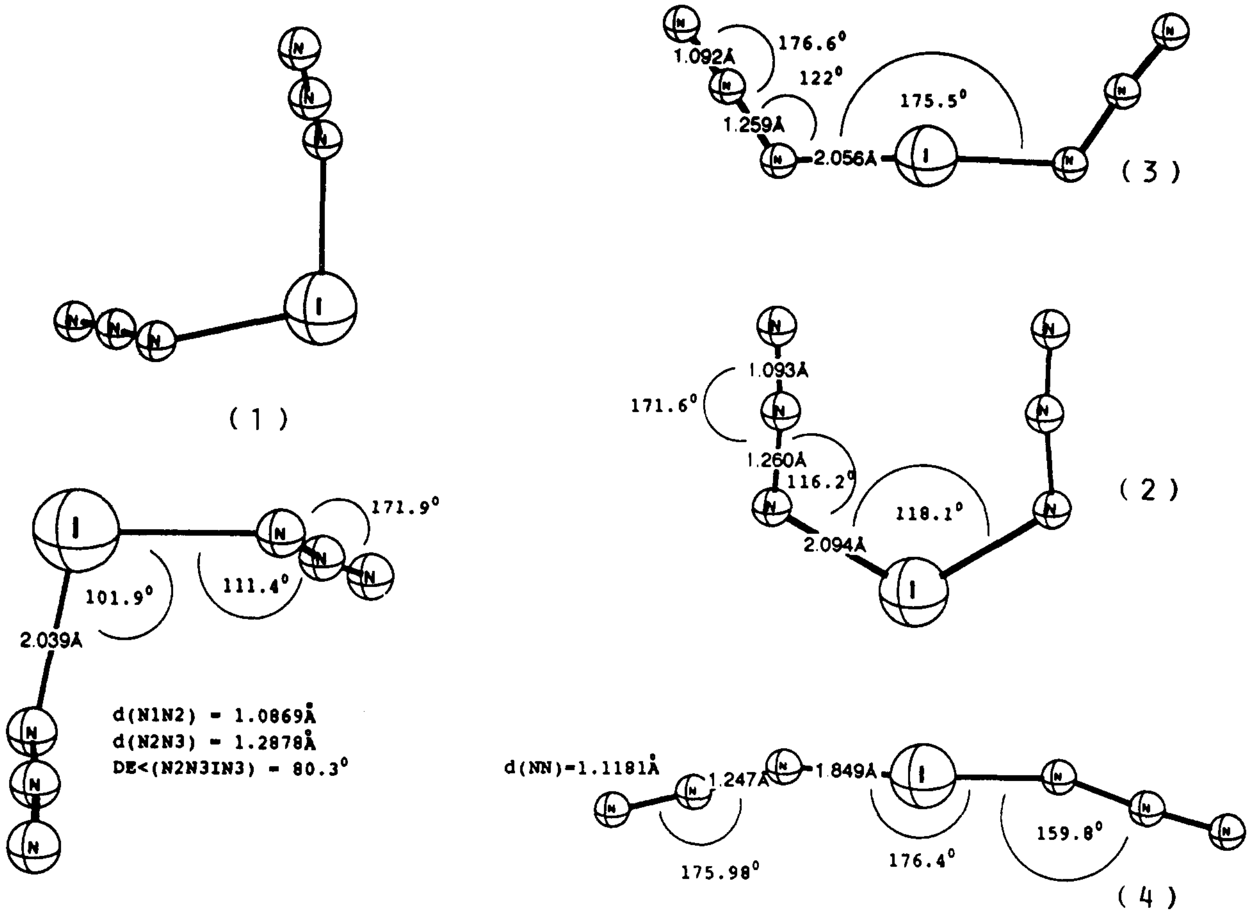
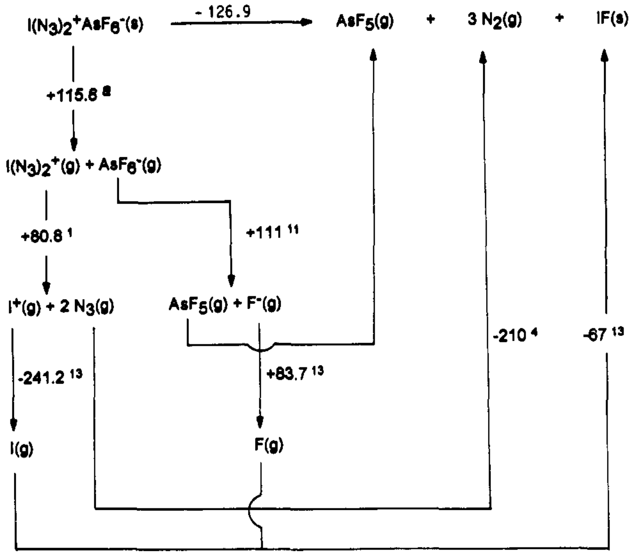


Figure 2. HF-optimized geometries for different geometrical configurations (1–4) of the $I(N_3)_2^+$ cation.

Scheme II. Energy Cycle for the Decomposition of $I(N_3)_2^+AsF_6^-$ (All Values in kcal mol^{-1})[a]



[a] $U_L(I(N_3)_2^+AsF_6^-)$ = 115.8 kcal/mol; see Scheme I.

Table II. Absolute and Relative Energies for Different Geometrical Configurations (1–4) for the $I(N_3)_2^+$ Cation (HF/6-31+G*)

	1	2	3	4
abs energy (–au)	337.310 26	337.283 03	337.219 20	337.159 16
rel energy (kcal/mol)	0.0	17.1	57.1	94.8

of $I(N_3)_2^+$. However, the $I(N_3)_2^+$ cation is thermodynamically highly unstable and decomposes even at –20 °C both in SO_2 solution and in the solid state. We observed an essentially quantitative reaction according to eq 2 (recovered yield of AgCl >85%), and we isolated the neat, yellow product from the reaction in SO_2 (eq 1; yield ≈20%). The decomposition reaction yielding N_2, AsF_5, and IF was estimated to be thermodynamically favorable ($\Delta H° = -127$ kcal/mol; Scheme II). (N.B. IF is unstable with respect to disproportionation, yielding I_2 and IF_5 in an exothermic process.)

In order to understand the $I(N_3)_2^+$ cation more fully, we computed several alternative geometrical configurations (**1**–**4**). The calculations were carried out with the Gaussian 92 program using the 6-31+G* standard basis set for nitrogen[19] and a quasirelativistic pseudopotential[20] with a [5s5p1d]/(3s3p1d)-(DZ+P) basis set for iodine.[21] The geometries were fully optimized at the HF level of theory by employing standard

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procedures.[22] The absolute and relative energies for **1**–**4** are summarized in Table II, and the optimized geometries are shown in Figure 2. The C_2 isomer (**1**) is favored substantially over the other geometries (**2**–**4**). As structures of **2**–**4** are by far higher in energy than **1**, we did not include vibrational calculations for these species (for comments concerning the vibrational frequencies and minimum structures, see above) and it may very well be that species **2**–**4** (especially **3** and **4**) are transition states rather than local minima. Therefore, with the minimum structure of **1**, the computations predict a bent $I(N_3)_2^+$ cation with two stereochemically active lone pairs at iodine and two slightly nonlinear N_3 units. The N–I bond distance (2.04 Å) is expected to be substantially shorter than that in the neutral, polymeric IN_3 (2.26(2) Å)[4] and resembles that in $I_2N_3^+$ (2.07 Å).[8]

Experimental Section

Equation 1. $I(N_3)_2^+AsF_6^-$ was prepared from $ICl_2^+AsF_6^-$ (0.145 g, 0.375 mmol) and Me_3SiN_3 (0.086 g, 0.10 mL, 0.750 mmol) in SO_2 solution (0.5 mL) at −40 °C (reaction time 30 min). The reaction was carried out in a 5-mm Raman capillary. Volatile product (Me_3SiCl) and SO_2 were removed under dynamic vacuum at −30 °C for 1 h, leaving a yellow solid, identified by its Raman spectrum as containing $I(N_3)_2^+$ (cf. Table I). Me_3SiCl was identified by ^1H NMR spectroscopy; no Me_3SiN_3 could be detected. The yellow solid was isolated in a yield of ca. 20%.

Equation 2. $I(N_3)_2^+AsF_6^-$ was prepared from $ICl_2^+AsF_6^-$ (0.058 g, 0.151 mmol) and AgN_3 (0.050 g, 0.334 mmol) in SO_2 solution at −50 °C (reaction time 30 min). The precipitated AgCl (ca. 0.037 g, 87%) was removed by low-temperature filtration. The solvent (SO_2) was removed under dynamic vacuum at −40 °C, leaving a yellow solid which was identified by Raman spectroscopy to be $I(N_3)_2^+AsF_6^-$. Thermal decomposition (20 °C) of the yellow SO_2 solution of the redissolved product led to the evolution of nitrogen (gas discharge) and the formation of iodine cations (I_2^+, identified by solution Raman spectroscopy; ν = 234 cm^{-1}).

Caution! AgN_3 and especially $I(N_3)_2^+AsF_6^-$ are highly explosive materials.

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