Electronic Supplementary Material for PCCP

Electronic Supplementary Information (ESI)

Spin-Spin Coupling Constants in Homonuclear Polynitrogen Species

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Table 1S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_2 and N_3^-. All calculations using the Dunning-type cc-pVXZ and aug-cc-pVXZ (X = D, T, Q, 5, 6) basis sets were performed with Gaussian 03; all calculations using the Huzinaga basis sets (Huz-X and Huz-X*su*n; X = II, III, IV and n = 2, 3, 4) were performed with Dalton 2.0. All data in Hz. Note that the implementations of the B3LYP functional in Gaussian03 and Dalton 2.0 differ slightly. See main text for references to geometries used in the calculations.

	N_2	N_3^-		
	$^{1}J(^{15}N,^{14}N)$	$^{1}J(^{15}N_{\alpha1},^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta},^{14}N_{\alpha2})$	$^{2}J(^{15}N_{\alpha1},^{14}N_{\alpha2})$
cc-pVDZ	3.51	5.05	6.10	-3.84
cc-pVTZ	-12.39	-5.64	-1.78	-2.54
cc-pVQZ	3.02	8.00	9.61	-1.98
cc-pV5Z	0.50	6.10	8.02	-2.17
cc-pV6Z	1.67	7.46	9.12	-2.15
aug-cc-pVDZ	-0.62	-1.09	-0.14	-3.07
aug-cc-pVTZ	-3.82	4.71	7.17	-1.26
aug-cc-pVQZ	2.44	7.98	9.66	-1.44
aug-cc-pV5Z	0.26	6.51	8.44	-1.73
aug-cc-pV6Z	1.53	7.59	9.27	-1.89
Huz-II	2.74	7.88	9.61	-2.48
Huz-III	1.78	7.06	8.71	-2.20
Huz-IV	1.33	6.59	8.23	-2.41
Huz-II*su*2	3.48	8.23	9.89	-2.81
Huz-III*su*3	1.75	7.06	8.74	-2.17
Huz-IV*su*4	1.56	6.97	8.65	-2.26
expt	∀(1.8 ∀ 0.6)	∀ 8.07 (average)	∀ 8.07 (average)	n.a.

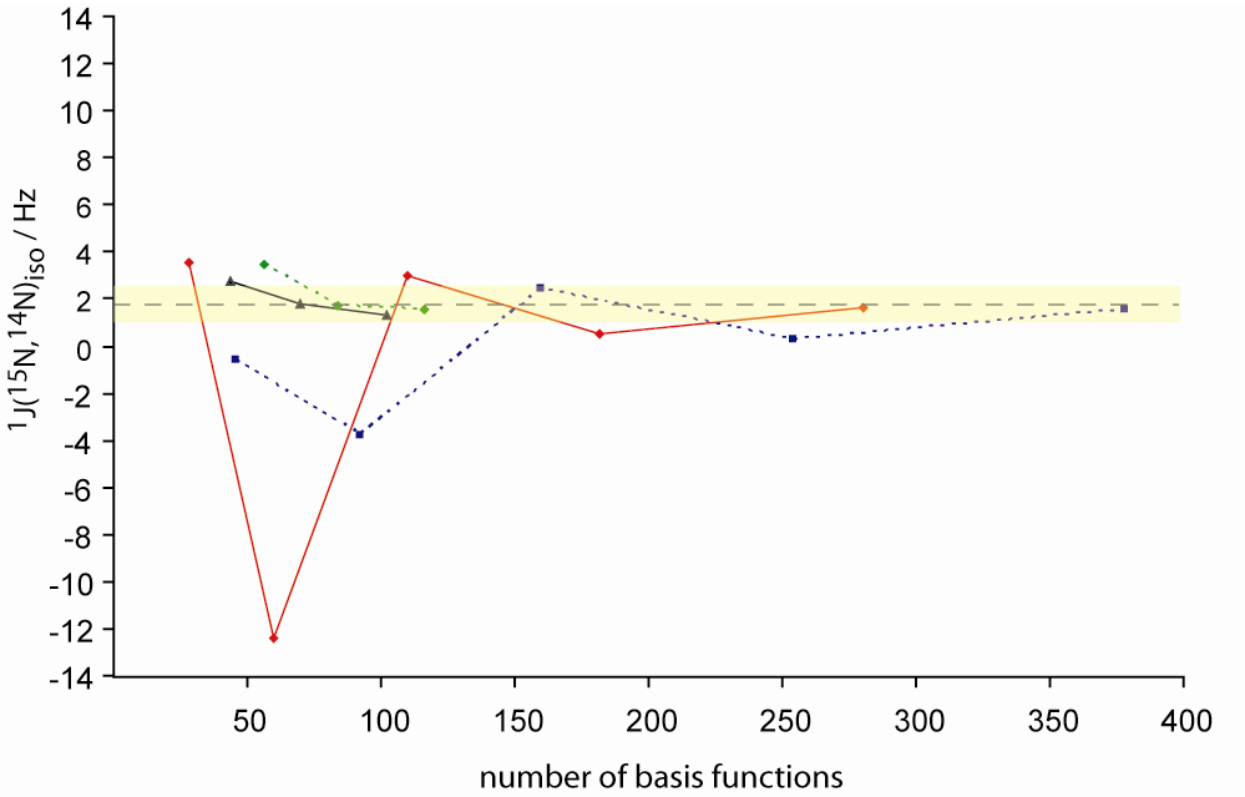

Figure 1S: Basis-set dependence of the isotropic nitrogen-nitrogen coupling constant in N_2. Calculations were performed using the B3LYP functional (data from Table 1S). The experimental value of 1.8 ∀ 0.6 Hz is highlighted in yellow. Results from the cc-pVXZ (X=D, T, Q, 5, 6) basis sets are shown in red; results from the aug-cc-pVXZ (X=D, T, Q, 5, 6) basis sets are shown in blue; results from the Huz-X (X=II, III, IV) basis sets are shown in black; results from the Huz-Xsu*n* (X=II, III, IV; *n* = 2, 3, 4) basis sets are shown in green.

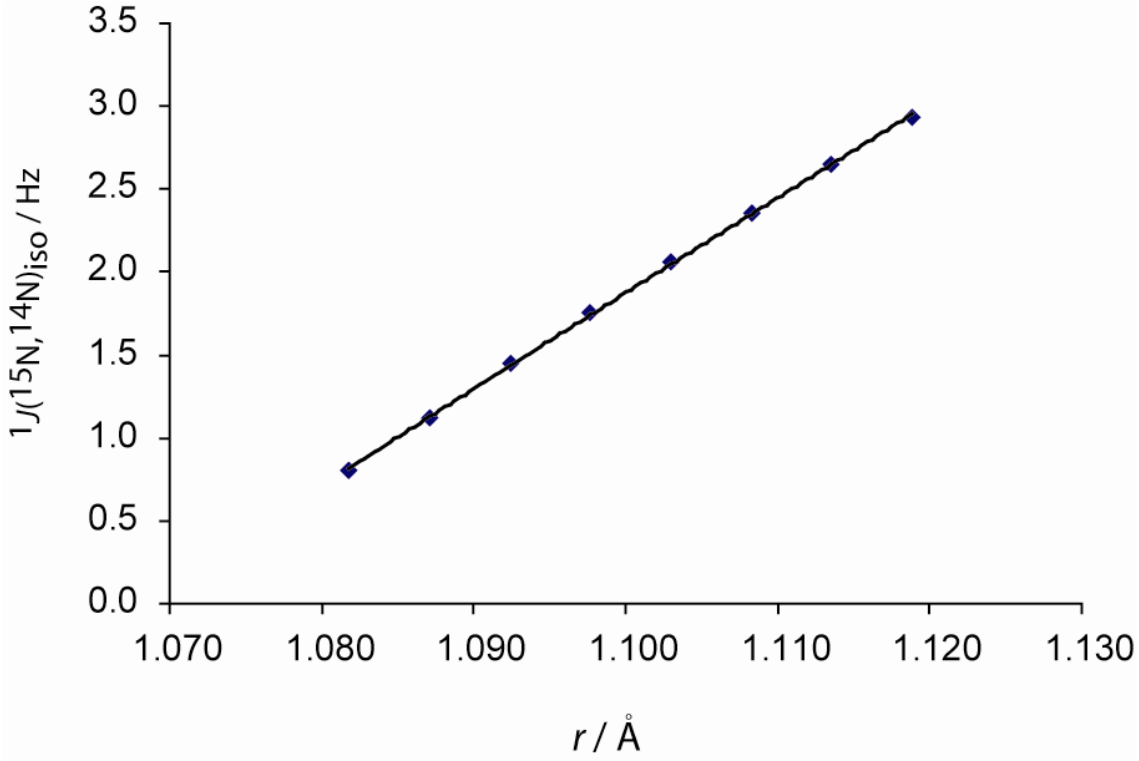

Figure 2S: Calculated (B3LYP/Huz-III*su*3) value of $^{1}J(^{15}N,^{14}N)_{iso}$ as a function of bond length in nitrogen, N_2. The equilibrium bond length is 1.09768 Δ. The function of best-fit is defined as $^{1}J(^{15}N,^{14}N)_{iso} = 63.405 \ln(r) - 4.1679$, where *r* is in Angstroms and *J* is in Hz. The correlation coefficient is $R = 0.9998$. The plot and equation suggest that a small change in bond length alone is not a dominant factor in determining the overall value of $^{1}J(^{15}N,^{14}N)_{iso}$ in a series of polynitrogen species.

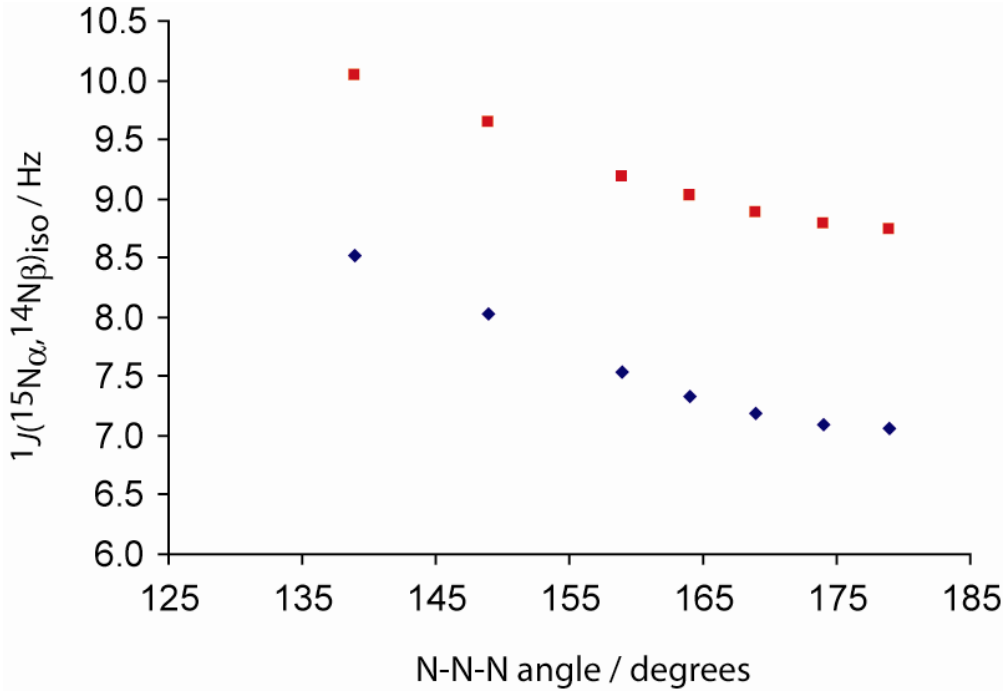

Figure 3S: Calculated (B3LYP/Huz-III*su*3) value of $^1J(^{15}N_\alpha,^{14}N_\beta)_{iso}$ in N_3^- as a function of the N-N-N angle. The two data sets correspond to $^1J(^{15}N_\alpha,^{14}N_\beta)_{iso}$ for the two crystallographically non-equivalent terminal nitrogen atoms ($^1J(^{15}N_{\alpha2},^{14}N_\beta)_{iso}$ and $^1J(^{15}N_{\alpha1},^{14}N_\beta)_{iso}$). The results suggest that a difference in bond angle is not a dominant factor in determining the overall value of the $^1J(^{15}N,^{14}N)_{iso}$ coupling constant for a range of polyatomic nitrogen species.

Table 2S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_2 and N_3^-, calculated using the second-order polarization propagator approximation (SOPPA) and SOPPA(CCSD). All calculations were performed with Dalton 2.0. All data in Hz. See main text for references to geometries used in the calculations.

	N_2	N_3^-		
	$^{1}J(^{15}N,^{14}N)$	$^{1}J(^{15}N_{\alpha 1},^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta},^{14}N_{\alpha 2})$	$^{2}J(^{15}N_{\alpha 1},^{14}N_{\alpha 2})$
SOPPA				
Huz-II	3.63	9.35	11.02	-0.05
Huz-III	2.98	8.24	9.81	0.22
Huz-IV	2.73	7.97	9.50	-0.10
Huz-II*su*2	4.43	9.70	11.30	-0.33
Huz-III*su*3	2.95	8.25	9.84	0.22
Huz-IV*su*4	2.93	8.39	9.98	0.07
SOPPA(CCSD)				
Huz-II	2.97	8.58	10.32	-1.32
Huz-III	2.37	7.53	9.17	-1.10
Huz-IV	2.09	7.28	8.88	-1.50
Huz-II*su*2	3.78	8.95	10.61	-1.58
Huz-III*su*3	2.34	7.53	9.19	-1.11
Huz-IV*su*4	2.27	7.67	9.33	-1.36
expt	∀(1.8 ∀ 0.6)	∀ 8.07 (average)	∀ 8.07 (average)	n.a.

Table 3S: One-bond nitrogen-nitrogen distances in polynitrogen species. There is a general trend that that magnitude of the coupling constant, $^{1}J(^{15}N, ^{14}N)_{iso}$ (presented here at the B3LYP/HuzIIIsu3 level), increases with increasing nitrogen-nitrogen distance; however it is clear that this is not the sole factor which accounts for the range of coupling constants. References for geometries are given in the main text.

	spin pair	$^{1}J(^{15}N, ^{14}N)_{iso}$ / Hz (calc)	r_{NN} / Δ
N_2		+1.75	1.09768
N_3^-	$N_{\alpha 1},N_{\beta}$	+8.75	1.176
	$N_{\alpha 2},N_{\beta}$	+7.06	1.155
N_4^{2+}	N_{α},N_{β}	+15.05	1.111
	N_{β},N_{β}	-11.33	1.285
N_5^+	N_{α},N_{β}	+6.34	1.12
	N_{β},N_{γ}	+19.1	1.33
N_6^{2+} (C_{2h})	N_{α},N_{β}	+9.69	1.102
	N_{β},N_{γ}	+27.6	1.391
	N_{γ},N_{γ}	+9.11	1.235

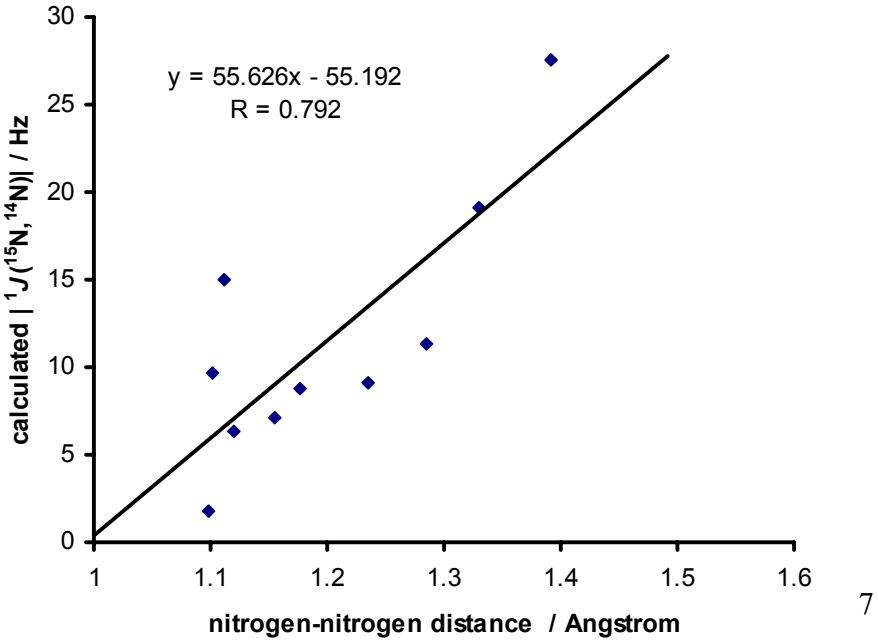

Figure 4S: Plot of the magnitude of the calculated values of $^{1}J(^{15}N, ^{14}N)_{iso}$ (B3LYP/HuzIIIsu3) for polynitrogen species as a function of the one-bond nitrogen-nitrogen distance. References for geometries are given in the main text. Data are from Table 3S.

Table 4S: Inclusion of solvent effects. Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_2. The following parameters were used to represent the solvent (hydrogen fluoride) within the Polarization Continuum Model (PCM): dielectric constant of 83.6; solvent radius of 0.91681 Δ; density of 0.0346265 particles per cubic Δ. All calculations were performed with the B3LYP functional in Gaussian 03. All data in Hz. See main text for a reference to the geometry used in the calculations. (*cf. Table 1S, where solvent is not included.)* These calculations were used to assess the effect of solvent on the magnitude of the coupling constant before proceeding to PCM calculations on N_5^+.

	N_2
	$^{1}J(^{15}N,^{14}N)$
cc-pVDZ	3.33
cc-pVTZ	-12.67
cc-pVQZ	2.99
cc-pV5Z	0.46
cc-pV6Z	1.66
aug-cc-pVDZ	-0.75
aug-cc-pVTZ	-3.88
aug-cc-pVQZ	2.43
aug-cc-pV5Z	0.22
aug-cc-pV6Z	1.52
expt	∀(1.8 ∀ 0.6)

Table 5S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_4^{2+}, and N_5^{+}. All calculations using the Dunning-type cc-pVXZ and aug-cc-pVXZ (X = D, T, Q, 5, 6) basis sets were performed with Gaussian 03; all calculations using the Huzinaga basis sets (Huz-X and Huz-X*su*n; X = II, III, IV and n = 2, 3, 4) were performed with Dalton 2.0. All data in Hz. Note that the implementations of the B3LYP functional in Gaussian03 and Dalton 2.0 differ slightly. Olah's[1] B3LYP/aug-cc-pVTZ optimized structure was used for N_4^{2+}; Christe's[2] B3LYP/6-311+G(2d) optimized structure was used for N_5^{+}.

	N_4^{2+}				N_5^{+}			
	$^{1}J(^{15}N_{\alpha1}, ^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta1}, ^{14}N_{\beta2})$	$^{2}J(^{15}N_{\alpha1}, ^{14}N_{\beta2})$	$^{3}J(^{15}N_{\alpha1}, ^{14}N_{\alpha2})$	$^{1}J(^{15}N_{\alpha}, ^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta}{}^{14}N_{\gamma})$	$^{2}J(^{15}N_{\alpha}, ^{14}N_{\gamma})$	$^{3}J(^{15}N_{\alpha1}, ^{14}N_{\beta2})$
cc-pVDZ	5.67	-17.60	6.33	-5.20	2.02	10.87	0.49	-0.49
cc-pVTZ	-2.79	-16.61	7.50	-5.12	-11.28	14.90	2.58	0.13
cc-pVQZ	17.23	-9.76	8.65	-5.65	7.65	19.33	2.83	0.07
cc-pV5Z	14.20	-11.18	9.02	-5.86	4.78	19.19	2.55	-0.13
cc-pV6Z	15.60	-11.56	9.10	-5.99	6.35	19.12	2.34	-0.21
aug-cc-pVDZ	2.86	-29.56	6.85	-5.16	-1.97	6.45	0.52	-0.62
aug-cc-pVTZ	11.36	-13.28	8.12	-4.39	2.27	18.22	2.89	0.08
aug-cc-pVQZ	17.06	-9.86	8.68	-5.68	7.46	19.23	2.80	0.05
aug-cc-pV5Z	14.43	-10.98	8.98	-5.89	5.09	19.35	2.52	-0.13
aug-cc-pV6Z	15.64	-11.56	9.06	-6.00	6.34	19.16	2.34	-0.21
Huz-II	15.81	-12.33	9.12	-5.50	6.59	19.91	2.57	-0.15
Huz-III	14.85	-10.93	8.84	-5.82	6.00	18.84	2.29	-0.23
Huz-IV	13.70	-10.67	8.65	-5.88	5.20	18.12	2.15	-0.23
Huz-II*su*2	15.23	-11.33	8.84	-5.51	6.54	19.61	2.32	-0.18
Huz-III*su*3	15.08	-11.35	8.99	-5.82	6.03	19.06	2.31	-0.25
Huz-IV*su*4	14.84	-11.18	8.96	-5.86	n.a.	n.a.	n.a.	n.a.
expt	n.a.	n.a.	n.a.	n.a.	small	∀18.0	n.a.	n.a.

[1] G. A. Olah, G. K. Surya Prakash, and G. Rasul, *J. Am. Chem. Soc.*, 2001, **123**, 3308.
[2] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem. Int. Ed.*, 1999, **38**, 2004.

Table 6S: Contributions from the Fermi-Contact (FC), Spin-Dipolar (SD), Paramagnetic Spin-Orbital (PSO), and Diamagnetic Spin-Orbital (DSO) terms to the total isotropic nitrogen-nitrogen coupling constant for homonuclear polyatomic nitrogen species. All results were obtained using Dalton 2.0 at the B3LYP/Huz-III*su*3 level. All data in Hz. (See also Figure 2 in the main text). Christe's[3] B3LYP/6-311+G(2d) optimized structure was used for N_5^+.

	coupling	FC	SD	PSO	DSO	total
N_2	$^1J(^{15}N,^{14}N)$	1.50	-2.54	2.77	0.03	1.75
N_3^-	$^1J(^{15}N_{\alpha1},^{14}N_{\beta})$	6.10	-0.56	1.53	-0.01	7.06
N_3^-	$^1J(^{15}N_{\alpha2},^{14}N_{\beta})$	7.80	-0.54	1.50	-0.02	8.75
N_3^-	$^2J(^{15}N_{\alpha1},^{14}N_{\alpha2})$	3.08	-2.98	-2.32	0.04	-2.18
N_4^{2+}	$^1J(^{15}N_{\alpha1},^{14}N_{\beta})$	21.4	-4.15	-2.17	0.00	15.1
N_4^{2+}	$^1J(^{15}N_{\beta1},^{14}N_{\beta2})$	-11.5	-0.43	0.65	-0.04	-11.3
N_4^{2+}	$^2J(^{15}N_{\alpha1},^{14}N_{\beta2})$	7.34	0.77	0.85	0.03	8.99
N_4^{2+}	$^3J(^{15}N_{\alpha1},^{14}N_{\alpha2})$	0.11	-2.30	-3.66	0.03	-5.82
N_5^+	$^1J(^{15}N_{\alpha},^{14}N_{\beta})$	10.0	-3.32	-0.66	0.00	6.03
N_5^+	$^1J(^{15}N_{\beta}{}^{14}N_{\gamma})$	17.5	0.30	1.32	-0.03	19.1
N_5^+	$^2J(^{15}N_{\alpha},^{14}N_{\gamma})$	2.59	-0.53	0.23	0.03	2.31
N_5^+	$^3J(^{15}N_{\alpha1},^{14}N_{\beta2})$	-0.47	0.17	0.04	0.02	-0.25
N_6^{2+}	$^1J(^{15}N_{\alpha},^{14}N_{\beta})$	14.5	-3.74	-1.11	0.00	9.69
N_6^{2+}	$^1J(^{15}N_{\beta}{}^{14}N_{\gamma})$	27.2	-0.23	0.70	-0.04	27.6
N_6^{2+}	$^1J(^{15}N_{\gamma1}{}^{14}N_{\gamma2})$	0.95	-0.31	8.48	-0.01	9.11
N_6^{2+}	$^3J(^{15}N_{\alpha1},^{14}N_{\gamma2})$	-0.15	-0.23	1.07	0.02	0.72
N_6^{2+}	$^3J(^{15}N_{\beta1},^{14}N_{\beta2})$	-13.8	-0.07	-0.03	0.01	-13.9

[3] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem. Int. Ed.*, 1999, **38**, 2004.

Table 7S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_5^+. Christe's[4] interpolated optimized structure was used for N_5^+. All calculations using the Dunning-type cc-pVXZ and aug-cc-pVXZ (X = D, T, Q, 5, 6) basis sets were performed with Gaussian 03; all calculations using the Huzinaga basis sets (Huz-X and Huz-X*su*n; X = II, III, IV and n = 2, 3, 4) were performed with Dalton 2.0.

	N_5^+			
	$^{1}J(^{15}N_{\alpha}, ^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta}, ^{14}N_{\gamma})$	$^{2}J(^{15}N_{\alpha}, ^{14}N_{\gamma})$	$^{3}J(^{15}N_{\alpha 1}, ^{14}N_{\beta 2})$
cc-pVDZ	2.20	12.63	0.66	-0.52
cc-pVTZ	-11.12	17.19	2.72	0.10
cc-pVQZ	7.91	21.37	2.99	0.05
cc-pV5Z	5.03	21.31	2.72	-0.16
cc-pV6Z	6.62	21.18	2.53	-0.25
aug-cc-pVDZ	-1.78	8.69	0.64	-0.65
aug-cc-pVTZ	0.25	20.02	3.02	0.06
aug-cc-pVQZ	7.73	21.28	2.96	0.02
aug-cc-pV5Z	5.35	21.46	2.69	-0.16
aug-cc-pV6Z	6.60	21.22	2.53	-0.24
Huz-II	6.83	22.06	2.73	-0.18
Huz-III	6.29	21.13	2.50	-0.28
Huz-IV	5.44	20.09	2.33	-0.26
Huz-II*su*2	6.79	21.68	2.49	-0.21
Huz-III*su*3	6.29	21.13	2.50	-0.28
expt	small	∀18.0	n.a.	n.a.

[4] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem. Int. Ed.*, 1999, **38**, 2004.

Table 8S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_5^+. Christe's[5] CCSD(T)/6-311+G(2d) optimized structure was used for N_5^+. All calculations using the Dunning-type cc-pVXZ and aug-cc-pVXZ (X = D, T, Q, 5, 6) basis sets were performed with Gaussian 03; all calculations using the Huzinaga basis sets (Huz-X and Huz-X*su*n; X = II, III, IV and n = 2, 3, 4) were performed with Dalton 2.0. All data in Hz.

	N_5^+			
	$^{1}J(^{15}N_{\alpha}, ^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta}{}^{14}N_{\gamma})$	$^{2}J(^{15}N_{\alpha}, ^{14}N_{\gamma})$	$^{3}J(^{15}N_{\alpha 1}, ^{14}N_{\beta 2})$
cc-pVDZ	2.64	14.52	0.74	-0.56
cc-pVTZ	-8.99	19.51	2.81	0.09
cc-pVQZ	8.96	23.58	3.08	0.04
cc-pV5Z	6.17	23.61	2.82	-0.18
cc-pV6Z	7.69	23.44	2.64	-0.27
aug-cc-pVDZ	-1.43	11.12	0.66	-0.69
aug-cc-pVTZ	3.93	21.95	3.07	0.05
aug-cc-pVQZ	8.77	23.50	3.06	0.01
aug-cc-pV5Z	6.48	23.73	2.80	-0.18
Huz-II	7.90	24.38	2.82	-0.20
Huz-III	7.26	23.07	2.58	-0.28
Huz-IV	6.41	22.23	2.44	-0.29
Huz-II*su*2	7.80	23.92	2.58	-0.23
Huz-III*su*3	7.32	23.38	2.60	-0.31
expt	small	∀18.0	n.a.	n.a.

[5] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem. Int. Ed.*, 1999, **38**, 2004.

Table 9S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_5^+. All calculations were performed with Gaussian 03. All data in Hz. Christe's[6] B3LYP/6-311+G(2d) optimized structure was used for N_5^+. For the spin-spin coupling tensor calculations, the following parameters were used to represent the solvent (hydrogen fluoride) within the Polarization Continuum Model (PCM): dielectric constant of 83.6; solvent radius of 0.91681 Δ; density of 0.0346265 particles per cubic Δ. (*Same as Table 5S, but with solvent effects included for the calculation of spin-spin coupling tensors.)*

	N_5^+			
	$^{1}J(^{15}N_{\alpha}, ^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta} ^{14}N_{\gamma})$	$^{2}J(^{15}N_{\alpha}, ^{14}N_{\gamma})$	$^{3}J(^{15}N_{\alpha 1}, ^{14}N_{\beta 2})$
cc-pVDZ	0.69	10.09	0.39	-0.52
cc-pVTZ	-13.23	14.25	2.41	0.09
cc-pVQZ	6.26	18.70	2.66	0.04
cc-pV5Z	3.30	18.53	2.37	-0.17
cc-pV6Z	4.93	18.45	2.18	-0.26
aug-cc-pVDZ	-3.21	5.71	0.44	-0.65
aug-cc-pVTZ	0.95	17.66	2.76	0.05
aug-cc-pVQZ	6.07	18.61	2.63	0.01
aug-cc-pV5Z	3.62	18.70	2.35	-0.17
aug-cc-pV6Z	4.92	18.49	2.17	-0.26
	small	∀18.0	n.a.	n.a.

[6] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem. Int. Ed.*, 1999, **38**, 2004.

Table 10S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_5^+. All calculations were performed with Gaussian 03. All data in Hz. Christe's[7] interpolated optimized structure was used for N_5^+. For the spin-spin coupling tensor calculations, the following parameters were used to represent the solvent (hydrogen fluoride) within the Polarization Continuum Model (PCM): dielectric constant of 83.6; solvent radius of 0.91681 Δ; density of 0.0346265 particles per cubic Δ. (*Same as Table 7S, but with solvent effects included for the calculation of spin-spin coupling tensors.)*

	N_5^+			
	$^{1}J(^{15}N_{\alpha}, ^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta} ^{14}N_{\gamma})$	$^{2}J(^{15}N_{\alpha}, ^{14}N_{\gamma})$	$^{3}J(^{15}N_{\alpha 1}, ^{14}N_{\beta 2})$
cc-pVDZ	0.89	11.85	0.58	-0.55
cc-pVTZ	-13.04	16.54	2.58	0.06
cc-pVQZ	6.56	20.76	2.84	0.01
cc-pV5Z	3.59	20.66	2.57	-0.20
cc-pV6Z	5.23	20.52	2.38	-0.29
aug-cc-pVDZ	-3.00	7.94	0.58	-0.68
aug-cc-pVTZ	1.22	19.46	2.91	0.02
aug-cc-pVQZ	6.37	20.66	2.81	-0.02
aug-cc-pV5Z	3.91	20.81	2.54	-0.20
aug-cc-pV6Z	6.62	21.18	2.53	-0.25
	small	∀18.0	n.a.	n.a.

[7] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem. Int. Ed.*, 1999, **38**, 2004.

Table 11S: Basis set dependence of the isotropic nitrogen-nitrogen coupling constants $^{n}J(^{15}N, ^{14}N)_{iso}$ in N_5^+. All data in Hz. The structure used was generated from a geometry optimization at the MP2/6-31+G* level; the optimization included hydrogen fluoride as a solvent using the PCM. Calculations of the spin-spin coupling tensors were subsequently performed in hydrogen fluoride solvent as well. The following parameters were used to represent the solvent (hydrogen fluoride) within the Polarization Continuum Model (PCM): dielectric constant of 83.6; solvent radius of 0.91681 Δ; density of 0.0346265 particles per cubic Δ. All calculations were performed using Gaussian 03.

	N_5^+			
	$^{1}J(^{15}N_{\alpha}, ^{14}N_{\beta})$	$^{1}J(^{15}N_{\beta}{}^{14}N_{\gamma})$	$^{2}J(^{15}N_{\alpha}, ^{14}N_{\gamma})$	$^{3}J(^{15}N_{\alpha1}, ^{14}N_{\beta2})$
cc-pVDZ	1.71	12.30	0.38	-0.59
cc-pVTZ	-7.42	16.67	2.64	0.13
cc-pVQZ	8.87	21.32	2.92	0.06
cc-pV5Z	6.22	21.25	2.59	0.17
aug-cc-pVDZ	-2.51	8.43	0.31	-0.73
aug-cc-pVTZ	4.68	19.98	2.97	0.08
aug-cc-pVQZ	8.68	21.23	2.89	0.03
aug-cc-pV5Z	6.53	21.42	2.56	-0.18
	small	∀18.0	n.a.	n.a.

Results of a B3LYP/Huz-IIIsu3 calculation based on the X-ray coordinates of the X-ray structure for $N_5^+Sb_2F_{11}^-$ (Vij et al., *J. Am. Chem. Soc.*, 2001, **123**, 6308):

$^{1}J(^{15}N_{\alpha1}, ^{14}N_{\beta1})$ = 5.45 Hz ; $^{1}J(^{15}N_{\beta1}{}^{14}N_{\gamma1})$ = 19.06 Hz
$^{1}J(^{15}N_{\alpha2}, ^{14}N_{\beta2})$ = 5.62 Hz ; $^{1}J(^{15}N_{\beta2}{}^{14}N_{\gamma2})$ = 18.12 Hz
$^{2}J(^{15}N_{\alpha1}, ^{14}N_{\gamma})$ = 2.56 Hz
$^{3}J(^{15}N_{\alpha1}, ^{14}N_{\beta2})$ = -0.25 Hz
$^{3}J(^{15}N_{\alpha2}, ^{14}N_{\beta1})$ = -0.30 Hz

Full reference 13: Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.