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References and Notes

- (1) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2306 (1953).
- (2) R. J. Gillespie and R. S. Nyholm, *Q. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Angew. Chem., Int. Ed. Engl.*, **6**, 819 (1967).
- (3) R. J. Buenker and S. P. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).
- (4) J. E. Lennard-Jones, *J. Chem. Phys.*, **20**, 1024 (1952).
- (5) H. B. Thompson, *J. Am. Chem. Soc.*, **97**, 5293 (1975).
- (6) L. C. Allen, *Theor. Chim. Acta* **24**, 117 (1972).
- (7) L. S. Bartell and V. Plato, *J. Am. Chem. Soc.*, **95**, 3097 (1973).
- (8) G. W. Schnuelle and R. G. Parr, *J. Am. Chem. Soc.*, **94**, 8974 (1972).
- (9) H. Nakatsuji, *J. Am. Chem. Soc.*, **95**, 345, 354, 2084 (1973).
- (10) C. Trindle and L. C. Weiss, *J. Phys. Chem.*, **79**, 2435 (1975).
- (11) C. A. Naleway and M. E. Schwartz, *J. Am. Chem. Soc.*, **95**, 8235 (1973).
- (12) R. F. W. Bader and H. J. T. Preston, *Can. J. Chem.*, **44**, 1131 (1966).
- (13) J. L. Bills and R. L. Snow, *J. Am. Chem. Soc.*, **97**, 6340 (1975).
- (14) H. H. Schmidtke and H. Preuss, *Z. Naturforsch. A*, **16**, 790 (1961); H. H. Schmidtke, *ibid.*, **17**, 121 (1962); **18**, 496 (1963).
- (15) The Slater-type orbitals were expanded in four Gaussian type functions according to R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).
- (16) M. Levy, T. Nee, and R. G. Parr, *J. Chem. Phys.*, **63**, 316 (1975).
- (17) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
- (18) P. O. Lowdin, *J. Chem. Phys.*, **18**, 365 (1950).
- (19) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
- (20) POLYATOM (III), QCPE Program No. 199, Indiana University, Bloomington, Ind.
- (21) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972).
- (22) M. Klessinger, *Chem. Phys. Lett.*, **4**, 144 (1969).
- (23) H. Nakatsuji, *J. Am. Chem. Soc.*, **96**, 24, 30 (1974).
- (24) D. M. Chipman, B. Kirtman, and W. E. Palke, *J. Chem. Phys.*, **65**, 2556 (1976).
- (25) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 120; C. A. Coulson, "Valence", 2nd ed, Oxford University Press, London, 1961, pp 163, 179, 221.
- (26) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).
- (27) J. Jarvie, W. Willson, J. Doolittle, and C. Edmiston, *J. Chem. Phys.*, **59**, 3020 (1973).
- (28) P. A. Christiansen and W. E. Palke, *J. Chem. Phys.*, **67**, 57 (1977).
- (29) M. B. Hall, *Inorg. Chem.*, **17**, 2261 (1978).

SCF MO Calculations of Nitromethane and Nitromethyl Anion

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Abstract: Ab initio SCF MO calculations with Pople's 4.31 basis set predict a planar structure as the most stable form of nitromethyl anion and a monotonic increase in energy as the hydrogens are bent out of the molecular plane. In contrast to previous ab initio calculations, the derived structure has high C=N double bond character and N-O single bond character. Surprisingly, it is found that Pople's 4.31 basis set yields *lower* energies than Murrell's Gaussian approximation to Clementi's double ζ STO basis in spite of the fact that Murrell's basis uses *more* Gaussians. The calculated ionization potentials (Koopman's theorem) for nitromethane are in reasonable agreement with those calculated by Murrell and in fair agreement with experiment. However, previous assignments, based on semiempirical calculations, are in poor agreement with the ab initio calculations.

The structure of nitromethyl anion is of considerable interest since substituent effects on equilibria involving the anion suggest a planar, delocalized structure,^{2a} while kinetic substituent effects have been interpreted to indicate that a pyramidal carbanion may exist as an intermediate in solution proton transfer reactions of nitroalkanes.^{2b} In this paper we report ab initio SCF MO calculations on nitromethyl anion and nitromethane and examine a portion of the potential surface for distorting a planar nitromethyl anion to a pyramidal structure with HCH and HCN angles similar to nitromethane. The optimized geometries and calculated energies of nitromethane and the planar and pyramidal anions are presented in Table I.

I. Calculated Energy and Geometry of Planar Nitromethyl Anion

The calculations were performed using the program GAUSS 70³ and a 4.31 basis set.⁴ As a starting point, a planar geometry was assumed with R_{NO} (N-O bond length) = 1.228 Å, $R_{\text{C-N}}$ = 1.397 Å, $R_{\text{C-H}}$ = 1.09 Å, $\angle\text{HCH}$ = 123°, $\angle\text{ONO}$ = 121°. These parameters were those found by Murrell, Vidal, and Guest⁵ (hereafter referred to as MVG) from a minimum basis set calculation for the planar anion.

The C-H bond lengths were fixed at 1.09 Å, while R_{CN} and R_{NO} were optimized sequentially. After R_{CN} was readjusted, the ONO and HCH angles were varied, followed by reoptimization of R_{NO} and R_{CN} . The final geometry parameters and

energy were found to be R_{CN} = 1.286 Å, R_{NO} = 1.314 Å, $\angle\text{HCH}$ = 123°, $\angle\text{ONO}$ = 119°, energy = -242.691 894 au. Further variations of R_{CN} , R_{NO} , $\angle\text{HCH}$, and $\angle\text{ONO}$ indicate that the bond lengths and angles have been optimized to ± 0.005 Å and $\pm 0.5^\circ$, respectively, while the energy is estimated (parabolic interpolation) to be less than 4×10^{-5} au from the minimum. The structure we derive for the planar anion has bond lengths much closer to typical C=N and N-O bonds than the MVG structure. For example, R_{CN} for formaldoxime is 1.276 Å²⁴ compared to 1.286 Å calculated for the planar anion, while the MVG value of R_{CN} = 1.397 is significantly closer to that for nitromethane (1.489 Å).²³ The N-O bonds follow a similar pattern as seen in Table I. R_{NO} for formaldoxime is 1.408 Å²⁴ which compares to R_{NO} = 1.314 Å calculated for the planar anion, R_{NO} = 1.224 Å measured for nitromethane,²³ and R_{NO} = 1.228 Å calculated by MVG for planar anion. The 4.31 results on the optimized structure suggest that nitromethyl anion is related more closely to *aci*-nitromethane than to nitromethane itself. It is in this regard a much more reasonable structure than that calculated by MVG.

Kresge and Csizmadia have reported 3-G calculations on nitromethyl anion and a 4.31 calculation at the optimized minimum basis set (3G) geometries.¹³ The latter calculation is included in Table I. The optimized 3-G geometry of the planar anion is comparable to that found by MVG and differs substantially from the optimized structure calculated with the 4.31 basis set.

Table I. Energies^f and Geometries of Nitromethyl Anion and Nitromethane

	planar anion (4.31 optimized)	planar anion (MVG optimized)	planar anion (4.31 at 3G geometry)	pyramidal anion (4.31 optimized)	pyramidal anion (MVG)	nitromethane (4.31)
R_{CN} , Å	1.286	1.397	1.350	1.349	1.451	1.451
R_{NO} , Å	1.314	1.228	1.337	1.281	1.228	1.228
$\angle HCH$, deg	123	123	121.74	112 (fixed)	112	112
$\angle ONO$, deg	119	121	119.30	121 (fixed)	121	121
$\angle HCN$, deg	118.5	118.5	119.13	107 (fixed)	107	107
E	-242.691 894	-242.662 62 (MVG) -242.674 19 (4.31) ^a	-242.687 257 ^b	-242.671 715	-242.657 47	-243.272 062 (4.31) ^c -243.259 04 (MVG) ^d -243.263 034 (ref 13) ^e

^a 4.31 calculation at MVG geometry. ^b 4.31 basis set using optimized geometries for 3-G basis set (ref 13). ^c This geometry is marginally different from experiment (ref 23): $R_{CN} = 1.489$ Å, $R_{NO} = 1.224$ Å, $\angle HCN = 107.2^\circ$, $\angle ONO = 125.3^\circ$. ^d MVG used geometry of ref 23 as in footnote *c* (vide supra). ^e Geometry given in ref 13. ^f Professor E. R. Davidson has informed us that the energy of the nitromethyl anion is more negative than the energy of the corresponding radical (private communication).

Table II. Atomic and Molecular Energies Calculated with Pople's 4.31 Basis vs. Clementi's STO Basis

C(3P)	N(4S)	O(3P)	F(2P)	H ₂ O	CH ₃ F	H ₂ CO	CH ₃ ^a
-37.636 918	-54.327 925	-74.705 481	-99.265 481	-75.903 24	-138.858 86	-113.691 71	-39.503 92 4.31 ¹⁸
-37.686 677 ⁶	-54.397 873 ⁶	-74.804 180 ⁶	-99.401 164 ⁶	-76.005 74 ¹⁹	-139.010 06 ²⁰	-113.7968 ²¹	-39.5471 ²² STO DZ ⁶

II. Comparison of 4.31 G and MVG Basis Sets for the Planar Anion

It is noteworthy that the energy calculated using the 4.31 basis set is significantly lower than that calculated by MVG using a *larger* basis set.⁵ MVG⁵ employ a 3-Gaussian expansion for each valence STO of Clementi's STO double ζ basis set⁶ and a 6-Gaussian expansion for the heavy atom 1s shells which are kept at the single- ζ basis. At the MVG geometry, their calculated energy of the planar anion using the Gaussian double ζ basis set is -242.662 62 au, while at the same geometry the 4.31 basis set gives -242.674 19 au; the 4.31 basis set yields a lower energy of over 10^{-2} au (30 kJ/mol). This is a significant difference since MVG uses 108 Gaussians to represent the valence orbitals of nitromethyl anion, whereas the 4.31 basis gives its lower energy with only 72 Gaussians. This result is the more interesting since Clementi's DZ Slater basis set is generally superior to the 4.31 basis in both atomic and molecular calculations (Table II) and might give lower energies for the nitromethyl anion and nitromethane as well.

The MVG calculation employs a single contraction of 6 Gaussians to represent the core of each heavy atom, instead of a single contraction of 4 Gaussians as in the 4.31 basis. Since the core molecular orbitals will be similar to the core basis functions, the MVG basis set probably gives a better description of the 1s shells than the 4.31 basis. However, since the total energy is lower for the 4.31, the description of the valence regions (and chemically important energy differences) may be significantly better than the lower energy of 10^{-2} au would indicate. The primary reason for this apparent anomaly may lie in the fact that Pople's 4.31 basis set uses Gaussian functions chosen to minimize the energy in atomic and molecular calculations,⁴ whereas the MVG Gaussians were selected to mimic the Slater functions in Clementi's DZ-STO basis set. Apparently, more of the flexibility necessary for describing valence orbitals has been lost in the MVG procedure for constructing a basis set than in Pople's procedure where the Gaussian functions and the contraction scheme are optimized specifically for molecular calculations.

The present comparison of basis sets, together with the results in Table II, suggest that the apparently common practice⁷⁻¹¹ of replacing STOs with Gaussian approximations may lead to worse results than would be obtained by using a fewer number of well-chosen Gaussian orbitals in molecular calculations.⁴ Such an outcome could have been anticipated from

the prior results of Dunning,^{12a} Pople,^{12b} Veillard,^{12c} and others.

III. Calculated Energy and Geometry of Pyramidal Nitromethyl Anion

Calculations on the pyramidal form of nitromethyl anion followed the same course taken for the planar geometry. Using the MVG geometry ($R_{NO} = 1.228$ Å, $R_{CH} = 1.09$ Å, $R_{CN} = 1.451$ Å, $\angle HCH = 112^\circ$, $\angle ONO = 121^\circ$, $\angle HCN = 107^\circ$), R_{CN} was optimized followed by R_{NO} , to give the following energy and bond lengths: $E = -242.671 715$ au, $R_{NO} = 1.281$ Å, $R_{CN} = 1.349$ Å. By varying R_{CN} at this geometry and by parabolic interpolation, it was estimated that R_{CN} is within ± 0.02 Å from the minimum, and that the calculated energy for the above geometry (fixed bond angles) is not further than 5×10^{-4} au from the minimum.

When $\angle HCH$ was changed¹⁴ to 109.47° , the energy increased, and as $\angle HCH$ was varied to 115° , the energy decreased. No minimum could be found for the pyramidal structure with respect to deformation of the HCH angle. The energy for the pyramidal structure with $\angle HCH$, $\angle HCN$, $\angle ONO$ characteristic of nitromethane and optimized C-N and N-O bond lengths is about 53 kJ/mol (12.7 kcal/mol) higher than our energy for the optimized planar structure (Table I), while the MVG energy difference is only 13.5 kJ/mol (3.2 kcal/mol) for their optimized structures. It is noteworthy that the calculated proton affinity of the pyramidal structure is nearly identical in both basis sets, while that for the planar structure indicates that the planar anion is substantially more stable relative to nitromethane in the 4.31 basis compared to the MVG basis. The pattern emerging from the three structures in Table II suggests that the MVG basis lacks some of the flexibility necessary for an adequate description of the valence orbitals in molecules, and that this lack of flexibility is most apparent for more delocalized structures.

The present calculations suggest that the planar anion is substantially favored over the pyramidal form and that there is no potential barrier blocking the conversion of the pyramidal structure to the planar one. However, the extension of this conclusion to the proton transfer reactions of nitroalkanes in solution is not yet clear, since the addition of solvent and/or cation could result in a kinetic barrier separating a pyramidal structure and the planar counterpart. This question is currently under investigation.

Table III. Experimental and Calculated^a Ionization Potentials of Nitromethane (eV)

4.31		MV basis ⁵		exp ¹⁶	exp ¹⁷
11.98	(1a ₂ π)	12.19	(1a ₂ π)	11.32	
13.38	(5b ₂ n)	13.47	(8a ₁ n)		11.5
13.61	(8a ₁ n)	13.72	(5b ₂ n)	11.73	
16.57	(2b ₁ π)	16.90	(2b ₁ π)	14.73	
					(15)
17.03	(4b ₂)CH	17.28	(4b ₂)	15.75	
19.86	(3b ₂)σ	19.90	(3b ₂)	17.45	17.5
20.52	(1b ₁ π)	20.73	(1b ₁ π)	19.1	
20.68	(7a ₁ n)	20.89	(7a ₁)		20.4
23.57	(6a ₁)	23.85	(6a ₁)		26.5
30.94	(5a ₁)	30.74	(5a ₁)		33.4
38.44	(2b ₂)	38.73	(2b ₂)		37.0
44.53	(4a ₁)	44.61	(4a ₁)		42.0

^a Koopmans' theorem.**IV. Comparison of 4.31 and MVG Orbital Energies for Nitromethane**

The photoelectron spectrum of nitromethane has been examined by several groups using both x-ray¹⁵ and UV techniques.^{16,17} Assignment of the ionization potentials to molecular orbitals has been made using semiempirical calculations as a guide, and all workers¹⁵⁻¹⁷ have concluded that the two lone pair orbitals (8a₁ and 5b₂) are split by 3.4 eV. MVG⁵ have pointed out that this magnitude for the splitting is inconsistent with all published semiempirical calculations on nitromethane and, on the basis of their ab initio calculation of the 8a₁, 5b₂ splitting (0.25 eV), have suggested that the previous assignments are incorrect.

The 4.31 calculations on nitromethane (Table III) agree with the small calculated 8a₁, 5b₂ splitting (0.23 eV) found by MVG, although the relative order of the 5b₂ and 8a₁ orbitals is reversed. The correspondence between the remaining calculated orbital energies is generally better than 0.2-0.3 eV, while the agreement between relative differences in the experimental and calculated ionization potentials is within 1-2 eV for the eight highest molecular orbitals. The current assignments^{5,15-17} of the nitromethane photoelectron spectra would require that the calculated splitting of 8a₁ and 5b₂ lone pair orbitals be in error by over 3 eV. This discrepancy would seem rather large⁵ compared to the agreement between the remaining experimental and calculated values, but is certainly

within the realm of possibility. While a reassignment of the spectrum based on the 4.31 or MVG calculations could be regarded as speculative, the present results indicate that the current assignment could stand reexamination.

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References and Notes

- (1) (a) University of California, Los Angeles; (b) University of California, Berkeley.
- (2) (a) F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *J. Am. Chem. Soc.*, **92**, 5926 (1970); (b) F. G. Bordwell and W. J. Boyle, Jr., *ibid.*, **97**, 3447 (1975).
- (3) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, No. 236, Chemistry Department, Indiana University, Bloomington, Ind.
- (4) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 5001 (1970).
- (5) J. N. Murrell, B. Vidal, and M. F. Guest, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1577 (1975).
- (6) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).
- (7) R. F. Stewart, *J. Chem. Phys.*, **50**, 2485 (1969).
- (8) D. T. Clark and J. Miller, *Theor. Chim. Acta*, **41**, 193 (1976).
- (9) D. B. Adams, *J. Chem. Soc., Faraday Trans. 2*, **72**, 383 (1976).
- (10) I. H. Hillier, J. Kendrick, F. E. Mabbs, and C. D. Gardner, *J. Am. Chem. Soc.*, **98**, 395 (1976).
- (11) J. M. Howell, A. R. Rossi, and R. Bissell, *Chem. Phys. Lett.*, **39**, 312 (1976).
- (12) (a) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971); (c) C. Salez and A. Veillard, *Theor. Chim. Acta*, **11**, 441 (1968).
- (13) P. G. Mezey, A. J. Kresge, and I. G. Csizmadia, *Can. J. Chem.*, **54**, 2526 (1976).
- (14) \angle HCN was held fixed at 107°. This is one way of increasing or decreasing the "s" character of the carbon "lone pair" as \angle HCH decreases or increases. An alternative is to vary \angle HCH and \angle HCN linearly from their values for the nitromethane geometry to the values for the planar anion geometry. When this was done, the energy dropped monotonically on going from the pyramidal structure to the planar structure.
- (15) T. Fujikawa, T. Ohta, and H. Kuroda, *Chem. Phys. Lett.*, **28**, 433 (1974).
- (16) J. W. Rabalais, *J. Chem. Phys.*, **57**, 960 (1972).
- (17) T. Kobayashi and S. Nagakura, *Chem. Lett.*, 903 (1972).
- (18) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
- (19) G. Alagona and R. Cimiriaglia, *Theor. Chim. Acta*, **29**, 93 (1973).
- (20) B. R. Appleman, T. Tokuhiro, and G. Fraenkel, *J. Chem. Phys.*, **58**, 400 (1973).
- (21) T. Tokuhiro, B. R. Appleman, G. Fraenkel, P. K. Pearson, and C. W. Kern, *J. Chem. Phys.*, **57**, 20 (1972).
- (22) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 1740 (1970).
- (23) A. P. Cox and S. Waring, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1060 (1972).
- (24) I. N. Levine, *J. Chem. Phys.*, **38**, 2326 (1963).