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A Density Functional Analysis of a Decomposition of 4-Nitro-1,2,3-Triazole
through the Evolution of N₂

by

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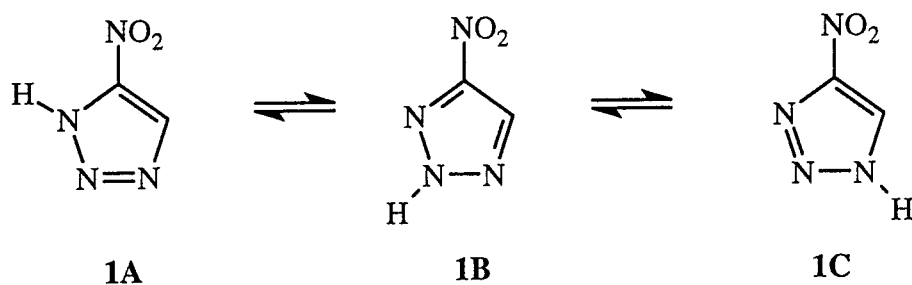
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13. ABSTRACT (Maximum 200 words) A density functional computational study shows that 4-nitro-1,2,3-triazole, which is highly impact sensitive, can decompose through ring opening and subsequent N ₂ evolution, with the net release of 12 kcal/mole. An input of 52 kcal/mole is required to initiate the process.														
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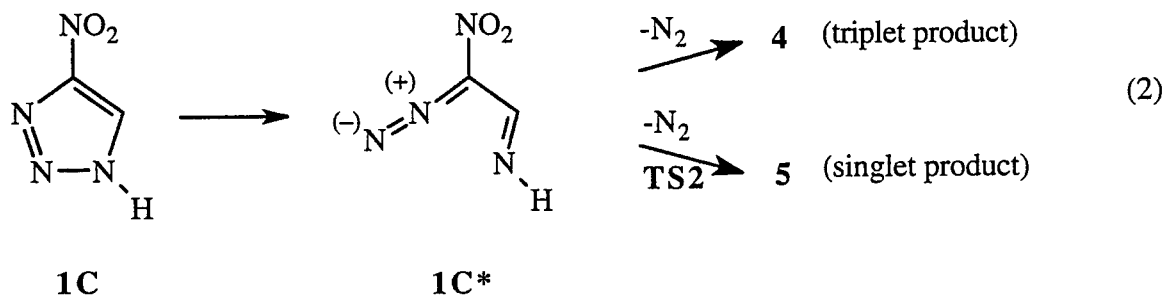
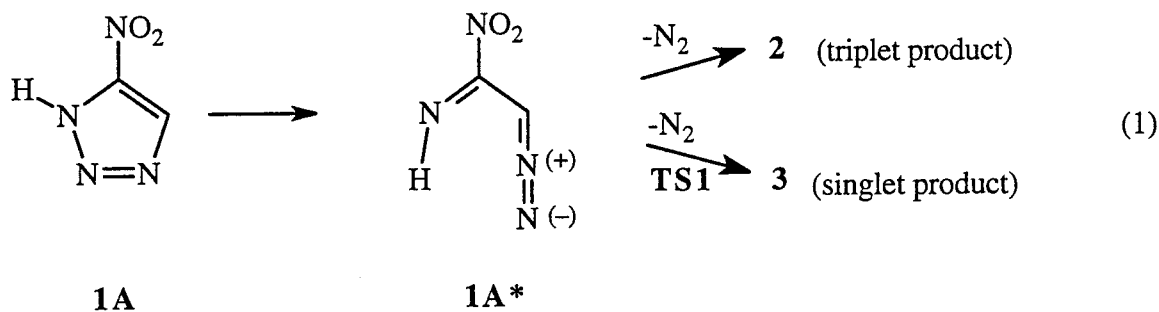
Introduction

There is currently considerable interest in high-nitrogen-content molecules as energetic materials.¹⁻¹⁷ A matter for potential concern, however, is the instability or sensitivity toward shock and/or impact that is frequently associated with the presence of several linked nitrogens.¹⁸ In some instances, for example certain picryl triazoles, it has been suggested that this instability is due to the availability of a relatively facile decomposition pathway involving the loss of N₂.¹⁹

We have accordingly investigated computationally the energetics of an N₂ evolution process in the case of the nitrotriazole **1**, which is known experimentally to be highly sensitive toward impact.²⁰ It has several tautomeric forms, as shown.



For **1A** and **1C**, one can envision decomposition routes through ring opening to give the intermediates **1A*** and **1C***,²¹ followed by the loss of N₂. This could leave either a singlet or a triplet product, and we have examined both possibilities in each case. The formation of the singlet products was found to involve transition states **TS1** and **TS2**.



Method

We have computed optimized geometries and energies for **1A**, **1B**, **1C**, **1A***, **1C***, **2**, **3**, **4**, **5**, **TS1** and **TS2** with the density functional option of the code Gaussian 92/DFT, revision G.2,²² using the Becke exchange²³ and the Perdew correlation²⁴ functionals and a 6-31G (d,p) basis set. The effectiveness of these functionals has been established through extensive comparisons with experimental and *ab initio* correlated studies.²⁵⁻³⁴ Zero-point energies were also determined. It was verified, by the absence of imaginary vibrational frequencies, that **1A**, **1B**, **1C**, **1A***, **1C*** and **2** - **5** all correspond to energy minima. **TS1** and **TS2** each have one imaginary frequency, confirming that they are transition states.

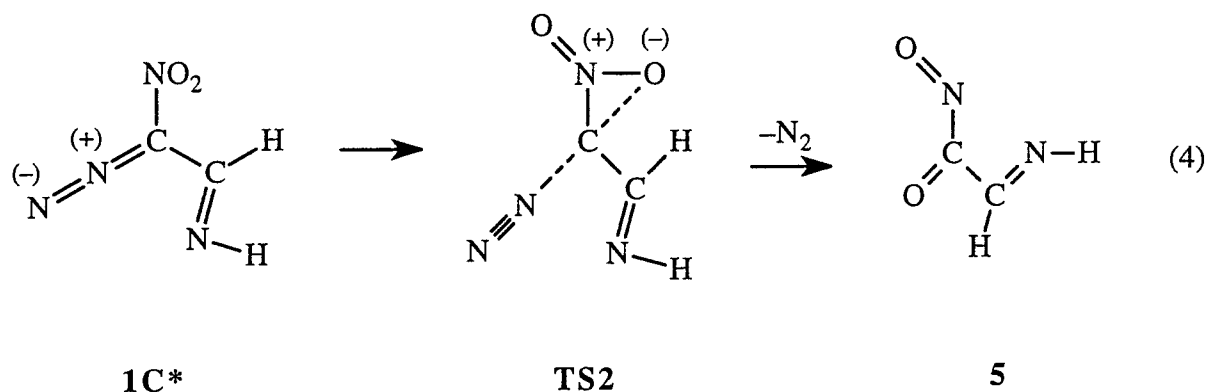
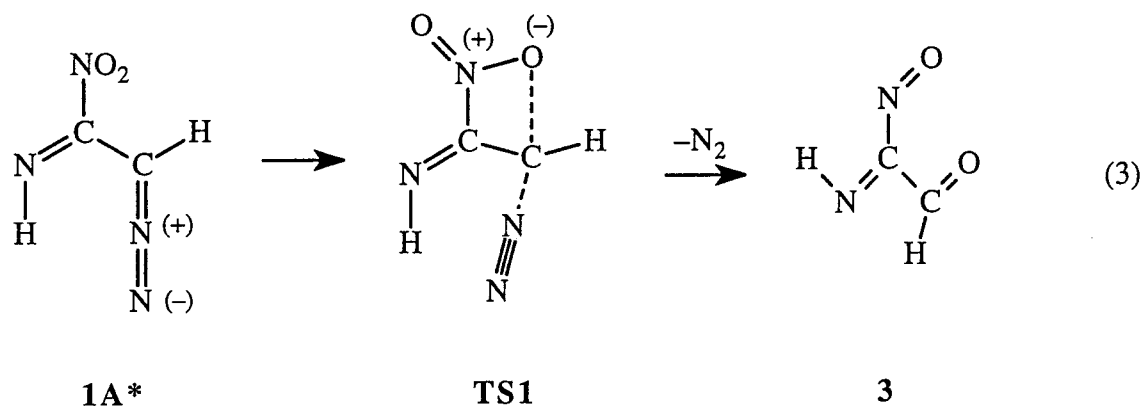
Results and Discussion

The resulting total and zero-point energies are given in Table 1, and the ΔE values for the individual steps in eqs. (1) and (2) are in Table 2. The energies of the tautomeric pair **1A** and **1C** are virtually equal (differing by only 0.6 kcal/mole) as are those of **1A*** and **1C*** (difference = 0.006 kcal/mole). Accordingly the energetics of the initial steps in eqs. (1) and (2), opening the triazole ring, are essentially identical, requiring an energy input of approximately 16 kcal/mole (Table 2).

The loss of N_2 from either **1A*** or **1C*** to form the triplet product **2** or **4** is simply a bond-breaking process; $\Delta E = +32.4$ and $+39.5$ kcal/mole, respectively (Table 2).



The formation of the singlet products **3** and **5**, on the other hand, involves structural rearrangements in which one of the oxygens of the nitro group migrates to the carbon from which the N_2 is leaving. This was found to proceed through the transition states **TS1** and **TS2**, as shown in eqs. (3) and (4). Table 2 shows that the energy barriers to these transition states, **1A*** \rightarrow **TS1** and **1C*** \rightarrow **TS2**, are $+38.0$ and $+32.4$ kcal/mole, respectively. Overall, however, the reactions represented by eqs. (3) and (4) release energy; for **1A*** \rightarrow **3** + N_2 , $\Delta E = -31.6$ kcal/mole, and for **1C*** \rightarrow **5** + N_2 , $\Delta E = -31.3$ kcal/mole.



An additional factor to be considered is the third tautomer, **1B**. It is prevented, for structural reasons, from forming an analog of **1A*** (and **1C***). However Table 2 shows that **1B** is about 3 kcal/mole more stable than **1A** and **1C**. We must therefore assume that there is a preference for the nitrotriazole **1** to exist as the tautomer **1B**.

Conclusion

On the basis of this study, we suggest that one plausible decomposition route for **1**, which could for example follow shock or impact, is that represented by eq. (5):



The first three steps in eq. (5) require $2.8 + 16.4 + 32.4 = 51.6$ kcal/mole of energy; however the overall ΔE is -12.1 kcal per mole of **1B**. The energy that must be provided to initiate this process is less than that typically needed to rupture a C-NO₂ linkage,³⁵⁻³⁸ which is believed to be the first step in the decomposition of many energetic materials.^{35,39-45} Furthermore, the reaction in eq. (5) results in the release of a significant amount of energy which can be used to promote further

decomposition. This appears, therefore, to be a reasonable interpretation of the high sensitivity that has been observed for the nitrotriazole **1**.²⁰

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Table 1. Calculated DFT energies, in hartrees.

System	Total energy, E	Zero-point energy, ZPE	E + ZPE
1A	-446.75903	+0.05933	-446.69970
1B	-446.76541	+0.06019	-446.70522
1C	-446.76004	+0.05933	-446.70071
1A*	-446.73015	+0.05563	-446.67452
1C*	-446.73074	+0.05623	-446.67451
2	-337.14470	+0.04314	-337.10156
3	-337.24779	+0.04418	-337.20361
4	-337.13425	+0.04405	-337.09020
5	-337.24743	+0.04433	-337.20310
N₂	-109.52670	+0.00536	-109.52134
TS1	-446.66559	+0.05158	-446.61401
TS2	-446.67360	+0.05078	-446.62282

Table 2. Energy changes corresponding to individual steps in reactions.
Differences in zero-point energies are taken into account.

Process	ΔE , kcal/mole
1B \rightarrow 1A	+3.5
1A \rightarrow 1A*	+15.8
1A* \rightarrow 2 + N₂	+32.4
1A* \rightarrow TS1	+38.0
1A* \rightarrow 3 + N₂	-31.6
1A \rightarrow 3 + N₂	-15.8
1B \rightarrow 1C	+2.8
1C \rightarrow 1C*	+16.4
1C* \rightarrow 4 + N₂	+39.5
1C* \rightarrow TS2	+32.4
1C* \rightarrow 5 + N₂	-31.3
1C \rightarrow 5 + N₂	-14.9