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Nitromethylene ($H–C–NO_2$): A Comparison of the Lowest Lying Triplet and Singlet States of a Highly Unconventional Carbene

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Abstract: The lowest lying triplet and single states of nitromethylene were studied with *ab initio* quantum mechanical methods employing large basis sets and high levels of theory. The lowest triplet state is predicted to have a planar C_s symmetry structure. The lowest singlet state displays C_s symmetry at the self-consistent field (SCF) and at the two-configuration self-consistent field (TCSCF) level of theory but shows C_1 symmetry at correlated levels of theory. With a basis set of triple-ζ plus double polarization (TZ2P) quality and using the configuration interaction method including all single and double excitations (CISD), the zero point vibrational energy (ZPVE) corrected energy separation between the two electronic states is 3.5 kcal/mol, with the triplet state lying lower. However, Davidson corrected energies and single point energies at CISD geometries using the coupled cluster method including all single and double excitations (CCSD) suggest that the singlet state is about 7 kcal/mol lower in energy than the triplet state. The inclusion of f functions at the SCF level of theory showed little effect on the geometry of nitromethylene.

Introduction

Nitrocarbenes ($R–C–NO_2$) have been of significant interest[1-11] in organic chemistry as proposed intermediates in various chemical reactions. Numerous attempts have been made to prepare and isolate these intermediates but with, at most, limited success. Nitromethylene, the simplest nitrocarbene, has proven to be an elusive intermediate and efforts to isolate, trap, and detect nitromethylene through thermal or photodecomposition of nitrodiazo compounds have only recently[1] realized partial success. Interest in nitromethylene has developed over the years as an intermediate used to form novel cyclopropane derivatives from electron-rich alkenes. The literature shows the first efforts to verify the existence of nitromethylene were made by Schöllkopf.[2,3]

Schöllkopf and Tonne[2] attempted to trap nitroethoxycarbonylcarbene with tetramethylethene by thermolysis and then by photolysis of ethylnitrodiazoacetate but without success. Schöllkopf and Markusch[3] later formed nitrodiazomethane in the hopes that they could trap nitromethylene with isobutene or with tetramethylethene by either thermolysis or photolysis of nitrodiazomethane to form cyclopropane derivatives. They were not able to accomplish their goals but they did present evidence[2,3] that thermolysis or photolysis of nitrodiazomethane did lead to mostly radical fragmentation and decomposition products.

Rahman and Clapp[4] furthered the interest and understanding of nitrocarbenes by proposing that the parent compound is an intermediate in the decomposition of potassium salts of 1,1-dinitroalkane derivatives. They also proposed[4] that the nitrocarbene intermediate will form a nitrile oxide intermediate in the presence of an alkene that will then react with an alkene to form an isoxazoline. If a nitrocarbene adds to an alkene, either an isoxaline *N*-oxide or a nitrocyclopropane should, at least initially, be formed. However, they found no evidence for the existence of isoxaline *N*-oxide as a precursor to isoxaline; so they reasoned, on the basis of the reaction's selectivity, that a nitrile oxide was formed.

Shiue,[5] too, fueled the interest in nitrocarbenes by reporting evidence for the formation of methylnitrocarbene ($CH_3–C–NO_2$) in the thermal decomposition of 1,1-dinitroethane in the presence of cyclohexene yielding 1-acetylcyclohexene. The formation of this ketone was considered evidence for methylnitrocarbene, which could react as a 1,3-dipole, giving as an intermediate a Δ^2-isoxazoline *N*-oxide[12] precursor to the ketone. These results were in direct contrast to those of Rahman and Clapp, who did not find any evidence for the existence of an isoxaline *N*-oxide.

The work of Alexandrou, Coutouli, and Varvoglis[6] and the work of Coutouli-Argyropoulou and Alexandrou[7] significantly developed the knowledge behind the mechanism used by nitrocarbenes when reacting with electron-rich alkenes. They concluded that nitrocarbenes were strongly electrophilic and reacted selectively with electron-rich alkenes and that in the presence of these alkenes nitrocarbenes should be expected to yield Δ^2-isoxazoline *N*-oxides, if considering the nitrocarbenes as 1,3-dipoles. Unfortunately they found that the reaction products of the sodium salts of arylbromonitromethanes with several alkenes were not Δ^2-isoxazoline *N*-oxides. Instead Δ^2-isoxazolines, identical with those obtained from 1,3-dipolar cycloaddition of the corresponding nitrile oxides and alkenes, were obtained as reaction products, in agreement with Rahman and Clapp.[4] However, nitrile oxides were ruled out as intermediates since Alexandrou *et al.*[6] were unable to isolate products known to be formed in the presence of nitrile oxides. Coutouli-Argyropoulou and Alexandrou[7] later reported that the silver salts of aryldinitromethanes in the presence of electron-rich alkenes, such as 1,1-diarylethylenes and phenyldinitromethane, did give mainly the corresponding Δ^2-isoxazoline *N*-oxides and in low yields the Δ^2-isoxalines. In the presence of electron-poor alkenes, however, only the Δ^2-isoxazolines were obtained. They[7] also showed that interconversion of Δ^2-isoxazolines and Δ^2-isoxazoline *N*-oxides did not take place under the experimental conditions. But of greatest importance Coutouli-Argyropoulou and Alexandrou[7] concluded that their results were most compatible with an arylnitrocarbene intermediate.

Recently, O'Bannon and Dailey have conducted the most rigourous experimental effort[1,8,9] in the identification and isolation

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of nitromethylene. They started their effort by trying to understand why the efforts of Schöllkopf and Markusch,[3] when adding nitrocarbene to olefins under either thermal or photochemical conditions, failed yielding only decomposition products. Examining the pathways of the fragmentation of the nitrocarbene, formed by the decomposition of nitrodiazomethane into formyl radical and nitric oxide, O'Bannon and Dailey performed a preliminary ab initio study[8] on the lowest lying electronic state of singlet nitromethylene, the transition state for [1,2] oxygen atom migration, and nitrosoformaldehyde, an intramolecular rearranged intermediate proposed by Tonne and Schöllkopf.[2] They concluded, based on their computations on singlet nitromethylene and the transition state for oxygen migration, that singlet nitromethylene spontaneously rearranges to nitrosoformaldehyde.

Assuming their theoretical predictions were correct, O'Bannon and Dailey[8,9] suggested that nitrosoformaldehyde should react as a dienophile in Diels–Alder reactions in a similar manner to acyl nitroso compounds, whose reactions are well-known in organic synthesis. However their attempts[8] to form Diels–Alder adducts by thermolysis of nitrodiazomethane with several different 1,3-dienes were without success. O'Bannon and Dailey also found[8] that they could react nitrodiazomethane with electron-rich olefins in the presence of a transition metal catalyst (rhodium(II) acetate), yielding nitrocyclopropanes, a result one would expect from a nitrocarbene intermediate. However, in the presence of electron-poor olefins no cyclopropanes were observed, similar to the results of Coutouli-Argyropoulou and Alexandrou.[6,7]

In their 1988 study, O'Bannon and Dailey[9] provided experimental evidence supporting their theoretical predictions that nitromethylene rearranges to nitrosoformaldehyde. Namely, reacting nitrodiazomethane with 9,10-dimethylanthracene yielded the Diels–Alder adduct that corresponded to nitrosoformaldehyde acting as the dienophile. This reaction occurred with and without a Rh(II) catalyst. O'Bannon and Dailey[9] then concluded that nitrodiazomethane may be a source of either nitromethylene or nitrosoformaldehyde depending on the substrate and reaction conditions.

Most recently, O'Bannon, Sulzle, Dailey, and Schwarz[1] have produced indirect experimental evidence for the existence of both nitromethylene and nitrosoformaldehyde despite their earlier predictions,[8] through the use of charge-reversal and neutralization–reionization mass spectrometry. They could not, however, determine the multiplicity of nitromethylene although they did suggest that it may be the triplet state, based on preliminary *ab initio* self-consistent-field (SCF) studies.[1] It should be noted that they did not determine the barrier for intramolecular rearrangement for the triplet state in any of their previous studies, which may leave the possibility that both the singlet and triplet states of nitromethylene are produced in their experiments[1] with the singlet state of nitromethylene rearranging to nitrosoformaldehyde and the triplet state of nitromethylene stable enough not to spontaneously rearrange.

In summary, nitromethylene, the simplest nitrocarbene, has only recently[1] been detected. Efforts[1,3,8,9] to isolate and detect nitromethylene through thermal decomposition and photodecomposition of nitrodiazo compounds have failed. However, recent experiments[1] by O'Bannon *et al.* using charge-reversal spectrometry have shown that nitromethylene does exist as a stable neutral molecule.

Theoretical Background

Several theoretical studies have been performed previously on nitromethylene. Hoffmann, Zeiss, and Van Dine[11] carried out semiempirical LCAO MO calculations of the extended Hückel type. They concentrated on the equilibrium geometries and distortions of the configurations that give rise to the lowest lying singlet and triplet states. Although they stated that their calculations cannot possibly make an outright prediction as to what will be the ground state of nitromethylene, their calculations did predict the lowest lying singlet state of nitromethylene to be a nonplanar C_s structure with the hydrogen being bent out of the CNO_2 plane. They also conclude that the lowest lying triplet state of nitromethylene should be a planar C_s structure with the hydrogen bent in plane.

The first *ab initio* theoretical study of nitromethylene was performed by O'Bannon and Dailey.[8] The results of this study, using third-order Moller-Plesset perturbation theory (MP3) and multiconfigurational self-consistent-field (MCSCF) single point energy calculations using a 6-31G* basis at the predicted 6-31G* self-consistent-field (SCF) optimized geometry, are very pertinent here. They concluded that singlet nitrocarbene spontaneously rearranges to nitrosoformaldehyde with the MP3 single point energies predicting no barrier and the MCSCF single point energies predicting a barrier very close to zero. The SCF level of theory, employing a 6-31G* basis set, predicted a 12.4 kcal/mol barrier height to rearrangement. O'Bannon and Dailey,[8] therefore, concluded that singlet nitromethylene spontaneously rearranges to nitrosoformaldehyde. A later limited *ab initio* study by O'Bannon, Sulzle, Dailey, and Schwarz[1] predicted that triplet nitromethylene was lower in energy than singlet nitromethylene by 10.4 kcal/mol.

Here we present a comprehensive theoretical study, using both large basis sets and high levels of theory, of the lowest lying triplet and singlet states of nitromethylene. Our motivation is to determine the relative stabilities of these two states and to provide predictions that will help in the spectroscopic detection of this molecule.

Theoretical Methods

Three different basis sets were used in this study. The DZP basis is a standard Huzinaga–Dunning[13,14] double-ζ basis set of contracted Gaussian functions augmented by a set of five Cartesian d-type polarization functions on carbon [$\alpha_d(C) = 0.75$], nitrogen [$\alpha_d(N) = 0.80$], and oxygen [$\alpha_d(O) = 0.85$] and a set of p-type polarization functions on hydrogen [$\alpha_p(H) = 0.75$]. The contraction scheme for this basis is:

C, N, O (9s5p1d/4s2p1d); H (4s1p/2s1p)

The triple-ζ plus double polarization (TZ2P) basis adds two sets of polarization functions per atom [$\alpha_d(C) = 1.5, 0.375$; $\alpha_d(N) = 1.7, 0.400$; $\alpha_d(O) = 1.8, 0.450$; $\alpha_p(H) = 1.5, 0.375$] to a standard Huzinaga–Dunning[13,15] basis that is of triple-ζ quality in the valence region. The contraction scheme is thus:

C ,N ,O (10s6p2d/5s3p2d); H (5s2p/3s2p)

The TZ2P+f basis is the result of appending a set of seven Cartesian f-type polarization functions to carbon [$\alpha_f(C) = 0.80$], nitrogen [$\alpha_f(N) = 1.00$], and oxygen [$\alpha_f(O) = 1.40$] and a set of five Cartesian d-type polarization functions on hydrogen [$\alpha_d(H) = 1.00$] to the previously described TZ2P basis.

The restricted Hartree–Fock (RHF) or self-consistent-field (SCF) method was initially employed in this study. The effects of electron correlation were taken into account using the method of configuration interaction including all single and double excitations from an SCF reference wave function (CISD), the couple-cluster method including all single and double excitations (CCSD), and the CCSD method with the effect of connected triple excitations included perturbatively [CCSD(T)]. Only the valence electrons have been explicitly correlated; the four lowest (carbon, nitrogen, and oxygen 1s-like) SCF molecular orbitals were constrained to be doubly occupied. In addition, the four highest virtual orbitals were deleted from the correlation procedure. With the TZ2P basis, this resulted in a total of 274 345 configurations for triplet

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Table I. SCF Results for the Planar $^3A''$ State of the Nitromethylene Molecule in C_s Symmetry. Harmonic Vibrational Frequencies (ω) and Their Respective Infrared Intensities Are Listed below Along with the Energy (hartree), Dipole Moment (D), Average Polarizability (Å^3), Bond Lengths (Å), and Bond Angles (deg)

basis set	DZP		TZ2P		TZ2P+f	
level of theory	SCF		SCF		SCF	
total energy	−242.43678		−242.47209		−242.48362	
dipole moment	3.58		3.44		3.45	
av polarizability	3.24		3.65		3.66	
bond lengths						
H–C	1.075		1.069		1.070	
C–N	1.427		1.422		1.421	
$N–O_4$	1.195		1.185		1.183	
$N–O_5$	1.198		1.188		1.187	
bond angles						
H–C–N	121.8		121.9		122.0	
$C–N–O_4$	116.9		117.0		117.0	
$C–N–O_5$	116.5		116.4		116.4	
$O_4–N–O_5$	126.6		126.6		126.6	
	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
H–C stretch	3417	7.4	3395	9.7	3387	9.5
N–O asym stretch	1836	733.1	1767	714.0	1791	723.8
N–O sym stretch	1637	148.4	1604	144.1	1617	145.3
H–C–N bend	1190	25.4	1187	30.1	1188	28.1
C–N stretch	1103	5.8	1096	5.1	1101	5.7
NO_2 twist	799	21.3	815	18.2	821	18.5
NO_2 scissors	755	34.0	760	28.4	764	29.2
NO_2 rock	508	2.9	515	3.5	513	3.4
NO_2 wag	413	9.9	422	10.3	424	10.3

nitromethylene (using C_s symmetry) and 448 878 configurations for singlet nitromethylene (using C_1 symmetry) in the CISD wave functions.

The molecular structure of singlet nitromethylene was fully optimized using closed-shell analytic gradient techniques at the SCF,[16-18] CISD,[19-21] CCSD,[22,23] and CCSD(T)[24,25] levels of theory. The structure of neutral triplet nitromethylene was fully optimized using open-shell analytic gradient techniques at the SCF and CISD levels of theory. In all cases, the residual Cartesian and internal coordinate gradients were less than 10^{-6} atomic units. At the CCSD and CCSD(T) levels of theory, only single point energies were given for triplet nitromethylene since no analytical gradient procedure is currently available in our laboratory for open-shell systems with these methods.[26] Harmonic vibrational frequencies were obtained using analytic SCF second-derivative techniques[27-29] and central finite differences of analytic CISD, CCSD, and CCSD(T) gradients. Dipole moments,[30,31] average polarizability,[32,33] and infrared intensities[31,33] were calculated and reported.

Relative energies designated CISD+Q were obtained for both singlet and triplet nitromethylene by adding the Davidson correction[34] for unlinked quadrupole excitations to the CISD energies. Improved estimates of the relative energy for triplet nitromethylene were determined using coupled-cluster methods at CISD optimized geometries. The following notation has been used in this paper to designate these single-point energies: a DZP CCSD(T) energy that was evaluated at the DZP CISD optimized geometry is labeled DZP CCSD(T)//CISD.

Geometries were optimized by the implementation of an automated surface walking algorithm using the BFGS update approach.[35-38] The initial electronic configurations were chosen through the consideration and application of MO and group theories.

Triplet State SCF Results

The lowest triplet state appears to be of C_s symmetry. The electron configuration for this triplet state of nitromethylene is

$$1a'^{2}2a'^{2}3a'^{2}4a'^{2}5a'^{2}6a'^{2}7a'^{2}8a'^{2}9a'^{2}1a''^{2}10a'^{2}11a'^{2}12a'^{2}2a''^{2}13a'3a''$$

The equilibrium bond distances and angles, harmonic vibrational frequencies, infrared intensities, dipole moment, and average polarizability for this state are given in Table I.

The SCF results for the planar $^3A''$ ground state of nitromethylene are mostly constant with respect to basis set size, showing near convergence. The predicted bond lengths display a small monotonic decrease with increasing basis set size with the exception of the H–C bond length which increases slightly, 0.001 Å, from the TZ2P to the TZ2P+f basis set. The bond angles are mostly constant with respect to increasing basis set size, with the largest range of change being 0.2° from the DZP to the TZ2P+f basis sets. The harmonic vibrational frequencies and infrared intensities also show mostly small variations from the DZP to the TZ2P+f basis set with the largest change in the frequencies being a 69 cm^{-1} or a 3.7% decrease for the N–O asymmetric stretching mode.

The most notable changes with respect to basis set are for the dipole moment and average polarizability. The change from the DZP to the TZ2P basis sets is a decrease of 0.14 D in dipole moment and an increase of 0.41 Å^3 for the average polarizability. There is little change, however, from the TZ2P to the TZ2P+f

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Table II. Correlated Results for the Planar $^3A''$ State of the Nitromethylene Molecule in C_s Symmetry. Harmonic Vibrational Frequencies (ω) and Their Respective Infrared Intensities Are Listed below Along with the Energy (hartree), Dipole Moment (D), Bond Lengths (Å), and Bond Angles (deg)

basis set	DZP	TZ2P
level of theory	CISD	CISD
total energy	−242.97369	−243.09241
CISD+Q energy	−243.04608	−243.17500
CCSD//CISD energy	−243.05749	−243.18925
CCSD(T)//CISD energy	−243.08239	−243.22495
dipole moment	3.29	3.21
bond lengths		
H–C	1.081	1.071
C–N	1.422	1.415
$N–O_4$	1.220	1.204
$N–O_5$	1.224	1.209
bond angles		
H–C–N	122.6	122.9
$C–N–O_4$	117.3	117.4
$C–N–O_5$	116.1	116.1
$O_4–N–O_5$	126.6	126.6

	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
H–C stretch	3360	9.6	3344	13.0
N–O asym stretch	1763	419.2	1701	455.5
N–O sym stretch	1508	132.0	1482	131.4
H–C–N bend	1125	17.7	1123	21.5
C–N stretch	1055	3.4	1052	3.4
NO_2 twist	740	15.0	758	13.3
NO_2 scissors	711	24.6	721	19.8
NO_2 rock	469	3.8	478	4.3
NO_2 wag	420	11.3	428	11.3

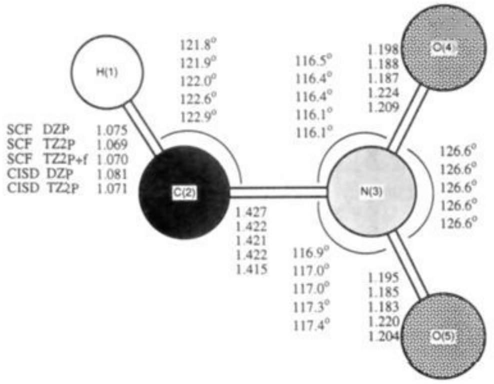

Figure 1. Summary of theoretical equilibrium geometries for the planar triplet state of the nitromethylene molecule. Bond distances are in Å and bond angles are in degrees.

basis sets for the same properties, namely a 0.01 D increase for the dipole moment and a 0.01 Å^3 increase for the average polarizability.

Triplet State Correlated Results

Summarized in Table II and Figure 1 are the C_s symmetry correlated results for the $^3A''$ ground state for nitromethylene. Upon comparison of the bond lengths in Tables I and II, one readily sees the characteristic trend of correlation to lengthen bonds with the noteworthy exception of the C–N bond length. In the latter case we instead see a small shortening of the DZP SCF bond distance, 0.005 Å, and a slightly larger decrease in the TZ2P bond distance, 0.007 Å, upon inclusion of the effects of correlation with the CISD method.

The increases in both lengths upon inclusion of correlation effects are small for the H–C bond length, 0.006 Å for the DZP basis set and 0.002 Å for the TZ2P basis set. However, the increases for the N–O bonds upon correlation are much larger. The increases for the $N–O_4$ and $N–O_5$ bond distances with the DZP basis set are 0.025 and 0.026 Å, respectively. With the TZ2P basis set, there N–O bond distance changes are slightly smaller, 0.021 and 0.022 Å, respectively.

The changes in bond angles due to electron correlation are much less pronounced than the changes in the bond lengths. The largest change in the bond angles is a 1.0° change for the H–C–N bend with the TZ2P basis set and a 0.8° change for the same angle for the DZP basis set. Little or no change is observed for the remainder of the bond angles upon explicit treatment of electron correlation effects.

Examination of the dipole moments using correlated methods showed a decrease of 0.29 D or 8.2% for the DZP basis set and a decrease of 0.23 D or 6.8% for the TZ2P basis set.

Comparison of the harmonic vibrational frequencies between the CISD and the SCF methods showed an average decrease of 4.7% for the DZP basis set and 4.4% for the TZ2P basis set. The largest percentage decreases due to correlation were seen for the N–O symmetric stretching, NO_2 rocking, NO_2 twisting, NO_2 scissoring, and H–C–N bending modes. Their respective percentage decreases were 7.9%, 7.8%, 7.4%, 5.8%, and 5.4% for the DZP basis set and 7.6%, 7.1%, 7.0%, 5.0%, and 5.4% for the same modes with a TZ2P basis set. In absolute terms, the respective decreases were 129, 39, 59, 44, and 64 cm^{-1} for the DZP basis set and 122, 37, 57, 38, and 64 cm^{-1} for the TZ2P basis set. However, not all of the frequencies decreased upon correlation. The NO_2 wagging mode showed instead a small increase, 6.6 cm^{-1} for the DZP basis set and 5.8 cm^{-1} for the TZ2P basis set.

The theoretical infrared intensities changed slightly upon inclusion of correlation with the exception of the N–O asymmetric stretching mode. This particular mode, which is notably of the strongest intensity, decreased markedly from 733 km/mol at the DZP SCF level of theory to 419 km/mol at the DZP CISD level of theory for a difference of 314 km/mol or 43%. This dramatic change was also observed with the TZ2P basis set giving a decrease of 258 km/mol or 36%.

Variations among the correlated results were not as dramatic as the changes between the SCF and CISD results for the $^3A''$ state. The CISD bond lengths showed relatively small characteristic decreases from the DZP to the TZ2P basis sets, 0.010, 0.007, 0.016, and 0.015 Å for the bond lengths H–C, C–N, $N–O_4$, and $N–O_5$, respectively. The bond angles also showed small changes (or no change at all) with the same basis size increase, the largest change in bond angle being an increase in 0.3° for the H–C–N bond angle.

In a comparison of the predicted dipole moments for the $^3A''$ state of nitromethylene with the CISD method, we see a small decrease of 0.08 D (DZP CISD → TZ2P CISD) as compared to the relatively larger change of 0.14 D for the same basis sets at the SCF level of theory. The harmonic vibrational frequencies and infrared intensities demonstrate relatively small deviations when comparing the results from the two basis sets at the CISD level of theory.

Singlet State SCF Results

The electronic configuration for the singlet state of nitromethylene in C_s symmetry is

$$1a''^2 1a'^2 2a'^2 3a'^2 4a'^2 2a''^2 5a'^2 6a'^2 7a'^2 3a''^2 8a'^2 4a''^2 9a'^2 5a''^2 10a'^2$$

SCF results for the $^1A'$ state of nitromethylene are given in Table III.

As with the $^3A''$ ground state, the SCF $^1A'$ results show only small deviations in geometry with respect to increasing basis set size with the possible exception of the N–O bond length which decreases 0.010 Å from the DZP to the TZ2P basis set. The harmonic vibrational frequencies and infrared intensities also show small deviations with respect to increasing basis set size.

The $^1A'$ state of nitromethylene also shows similar trends to those for the $^3A''$ state for the dipole moment. From the DZP to the TZ2P basis sets, we see a decrease of 0.17 D and between

Table III. SCF Results for the Nonplanar $^1A'$ State of the Nitromethylene Molecule in C_s Symmetry. Harmonic Vibrational Frequencies (ω) and Their Respective Infrared Intensities Are Listed below Along with the Energy (hartree), Dipole Moment (D), Average Polarizability (Å^3), Bond Lengths (Å), Bond Angles (deg) and Torsion Angles (deg)

basis set	DZP	TZ2P	TZ2P+f
level of theory	SCF	SCF	SCF
total energy	−242.41229	−242.44970	−242.46105
dipole moment	2.98	2.82	2.83
av polarizability	3.55	3.60	3.94
bond lengths			
H–C	1.094	1.089	1.090
C–N	1.426	1.422	1.420
N–O	1.193	1.183	1.182
bond angles			
H–C–N	103.8	103.8	104.0
C–N–O	115.6	115.6	115.6
torsion angles			
H–C–N–O	90.8	90.7	90.7

	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
H–C stretch	3238	4.9	3203	1.4	3198	1.5
N–O asym stretch	1816	836.4	1752	807.9	1776	814.9
N–O sym stretch	1652	135.5	1626	124.0	1637	128.1
H–C–N bend	1298	49.3	1311	52.8	1303	50.4
C–N stretch	1089	4.2	1078	4.3	1084	5.3
NO_2 twist	737	32.3	751	31.6	754	31.2
NO_2 scissors	692	59.3	695	50.6	699	52.9
NO_2 wag	566	60.9	590	55.3	592	55.3
NO_2 rock	215	5.7	218	4.9	208	5.4

Table IV. CISD Results for the Nonplanar $^1A'$ State of the Nitromethylene Molecule in C_s Symmetry. Harmonic Vibrational Frequencies (ω) and Their Respective Infrared Intensities Are Listed below Along with the Energy (hartree), Dipole Moment (D), Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg)

basis set	DZP	TZ2P
level of theory	CISD	CISD
total energy	−242.96442	−243.08539
dipole moment	2.62	2.52
bond lengths		
H–C	1.103	1.092
C–N	1.427	1.417
N–O	1.216	1.200
bond angles		
H–C–N	102.8	103.3
C–N–O	115.5	115.5
torsion angles		
H–C–N–O	91.2	91.0

	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
H–C stretch	3157	9.7	3137	2.6
N–O asym stretch	1763	524.6	1704	546.1
N–O sym stretch	1564	95.8	1545	89.0
H–C–N bend	1249	57.0	1254	64.6
C–N stretch	1035	1.2	1027	5.2
NO_2 twist	679	21.9	695	23.1
NO_2 scissors	650	50.4	657	44.1
NO_2 wag	539	53.2	576	50.9
NO_2 rock	142*i*	6.4	138*i*	5.4

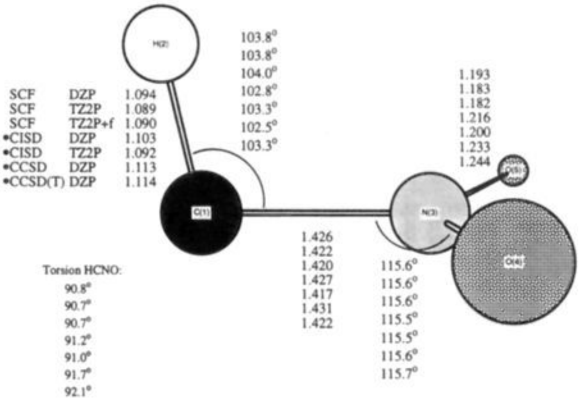

Figure 2. Summary of theoretical equilibrium geometries for the lowest singlet state of the nitromethylene molecule in C_s symmetry. Bond distances are in Å and bond angles are in degrees. An asterisk indicates that this particular structure is a transition state. The molecule below has been rotated 15° toward the reader.

the TZ2P and TZ2P+f basis sets an increase of 0.01 D. However, a much different trend is shown for the average polarizability. As with the $^3A''$ state, there is an increase, although small, for the $^1A'$ state from the DZP to the TZ2P basis set, 0.05 Å^3, but the change from the TZ2P to the TZ2P+f basis set is much larger, an increase of 0.34 Å^3.

Singlet State Correlated Results

The correlated results for the $^1A'$ state in C_s symmetry are summarized in Tables IV and V and Figure 2. Upon inspection of these results one immediately sees the absence of an equilibrium geometry for the $^1A'$ C_s structure at correlated levels. One instead sees that the C_s structure is a transition state, denoted by the presence of a single imaginary frequency. This imaginary vibrational frequency corresponds mostly to the molecule's desire to have unequal values for the C–N–O angles. However, a retrospective search for a C_1 symmetry structure, using the predicted ^1A DZP CISD geometry as a starting point, at the SCF level of theory was unsuccessful. Only the previously described C_s structure could be found.

The two-configuration self-consistent-field (TCSCF) method was then applied to singlet nitromethylene by fully optimizing the structure using analytic gradient techniques. The second configuration used is

$$1a''^2 1a'^2 2a'^2 3a'^2 4a'^2 2a''^2 5a'^2 6a'^2 7a'^2 3a''^2 8a'^2 4a''^2 9a'^2 5a''^2 6a''^2$$

The C_s structure was reexamined and we again searched for an equilibrium C_1 structure. The TCSCF results are summarized in Table VI. This method too predicted a C_s structure and evidence for a C_1 structure was never found. In fact the DZP TCSCF results show little deviation from the DZP SCF results. Previous theoretical studies[1,9,12] never noted an equilibrium C_1 structure. This is due to the deficiencies of the SCF and TCSCF methods and the reliance on single point energies at correlated levels of theory.

The singlet ground state was then carefully examined at correlated levels in C_1 symmetry. The results can be viewed in

Table V. Further Results for the $^1A'$ Ground State of the Nitromethylene Molecule in C_s Symmetry. Harmonic Vibrational Frequencies (ω) and Their Respective Infrared Intensities Are Listed below Along with the Energy (hartree), Dipole Moment (D), Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg)

basis set	DZP	DZP	DZP	DZP
level of theory	SCF	CISD	CCSD	CCSD(T)
total energy	−242.41229	−242.96442	−243.05838	−243.08803
dipole moment	2.98	2.62	2.35	2.18
bond lengths				
H–C	1.094	1.103	1.113	1.114
C–N	1.426	1.427	1.431	1.422
N–O	1.193	1.216	1.233	1.244
bond angles				
H–C–N	103.8	102.8	102.5	103.3
C–N–O	115.6	115.5	115.6	115.7
torsion angles				
H–C–N–O	90.8	91.2	91.7	92.1

	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
H–C stretch	3238	5.0	3157	9.7	3051	15.2	3036	14.5
N–O asym stretch	1816	836.4	1763	524.6	1635	393.3	1556	250.1
N–O sym stretch	1652	135.5	1564	95.8	1477	47.0	1421	20.9
H–C–N bend	1298	49.3	1249	57.0	1205	55.9	1159	62.4
C–N stretch	1089	4.2	1035	1.2	982	0.4	959	0.4
NO_2 twist	737	32.3	679	21.9	638	14.5	614	9.2
NO_2 scissors	692	59.3	650	50.4	619	40.3	598	34.6
NO_2 wag	566	60.3	539	53.2	521	44.1	523	42.5
NO_2 rock	215	5.7	142*i*	6.4	200*i*	4.1	276*i*	2.0

Table VI. Comparison of SCF and TCSCF Results for the Nonplanar $^1A'$ State of the Nitromethylene Molecule in C_s Symmetry. Harmonic Vibrational Frequencies (ω) and Their Respective Infrared Intensities Are Listed below Along with the Energy (hartree), Dipole Moment (D), Average Polarizability (Å^3), Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg)

basis set	DZP[a]	DZP[a]
level of theory	SCF	TCSCF
total energy	−242.41346	−242.43415
dipole moment	2.97	2.97
av polarizability	3.56	3.55
bond lengths		
H–C	1.094	1.097
C–N	1.427	1.440
N–O	1.194	1.193
bond angles		
H–C–N	103.7	102.5
C–N–O	115.6	115.7
torsion angles		
H–C–N–O	90.8	90.7

	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
H–C stretch	3238	4.9	3207	9.6
N–O asym stretch	1808	834.8	1817	848.2
N–O sym stretch	1649	135.2	1657	119.4
H–C–N bend	1297	49.5	1330	31.3
C–N stretch	1086	4.2	1077	1.6
NO_2 twist	734	31.6	730	25.3
NO_2 scissors	691	59.2	689	64.2
NO_2 wag	566	60.3	538	49.9
NO_2 rock	217	5.8	266	2.8

[a] This basis set uses a set of six Cartesian d-type polarization functions rather than the five Cartesian d-type polarization functions described previously.

Table VII and Figure 3. One may notice that these results are significantly changed from the results for the $^1A'$ structure in C_s symmetry. The differences in geometry between the SCF results in C_s symmetry and the correlated results in C_1 symmetry are very substantial.

The most significant change between the C_s symmetry SCF results and the C_1 symmetry correlated results is in the predicted C–N–O bond angles. The C–N–O bond angles change from 115.6° at the DZP SCF level of theory to 88.2° and 141.4° at the DZP CISD level of theory. These changes are typical of those found at the DZP CCSD and the TZ2P CISD levels of theory.

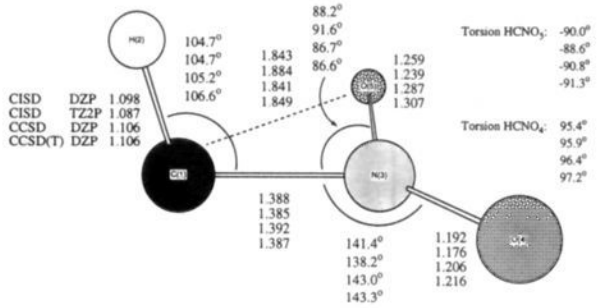

Figure 3. Summary of theoretical equilibrium geometries for the lowest-lying singlet state of the nitromethylene molecule in C_1 symmetry. Bond distances are in Å and bond angles are in degrees. The molecule below has been rotated 30° toward the reader.

The torsion angles also differ, although not to as great an extent as the changes for the C–N–O bond angles. We see a change in the H–C–N–O torsional angles from 90.8° and −90.8° at the DZP SCF $^1A'$ structure to 95.4° and −90.0° at the DZP CISD ^1A structure. Similar results are predicted at the DZP CCSD and the TZ2P CISD levels of theory.

Another interesting change in geometry ($C_s \rightarrow C_1$) is clearly noticed in the divergence of the N–O bond lengths. When comparing the N–O bonds in the DZP SCF $^1A'$ and the DZP CISD ^1A structures, there is a decrease of 0.001 Å in the N–O_4 bond and an increase of 0.066 Å in the N–O_5 bond. Comparison of the TZ2P SCF and TZ2P CISD results shows similar trends for the analogous N–O bonds. However, the decrease is more pronounced, 0.006 Å, and the increase is smaller, 0.057 Å. As for the C–N bond, we see a decrease of 0.038 Å from the DZP SCF $^1A'$ structure to the DZP CISD structure. A comparable change in the C–N bond length is given when using a TZ2P basis set at the same levels of theory.

Also significant is the relative large change in the dipole moment. We see a large decrease of 0.98 D from the DZP SCF $^1A'$ result to the DZP CISD ^1A result. A similar change occurs with the TZ2P basis set, 0.82 D.

The different correlated results for the C_1 symmetry structures show mostly small changes in both lengths and bond angles. The dipole moments are mostly constant at the CISD level of theory, although there is a change of 0.16 D from the DZP CISD to the DZP CCSD levels of theory. The vibrational frequencies also

Table VII. Correlated Results for the Lowest-Lying ^{1}A State of the Nitromethylene Molecule in C_1 Symmetry. Harmonic Vibrational Frequencies (ω) and Their Respective Infrared Intensities Are Listed below Along with the Energy (hartree), Dipole Moment (D), Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg)

basis set	DZP	DZP	DZP	TZ2P
level of theory	CISD	CCSD	CCSD(T)	CISD
total energy	−242.96629	−243.06188	−243.09102	−243.08662
dipole moment	2.00	1.84	1.80	2.01
bond lengths				
H–C	1.098	1.106	1.106	1.087
C–N	1.388	1.392	1.387	1.385
N–O_4	1.192	1.206	1.216	1.176
N–O_5	1.259	1.287	1.307	1.239
bond angles				
H–C–N	104.7	105.2	106.6	104.7
C–N–O_4	141.4	143.0	143.3	138.2
C–N–O_5	88.2	86.7	86.6	91.6
torsion angles				
H–C–N–O_4	95.4	96.4	97.2	95.9
H–C–N–O_5	−90.0	−90.8	−91.3	−88.6

	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)	frequency (cm^{-1})	intensity (km/mol)
H–C stretch	3193	6.8	3104	8.8	3174	2.0
N_3–O_4 stretch	1876	454.3	1775	372.2	1818	462.7
N_3–O_5 stretch	1409	114.7	1294	88.7	1406	115.4
H–C–N bend	1189	95.6	1115	92.2	1206	96.4
C–N stretch	1040	13.8	989	25.5	1031	8.2
t_{HCNO_5}	938	49.0	890	71.7	924	43.5
NO_2 scissors	622	5.4	572	0.6	643	4.8
t_{HCNO_4}	526	41.3	503	33.9	544	42.0
NO_2 rock	236	33.8	271	14.7	212	36.2

Table VIII. Energy Separation between the Lowest Triplet and Singlet States of Nitromethylene

	total energy[a]		ΔE(triplet–singlet)		ΔZPVE	ΔE − ΔZPVE
level of theory	^{3}A″ state	^{1}A state	mhartrees	kcal/mol	(kcal/mol)	(kcal/mol)
DZP SCF	−242.436 758	−242.412 285[b]	24.47	15.36	0.51	14.85
TZ2P SCF	−242.472 086	−242.449 702[b]	22.38	14.05	0.48	13.56
TZ2P+f SCF	−242.483 617	−242.461 053[b]	22.56	14.16	0.51	13.65
DZP CISD	−242.973 685	−242.966 289	7.40	4.64	0.18	4.46
TZ2P CISD	−243.092 410	−243.086 625	5.78	3.63	0.18	3.45
DZP CISD+Q[c]	−243.046 081	−243.046 441	−0.36	−0.23		
TZ2P CISD+Q[c]	−243.175 004	−243.176 709	−1.70	−1.07		
DZP/CCSD//CISD	−243.057 492	−243.060 688	−3.20	−2.01		
TZ2P CCSD//CISD	−243.189 250	−243.194 298	−5.05	−3.17		
DZP CCSD(T)//CISD	−243.082 393	−243.091 019	−8.63	−5.41		
TZ2P CCSD(T)//CISD	−243.224 949	−243.236 038	−11.09	−6.96		

[a] Total energy in hartrees. [b] This particular equilibrium structure corresponds to the C_s symmetry ^{1}A′ state. [c] Davidson corrected energy.

show mostly small changes and the infrared intensities are relatively constant with the possible exception of the N–O stretching modes, which decrease, and the HCNO$_5$ torsional mode, which increases somewhat at the DZP CCSD level of theory.

Energetic Comparisons

Table VIII gives a summary of the triplet and singlet energies at the various levels of theory and their energy separations. One can immediately see that at fully optimized geometries, the triplet state is lower by 4.6 kcal/mol at the DZP CISD level of theory and by 3.6 kcal/mol at the TZ2P CISD level of theory. When zero-point vibrational energy corrections are factored in the energy separations decrease to 4.5 and 3.4 kcal/mol, respectively. However, differences in Davidson corrected energies and single point energies at higher levels of theory predict that the singlet state is lower in energy than the triplet state.

The Davidson corrected energies suggest that the singlet state is lower in energy by 0.2 kcal/mol at the DZP CISD level of theory and by an even larger 1.1 kcal/mol at the TZ2P CISD level of theory. Single point energies at the CCSD level of theory continue the above trend with even greater energy separations between the singlet and triplet states. Single point energies using the DZP CCSD level of theory with the DZP CISD optimized geometry (DZP CCSD//CISD) show the single state to be lower by 2.0 kcal/mol. The TZ2P CCSD//CISD single point energies give an even larger energy separation of 3.2 kcal/mol. This trend is further continued by single point energies at the DZP CCSD(T)//CISD and TZ2P CCSD(T)//CISD levels of theory yielding energy separations of 5.4 and 7.0 kcal/mol, respectively.

The large difference (7.0 − 1.1 = 5.9 kcal/mol) between the Davidson corrected CISD and the CCSD(T) singlet–triplet separations appears to be unprecedented for carbenes. Generally speaking, the Davidson corrected CISD method yields ΔE(S–T) values within 2 kcal/mol of the exact results for a given basis set.[38,39] This is further evidence that nitromethylene has an exceptionally complicated structure.

Upon the inclusion of the effects of correlation with the CISD method, one can see the trend at fully optimized geometries is to decrease the energy separation between the singlet state and the triplet state. An increase in basis set size further decreases the singlet–triplet energy separation and as ZPVE corrections are factored in the energy separation decreases even more. Davidson corrected energies (CISD+Q) and single point energies at the CCSD and CCSD(T) levels of theory imply that the energy

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(39) Gilles, M. K.; Lineberger, W.; Ervin, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 1031–1038.

(40) DeLeeuw, B. J.; Fermann, J. T.; Xie, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1993**, *115*, 1039–1047.

Table IX. Energy Separation between the Singlet State C_s and C_1 Symmetry Stationary Point Structures at Correlated Levels

theory	total energy[a]		$\Delta E(C_s–C_1)$	
	$^1A'$ state	^1A state	mhartrees	kcal/mol
DZP CISD	–242.964 420	–242.966 289	–1.90	–1.19
DZP CISD+Q	–243.042 129	–243.046 441	–4.31	–2.70
DZP CCSD	–243.058 384	–243.061 880	–3.50	–2.19
DZP CCSD(T)	–243.088 033	–243.093 939	–5.91	–3.69
TZ2P CISD	–243.085 392	–243.086 625	–1.23	–0.77
TZ2P CISD+Q	–243.173 422	–243.176 709	–3.29	–2.06
TZ2P CCSD//CISD	–243.191 865	–243.194 298	–2.43	–1.53
TZ2P CCSD(T)//CISD	–243.231 618	–243.236 038	–4.42	–2.77

[a] Total energy in hartrees.

of the singlet state is lower than that of the triplet state. Increases in basis set size with these single point energies at higher levels of theory work only to further increase the stability of the singlet state relative to the triplet state. It would appear that these trends in singlet–triplet energy separation with increasing basis set size and higher levels of theory work only to the advantage of the singlet state. Note that a singlet ground state for nitromethylene was not anticipated in previous theoretical studies.[1,9,12]

One may wonder how much lower lying in energy is the C_1 symmetry singlet state equilibrium structure relative to the C_s symmetry singlet state transition structure. This information is provided in Table IX. In this table we see that the use of higher levels of theory increases the C_1–C_s energy difference. However, an increase in basis set size decreases the energy separation in the direction of the return to a C_s symmetry structure. The most reliable C_1–C_s energy difference is 2.8 kcal/mol, predicted at the TZ2P CCSD(T)//CISD level of theory. It would appear though that if even larger basis sets were to be used with correlated levels of theory, there still would not be a return to a C_s symmetry structure as the equilibrium structure.

Discussion

This study has shown the lowest lying triplet state of nitromethylene to be of C_s symmetry. The singlet state was predicted to be of C_s symmetry at the SCF and TCSCF levels of theory and C_1 symmetry at the CISD, CCSD, and CCSD(T) levels of theory.

The singlet state of nitromethylene has been shown to be lower in energy than the triplet state. It is well-known that the triplet ground state of methylene (CH_2) is 9.1 kcal/mol lower in energy than the lowest lying singlet state.[41–43] Nitromethylene is an example of the effect of a substituent, in this case a nitro group, to stabilize the singlet state with respect to the triplet state. This result is similar to that found for the halocarbenes[44–46] which are predicted to have a singlet ground state between 4.1 and 13.2 kcal/mol lower in energy than the lowest lying triplet state.

The C_1 structure for singlet nitromethylene is truly interesting and one may wonder if there is some sort of interaction between the "partially" bridged oxygen (O_5) and the carbon and/or the hydrogen. We do see significant reductions in the H–O_5 and C–O_5 distances in going from the C_s to the C_1 structure. When comparing the $^1A'$ DZP SCF and ^1A DZP CISD structures, there is a reduction of 0.377 Å in the C–O_5 distance, from 2.220 to 1.843 Å, and a reduction of 0.344 Å in the H–O_5 distance, from 2.678 to 2.334 Å. The presence of an intramolecular interaction may explain the lengthened N–O_5 bond. An interaction between C–O_5 and/or H–O_5 would reduce the electron density in the N–O_5 bond, making the bond longer. At the same time, this would allow the nitrogen to strengthen its bonds with the carbon and the other oxygen (O_4), demonstrated by C–N and N–O_4 bond lengths decreasing (instead of the characteristic increase) upon inclusion of the effects of correlation. Therefore, it is not too farfetched to reason that there is in fact some form of intramolecular interaction between carbon and the interacting oxygen (O_5). An intramolecular interaction explains the dramatic decrease in the carbon–nitrogen–oxygen bond angle (C–N–O_5) to 88.2° with the DZP CISD ^1A structure from the 115.6° predicted for the DZP SCF $^1A'$ structure. This represents a significant bond angle decrease of 27.4°. This interaction appears to become even stronger at the DZP CCSD level of theory, as shown by the further decrease in bond angle to 86.7° and a further, although slight, decrease in carbon–oxygen separation to 1.841 Å. The SCF and TCSCF levels of theory do not yield a C_1 stationary point and apparently were not able to describe this interaction, due to the limited number of configurations used to describe this molecule.

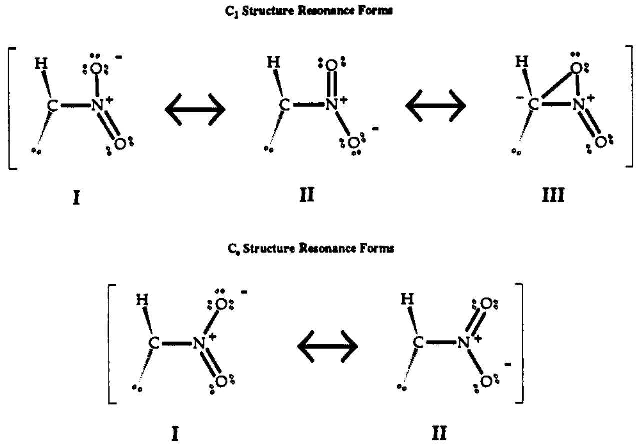

Figure 4. Resonance schemes for the singlet C_1 symmetry and singlet C_s symmetry structures.

There is a significant increase in the N–O_5 bond length when comparing the DZP SCF C_s structure to the DZP CISD C_1 structure. This increase of 0.066 Å is most likely due to the nature of the bonding interaction between the carbon and the oxygen (O_5) atoms. The oxygen (O_4) also undergoes significant changes from the DZP SCF C_s structure to the DZP CISD C_1 structure. The carbon–nitrogen–oxygen (C–N–O_4) bond angle undergoes an increase of 25.8° and the bond length (N–O_4) a decrease of 0.001 Å.

One may question the validity of this singlet C_1 symmetry structure and why it is predicted as the lowest lying singlet state instead of the expected singlet C_s symmetry structure. We are convinced that this singlet C_1 structure is valid and can be adequately explained through the use of simple resonance structures and a comparison of electron density plots between the ^1A DZP CISD and the $^1A'$ DZP SCF structures.

The singlet C_1 symmetry structure shows some form of an interaction between the carbon and the oxygen (O_5), resembling a donor–acceptor interaction between the lone pair on the oxygen and the empty orbital on the carbon. The donation of the lone pair to the empty orbital can be visualized and explained in terms of the singlet C_1 symmetry resonance scheme, demonstrated in Figure 4. Also shown in Figure 4 is the typical resonance scheme one would expect for the singlet C_s symmetry structure of nitromethylene.

We can see from these resonance structures that the singlet C_1 symmetry structure achieves further stabilization (over the singlet C_s symmetry structure) through the contributions of a greater number of important resonance forms. The contribution of a new important resonance form, denoted as III in Figure 4, is of importance in the understanding of the singlet C_1 structure. The

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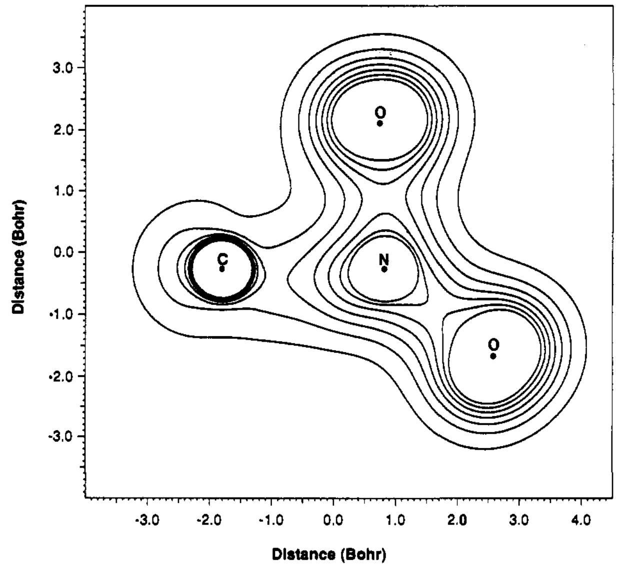

Figure 5. Electron density plot for the DZP CISD singlet C_1 symmetry structure in the C–N–O(5) plane. Contour lines correspond to a 0.05 change and range from 0.00 to 0.40. The black dots correspond to the location of the nuclei.

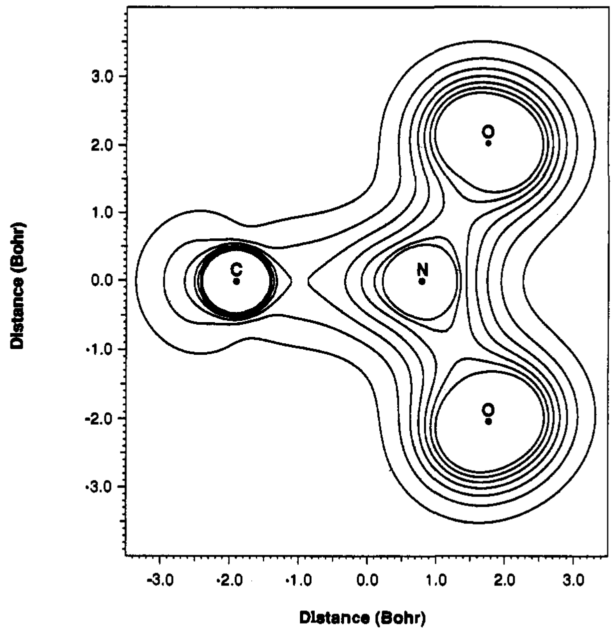

Figure 6. Electron density plot for the DZP SCF singlet C_s symmetry structure in the C–N–O(5) plane. Contour lines correspond to a 0.05 change and range from 0.00 to 0.40. The black dots correspond to the location of the nuclei.

addition of resonance form III to the expected resonance forms of the C_s symmetry singlet structure, denoted as I and II in Figure 4, gives the C_1 symmetry singlet structure monobridged character and helps explain why there is a shortening of the C–N and N–O_4 bonds, lengthening of the N–O_5 bond, and drastic changes in the C–N–O bond angles.

A comparison of the contour plots of the total electron density in the C–N–O_5 plane for the singlet C_1 symmetry structure, shown in Figure 5, and the C_s symmetry structure, shown in Figure 6, reveals that the C–N bond is actually bent in the singlet C_1 symmetry structure. Bent bonds usually result from angle strain and are present in three-membered rings.[47] A bent bond would partially explain the large difference in the C–N bond length between the ^1A and $^1A'$ structures, a difference of 0.039 Å at the DZP CISD level of theory. This difference is largely due to what was actually being predicted, namely the distance between two respective nuclei. If the bond path lengths,[48] measure along the maximum of electron density, were instead predicted, the two values would be more similar. One normally takes it for granted that the maximum of electron density is the distance between the two respective muclei but, in the case of bent bonds, this cannot be assumed,[47,48] thus helping to explain the difference in the C–N bond length.

The contribution of the monobridged resonance form III is largely responsible for the large change in C–N–O bond angles. The C–N–O_5 bond angle will naturally decrease so that the lone pair can better interact with the empty p-orbital on the carbon atom. The shortening of the C–N distance is a direct result of bending the bond, where the bond bending results from the angle strain caused by the large decrease in the C–N–O_5 bond angle. The N–O_5 bond length increases more than would be expected due to the oxygen's ability to interact with the carbon, the large decrease in C–N–O_5 angle, and, as viewed in resonance form III, less double bond character. The N–O_4 bond length decreases slightly due to the increased bonding with nitrogen and is depicted in the resonance scheme as the result of increased double bond character between nitrogen and oxygen (O_4).

Let it be noted that not one of the resonance forms shown in the C_1 resonance scheme dominates. We instead see a superposition of the three forms. The effects of resonance form III are clearly important in the understanding of the singlet C_1 structure and help explain its "partially" monobridged character. One may wonder why a "fully" monobridged structure does not form. One possible explanation may be visualized through the use of formal charges. We see that the monobridged resonance form III carries a formal negative charge on the carbon and a formal positive charge on the nitrogen. It is well-established, however, that nitrogen is more electronegative than carbon. Therefore we would expect that this monobridged resonance form III will affect the geometry less than the nonbridged resonance forms I and II. This does not decrease the importance of the monobridged resonance form III but may explain why we did not obtain a truly monobridged C_1 symmetry singlet structure instead of the "partially" monobridged C_1 symmetry structure predicted here. It should also be noted that the singlet C_s symmetry structure is a transition state for the interconversion into the mirror image of the singlet C_1 symmetry structure.

Conclusion

We have shown the lowest lying singlet state of nitromethylene is lower in energy that the lowest lying triplet state of nitromethylene. We estimate the singlet state to be lower in energy by 7 kcal/mol. The singlet C_1 symmetry structure has been shown to be the equilibrium geometry, instead of the nonplanar C_s symmetry structure, for two major reasons. First, the lone pair on the "partially" bridged oxygen donates electron density to the electron deficient carbon atom. Second, the C_1 structure allows a more favorable electrostatic interaction between the "partially" bridged oxygen and the hydrogen by bringing those two atoms in the usual range of strong hydrogen bonding (2.2–2.5 Å). Lastly, provided the C_1 structure is the global minimum, then the nonplanar C_s structure is the transition state for the interconversion into the mirror image of the first C_1 structure.

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