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Dr. Richard S. Miller

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COMPUTATIONAL ANALYSIS OF SOME ASPECTS OF A
SYNTHETIC ROUTE TO AMMONIUM DINITRAMIDE

by

Tore Brinck and Peter Politzer

Department of Chemistry
University of New Orleans
New Orleans, LA 70148

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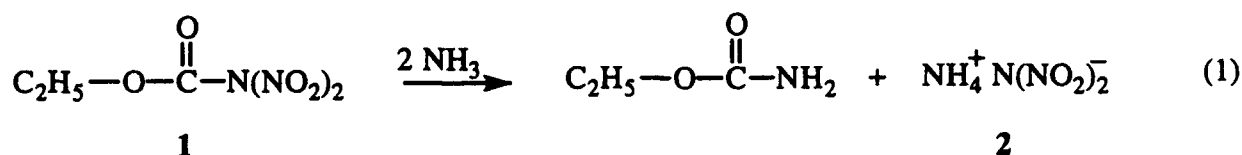
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13. ABSTRACT (Maximum 200 words) The optimized geometry of 1, $C_2H_5-O-\overset{O}{C}-N(NO_2)_2$, a precursor to ammonium dinitramide, has been computed at the <u>ab initio</u> HF/6-31G* level. We find no structural evidence that 1 exists in the ionic form, $C_2H_5-O-C\equiv O^+ N(NO_2)_2^-$. The reaction of 1 with NH_3 passes through a transition state that is consistent with a concerted substitution (Ingold mechanism) in which $N(NO_2)_2^-$ is the leaving group.									
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Introduction

Eq. (1) shows the final step in a synthetic route to ammonium dinitramide:

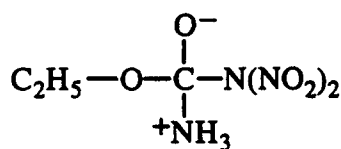


In this work, we have addressed two questions:

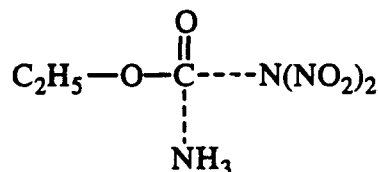
(1) Is there any evidence to indicate that **1** may actually be in the ionic form **1B**?



(2) Does eq. (1) proceed through the tetrahedral intermediate (or transition state) **3**, or is it a concerted substitution (Ingold mechanism) which goes through the transition state **4**, with $\text{N}(\text{NO}_2)_2^-$ being the leaving group?



3



4

Methods

All geometries were optimized at the *ab initio* HF/6-31G* level, using the GAUSSIAN 92 code [1]. The HF/6-31G* vibration frequencies were calculated for each structure, in order to determine whether it corresponds to a local energy minimum (zero imaginary frequencies) or to a transition state (one imaginary frequency).

Results and Discussion

Figure 1 shows our computed structure for **1**. It has no imaginary frequencies, confirming that it corresponds to an energy minimum. The C=O and C-N(NO₂)₂ distances are quite reasonable for these types of bonds at the HF/6-31G* computational level [2], and do not support

the idea that **1** may be in the form **1B**, for which one would anticipate an anomalously short C=O bond and long C-N(NO₂)₂. Furthermore, when we attempted to compute an optimized geometry for the cationic portion of **1B**, treating it as a separate entity, it broke up into CO₂ and C₂H₅⁺.

Our calculated structure for the transition state in eq. (1), formed by allowing NH₃ to interact with the central carbon in **1**, is given in Figure 2. It is indeed a transition state (not an intermediate), with one imaginary frequency corresponding to a vibrational mode involving the C-NH₃ and C-N(NO₂)₂ bonds. The bond angles around the central carbon are 100.6, 102.4, 117.0 and 125.1 degrees; these indicate a significant deviation from tetrahedral symmetry, for which they would all be 109.5°. In addition, the C=O distance (1.201 Å) is only 0.027 Å longer than in **1** and is quite compatible with this still being a double bond, whereas structure **3** suggests a single bond. On the other hand, the C-N(NO₂)₂ bond length has increased to 1.660 Å, compared to 1.450 Å in **1**. The C-NH₃ distance is almost as great, 1.615 Å. All of these results indicate that structure **4** is a better representation of the transition state than is **3**, despite many examples of nucleophilic interactions with carboxyl derivatives proceeding by tetrahedral mechanisms [3,4].

An interesting feature of the transition state is a hydrogen bond between an ammonia hydrogen (H₂₁) and a nitro oxygen (O₉), as indicated by the dashed line in Figure 2. The H₂₁...O₉ distance is 2.093 Å. For that nitro group, the N-NO₂ distance is 1.366 Å, which is less than the 1.414 Å - 1.423 Å range of the other N-NO₂ bonds in **1** and **4**. As the incipient C-NH₃ bond becomes shorter and stronger, H₂₁ may migrate to O₉, forming an isomer of dinitraminic acid which could subsequently react with a second NH₃ to give the product, ammonium dinitramide (**2**).

References

- [1] GAUSSIAN 92, Revision C, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1992.
- [2] W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, Ab Initio Molecular Orbital Theory, John Wiley and Sons, New York, 1986.
- [3] S. J. Weininger and F. R. Stermitz, Organic Chemistry, Internat. Ed., Academic Press, New York, 1984, section 17:5.
- [4] J. March, Advanced Organic Chemistry, 3rd. ed., Wiley-Interscience, New York, 1985, ch. 10.

Bond Lengths (Å)

O 1- C 2 1.292
 O 1- C 3 1.443
 C 2- O 4 1.174
 C 2- N 5 1.450
 C 3- C 12 1.511
 C 3- H 13 1.080
 C 3- H 14 1.080
 N 5- N 6 1.414
 N 5- N 7 1.417
 N 6- O 8 1.180
 N 6- O 9 1.176
 N 7- O 10 1.175
 N 7- O 11 1.183
 C 12- H 15 1.084
 C 12- H 16 1.083
 C 12- H 17 1.083

Bond Angles (deg)

C 2- O 1- C 3 117.2
 O 1- C 2- O 4 129.4
 O 1- C 2- N 5 108.4
 O 1- C 3- C 12 107.0
 O 1- C 3- H 13 107.9
 O 1- C 3- H 14 108.0
 O 4- C 2- N 5 122.2
 C 2- N 5- N 6 114.3
 C 2- N 5- N 7 116.1
 C 12- C 3- H 13 112.5
 C 12- C 3- H 14 112.3
 C 3- C 12- H 15 109.3
 C 3- C 12- H 16 110.8
 C 3- C 12- H 17 110.8
 H 13- C 3- H 14 108.9
 N 6- N 5- N 7 112.5
 N 5- N 6- O 8 117.2
 N 5- N 6- O 9 113.6
 N 5- N 7- O 10 114.9
 N 5- N 7- O 11 116.2
 O 8- N 6- O 9 129.2
 O 10- N 7- O 11 128.9
 H 15- C 12- H 16 108.6
 H 15- C 12- H 17 108.5
 H 16- C 12- H 17 108.8

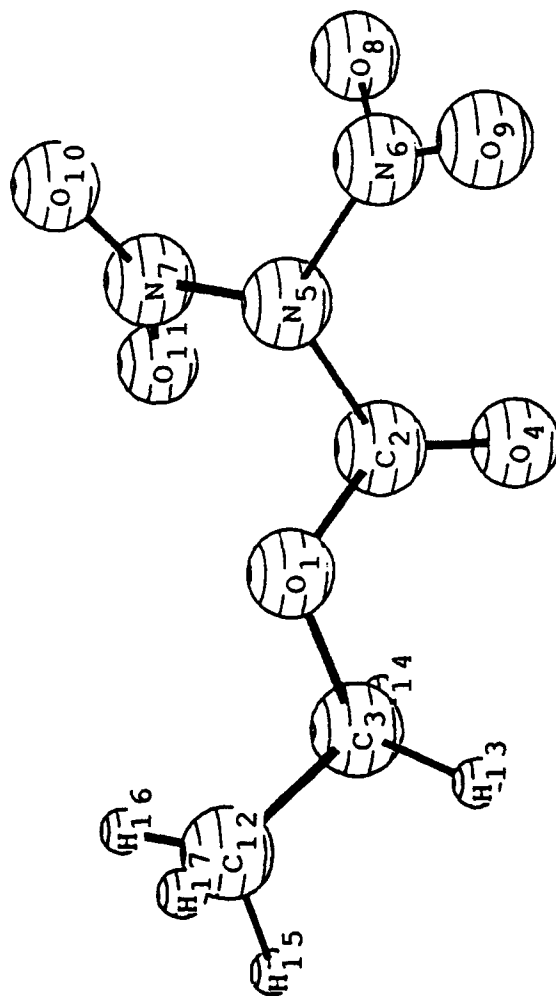


FIGURE 1. HF/6-31G* optimized geometry of 1.

Bond Lengths (Å)

0	1-	C	2	1	.350
0	1-	C	3	1	.436
C	2-	0	4	1	.201
C	2-	N	5	1	.660
C	2-	N	8	1	.615
C	3-	C	12	1	.513
C	3-	H	13	1	.082
C	3-	H	14	1	.077
N	5-	N	6	1	.366
N	5-	N	7	1	.423
N	6-	0	8	1	.182
N	6-	0	9	1	.198
N	7-	0	10	1	.180
N	7-	0	11	1	.183
C	12-	H	15	1	.085
C	12-	H	16	1	.083
C	12-	H	17	1	.084
N	18-	H	19	1	.006
N	18-	H	20	1	.007
N	18-	H	21	1	.009

Bond Angles (deg)

C 2- 0 1- C 3	116.3
0 1- C 2- 0 4	125.1
0 1- C 2- N 5	100.6
0 1- C 2- N 8	102.4
0 1- C 3- C 12	106.9
0 1- C 3- H 13	108.6
0 1- C 3- H 14	109.0
0 4- C 2- N 5	117.0
0 4- C 2- N 8	111.9
N 5- C 2- N 8	95.0
C 2- N 5- N 6	115.6
C 2- N 5- N 7	112.9
C 2- N 8- H 19	112.6
C 2- N 8- H 20	106.9
C 2- N 8- H 21	107.3
C 12- C 3- H 13	111.8
C 12- C 3- H 14	111.9
C 3- C 12- H 15	109.7
C 3- C 12- H 16	110.6
C 3- C 12- H 17	111.1
H 13- C 3- H 14	108.5
N 6- N 5- N 7	110.5
N 5- N 6- 0 8	119.3
N 5- N 6- 0 9	114.3
N 5- N 7- 0 10	114.9
N 5- N 7- 0 11	117.4
0 8- N 6- 0 9	126.3
0 10- N 7- 0 11	127.7
H 15- C 12- H 16	108.5
H 15- C 12- H 17	108.4
H 16- C 12- H 17	108.5
H 19- N 8- H 20	110.0
H 19- N 8- H 21	110.3
H 20- N 8- H 21	109.7

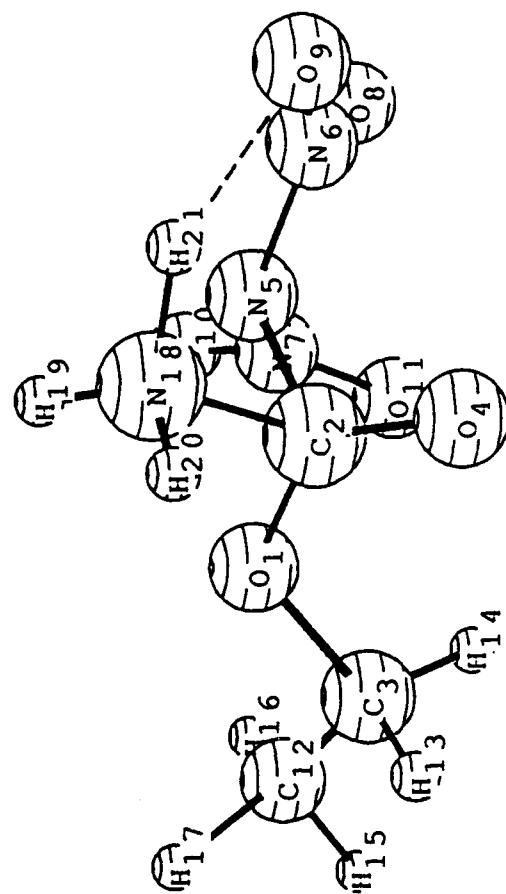


FIGURE 2. HF/6-31G* optimized geometry of transition state.