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Methylnitrene: Theoretical Predictions of Its Molecular Structure and Comparison with the Conventional C–N Single Bond in Methylamine

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Abstract: Ab initio quantum mechanical methods have encountered difficulties in predicting the short C–N bond distance in methylnitrene, particularly in comparison with the normal C–N single bond distance in methylamine. It is shown that the origin of the problem lies with unexpected dependencies on basis set and the treatment of electron correlation. Specifically, correlation effects *shorten* the predicted C–N bond distance in CH_3N. An ab initio bond distance within 0.01 Å of experiment is finally achieved by using configuration interaction including all single and double excitations (CISD) in conjunction with a basis set of quality quadruple-ζ plus double polarization plus f functions on the C and N atoms (QZ+2P+f).

Much of the intellectual challenge to the science of chemistry is related to the fact that the subject is constantly changing. The simple molecule methylnitrene

$$CH_3{-}\underset{\cdot\cdot}{\dot{N}}\cdot$$

provides an example of this sort of metamorphosis. Among the general category of nitrenes, the arylnitrenes (e.g., phenylnitrene[1]) are the best characterized.[2] However, as early as 1970, Berry[3] suggested that the alkylnitrenes should have electronic states similar to those of the NH diatomic molecule, which has been rather well-characterized by spectroscopists.[4]

The first ab initio theoretical study of the different electronic states of methylnitrene was reported in 1974 by Yarkony and Rothenberg (YSR).[5] YSR confirmed in reasonable detail the qualitative prediction of Berry[3] that the $^3A_2$, ^1E, and $^1A_1$ electronic states of CH_3N are analogous to the known $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ states of the diatomic NH molecule. However YSR explicitly stated "One problem we have intentionally avoided is that of why CH_3N has been so difficult to isolate in the laboratory". A possible reason for the short life[3] of CH_3N might be its rapid isomerization to methyleneimine.

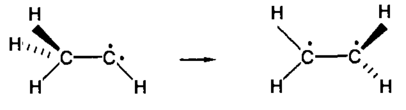
$$CH_3N \rightarrow CH_2{=}NH \qquad (1)$$

During the period 1974–1980, no experimental evidence for the existence of alkylnitrenes appeared, beyond the 1960's matrix-isolation electron spin resonance (ESR) spectra of Wasserman, Smolinsky, and Yager[6] and the seldom-noticed tentative UV spectrum of CH_3N reported by Franken, Perner, and Bosnali[7] in 1970. This absence of evidence confirmed many[8,9] in the early view[10-12] that the existence of alkylnitrenes as stable minima on potential energy hypersurfaces was tenuous at best.

An important theoretical discovery during the late 1970's was that the triplet states of vinylidenes and carbenes undergo 1,2 hydrogen shifts, i.e.

(2)

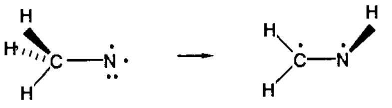
and



(3)

very slowly.[13] Specifically, the activation energies for the unimolecular processes (2) and (3) are of the order of 50 kcal/mol.

With this background in mind, in 1980 Demuynck, Fox, and Yamaguchi, (DFYS)[14] undertook the first ab initio study of the unimolecular rearrangement of ground state triplet methylnitrene, i.e.



(4)

The result of this theoretical study was the prediction of an activation energy in excess of 40 kcal/mol. The title of the DFYS paper clearly reflected their finding—Triplet Methylnitrene: An Indefinitely Stable Species in the Absence of Collisions.

Striking confirmation of the theoretical prediction by DFYS was given in 1984 in the important experimental paper by Carrick and Engelking,[15] representing the first unequivocal spectroscopic identification (via the electronic UV emission spectrum) of methylnitrene. In 1987 Ferrante[16] provided the first infrared spectrum of CH_3N, trapped in a solid nitrogen matrix at 10 K. Later the same year Carrick, Brazier, Bernath, and Engelking[17] (CBBE) were able to report the first experimental molecular structure for methylnitrene. In the most recent experimental paper

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† Contribution CCQC No. 39.

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Chappell and Engelking[18] have provided much new spectroscopic information relating to the $\tilde{A}\ ^3E$ -$\tilde{X}\ ^3A_2$ ultraviolet emission spectrum. Thus in a period of 4 years, the methylnitrene molecule has gone from the "tenuous" category to what must now be considered the best characterized of all known organic nitrenes.

The Experimental Molecular Structure of CBBE[17]

In many respects, the above story represents an ideal example of the constructive interaction between theory and experiment: (a) theory insists that an unknown molecule should be stable[14] and (b) experiment confirms,[15] opening up a new sub-branch of chemistry. Unfortunately for theory, this story has one bittersweet aspect.

Using a double-ζ (DZ) basis set in conjunction with restricted self-consistent-field (SCF) theory, DFYS[14] predicted the following equilibrium structure for triplet CH_3N: r_e(C–N) = 1.471 Å, r_e(C–H) = 1.084 Å, Θ_e(HCN) = 110.0°. On the basis of hundreds of comparisons with experiment for closed-shell molecules, the DZ SCF level of theory was expected to provide reasonably reliable molecular structures.[19]

The analysis of Engelking and co-workers[17] provides a rather different C–N bond distance, namely 1.411 Å. If the C–H distance is assumed to be 1.09 Å (in reasonable agreement with DFYS[14]), then the HCH angle is found in the experimental analysis to be 106.7°, in disappointing agreement with the 108.9° predicted from theory by the Berkeley group.

At least one theoretical study of CH_3N subsequent to that of DYFS should be noted here, the 1983 work of Pople, Raghavachari, Frisch, Binkley, and Schleyer[20] (PRFBS). Using the unrestricted SCF level of theory in conjunction with their 6-31G* basis set (roughly comparable to adding d functions to the C and N atoms in the DZ basis of DFYS[14]), their equilibrium C–N distance for

$$CH_3\text{—}\underset{..}{\dot{N}}\cdot$$

is 1.433 Å, much closer to the 1987 experiment by CBBE.[17] However, as noted by Chappell and Engelking,[18] PRFBS predict the conventional C–N single bond distance in methylamine (CH_3NH_2) to be 1.453 Å, or 0.010–0.020 Å less than experiment.[21-24] Thus PRFBS account theoretically for only 0.020 Å of the experimental C–N bond distance difference of 0.051–0.063 Å between CH_3N and CH_3NH_2. Thus Chappell and Engelking[18] make the seemingly reasonable statement: "so far, no calculation has accounted for the short C–N bond in CH_3N".

The purpose of the present paper is to attempt to account for the differences between the experimental CH_3N ground-state structure of Carrick, Brazier, Bernath, and Engelking[17] (CBBE) and the three existing theoretical studies.[5,14,20] Quantum chemistry has made sufficient progress since 1983 that it should be possible to make a definitive theoretical prediction of the molecular structure of methylnitrene. We concur with Chappell and Engelking[18] that the difference between C–N bond distances in CH_3N and CH_3NH_2 is critical in qualitatively understanding the bonding in methylnitrene. Therefore, we have carried out parallel theoretical studies of the conventionally single-bonded species methylamine.

Basis Sets

The smallest basis set used in this research was the standard double-ζ plus polarization (DZ+P) set of Huzinaga[25] and Dunning.[26] Thus every level of theory presented here exceeds those earlier reported.[5,14,20] Specifically the C,N(9s5p1d/4s2p1d), H(4s1p/2s1p) set was chosen with polarization function orbital exponents of $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_p(H) = 1.0$. Hydrogen primitive gaussian s functions were scaled by a factor of $(1.2)^2 = 1.44$ in the DZ+P basis set. A triple-ζ plus polarization (TZ+P) basis, designated C,N(9s5p1d/5s3p1d), H(4s1p/3s1p), differs only in the more flexible contraction of the Huzinaga primitive sets.

Also used extensively in this work was a quadruple-ζ plus double polarization (QZ+2P) basis set. The (sp) primitive sets for C and N are the (11s7p) sets of van Duijneveldt,[27] and these have been contracted to (6s4p). The sp contractions have attempted to maintain maximum flexibility in the valence region, i.e., the s contractions are (611111) [the six primitive gaussians with the highest orbital exponents are taken in a fixed 1s-like linear combination] and the p contractions (4111). Similarly the hydrogen s basis set is (6s/4s). The polarization functions added to this QZ basis were[27] $\alpha_d(C,N) = 1.5, 0.35$ and $\alpha_p(H) = 1.4, 0.25$. All six cartesian d-like functions (x^2,y^2,z^2,xy,xz, and yz times $e^{-\alpha r^2}$) were used throughout. The technical designation for the QZ+2P basis is thus C,N(11s7p2d/6s4p2d), H(6s2p/4s2p).

In the largest basis set used here, a set of ten f-like functions ($x^3,y^3,z^3,x^2y,x^2z,xy^2,y^2z,xz^2,yz^2$, and xyz multiplied by $e^{-\alpha r^2}$) was added to each atom. Following Frisch, Pople, and Binkley,[28] the gaussian orbital exponents for these functions were $\alpha_f(C) = 0.8$ and $\alpha_f(N) = 1.0$. This largest basis set may be labeled QZ+2P+f and includes 110 contracted gaussian functions for CH_3N and 130 functions for CH_3NH_2. The technical designation for the QZ+2P+f basis is C,N(11s7p2d1f/6s4p2d1f) and H(6s2p/4s2p).

Self-Consistent-Field (SCF) Results

Single configuration SCF gradient methods[29] were used to optimize the molecular structures of the ground states of methylnitrene (CH_3N)

$$\tilde{X}\,^3A_2 \qquad 1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1^2 2e^2 \tag{5}$$

and methylamine (CH_3NH_2)

$$\tilde{X}\,^1A' \qquad 1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 1a''^2 6a'^2 7a'^2 2a''^2 \tag{6}$$

The results of these structural predictions are summarized in Table I.

The predicted SCF molecular structures for CH_3N and CH_3NH_2 are not strongly dependent on basis set. For example, the C–N distance in methylnitrene decreases by only 0.009 Å in going from DZ+P SCF to QZ+2P+f SCF. For methylamine, the analogous basis set variation is even less, 0.004 Å. The changes in HCH bond angles are very small as a function of basis set, namely 0.1° or less.

Before moving on to a discussion of the critical C–N bond distances, let us examine more carefully the experimental data. CBBE[17] state that the CH_3N bond distance is 1.4106 ± 0.0009 Å. This determination was based on experimental rotational constants B for CH_3N and CD_3N and the *assumption* that the CH bond distance is 1.09 Å. It should be noted that a substitution structure is not precisely the same concept as the equilibrium geometry predicted here theoretically.[30] Our own assessment is that the experimental r(C–N) = 1.4106 Å should not be expected to lie closer than ±0.01 Å to the true r_e(C–N) for methylnitrene.

There are at least three experimental values for the C–N bond distance in methylamine. The 1971 structure of Takagi and Kojima[22] incorporates earlier microwave studies[21] and concludes that r(C–N) = 1.471 ± 0.002 Å. The electron diffraction work (1965) by Higginbotham and Bartell[23] finds r(C–N) = 1.465 ± 0.002 Å. A more recent (1986) electron diffraction study[24] by Iijima, Jimbo, and Taguchi gives 1.472 ± 0.003 Å for the C–N

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Table I. Self-Consistent-Field (SCF) Predictions of the Molecular Structures of Methylnitrene and Methylamine

basis set	E (hartrees)	r_e(CN) (Å)	θ_e(HCH) (deg)	Δr_e(CN) (Å) [CH_3NH_2-CH_3N]
		$\tilde{X}^3A_2$ CH_3N		
DZ+P	-94.01645	1.440	108.8	
TZ+P	-94.01829	1.437	108.8	
TZ+2P	-94.02168	1.434	108.8	
QZ+2P	-94.03146	1.432	108.9	
TZ+2P+f	-94.02374	1.432	108.8	
QZ+2P+f	-94.03283	1.431	108.8	
experiment[a]		1.411 ± 0.001	106.7 ± 0.7	
		$\tilde{X}^1A'$ CH_3NH_2		
DZ+P	-95.23922	1.456	107.3, 108.0	0.016
TZ+P	-95.24115	1.456	107.3, 108.0	0.019
TZ+2P	-95.24622	1.456	107.4, 108.1	0.022
QZ+2P	-95.25751	1.454	107.4, 108.1	0.022
TZ+2P+f	-95.24879	1.452	107.4, 108.0	0.020
QZ+2P+f	-95.25945	1.452	107.4, 108.0	0.021
experiment		1.471 ± 0.002[b] 1.465 ± 0.002[c]	108.0 ± 0.5[b]	0.058 ± 0.02[a-d]

[a] Reference 17. [b] Reference 22. [c] Reference 23. [d] This error bar estimated by present authors; see text.

bond distance. Again none of these studies results in a value of r_e. *Our assessment* is that the average of the three measurements, namely 1.469 Å, should not be expected to lie closer than ±0.01 Å to the true r_e(C–N) for methylamine.

Therefore, we conclude that, even if one accepts the existing experimental analyses[17,22,23] for CH_3N and CH_3NH_2, the most they say about the true r_e values is

$$r_e(CH_3N) = 1.411 \pm 0.01 \text{ Å} \quad (7)$$

$$r_e(CH_3NH_2) = 1.469 \pm 0.01 \text{ Å}$$

Thus the difference between the C–N bond distances in methylnitrene and methylamine is at best only known to be Δr_e(C–N) = 0.058 ± 0.02 Å.

Even with the relatively loose error bars suggested here, Table I shows that restricted Hartree–Fock theory does not reproduce the experimental difference between C–N bond lengths for CH_3N and CH_3NH_2. Each of the basis sets properly predicts that the methylnitrene distance is shorter than that for methylamine. And the methylamine C–N SCF bond distance with the largest basis set (QZ+2P+f) lies shorter than experimental, as generally expected as one approaches the Hartree–Fock limit.[19]

What is surprising in Table I is that for CH_3N the near-Hartree–Fock C–N bond distance, 1.431 Å, is still 0.02 Å longer than experiment. Thus the difference in C–N distances between CH_3N and CH_3NH_2 is predicted to be 0.021 Å (QZ+2P+f SCF), much less than the experimental 0.058 ± 0.02 Å. Even if one takes the lower estimated limit 0.038 Å, there still appears to be a significant error at the Hartree–Fock level of theory.

Configuration Interaction (CI) Molecular Structures

The CI wave functions included all single and double excitations with respect to the SCF reference configurations (5) and (6). For methylnitrene (a triplet ground state) only the Hartree–Fock interacting configurations[31] were included. All CISD wave functions were determined within the confines of C_s symmetry. For CH_3N, the numbers of configurations included in CISD were 16696 (DZ+P basis), 27944 (TZ+P), 76519 (QZ+2P), and 118749 (QZ+2P+f). For methylamine the sizes of CISD were 26586 (DZ+P), 43732 (TZ+P), and 122437 (QZ+2P).

Comparison of the SCF (Table I) and CISD (Table II) molecular structures shows that the structure of methylnitrene is indeed atypical. Stable closed-shell molecules (methylamine is a good example) virtually always show bond distance increases when electron correlation is taken into account.[19] However, a mixed picture emerges for CH_3N. With the DZ+P basis set, CISD increases the SCF C–N bond distance by only 0.002 Å. With the TZ+P basis set, the same bond lengthening is even less, 0.0004 Å. And with the TZ+2P basis set, the C–N bond distance actually *decreases*, by 0.002 Å. With the larger QZ+2P basis, the decrease in bond distance due to electron correlation is greater, 0.004 Å. Adding f functions to the QZ+2P basis set has a profound relative impact, with the effect of correlation now being to reduce the C–N distance by 0.008 Å. This surprising behavior as a function of level of theory, culminating in a decrease (due to correlation effects) in the bond distance, would appear to identify methylnitrene as having a peculiar molecular structure.

Table II. Single and Double Excitation Configuration Interaction (CISD) Predictions of the Molecular Structure of Methylnitrene and Methylamine

basis set	E (hartrees)	r_e(CN) (Å)	θ_e(HCH) (deg)	Δr_e(CN) (Å) [CH_3NH_2-CH_3N]
		$\tilde{X}^3A_2$ CH_3N		
DZ+P	-94.28170	1.442	108.7	
DZ+2P	-94.30219	1.438	108.5	
TZ+P	-94.29968	1.438	108.7	
TZ+2P	-94.31681	1.432	108.7	
TZ+2P+f	-94.34004	1.425	108.6	
QZ+P	-94.31551	1.432	108.8	
QZ+2P	-94.33125	1.427	108.6	
QZ+2P+f	-94.35393	1.424	108.7	
experiment[a]		1.411 ± 0.001	106.7 ± 0.7	
		$\tilde{X}^1A'$ CH_3NH_2		
DZ+P	-95.56508	1.466	107.3, 108.0	0.024
TZ+P	-95.58362	1.464	107.4, 108.1	0.026
TZ+2P	-95.60551	1.465	107.4, 108.1	0.033
QZ+2P	-95.62176	1.461	107.3, 108.1	0.034
experiment		1.471 ± 0.002[b] 1.465 ± 0.002[c]	108.0 ± 0.5[b]	0.058 ± 0.02[a-d]

[a] Reference 17. [b] Reference 22. [c] Reference 23. [d] This error bar estimated by present authors; see text.

At the highest level of theory (QZ+2P CISD) applied to both molecules, the C–N distance in methylnitrene is 1.427 Å or 0.016 Å longer than experiment. Our earlier discussion indicated that the experimental C–N distance (obtained from rotational constants for CH_3N and CD_3N) could lie 0.01 Å away from the true equilibrium r_e value. Thus the absolute agreement between theory and experiment for this bond distance is probably acceptable.

But what about the *difference* between methylnitrene and methylamine bond distances? With the DZ+P basis set the SCF and CISD bond distance differences are 0.016 and 0.024 Å, respectively. Thus correlation effects are moving things in the right direction. With the TZ+P basis, the analogous differences in C–N bond distances are 0.019 (SCF) and 0.026 Å (CISD). The TZ+2P basis predicts the differences in distances between CH_3N and CH_3NH_2 to be 0.022 (SCF) and 0.033 Å (CISD). Finally, the QZ+2P set predicts differences of 0.022 (SCF) and 0.034 Å (CISD). The last result, 0.034 Å (QZ+2P CISD), is beginning to approach the experimental range 0.038–0.078 Å.

For the CH_3N molecule only, a CISD structural optimization was carried out with the largest basis set, QZ+2P+f. A reduction of the C–N distance by 0.004 Å is seen (Table II, Figure 3) due to f functions. This final theoretical structure is compared to experiment in Figure 3. For the C–N bond distance, theory (1.4236 Å) is finally in acceptable agreement (0.013 Å) with experiment (1.411 Å). What remains a bit surprising is that the QZ+2P+f CISD bond angle (108.7°) is still 2.0 ± 0.7° larger than experiment. Furthermore, examination of Table II shows that the ab initio HCH angles are quite insensitive to the level of theory applied. In fact, the entire theoretical range of HCH angles for CH_3N is 108.5–108.7°. Thus it is possible that the methyl group in CH_3N might be a bit less strongly pyramidal than concluded by CBBE.[17]

To what degree can we pinpoint the contributors to a proper description of the C–N bond distance in CH_3N? With a simple DZ basis set (no polarization functions at all) the CISD bond distance is 1.493 Å, more than 0.08 Å too long. The DZ+P basis (one set of polarization functions) decreases this distance by 0.051

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(31) Bunge, A. *J. Chem. Phys.* **1970**, *53*, 20. Bender, C. F., Schaefer, H. F. *J. Chem. Phys.* **1971**, *55*, 4798.

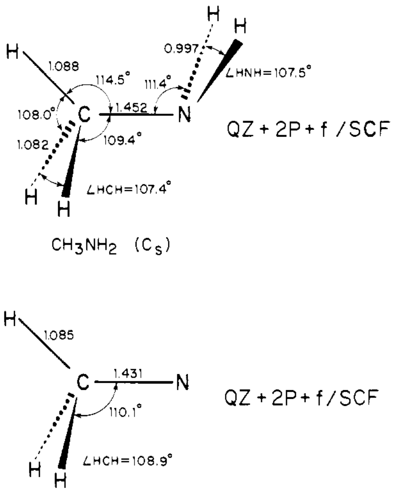

Figure 1. Ab initio self-consistent-field (SCF) equilibrium geometries for methylnitrene and methylamine with the largest basis set used here. The quadruple-ζ plus double polarization plus f functions (QZ+2P+f) basis set is described in the text. All bond distances are given in Å.

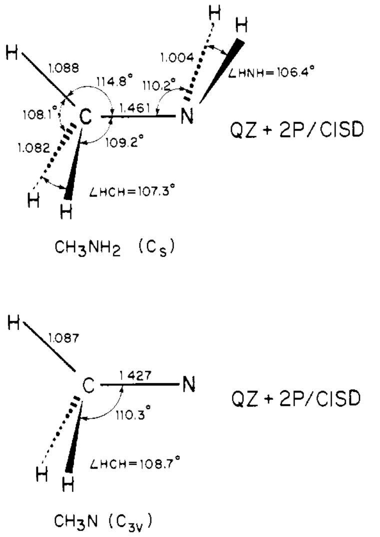

Figure 2. Equilibrium geometries for methylnitrene and methylamine from the configuration interaction method including all single and double excitations (CISD). The quadruple-ζ plus double polarization (QZ+2P) basis set was the largest with which the structure of methylamine was optimized. As seen in Figure 3, the CISD structure of CH_3N was optimized with a larger basis set.

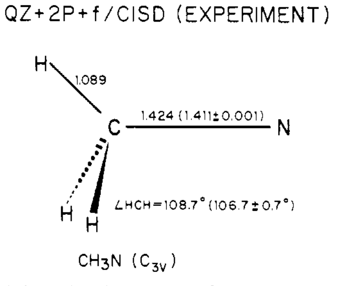

Figure 3. The highest level theoretical prediction of the molecular structure of methylnitrene. In parentheses is the experimental structure of Carrick, Brazier, Bernath, and Engelking.[17]

Å. Addition of a second set of polarization functions (DZ+2P) is seen in Table II to result in a further decrease in r_e(C–N) of 0.004 to 1.438 Å.

If one takes as a base line the DZ+P CISD result, Table II allows us to see the effects of increasing the C,N(sp) and H(s) atomic basis sets. Going from DZ+P to TZ+P reduces r_e(C–N) by 0.004 Å, and going from TZ+P to QZ+P gives an even larger decrease, 0.006 Å. Finally QZ+P → QZ+2P gives a Δr_e of 0.005, while QZ+2P → QZ+2P+f yields the final difference of 0.004 Å. One concludes that all of these basis set enhancements are significant and that none can be neglected.

Concluding Remarks

The present study establishes that Hartree–Fock theory is not capable of reproducing the large C–N single bond distance difference (0.058 Å) between

$$CH_3-\underset{\cdot\cdot}{\dot{N}}\cdot$$

and CH_3NH_2. This is because the effects of electron correlation on the C–N bond distance are opposite for these two molecules. For methylamine one sees the usual effect, namely that electron correlation increases the C–N bond distance.[19] This may be qualitatively understood in terms of correlation effects due to antibonding orbitals not occupied in the Hartree–Fock wave function. However, for CH_3N electron correlation decreases the C–N single bond distance. This may be qualitatively understood in terms of the electronically unsaturated character of CH_3N. That is, the lowest lying incompletely occupied orbitals of CH_3N are not antibonding (as with CH_3NH_2) but nonbonding. In fact, were the CH_3 group not locally saturated, these unfilled orbitals on nitrogen could be used to form two more bonds to carbon. The incorporation of these incompletely occupied SCF orbitals into the wave function via CISD decreases the C–N bond distance in CH_3N.

At the highest level of theory (QZ+2P CISD) used to predict the molecular structures of both molecules, the difference in C–N bond distances is still only 0.034 Å, as opposed to experiment 0.058 ± 0.02 Å. However, the addition of f functions decreases the C–N distance in CH_3N by another 0.004 Å. Higher order correlation effects (triple and quadruple excitations) are expected to further reduce the C–N distance.

For the closed-shell methylamine molecule we have explicitly shown that higher excitations increase the ab initio C–N distance. With the DZ+P basis set, a complete geometry optimization has been carried out for CH_3NH_2 with the coupled cluster single and double excitation (CCSD) method.[32] The CCSD method explicitly includes unlinked triple and quadruple excitations. The DZ+P CCSD methylamine C–N bond distance is 1.471 or 0.005 Å longer than predicted via CISD with the same basis set. It should be noted that connected (linked) triple excitations are not included in the CCSD model, although they have been shown to be important.

Adding the 0.004 Å decrease in CH_3N due to f functions to the 0.005 Å increase for CH_3NH_2 due to higher order correlation effects one obtains a widening of 0.009 Å in the difference between C–N bond distances for the two molecules. Adding this to the QZ+2P CISD prediction of 0.034 Å, one obtains a final ab initio difference in C–N bond distances 0.043 Å, compared to experiment 0.058 ± 0.02 Å.

From a theoretical point of view the only significant deficiency of this work is the restriction for triplet methylnitrene to single and double excitations from the Hartree–Fock reference function. However, it is possible to make some further remarks as to the likely importance of higher excitations for methylnitrene. With the QZ+2P CISD method the coefficients of the SCF reference configurations in the CI (at the predicted equilibrium geometries) are 0.954 for CH_3N and 0.950 for CH_3NH_2. However, for methylnitrene there are ten configurations (C_s symmetry, canonical SCF orbitals) with coefficients ranging from 0.0251 (the largest after C_0) to 0.0184. For methylamine the largest CI coefficient following the Hartree–Fock configuration is smaller, only 0.0183. These observations support our suggestion that orbital correlation effects are more important for CH_3N than CH_3NH_2.

The C–N bond distance comparison between CH_3N and CH_3NH_2 is obviously a pathological one for the more standard

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methods of ab initio quantum chemistry. However, it serves a purpose in warning one to be careful of situations in which correlation effects will have opposing ramifications. An obvious closely related problem would be the comparison between the C–C single bond distances of triplet methylcarbene (CH_3–CH) and ethane. Since experiments of the type reported by Engelking, Bermath, and co-workers[15,17,18] may soon be possible for triplet methylcarbene, one should make note of this problem in advance.

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Registry No. CH_2=NH, 27770-42-9; NCH_3, 74-89-5.

Electron-Transfer Reactions of Rhenium Carbonyl Radicals with *N*-Methylpyridinium Cations: Application of Marcus-Type Relationships

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Abstract: Rhenium carbonyl radicals, $Re(CO)_4L^{\bullet}$ (L = PMe_3 or P(O-*i*-Pr)$_3$), generated via flash photolysis at 22 °C of acetonitrile solutions of the corresponding dinuclear compounds, $Re_2(CO)_8L_2$, are observed to undergo electron transfer to substituted *N*-methylpyridinium cations. Reaction rates were measured by observing the disappearance of the transient absorption due to $Re(CO)_4L^{\bullet}$ or appearance of the absorption due to the product pyridinyl radical. Measured bimolecular rate constants, k_T, for electron transfer of the $Re(CO)_4PMe_3^{\bullet}$ radical fall in the range 2.6×10^9–4.0×10^6 M^{-1} s^{-1}. For $Re(CO)_4P(O\text{-}i\text{-}Pr)_3^{\bullet}$ the rate constants fall in the range 6.0×10^8–3.5×10^6 M^{-1} s^{-1}. Correlation of the relationship between log k_T and $-E_{p,c}$, the cathodic peak potential for reduction of the pyridinium cations, using both the Marcus/Agmon–Levine and Marcus quadratic equations led to values of the intrinsic barrier, $\Delta G^{*}(0)$, of approximately 3 kcal mol^{-1} for each rhenium radical. Application of the above-mentioned equations to extant transition-metal-mediated electron transfer returns *C* parameters (essentially the oxidation potential of the electron-donor species) in reasonable agreement with values estimated in other ways. The electron-transfer results provide insight into the differences in the electron-transfer and atom-transfer processes for the carbonyl radicals.

The chemistry of metal carbonyl radicals now encompasses a wide variety of reaction types, including disproportionation,[1] recombination,[2] ligand substitution,[3] and atom transfer.[2e,3c,4] Interestingly, and in spite of the premise that these radicals are both better oxidants and reductants than their parent molecules, the electron-transfer chemistry of metal carbonyl radicals remains largely unexplored.[4b,5] These transient organometallic species are ideal subjects for study employing flash photolysis methods; the radicals can be generated from metal–metal bonded dinuclear precursors via irradiation into the $\sigma_{M-M} \rightarrow \sigma^{*}_{M-M}$ manifold.[6] In this manner, the oxidation of $Mn(CO)_5^{\bullet}$ by several pyridinium complexes has been studied.[5b] The rate of electron transfer exhibits a monotonic dependence on the pyridinium reduction potential. An analogous trend has been observed elsewhere where pyridinium ions serve as the electron acceptor.[7] The attractiveness of pyridinium complexes as acceptors resides in their high electron affinity and, of equal importance, the potential for modifying the reduction potential while maintaining a fairly fixed structure. In addition, the product of electron transfer, the pyridinyl radical,[8] is generally a stable entity with characteristic absorptions in the UV–visible region, which in favorable cases provide a useful probe in the flash photolysis experiment.

Recent efforts from our laboratory have centered on both the atom[4d-g]- and electron[5c]-transfer reactivities of $M(CO)_4L^{\bullet}$ radicals (M = Mn, Re; L = CO, phosphine, phosphite, arsine). Particular attention has been paid to the applicability of Marcus theory[9] and related models[10] to the halogen atom transfer reactions of Re-

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