

Ab Initio and MNDO Study of Nitromethane and the Nitromethyl Radical

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Abstract: Ab initio and MNDO calculations have been performed to study the geometry and vibrational frequencies of nitromethane and the nitromethyl radical. For nitromethane the two rotational conformers are predicted to differ in energy by only 0.01 kcal/mol (MP2/6-31G*). Vibrational frequencies of the staggered and eclipsed conformations have been calculated and compared with the experimental frequencies. Similar studies were carried out for the nitromethyl radical where it was found that the UHF solution was internally unstable, and a lower energy solution was found with symmetry relaxation. However, the distortion from C_{2v} is predicted to be energetically unfavorable when correlation is included (UMP2/3-21G). Vibrational frequencies of CH_2NO_2 were calculated at the C_{2v} geometry and compared with a recent experimental study. At the scaled 6-31G* level the average absolute error in vibrational frequencies is 23 and 12 cm^{-1} for CH_3NO_2 and CH_2NO_2 , respectively, if the two NO stretches are omitted. The calculated C-N stretching frequency of 995 cm^{-1} (scaled UHF/6-31G*) is only 48 cm^{-1} higher than the C-N stretch in CH_3NO_2 and does not suggest significant π -bond character. Disagreement between calculated and observed NO stretching frequencies is traced to the neglect of a contributing configuration. The MNDO results parallel 3-21G and 6-31G* results. However, when compared with experimental values the 6-31G* basis is uniformly superior.

The nitro group is well recognized to exert significant electronic effects as a substituent. The group acts as an electron sink where negative charge can accumulate on the oxygen atoms. Several authors¹⁻³ using MCSCF methods have shown that a second configuration is important in the description of nitromethane, the simplest organo-nitro compound. In one study¹ it was found that at the STO-3G level several configurations are required before the correct order of the singlet and triplet state is given. If a near double- ζ basis set is used (3-21G), the correct order is given with a single configuration. In addition, with increasing sophistication of the basis set, the leading configuration becomes more dominant.⁴

In the present study a comparison is made of the properties of nitromethane and the nitromethyl radical calculated with different basis sets (3-21G, 6-31G*, MNDO). It is found that for accurate prediction of geometry and vibrational frequencies a single configuration at the 6-31G* level is sufficient. Deviations in the bond length and stretching frequencies of NO, however, can be attributed to the neglect of the second contributing configuration.

A very recent study^{5,6} of the reactions of nitropropene has been made with MNDO. In order to further test the reliability of MNDO for nitro compounds, it was decided to include MNDO in the present study to rigorously compare the predictions of the semiempirical calculations with more sophisticated ab initio ones.

Experimental frequencies of the nitromethyl radical^{7,8} have been obtained⁹ by observing the IR spectra of species resulting from the reaction of F and CH_3NO_2 in an argon matrix. The new bands were largely assigned to HF, H_2CO , and CH_2NO_2 which are reaction products; however, the bands due to the free nitromethyl radical were only partially assigned. To aid in the vibrational assignment of the nitromethyl radical a systematic study of the

Table I. Total Energies (-Hartrees) and Differences (kcal/mol) Associated with Conformation Change in Nitromethane

	staggered	eclipsed	Δ^a
MNDO	3.5027 ^b	3.5022 ^b	-0.0005
3-21G	242.25586	242.25585	-0.01
MP2/3-21G	242.74772	242.74767	-0.03
6-31G*	243.66199	243.66198	-0.01
MP2/6-31G*	244.337942	244.337925	-0.01

^a Staggered - eclipsed in kcal/mol. ^b ΔH_f° (kcal/mol).

vibrational frequencies of nitromethane and the nitromethyl radical at different computational levels was undertaken. At the highest level (6-31G*) the agreement between theory and experiment (including isotope shifts) is excellent, allowing for the first time complete assignment of the vibrational spectrum for the nitromethyl radical.

Results and Discussion

All calculations were carried out with the GAUSSIAN 82 program system¹⁰ and the MNDO program.¹¹ Geometries were completely optimized within the appropriate point group with analytical derivatives. Vibrational frequencies were obtained by solving the coupled perturbed Hartree-Fock equations¹² to obtain the analytical second derivatives of energy with respect to geometric distortion. The level of theory used to determine energies is sometimes different from the level of theory used to determine geometries. In the basis set notation used below, the first basis set indicates the level of the single point calculation while the basis set following "//" indicates the level used in geometry optimization.

The measured rotational barrier of nitromethane is 0.0061 kcal/mol¹³ which compares to a theoretical barrier of 0.01 kcal/mol (MP2/6-31G*//6-31G*). The staggered conformation

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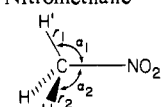
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Table II. Calculated and Observed Geometric Parameters for Nitromethane (Angstroms and Degrees)

conformation	method	C-N	CH'	CH	NO'/NO''	H'CN	HCN	CNO'/CNO''	ONO
staggered	MNDO	1.546	1.110	1.108	1.210	107.8	109.3	119.3	121.4
	3-21G	1.492	1.080	1.074	1.240	106.8	107.1	116.9	126.2
	6-31G*	1.478	1.080	1.076	1.192	106.5	108.0	117.1	125.8
eclipsed	MNDO	1.546	1.108	1.109	1.209/1.210	109.7	108.4	119.6/118.9	121.4
	3-21G	1.493	1.073	1.078	1.239/1.242	107.4	106.8	117.7/116.1	126.2
	6-31G*	1.479	1.076	1.079	1.191/1.193	108.4	107.0	117.7/116.5	125.3
	obsd ^a	1.489			1.224	av	107.5		125.3

^aReference 13.**Table III.** Predicted Geometric Changes Associated with Conformation Change in Nitromethane


conformation	method	ΔCH_4^a	ΔCH^b	Δangle^c
staggered	MNDO	+0.005	+0.002	-1.5
	3-21G	+0.007	+0.006	-0.3
	6-31G*	+0.007	+0.004	-1.5
eclipsed	MNDO	+0.005	-0.001	1.3
	3-21G	+0.007	-0.005	0.6
	6-31G*	+0.006	-0.003	1.4

^a $\Delta\text{CH}_4 = r - (r_1 + 2r_2)/3$, where r = the CH bond distance in CH_4 .
^b $\Delta\text{CH} = r_1 - r_2$. ^c $\Delta\text{angle} = \alpha_1 - \alpha_2$.

1 is slightly more stable (Table I).

The HOMO of CH_3NO_2 is of a'' symmetry in both the staggered (**1**) and eclipsed (**2**) conformation while the LUMO is a'' symmetry in the eclipsed conformation and of a' symmetry in the staggered conformation. The interaction diagram¹⁴ is given in

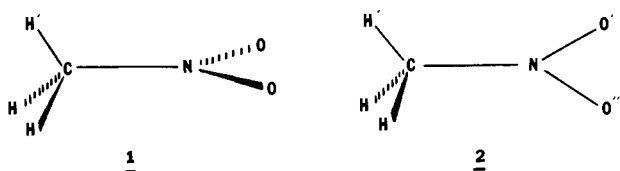


Figure 1. The methyl group is expected to interact strongly with the LUMO as that orbital has a significant coefficient on nitrogen in contrast to the HOMO where the coefficient is zero by symmetry. The resulting interaction causes a methyl tilt away from the nitro group (Figure 1a) to improve the overlap of the occupied orbital of the methyl group with the unoccupied orbital on nitrogen (Tables II and III). In **2** the interaction of the occupied a' orbital of the methyl group with the unoccupied a' orbital mainly on nitrogen (Figure 1b) causes a tilt in a direction opposite to the tilt in **1**. Another effect of hyperconjugation is seen in the C-H bond lengths. All C-H bonds are shorter than those found in CH_4 (Table III) due to electrostatic bond shortening caused by electron withdrawal by the nitro group. However, in staggered nitromethane the unique hydrogen is 0.004 Å longer (6-31G*) than the two equivalent hydrogens due to donation into the LUMO on nitrogen. In the eclipsed conformation, the unique hydrogen is 0.003 Å shorter (6-31G*) than the two equivalent hydrogens because it cannot interact with the LUMO (Table III).

With respect to basis set effects, it can be seen that all basis sets predict the two conformations to be very close in energy (Table I). In comparing the ab initio bond length and angles with the experimental structure derived from the microwave spectrum,¹³ it is seen that the 3-21G and 6-31G* distances bracket the experimental values (Table II), the 3-21G values being too long and the 6-31G* values being too short. The N-O distances showed the largest change on going from 3-21G to 6-31G* with a shortening of 0.048 Å, while in comparison, the C-N bond shortens 0.014 Å. Angles are reproduced to within 0.5° by the 6-31G* basis set. Except for the C-N bond which is predicted to be too long by almost 0.06 Å and the ONO angle which is predicted to

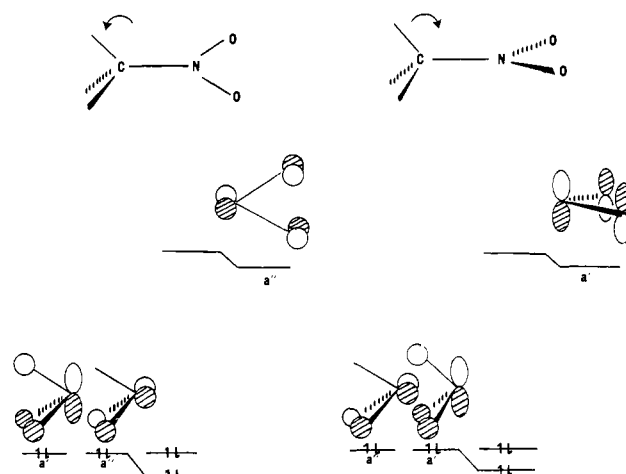


Figure 1. Interaction diagram for (a) eclipsed nitromethane and (b) staggered nitromethane. The direction of the methyl group tilt is indicated by a curved arrow. Movement in this direction involves a favorable interaction of the HOMO of the CH_3 fragment with the LUMO of the NO_2 fragment.

be too small by 4°, the MNDO geometry is also in good agreement with experiment.

The vibrational frequencies of nitromethane calculated by different methods are compared with experimental frequencies¹⁵ in Table IV. For the eclipsed conformation there are ten a' and five a'' modes while for the staggered conformation there are nine a' and six a'' modes. Some of the modes have different designations for the two conformations. The antisymmetric NO_2 stretch is of a' symmetry in the eclipsed conformation and of a'' symmetry in the staggered conformation. The NO_2 wag and rock also have different assignments in the two conformations.

Compared mode for mode the staggered and eclipsed conformation have nearly the same values at the same computational level. There is a trend toward higher frequencies on going from 3-21G to 6-31G*. This parallels the bond shortening that is generally observed when polarization functions are added. The MNDO values are often intermediate between the 3-21G value and the 6-31G* value.

For comparison with the observed frequencies of CH_3NO_2 , the 6-31G* frequencies are scaled by a factor of 0.9. The agreement is exceptional except for the NO stretches which will be discussed below. The average difference of the scaled 6-31G* values¹⁶ and the observed frequencies is 37 cm^{-1} (23 cm^{-1} when the two NO stretches are omitted).

An interesting aspect of the frequency calculation is the prediction of the methyl torsion. When the normal convergence criterion was used^{17a} in the optimization of the eclipsed confor-

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Table IV. Vibrational Frequencies of Nitromethane Calculated by Different Methods and Observed

	eclipsed (1)			staggered (2)				obsd ^b	Δ^c	mode ^d
	MNDO	3-21G	6-31G* ^a	MNDO	3-21G	6-31G*	6-31G* ^a			
a'	3333	3393	3404	3333	3352	3369	3032	3065	33	CH ₃ stretch
	3283	3261	3274	3279	3258	3272	2945	2967	22	CH ₃ stretch
	2114	1483	1880	1840	1381	1689	1520	1402	-118	NO ₂ stretch
	1839	1381	1688	1484	1643	1620	1458	1426	-32	CH ₃ deformation
	1484	1646	1609	1406	1565	1571	1414	1379	-35	CH ₃ deformation
	1404	1565	1570	1156	1251	1271	1144	1103	-41	CH ₃ rock
	1162	1152	1232	1038	911	1052	947	917	-30	CN stretch
	1038	911	1051	678	666	744	670	655	-15	NO ₂ scissor
	677	659	736	583	603	690	621	607	-14	NO ₂ wag
	478	468	527							
a''	3280	3347	3367	3284	3392	3404	3064	3045	-19	CH ₃ stretch
	1410	1640	1619	2115	1483	1880	1694	1561	-131	NO ₂ stretch
	1157	1250	1270	1407	1642	1607	1446	1426	-20	CH ₃ deformation
	478	615	702	1162	1152	1233	1110	1103	-7	CH ₃ rock
	-88	-16	-21	478	471	529	476	480	4	NO ₂ rock
				12	13	26				CH ₃ torsion

^aScaled by 0.9. ^bReference 15. ^cObserved frequencies minus frequencies for staggered conformation scaled by 0.9. ^dAssignments are for staggered conformation.

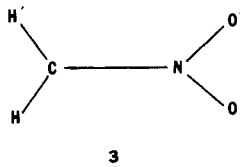
Table V. Predicted Geometries and Energies for the Nitromethyl Radical (Angstroms, Degrees, and Hartrees)

geometry	CN	CH/CH'	NO/NO'	HCN/H'CN	ONC/O'NC	UHF energy	UMP2 energy
MNDO (<i>C_s</i>)	1.466	1.083/1.083	1.221/1.227	118.3/118.4	120.6/119.2	33.8 ^a	
MNDO (<i>C_{2v}</i>)	1.476	1.083	1.213	118.3	119.3	35.2 ^a	
UHF/3-21G (<i>C_s</i>)	1.391	1.065/1.064	1.288/1.362	117.1/117.1	124.5/115.1	241.66365	242.05481
UMP2/3-21G (<i>C_s</i>)	1.352	1.076/1.076	1.304/1.391	116.9/118.7	125.5/111.7	241.66100	242.05646
UHF/3-21G (<i>C_{2v}</i>)	1.408	1.065	1.257	116.6	117.1	241.62566 ^b	242.09127 ^c
UMP2/3-21G (<i>C_{2v}</i>)	1.470	1.077	1.291	116.3	116.5	241.62043	242.09675
UHF/6-31G* (<i>C_{2v}</i>)	1.418	1.067	1.198	116.5	117.1	243.02981	243.67759

^akcal/mol. ^bBroken symmetry solution is 17.8 kcal/mol lower. ^cBroken symmetry solution is 31.9 kcal/mol higher.

mation and the frequencies calculated, the resulting torsion was calculated to be positive (20 cm⁻¹; 6-31G*). When a stricter convergence criterion was used,^{17b} the 6-31G* energy was lowered only 3×10^{-4} kcal/mol. However, the vibrational frequencies using this geometry yielded a negative frequency for the torsion (-21 cm⁻¹; 6-31G*). Also, the calculated MP2/6-31G* energy actually increased 0.02 kcal/mol on using the geometry obtained from the stricter criterion. This emphasizes that a very rigorously optimized geometry is required for calculating analytical second derivatives when very low frequency modes are involved.

The nitromethyl radical, **3**, was studied next. Previous calculations have been performed¹⁸ with a MCSCF/6-31G wave function. The results show that there are several low-lying



electronic states and that several of these states require more than one configuration to be properly described. It was found that the ²B₁ and ²A₂ electronic states interact via a second-order Jahn-Teller distortion, reducing the symmetry from *C_{2v}* to *C_s*. Also, for a *C_{2v}* geometry it was found that the UHF solution exhibited internal instability and reducing the symmetry from *C_{2v}* led to a lower energy solution in *C_s* symmetry. We are confining our attention here to the planar ²B₁ state and a planar state of ²A'' symmetry. In the MCSCF calculation it was found that the former state was dominated by one configuration, which contributed 95% while the ²A'' state had a leading configuration with a contribution of 90%.

It has been shown¹⁸ that by using one configuration, the ²A₂ state of CH₂NO₂ is 17.7 kcal/mol lower than the ²B₁ state

(UHF/3-21G//3-21G); however, correlation reverses the stability such that the ²B₁ state was 31.0 kcal/mol lower (UMP3/6-31G//3-21G). The ²A'' state was the global minimum on the UHF/3-21G surface, 6.1 kcal/mol lower than the ²A₂ state and characterized by an exaggerated distortion of the NO₂ group (Table V). However, with correlation (UMP3/6-31G//3-21G), the ²A'' state is 12.4 kcal/mol higher than the ²B₁ state. This would indicate that the distortion which is favorable at the UHF/3-21G level is *not* favorable when correlation is included. This is in disagreement with the MCSCF treatment¹⁸ where the ²A'' state (using the 3-21G geometry) was eventually found to be lower in energy. It has been pointed out¹⁹ that single configurational ab initio methods often underestimate the interaction of low-lying electron states. For a closer look at interacting states in a similar system see ref 20.

In this work it was decided to determine the effect of correlation on the geometry of the radical and, therefore, UMP2/3-21G optimizations were carried out starting from the UHF/3-21G geometries. The results in Table V show that correlation generally lengthens bond lengths, but the energy changes are minimal for the *C_{2v}* ²B₁ state where the UMP2/3-21G energy is lowered 3.4 kcal/mol upon optimizing the UHF/3-21G geometry with correlation. In contrast the *C_s* geometry, a ²A'' state, is lowered only 1.0 kcal. Interestingly, the C-N bond length of the ²B₁ state increases significantly upon optimizing with correlation, probably indicating a smaller mixture of states for which a resonance structure containing a carbon-nitrogen double bond can be written. The spin-squared values of 0.80 for the *C_{2v}* geometry and 1.44 for the *C_s* geometry indicate that the latter geometry has more extensive spin polarization.

The UMP2/3-21G optimized *C_{2v}* geometry is 25.3 kcal/mol more stable than the UMP2/3-21G optimized *C_s* geometry. It

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(17) (a) The Normal criterion for GAUSSIAN 82 is for all internal forces to be smaller than 4.5×10^{-4} hartree/bohr or hartree/rad. (b) The stricter criterion is for all internal forces to be smaller than 1.5×10^{-5} hartree/bohr or hartree/rad.

Table VI. Vibrational Frequencies of the Nitromethyl Radical (cm⁻¹)

	MNDO		3-21G		6-31G*		obsd	Δ^a	mode
	C _s	C _{2v}	C _s	C _{2v}	C _{2v}	C _{2v} scaled			
A ₁	3412	3415	3371	3367	3391	3052	3055	3	CH ₂ stretch
	1608	1647	857	1203	1586	1427	1297	-130	NO ₂ stretch
	1432	1431	1544	1528	1546	1392	1419	27	NO ₂ stretch
	1161	1144	1053	976	1106	995	986	-9	CN stretch
	680	674	581	652	756	680	693	13	NO ₂ scissor
A ₂	148	154	253	343	291	262			CH ₂ torsion
B ₁	758	762	350	673	789	710	719	9	CH ₂ wag
	536	525	429	559	457	411			NO ₂ wag
B ₂	3456	3452	3527	3533	3554	3199	3200	1	CH ₂ stretch
	2066	2135	1486	1431	1845	1660	1461	-199	NO ₂ stretch
	1122	1122	1208	1096	1194	1075	1095	20	CH ₂ rock
	494	491	461	497	555	500			NO ₂ rock

^a Observed frequencies minus 6-31G* frequencies scaled by 0.9.

Table VII. Change in CN Bond Length (Å) and Frequency (cm⁻¹) from CH₃NO₂ to CH₂NO₂

method	C-N length	C-N frequency
MNDO	-0.060	106
3-21G	-0.084	65
6-31G*	-0.080	54 (48) ^a
obsd		69

^a Frequency scaled by 0.9.

must be remembered that the UMP2 perturbational treatment used to obtain the C_{2v} and C_s optimized geometries is based upon very different starting wave functions. It is therefore possible that the C_s minimum may be an artifact of the calculation and that the C_s structure would collapse to the C_{2v} structure if the starting orbitals were more closely related to the C_{2v} orbitals rather than obtained from a broken symmetry solution.

At present the geometry of the radical is still a point of uncertainty. MCSCF treatments suggest a planar C_s structure while the UMP treatment predicts a C_{2v} geometry. The MCSCF results¹⁸ for the C_s structure used eight configurations to form a reference state, and a CI of 1176 configurations was made from that reference state. The correlation results here involve a perturbational approach and require a dominant contribution from one configuration. In any case, if the radical is only slightly distorted from C_{2v} symmetry, the observed frequencies should be comparable with those calculated from a C_{2v} structure.

The vibrational frequencies of the C_{2v} geometry and C_s geometry are given in Table VI. The vibrational frequencies produced from the C_s minimum indicate a very weakened oxygen-nitrogen bond. The bond length has increased 0.1 Å and the stretching frequency is calculated to be 857 cm⁻¹ (3-21G). The C-N distance decreases 0.017 Å and the C-N vibrational frequency increases 77 cm⁻¹ from the value in the C_{2v} geometry (3-21G). Even though the energy is calculated to be lower at a C_s geometry, the vibrational frequencies of the C_{2v} geometry indicate a minimum for all wave functions used. MNDO also predicts two different solutions, one in C_{2v} symmetry and one in C_s symmetry 1.4 kcal/mol lower in energy. In this case the geometric changes are much smaller than

the changes predicted by 3-21G in going from the C_{2v} to the C_s structure, and as can be seen in Table III, the predicted vibrational frequencies are very similar.

When the 6-31G* scaled frequencies (0.9 scaling factor) calculated at the C_{2v} structure are compared to the observed frequencies (Table VI), the agreement is excellent and as will be seen shortly the assignments are consistent with observed shifts upon substitution of ¹³C, ¹⁵N, and ²H in the molecule. (The average absolute error is 46 cm⁻¹ which is reduced to 12 cm⁻¹ if the two NO stretches are eliminated.) The scaled frequencies of the NO stretches are still overestimated and would require a MCSCF treatment to be correctly described. It has been found¹⁸ with a MCSCF approach that an orbital which is nitrogen-oxygen antibonding and unoccupied in the single configurational studies actually contains 0.2 electron. A description based on the MCSCF treatment would then yield weaker N-O bonds and hence lower vibrational frequencies for the NO stretches.

The large increase of the NO stretching frequencies on going from 3-21G to 6-31G* parallels the large decrease in bond distance. The antisymmetric NO₂ stretch increases 308 cm⁻¹ while the symmetric NO₂ stretch increases 397 cm⁻¹.

The C-N bond stretch of CH₂NO₂ is of particular interest since resonance forms can be written in which there is either a single bond or a double bond between the two atoms. The 6-31G* scaled results predict the C-N stretch at 995 cm⁻¹ in good agreement with an observed band at 986 cm⁻¹.

The MNDO and ab initio results indicate that the C-N bond lengths in CH₃NO₂ decreases considerably upon losing a hydrogen atom; however, the vibrational frequency increases only slightly (Table VII). The C-N stretch of CH₃NO₂ is calculated to increase 48 cm⁻¹ on losing a hydrogen atom to form CH₂NO₂ which is close to the observed increase of 69 cm⁻¹. This suggests little multiple bonding.

The symmetric NO₂ stretch in CH₂NO₂ is predicted too high by 130 cm⁻¹ (6-31G* scaled 1427 cm⁻¹, obsd 1297 cm⁻¹), while the analogous NO₂ stretch in CH₃NO₂ is predicted too high by 118 cm⁻¹ (6-31G* scaled 1520 cm⁻¹, obsd 1402 cm⁻¹). The lowering of the symmetric N-O stretch on losing a hydrogen atom (CH₃NO₂ → CH₂NO₂) is likely due to conjugation, which reduces

Table VIII. MNDO, 6-31G*-Scaled^a and (Observed) Frequency Shifts (cm⁻¹) for Isotopes of the Nitromethyl Radical

type	CD ₂ NO ₂		¹³ CH ₂ NO ₂			CH ₂ ¹⁵ NO ₂			mode	
A ₁	-957	-849	-4	-4	(-5)	0	0	(b)	CH ₂ stretch	
	-1	-1	(-1)	0	-1	(0)	-23	-24	(-25)	NO ₂ stretch
	-270	-299		-4	-0	(-6)	0	-1	(-6)	CH ₂ scissor
	-130	-65	(-81)	-20	-11	(-12)	-9	-7	(-4)	CN stretch
	-12	-25	(-24)	-6	-10	(-8)	-3	0	(-3)	NO ₂ scissor
A ₂	-42	-71		0	0	(b)	0	0	(b)	CH ₂ torsion
B ₁	-133	0		-7	-1	(-5)	-1	-18	(-10)	NO ₂ wag
	-878	-98		-1	-3	(b)	-13	0	(b)	CH ₂ wag
B ₂	-2	-797		-15	-14	(-15)	0	0	(0)	CH ₂ stretch
	-235	-7	(-1)	0	-1	(-10)	-47	-38	(-26)	NO ₂ stretch
	-45	-203		-9	-9	(-7)	1	0	(-1)	CH ₂ rock
	-45	-60		-4	-4	(b)	-2	-1	(b)	NO ₂ rock

^a Frequency scaled by 0.9 ^b Not reported.

electron density in the nitro group. The asymmetric NO₂ stretch is overestimated by 199 cm⁻¹ in CH₂NO₂ compared to 130 cm⁻¹ in CH₃NO₂. For both NO₂ stretches the error is due to neglecting a low-lying configuration, which contains two electrons in an orbital which is N-O antibonding.

The isotope frequency shifts were calculated with the 6-31G* force constants and are reported in Table VIII. One can clearly see that the calculated shifts support the present assignment. The CN stretch, which was previously thought to be much higher, has only a small isotope shift for ¹³C and ¹⁵N. For a pure C-N mode with a frequency of 986 cm⁻¹ the isotope shift for ¹³C and ¹⁵N would be 21 and 15 cm⁻¹, respectively. The calculated and observed shifts are less due to coupling with the hydrogens and oxygens. In fact, the isotope shift with deuterium is calculated to be 65 cm⁻¹ for the CN stretch (observed 81 cm⁻¹), which also suggests coupling. The observed isotope shifts have been reported where it was clear that the new band was shifted from one which was identifiable in the normal isotope spectrum. The MNDO isotope shifts are also presented in Table VIII. Although the agreement is not as good as the 6-31G* scaled results, the trends are generally the same. One exception is the shifts for the B₁ wags. The 6-31G* scaled results show a considerable shift as a result of substituting ¹⁵N for ¹⁴N for the first (higher frequency) wag

as compared to the second wag while MNDO results predicts the opposite effect. This clearly shows that MNDO predicts CH₂ wag > NO₂ wag in contradiction to the 6-31G* scaled results. Unfortunately the lower frequency wag was not observed in the experimental spectrum.

Conclusion

Ab initio results predict that the methyl group tilt is controlled by CH₃ donation into a vacant nitrogen orbital in the LUMO and that the rotational barrier is extremely small. The CH₂NO₂ radical is predicted to be of C_{2v} symmetry at the UMP2/3-21G level. The UHF solution, on the other hand, contains an internal instability which when removed leads to a broken symmetry solution in C_s symmetry, and which is further stabilized by a geometric distortion of the NO₂ group. Comparing vibrational frequencies calculated with several wave functions, it is found that scaled 6-31G* frequencies can be used to assign the character of CH₂NO₂ frequencies. Although not of quantitative quality, the MNDO frequencies may be of sufficient accuracy to help interpret and assign vibrational frequencies.

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Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 2. Use of Second-Order Correlation Energies

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Abstract: The heats of formation of 15 representative strained and unstrained hydrocarbons have been calculated by ab initio molecular orbital theory with the 6-31G* basis set. It is shown that RMP2 energies computed at SCF geometries in conjunction with homodesmotic reactions furnish heats of formation within 3 kcal/mol of experiment; the root-mean-square (rms) error is 1.3 kcal/mol. An exception is benzene, for which homodesmotic cycles using single- and double-bonded carbons are probably inadequate. Calculations are also reported for isodesmotic reactions, the rms error being 2.1 kcal/mol. Heats of formation calculated at the 6-31G*(SCF) level are in error to a substantially greater degree.

In the first paper of this series¹ we investigated the possibility of using ab initio molecular orbital theory to calculate accurate heats of formation of the medium-sized hydrocarbons cyclohexane, adamantane, cubane, and dodecahedrane. The highest level of calculation employed 6-31G* (SCF) energies² and homodesmotic reactions³ of the molecules of interest. While the deviations of the calculated $\Delta H_f(298\text{ K})$ from the experimental values for the relatively unstrained hydrocarbons cyclohexane and adamantane were reasonably good (0.7 and 2.1–2.8 kcal/mol, respectively), the calculated $\Delta H_f(298\text{ K})$ for cubane with three different thermochemical cycles were 9 to 16 kcal/mol in error. This persistent and appreciable error is disturbing in view of the importance of the application of ab initio calculation to the thermochemistry of highly strained systems, whose preparation in

quantity is often difficult or impossible. The present work describes a systematic study of the heats of formation of a number of representative strained and unstrained hydrocarbons with 6-31G* SCF and RMP2⁴ energies in conjunction with both isodesmotic⁵ and homodesmotic³ reactions. With the exception of benzene, heats of formation calculated from RMP2 ab initio energies are in excellent agreement with experiment, even for highly strained systems such as cubane.

Methods

All RMP2 calculations were performed at 6-31G*(SCF)-optimized geometries with the frozen-core approximation,^{5c} which excludes correlation contributions from carbon 1s-like molecular orbitals. The calculations were performed with optimized programs developed by us (The Queens College Quantum Chemistry Package). Heats of reaction at 0 K are computed from the ab initio energy differences corrected for

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