Supplementary material to manuscript:

‘Does $[I_3]^+$ act as an ‘$[I]^+$’ Donor to CH_3CN and N_2O ? Structure of $[H_3CCN\text{-}I\ NCCH_3]^+[AsF_6]^-$‘

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Computational Methods

All calculations were carried out using the program package G03W.[1] The structure and frequency calculations were performed with Becke’s B3 three parameter hybrid functional using the LYP correlation functional (B3LYP).[2] For all H, C, N and O a correlation consistent polarized triple-zeta basis set was used (cc-pVTZ).[3] For I an energy consistent multi-electron Wood-Boring pseudopotential (ECP-46-MWB) treating 46 core electrons was used.[4] The valence electrons of iodine were calculated with a basis set using the following contraction: (16s12p4d2f)/[3s3p2d2f].[5]

Table S1. Computational results for $[H_3CCNI]^+$ and $[H_3CCN\text{-}I\text{-}NCCH_3]^+$ at B3LYP level of theory.

	$[H_3CCNI]^+$	$[H_3CCN\text{-}I\text{-}NCCH_3]^+$
symmetry	C_{3v}	D_{3d}
electronic state	$^1A_1$	^1A
-*E* / a.u.	143.923796	276.784928
NIMAG	0	0
zpe / kcal mol^{-1}	29.2	58.5
μ / D	6.4	0
d(C-H) / Å	1.092	1.090
d(C-C) / Å	1.439	1.446
d(C-N) / Å	1.147	1.145
d(N-I) / Å	1.988	2.226
< (HCH) / °	109.6	109.4
< (HCC) / °	109.3	109.5

Table S2. Calculated vibrational data for $[H_3CCNI]^+$ and $[H_3CCN\text{-}I\text{-}NCCH_3]^+$ at B3LYP level of theory.

$[H_3CCNI]^+$ [a)]	$[H_3CCN\text{-}I\text{-}NCCH_3]^+$ [a)]	Assignment
	A 22 (0/0)	ω (CH_3)
	E 37 (14/0)	δ (R-I-R)
E 140 (4 / 0)	E 106 (0/0)	δ (C-N-I)
	A 169 (81/0)	υ_{as} (N-I)
	E 222 (5/0)	δ (N-I-N)
A_1 375 (0 / 0)	A 254 (0/0)	υ_{sym} (N-I)
E 411 (2 / 1)	E 407 (0/3)	δ (N-C-C)
	E 431 (5/0)	δ (N-C-C)
A_1 978 (0 / 10)	A 936 (32/0)	υ_{as} (C-C)
	A 955 (0/19)	υ_{sym} (C-C)
E 1040 (10 / 1)	E 1053 (2/2)	δ (H-C-H)
	E 1054 (10/0)	δ (H-C-H)
A_1 1398 (7 / 35)	A 1406 (3/0)	τ (CH_3)
	A 1407 (0/64)	τ (CH_3)
E 1437 (17 / 8)	E 1454 (6/13)	δ (H-C-H)
	E 1454 (24/6)	δ (H-C-H)
A_1 2390 (102 / 540)	A 2388 (328/0)	υ_{as} (C-N)
	A 2395 (0/1285)	υ_{sym} (C-N)
	A 3047 (30/44)	υ_{as} (C-H)
A_1 3032 (44 / 287)	A 3047 (2/627)	υ_{sym} (C-H)
E 3110 (17 / 83)	E 3124 (6/94)	υ_{as} (C-H)
	E 3124 (6/89)	υ_{as} (C-H)

a) IR and Raman frequencies in cm^{-1}; (IR intensities / Raman scattering activities) in km mol^{-1} (IR) and $Å^4$ amu^{-1}.

Table S3. Computational results for $[IN_2O]^+$ and $[ION_2]^+$ at B3LYP level of theory.

	$[IN_2O]^+$	$[ION_2]^+$
symmetry	C_s	C_s
electronic state	^{1}A'	^{1}A'
-*E* / a.u.	195.779005	195.765508
ΔE / kcal mol^{-1}	0.0	+8.5
NIMAG	0	0
zpe / kcal mol^{-1}	7.7	7.3
μ / D	1.6	2.7
d(I-N) / Å	2.024	
d(N-N) / Å	1.128	1.106
d(N-O) / Å	1.150	1.239
d(I-O) / Å		2.154
< (INN) / °	160.2	
< (NNO) / °	175.7	174.7
< (ION) / °		118.2

Table S4. Calculated vibrational data for $[IN_2O]^+$ and $[N_2OI]^+$ at B3LYP level of theory.

$[IN_2O]^{+}$ a)	$[ION_2]^{+}$ a)
91 (5/1) δ(INN)	149 (0/6) δ(ION)
344 (1/1) ν(I-N)	353 (8/9) ν(I-O)
522 (10/0) $\delta(NNO)_{o.o.p.}$	508 (4/1) $\delta(ONN)_{o.o.p.}$
543 (15/2) $\delta(NNO)_{i.p.}$	610 (2/4) $\delta(ONN)_{i.p.}$
1437 (75/140) $\nu(NNO)_{"sym."}$	1125 (166/1) $\nu(ONN)_{"sym."}$
2465 (710/38) $\nu(NNO)_{"as."}$	2361 (113/142) $\nu(ONN)_{"as."}$

a) IR and Raman frequencies in cm^{-1}; (IR intensities / Raman scattering activities) in km mol^{-1} (IR) and $Å^4$ amu^{-1}.

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