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An *ab initio* Molecular Orbital Study of the Nitromethyl Anion

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The anion CH_2NO_2^- has been studied with *ab initio* molecular orbital calculations. The structures of various CH_2NO_2^- isomers and other related species have been determined by full geometry optimization at the Hartree-Fock level with the diffuse-function augmented basis sets 3-21+G and 6-31+G*. In addition, improved energy comparisons have been obtained at the MP3/6-31++G** level, and vibrational frequency analysis of the various species have been carried out in order to characterize the stationary points, as well as to determine the zero-point vibrational energies of these species.

The rotation around C-N bond for CH_2NO_2^- has been calculated to have a barrier of 128 kJ mol⁻¹. The transition structure of this process is found to have C_s symmetry. In addition, the electron affinity of CH_2NO_2^- is calculated to be 168 kJ mol⁻¹, not in very good agreement with the experimental estimate. The C-proton and O-proton affinities of CH_2NO_2^- have been calculated to be 1579 and 1512 kJ mol⁻¹, respectively. The former is in very good agreement with the experimental result.

INTRODUCTION

In the past few years, some significant advances have been made in the theoretical study of carbanions. In particular, it has been found that quantitatively useful chemical information can be obtained for anions from calculations with sufficiently large basis sets (such as diffuse-function augmented sets) and with adequate incorporation of electron correlation.¹ At such high levels of theory, properties such as ion structures and energies of reactions involving closed-shell species may be determined with an accuracy comparable to that achievable for cations or neutral molecules.

The nitromethyl anion has been investigated using *ab initio* molecular orbital many times. In these studies, the basis sets used include STO-3G^{2,3,4}, 3-21G⁴, 4-31G^{2,4,5,6,7}, 3-21+G^{8,9}, 4-31+G¹⁰, and 6-31G*⁴ (a »less extensive optimization«). Also, the best relative energies obtained so far are at the levels of 4-31+G//4-31+G¹⁰ and 6-31G*//6-31G*.⁴ In other words, in the studies carried out so far, none of the basis sets includes both polarization and diffuse functions. Furthermore, electron correlation has not been taken into consideration and none of the stationary points has been charac-

terized with vibrational frequency calculations. Hence, it appears to be desirable to rectify this situation by studying this anion with better basis functions and with the inclusion of correlation effects and vibrational frequency analysis.

It is the purpose of this note to study the rotational barrier and the C-proton and O-proton affinities of the nitromethyl radical. Wherever possible, the results obtained will be compared with those of other theoretical studies and experimental findings.

METHOD OF CALCULATION AND RESULTS

The *ab initio* molecular orbital calculations have been carried out using the Gaussian 86 system of programs.¹¹ Geometries of all species have been determined at the Hartree-Fock (HF) level by employing the gradient optimization technique with basis sets 3-21+G and 6-31+G*. These diffuse-function augmented basis sets have been shown to yield satisfactory results for anionic systems.¹ It has been demonstrated that the inclusion of diffuse functions to split-valence basis sets improves anion energy calculations significantly.

In order to characterize the stationary points found as minima (equilibrium structures) or saddle points (transition structures) and to include the effects of zero-point vibrational energies (ZPVEs) in estimating the relative energies of various structures, harmonic vibrational frequencies have been calculated at the HF level with the 3-21+G basis using geometries optimized

TABLE I
Calculated total-energies (Hartrees) and zero-point vibrational energies (ZPVE, kJ mol⁻¹)^a

Species	HF/3-21+G ^b	HF/6-31+G*	HF/6-31++G**	MP2/6-31++G**	MP3/6-31++G**	ZPVE ^c
1 (CH ₂ NO ₂ ⁻)	-241.77186	-243.08510	-243.08914	-243.78496	-243.77790	99
2 (CH ₂ NO ₂)	-241.67752	-243.00964	-243.01518	-243.71300	-243.70426	89
3 (CH ₂ NO ₂ ⁻)	-241.69741	-243.03587	-243.03982	-243.73257	-243.72607	91
4 (CH ₂ NO ₂ ⁻)	-241.68983	-243.03948	-243.04278	-243.69958	-243.69519	96
5 (CH ₂ NO ₃)	-242.31737	-243.67119	-243.67615	-244.36698	-244.36266	136(143) ^d
6 (CH ₂ NO ₂ H)	-242.31894	-243.64028	-243.65076	-244.33744	-244.33988	135
[•] CH ₃ ^e	-39.34604	-39.56110	-39.56679	-39.69651	-39.71392	82
⁻ CH ₃ ^f	-39.29075	-39.50415	-39.51055	-39.68119	-39.69462	79

^a Geometries optimized using 6-31+G* basis set unless otherwise noted.

^b Geometry optimized using the 3-21+G basis set.

^c Calculated at the 3-21+G//3-21+G level unless otherwise noted.

^d Value in the parentheses was calculated at the 6-31+G*/6-31+G* level.

^e The structure of CH₃[•] has D_{3h} symmetry: C-H = 1.073 Å (6-31+G*) or 1.072 Å (3-21+G).

^f The structure of CH₃⁻ has C_{3v} symmetry: C-H = 1.097 Å (6-31+G*) or 1.091 Å (3-21+G), <HCH = 112.9° (3-21+G) or 109.2° (6-31+G*).

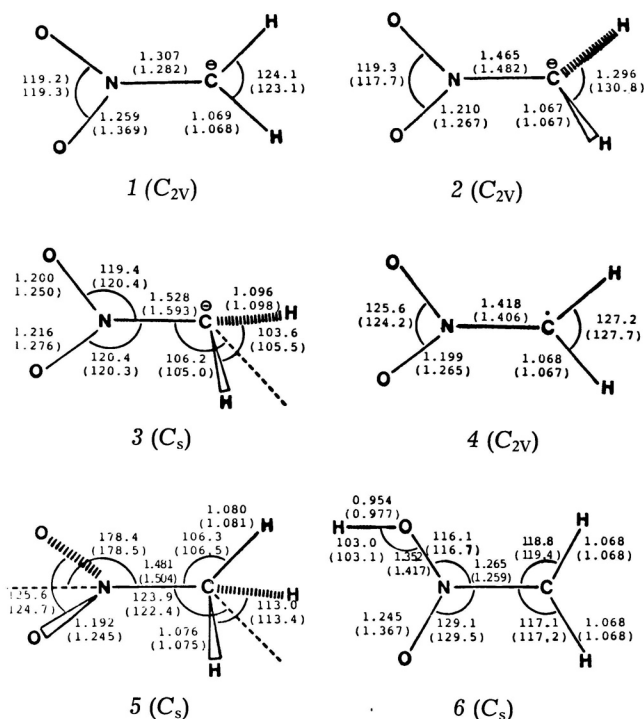


Figure 1. Optimized structures (HF/6-31+G*) of various isomers of CH_2NO_2^- (1, 2, 3), CH_2NO_2^+ (4), CH_3NO_2 (5), and $\text{CH}_2\text{NO}_2\text{H}$ (6). Structural parameters determined at the HF/3-21+G level are enclosed in parentheses. Bond lengths are given in Ångströms and angles in degrees.

with this basis set. In addition, the effects of valence-electron correlation on relative energies have been determined from the third-order Møller-Plesset perturbation theory^{12,13} (MP3) calculations with the 6-31++G** basis set, using the structures optimized at the HF/6-31+G* level. In other words, the best energies reported are the MP3/6-31++G**//HF/6-31+G* values.

Optimized geometries of the various species are shown in Figure 1. Calculated total energies, ZPVEs and relative energies are summarized in Tables I and II, and calculated frequencies are listed in Table III. Unless otherwise noted, relative energies quoted in the text correspond to MP3/6-31++G** values, together with ZPVE contributions.

DISCUSSION

The Nitromethyl Anion and Its Rotational Barrier

Three isomers of CH_2NO_2^- , with planar C_{2v} (1), non-planar C_{2v} (2), and C_s (3) structures, have been studied in this work. Upon calculating the vibrational frequencies of these species, it was found that 1 and 3 represent an equilibrium structure and a transition structure, respectively. On the other hand, structure 2, with two imaginary vibrational frequencies, represents a second-order saddle point and hence is of no interest to us.

TABLE II

Relative energies (kJ mol^{-1}) calculated from total energies

Species	HF/3—21+G	HF/6—3HG*	HF/6—31++G**	MP2/6—31++G*	MP3/6—31**G*	MP3/6—31++G**
1 (CH_2NO_2^-)	0	0	0	0	0	0
2 (CH_2NO_2)	248	198	194	189	193	183
3 (CH_2NO_2)	195	129	129	138	136	128
EA^b	215	120	122	224	217	214
EA^c	78	-21	-18	192	174	168
PA (C) ^d	1432	1538	1541	1528	1535	1579
PA (O) ^d	1436	1458	1475	1451	1476	1512

^a Including zero-point vibrational correction.^b Electron affinity of CH_2NO_2^- calculated by direct subtraction.^c Electron affinity of CH_2NO_2^- calculated via reaction (1).^d Proton affinity of 1 calculated by direct subtraction without temperature correction.

TABLE III

Calculated vibrational frequencies (cm^{-1})^a

1 (CH_2NO_2^-)	525(a ₁)	547(b ₂)	684(b ₁)	757(a ₂)	853(a ₁)
	961(b ₁)	961(b ₂)	1353(b ₂)	1526(a ₁)	1656(a ₁)
	3345(a ₁)	3461(b ₂)			
2 (CH_2NO_2)	967i(a ₂)	842i(b ₂)	540(b ₂)	624(b ₁)	676(a ₁)
	884(a ₁)	1193(b ₁)	1257(b ₂)	1301(a ₁)	1470(a ₁)
	3346(a ₁)	3516(b ₁)			
3 (CH_2NO_2)	422i(a'')	460(a')	502(a')	611(a'')	812(a')
	1111(a')	1240(a')	1333(a'')	1382(a')	1593(a')
	3046(a')	3089(a'')			
4 (CH_2NO_2)	381(a ₂)	514(b ₂)	644(a ₁)	645(b ₁)	736(b ₁)
	970(a ₁)	1107(b ₂)	1169(a ₁)	1417(b ₂)	1540(a ₁)
	3354(a ₁)	3522(b ₂)			
5 (CH_3NO_2)	33i(a'')	476(a'')	620(a')	659(a')	899(a')
	1148(a'')	1256(a')	1380(a')	1452(a'')	1574(a')
	1624(a'')	1624(a')	3246(a')	3345(a')	3387(a'')
5 (CH_3NO_2) ^b	21(a'')	527(a'')	687(a')	738(a')	1944(a')
	1232(a'')	1268(a')	1569(a')	1605(a'')	1616(a')
	1679(a')	1842(a'')	3272(a')	3369(a')	3405(a'')
6 ($\text{CH}_2\text{NO}_2\text{Fi}$)	415(a'')	488(a')	502(a')	590(a'')	799(a'')
	811(a')	999(a')	1155(a'')	1342(a')	1439(a')
	1591(a')	1870(a')	3365(a')	3491(a')	3762(a')
CH_3^+	499(a ₂ '')	1531(e')	3246(a ₁)	3421(e')	
CH_3^-	653(a ₁)	1582(e)	3080(a ₁)	3168(e)	

^a Calculated at the 3—21+G//3—21+G level unless otherwise noted.^b Calculated at the 6—31+G**//6—31+G* level.

From these results it can be concluded that rotation about the formal C—N single bond does not proceed *via* the perpendicular structure 2, but rather *via* 3, which has a pyramidal configuration at carbon. The barrier of rotation has been calculated to be 128 kJ mol⁻¹. At the minimum basis level,⁴ this barrier has a value of 67 kJ mol⁻¹.

Examining the structures of 1 and 3, it is seen that, when CH₂NO₂⁻ rotates around its C—N bond, the C—N bond lengthens from 1.307 Å to 1.528 Å at the transition structure. Also, the N—O bonds shorten from 1.259 Å to the 1.20—1.22 Å range. This picture is consistent with the idea that the C—N π-system is broken upon internal rotation.

Electron Affinity of the Nitromethyl Radical

In this section we address the question of whether the nitromethyl anion is stable towards the spontaneous loss of an electron. Additionally, if the answer is in the affirmative, what is the electron affinity (*EA*) of the nitromethyl radical (4)?

The *EA* of a radical is the energy difference between the radical and its anion. However, the *EAs* obtained in this way are not always very accurate, especially for species leading to localized anions. Hence, in the results reported below, we have also included the approach of Schleyer and co-workers¹⁴ by calculating the enthalpy change for the isogyric¹⁵ reaction



This enthalpy change gives the *EA* of X⁻ relative to that of CH₃⁻. Taking the experimental value¹⁶ (8 ± 2 kJ mol⁻¹) for the *EA* of CH₃⁻ allows the *EA* of X⁻ to be calculated. In principle, evaluation of *EAs* in this manner should be most effective when X⁻ is similar to CH₃⁻. Thus, it is not certain whether the *EA* for CH₂NO₂⁻ obtained *via* reaction (1) is more or less accurate than the directly calculated value.

Examining Table II, it is seen that the *EA* for CH₂NO₂⁻ is calculated to be 168 kJ mol⁻¹ [*via* reaction (1)] or 214 kJ mol⁻¹ (direct subtraction). While these results are considerably different from the experimental »estimate« of 50 kJ mol⁻¹,¹⁷ they are still better than the one³ obtained with the STO—3G (with polarization functions) basis set, 238 kJ mol⁻¹. In any event, a more accurate experimental value is urgently needed.

At this point, it should be mentioned that both the experimental and the theoretical *EAs* reported here may not be entirely reliable. For the former, in their mass spectroscopic study for the estimate of the *EA* of CH₂NO₂⁻, Tsuda and co-workers arbitrarily assumed the dissociation energy of the C—H bond in CH₃NO₂ to be 4.4 eV. As far as the theoretical results are concerned, the fact that the two methods used in this work give considerably different *EAs* indicates that there is inherent difficulty in the proposed methods. In addition, the unrestricted Hartree-Fock scheme used in the calculation of the radical CH₂NO₂ may also be a source of errors, specially when there is a high degree of spin contamination.¹⁸

In passing, it is of interest to examine the optimized structure of CH₂NO₂⁻. When CH₂NO₂⁻ loses an electron to become CH₂NO₂[·], the C—N bond lengthens appreciably from 1.307 Å to 1.418 Å, while the N—O bonds shorten from

1.259 Å to 1.199 Å, indicating the π -system is more localized in the radical than in the anion.

The Proton Affinities of the Nitromethyl Anion

Protonation of the nitromethyl anion can occur at C or O, leading to CH_3NO_2 or $\text{CH}_2\text{NO}_2\text{H}$, respectively. The experimental gas-phase proton affinity at C [$PA(\text{C})$] is approximately 1500 kJ mol^{-1} ,¹⁹ while there is no experimental value for $PA(\text{O})$. Examining Table II, it is seen that $PA(\text{C})$ is calculated to be 1579 kJ mol^{-1} , in excellent agreement with the experimental value. Also, the calculated $PA(\text{O})$, 1512 kJ mol^{-1} , is very close to the $PA(\text{C})$ value.

In the literature, only one $PA(\text{O})$ result can be found: 1486 kJ mol^{-1} at the 4-31G//4-31G level. On the other hand, many $PA(\text{C})$ results have been reported: 1989 (STO-3G)⁹, 1485 (double zeta)⁵, 1510-1530 (4-31G and 6-31G)^{2,5,6,7}, 1432-1466 (3-21+G and 4-31+G)^{8,9,10}, and 1596 (6-31G*)⁷ kJ mol^{-1} .

Finally, upon examining Table III, it is seen that, at the 3-21 + G//3-21 + G level, the optimized structure for CH_3NO_2 has one imaginary vibrational frequency. However, at the 6-31 + G*/6-31 + G* level, all the vibrational frequencies are real, indicating that the structure optimized is an equilibrium structure.

CONCLUDING REMARKS

The rotational barrier around the C-N bond in CH_2NO_2^- has been calculated to be 128 kJ mol^{-1} . Also, the transition structure of this process is found to have C_s symmetry. On the other hand, the »best« calculated EA of CH_2NO_2^- has been calculated to be 168 kJ mol^{-1} , still considerably different from the experimental »estimate« of 50 kJ mol^{-1} . Finally, the $PA(\text{C})$ and $PA(\text{O})$ of CH_2NO_2^- have been calculated to be 1579 and 1512 kJ mol^{-1} , respectively; the former is in very good agreement with the experimental value.

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SAŽETAK

Ab initio molekularno-orbitalni račun za nitrometilni anion

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Proveden je *ab initio* molekularno-orbitalni račun za CH_2NO_2^- . Izračunana je visina energijske barijere za rotaciju oko veze C-N: ona iznosi 128 kJ mol^{-1} . Prijelazna struktura u tom procesu ima C_s simetriju. Izračunana vrijednost protonskog afiniteta (168 kJ mol^{-1}) za nitrometilni anion daleko je od eksperimentalno predložene vrijednosti (cca 50 kJ mol^{-1}). Predložene su također i strukture različitih izomera nitrometilnog aniona i srodnih spojeva.