X $^3A_2$, a ^1E, and b $^1A_1$ Electronic States of Methylnitrene

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Abstract: An *a priori* theoretical study of the electronic structure of methylnitrene has been carried out. Using a double ζ basis set, the geometries of the lowest $^3A_2$, ^1E, and $^1A_1$ states have been predicted at the self-consistent-field level of theory. The three states, all of which arise from the same electron configuration $1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1^2 2e^2$, are predicted to have very similar geometries. For the ground $^3A_2$ state, we predict $r(CH) = 1.09$ Å, $R(CN) = 1.47$ Å, $\theta(NCH) = 110°$. At the predicted $^3A_2$ equilibrium geometry, several molecular properties were calculated using a larger basis set including d functions on C and N and p functions on hydrogen. The predicted dipole moments are substantial: 2.11 D ($^3A_2$), 2.23 D (^1E), and 2.36 D ($^1A_1$). The ^1E and $^1A_1$ states are predicted to lie 14,200 and 27,700 cm^{-1} above the $^3A_2$ ground state. Comparisons are made with the properties of the simplest nitrene, NH.

Nitrenes, molecules of the type R–N, are short-lived intermediates of increasing importance in organic and inorganic chemistry.[2-5] This interest has in part been motivated by certain similarities between nitrenes and another class of free radicals, the carbenes.[6] Both nitrenes and carbenes usually have small energy separations between their lowest singlet and triplet electronic states. In addition, both classes of molecules seem to conform to the idea of Skell[7] that singlet states should insert into double bonds in a stereospecific manner, while triplets insert nonstereospecifically.

The simplest nitrene, NH, is perhaps the most thoroughly studied, both from an experimental and theoretical point of view. The X $^3\Sigma^-$ state is known to be the ground state, but the precise position of the first excited a $^1\Delta$ state has not been established experimentally.[4] The b $^1\Sigma^+$ state is known to lie 8650 cm^{-1} above a $^1\Delta$, and all three of these states arise from the electron configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2 \qquad (1)$$

As might be expected, the three states have rather similar geometries,[8] the bond distances varying by only 0.004 Å. Although the triplet–singlet separation is not known from experiment, several theoretical studies[9-11] suggest a value of ~ 1.5 eV or 12,000 cm^{-1}.

Huo[10] has predicted the values of a number of molecular properties of NH, including the dipole moment: 1.63 D ($^3\Sigma^-$), 1.64 D ($^1\Delta$), and 1.66 D ($^1\Sigma^+$). The experimental value is known[12] (1.49 D) for the $^1\Delta$ state

and the agreement with theory is seen to be quite good. The sign of the theoretical dipole is N$^-$H$^+$ in each case.

Of the multitude of conceivable larger nitrenes, the alkylnitrenes, arylnitrenes, and carbonylnitrenes have been of particular interest.[13] Of these three groups, the alkylnitrenes have been by far the most elusive to experimentalists. In fact, it appears that no electronic spectra have been reported to date for the alkylnitrenes. However, Berry[13] has suggested, reasonably enough, that the electronic states of the alkylnitrenes should be analogous to those of NH. For the prototype system CH$_3$N, the lowest electron configuration analogous to (1) for NH is

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1^2 2e^2 \qquad (2)$$

In this way the $^3A_2$, ^1E, and $^1A_1$ states can be predicted to be the three lowest states of CH$_3$N, in analogy with the $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ states of NH. The fact that Wasserman, Smolinsky, and Yager[14] were able to observe the esr spectra of *n*-propylnitrene (and several larger nitrenes) implies a probable triplet ground state for the alkylnitrenes. In any event, for the alkylnitrenes studied,[14] there must be a triplet electronic state within a few wave numbers of the ground state.

Our concern in the present theoretical paper is the prototype alkylnitrene, methylnitrene. Despite its relative simplicity, we know of only two *a priori* theoretical studies of CH$_3$N. Harrison[15] has studied CH$_3$N in order to provide a model for the interpretation of the zero-field splitting data[14] of the alkylnitrenes. As a part of a comprehensive study of ABH$_n$ molecules, Pople and coworkers[16] have predicted the ground state geometry of CH$_3$N using a minimum basis set. Our emphasis here is on a comparison of the properties of CH$_3$N with those of NH. In addition, by using an extended basis set, we hope that the molecular properties predicted will be close to their limiting Hartree–Fock values.

Details of the Calculations

For the geometry optimizations, a double ζ basis set

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was chosen in analogy with our previous work[17] on the methoxy radical CH_3O. For C and N, the (9s 5p) primitive Gaussian basis sets of Huzinaga[18] were contracted to (4s 2p) *via* Dunning.[19] Similarly a H (4s) basis was contracted to (2s) and scaled by a factor of 1.2. Experience suggests[20] that if one does not intend to go beyond the Hartree–Fock approximation (*i.e.*, explicitly consider electron correlation[21]), then this type of double ζ basis is nearly optimum for geometry predictions.

For the prediction of molecular properties, the above basis was augmented with polarization functions. That is, six d-like functions (x^2, y^2, z^2, xy, xz, yz) $e^{-\alpha r^2}$ were centered on C ($\alpha = 0.75$) and N ($\alpha = 0.80$); p_z, p_y, and p_z functions ($\alpha = 1.0$) were centered on each of the three hydrogen atoms.

Roothaan self-consistent-field wave functions[22] were obtained using the MOLE system of programs.[23] The couplings of the outermost two electrons in the three electronic states are

$$2e_z\alpha 2e_y\alpha \quad ^3A_2 \qquad (3)$$

$$\frac{1}{\sqrt{2}}(2e_x\alpha 2e_z\beta - 2e_y\alpha 2e_y\beta) \text{ and } \frac{1}{\sqrt{2}}(2e_z\alpha 2e_y\beta - 2e_z\beta 2e_y\alpha) \, ^1E \quad (4)$$

$$\frac{1}{\sqrt{2}}(2e_z\alpha 2e_z\beta + 2e_y\alpha 2e_y\beta) \, ^1A_1 \qquad (5)$$

Results and Discussion

(A) Geometries. The predicted geometries are shown in Table I, where the ground state geometry of

Table I. Predicted Geometries and Energies for Methylnitrene, CH_3N^a

Electronic state		Energy, hartree	T_e, cm^{-1}	r(CH)	R(CN)	θ(NCH), deg
Pople[16]	$^3A_2$	−92.8604	0	1.09	1.51	109
This work	$^3A_2$	−93.9791	0	1.09	1.47	110
	^1E	−93.9135	14,400	1.09	1.46	110
	$^1A_1$	−93.8515	28,000	1.09	1.44	111

^{a} Bond distances are given in Å. These results were obtained with a double ζ basis set.

Pople[16] is also given. Note first that the present geometry prediction is very similar to that of Pople,[16] except for the CN distance, which is 0.04 Å shorter in the present study. Second, the geometries of all three low-lying states of CH_3N are predicted to be very similar. This is completely consistent with the known geometries of the $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ state of NH. In addition, these close similarities reinforce one's intuitive feeling that electronic states arising from the same electron configuration should have similar geometries.[24]

The CH bond distances and NCH bond angles for the methylnitrene states are relatively uninteresting, being essentially the same as those in the conventional molecule CH_3OH.[25] However, one does not expect the CN

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(22) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
(23) S. Rothenberg, P. Kollman, M. E. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem., Symp.*, **3**, 715 (1970).
(24) A. D. Walsh, *J. Chem. Soc., London*, 2260 (1953).

bond to be a conventional single bond. In this light it is somewhat surprising that the predicted 1.47-Å bond distance is indistinguishable from that of methylamine[26] CH_3NH_2, with R(C–N) = 1.474 Å. By this standard, then, there is no trace of multiple bond character in the CN bond of methylnitrene.

(B) Energy Results. Table II summarizes the

Table II. Energy Quantities for Methylnitrene, Obtained from Self-Consistent Field Calculations Employing a Double ζ Plus Polarization Basis Set[a]

Property	State		
	$^3A_2$	^1E	$^1A_1$
E, hartree	−94.0166	−93.9518	−93.8902
Vertical excitation energy. cm^{-1}	0	14,200	27,700
Potential energy	−187.9529	−187.7956	−187.6456
One-electron potential energy	−280.0771	−279.8927	−279.7158
Two-electron potential energy	62.0835	62.0565	62.0296
Nuclear repulsion	30.0406	30.0406	30.0406
Kinetic energy	93.9363	93.8438	93.7554
$-V/T$	2.00086	2.00115	2.00144
Orbital energies			
1a$_1$	−15.5882	−15.6089	−15.6277
2a$_1$	−11.2613	−11.2660	−11.2709
3a$_1$	−1.1076	−1.1136	−1.1191
4a$_1$	−0.8434	−0.8478	−0.8520
1e	−0.5927	−0.5967	−0.6007
5a$_1$	−0.5045	−0.5113	−0.5174
2e	−0.4963	−0.4270	−0.3621

^{a} All three calculations were carried out at the predicted $^3A_2$ equilibrium geometry.

SCF energies obtained using the double ζ plus polarization basis set. We predict the ^1E state of CH_3N to lie at 14,200 cm^{-1} and the $^1A_1$ state to lie at 27,700 cm^{-1}. Note from Table I that the geometries of the three states are so similar that there is little difference between the vertical and adiabatic excitation energies. Although the ground state total energy is lowered (with respect to the double ζ calculation) by 0.0375 hartree = 8200 cm^{-1}, the term splittings from the two sets of calculations agree to within a few hundred wave numbers.

It is interesting to compare our excitation energies with the SCF predictions of Huo[10] for the analogous states of NH. She predicts the a $^1\Delta$ and b $^1\Sigma^+$ states of NH to lie at 14,800 and 28,800 cm^{-1}. In this regard, then, CH_3N and NH are remarkably similar, even more so than could have been anticipated qualitatively.[13]

The ordering of orbital energies is the same for the $^3A_2$, ^1E, and $^1A_1$ states. The largest difference in the three results is the fact that ϵ(2e) is significantly higher for the excited states. *Via* Koopmans' theorem, of course, this indicates the decrease in ionization potential for the excited states. Also evident from inspection of the orbital energies is the probable existence of ^3E and ^1E excited states arising from the electron configuration

$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1 2e^3 \qquad (6)$$

These states are analogous to the A $^3\Pi$ and c $^1\Pi$ states of NH, which lie[8] at 29,800 and ~42,000 cm^{-1}.

(25) E. V. Ivash and D. M. Denninson, *J. Chem. Phys.*, **21**, 1804 (1953).
(26) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand-Reinhold, New York, N. Y., 1966.

(C) Population Analyses. Table II indicates gross atomic populations for the three lowest states of methylnitrene. There it is seen that these three states have very similar electronic structures. The atomic "charges" obtained in this way are: H(+0.14 to +0.15), C(−0.29), N(−0.14 to −0.17). These results are consistent with a classical picture of bonding in methylnitrene.

$$
\begin{array}{c}
H \\
\diagdown \\
H-C-N\cdot \\
\diagup \\
H
\end{array}
\qquad (7)
$$

The carbon atom valence shell populations are of the form $s^{1.24}p^{2.96}$, in reasonable agreement with the traditional sp^3. For nitrogen the analogous result is $\sim s^{1.85}$ $p^{3.27}$. The Mulliken populations[27] of Table III also

Table III. Population Analyses for the Three Lowest States of CH_3N

	$^3A_2$	^1E	$^1A_1$
Hydrogen s	2.527	2.515	2.500
Hydrogen p	0.046	0.046	0.046
Total (per atom)	0.858	0.854	0.849
Carbon s	3.238	3.238	3.239
Carbon p	2.967	2.962	2.959
Carbon d	0.085	0.087	0.088
Total	6.290	6.287	6.287
Nitrogen s	3.847	3.850	3.853
Nitrogen p	3.257	3.270	3.284
Nitrogen d	0.033	0.031	0.030
Total	7.137	7.152	7.167

indicate the relative unimportance of polarization functions. Carbon d functions appear to be most effective in this regard.

A more detailed population analysis is given in Table IV for the $^3A_2$ ground state. As expected the $1a_1$ orbital

Table IV. Detailed Population Analysis for $^3A_2$ CH_3N

	H		C			N		
	s	p	s	p	d	s	p	d
$1a_1$	0.00	0.00	0.00	0.00	0.00	2.00	0.00	0.00
$2a_1$	0.00	0.00	2.00	0.00	0.00	0.00	0.00	0.00
$3a_1$	0.05	0.00	0.70	0.06	0.03	0.93	0.09	0.03
$4a_1$	0.16	0.00	0.54	0.26	0.02	0.68	0.03	0.00
$1e$	0.58	0.01	0.00	2.15	0.02	0.00	0.05	0.01
$5a_1$	0.04	0.00	0.00	0.50	0.01	0.23	1.15	0.00
$2e$	0.02	0.00	0.00	0.00	0.01	0.00	1.94	0.00
Totals	0.85	0.01	3.24	2.97	0.09	3.84	3.26	0.04

is essentially a nitrogen 1s orbital, while the $2a_1$ orbital is carbon 1s. The $3a_1$ orbital approximates the form

$$3a_1 \approx x2s_C + y2s_N$$

where x corresponds to $\sim 30\%$ and y to $\sim 46\%$ of the molecular orbital. This orbital is then not terribly different from the $3\sigma_g$ orbital of N_2. Similarly, the $4a_1$ orbital has a marked similarity with the $2\sigma_u$ orbital of N_2. The $1e$ orbital is seen to be of CH bonding character, the populations being about equally split between C 2p and H 1s functions. The $5a_1$ orbital is very similar to the $5a_1$ orbital of the CH_3O radical,[17] namely $2pc^{0.55}$ $2p_N^{1.15}$. However, the $2e$ orbital of CH_3N is almost

(27) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

Table V. Molecular Properties of Methylnitrene, Obtained with a Double ζ Plus Polarization Basis Set[a]

Moments (with respect to the center of mass) of the electronic charge distribution	$^3A_2$	^1E	$^1A_1$
$\langle z \rangle$	2.13	2.08	2.03
$\langle x^2 \rangle = \langle y^2 \rangle$	−14.75	−14.82	−14.90
$\langle z^2 \rangle$	−48.18	−48.16	−48.13
$\langle x^3 \rangle = -\langle xy^2 \rangle$	−4.47	−4.44	−4.41
$\langle z^3 \rangle$	11.21	10.86	10.50
$\langle x^2 z \rangle = \langle y^2 z \rangle$	11.79	11.53	11.27
Multipole moments			
$\mu_z \ (+CN-)$	0.831	0.876	0.93
$\theta_{xx} = \theta_{yy}$	0.86	0.81	0.76
θ_{zz}	−1.71	−1.62	−1.51
$\Omega_{xxx} = -\Omega_{xyy}$	2.32	2.38	2.46
Ω_{zzz}	−2.23	−1.81	−1.37
$\Omega_{xxz} - \Omega_{yyz}$	1.11	0.91	0.69
Potential at nucleus			
$\Phi(H)$	−1.095	−1.091	−1.085
$\Phi(C)$	−14.70	−14.69	−14.69
$\Phi(N)$	−18.36	−18.34	−18.32
Electric field at nucleus			
$E_z(H)$	0.010	0.011	0.012
$E_z(H)$	−0.002	−0.002	−0.003
$E_z(C)$	−0.008	−0.007	−0.005
$E_z(N)$	0.072	0.071	0.070
Diamagnetic susceptibility tensor			
$\chi_{xx}{}^d = \chi_{yy}{}^d$	−62.92	−62.98	−63.03
$\chi_{zz}{}^d$	−29.49	−29.65	−29.80
$\chi_{av}{}^d$	−51.78	−51.87	−51.96
Diamagnetic shielding tensor			
$\sigma_{xx}{}^d(H)$	−3.19	−3.19	−3.19
$\sigma_{yy}{}^d(H)$	−0.94	−0.93	−0.93
$\sigma_{zz}{}^d(H)$	−2.25	−2.24	−2.24
$\sigma_{xz}{}^d(H)$	1.27	1.27	1.27
$\sigma_{av}{}^d(H)$	−2.12	−2.12	−2.12
$\sigma_{xx}{}^d(C) = \sigma_{yy}{}^d(C)$	−5.65	−5.65	−5.65
$\sigma_{zz}{}^d(C)$	−7.37	−7.37	−7.36
$\sigma_{av}{}^d(C)$	−6.22	−6.22	−6.22
$\sigma_{xx}{}^d(N) = \sigma_{yy}{}^d(N)$	−6.36	−6.35	−6.34
$\sigma_{zz}{}^d(N)$	−8.56	−8.56	−8.56
$\sigma_{av}{}^d(N)$	−7.09	−7.08	−7.08
Electric field gradient tensor			
$q_{xx}(H)$	−0.259	−0.259	−0.260
$q_{yy}(H)$	0.163	0.164	0.163
$q_{zz}(H)$	0.095	0.096	0.096
$q_{xz}(H)$	0.149	0.149	0.150
$q_{xx}(C) = q_{yy}(C)$	0.086	0.090	0.091
$q_{zz}(C)$	−0.172	−0.179	−0.181
$q_{xx}(N) = q_{yy}(N)$	−0.195	−0.272	−0.340
$q_{zz}(N)$	0.389	0.543	0.681

[a] The z coordinate lies along the C_3 axis of the molecule. and one of the H atoms has been placed at $y = 0$. Atomic units[28] are used throughout.

entirely nonbonding nitrogen 2p, whereas in CH_3O this orbital has a significant fraction (15%) of hydrogen s character. Nevertheless, the overall picture of the electronic structure of CH_3N is quite similar to that of methoxy, with the obvious deletion of one electron from the 2e orbital.

(D) Molecular Properties. A number of molecular properties are tabulated in Table V. For the conversion factors between atomic units (used here) and conventional units, the reader is referred to the paper by Rothenberg and Schaefer.[28] Due to the fleeting nature of CH_3N, none of its molecular properties have been

(28) S. Rothenberg and H. F. Schaefer, *J. Chem. Phys.*, **53**, 3014 (1970).

measured, and the results of Table V are thus true predictions.

The dipole moments of the $^3A_2$, ^1E, and $^1A_1$ states are predicted to be 2.11, 2.23, and 2.36 D. These dipoles are significantly larger than those predicted by Huo[10] for the analogous states of NH (1.63, 1.64, and 1.66 D), but the values of μ show the same increase with excitation energy. Based on the good agreement with experiment found for $^1\Delta$ NH and Green's analysis,[29] we are hopeful that the predicted dipole moments are reliable to within ± 0.2 D. It is certainly worth noting that the trend in the dipole moments can be perfectly correlated with the N atom gross populations. Interestingly, the C atom populations stay nearly constant, with the N population changes (accompanying electronic excitation) being compensated by increasingly positive charges on the H atoms.

The predicted quadrupole and octupole moments also vary essentially linearly with electronic excitation energy. These variations are most pronounced for the octupole moment tensor elements Ω_{zzz} and Ω_{xxz} which for the $^1A_1$ state are only $\sim 62\%$ of the ground state values.

Most of the remaining properties are nearly identical for the three different electronic states. Perhaps the best example of this sameness can be seen in the diamagnetic shielding tensors. Similar field gradients at hydrogen differ very little, while the carbon atom values of q vary to only a small degree.

However, the nitrogen electric field gradients are quite different for the $^3A_2$, ^1E, and $^1A_1$ states. It is well known, of course, that predicted field gradients are quite sensitive to the form of the wave function used.[30] By assuming[31] the nuclear electric quadrupole moment

of N to be 0.0156 barn, we predict the following quadrupole coupling constants

$$eq_{xx}Q(^{14}N) = -0.72, -1.00, -1.25 \text{ MHz} \qquad (8)$$

$$eq_{zz}Q(^{14}N) = 1.43, 1.99, 2.50 \text{ MHz} \qquad (9)$$

for the three electronic states. Thus the microwave spectrum of CH_3N should be quite interesting, when it becomes accessible experimentally.

Concluding Remarks

The predicted properties of CH_3N appear to be sufficiently interesting as to justify renewed efforts to characterize this radical. One problem we have intentionally avoided is that of why CH_3N has been so difficult[13] to isolate in the laboratory. A possible reason for the short life of CH_3N might be its rapid isomerization to methylimine

$$CH_3N \longrightarrow CH_2{=}NH \qquad (10)$$

Since the thermodynamics of reaction 10 are not known, we carried out a double ζ geometry optimization for the imine. The CH_2 group was constrained to have the experimental geometry of ethylene. The following parameters were then determined: $R(CN) = 1.27$ Å, $\theta(CNH) = 116°$, and $r(N-H) = 1.00$ Å. The computed total energy at this equilibrium geometry is -93.9948 hartrees, or 9.9 kcal/mol below CH_3N. Thus methylnitrene is unstable with respect to CH_2NH. However, it is quite possible that a substantial barrier height exists for the rearrangement (reaction 10). In that case methylnitrene could be isolated, in the same way that CH_3NC may be prepared despite its thermodynamic instability with respect to CH_3CN.

(29) S. Green, *Advan. Chem. Phys.*, **25**, 173 (1974).

(30) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results," Addison-Wesley, Reading, Mass., 1972.

(31) A. D. McLean and M. Yoshimine, *Bull. Amer. Phys. Soc.*, **13**, 373 (1968); C. T. O'Konski and T. K. Ha, *J. Chem. Phys.*, **49**, 5354 (1968).