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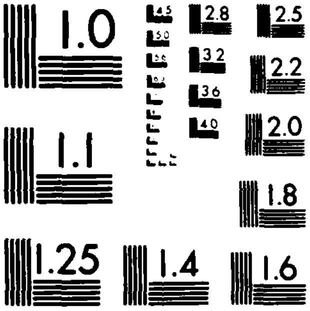

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FRANK J. SEILER RESEARCH LABORATORY

FJSRL-TR-83-0009

September 1983

A Study of the CH_2NO_2 Radical Using A Multiconfigurational Self-Consistent Field Approach

Michael L. McKee

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The CH_2NO_2 radical is used as a model for first likely reactive species in the decomposition of high energy materials such as TNT (1,3,5-trinitrotoluene) or HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-Tetrazocine). Radical species can be observed in an ESR cavity during the inductive phase of decomposition however their identity is not clearly established. Semiempirical, single configurational, and eventually multi-configurational ab initio calculations were carried out to determine the ground electronic state and the electronic distribution. Ab initio

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calculations based on a single configuration plus correlation could not distinguish the ground state. The MCSCF results indicate that the ground state is a planar $^2A''$ state which results from the interaction of the planar $^2B_1$ and $^2A_2$ states that cross at a common C_{2v} geometry and which leads to a favorable asymmetric distortion from C_{2v} symmetry to a lower C_s symmetry. A similar distortion was observed by Davidson and coworkers for NO_2. The $^2A''$ state is 14.6 kcal/mol more stable than the $^2B_1$ state and 19.9 kcal/mol more stable than the $^2A_2$ state. The staggered $^2B_2$ state which is the C_{2v} ground state is 6.8 kcal/mol higher than $^2A''$ state. The planar $^2A''$ ground state has considerable spin density on the carbon and some on one oxygen in agreement with ESR results.

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A STUDY OF THE CH_2NO_2 RADICAL USING A MULTICONFIGURATIONAL SELF-CONSISTENT FIELD APPROACH

Michael L. McKee

September 3, 1983

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I. INTRODUCTION:

The nitromethyl radical has been postulated to be involved in a number of different phenomena. In a study[1] of nitromethylation of aromatic compounds it was determined that the radical had appreciable electrophilic character. The only products formed were through reactions at the carbon suggesting that it was the more reactive center. Interestingly in the reaction with manganese (III) acetate and nitromethane the authors[1] suggested that it might be the aci form (CH_3ONO) that underwent oxidation followed by tautomerization.

The radical could be produced in the following reaction:

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2$$

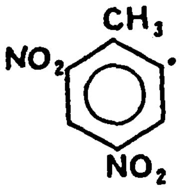
which has been suggested[2] to explain the appearance of methane as a major product in the decompostion of nitromethane. Once formed the nitromethyl radical is believed to effect the thermal decomposition of nitromethane in condensed phase systems[3]. Such systems include propellant ignition and explosive initiation. Nitromethyl radical may even play a role in the chemistry of the upper troposphere through the degradation of nitromethane formed from the possible reaction of CH_3 and NO_2[4].

Very recently the vibrational spectrum of CH_2NO_2 was reported by Jacox[4] who codeposited F atoms and nitromethane in an Argon matrix at 14 K and analyzed the changes in the IR spectra. Different isotopes of nitromethane were used in the study to help assign the bands.

The heat of formation of gaseous nitromethyl radical has been estimated[5] to be 37.5 kcal/mol.

The ESR spectrum of the nitromethyl radical has been interpreted[6] as supporting a nonplanar geometry. However, the only reported theoretical calculation on CH_2NO_2 was an INDO calculation[7] which predicted a planar structure.

The motivation for this study was not only to gain an understanding of this particular system as a reactive intermediate, but also to view the system as a model for the radicals produced from high energy species such as TNT (1,3,5-trinitrotoulene) where radical intermediates[8] as 1 or 2 might occur.



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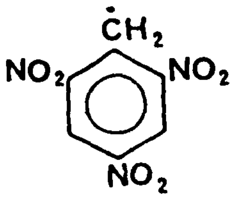

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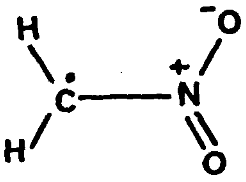
The two valence structures which can be written for planar CH_2NO_2 are: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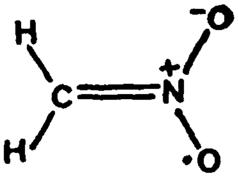
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A theoretical study[9] on radicals of this nature involving structures with comparable energies but inequivalent assignments of π bonds and the lone electron suggest that accurate results require substantial effort to correctly predict their relative energy. Indeed this could be predicted by the sophisticated basis sets needed[10] to predict the states of NO_2.

II. OBJECTIVES OF THE RESEARCH EFFORT:

The object of this work was to study the types of radicals that could be generated by thermal or photolytic decomposition of high energy materials. Specifically the radicals produced from polynitrated systems as TNT or HMX. To do this one must determine which is the most economical method that will produce results of sufficient quality or accuracy to answer the particular chemical problem. If empirical methods are not sufficiently accurate and more sophisticated methods too costly, one may ask if there are trends which could still allow the empirical methods to be used predictively with some confidence. The objectives of this study were as follows:

(1) To study the electronic states of the CH_2NO_2 radical with the semiempirical method MNDO to determine the ground state and electronic configuration.

(2) To study the problem using ab initio methods with geometry optimization and correlation.

(3) To determine the extent that other configurations play in determining the properties of the electronic states by using a MCSCF method.

III. RESULTS AND DISCUSSION:

The first method used to study the electronic states of CH_2NO_2 was the MNDO method, a semiempirical method based on the NDDO approximation[11] and very successfully parameterized by Dewar and Thiel[12]. All calculations were carried out using the unrestricted SCF formalism.

The heats of formation and geometries for C_{2v} species are given in Table 1. The most stable state is the planar $^2B_1$ followed very closely by the staggered $^2B_2$. These two states simply correspond to rotation of the singly occupied p orbital on carbon. The other states were obtained by starting with a bond order generated from an orbital guess in which selected orbitals were occupied. During the iteration to self consistency the switched orbital was monitored to insure that it remained occupied. Unfortunately in many instances the wavefunction lost the initial C_{2v} symmetry and it proved to be impossible to obtain those states.

The planar $^2A_2$ solution was found to be 18.3 kcal/mol higher in energy than the planar $^2B_1$ state. Roughly, these two states correspond to valence structures 3 and 4. The unrestricted solution obtained for $^2A_1$ was characterized by three singly occupied orbitals; a b_2 and a_2 orbital of alpha spin and a b_1 orbital of beta spin.

The assumption of C_{2v} symmetry for CH_2NO_2 radical seems intuitively obvious but due to the interaction of closely related electronic state this assumption may be wrong. It has previously been noted[10a,b] that under certain conditions electronic states in C_{2v} symmetry may mix by an asymmetric distortion and lead to a lower energy in C_s symmetry. The conditions which must be met are:

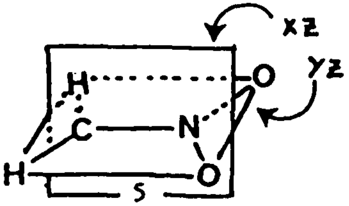
1) the two states in C_{2v} symmetry must transform as the same irreducible representation in the C_s point group;

2) there must be a surface crossing at some nearby C_{2v} geometry;

3) the leading configurations must differ by only one spin orbital.

The $^2A_1$ and $^2B_2$ states of NO_2 meet the above conditions and it is found[10a,b] that an asymmetric distortion does lead to a lower energy.

If we look at the C_{2v} point group table we see that the C_{2v} symmetry can be reduced to C_s by the loss of the sigma (yz) plane or the sigma (xz) plane (5)



If the xz symmetry plane is lost then the A_2 and B_1 states transform as A" while A_1 and B_2 states transform as A'. If the yz symmetry plane is lost then A_2 and B_2 transform as A" while the A_1 and B_1 transform as A'.

The MNDO wavefunctions were tested for stability under C_s distortions and the results are presented in Table 2 and 3.

Table 1 MNDO Heats of Formation (kcal/mol) and Geometries[a] of CH_2NO_2 radicals in C_{2v} symmetry

State	ΔH_f	CN	NO	CH	ONH	HCN
${}^2B_1^b$	35.2	1.476	1.214	1.084	119.3	118.3
${}^2A_2^b$	53.5	1.414	1.266	1.084	122.3	119.0
${}^2B_2^c$	35.6	1.482	1.219	1.082	119.4	117.6
${}^2A_1^{c,d}$	63.1	1.454	1.264	1.084	121.5	118.2

a) Distances are given in Angstroms and angles are given in degrees.

b) Planar geometry.

c) Staggered geometry.

d) The ${}^2A_1$ state has b_2, a_2, and b_1 orbitals singly occupied.

Table 2 MNDO Heats of Formation (kcal/mol) on distortion from C_{2v} Symmetry to C_s Symmetry

Element of symmetry kept	Symmetry in C_{2v}	Symmetry in C_s	ΔH_f^a	ΔH_f^b
sigma(yz)	${}^2A_2$, ${}^2B_1$	${}^2A"$	33.8^c (1.4)	71.0
	${}^2A_1$, ${}^2B_2$	${}^2A'$	---	d

sigma(xz)	$^2A_2$, $^2B_2$	$^2A''$	33.8^c (1.8)	d
	$^2A_1$, $^2B_1$	$^2A'$	d	61.6 (1.5)

a) Planar geometry. Number in parenthesis refers to lowering in kcal/mol with respect to the lower of the two C_{2v} states.

b) Staggered geometry. Number in parenthesis refers to lowering in kcal/mol with respect to the lower of the two C_{2v} states.

c) The wavefunction exhibited only C_1 symmetry.

d) A distortion from C_{2v} symmetry was not energetically favorable.

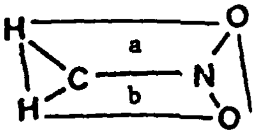
Table 3 MNDO Geometries[a]

of CH_2NO_2 radicals in C_s symmetry

Geometry	ΔH_f	CN	NO	CH	ONC	HCN	Dihedral
6	33.8	1.466	1.221	1.083	120.5	118.3	
			1.227	1.083	119.1	118.5	
6a	61.6	1.465	1.268	1.084	118.0	120.2	72.8
				1.082		116.4	
7	71.0	1.452	1.226	1.084	125.3	118.0	88.9
			1.306		116.6		

a) When two values for a variable are given, the first value corresponds to the bond distance or bond angle on the side of the CN bond denoted 'a' in figures 6, 6a, and 7 while the second value corresponds to the side denoted 'b'.

The global minimum was a distorted planar structure 6 but since the wavefunction did not possess C_s symmetry, the state could not be definitively assigned. Although the staggered $^2A_2$ and $^2B_1$ solutions could not be found, the MNDO value of 71.0 kcal/mol for the heat of formation of the distorted structure 6a is a lower bound for the lower of the C_{2v} states. When the sigma (yz) plane of symmetry is lost the $^2A_1$ and $^2B_1$ states interact and lead to a $^2A'$ state 7 1.5 kcal/mol lower in energy than the $^2A_1$ state.



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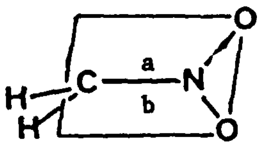

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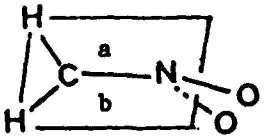

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Since the relative energies of NO_2 and related compounds are particularly sensitive to the basis set[10], ab initio calculations were performed on the CH_2NO_2 system[13]. Geometries were completely optimized within either the C_{2v} or C_s point group using the 3-21G basis[14] and single point calculations were then made including correlation at the UMP3 level[15]. The energies relative to the staggered $^2B_2$ are presented in Table 4, absolute energies in Table 5, and geometries in Table 6. From Table 4 one can determine that the $^2A_2$ - $^2B_1$ (planar) separations calculated at the UHF/3-21G, UHF/6-31G, UMP2/6-31G, and UMP3/6-31G are respectively; -17.7, -4.6, 49.4, and 31.0 kcal/mol. This compares to the MNDO value of 18.3 kcal/mol from Table 1.

Table 4 Relative Energies (kcal/mol) for Different States of CH_2NO_2 Based on Single Configuration Calculation

		UMP3/6-31G	UMP2/6-31G	UHF/6-31G	UHF/3-21G
Planar	$^2A_2$	24.3	45.1	-12.7	-26.5
	$^2B_1$	-6.7	-4.3	-8.1	-8.8
	$^2B_2$	16.5	29.8	9.2	0.3
	$^2A_1$				122.9
	$^2A''$	5.7	23.3	-22.8	-32.6
	$^2A'$	37.5	57.9	9.0	-16.0
Stagg.	$^2A_2$	75.4	87.7	58.2	45.4
	$^2A_2$	110.4	133.0	76.0	53.1
	$^2B_1$	58.1	71.6	38.6	30.9
	$^2B_2$	0	0	0	0
	$^2A_1$				80.7
	$^2A''$	52.5	73.7	15.5	0.9
	$^2A'$	18.0	36.9	-14.4	-24.6

Table 5 Total Energies (Hartrees) for Different States of CH_2NO_2 Based on Single Configuration Calculation

State	config.[a]	UMP3/6-31G	UMP2/6-31G	UHF/6-31G	UHF/3-21G
Planar					
$^2B_1$	16/3/2/10	243.33871	243.35832	242.89561	241.62565
$^2B_2$	16/4/2/9	243.30166	243.30401	242.86808	241.61118
$^2A_2$	16/4/1/10	243.28929	243.27959	242.90298	241.65386
$^2A_1$	16/5/1/9				241.41585
$^2A''$[b]	26/5	243.31891	243.31428	242.91899	241.66365
					(6.1)[c]
$^2A'$[d]	25/6	243.26825	243.25916	242.86835	241.63718
					(16.3)[c]
Staggered					
$^2B_1$	16/5/2/8	243.23547	243.23744	242.82115	241.56241
$^2B_2$	16/4/2/9	243.32802	243.35148	242.88272	241.61165
$^2A_2$	15/5/2/9	243.20787	243.21167	242.78989	241.53924
$^2A_2$	16/4/1/10	243.15204	243.13955	242.76159	241.52701
$^2A_1$	16/5/1/9				241.48298
$^2A''$[e]	24/7	243.24441	243.23404	242.85805	241.61020
					(30.0)[c]
$^2A'$[f]	25/6	243.29926	243.29263	242.90567	241.65085
					(24.6)[c]

a) The notation refers to the number of electrons in the a_1, b_1, a_2, and b_2 orbitals respectively. The notation for $^2A''$ and $^2A'$ refers to the number of electrons in a' and a" orbitals respectively

b) Involves the interaction of planar states $^2B_1$ and $^2A_2$ and the loss of the sigma (xz) plane of symmetry.

c) The number in parenthesis refers to the lowering in kcal/mol with respect to the lower of the two interacting C_{2v} states for the 3-21G energies.

d) Involves the interaction of planar states $^2B_2$ and $^2A_1$ and the loss of the sigma (xz) plane of symmetry.

e) Involves the interaction of staggered states $^2B_1$ and $^2A_2$ and the loss of the sigma (xz) plane of symmetry.

f) Involves the interaction of staggered states $^2B_2$ and $^2A_1$ and the loss of the sigma (xz) plane of symmetry.

Table 6 Ab initio UHF/3-21G Geometries of CH_2NO_2 radicals in C_{2v} Symmetry and the Spin Squared Values (without projection)

	State	S^2	CN	NO	CH	ONC	HCN	Dihedral
Planar	$^2A_2$	1.59	1.377	1.360	1.065	122.5	117.2	
	$^2B_1$	0.79	1.408	1.257	1.065	117.1	116.6	
	$^2B_2$	1.08	1.281	1.369	1.066	129.2	118.3	
	$^2A_1$	1.80	1.384	1.428	1.064	138.6	116.1	
	$^2A''^a$	1.47	1.391	1.288	1.065	124.5	117.1	
				1.362	1.064	115.1	117.1	
	$^2A'^a$	1.37	1.341	1.458	1.065	115.0	118.9	
				1.284	1.066	129.8	116.5	
Stagg.	$^2A_2^b$	1.54	1.336	1.454	1.068	128.4	117.2	
	$^2A_2^b$	1.84	1.425	1.370	1.068	115.2	116.7	
	$^2B_1$	1.84	1.413	1.363	1.070	128.2	117.8	
	$^2B_2$	0.76	1.456	1.241	1.067	117.0	116.5	
	$^2A_1$	1.84	1.402	1.419	1.071	124.7	118.0	
	$^2A''^c$	1.76	1.419	1.472	1.070	111.8	118.7	90.6
				1.299		128.9		
	$^2A'^c$	1.63	1.431	1.319	1.070	120.8	118.0	96.1
				1.328		118.7		

a) See Table 3 and Figure 6.

b) The geometries for the two perpendicular states of $^2A_2$ symmetries differ in the orbital occupancy. The first entry was obtained with 3 open shells, and the second with one open shell(see text).

c) See Table 3 and Figure 8.

The rotational barrier of planar $^2B_1$ to staggered $^2B_2$ is fairly insensitive to the level of calculation (7-9 kcal/mol). The rotational barrier of planar $^2A_2$ to staggered $^2A_2$ is also insensitive to correlation if the same configuration is used. The barrier at the UHF/6-31G level is 79.6 kcal/mol compared to 86.1 kcal/mol at the UMP3/6-31G level. The high barrier reflects the multiple bond character of the C-N bond. At the single determinant level, however, the $[8a_1^2 2b_1^2 5b_2^2]1a_2^1$ configuration leads to a higher energy than the $[7a_1^2 2b_1^2 1a_2^2 4b_2^2]8a_1^1 3b_1^1 5b_2^1$ configuration[16]. The energy difference between the two solutions varied from 10-30 kcal/mol depending on level of calculation (see Table 4).

Of course the true $^2A_2$ staggered state will be some linear combination of these two states plus other configurations of the correct symmetry. The proper treatment of such states must be based on either an MCSCF approach or a full configuration interaction approach.

As seen in Table 6 the CN bond length of the planar $^2B_1$ states elongates 0.05 Å upon twisting to the staggered $^2B_2$ state. This suggests that the 6.7 kcal/mol required for rotation (UMP3/6-31G) may be due either to elimination of conjugation in the planar structure or increased repulsion of the electron in the singly occupied orbital with the oxygen atoms in the staggered structure.

It must be remembered that this is not an electronic transition between states but rather a conformational change. The states $^2B_1$ and $^2B_2$ are antisymmetric with respect to C_2 rotation while A_2 state is symmetric.
In the former case a rotation will split the $^2B_1$ and $^2B_2$ planar states into $1^2A''$ and $2^2A''$ which may interact. The rotation continues until at 180 degrees the states become noninteracting with new designations of $^2B_2$ and $^2B_1$. The interaction could lead to a weak minimum for the lower state or a slight maximum in the higher state. However in this paper rotational barrier refers to the energy difference in the two C_{2v} electronic states. For $^2A_2$ rotation the same applies to the interaction of $^2A_2$ and $^2A_1$ as $1^2A'$ and $2^2A'$. In this case the energy separation between the two states makes mixing unlikely.

The shortest CN bond occurs in the planar $^2B_2$ state, 0.10 Å shorter than the CN bond in the planar $^2A_2$ state $\underline{4}$ whose valence structure can be drawn with a double bond. The shorter CN bond is due to removing an electron (with respect to the $^2A_2$ configuration) from the CN antibonding $5b_2$ orbital and putting it in the CN bonding $1a_2$ orbital. The loss of a electron from the $5b_2$ orbital also causes the CNO bond angle to increase about 6 degrees when compared to the planar $^2A_2$ geometry.

The spin squared values for the 3-21G wavefunctions are given in Table 6. The only states which approach the ideal 0.75 value (S(S+1)) are the planar $^2B_1$ state and the staggered $^2B_2$ state. In these states the extra alpha spin electron is almost completely localized in a p orbital perpendicular to the CH_2 plane. The other states indicate a large amount of spin polarization where alpha and beta spins localize in different regions of the molecule. This gives some indication that a restricted program must use additional configurations to achieve the same result.

It was found that the 3-21G optimized geometries are unstable with respect to distortions from C_{2v}. The results are also presented in Table 4, 5, and 6. The distortions and energy changes are larger than found for MNDO. When correlation is used the distortion becomes unfavorable.

A perturbational correlation treatment such as the UMP3 method becomes ineffective when the single Hartree-Fock configuration is not the dominant configuration in the wavefunction. Since it is known that there are several configurations of the same symmetry and of comparable energy, a MCSCF treatment was used to continue the study. The program ALIS[17] developed by Klaus Ruedenberg and coworkers and sponsored by the U.S. Department of Energy was used to determined MCSCF energies and wavefunctions.

In order to 'feel out' the potential surface and determine which configurations were important for the different states MCSCF calculations were made using a STO-3G basis[18]. In all calculations reported below the 3-21G geometries were used[19]. It was later confirmed that the largest contribution to the wavefunction was the configuration used to generate the geometry. It can be argued that using geometries optimized with a single configuration might 'favor' that configuration in a MCSCF scheme, however the extra expense of optimizing at this level was not feasible. MCSCF calculations were performed on the two staggered $^2A_2$ states obtained at the 3-21G level (vide supra) using different configurations. For the geometry obtained with 3 open shells, the leading contribution (one space orbital with two spin functions) also contained the 3 open shells (a_1, b_1, b_2) and accounted for 63% of the wavefunction. For the geometry obtained with one open shell (a_2), the same configuration accounted for 49% of the wavefunction.

The steps taken to obtain the MCSCF energy[20] are given below. An initial guess of orbitals is made by doing a restricted open shell calculation. For the STO-3G basis the energy normally converged but for the 6-31G basis the energy diverged. In the latter case it was necessary to stop the SCF at the point of divergence and orbital improvement was made at the expense of extra MCSCF microiterations. Next a limited MCSCF was performed with a few intuitive configurations. Using this wavefunction a CI in a larger space (approximately 500 Spin Adapted Antisymmeterized Products) was made to determine which configurations made substantial contributions to the wavefunction. These configurations were then used in another MCSCF calculation with the CI orbitals as the initial guess. The process was repeated until the MCSCF and CI had the same dominant configurations and until no configuration in the CI which was not included in the MCSCF contributed 1% or more to the wavefunction. The final MCSCF was carried out with between 5 and 11 spin adapted configurations. This provides an approximation to the full 500 configuration MCSCF as the most important configurations have been iteratively selected.

The MCSCF/STO-3G results are presented in Table 7. The first column represents the restricted open shell energies while the second column gives the MCSCF energy with the number of configurations in parenthesis and the per cent contribution of the most important configuration. The third column gives the CI energy with the number of spin adapted configurations in parenthesis (8 orbitals and 7 electrons in C_{2v} symmetry). It has been pointed out that in some cases carrying out a calculation in C_{2v} symmetry may lead to a higher energy than if only C_s symmetry were used, but in the calculations[10a,b] for NO_2 it was found that the C_{2v} solution was the same as the C_s solution. For this reason plus economics, the C_{2v} point group was used when possible.

Relative energies are presented in Table 9. In contrast to MNDO and ab initio results, the planar $^2A_2$ state is predicted to be the most stable of the C_{2v} states followed by the planar $^2B_1$ state 8.0 kcal/mol higher. The rotational barrier for the $^2B_1$ to $^2B_2$ conformational change is 18.6 kcal/mol, considerablely higher than the MNDO (0.4 kcal/mol) or the UMP3/6-31G (6.7 kcal/mol) barrier. The barrier for the rotation of the $^2A_2$ state (45.1 kcal/mol) is larger than the UMP3/6-31G value (51.1 kcal/mol).

Table 7 Total Energies for Different States of CH_2NO_2 Based on Multiconfigurational STO-3G Wavefunction

	State	RSCF	MCSCF	#conf.	$\%^a$	CI	#conf.	$\%^b$
Planar	$^2A_2$	239.7296	239.79270	(4)		239.86545	(582)	11%
			239.88456	(6)	65%	239.90642	(582)	< 1%
	$^2B_1$	239.7699	239.86848	(6)	81%	239.89358	(588)	< 1%
	$^2B_2$	239.7512	239.82680	(5)	87%	239.83138	(594)	6%
			239.84988	(9)		239.85617	(594)	< 1%
Stagg.	$^2A_2$	239.5864	239.79005	(8)	52%	239.79205	(584)	< 1%
	$^2B_1$	No SCF	239.73403	(7)		239.79018	(588)	6%
			239.81702	(11)	30%	239.82255	(588)	< 1%
	$^2B_2$	239.7633	239.85302	(5)	83%	239.86399	(594)	< 1%

a) Largest contribution from a single configuration in the MCSCF wavefunction.

b) Largest contribution from a single configuration in the CI which was not optimized in the MCSCF wavefunction.

The STO-3G minimal basis set is known to be inferior to the near double zeta quality 6-31G basis set[21]. For this reason the calculations were repeated with the larger basis set. It was felt that most of the important configurations would already be identified from the STO-3G basis allowing rapid convergence to the most important configurations in the expanded basis.

The absolute energies for the MCSCF/6-31G calculations are presented in Table 8 and the relative energies are presented in Table 9. The restricted open shell energies are not given as the SCF diverged. The percent contribution of the single largest contributing configuration clearly indicates that a single determinant cannot be adequate. The planar $^2B_1$ and staggered $^2B_2$ states have one configuration comprising approximately

Table 8 Total Energies for Different States of CH_2NO_2 Based on Multiconfigurational 6-31G Wavefunction

	State	MCSCF	#conf.	$\%^a$	CI	#conf.	$\%^b$
Planar	$^2A_2$	242.86061	(6)		242.89866	(582)	less 1%
		242.9238	(8)	73%	242.94688	(582)	less 1%

	$^2B_1$	242.8978 (7)		242.90731 (588)	< 1%
		242.94927 (7)	89%	242.95541 (588)	< 1%
	$^2B_2$	242.86 (5)		242.90560 (594)	< 1%
		242.92690 (8)	91%	242.94086 (594)	< 1%
	$^2B_1^c$	242.92308 (7)	81%	242.92988 (588)	< 1%
	$^2A_2^c$	242.90617 (8)	70%	242.92207 (582)	< 1%
	$^2A''$	242.92 (7)		242.92671 (68)	8%
		242.93088 (8)		242.95703 (1176)	< 1%
		242.96236 (8)	90%	242.97867 (1176)	< 1%
Stagg.	$^2A_2$	242.6 (6)		242.62593 (584)	34%
		242.80496 (7)		242.81163 (584)	3%
		242.80498 (9)	24%	242.81155 (584)	< 1%
	$^2A_2$	242.8238 (9)		242.83152 (584)	< 1%
		242.82383 (9)	52%	242.83165 (584)	< 1%
	$^2B_1$	242.84862 (11)		242.86150 (588)	< 1%
		242.84806 (11)	49%	242.86847 (588)	< 1%
	$^2B_2$	242.93351 (5)	90%	242.96780 (594)	< 1%

a) Largest contribution from a single configuration in the MCSCF wavefunction.

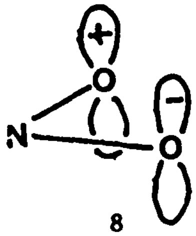
b) Largest contribution from a single configuration in the CI which was not optimized in the MCSCF wavefunction.

c) The $^2B_1$ calculation was at the $^2A_2$ geometry and the $^2A_2$ calcuation was at the $^2B_1$ geometry(see text).

Table 9 Relative Energies (kcal/mol) for Different States of CH_2NO_2 Based on MCSCF/STO-3G and MCSCF/6-31G

	State	MCSCF/STO-3G	+CI	MCSCF/6-31G	+CI
Planar	$^2A_2$	-19.8	-26.6	6.1	13.1
	$^2B_1$	-9.7	-18.6	-9.9	7.8
	$^2B_2$	2.0	4.9	4.1	16.9
	$^2A''$			-18.1	-6.8
Stagg.	$^2A_2$	39.5	45.1	80.6	98.0
	$^2A_2$			68.8	85.4
	$^2B_1$	22.6	46.3	53.6	62.3
	$^2B_2$	0	0	0	0

90% of the wavefunction. These corresponds to one electron in a p orbital perpendicular to the CH_2 plane and are the same states that produced 'normal' S^2 values. Even for these two states the orbitals occupations showed a significant population of a 'virtual' orbital. In Figure 8 and 9 the nonbonding oxygen b_2 orbital contained 1.8 electrons while the antibonding (bonding across oxygen) contained 0.2 electrons.



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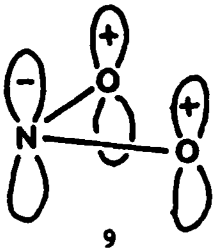

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This suggests that there may be some stabilization through pi overlap of the oxygen p orbitals.

The MCSCF/6-31G plus CI lead to a predicted staggered $^2B_2$ C_{2v} ground state for the nitromethyl radical. This is different from each of the previous methods. The planar $^2B_1$ state is 7.8 kcal/mol less stable and the planar $^2A_2$ state is 13.1 kcal/mol above the staggered $^2B_2$ state. The difference between the $^2A_2$ states is 72.3 kcal/mol which is almost identical to the STO-3G difference and greater than that predicted by UMP3/6-31G.

The relative energies have not converged with respect to increasing the sophistication of the basis set. Therefore it is premature to give the definitive electronic state ordering. In particular polarization functions as well as a more complete CI may make significant contributions to the relative energies.

Another possible influence on relative energies could be distortions from C_{2v}. This was found to be favorable in the MNDO approximation and at the UHF/3-21G and UHF/6-31G levels (though not at the UMP2/6-31G or UMP3/6-31G levels). In order to see if the planar $^2A_2$ and $^2B_1$ states might interact upon loss of the sigma (xz) plane (vide supra), MCSCF calculations were carried out on the planar $^2A_2$ state at the $^2B_1$ geometry and on the $^2B_1$ state at the $^2A_2$ geometry. The results shown in Figure 10 (see Table 8 for absolute energies) indicate that a crossing must occur somewhere between the two geometries along a C_{2v} reaction coordinate.

A MCSCF calculation was carried out on the distorted C_{2v}

geometry optimized with the UHF/3-21G basis (see Table 6). The results given in Table 8 and 9 indicate that the distortion is favorable and yields a $^2A''$ state 14.6 kcal/mol more stable than the planar $^2B_1$ state. This is 6.8 kcal/mol more stable than the staggered $^2B_2$ and thus becomes the ground state. It would be important to precisely determine the C_s minimum before structural predictions are made as the UHF/3-21G optimized geometry may not be accurate, but it is felt that such optimization would not qualitatively change this result.

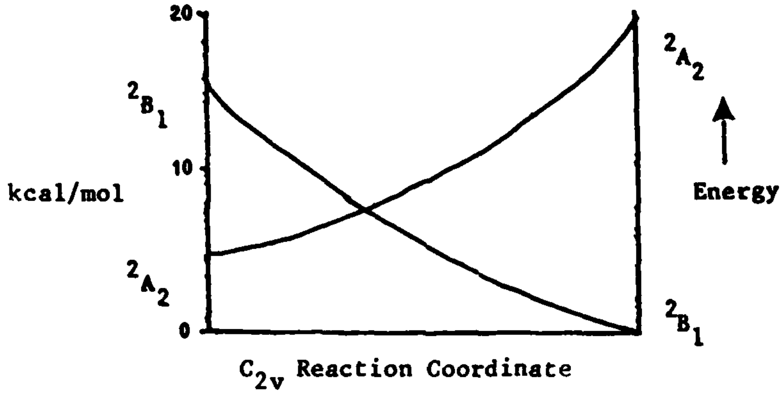

Figure 10. Illustration of C_{2v} Energy Crossing with the MCSCF calculations at the four labeled points.

RECOMMENDATIONS

On the basis of the above study the following recommendations can be made:

(1) That single determinant methods for the nitromethyl radical may neglect important contributions to the wavefunction and must be used with some caution in making structural and energetic predictions.

(2) That semi-empirical and ab initio methods provide similar qualitative predictions, however it is more difficult to obtain different electronic states with the MNDO method.

(3) That distortions from C_{2v} symmetry must be considered when states differing by only one spin orbital cross at some C_{2v} geometry.

(4) That unrestricted ab initio results without correlation probably overestimate such distortions.

(5) That a similar study be undertaken at the ab initio level for the radicals derived from 1-nitropropene which may be a more realistic model for the radicals produced from TNT.

(6) That in order to study the decomposition mechanism for nitromethane the reaction pathway from the nitromethyl radical to CH_2 plus NO_2 and to CH_2O plus NO be studied.

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REFERENCES

(1) Kurz, M. E.; Chen, T.-Y. R. J. Org. Chem. 1978, 43, 239.

(2) Cottrell, T. L.; Graham, T. E.; Reid, T. J. Trans. Faraday Soc. 1951, 47, 584.

(3)(a) Nazin, G. B.; Manelis, G. B.; Dubovitskii, F. I. Russ. Chem. Rev. 1968, 37, 603. (b) Crawforth, C. G.; Waddington, D. J. Trans. Faraday Soc. 1969, 65, 1334. (c) Dubovitskii, F. I.; Korsunskii, B. L. Russ. Chem. Rev. 1981, 50, 958.

(4) Jacox, M. E. J. Phys. Chem. 1983, 87, 3126.

(5) Knobel, Yu. K.; Miroshnichenko, E. A.; Lebedev, Yu. A. Izv. Akad. Nauk. SSSR, Ser. Khim. 1971, 485.

(6)(a) Chachaty, C. J. Chim. Phys. 1965, 62 728. (b) Chachaty, C.; Rosilio, C. J. Chim. Phys. 1967, 64, 777.

(7) Bolsman, T. A. B. M.; Verhoeven, J. W.; De Boer, Th. J. Tetrahedron, 1975, 81, 898.

(8)(a) Guidry, R. M.; Davis, L. P. Themochimica Acta 1979, 32, 1. (b) Davis, L. P.; Wilkes, J. S.; Pugh, H. L.; Dorey, R. C. J. Phys. Chem. 1981, 85, 3505. (c) Davis, L. D.; Turner, A. G.; Carper, W. R.; Wilkes, J. S.; Dorey, R. C.; Pugh, H. L.; Siegenthaler, K. E. "Thermochemical Decomposition of TNT: Radical Identification and Theoretical Studies," FJSL TR 81-0002, April 1981.

(9) Baird, N. C.; Taylor, K. F. Can. J. Chem. 1980, 58, 733.

(10)(a) Jackels, C. F.; Davidson E. R. J. Chem. Phys. 1976, 64, 2908. (b) Jackels, C. F.; Davidson E. R. J. Chem. Phys. 1976, 65, 2941. (c) Handy, N. C.; Goddard, J. D.; Schaefer, H. F. III J. Chem. Phys. 1979, 71, 1979. (d) Benioff, P. A. J. Chem. Phys. 1978, 68, 3405. (e) Krauss, M.; Hopper, D. G.; Fortune, P. J.; Wahl, A. C.; Tiernan, T. O. "Potential Energy Surfaces for Air Triatomics, Vol I," June 1975, Final Report ARL TR 75-0202, Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio.

(11) Pople, J. A.; Segal, G. A. J. Chem. Phys. 1965, 43, S129.

(12) Dewar, M. J. S.; Thiel, W. J. Am. Chem. Soc. 1977, 99 4899.

(13) The Gaussian 80 program was used; Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. QCPE 1981, 13, 406.

(14) Binkley, J. S.; Pople, J. A.; Hehre, W. J. J. Am. Chem. Soc.

1980, 102, 939.

(15) Pople, J. A.; Binkley, J. S.; Seeger, R. Int. J. Quantum Chem. Symp. 1976, 10, 1.

(16) The orbitals in brackets indicate the highest doubly occupied orbital of each type.

(17) Elbert, S. T.; Cheung, L. M.; Ruedenberg, K. NRCC Software Catalog, Vol 1., Program No. QM01 (ALIS) (Ames Laboratory-Iowa State University). The MCSCF method used is described in: Ruedenberg, K.; Cheung, L. M.; Elbert, S. T. Int. J Quantum Chem. 1979, 16 1069.

(18) Hehre, W. J.; Stewart, R. F.; Pople, J. A. J. Chem. Phys. 1969, 51, 2657.

(19) The following paper finds that large spin contaminations is associated by poor geometry predictions. Farnell, L.; Pople, J. A.; Radom, L. J. Phys. Chem. 1983, 87, 79.

(20) Feller, D. F.; Schmidt, M. W.; Ruedenberg, K. J. Am. Chem. Soc. 1982, 104, 960.

(21) Ditchfield, R.; Hehre, W. J.; Pople, J. A. J. Chem Phys. 1971, 54, 724.

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