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First Calculations of $^{15}N-^{15}N$ *J* Values and New Calculations of Chemical Shifts for High Nitrogen Systems: A Comment on the Long Search for HN_5 and Its Pentazole Anion

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In the potential solution observation of the long-sought-after pentazole anion (N_5^-), the principal experimental tool used for detection is NMR. However, in two experiments, very different conclusions were reached. To assist in the interpretation, we report predictive level coupled-cluster results for the spin−spin coupling constants and chemical shifts for all of the key species, which include NO_3^-, N_5^-, HN_5, N_3^-, and $MeOC_6H_5N_3$. In the case of the shifts, an empirical estimate based on the molecule polarity enables comparison of gas-phase and observed values with expected error bars of ∼ ±10 ppm. For the scalar couplings, the evidence is that the solution effects are modest, enabling the gas-phase values (with error bars are ∼ ±5 Hz) to be accurate. The latter supports the observation of centrally ^{15}N labeled N_3^- in the cerium(IV) ammonium nitrate (CAN) solution which could only occur if the pentazole anion had been created in the experiment, yet with too short a lifetime to be observed in NMR.

Introduction

The pentazole anion[1−4] has a rich, though controversial history. Its first observation was reported in 1915,[1,2] although that proved to be false. It is isoelectronic with the cyclopentadienyl anion, is aromatic, and has D_{5h} symmetry, and state-of-the-art theoretical calculations[5] predict that it is a minimum on its potential energy surface with an activation barrier of 27 kcal/mol to prevent autodecomposition. Despite the fact that all of the evidence points to its viability as an isolable chemical species, all efforts to prepare it or its salts have been a challenge; however, the existence of the pentazole anion deserves attention even in freshman chemistry.

The long-sought-after pentazole anion[1−4] (see Figure 1) has now been observed in negative ion mass spectra,[6,7] followed by a potential NMR observation in solution.[8] However, the NMR results have been controversial. They were disputed by Schroer et al.[9] Subsequent work by Butler et al.[10] concluded that their prior paper[8] did not observe the pentazole anion because it was too short-lived. However, they argue that it was made in the experiment as proven by its unique byproduct of an isotopically labeled azide anion. The latter could only appear from the terminally labeled *para*-methoxyphenylpentazole (4-$MeOC_6H_4N_5$) precursor. The difference in opinion arises from the different NMR assignments made by Butler and Schroer et al.[8,9,11]

Predictive, coupled-cluster theory offers a third voice that can contribute to understanding these experimental observations, and whether HN_5/N_5^- was indeed generated in the Butler et al.[8] NMR experiment is significant. The discrepancies between the observations warrant further analysis using predictive level coupled-cluster theory, which we report. Furthermore, we argue that an observation of the spin−spin coupling constants, as predicted here, will help to resolve the conflicting observations.

Prior to presenting our results, let us briefly revisit the experimental evidence Butler and Schroer et al.[8,9] cite to advance their arguments. Butler et al.[8] report that when a fully deuterated methanol and water solution containing $(NH_4)_2Ce(IV)(NO_3)_6$ (CAN) and $Zn(NO_3)_2$, and the precursor 4-$MeOC_6H_4N_5$, is heated to −40 °C, a new signal at −10 ± 2 ppm is observed in ^{15}N NMR. Furthermore, it is noted that upon heating to −20 °C three NMR signals appear at −72 ppm corresponding to N_2 gas and at −283 and −147 ppm which were assigned to the terminal and central nitrogen atoms (henceforth designated as N_t and N_c) of N_3^-, respectively. Since the precursor 4-$MeOC_6H_4N_5$ is prepared with ^{15}N labeled N_3^- at N_t, Butler et al.[8] cite that the N_3^- with $^{15}N_c$ could not be present unless it is formed from a decomposition of N_5^-, and consequently assign the −10 ± 2 ppm signal to N_5^-. The theoretically computed ^{15}NMR shift of −1.7 ± 20 ppm of N_5^- at the DFT[12] (the computed values are believed to have error bars of ±20 ppm, as described by Burke et al.[12]) level is quoted as further supporting evidence for the assignments. On the other hand, Schroer et al.[9] who subsequently duplicated Butler's experiment report that there is no evidence to support the formation of N_5^- or the N_3^- anion, but the observed species are instead NO_3^- and NH_4^+. Schroer et al.[9] assigned the NMR signal observed at −11 ppm in their experiment to NO_3^-, disputing the Butler et al.[8] assignment of it to N_5^-. The other key feature in the first experiment is that the ^{15}N NMR signal assigned to the N_c atom in N_3^- has also been questioned. First, it is argued that the excess CAN used in the first experiment would have oxidized N_3^- to N_2 before detection, and second, that 4-$MeOC_6H_4N_3$, a decomposition product of 4-$MeOC_6H_4N_5$, also has an NMR signal of −148.16 ppm for N_γ (a solution of 4-$MeOC_6H_4N_\gamma{=}N_\beta{=}N$ in CH_3OH), close to the −147.2 ppm which was incorrectly

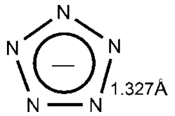

Figure 1. CCSD(T)/aug-cc-pVQZ structure of N_5^-. The CCSD(T)/aug-cc-pVQZ vibrational frequencies in cm^{-1} are 766.5, 766.5, 1021.9, 1021.9, 1102.1, 1102.1, 1169.8, 1231.5, and 1231.5.

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TABLE 1: Computed and Measured (Experimental Gas-Phase Data Shown in Bold) Chemical ^{15}N Shifts of the Molecules of Interest (in ppm with Respect to CH_3NO_2 Internal Standard)[a]

	cc-pVTZ	cc-pVQZ	PZ3D2F	CP corrected	experiment
N_2	−85.8	−80.1	−77.5	−70.5	**−75.3**,[27] −70.2[27]
N_tN_cO	−251.4 (N_t)	−246.3	−244.9	−227.4	**−232.3**,[27] −225.0[27]
	−159.1 (N_c)	−152.7	−149.9	−143.9	**−148.0**,[27] −140.0[27]
NH_3	−410.7	−408.7	−407.2	−389.7	**−400.1**,[27] −380.2[25,27,28]
CH_3CN	−137.6	−134.4	−132.3	−137.3	**−126.7**,[27] −137.1[28]
ClCN	−150.3	−147.0	−145.0	−139.0	−144.0[27]
HCN	−127.3	−125.2	−123.0	−128.0	−127.5[27]
NO_3^-	−11.7	−2.6	1.5	−5.5	−11.5,[8] −4.0[27]
$N_t(N_cN)^-$	−310.6 (N_t)	−309.0	−309.1	−291.6	−283,[7] −282.2[8]
	−145.1 (N_c)	−136.2	−131.9	−126.9	−147,[7] −133.6,[8] −130[28]
NH_4^+	−380.7	−382.4	−381.3	−363.8	−359.8,[8] −359.6[27]
N_5^+	−111.7 (N_1)	−105.7	−103.1	−98.1	−100.4[29]
	−179.0 (N_2)	−174.2	−171.7	−165.7	−165.3[29]
	−264.1 (N_3)	−262.4	−260.8	−243.3	−237.3[29]
N_5^-	−22.8	−16.5	−13.5	−6.5	
N_5H	−136.7 (N_1)	−131.3	−128.5	−121.5	
	−44.0 (N_2)	−37.6	−34.6	−27.6	
	−8.7 (N_3)	−0.5	3.3	10.2	
$MeOC_6H_4N_3$	−295.9 (N_1)			−278.4	
	−139.5 (N_2)			−133.5	−135.5[8]
	−137.2 (N_3)			−131.2	−148.2[8]
$MeOC_6H_4N_5$	−87.8 (N_1)			−92.8	
	−27.0 (N_2)			−34.0	−26.7[7]
	13.9 (N_3)			6.9	5.6[7]

[a] The unique N atoms of N_5^+, N_5H, $CH_3OC_6H_5N_3$, and $CH_3OC_6H_5N_5$ are labeled as N_1, N_2, and N_3 in accordance with the literature.

assigned to the N_c of N_3^- in the previous experiment. The absence of the signal corresponding to N_β (−135.5 ppm 4-$MeOC_6H_4N_3$ in CH_3OH) is explained as a result of the small signal-to-noise ratio based on the fact that, in the Schroer et al.[9] experiment, N_β has a much smaller peak height than does N_γ. Both groups agree that the signal at −283 ppm is from the ^{15}N labeled N_3^- at N_t but disagree on its origin: for Schroer et al.,[9] it is from the unreacted N_3^- present in the reaction mixture, while, for Butler et al.,[8] it arises from the decomposition of N_5^-.

In an exhaustive follow-up study, Butler and co-workers[10] reexamined the CAN mediated N-dearlyation of N-*p*-anisylazoles in order to firmly establish the presence of N_3^- ^{15}N labeled at the N_c position and rule out the possibility that the NMR signal that they assigned to N_3^- in their first experiment is not due to 4-$MeOC_6H_4N_3$, as Schroer and co-workers[9] have claimed. Using both mono- and dilabeled 4-$MeOC_6H_4N_5$, they have shown that the signal that they assigned to the ^{15}N labeled N_c of N_3^- is a strong singlet and a weak overlapping doublet, a pattern which could only arise from neighboring symmetry equivalent ^{15}N nitrogen atoms as in N_3^-. Furthermore, they demonstrate that the strong singlet for N_c is particularly significant, since it can arise for N_3^- only from the decomposition of HN_5/N_5^-, and not from any ^{15}N labeled Ar−N_3 fragments. Butler and co-workers[10] showed that the N_β ^{15}NMR signal of 4-$MeOC_6H_4N_3$ is more intense than N_γ, which invalidates the claim of Schroer et al.[9] that the signal due to N_β is not observed in the previous Butler et al.[8] experiment because of its low intensity. It is shown that the Schroer et al.[8] observation that N_β of $MeOC_6H_4N_3$ has twice as strong a ^{15}NMR signal as N_γ is an artifact due to the contaminant Ar−N_3. As for the Schroer et al.[9] claim that the −248 ppm ^{15}N NMR signal of N_3^- ^{15}N labeled at N_t is from the residual N_3^- from the reaction to synthesize $MeOC_6H_4N_5$ rather than decomposition of HN_5/N_5, Butler et al.[10] note that it is unlikely that it could only appear after the CAN treatment, since had it been a contaminant its signal should have been present throughout the experiment.

Both aspects of NMR spectra in the gas phase, namely, the vector chemical shifts[13,14] and the scalar spin−spin coupling constants,[15,16] can be very accurately described by coupled-cluster theory. Calculations of the former have been shown to be accurate to ∼1−2 ppm for ^{13}C,[15] with calculations of the latter accurate to ∼5 Hz for a variety of molecules.[15,16] However, a similar calibration for ^{15}N shifts, required to address the N_5^- problem, has not been made. Furthermore, the observation of the shifts in solution is subject to dramatic changes compared to the gas phase. Hence, to offer a meaningful theoretical comparison, suitable estimates of the chemical shifts in solution have to be made. For the scalar term, though, solution effects have generally been found to be less significant, so their observation can offer a more reliable assessment of the potential observation of the pentazole anion.

Computational Details

The UF and MAB versions[17,18] of the ACES II program are used for all calculations. The geometry optimizations are performed using single- and double-excitation coupled-cluster methods that include noniterative triple excitations (CCSD(T)) with basis sets:[19−21] aug-cc-pVQZ for N_5^-, cc-pVQZ for N_5H, N_3^-, NO_3^-, NH_4^+, N_2, N_2O and at cc-pVTZ level for CH_3NO_2. The ^{15}N NMR shieldings are computed at the CCSD(T) level with gauge-including atomic orbitals (GIAOs)[11,12] using cc-pVTZ, cc-pVQZ, and pz3d2f basis sets.[22] Experimental absolute shielding of nitromethane standard (135.8 ppm) was used as the reference to obtain the calculated chemical shifts.

Results and Discussion

Prior knowledge of the expected accuracy of the computed chemical shifts is a prerequisite for helping experimental assignments or making new assignments. It is established by comparing computed results with a series of experimentally known chemical shifts. For example, the CCSD(T)/pz3d2f level has been shown to have a standard deviation of ±1 ppm for ^{13}C chemical shifts,[23] but no such data for ^{15}N shifts are

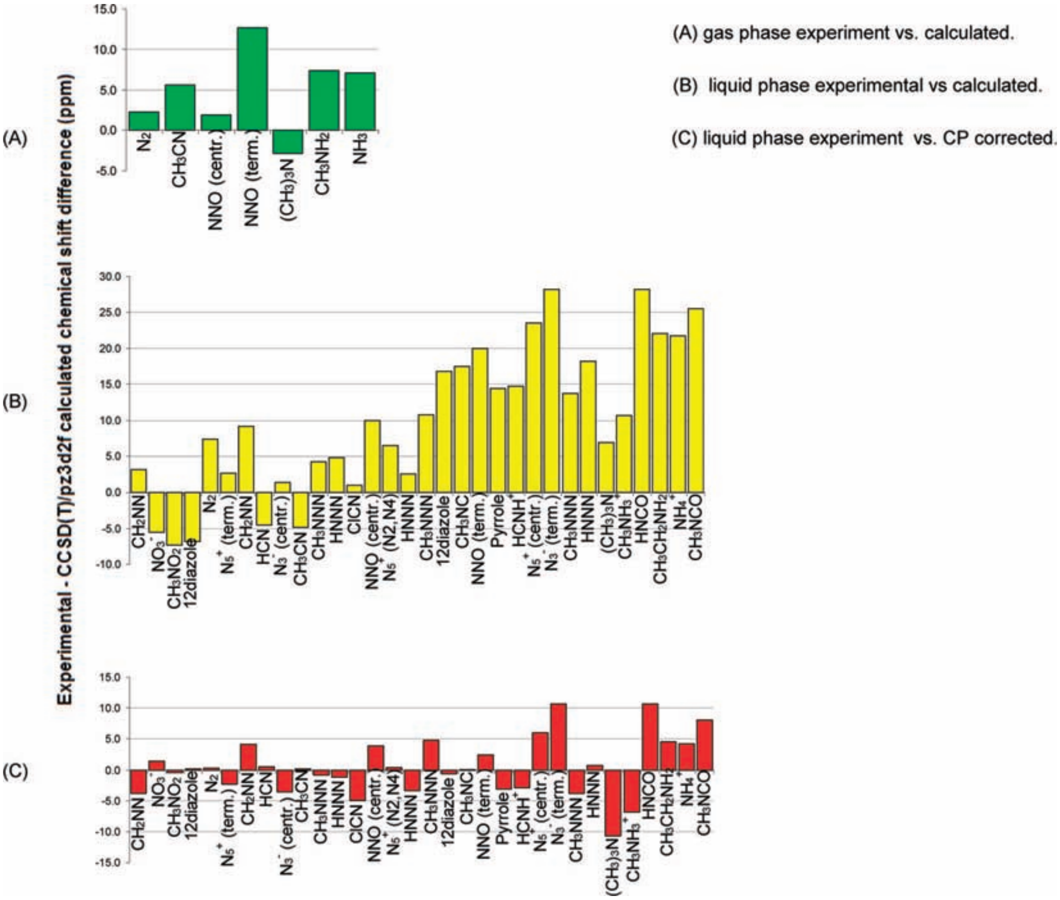

Figure 2. Computed absolute shieldings vs chemical shift difference between gas-phase computed results and experiment.

available. Hence, an exhaustive study to establish the accuracy of the computed ^{15}N shifts was performed and further details of the error bars quoted above will be published elsewhere.[24] However, a selected set of computed chemicals shifts at the CCSD(T)/pz3d2f level, which are of interest in this context, are shown in Table 1 along with the experimental values. Those that are highlighted in boldface in Table 1 are well established gas-phase experimental values for the respective molecules. They are part of the selection used in order to calibrate the basis set and the theoretical method and to establish error bars (we have not used data from the two disputed experiments to establish error bars). There are no practically significant variations among the results for the three basis sets, and the cc-pVTZ and cc-pVQZ results converge toward the pz3d2f results. The situation with ^{15}N shifts is more complex than that found for ^{13}C NMR. For example, among the set of benchmark molecules, only the N_2 and the central atom of N_2O CCSD(T)/pz3d2f ^{15}N chemical shifts are within ±1 ppm from gas-phase measurements. On the other hand, the computed shifts for NH_3 and the terminal atom of N_2O show much larger deviations: 7 (2%) and 12 (5%) ppm, respectively, from gas-phase experiments.

Furthermore, both Butler and Schroer et al.[8,9] experiments are conducted in the liquid phase. The ^{15}N chemical shifts are known to have a much more pronounced influence from the medium effects compared to ^{13}C shifts,[25] so a correction to account for the medium effects must be established. In Figure 2 (plots A and B), we have shown a plot of the deviation of computed data from experiment (both liquid- and gas-phase experimental data). We have noted that the errors of the computed results increase as the medium becomes more polar, and can be related to the absolute shielding, which is a measure of the polarity of the N atoms of interest. For example, when the N atoms are in a nonpolar bond as in N_2, the error in the gas-phase result is about 2 ppm, and when they are in a polar bond as in NH_3, the error is 7 ppm. When these two groups of N atoms are in polar solvents, the errors increase to 7 and 27 ppm, respectively. Another noteworthy feature is that, for negative absolute shieldings, the error can be either positive or negative depending upon whether the N atom is internally polarized (the error is negative as in HCN) or neutral (the error is positive as in N_2), and when the absolute shielding is positive, the error is always positive as well.

These observations further affirm that a correction must be applied to the CCSD(T)/pz3d2f results to account for medium effects, and the correction has to be chosen on the basis of the nature (internal polarity) of the nitrogen atom and the polarity of the medium. By analyzing the variations between the computed absolute shielding and the deviation of the corresponding good approximation, the lower and upper bound for the errors are 1 and 11 ppm for the absolute shielding in the range of 0−50 ppm and 7 and 28 ppm for absolute shielding in the range of 50 ppm and above. In Figure 2 (plot C), we show that the deviation of the computed solution-phase shifts from experiment with and without the correction, and note that the average deviation decreases from 12.6 to 3.6 ppm (±10 ppm maximum deviation) as a result of the correction applied to account for the influence of the medium. Details of a comprehensive study of CCSD(T) ^{15}N NMR shifts that lead to the error bars quoted above are published elsewhere.[24]

Having established the bounds for the errors in the computed gas-phase values, we are now in a position to assess the assignments of the two experiments in question. Purely from the point of view of considering the nature of the solvents used, especially CAN, the experimental medium is complex and highly polar and the errors in the computed values approach the upper limit. There is also quantitative evidence to support that assessment. Independent experiments show that the ^{15}N shift of NO_3^- in polar solvents can be as low as −17 ppm and as high as −5 ppm as the polarity of the medium decreases. Neither of the two experiments show any NMR signal higher than −10 ppm, which could be assigned to NO_3^-, supporting the assessment that the medium is highly polar.

As shown in Table 1 (labeled as condensed-phase (CP) corrected), the computed NMR shifts of N_5^- and NO_3^- are −6.5 and −5.5 ppm, respectively (both values include a −7 ppm correction). As we have noted earlier, the measured ^{15}N chemical shifts of NO_3^- can vary from −5 to −17 ppm depending on the temperature and the polarity of the medium. This seems to indicate that the computed NO_3^- shift matches observed shifts in less polar solvents. The computed value for N_c of N_3^-, −126.8 ppm, is in good agreement with the Schroer et al.[9] result (−133.5 ppm) though in less good agreement with the Butler et al.[10] 144 ± 3 ppm value for N_c. Both groups have reported similar values (−283,[8] −282.1,[9] and −281 ± 2[10] ppm) for N_t, which are in reasonable agreement with the computed value −291.6. We note that the computed shifts for N_5^+ and $MeOC_6H_4N_5$ are also in excellent agreement with measured values.

Let us first consider the computed shifts for N_5^- and NO_3^- and the conflicting assignments proposed. Both groups observe a ^{15}N NMR signal in the region of −10 ppm. As mentioned above, the computed shift for NO_3^- can vary greatly with polarity: experimentally from −11.5 to −4.0 ppm, but only NO_3^- falls in this range, except for pentazole itself. On the basis of the agreement shown by our corrected shifts of N_5^+ and $MeOC_6H_4N_5$ with experiment, we expect a similar agreement of computed and observed N_5^- shifts. This led us to conclude that the observed NMR signal in the −10 ppm region is indeed due to NO_3^- rather than N_5^-. As noted before, the chemical shifts for N_c and N_t of N_3^- are close to what is reported for their chemical shifts by both groups. The ^{15}N chemical shifts of $MeOC_6H_4N_3$ are also in the same region as N_3^-, further complicating the assignments. Nevertheless, Schroer et al.[9] assign the shifts in the first experiment to $MeOC_6H_4N_3$, and concluded that the N_3^- shifts should be −133.6 ppm (N_c) and −282.2 ppm (N_t). Schroer et al.[9] also question the presence of N_3^- in a highly oxidative medium such as CAN. Despite these above-mentioned coincidences, the presence of the centrally ^{15}N labeled N_3^- is a key piece of evidence that supports the presence of N_5^-, though of too short a lifetime to be seen in NMR.

To resolve this remaining question, we suggest an analysis of the scalar NMR spin−spin coupling constants. The NMR spin−spin couplings constants that would help to unambiguously resolve the disputed evidence and establish whether the N_5^- is formed are $^1J(^{15}N^{17}O)$ of NO_3^- and $^1J(^{15}N_t{}^{15}N_c)$ of N_3^-. The computed values for those couplings for qz2p[22] and pz3d2f basis sets are shown in Table 2. Both basis sets give the same results, indicating that they are essentially converged (the qz2p basis has been previously calibrated and shown to be well suited for NMR coupling constants,[16] and the pz3d2f basis set is used to maintain consistency with shift calculations). Also shown in Table 2 are the computed $^1J(^{15}N^{15}N)$ coupling constants of $MeOC_6H_4N_3$ (and $C_6H_5N_3$), and these coupling constants are also relevant to resolve the disputed shift assignments. Unlike chemical shifts, the spin−spin couplings are less sensitive to the medium effects, and it is our experience that their computed EOM-CCSD values are accurate to within ±5 Hz. However, we must note that the comparatively large number of nuclei in $MeOC_6H_4N_3$ constrains the quality of the basis set that we can use for the spin−spin coupling constant calculations and the reported values have larger uncertainties than those for the N_3^- (see footnote of Table 2 for more details). As we can see from Table 2, the computed $^1J(^{15}N_2{}^{15}N_3)$ of $MeOC_6H_4N_3$ and $^1J(^{15}N_t{}^{15}N_c)$ are nearly identical and it would be impossible to unambiguously assign the observed NMR based on the magnitude of the coupling constant alone. However, due to the two symmetry equivalent terminal nitrogen atoms, the NMR signal of the central nitrogen of the N_3^- anion should show the characteristic doublet triplet pattern, while such splitting pattern is not possible for $MeOC_6H_4N_3$. Thus, further experimental observations to measure the relevant coupling constants would resolve the disputed assignments and conclusively establish whether the N_5^- had been made in solution.

TABLE 2: $^1J(^{15}N^{17}O)$ and $^1J(^{15}N^{15}N)$ (in Hz) Spin−Spin Coupling Constants of NO_3^-, N_3^-, and N_5H (FC, PSO, SD, and DSO Are Fermi-Contact, Paramagnetic Spin-Orbit, Spin-Dipole, and Diamagnetic Spin-Orbit Contributions) (Only Couplings That Are >1 Hz Are Shown)

	coupling	FC	PSO	SD	DSO	total
NO_3^-	$^1J(^{15}N^{17}O)$	−34.4	−7.6	−0.2	0.1	−42.1
		−32.5	−7.7	−0.3	0.1	−40.4
	$^1J(^{17}O^{17}O)$	1.6	−7.3	1.7	0.0	−4.0
		1.5	−7.4	1.7	−0.1	−4.1
$N_tN_cN^-$	$^1J(^{15}N_t{}^{15}N_c)$	−12.3	−2.0	0.6	0.0	−13.7
		−11.2	−2.0	0.6	0.0	−12.6
	$^2J(^{15}N_t{}^{15}N_t)$	−3.6	2.7	3.4	−0.1	2.4
		−3.8	2.9	3.5	−0.1	2.7
N_5H[a]	$^1J(^{15}N_1{}^1H)$	−113.1	−0.7	−0.2	−0.5	−114.4
	$^1J(^{15}N_1{}^{15}N_2)$	−13.3	−3.3	0.1	0.0	−16.5
	$^2J(^{15}N_2{}^1H)$	−10.3	0.7	0.0	0.3	−9.3
	$^1J(^{15}N_2{}^{15}N_3)$	−13.2	−4.8	0.5	0.0	−17.5
	$^1J(^{15}N_3{}^{15}N_4)$	−15.9	−4.1	0.3	0.0	−19.7
$C_6H_5N_3$[b]	$^1J(^{15}N_1{}^{15}N_2)$	−12.5	−1.8	1.8	0.0	−12.4
	$^1J(^{15}N_2{}^{15}N_3)$	−14.1	−2.3	0.0	0.1	−11.7
$MeOC_6H_4N_3$[b]	$^1J(^{15}N_1{}^{15}N_2)$	−12.8	−1.9	0.5	0.0	−14.1
	$^1J(^{15}N_2{}^{15}N_3)$	−12.6	−1.8	1.0	0.0	−13.4

[a] The N_5H coupling constants are obtained with the qz2p basis set[23] only. [b] Coupling constant calculations of $MeOC_6H_4N_3$ (and $C_6H_5N_3$) are not as straightforward as the others because of their size: there are 28, 64, and 228 FC, PSO, and SD perturbations, respectively. As a result, it is not practically viable to use the same basis set consistently for all three components or to use the qz2p basis set for all of the atoms. It has been shown previously that the basis set requirements for the PSO and SD terms are not as severe as those for the FC term and we could use smaller basis sets to obtain their values.[14] We have taken advantage of the fact the basis set we use for the other atoms except for the N_3 moiety can be of smaller size, since their effects on the spin−spin couplings on N have been shown to be smaller. The possibility of saturating the N_3 moiety by using ghost atom basis sets on nitrogen atoms is also considered, and we observed that one could use a smaller basis set for nitrogen when there are ghost atom basis functions in their vicinity. The FC results reported in the table use the tzp basis set on N and dzp basis set on two ghost atoms directly bonded to two terminal nitrogen atoms of 0.5 Å distance. We use a dz quality basis set for all of the other atoms. The PSO and SD terms are computed with a dzp basis set on N while keeping the basis sets on other nuclei the same as those for the FC term (the basis sets used here are developed by Ahlrichs and co-workers[23]).

Upon request from us, Prof. Butler extracted the observed ^{15}N spin−spin coupling constants of N_3^- and $MeOC_6H_4N_3$ from their spectra.[26] Those are |13 ± 0.5| and |11.4 ± 0.5| Hz in CD_3OD-D_2O for N_3^-, with and without Ce^{3+}, respectively, which are in near perfect agreement with our prediction for N_3^-. The observed values for $MeOC_6H_4N_3$ are reported to be |14.0| and |7.0| Hz for $^1J(^{15}N_1{}^{15}N_2)$ and $^1J(^{15}N_2{}^{15}N_3)$, respectively. While the computed value for $^1J(^{15}N_1{}^{15}N_2)$ also shows near perfect agreement with the observed value, theory differs by as much as 6 Hz for $^1J(^{15}N_2{}^{15}N_3)$. [Prof. Butler in a private communication commented on the disagreement between the computed and measured value of $^1J(^{15}N_2{}^{15}N_3)$. On the basis of his comment, "the synthesis of ^{15}N labeled samples like these is extremely difficult and there are none in the literature. We only happened on these samples by accident as side byproducts from our work; we were not trying to make them and we did not pursue them or get spectra of pure samples", we conclude that in this case both the theoretical and experimental values have large uncertainties and should be reevaluated. Also, for $Ph-N_3$, the calculated $^1J(^{15}N_1{}^{15}N_2)$ and $^1J(^{15}N_2{}^{15}N_3)$ values are 12.4 and 11.7 Hz, with the latter being smaller than the former, which is at least in line with the crude experimental *J* values for $^1J(^{15}N_2{}^{15}N_3)$.] The combination of the computed and measured spin coupling constants plus the observed characteristic doublet triplet pattern for the central nitrogen offers substantial evidence to support the presence of centrally ^{15}N labeled N_3^- which could only be possible had N_5^- also been present. [Our preliminary data was presented at a meeting sponsored by AFOSR on September 15, 2006, at the Locker Hydrocarbon Research Institute and proposed measuring the spin−spin coupling constants as a means of resolving the conflicting assignments and predicted both $^1J(^{15}N^{17}O)$ of NO_3^- and $^1J(^{15}N^{t15}N^c)$ of N_3^- as well as N_5H coupling constants. Our results were made available to both groups.]

Summary and Conclusions

To summarize, high-level coupled-cluster theory has been applied to the chemical shifts for ^{15}N containing species in the gas phase to calibrate the tool for such applications. Augmented with an empirical estimate of polarity based solution effects on ^{15}N shifts in solutions, estimates of chemical shifts accurate to ±10 ppm are obtained. These provide results that support the assignments of N_3^- central and terminal shifts that support the experimental assignments for N_3^- observed in its CAN solution by Schroer et al.[9] and Butler et al.[8] We predict that N_5^- will have a gas-phase value of −13.5 ppm and a solution value of −6.5 ppm. We also predict the scalar couplings for all relevant species, and conclude that, for N_3^-, the predicted results fall ±1 Hz from those observed. Due to the short lifetime of N_5^- in solution, perhaps other spectroscopic techniques could be used to spectroscopically characterize the transient N_5^- in the experiment.

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